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Proceedings of the 2<sup>nd</sup> Jožef Stefan International Postgraduate School Students Conference

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Zbornik 2. Študentske konference Mednarodne podiplomske šole Jožefa Stefana  
(Proceedings of the 2<sup>nd</sup> Jožef Stefan International Postgraduate School Students Conference)

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**2. ŠTUDENTSKA KONFERENCA  
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## Z znanjem do inovativnih rešitev

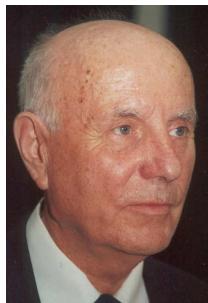
Prva študentska konferenca Mednarodne podiplomske šole Jožefa Stefana je pokazala, da tako študentje kot tudi predstavniki iz gospodarstva potrebujemo dogodke, namenjene povezovanju znanja iz različnih sfer. Zato je bila odločitev Študentskega sveta tokrat veliko lažja: »Konferenca seveda bo«.

Za rdečo nit letošnje študentske konference smo si postavili izziv, kako z znanjem do inovativnih rešitev. Odgovore bomo poiskali s povezovanjem - povezovanjem med nami, študenti, povezovanjem z mentorji, ki usmerjajo naše delo, in ne nazadnje s povezovanjem z vrhunskimi slovenskimi raziskovalnimi in razvojnimi laboratoriji. Drug drugemu in širokemu krogu strokovnjakov iz vodilnih slovenskih organizacij želimo pokazati svoje delo. Želimo premisliti tudi o tem, kakšno pot bomo ubrali, ter na kakšen način lahko s svojim pridobljenim znanjem prispevamo svoj kamenček v mozaik uspešnosti slovenskega gospodarstva.

Mladi raziskovalci v času študija usmerjamo rezultate svojega dela predvsem v znanstvene publikacije v najboljših mednarodnih revijah. Velikokrat se niti ne zavedamo, kako bi svoje znanje in izsledke uporabili za izboljšavo določenega izdelka, v razvoju novih materialov, delovnih in poslovnih procesov ali za čistejše okolje. Prav v tem segmentu je študentska konferenca svojevrstna, saj je njen namen povezovanje inštitucije znanja s slovenskim gospodarstvom. Upamo, da bodo tako študentje kot tudi predstavniki iz gospodarstva na tej konferenci našli svoje sogovornike in da se bo ob predstavljenih posterjih razvila plodna debata, ki bo morda vodila v kasnejše tesno sodelovanje in ne nazadnje, inovacije.

V letošnjem letu nam je uspel velik premik naprej: 37 študentskih prispevkov in preko 40 obiskovalcev iz vodilnih slovenskih podjetij kaže na to, da je tako srečanje v današnjem času ekonomske negotovosti, ko je glavno gonilo razvoja prav v inovacijah, raziskavah, novih izdelkih in izboljšanih storitvah, še kako potrebno. Uspeh te konference pa ni samo stvar organizatorjev. Brez vsestranske podpore Mednarodne podiplomske šole Jožefa Stefana z dekanom prof. dr. Robertom Blincem ne bi šlo tako gladko. Prav tako sta za uspeh konference v veliki meri zasluzna prof. dr. Aleksandra Kornhauser, prodekanica MPŠ za sodelovanje z industrijo, ki je tudi v letošnjem letu prevzela skrb za pregled vseh prispevkov, in dr. Emil Rojc, ki nam je priskočil na pomoč s številnimi kontakti v razvojno-raziskovalnih oddelkih podjetij. Veseli smo, da so se slovenska podjetja v tako veliki meri odzvala na vabilo. Predvsem pa gre zahvala vsem mentorjem, ki nas usmerjajo na naši raziskovalni poti.

Programski odbor



## Beseda dekana

Živimo v času globalizacije, kjer je znanstvena uspešnost države pogoj za ekonomsko uspešnost in celo za neodvisnost. Razlogi za ustanovitev Mednarodne podiplomske šole Jožefa Stefana (MPŠ) so prav v tem, to je v izjemno hitrem razvoju znanosti in nastanku novih znanstvenih področij ter potrebi po hitrem prenosu novih znanj v uporabo. MPŠ gradi na projektno usmerjenem izobraževanju, kjer študenti skupaj z mentorji prispevajo k prenosu vrhunskih znanj v procese dela in k uvajanju novih okolju prijaznih tehnologij ter mednarodnemu sodelovanju z vrhunkimi raziskovalci tujih univerz. Področja dela so zlasti nanotehnologija in bioznanosti, informacijska in komunikacijska tehnologija, ekotehnologija in menedžment tehnologij. Gre za doseganje odličnosti v temeljnih raziskavah, po drugi strani pa za posodabljanje postopkov in proizvodov, ki naj privedejo k večji ekonomski učinkovitosti in okoljski sprejemljivosti.

MPŠ je bila ustanovljena leta 2004 kot samostojni visokošolski zavod, na njej pa je sedaj doktoriralo 40 doktorjev znanosti in magistriralo 17 magistrov. Študenti so skupaj z mentorji objavili okoli 200 znanstvenih del v revijah, ki jih citira *Science Citation Index*.

MPŠ kot vsaka druga univerza je tako dobra, kot so dobri njeni študenti. Pred letom dni je bila organizirana prva študentska konferenca, ki je prikazala nekatere rezultate dela študentov in je bila zelo uspešna. Tokrat organizirajo študenti drugo študentsko konferenco, za katero smo prepričani, da bo prav tako uspešna kot prva in bo prispevala k povezovanju akademske in industrijske sfere.

Prof. dr. Robert Blinc  
Dekan MPŠ



## Beseda predstavnika industrije

Glavni razlog za močno podporo slovenske industrije pri snovanju in ustanavljanju Mednarodne diplomske šole Jožefa Stefana –MPŠ – je bil njen cilj:

*Gojiti vrhunsko raziskovanje  
in dosežke temeljnih raziskav neposredno vključevati  
v raziskovalne in razvojne projekte gospodarstva.*

Zato smo v slovenskih industrijskih podjetjih lani z veseljem pozdravili akcijo študentov MPŠ za širšo predstavitev njihovih raziskovalnih naporov in dosežkov s poudarkom na obetih za izboljšanje – ali celo uvajanje novih – postopkov in proizvodov.

Letošnja druga študentska konferenca kaže porast obsega in kakovosti predstavljenih dosežkov. To je dokaz, da tudi nova generacija študentov MPŠ sprejema to predstavitev kot obveznost ter kot priložnost za prenos znanja – ne nazadnje tudi za uveljavljanje mladih raziskovalcev.

Gospodarstveniki bomo veseli, če bo čimveč dosežkov prodrlo v našo industrijo v obliki novih izdelkov in storitev. Še posebej pa bomo z veseljem pozdravili mlade raziskovalce v svoji sredi. Kajti samo s skupnimi naporji mladih raziskovalcev in izkušenih razvojno vodilnih gospodarstvenikov bomo ustvarili dosežke, ki jih želimo in potrebujemo.

Uresničiti jih bomo poskušali z razvojno strategijo, ki bo večala pomen in možnosti raziskovanja, seveda tudi z usklajevanjem neogibnih omejevalnih faktorjev kot sta za to potreben čas in denar.

Od Vas pa pričakujemo, da boste prinašali svežino, dinamičnost in tudi sanje.

Franjo Bobinac  
Predsednik Uprave Gorenje



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# **Ekotehnologija (Ecotechnology)**

# Združitev kemijske analize in bioloških testov za preučevanje steroidnih estrogenov in drugih biološko aktivnih snovi

Miha Avberšek<sup>1,2</sup>, Bojana Žegura<sup>3</sup>, Metka Filipič<sup>3</sup>, Ester Heath<sup>1</sup>

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Biološko aktivne snovi igrajo v življenju človeka in drugih živih organizmov pomembno vlogo, ki je lahko pozitivna (zdravilne učinkovine) ali pa negativna (škodljiva prisotnost v okolju). Onesnaževanje okolja je že več desetletij pomembna tema in predmet raziskav, pa vendar raziskovalci v Evropi in svetu ugotavljajo, da v okolju prepoznavamo vse več novih organskih in anorganskih biološko aktivnih onesnažil. Prav tako se nezadržno širi tudi spisek zdravilnih učinkovin, ki imajo poleg želenih tudi neželene učinke. Ker se biološko aktivne snovi ponavadi pojavljajo v kompleksnih vzorcih, je poleg vsebnosti posameznih spojin pomemben tudi podatek o celotnem biološkem učinku vzorca. Osnovni metodologiji, ki se uporablja za preučevanje zdravilnih učinkovin ter prisotnosti, kroženja in vpliva biološko aktivnih snovi v okoljskih vzorcih, sta kemijska analiza in biološko testiranje – biotesti.

Kemijska analiza, ki se najpogosteje uporablja za dokazovanje spojin v kompleksnih vzorcih, nam poda informacijo o kemijski sestavi vzorca, to je o vsebnosti posameznih spojin v vzorcu, ne pa tudi o njihovem dejanskem učinku in medsebojnih interakcijah. Celotni biološki učinek merimo z biotesti, ki pa nam sami ničesar ne povedo o vsebnosti posameznih spojin v vzorcu. Kvalitetnejše rezultate lahko zagotovimo z združitvijo kemijske analize in biološkega testiranja, v kolikor sta metodi smiselno združeni in prilagojeni ena drugi.

Del našega raziskovalnega dela pokriva preučevanje prisotnosti steroidnih estrogenov v okoljskih vzorcih s kemijsko analizo (plinska kromatografija z masno spektrometrično detekcijo, GC-MSD), kar kombiniramo z biološkimi testi za določanje celokupne estrogenosti vzorcev (ER-Calux®). Običajno raziskovalci kemijsko analizo in biološke teste obravnavajo ločeno, kar posledično pomeni ločeno in dvojno pripravo vzorcev. V našem laboratoriju smo s prilagajanjem posameznih metod (npr. uporaba enakega topila v obeh metodah, prilagoditev količine uporabljenega topila) združili oba postopka in dosegli več kot 90 % ujemanje rezultatov, pri čemer smo zmanjšali čas in stroške analize. V prihodnje bomo kombinirano metodo uporabili za preučevanje kroženja steroidnih estrogenov v okoljskih vzorcih (odpadna voda iz komunalnih čistilnih naprav in površinske vode) in njihov doprinos k celokupni estrogenosti vzorcev.

Preučevanje povezave med kemijsko sestavo vzorca in celokupnim biološkim učinkom vzorca je uporabno tako za preučevanje onesnaženosti okolja (strupene snovi, endokrini motilci ipd.), kot tudi za testiranje biološkega učinka zdravilnih učinkovin. Hkrati pa lahko s primerno kombinacijo analizne metode in biološkega testa odkrijemo neznane spojine, ki jih lahko s frakcioniranjem izoliramo in identificiramo. Tovrstni pristopi so pomembni pri iskanju novih biološko aktivnih zdravilnih učinkovin, v okolju pa za zaznavanje novih onesnažil. Združitev kemijske analize in biološkega testa pomeni kvalitetnejšo informacijo z nižjimi možnimi stroški in krajšim porabljenim časom.



# Združitev kemijske analize in bioloških testov za preučevanje biološko aktivnih snovi

Miha Avberšek<sup>1</sup>, Bojana Žegura<sup>2</sup>, Metka Filipič<sup>2</sup>, Ester Heath<sup>1</sup> (mentor)

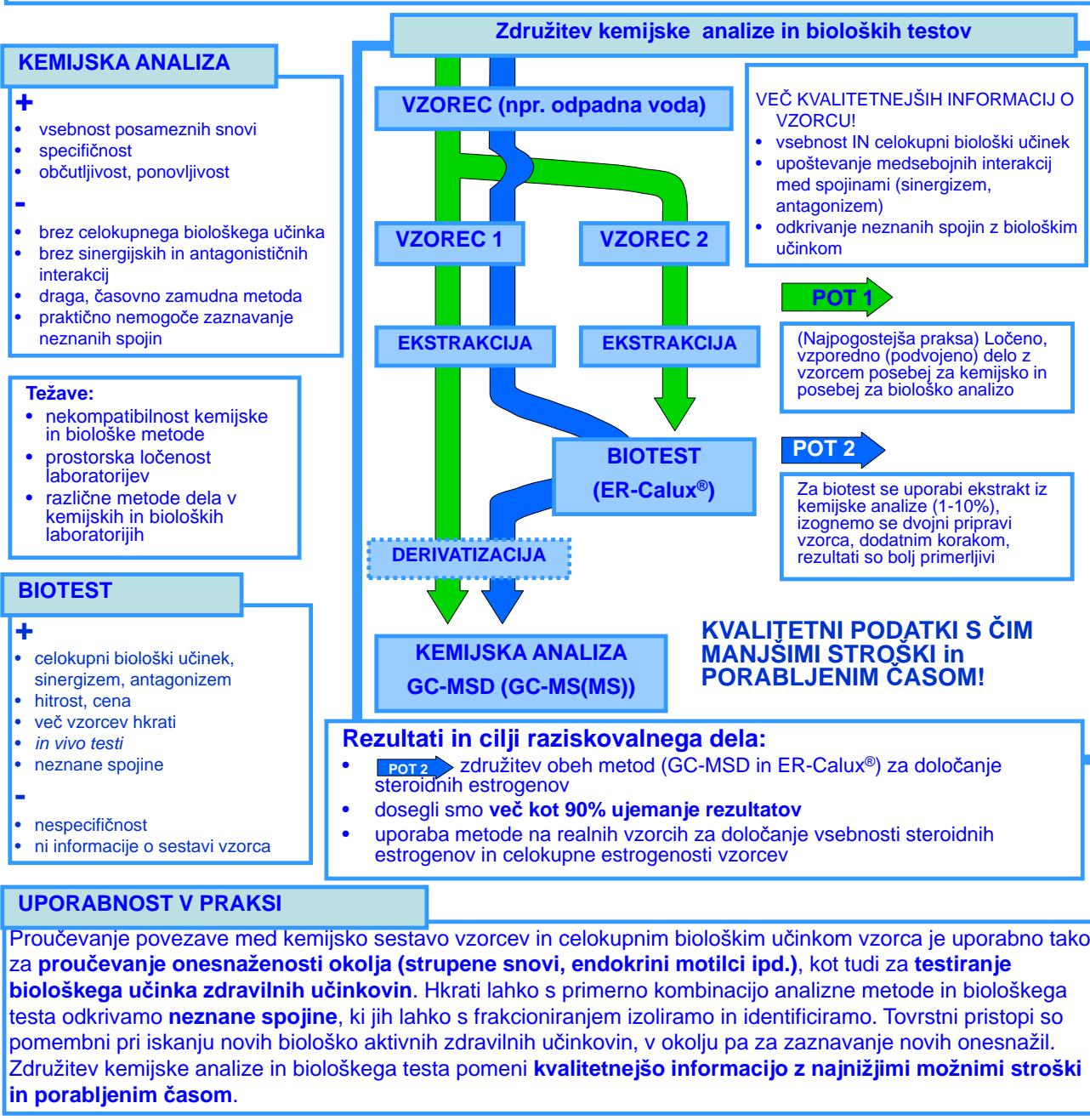
<sup>1</sup>Institut Jožef Stefan; Mednarodna podiplomska šola Jožefa Stefana; Smer: Ekotehnologija; miha.avbersek@ijs.si



## UVOD

<sup>2</sup>Nacionalni inštitut za biologijo

Biološko aktivne snovi igrajo v življenju človeka in drugih živilih organizmov pomembno vlogo, ki je lahko pozitivna (zdravilne učinkovine) ali pa negativna (škodljiva prisotnost v okolju). Onesnaževanje okolja je že več desetletij pomembna tema in predmet raziskav, pa vendar raziskovalci v Evropi in svetu ugotavljajo, da v okolju prepoznavamo vse več novih organskih in anorganskih, biološko aktivnih onesnažil. Prav tako se nezadržno širi tudi spisek zdravilnih učinkovin, ki imajo poleg želenih, tudi neželene učinke. Ker nam kemijska analiza in biološki testi vsak zase ne podajajo celovite informacije o vsebnosti in biološki aktivnosti posameznih spojin oz. kompleksnih vzorcev, je smiselno hkratno testiranje vzorcev z obema metodama. Združitev kemijske analize in biološkega testiranja nam omogoča kvalitetnejše rezultate, v kolikor sta metodi smiselno združeni in prilagojeni druga drugi.



# Microbiological transformations of mercury species in aquatic environments

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Biogeochemical cycle of mercury (Hg) is a complicated series of biotic and abiotic reactions, from which formation of monomethylmercury (MeHg) is widely considered as the most important, due to the proven toxicity of MeHg [1]. Organomercury forms have a pronounced capability of bioaccumulation (incorporation in cells and tissues of living organisms) and biomagnification (transport through trophic levels) [1]. In order to understand how the MeHg enters food resources, transformation of mercury and its species in the aquatic environment needs to be understood. Microorganisms play a fundamental role in mercury transformation processes (reduction, oxidation, methylation, demethylation). Hg transport and transformations are also governed by the physical and chemical properties that characterize the aquatic environment (pH, redox potential, temperature, salinity, dissolved oxygen, presence of dissolved organic matter, etc...).

The objective of this research is to better understand the role of microorganisms in mercury cycling in typical Slovenian surface water bodies as a response to mercury loads from air and water born sources. The work plan involves the following steps: (i) acquisition of measurement data on mercury analysis and speciation in precipitation and surface waters; (ii) use of chemical analytical methods for mercury analysis and speciation and transformation processes using radiotracers; (iii) application of microbiological and molecular tools to understand the role and response of microbial population to mercury stress.

The initial research has been focused on the coastal and estuarine environment of the Gulf of Trieste, which has been extensively studied in recent years [2-5]. The Gulf of Trieste is still receiving higher loads of Hg due to now closed mercury mine in Idrija and is therefore of special ecological interest. Latest results from measurements from Gulf of Trieste indicate that approximately 1-7 % of total Hg (THg) is in the form of MeHg in pore waters and water column, whereas in sediments, between 0.01 and 0.1 % of total Hg is present in methylated form (data not published). THg concentrations in marine waters are in range from 2 ng/L in surface layers to 15 ng/L at the bottom layer. Interesting values are those of dissolved elemental Hg in waters, which are not only of the same order of magnitude as MeHg, but are approximately of the same concentration as well, and are in some cases higher than MeHg. Surface waters have generally more dissolved Hg than bottom waters. Concentrations of THg in pore waters are somewhat higher and range from 4 ng/L to 32 ng/L. Sediments have the highest THg concentrations, ranging from 2700 to 17000 ng/g of sediment dry weight, however in this case, higher concentrations in top layers can be observed. These are relatively high values, indicating present (and constant) input of Hg into Gulf of Trieste. More measurements are required to estimate which are the controls over the Hg cycling in this environment. In addition to that, seasonal variations need to be investigated.

## References:

- [1] T. Barkay and I. Wagner-Dobler. Microbial transformations of mercury: potentials, challenges and achievements in controlling mercury toxicity in the environment. *Advances in applied microbiology*, 57:1-52, 2005
- [2] M. Horvat, S. Covelli, J. Faganeli, M. Logar, V. Mandič, R. Rajar, A. Širca, D. Žagar. Mercury in contaminated coastal environments; a case study: the Gulf of Trieste. *The Science of the Total Environment*, 237/238:43-56, 1999
- [3] S. Covelli, J. Faganeli, M. Horvat, A. Brambati. Mercury contamination of coastal sediments as a result of long-term cinnabar mining activity (Gulf of Trieste, northern Adriatic sea). *Applied Geochemistry*, 16:541-558, 2001
- [4] M. E. Hines, M. Horvat, J. Faganeli, J-C. J. Bonzongo, T. Barkay, E. B. Major, K. J. Scott, E. A. Bailey, J. J. Warwick, W. Lyons. Mercury Biogeochemistry in the Idrija River, Slovenia from above the Mine into the Gulf of Trieste. *Environmental Research Section A*, 83:129-139, 2000



## Microbiological transformations of mercury species in aquatic environments

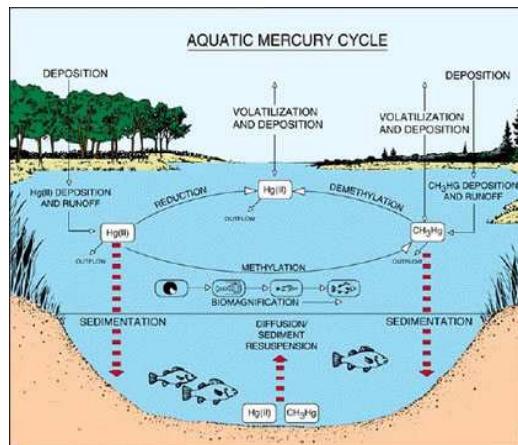


Figure 1: Simplified mercury water cycle.

Source: Internet

In September 2009, water was collected from the boat with precleaned bottles and sediment was collected with corers. They were kept in cooling boxes and transported back to the laboratory. First, measurements of dissolved elemental Hg were conducted. Sample preparations for MeHg measurements were carried out in inert nitrogen atmosphere.

During aquatic part of Hg cycle many different transformations occur, which have profound influence on Hg bioavailability. Very important are especially methylation and complexation processes. They are responsible for the increased toxicity and decreased bioavailability and transport, respectively. Note that besides sedimentation and volatilization, no other process removes Hg permanently from aquatic system. Hg, bound in biota, is considered only temporarily immobilized (Figure 1).



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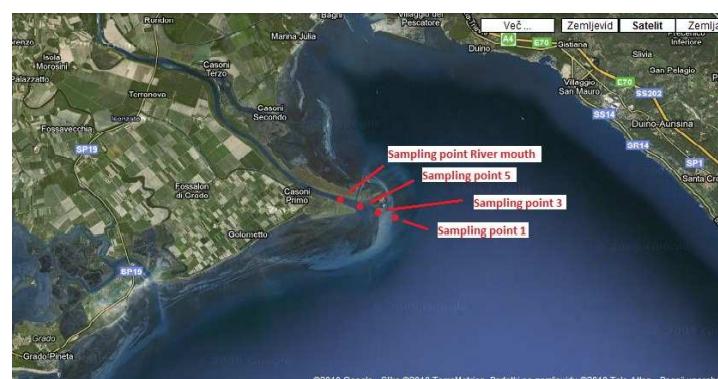


Figure 2: Sampling points in Gulf of Trieste. Source: Google Maps

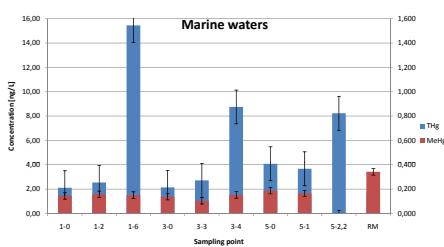


Figure 1: MeHg and THg concentrations in sea water

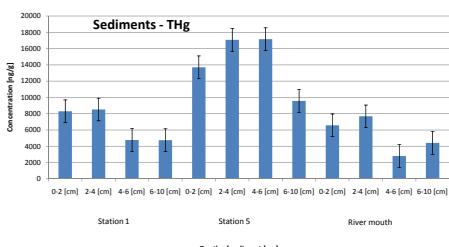


Figure 2: THg concentrations in sediments.  
Sampling point 3 is missing from analyses.

The authors would like to acknowledge help and effort from V. Fajon, N. Ogrinc, J. Kotnik and D. Kocman, without whose assistance this work would not be possible.

Figures 3-6 show results from sampling in September 2009. Different Hg species were measured at different water depths and sediment at 4 sampling points. DGM was measured only in water column. Results indicate gradual increase of THg concentrations towards bottom and higher concentrations in upper layers of sediment. Other values do not exhibit clear trends in the sampling period.

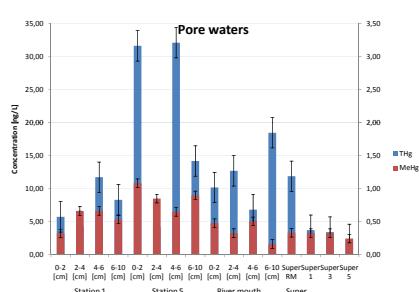


Figure 3: MeHg and THg in sediment pore waters

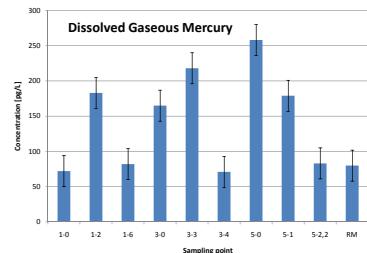


Figure 4: DGM concentrations in sea water.

# Fitoremediacija, kot ekotehnološki način za čiščenje z radionuklidi onesnaženih tal in voda

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Vstop radionuklidov v okolje kot posledica aktivnosti v energetiki ali jedrske industriji in posledično njihova razporeditev in kroženje v ekosistemih je globalni problem, ki se odraža na različnih ravneh. V okolini uranovih rudnikov so specifične aktivnosti lahko močno povečane, ker uranovi razpadni produkti ( $^{226}\text{Ra}$ ,  $^{230}\text{Th}$ ,  $^{210}\text{Pb}$ ,  $^{210}\text{Po}$ ) prehajajo v okolje z odlaganjem rudniških jalovin. Na takih območjih lahko radionuklidi predstavljajo radiološko nevarnost ljudem in živalim zaradi možnosti zaužitja onesnažene hrane ali vode, vdihavanja na prašnate delce vezanih radionuklidov ali radioaktivnega sevanja. Radionuklidi so v tesni povezavi z lastnostmi tal (organska snov, glineni minerali, kationska izmenjevalna kapaciteta, pH vrednost...), ki določajo obnašanje radionuklidov v tleh in vplivajo na njihovo biološko dostopnost [1]. Nekatere rastline, ki rastejo na rudniških jaloviščih ali v bližini uranovih rudnikov lahko kopičijo radionuklide tudi v večjih koncentracijah v koreninah in nadzemnih delih [2]. To so tako imenovane akumulatorske rastline, ki so razvile različne načine tolerance na toksične kovine in radionuklide [3]. Nekatere akumulatorske rastline iz družine križnic in trav se v zadnjih letih vse več uporabljajo v ekotehnološke namene, kot je fitoremediacija, kar pomeni uporabo rastlin za čiščenje onesnaženih tal ali voda. Med rastlinami primernimi za fitoremediacijo radionuklidov, v literaturi pogosto omenjajo sončnico (*Helianthus annus* L.), rjavo gorjušico (*Brassica juncea*), oljno ogrščico (*Brassica napus*), amaranthus (*Amaranthus* sp.), navadno trsje (*Phragmites australis*), širokolistni rogoz (*Typha latifolia*), nekatere vrste praproti (*Pteris vittata*)... Tradicionalne metode remediacij, kot so fizikalne (solidifikacija, izpiranje, aeracija...) in kemijske (ekstrakcija, imobilizacija, oksidacija/redukcija ...) so dražje in lahko negativno vplivajo na kakovost tal in na ekosistem, zato je fitoremediacija dobra alternativa za manj onesnažena področja, ker je okoljsko in ekonomsko trajnostna. Fitoremediacija se glede na namen biološkega čiščenja še naprej deli na fitoekstrakcijo, fitostabilizacijo, rizofiltracijo in fitovolatizacijo.

## Literatura:

- [1] C. Tamponnet, A. Martin-Garin, M-A. Gonze, N. Parekh, R. Vallejo, T. Sauras-Yera, J. Casadesus , C. Plasard, S. Staunton, M. Norden, R. Avila, G. Shaw. An overview of BORIS: Bioavailability of Radionuclides in Soils. *Journal of Environmental Radioactivity*, 99: 820-830, 2008
- [2] P. Soudek, P. Petřík, M. Vágner, R. Tykva, V. Plojhar, P. Petrová and T. Vaněk. Botanical survey and screening of plant species which accumulate  $^{226}\text{Ra}$  from contaminated soil of uranium waste depot. *European Journal of Soil Biology*, 43: 251-261, 2007
- [3] W.A. Peer, I.R. Baxter, E.L. Richards, J.L. Freeman, A.S. Murphy. Phytoremediation and hyperaccumulator plants. In: Tamás MJ, Martinoia E (Eds.), Molecular Biology of Metal Homeostasis and Detoxification: Topics in Current Genetics, Springer-Verlag Berlin Heidelberg, 14, 2005



## FITOREMEDIACIJA, KOT EKOTEHNOLOŠKI NAČIN ZA ČIŠČENJE Z RADIONUKLIDI ONESNAŽENIH TAL IN VODA

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### 1 UVOD

Vstop radionuklidov v okolje kot posledica aktivnosti v energetiki ali jedrski industriji in posledično njihova razporeditev in krojenje v ekosistemih je globalni problem, ki se odraža na različnih nivojih. Radionuklidi predstavljajo problem v okolju pri večjih koncentracijah v tleh in vodah zaradi možnosti ingestije onesnažene hrane in vode ter inhalacije na proračne dele vezanih radionuklidov. Eden pogostejših vzrokov prenosa radionuklidov v okolje je dejavnost uranovih rudnikov kjer z odlaganjem sive jalovine v okolje prehajajo uranove razpadni produkti (Ra-226, Th-230, Pb-210, Po-210). Tudi pretekli poskusi z jedrskimi bombami in jedrska nesreča v Černobilu sta še dva od pomembnejših vzrokov zaradi katerih so v okolju še vedno povečane specifične aktivnosti Sr-90 in Cs-137. Čiščenje z radionuklidimi onesnaženih območij je težavno pri večji onesnaženosti zato so po svetu razvili različne metode remediacij za onesnažena tla ali voda, ki običajno temeljijo na fizikalnih ali kemijskih procesih. Te metode so drage, ker zahtevajo dodatno tehnologijo, prav tako pa lahko negativno vplivajo na kakovost ali v talni ekosistem. V zadnjih 20 letih se zato vse bolj uveljavljajo ekotehnološki načini remediacij, ki temeljijo na naravnih procesih in uporabi akumulatorskih organizmov, ki lahko kopijo radionuklide v svojih tkivih v večjih koncentracijah. Fitoremediacija je med bolj razširjenimi ekotehnološkimi načini in pomeni uporabo rastlin za čiščenje onesnaženih tal ali voda [1]. V primerjavi z tradicionalnimi metodami remediacij je fitoremedacija cenovno ugodnejša, ne zahteva dodatne tehnologije in je okoljsko trajnostna, vendar je primera na le za manj onesnažena območja. Glede na namen čiščenja se fitoremediacija deli na fitoekstrakcijo, fitostabilizacijo, fitovolatizacijo in rizofiltracijo od katerih je vsak tip primera le pri določenih rastlinskih vrstah.

### 2 ZNAČINOSTI RASTLIN PRIMERNIH ZA FITOREMEDIACIJO

Nekatere rastline, ki rastejo v bližini uranovih rudnikov ali na samih jalovčiščih lahko kopijo radionuklide tudi v večjih koncentracijah v koreninah in nadzemnih delih [2]. Veliko teh rastlinskih vrst je razvilo ekotipe, prilagojene na večjo vsebnost toksičnih kovin v tleh. Takšna prilagoditev je vezana na ekspresijo specifičnih genov za določeno kovino v rastlinah. Ekotipi z takšnimi prilagoditvami imajo razvite različne načine toleranca na večje koncentracije radionuklidov ali toksičnih kovin v tleh in se delijo na naravne akumulatorje, indikatorje in izločevalce. [3]

• **Akumulatorji** so rastline, ki kopijo radionuklide v večjih koncentracijah v koreninah in nadzemnih delih in so tako primerne za ekstrakcijo radionuklidov iz tal ali voda. Primer so rjava goriščica (*Brassica juncea*), oljna ogriščica (*Brassica napus var. napus*), oljna repica (*Brassica rapa subsp. campestris*), amaranthus (*Amaranthus tricolor*), mnogolistni volčji bob (*Lupinus polyphyllus*), navadno korenje (*Daucus carota*), plazeči petoprstnik (*Potentilla reptans*), navadno trsje (*Phragmites australis*), širokolistni rogoz (*Typha latifolia*), grbasti vodna leča (*Lemna gibba*), lokvanji (*Nymphaea violacea*), nekatere vrste paprati (*Pteris vittata*, *Woodwardia areolata*)...

• **Indikatorji** kopijo radionuklide v nadzemnih delih v majhnih koncentracijah in tako služijo za indikacijo močno onesnaženih ali naravno založenih tal z radionuklidi.

• **Izločevalci** pa s svojimi mehanizmi onemogočajo sprejem radionuklidov v rastlini in so v nekaterih primerih primerne za fitostabilizacijo radionuklidov v tleh, ker s svojimi izločki zmanjšajo njihovo mobilnost v tleh. Rastline primerne za fitostabilizacijo so npr. trave iz rodu *Festuca*, *Agrostis* in *Hyparrhenia*, nekatere mikorizne rastline, topoli...

### 3 PRIVZEM IN KOPIČENJE RADIONUKLIDOV V RASTLINAH

Za fitoekstrakcijo je pomembno, da se morajo radionuklidi v tleh nahajati v dostopni obliki, kar pomeni, da se morajo nahajati v topni oblikah v talni raztopini. Odziv rastlin na povečano vsebnost radionuklidov ali toksičnih kovin v tleh je prikazan na spodnji sliki :

a) Absorpcija – mobilizacija radionuklidov v tleh s pomočjo zakisanja

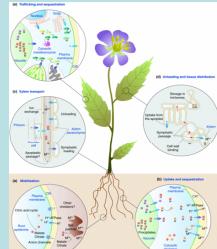
rizosfer in helatiranja radionuklidov z rastlinskimi izločki

b) Privzem in sekvestracija – privzem helatiranih ali hidratiranih radionuklidov

c) Transport radionuklidov po ksilemu

d) Razporeditev radionuklidov po tkivih – npr. kopiranje v trihomih

e) Kopiranje radionuklidov v celičnih organelah



### 5 NOVI TRENDI POVEZANI Z FITOREMEDIACIJO

- V svetu se razvijajo novi načini izboljšanja fitoekstrakcije z dodajanjem najrazličnejših dodatkov v onesnažena tla z namenom povečanja biodostopnosti radionuklidov ali toksičnih kovin v tleh za rastline
- proučevanje genov, ki so odgovorni za toleranco akumulatorskih rastlin na večje koncentracije radionuklidov ali toksičnih kovin v tleh
- uporaba transgenih rastlin z izboljšano toleranco na toksične kovine in izboljšanim akumulacijskim potencialom

### 6 LITERATURA

- [1] P. K. Padmavathiamma and Y.L. Loretta. Phytoremediation Technology: Hyper-accumulation Metals in Plants. *Water Air Soil Pollution*, 184: 105-126, 2007
- [2] P. Sodek, P. Petřík, M. Vágner, R. Tykva, V. Plojhar, P. Petrová and V. Vaněk. Botanical survey and screening of plant species which accumulate Ra-226 from contaminated soil of uranium waste depot. *European Journal of Soil Biology*, 43: 251-261, 2007
- [3] W.A. Peer, I.R. Baxter, E.L. Richards, J.L. Freeman, A.S. Murphy. Phytoremediation and hyperaccumulator plants. In M.J. Tamás, E. Martínoia (Eds), *Molecular Biology of Metal Homeostasis and Detoxification: Topics in Current Genetics*, Springer-Verlag, Berlin, Heidelberg, 14, 2005

### 4 TIPI FITOREMEDIACIJE

#### 4.1 FITOEKSTRAKCIJA

- Je uporaba akumulatorskih rastlin za ekstrakcijo radionuklidov iz tal v koreninah in nadzemne dele
- primerne so hitrorostične rastline, ki razvijajo veliko biomaso in kopijo radionuklide v večjih koncentracijah v nadzemnih delih
- poznamo trajno fitoekstrakcijo, kjer se uporablajo naravne akumulatorske rastline z velikim akumulacijskim potencialom in kemijsko-inducirano, kjer se tlor dodaja najrazličnejše dodatki, ki povečajo dostopnost radionuklidov v tleh ob uporabi kultiviranih rastlin, ki razvijajo veliko biomaso, vendar ni nujno da so akumulatorske in morajo imeti razvito naravno toleranco na radionuklide ali toksične kovine
- primeri rastlin za fitoekstrakcijo U-238 in Ra-226



*Brassica juncea*



*Helianthus annuus*



*Amaranthus sp.*

#### 4.2 FIOSTABILIZACIJA

- To je proces, kjer rastline radionuklidov v svojih tkivih ne kopijo, temveč s svojimi izločki zmanjšajo njihovo mobilnost v tleh in jih na ta način stabilizirajo
- rastline morajo imeti razvito dobro toleranco na večje koncentracije radionuklidov v tleh, katerih na smejo premeščati v nadzemne dele
- primeri rastlin za fitostabilizacijo toksičnih kovin



*Agrostis tenius*



*Festuca rubra*



*Hyparrhenia hirta*

#### 4.3 RIZOFILTRACIJA

- Je uporaba akumulatorskih vodnih in močvirskih rastlin za čiščenje vodnih ekosistemov
- primeri rastlin za rizofiltracijo U-238 in Ra-226



*Lemna gibba*



*Nymphaea violacea*



*Phragmites australis*

#### 4.4 FITOVOLATIZACIJA

- je proces, kjer se radionuklidi po ekstrakciji iz tal v telesu rastline pretvorijo v haplo obliko, ki nato izhlapi v ozračje (primer H-3)

# Organska snov v jezerskih sedimentih

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Jezera so edinstvena vodna sedimentacijska okolja, ki predstavljajo zelo občutljive, z okolico tesno povezane ekosisteme. Osnovni problem jezer predstavlja eutrofikacija, ki jo pospešuje človek z intenzivnimi posegi v okolje. Zaradi povečanega vnosa hranil v jezero se poruši ravnotežje, posledica pa je povečanje primarne produkcije. Organska snov, ki nastaja v površinski plasti vodnega stolpca (epilimniju), počasi tone in se razgrajuje v spodnjem delu vodnega stolpca (hipolimniju). Organska snov, ki doseže dno, je pomemben vir hranil in se lahko vgradi v sediment, kjer je izpostavljena nadaljnjam diagenetskim spremembam (fizikalni, kemijski, biološki in mehanski procesi, ki so prisotni v fazi, ko iz sedimenta nastaja kamnina). To poteka s pomočjo mikrobnih procesov, in tako neposredno vpliva na koncentracijo hranil v vodnem okolju.

Raziskave organske snovi v sedimentu nam omogočajo določiti njen izvor in depozicijske pogoje, ki so vladali v času, ko se je organska snov vgradila v sediment. Študije organske snovi v jezerskih sedimentih so pomembne, ker pokažejo, kakšne so bile spremembe v produktivnosti jezera ter nakažejo klimatske razmere in spremembe v preteklosti. Uporablajo se različne metode, od analiz spremembe izotopske sestave organske snovi ( $\delta^{13}\text{C}$  vrednosti) in določitve razmerij C/N, na osnovi katerih lahko določimo izvor celotne organske snovi, do določitve posameznih organskih spojin, ki so dovolj odporne in stabilne, da »preživijo« prve stopnje procesov razgradnje in nam lahko podajo bolj specifičen izvor organske snovi. Čeprav so bile prve raziskave biomarkerjev v jezerskih sedimentih opravljene že v osemdesetih letih, so te študije aktualne tudi danes, predvsem zaradi vedno novih odkritij lipidov iz alg, bakterij, zooplanktona in ostalih organizmov, ki jih lahko uporabimo za zelo specifično identifikacijo izvora organske snovi.

Iz sestave lipidne frakcije organske snovi v sedimentu dobimo zelo uporabne informacije o izvoru organske snovi in o njenih spremembah, ki so posledica diagenetskih procesov. Lipidni ekstrakti iz jezerskih sedimentov vsebujejo različne frakcije, kot so alifatiki ogljikovodiki (CH), alkoholi (COH), aldehydi, ketoni, steroli (ST), maščobne kisline (FA) in sorodne spojine, ki vsebujejo 10 in več C atomov.

Cilj naših raziskav je določitev izvora organske snovi v sedimentih in v suspendirani organski snovi v Blejskem jezeru. V ta namen smo v sedimentu Blejskega jezera določili CH, COH, ST in FA. Za ekstrakcijo sedimenta smo medseboj primerjali dve različni ekstrakcijski tehniki – ekstrakcijo s Soxhletom in ekstrakcijo z mikrovalovi. Za ločitev in identifikacijo komponent smo uporabili plinski kromatograf sklopljen s plamensko ionizacijskim detektorjem (GC-FID) in plinski kromatograf z masnim detektorjem (GC-MS). Za določitev izotopske sestave biomarkerjev v Blejskem jezeru smo uporabili plinski kromatograf sklopljen z masnim spektrometrom za določevanje stabilnih izotopov preko sežigne enote (GC-C-IRMS). Rezultati kažejo, da avtohtoni lipidi s krajšimi verigami, ki so planktonskega in bakterijskega izvora, prevladujejo v vrhnjih plasteh sedimentov, globlje pa prevladujejo kopenski lipidi z daljšimi verigami. Ta porazdelitev je večinoma posledica diagenetskih procesov, saj so kopenski lipidi težje razgradljivi. Izotopska sestava alifatiskih ogljikovodikov ( $n\text{-C}_{25} - n\text{-C}_{33}$ ) se giblje med -34,0 in -37,0 ‰, kar kaže na njihov kopenski izvor. Podobno kot alifatiki ogljikovodiki, so tudi alifatiki alkoholi z daljšimi verigami kopenskega izvora. Njihova  $\delta^{13}\text{C}$  vrednost znaša med -35,0 in -36,0 ‰.

Uporabo stabilnih izotopov in določitev izotopske sestave maščobnih kislin, smo uspešno uporabili tudi v industrijske namene, kjer z določitvijo maščobnih kislin v oljčnih oljih ugotavljamo pristnost in geografsko poreklo oljčnih olj.



# MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA

JOŽEF STEFAN  
INTERNATIONAL  
POSTGRADUATE SCHOOL

## ORGANSKA SNOV V JEZERSKIH SEDIMENTIH

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### UVOD

Organska snov predstavlja majhen del jezerskih sedimentov. Vir organske snovi so lahko ostanki vodnih organizmov iz vodnega stolpca in sedimenta (avtohtona organska snov), ostanki kopenskih organizmov, predvsem rastlin, ki se v jezero spirajo iz njegove okolice (alohtona organska snov) ter produkti, ki so posledica mikrobine aktivnosti v vodi in sedimentu. Organsko snov sestavljajo zelo obstojne (nereaktivne) komponente in lahko razgradljive (reaktivne) komponente, ki se relativno hitro odstranijo.

Lipidni ekstrakti iz jezerskih sedimentov vsebujejo različne frakcije, kot so ogljikovodiki, alkoholi, ketoni, aldehidi, steroli, maščobne kisline in sorodne spojine, ki vsebujejo 10 in več C atomov.

Iz sestave lipidne frakcije organske snovi v sedimentu lahko dobimo zelo uporabne informacije o izvoru organske snovi in o njenih spremembah, ki so posledica diagenetskih procesov.

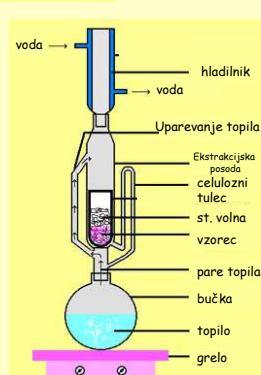
### CILJI

- določitev izvora organske snovi v sedimentih in v suspendirani organski snovi v Blejskem jezeru
- določitev lipidnih biomarkerjev: alifatskih ogljikovodikov (CH), alkoholov (OH), sterolov (ST) in maščobnih kislin (FA)
- primerjava dveh različnih ekstrakcijskih tehnik - ekstrakcijo s Soxhletom in ekstrakcijo z mikrovalovi
- za ločitev in identifikacijo komponent in stabilnih izotopov smo uporabili GC-FID, GC-MS in GC-C-IRMS

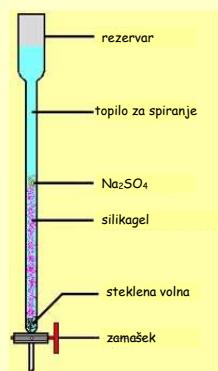
### EKSPERIMENTALNI DEL



1. Vzorčevanje



2. Ekstrakcija



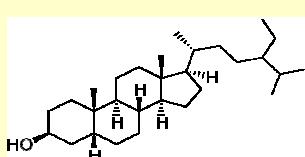
3. Frakcionacija



4. Detekcija

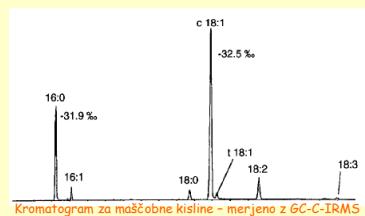
### REZULTATI

V površinskih anoksičnih sedimentih prevladujejo lipidi s krajšimi verigami. Najpogostejši so ST in FA. V oksičnem sedimentu



24-ethylcoprostanol (24-ethyl 5 $\beta$ -cholest-3 $\beta$ -ol)

Ta ST predstavlja fekaliski onesnaženje. Glede na naše rezultate, je prisoten samo na površini, medtem ko ga globje ni, kar pomeni, da je do onesnaženja jezera prislo v zadnjih nekaj letih.



Kromatogram za maščobne kisline - merjeno z GC-C-IRMS

Uporabo stabilnih izotopov in določitev izotopske sestave maščobnih kislin, smo uspešno uporabili tudi v industrijske namene, kjer z določitvijo maščobnih kislin v oljčnih oljih ugotavljamo pristnost in geografsko poreklo oljčnih olj.

# A model for prediction of radon concentration in the Postojna cave

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Postojna Cave is the biggest of 12 show caves in Slovenia. Because of elevated radon concentrations, it has been under permanent radon survey since 1995 [1]. The driving force for air movement in the cave, and thus the inflow of fresh air and release of the cave air to the atmosphere, is the temperature difference between the cave air and outdoors [2]. In our study, we intend to predict radon concentration in the cave air on the basis of this temperature difference.

Measurements of radon concentration in the Postojna Cave were carried out continually (recorded once per hour) from July 2005 to October 2009 in the Great Mountain hall. Outdoor temperature has been recorded at the Postojna meteorological station and provided by the Environmental Agency of the Republic of Slovenia.

The cave behaves as a large chimney, and in the cold period the warmer radon-rich cave air is released to the colder outdoor atmosphere, allowing the inflow of fresh air with low radon levels. The radon levels in the cave are the highest when the outdoor temperature is similar to the cave temperature (10 °C) and, hence, the air movement is very low. Our calculations have shown that the effect of the difference between outdoor and cave temperature on radon concentration was delayed for three days, presumably because of the distance of the Great Mountain from the entrance (ca. 2 km). When daily outdoor temperature drops below – 6 °C, radon concentration grows higher resulting in an average value of  $644 \pm 235 \text{ Bq m}^{-3}$ . It is assumed that ice and snow on the surface above the cave prevent the cave air from escaping the cave. In summer, the vertical air movement stops or is minimal and the horizontal air movement has the main influence on radon concentration in the cave.

For data analysis, the one dimensional transport equation provided by Nazaroff [3] has been used:

$$\frac{dC}{dt} \approx -\frac{k_i |\Delta T| C}{L} - \lambda C + \phi \quad (1)$$

Here,  $C$  is the radon concentration [ $\text{Bq m}^{-3}$ ],  $t$  is time [s],  $\Delta T$  is the difference between outdoor temperature and cave temperature [K],  $L$  is the distance from the entrance to the Great Mountain [m],  $\lambda$  is radon decay constant ( $2.1 \times 10^{-6} \text{ s}^{-1}$ ) and  $\phi$  is radon source term [ $\text{Bq m}^{-3} \text{ s}^{-1}$ ]. Based on the temperature difference, this equation predicts radon concentration. In the analysis of the dataset from July 2005 to October 2007, the concentration reached its maximum ( $2,800 \text{ Bq m}^{-3}$ ) in summer when the air draught in the cave was minimal or zero. Under these conditions, the radon source term of  $5.9 \times 10^{-3} \text{ Bq m}^{-3} \text{ s}^{-1}$  was obtained. The  $k$  values were calculated for the summer ( $k_1$ ) and winter regime ( $k_2$ ) separately, and the averages of  $0.19 \pm 1.07 \text{ mm s}^{-1} \text{ K}^{-1}$  and  $0.93 \pm 31.13 \text{ mm s}^{-1} \text{ K}^{-1}$ , respectively, were obtained.

The model, developed using the results of our previous long-term radon monitoring in the Postojna Cave, provides a relatively good prediction of radon concentration in the cave air, simply on the basis of the difference in air temperature in the cave and outdoors. Although successful, the model may certainly not replace the measurements but could reduce markedly their number, without diminishing the level of reliability of data needed for dose estimates for the personnel working in the cave.

## References:

- [1] J. Vaupotič. Nanosize radon short-lived decay products in the air of the Postojna Cave. *Science of the Total Environment*, 393(1): 27-38, 2008.
- [2] J. Hakl, et al. Radon transport phenomena studied in Karst caves-international experiences on radon levels and exposures. *Radiation Measurements*, 28(1-6): 675-684, 1997.
- [3] W. W. Nazaroff. Radon transport from soil to air. *Reviews of Geophysics*, 30(2): 137-160, 1992.



## A MODEL FOR PREDICTION OF RADON CONCENTRATION IN THE POSTOJNA CAVE

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### Introduction

Postojna Cave is the biggest of 12 show caves in Slovenia. Because of elevated radon concentrations it has been under permanent radon survey since 1995 (Vaupotič, 2008). The influence of meteorological conditions on the radon levels and their temporal variations depends mostly on the shape of the cave, and the number and directions of cracks, corridors and fissures connecting the cave rooms with the outdoor atmosphere. The driving force for air movement in the cave, and thus the inflow of fresh air and release of the cave air to the atmosphere, is the temperature difference between the cave air and outdoors (Hakl et al., 1997). In our study, we intend to predict radon concentration ( $C_{Rn}$ ) in the cave air on the basis of this temperature difference.

### Experimental

Measurements of  $C_{Rn}$  in the Postojna Cave were carried out continually (recorded once per hour) from July 2005 to October 2009 in the Great Mountain hall (with some interruptions because of failure of instrument. Outdoor temperature ( $T_{out}$ ) has been recorded at the Postojna meteorological station and provided by the Environmental Agency of the Republic of Slovenia.

#### 1. Seasonal pattern

Winter regime:  $T_{out} < T_{cave}$

- Chimney effect: the warmer radon-rich cave air is released to the colder outdoor atmosphere, allowing the inflow of fresh air with low  $C_{Rn}$  (Fig. 3).
- $T_{out} \approx T_{cave}$ : The air movement is very low  $\rightarrow C_{Rn}$  reaches its maximum
- $T_{out} < -6^\circ\text{C}$ : ice and snow on the surface above the cave prevent the cave air from escaping the cave  $\rightarrow C_{Rn}$  grows higher.

Summer regime:  $T_{out} > T_{cave}$

- The vertical air movement stops or is minimal and the horizontal air movement has the main influence on  $C_{Rn}$  in the cave.

The effect of the difference between  $T_{out}$  and  $T_{cave}$  on  $C_{Rn}$  is delayed for 3 days, presumably because of the distance of the Great Mountain from the entrance (cca 2 km).

#### 2. Building the model

- Dataset: July 2005 to October 2007
- The one dimensional transport equation provided by Nazaroff (1992) can be transformed to the following equation:
$$\frac{dC}{dt} \approx -\frac{k_1 |\Delta T| C}{L} - \lambda C + \Phi$$

$C$  ... radon concentration ( $\text{Bq m}^{-3}$ )  
 $t$  ... time (s)  
 $\Delta T$  ... the difference between  $T_{out}$  and  $T_{cave}$  (K)  
 $\lambda$  ... radon decay constant ( $\text{s}^{-1}$ )  
 $\Phi$  ... radon source term ( $\text{Bq m}^{-3}\text{s}^{-1}$ )
- $C_{Rn}$  reached its maximum ( $2800 \text{ Bq m}^{-3}$ ) in summer when the air draught in the cave was minimal or zero  $\rightarrow \Phi$  was calculated:  $5.9 \times 10^{-3} \text{ Bq m}^{-3}\text{s}^{-1}$ .
- The  $k$  values were calculated for the summer ( $k_1$ ) and winter regime ( $k_2$ ) separately (Table 1).

$k_1$	$T_{out}$	$k$ ( $\text{mm s}^{-1}\text{K}^{-1}$ )	$C_{Rn}$ ( $\text{Bq m}^{-3}$ )
$k_1$	$T_{out} > 10^\circ\text{C}$	$0.193 \pm 1.072$	
$k_2$	$-6^\circ\text{C} < T_{out} < 10^\circ\text{C}$	$1.8 \pm 31.137$	
	$T_{out} < -6^\circ\text{C}$		$644 \pm 235$

Table 1: Constant  $k$  for summer and winter regime.

#### 3. Testing the model

For testing the model the dataset from November 2007 to October 2009 was used. The correlation coefficient between measured and predicted  $C_{Rn}$  is **0.76**.

### Results

Our results have shown a good agreement between the measured and predicted radon concentration (Fig. 1). However this agreement is better in summer and winter months, whereas in the transitional period (from March to April and from October to November) the error of prediction is higher.

### Conclusion

The model, developed on the results of our previous long-term radon monitoring in the Postojna Cave, provides a relatively good prediction of radon concentration in the cave air, simply on the basis of the difference in air temperature in the cave and outdoors. Although successful, the model may certainly not replace the measurements but could reduce markedly their number, without diminishing the level of reliability of data needed for dose estimates for the personnel working in the cave.

### References

- Hakl, J., Hunyadi, I., Csige, I., Géczy, G., Lénárt, L., and Várhegyi, A.: Radon transport phenomena studied in Karst caves-international experiences on radon levels and exposures, Radiat. Meas., 28, 675-684, 1997.  
Nazaroff, W. W.: Radon transport from soil to air, Reviews of Geophysics, 30, 137-160, 1992.  
Vaupotič, J.: Nanosize radon short-lived decay products in the air of the Postojna Cave, Sci. Total Environ., 393, 27-38, 2008.

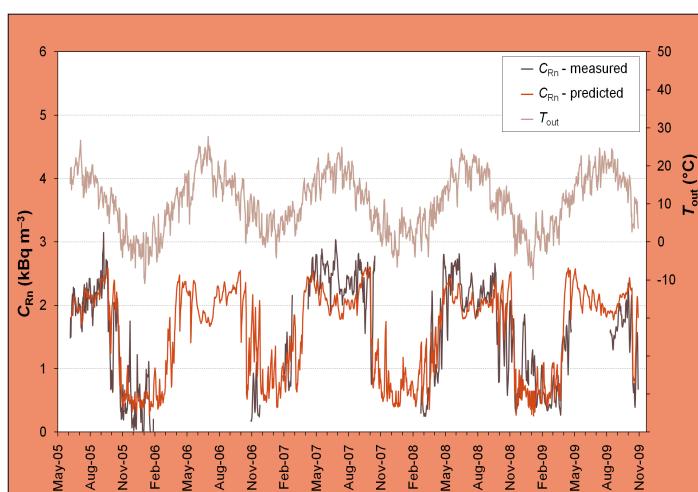


Figure 1: Comparison of predicted and measured  $C_{Rn}$  from July 2005 to October 2009.

# Fluor: Koristen ali škodljiv? Čaj kot potencialni vir vnosa fluora v človeško telo

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Čajevec (*Camellia sinensis* L.; družina Theaceae) lahko iz zemlje privzema fluor, ki ga akumulira v listih, iz katerih se med ekstrakcijo zlahka sprosti [1,2]. Pitje večjih količin pravega čaja lahko tako bistveno prispeva k dnevnemu vnosu fluora v telo. Primeren dnevni odmerek fluora iz vseh virov naj bi bil 0,05 mg/kg telesne teže/dan za vse starosti više od 6 mesecev [3], v primeru višjih vnosov pa se poveča tveganje za pojav fluoroze.

Zanimala sta nas razlike med vsebnostjo celotnega fluora in sproščenega fluora v pripravljenem čaju v nekaterih najbolje prodajanih pravih čajih v Sloveniji, ter količina čaja, ki ga lahko zaužijemo, ne da bi presegli primeren dnevni vnos fluora.

Največ fluora vsebujejo črni čaji (68–435 mg/kg), manj rdeči (83–238 mg/kg), najmanj pa zeleni (53–293 mg/kg). Pripravljeni napitki črnih čajev vsebujejo 0,56–3,55 mg/L, rdečih 50–134 mg/L in zelenih 0,44–1,52 mg/L prostega fluora. Primeren dnevni vnos, če zauživamo fluor le s čajem, je v primeru uživanja 1 L čaja (za osebo s težo 70 kg) presežen le pri črnem čaju, v primeru večjega vnosa čaja in pri lažjih osebah pa je primeren vnos fluora zlahka presežen tudi pri drugih vrstah čaja.

V skladu s pričakovanji sem ugotovila tudi, da je vsebnost celotnega fluora višja od vsebnosti prostega fluora, pokazala pa sem tudi, da se koncentracije fluora v infuzijah glede na način priprave čaja razlikujejo. Rezultati eksperimentov kažejo, da lahko samo s pitjem petih skodelic (1000 mL) nekaterih vrst čajev že presežemo priporočen dnevni vnos fluora.

Fluor dokazano prehaja preko placente in materinega mleka [4], pojav zobne fluoroze pa je najpogosteji pri otrocih do 7-8 leta starosti (ko se zobje formirajo) [5–6], zato bom v prihodnje določila vsebnosti fluora v čajih za nosečnice in doječe matere in v otroških čajih. Ravno pri zadnjih je količina vnešenega fluora izjemno pomembna, saj lahko le-ta že v nizkih koncentracijah bistveno vpliva na dojenčkovo zdravje in razvoj.

Fluor je eden najbolj pogostih elementov v sledih v naravi, kjer se nahaja v višjih koncentracijeh. Poleg naravnih virov (tudi vulkanski izbruhi) so za človekovo zdravje pomembne predvsem koncentracije fluora v okoljih, ki so kontaminirana z industrijskimi viri fluora. Določitev le-teh je tudi cilj bodočih raziskav.

## References:

- [1] P. Gulati, V. Singh, M.K. Gupta, V. Vaidya, S. Dass and S. Prakash. Studies on the leaching of fluoride in tea infusions. *Sci. Total Environ.* 138: 213–222, 1993
- [2] Z.M. Xie, Z.H. Ye, M.H. Wong. Distribution characteristics of fluoride and aluminum in soil profiles of an abandoned tea plantation and their uptake by six woody species. *Environ. Int.* 26: 341–346, 2001
- [3] Standing Committee on the Scientific Evaluation of the Dietary Reference Intakes, Dietary Reference Intakes (DRI) for Calcium, Phosphorus, Magnesium, Vitamin D, and Fluoride, National Academy Press, Washington D.C., 1997
- [4] Y. W. Shen, D. R. Taves. Fluoride concentrations in the human placenta and maternal and cord blood. *Am. J. Obstet. Gynecol.* 119: 205-207, 1974
- [5] O. Fejerskov, A. Thylstrup, M. J. Larsen. Clinical and structural features and possible pathogenic mechanisms of dental fluorosis. *Scand. J. Dent. Res.*, 85:510-534, 1977
- [6] T. Ishii, G. Suckling. The severity of dental fluorosis in children exposed to water with a high fluoride content for various periods of time. *J. Dent. Res.*, 70:952-956, 1991



## FLUOR: KORISTEN ali ŠKODLJIV?? ČAJ KOT POTENCIALNI VIR VNOSA FLUORA V ČLOVEŠKO TELO

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### ZNANSTEVNI TEMELJI

**FLUOR** je esencialni element, ki ima pri vnosu nižjih koncentracij bistven pomen pri mineralizaciji zob (najpomembnejši je vnos fluora pri otrocih do 7-8 leta starosti) in tvorbi kosti.

Fluor vnašamo v telo s **HRANO**, pitno **VODO** in različnimi fluoriranimi sredstvi za nego zob. Priporočen dnevni vnos fluora je **0.05 mg/dan/kg telesne teže**.

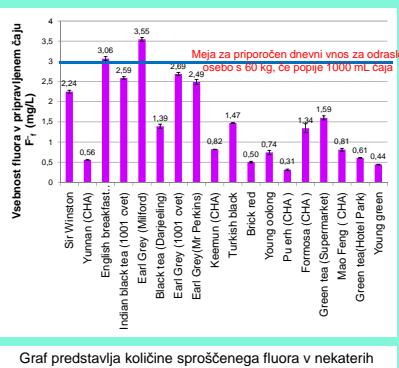
Kroničen vnos višjih koncentracij fluora pa lahko povzroči pojav **zobne oziroma kostne fluoroze**.



Čajevec (*Camellia sinensis*; family Thaece) dokazano privzema višje koncentracije fluora iz zemlje in ga akumulira v listih iz kjer se zlahka sprosti med pripravo čaja.



Že s samo pitjem nekaterih čajev lahko presežemo priporočen dnevni vnos fluora...



Kaj pa v primeru:

➤ Niže telesne teže, Uživanja večjih količin čaja

➤ Vnosa fluora iz hrane, vode in izdelkov ustne nege ??

### DOLOČANJE fluora v s fluorom bogatih virih je POMEMBNO za:

- ➡ Določitev dnevnega vnosa fluora v človeško telo iz različnih virov hrane – v katerih primerih je ta vnos previsok??
- ➡ Določitev meje med koristnim in škodljivim odmerkom fluora

Vnos fluora ima največji vpliv pri **majhnih otrocih** in **dojenčkih**, saj lahko že nizke koncentracije vplivajo na zdravje in razvoj

Fluor dokazano prehaja preko placente in preko materinega mleka na otroka...



Količine fluora v otroških čajih, v čajih za nosečnice in doječe matere

### Preučiti smotrnost uporabe fluorovih tablet pri otrocih in dodajanja fluora v sredstva za nego zob

Fluor je prisoten povsod v okolju, še posebno ob večjih naravnih virih → tudi prst kontaminirana z vulkanskim pepelom ter v okoljih kontaminiranih z različnimi industrijskimi viri fluora

### Preučiti obremenjenost Slovenskega okolja z industrijskimi viri fluora in njihov vpliv na človekovo zdravje

# Asfaltni in cementni kompoziti z dodatkom filtrskega prahu iz elektroobločne peči: študij vplivov na okolje

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V jeklarski industriji nastaja v proizvodnem procesu poleg ostalih odpadkov tudi filtrski prah iz elektroobločne peči, ki zaradi prašnate narave in velike količine močno obremenjuje odlagališča in okolje. V razvitih državah v zadnjih desetletjih industrijske odpadne surovine intenzivno uporabljajo kot alternativne materiale, ki uspešno nadomeščajo naravne surovine v gradbeništvu [1] in cestogradnji [2]. S tem se ohranjajo naravne surovine in zmanjšuje obremenitev odlagališč in okolja. Tovrstna uporaba odpadnih surovin ima tudi pozitivne ekonomske učinke. Pred kakršnokoli uporabo pa je potrebno podrobno preučiti in kritično oceniti dolgoročne vplive tako nastalih novih materialov na okolje. Pri oceni dolgoročnih vplivov novih materialov na okolje moramo upoštevati tudi, da sta biološka dostopnost in toksičnost posameznega elementa odvisni od kemijske oblike, v kateri se ta element nahaja (npr. trivalentni krom je esencialen, medtem ko je šestivalentni krom toksičen).

Preučili smo uporabnost filtrskega prahu za pripravo asfaltnih in cementnih kompozitov, ki bi jih lahko uporabljali v cestogradnji in gradbeništvu. V ta namen smo pripravili stabilne kompaktne in zdrobljene asfaltne kompozite z dodatkom 2 % filtrskega prahu, ter kompaktne in zdrobljene cementne kompozite brez in z dodatkom 1,5 % filtrskega prahu. Dolgoročne vplive materialov, ki vsebujejo filtrski prah smo preučili z izlužitvenimi testi na osnovi difuzije. Kot izluževalno sredstvo smo uporabili vodo in slano vodo ter časovno (pol leta) sledili izluževanju celotnega in šestivalentnega kroma. Na koncu poskusa smo v izlužkih določili tudi koncentracije nekaterih ostalih kovin (Mo, Co, V, Cu, Zn, K, Cd, Pb, Ni, Fe, Ca, Mg, Mn).

Rezultati so pokazali, da je krom v izlužkih asfaltnih in cementnih kompozitov prisoten skoraj izključno v šestivalentni obliki. Ugotovili smo, da se je šestivalentni krom izlužil le iz zdrobljenih asfaltnih kompozitov z dodatkom filtrskega prahu. Koncentracija izluženega šestivalentnega kroma v vodi po šestih mesecih ni presegla  $220 \mu\text{g L}^{-1}$  in v slani vodi  $150 \mu\text{g L}^{-1}$ . Pri cementnih kompozitih se je šestivalentni krom izlužil le iz zdrobljenih cementnih kompozitov z dodatkom filtrskega prahu v slani vodi. Po šestih mesecih koncentracija šestivalentnega kroma ni presegla  $100 \mu\text{g L}^{-1}$ . Iz rezultatov je bilo razvidno, da se šestivalentni krom izlužuje pretežno iz cementa in le v manjšem deležu iz filtrskega prahu. Izluževanje nekaterih ostalih kovin (Mo, Co, V, Cu, Zn, K, Cd, Pb, Ni, Fe, Ca, Mg, Mn) je bilo zamemarljivo.

Na osnovi naše raziskave lahko zaključimo, da asfalti in cementi z dodatkom filtrskega prahu ne predstavljajo nevarnosti za okolje in jih lahko uporabimo za različne namene v cestogradnji in gradbeništvu.

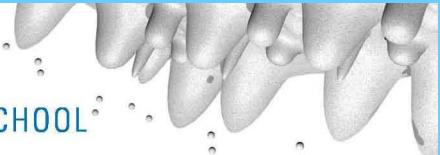
## Literatura:

- [1] T. Šturm, R. Milačič, S. Murko, M. Vahčič, A. Mladenovič, J. Strupi-Šuput, J. Ščančar. The use of EAF dust in cement composites : assessment of environmental impact. *J. hazard. mater.*, vol. 166, pp. 277-283, 2009.
- [2] M. Vahčič, R. Milačič, A. Mladenovič, S. Murko, T. Zuliani, M. Zupančič in J. Ščančar. Leachability of Cr(VI) and metals from asphalt composites with addition of filter dust. *Waste Manag.*, vol. 12, pp. 2667-2674, 2008.



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## ASFALTNI IN CEMENTNI KOMPOZITI Z DODATKOM FILTRSKEGA PRAHU IZ ELEKTROOBLOČNE PEČI: ŠTUDIJ VPLIVOV NA OKOLJE

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### NAMEN DELA

Preučiti uporabnost filtrskega prahu iz elektroobločne peči za pripravo asfaltnih in cementnih kompozitov, ki bi jih lahko uporabljali v cestogradnji in gradbeništvu.

Kritično oceniti okoljske vplive stabilnih asfaltnih in cementnih kompozitov z dodatkom filtrskega prahu.

### REZULTATI

- Izluženi krom je skoraj povsem v šestvaletni obliki
- Cr(VI) se je izlužil le iz zdrobljenih asfaltnih kompozitov z dodatkom filtrskega prahu (v vodi 220 µg/L, v slani vodi pa 150 µg/L)
- Cr(VI) se je izlužil le iz zdrobljenih cementnih kompozitov z dodatkom filtrskega prahu v slani vodi (100 µg/L) à Cr(VI) se je izlužil pretežno le iz cementa
- Izluževanje nekaterih kovin je bilo zanemarljivo

### EKSPERIMENT

Pripravili smo:

- Asfaltne kompozite brez in z dodatkom 2% filtrskega prahu
- Zdrobljene asfaltne kompozite brez in z dodatkom 2% filtrskega prahu
- Cementne kompozite brez in z dodatkom 1,5% filtrskega prahu
- Zdrobljene cementne kompozite brez in z dodatkom 1,5% filtrskega prahu

Dolgoročni vplivi novih materialov z dodanim filtrskim prahom na okolje smo preučevali z izlužitvenim testom na osnovi difuzije (izluževalno sredstvo je voda in slana voda).

-V izlužkih smo določili pH, koncentracije celotnega Cr in Cr(VI), ter na koncu poskusa še koncentracije nekaterih izbranih elementov.

### ZAKLJUČEK



Asfaltni in cementni kompoziti z dodatkom filtrskega prahu ne predstavljajo nevarnosti za okolje in jih lahko uporabimo za različne namene v cestogradnji in gradbeništvu.

# Stabilni izotopi dušika – možnost uporabe pri kontroli ekološke pridelave zelenjave

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Ekološko pridelana zelenjava na trgu dosega višje cene v primerjavi s tisto, pridelano na konvencionalen način. Ker zaradi želje pridelovalcev po doseganju večjih dobičkov obstaja možnost goljufij oziroma nepravilnega označevanja konvencionalno pridelane zelenjave z oznako "ekološki", se pojavlja potreba po metodah za preverjanje avtentičnosti ekoloških pridelkov. Z metodo izotopske masne spektrometrije (IRMS) smo ugotavljali primernost uporabe izotopske sestave dušika ( $\delta^{15}\text{N}$ ) kot potencialnega indikatorja ekološke pridelave, in sicer na primeru lončnega poskusa s solato (*Lactuca sativa* L.) ter na vzorcih zelenjave (endivija, motovilec, rabič, por, peteršilj, itd.), kupljene na slovenskem trgu. Študija temelji na predpostavki, da imajo konvencionalno pridelane rastline nižje  $\delta^{15}\text{N}$  vrednosti v primerjavi z enakimi rastlinami, gnojenimi z organskim gnojilom, saj imajo zaradi različnih procesov izdelave gnojil sintetična gnojila nižje  $\delta^{15}\text{N}$  vrednosti (okrog 0‰) od organskih (med +10‰ in +25‰). V lončnem poskusu se je  $\delta^{15}\text{N}$  izkazal kot hiter in relativno poceni indikator gnojenja s sintetičnim dušikovim gnojilom, vendar samo v primeru enkratne aplikacije gnojila. Srednja izmerjena  $\delta^{15}\text{N}$  vrednost v solati, gnojeni z organskim gnojilom, je bila 9,6‰, v solati, gnojeni s sintetičnim gnojilom pa 5,3‰. V primeru dognojevanja kombinirane uporabe organskih in sintetičnih gnojil pa z uporabljeno IRMS metodo nismo mogli zanesljivo potrditi, kar pomeni, da bi pridelovalci solate lahko prikrili uporabo sintetičnega gnojila, če bi letega uporabili v kombinaciji z organskim gnojilom. Preliminarni rezultati analiziranih vzorcev zelenjave, kupljene na slovenskem trgu, kažejo jasne razlike v  $\delta^{15}\text{N}$  med konvencionalno pridelano zelenjavo (nižje  $\delta^{15}\text{N}$  vrednosti) ter zelenjavo, ki naj bi bila pridelana ekološko (višje  $\delta^{15}\text{N}$  vrednosti), kar kaže na to, da je bila analizirana zelenjava označena pravilno.



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## STABILNI IZOTOPI DUŠIKA - MOŽNOST UPORABE PRI KONTROLI EKOLOŠKE PRIDELAVE ZELENJAVE

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# IPSSC: Razvoj metod za speciacijo organokositrovih spojin z GC-ICP-MS

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Kositer in kositrove zlitine so v uporabi od bronaste dobe dalje. Sprva so se kositer in njegove zlitine uporabljali predvsem za izdelavo raznih uporabnih izdelkov (posode, orožje..), danes pa se večina kositra porabi za sintezo organokositrovih spojin (OKS).

Prve (OKS) je sintetiziral sir Edward Frankland leta 1849. OKS vsebujejo centralni kositrov (Sn) atom, na katerega so vezane do štiri organske skupine (alkilne ali arilne). Spadajo v skupino organokovinskih spojin, splošno pa jih lahko zapišemo z formulo  $R_{4-n}SnX_n$ . Prve praktične aplikacije OKS so razvili leta 1940, ko so v industriji plastike ugotovili, da OKS zelo dobro stabilizirajo plastične mase. Te pod vplivom svetlobe in toplote razpadajo (postanejo krhke in izgubijo barvo). V petdesetih so ugotovili, da imajo OKS spojine tudi biocidne lastnosti, tako jih danes uporabljam za zaščito lesa, fungicide, miticide ter strupe za glodalce in insekte [1], [2].

OKS spojine so zelo strupene že pri nizkih koncentracijah (ng/L). Povzročajo spremembo spola pri nekaterih vrstah morskih polžev in okvare pri tvorbi lupin školjk, pri sesalcih pa okvare imunskega in živčnega sistema ter encimatske aktivnosti. Zaradi široke uporabe in dolge razpolovne dobe so OKS danes prisotne v različnih ekosistemih [2], [3].

Po strupenosti si sledijo OKS spojine v naslednjem zaporedju: trisubstituirane OKS > disubstituirane OKS > mosubstituirane OKS > tetrasubstituirane OKS > anorganski Sn [3].

Speciacija OKS spojin je izjemnega pomena za varovanje okolja in zdravja ljudi. Za določanje posameznih zvrsti OKS so danes najbolj razširjene kromatografske tehnike sklopljene z različnimi masnimi detektorji (ICP-MS, MS, PFPD,...).

Cilj dela je bil razviti hitreje in učinkovitejše analizne metode za hkratno speciacijo 12 najpogostejših OKS (metil-, butil-, fenil- in oktil- kositrovih spojin) v različnih okoljskih vzorcih (vode, sedimenti, zemlje, organski vzorci). Razvoj speciacijskih metod je vključeval preizkušanje različnih pufrov, ekstrakcijskih reagentov, derivatizacijskih reagentov ter optimizacijo pogojev derivatizacije, ekstrakcije in kromatografskih pogojev. Za ločbo in detekcijo OKS smo uporabili plinsko kromatografijo sklopljeno z masno spektrometrijo z induktivno sklopljeno plazmo (GC-ICP-MS). Z razvitimi metodami smo uspešno ločili in kvantitativno določili metil-, butil-, fenil- in oktil- kositrove spojine v okoljskih vzorcih. Razvite analizne metode so občutno skrajšale analizni čas in omogočile hkratno določitev 12 OKS spojin v okoljskih vzorcih.

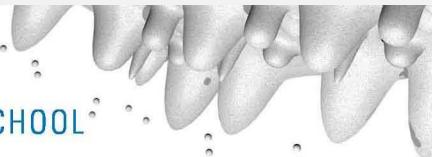
## References:

- [1] M. Hoch, Organotin Compounds in the environment – an overview, Applied Geochemistry, 16 (2001), 719-743.
- [2] J.M. Batt, The world of organotin chemicals: Applications, Substitutes and the environment, [www.ortepa.org/WorldofOrganotinChemicals.pdf](http://www.ortepa.org/WorldofOrganotinChemicals.pdf)
- [3] K. Fent, Ecotoxicology of organotin compounds, Crit. Rev. Toxicol. 26 (1996) 1.



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## RAZVOJ METOD ZA SPECIACIJO ORGANOKOSITROVIH SPOJIN Z GC-ICP-MS

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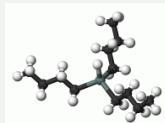
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### Uvod:

Organokositrove spojine (OKS) sodijo med industrijsko najširše uporabljane organokovinske spojine. Prva in še danes najpomembnejša aplikacija OKS je stabilizacija plastičnih mas, sledi uporaba za zaščitne premaze, katalizo itd... Zaradi dolgega razpolovnega časa in širokega spektra uporabe so OKS posledično zelo razširjene v okolju. Ker so poleg uporabnosti te spojine tudi zelo toksične, tako za morske organizme (povzročajo spremembo spola pri polžih, nepravilnosti pri tvorbi lupin, ...) kot za sesalce (okvare imunskega, endokrinega in živčnega sistema) je njihov stalen nadzor in speciacija izjemnega pomena za varovanje okolja in zdravje ljudi.



Lastnosti in toksičnost OKS so funkcija substitucije centralnega Sn atoma, na katerega so lahko vezane do štiri organske skupine (alkilne ali arilne). Splošno lahko OKS zapišemo s formulo  $R_{4-n}SnX_n$ . Toksičnost pada v smeri : tri- > di- > mono- > tetra-substituiranim.



Tributil kositer

Nezaščiten ladijski trup

Cilj dela je bil razvoj hitrejših in učinkovitejših metod za simultano speciacijo 12 napogostejših OKS (metil-, butil-, fenil- in oktil-kositrov) v različnih okoljskih vzorcih z uporabo 15 m GC kolone, testiranjem različnih ekstrakcijskih pogojev in pufrov. Razvite metode uporabljamo za analizo realnih vzorcev (rečne, morske, odpadne, izcedne vode).

### Speciacija OKS

Ekstracija OKS iz vzorca

Derivatizacija

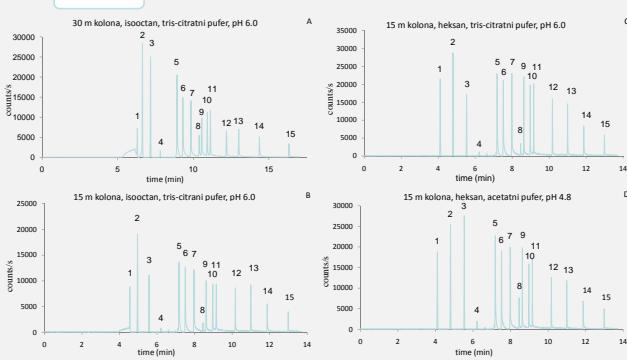
Prenos v organsko fazo

Ločba in analiza organske faze z GC-ICP-MS

### Razvoj analiznega postopka



### Rezultati



### Lastnosti GC-ICP-MS

#### Prednosti Uporabe

Odstranitev interferenc ki se pojavljajo pri GC-MS ali GC-PFPD

Nizka meja detekcije

Veliko linearno območje

#### Slabosti tehnike

Dražja

Zahtevnija za uporabo

### Zaključki in ugotovitve

- Razvite metode so občutno skrajšale čas analize z GC-ICP-MS
- Posledica je prihranek energije, časa in možnost analize večje količine vzorcev v istem času
- Metoda omogoča simultano določanje 12 OKS v okoljskih vzorcih.
- Fostatni in karbonatni pufer nista uporabna za ekstrakcijo OKS v morskih vzorcih zaradi izobarjanja soli.
- Ugotovili smo da je TRIS/citratni pufer pri pH 6.0 optimalni za analizo OKS v okoljskih vodenih vzorcih.
- Ekstrakcija z heksanom je reproducibilna in da stabilen signal preiskovanih OKS.



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## **Informacijske in komunikacijske tehnologije (Information and Communication Technologies)**

# Providing Trust and Reputation in Peer-to-Peer Networks

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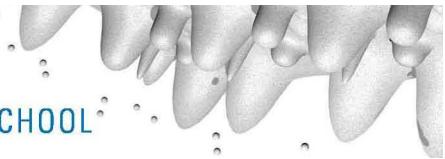
The Internet has already set its users free of any kind of building infrastructure. It has evolved beyond e-mail, content, and e-commerce, becoming a true platform that combines the qualities of service of enterprise computing with the ability to share resources across the web. Moreover, Internet is becoming more and more distributed, and so are the expectations for its aligning protocols. According to Ipoque Internet Study for 2008/09, P2P generates most of the Internet traffic in all regions (even up to 70% in Eastern Europe), with predictions that it will account for more than 90% by 2013. This huge amount of P2P usage is due to its open, anonymous and self-organizing nature. P2P computing has incredibly wide range of usage: from simple every-day communication (Skype), content sharing (BitTorrent), and e-commerce (eBay), to great research projects that require the processing power of numerous interconnected computers (SETI@Home). The whole area of distributed computing is a hot bed of significant development that has been generating amazing advances [3] [4].

Nevertheless, P2P systems are not just about distributing information. Their open nature has attracted vast amount of users and dragged even greater attention to attackers who use impressive amount of resources trying to subvert these systems. There is now a strategic shift by the attackers that mainly target personal computers with high Internet connectivity that can be useful for the miscreants. The complexity of distributed networks brings equally complex issues for defending them against attacks [1] [2]. Future systems are not likely to ease that job, as new threats will emerge due to the billions of components comprising them. In this new “world of emerging technological opportunities”, reputation is one of the few tools that can still provide trust: trust among the users of distributed services, and even the trust necessary to maintain reliability and accountability of these services [3].

Our contribution is attributed through BarterCast, a fully distributed reputation mechanism that is part of the NextShare software developed in the P2P-Next project [4]. We have mapped BarterCast’s design onto the Taxonomy of Trust proposed by the Stanford Peer Research group and obtained important conclusions mainly related to the design and partially to the purpose of the mechanism [3]. While BarterCast is more reputation oriented (choosing appropriate collaborator based on her past behavior and performance, incentivizing collaborative behavior etc.), there are security issues that have not been tackled yet in the present design. Some of them are identity and trust management, threat modeling, information integrity check and information time convergence. Our research not only considers the social aspect of a reputation system design, but also strives to base users’ collaboration on strong security mechanisms. Fostered reputable and trustworthy collaboration would lead any Internet based application closer to its “Future Internet” ideal.

## References:

- [1] Meulpolder, M. and Pouwelse, J. A. and Epema, D. H. J. and Sips, H. J., BarterCast: A Practical Approach to Prevent Lazy Freeriding in P2P Networks, Proc. of the 6th International Workshop on Hot Topics in Peer-to-Peer Systems (Hot-P2P’09) in conjunction with IPDPS 2009, May, 2009, 1-8,
- [2] J. A. Pouwelse and P. Garbacki and D.H.J. Epema and H. J. Sips, The BitTorrent P2P File-Sharing System: Measurements and Analysis, , 2005,
- [3] Marti, Sergio and Garcia-Molina, Hector, Taxonomy of trust: Categorizing P2P reputation systems, Management in Peer-to-Peer Systems, Computer Networks, 50, 4, March, 2006, 50, 472--484, <http://dx.doi.org/10.1016/j.comnet.2005.07.011>;



## PROVIDING TRUST AND REPUTATION IN PEER-TO-PEER SYSTEMS

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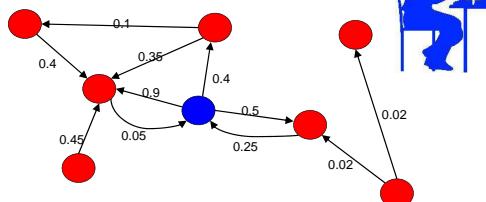
### WHY?

Distributed computing: hot bed of significant development that is generating amazing advances

P2P computing: distributed computing paradigm of sharing resources on the Internet

P2P open and anonymous nature  
⇒ an ideal medium for attackers to spread malicious content

Information asymmetry in on-line collaboration

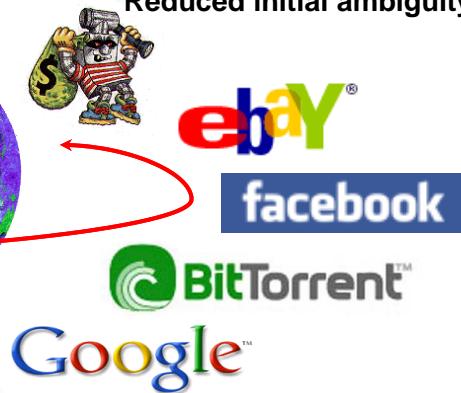
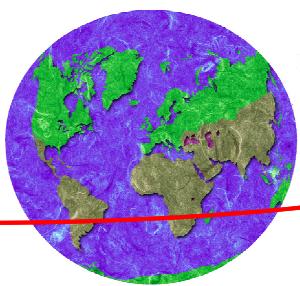


### HOW?

Reputation mechanisms  
[ BarterCast: Fully distributed BitTorrent-based ] \*

Reputation rationale:

- Past behavior predicts future behavior
- Poor behavior deterred by loss of future business



### RESULT

Minimized privacy concerns and cost

Data protection

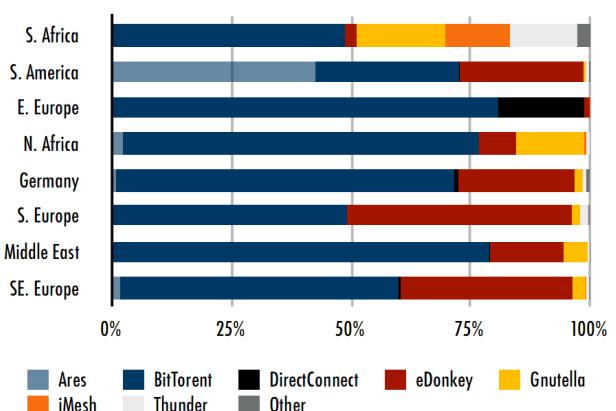
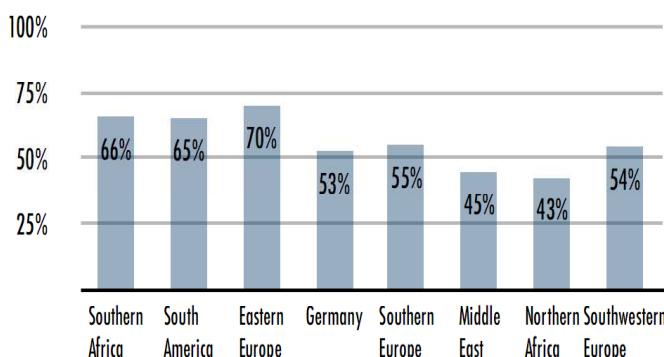
Maximized resource and data relevance and ease of use

Reduced initial ambiguity

### OBJECTIVES

The problem of deciding whether to interact is a process of judging how cooperatively prospective partners are likely to be with respect to the expected outcome.

Principals gather information, evaluate and enforce agreed upon policies (if necessary) without reliance on central management authority.



\* <http://www.p2p-next.org/>

# Multiobjective genetic discovery of driving strategies

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Vehicle driving consumes time and energy (fuel, electricity etc.). Usually both have to be minimized. Minimizing the consumption of one of them leads to increasing the consumption of the other. To find driving strategies that take into consideration both objectives, we have implemented a multiobjective genetic algorithm that constructs driving strategies as sets of rules. Optimal sets of rules consist of non-dominated solutions and therefore cannot be sorted based on quality since each solution represents a particular trade-off between the two objectives. The final strategy selection is done by the user who uses higher-level information to select the most preferred strategy from the found best solutions.

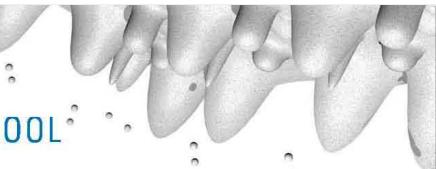
To test the strategies, we implemented a vehicle simulator. It is defined with the engine, transmission, aerodynamics, braking and wheel characteristics. It simulates driving on a predefined route that consists of segments. Each segment is defined with its length, inclination, radius and velocity limit. Vehicle driving is controlled with a strategy consisting of a set of rules. Each rule has the following form: IF vehicle characteristics INSIDE interval1 AND segment characteristics INSIDE interval2 THEN USE throttle percentage AND gear OR braking percentage.

The implemented multiobjective genetic algorithm is based on NSGA-II [1]. It has the characteristics of genetic algorithms [2] as follows. It randomly initializes a set of driving strategies. Then these strategies are improved over generations where in each generation pairs of strategies are randomly selected, their information is exchanged, their rules are randomly changed, a randomly selected rule is removed and a randomly created rule is added, and the strategies are finally evaluated and added to the set of strategies [3]. This is done in such a way that each strategy is selected once on average in each generation. In addition to these classical genetic algorithm mechanisms, the NSGA-II has dedicated mechanisms in order to meet the multiobjective algorithm requirements: in addition to minimization of the objectives, it preserves the diversity of the strategies with respect to the objectives. This is done using the non-dominated sorting and the crowding distance mechanisms known from the NSGA-II.

Using the described algorithm, we performed preliminary numerical experiments in multiobjective discovery of driving strategies for several predefined simple routes [4]. The results in the form of nondominated sets of solutions are promising and stimulative for further investigation in this problem domain. Future work will include improvements of the algorithm efficiency, its testing on the routes defined with real data, and comparison of our results with the results of other algorithms.

## References:

- [1] K. Deb, S. Agrawal, A. Pratap, and T. Meyarivan. A fast elitist non-dominated sorting genetic algorithm for multi-objective optimisation: NSGA-II. *Proceedings of the 6th International Conference on Parallel Problem Solving from Nature*, pp. 849–858, 2000.
- [2] A. E. Eiben and J. E. Smith. *Introduction to Evolutionary Computing*. Springer, 2003.
- [3] K. A. De Jong. *Evolutionary Computation: A Unified Approach*. MIT Press, 2006.
- [4] E. Dovgan, M. Javorski, and B. Filipič. A Multiobjective Genetic Algorithm for Discovering Car Driving Strategies. Technical Report IJS-DP 10402. Jožef Stefan Institute, Ljubljana, 2010.



## MULTIOBJECTIVE GENETIC DISCOVERY OF DRIVING STRATEGIES

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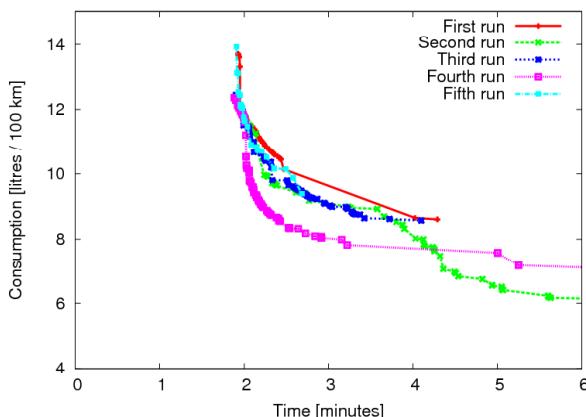
### Problem Description

- Vehicle driving on a route from location A to location B
- Vehicle defined with:
  - engine characteristics
  - transmission characteristics
  - aerodynamic characteristics
  - braking characteristics
  - wheel characteristics
- Route consists of segments
- Segment defined with:
  - length
  - inclination
  - radius
  - velocity limit

### Goal

- Find driving strategies regarding two objectives that have to be minimized:
  - traveling time
  - fuel consumption
- Find set of strategies:
  - not worse with respect to both objectives
  - heterogeneous with respect to both objectives

Solutions for a given route found in five experimental runs



### Representation of Driving Strategies

- Strategies as sets of rules
- Rule form:
  - IF vehicle characteristics INSIDE interval1 AND segment characteristics INSIDE interval2 THEN USE throttle percentage AND gear OR braking percentage

### Solving the Problem

- Find strategies with a multiobjective genetic algorithm based on NSGA-II
- First, random initialization of strategies
- Then, strategy improvement step-by-step, in each step:
  - randomly select two strategies and two rules of these strategies
  - exchange information between the selected rules
  - randomly change the rules
  - delete a randomly selected rule
  - add a randomly created rule
  - evaluate the obtained strategies
  - add these strategies to the set of existing strategies
- Periodically remove the worst and too similar strategies with respect to the objectives

### Car driving interface



# Context-Aware MAS for Remote Elderly Care

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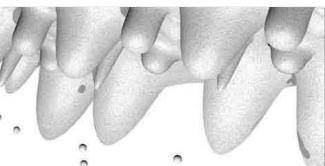
The population of developed societies is rapidly aging and there is an increased pressure on the working-age population to take care for the elderly people. Several systems were introduced in recent years addressing some issues related to this problem. However, most of the systems developed in this context are based on pre-defined fall detection [1, 4, 5], meaning that they are capable of recognizing simple hazardous situations and triggering alarms. We aim at augmenting the scope of detection and user-adaptation of the system by enriching it with more complex schemes for reconstruction, interpretation and adaptation. In particular, we are exploring the possible applications of intelligent agents in home environment, studying how they can be employed to realize cognitively-enhanced multi-agent system (MAS) which is capable of robust and reliable monitoring the elderly person in his or her daily activities. Not only the elderly will profit from the system, but also their families and caregivers, since the burden on them will be substantially reduced.

In this context, our efforts are endeavoring to integrate state-of-the-art technology in the fields of multi-agent systems, filtering, machine learning and outlier detection in order to produce a single, multi-functional system to be deployed in a home environment. The system is composed of a multitude of agents that are arranged hierarchically, providing increasingly more abstract situational awareness, and in parallel, exploiting the principle of multiple knowledge. We present the following groups of agents: the *refining* agent group where the agents filter noise, compute derived attributes and map raw data with the human body model; the *reconstruction* agent group, a set of agents which reconstruct a user's 3D position and a posture in the environment [3]; the *interpretation* agent group, which provides the awareness by explaining the reconstruction results and reacts to emergency or hazardous situations when detected; the *prevention* agent group, a swarm of agents monitoring a variety of measurable user parameters ranging from posture characteristics to daily activities, and reacts to contingencies and foreseeing inconsistencies in the user's behavior indicating a decreased psychophysical state or even a disease; and finally, the *cognitive* agent group which is able to construct the cognitive state of the integrated system from increasingly more abstract context awareness, and perform reasoning on a wider spectrum of information with an integrated reasoning strategy.

The system has been tested in several on-line demonstrations. The results in the fall detection experiment showed that context dependent reasoning can detect the complex scenarios usually misinterpreted by acceleration-based systems [2]. In addition, the preliminary results on disability detection are encouraging, showing a potential for premature discovery of a potential health problem that may lead to a perilous condition.

## References:

- [1] A. K. Bourke and G. M. Lyons. A threshold-based fall-detection algorithm using a bi-axial gyroscope sensor. *Medical Engineering & Physics*, 30(1):84–90, 2008.
- [2] Bostjan Kaluza, Violeta Mirchevska, Mitja Lustrek, Igone Velez, and Matjaz Gams. Ubiquitous care system to support independent living: Preliminary results. In: *Roots for the future of amb. intelligence*, pp. 308–315, 2009.
- [3] Mitja Luštrek and Boštjan Kaluža. Fall detection and activity recognition with machine learning. *Informatica*, 33(2):197–204, 2009.
- [4] J. I. Pan, C. J. Yung, C. C. Liang, and L. F. Lai. An intelligent homecare emergency service system for elder falling. In: *World Congress on Medical Physics and Biomedical Engineering 2006*, pp. 424–428, 2006.
- [5] T. Zhang, J. Wang, J. Liu, and P. Hou. Fall detection by wearable sensor and one-class SVM algorithm. In: *Lecture Notes in Control and Information Science*, pp. 858–863, 2006.



## Context-Aware MAS for Remote Elderly Care

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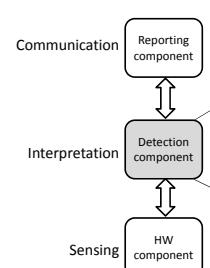
### MULTI-AGENT SYSTEM (MAS)

A multi-agent system is a collection of software agents that work in conjunction with each other cooperatively or competitively to achieve some individual or collective task. Multi-agent systems can be used to solve problems which are difficult or impossible for an individual agent or monolithic system to solve.

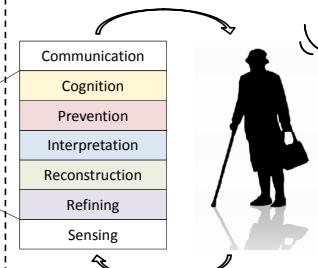
### REMOTE ELDERLY CARE

Care at home is often preferable to patients and is usually less expensive for care providers than institutional alternatives. New developments in assistive technology are likely to make an important contribution to the remote care of elderly people improving older people's safety, security and ability to cope at home. Systems introduced in this context are mainly focused on fall detection, meaning that they are capable of recognizing simple hazardous situations, triggering alarms and notifying caregivers or relatives.

### Components of a typical care system architecture

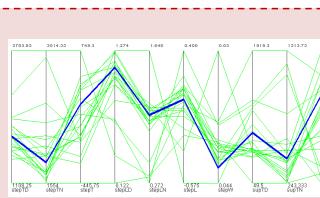


### Cognitively-enhanced architecture

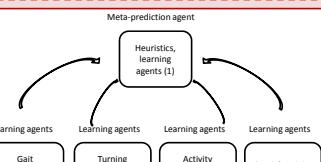


### OUR SOLUTION

We aim at augmenting the scope of detection component (marked gray) by enriching it with more complex schemes for reconstruction, interpretation and prevention. In particular, we present a complex MAS architecture able not only to detect falls from sensor data but also to reason from context and moreover, to recognize unusual behavior as an indicator of a potential health problem. On the right is illustrated the subsumption architecture that organizes agents into groups, and groups into hierarchical context awareness. The architecture is further elaborated below in the middle figure presenting interactions between agent groups. Particular group is presented in one of the surrounding boxes with corresponding color.



Meta-prediction agent



### PREVENTION AGENTS

A set of agents observe user's behavior, where each of them collects specific subset of behavior data ranging from posture characteristics to daily activities. These agents automatically build behavior models that are constantly updated and classify the current behavior to recognize changes that might lead to a disease or illness. Since each agent only partially observes user's behavior, an integration agent collects their observations and merges them into the final behavior observation. Figure on the right shows measured behavior of gait characteristics agents. Each measured attribute is presented on one vertical axis, while green intersecting lines are previous measurements of normal behavior. New measurement, marked with blue line, represents new measurement.

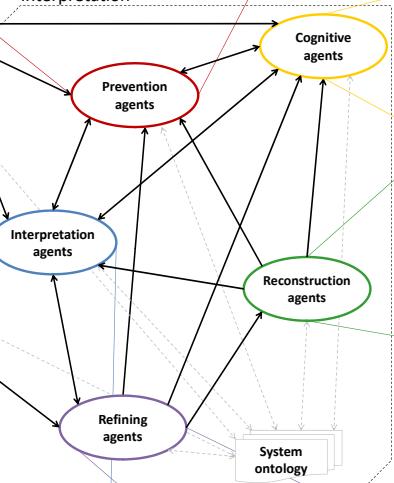
### RESULTS

We have designed two sets of experiments showing the capabilities of the interpretation and prevention group of agents. The first experiment was devoted to fall detection where we presented complex situations that can be easily misinterpreted by an acceleration-based fall detector. The system successfully recognized all falls and had some problems recognizing sliding from the chair. However, the system raised only one false alarm, achieving overall accuracy of 91.33 %. The second experiment verified how the prevention group of agents adapts to a person and detects disabilities. After two training days, the user started limping (third day) and walking slow (fourth day), which was successfully recognized by at least one statistics-agent group.

### Communication



### Interpretation



### Cognitive agents



### COGNITIVE AGENTS

The system design includes the cognitive state of the user, although not implemented yet in the tested version. The cognitive layer will include the attributes related to the cognitive state of the user (heart rate, blood pressure, voice etc.), thus constructing not only the physical, but also the cognitive state of the user. These agents use the cognitive state to perform reasoning on a wider spectrum of information with an integrated reasoning strategy.

### Reconstruction agents



### RECONSTRUCTION AGENTS

The reconstruction agents determine location and posture of a person at a specific time. There are two competitive agent groups performing this task, namely machine-learning and expert-knowledge agents. The final decision is made by meta-prediction agents that combine their classifications by exploiting the power (accuracy) of particular agents.

Three figure below show: top view of the apartment (left) indicating area where the user is; side view (middle) showing skeleton of the user as seen; and recognized activity (right), i.e. how the system perceives the current posture of the user by various agents.

### INTERPRETATION AGENTS

The interpretation group of agents contracts physical awareness of a person in the environment and detects emergency situations which are caused by a fall or a sudden health problem. These situations are reflected by a person lying or sitting at an inappropriate place (e.g. on the ground) for a prolonged period of time. The group is structured similar as the reconstruction agent group: it consists of expert knowledge agents, prediction agents based on machine-learning algorithms, while the final decision is made by the meta-prediction agent.

The image below group architecture shows explanations of alarm messages triggered by the particular subgroup.



Rules:

FALLING DETECTED AND PERSON LYING AT IMPROPRIATE PLACE!

Machine Learning:

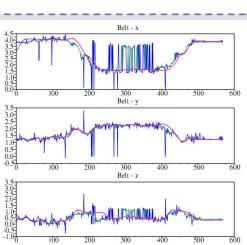
Final:

FALLING DETECTED AND PERSON LYING AT IMPROPRIATE PLACE!

ALERT

### REFINING AGENTS

These agents filter noise (using not only one method such as Kalman's filter, but five independent methods in the form of agents that provide their observations), compute derived attributes and map raw data with the human body model. In this way they provide a uniform presentation of all available data of the body. Three graphs on the right present x, y and z coordinates of a tag attached to the belt. The vertical axis is distance (meters) while horizontal axis is time (1/10 of a second). The blue line presents original data as provided by sensing agent, the green line is after the median filtering is applied and the red line after the agent that takes into account constraints of human body.



ACKNOWLEDGMENTS: This work was partly supported by the Slovenian Research Agency under the Research Programme P2-0209 Artificial Intelligence and Intelligent Systems, and partly from the European Community's Framework Programme FP7/2007–2013 under grant agreement No. 214986. The work of Violeta Mirchevska was partly financed by the European Union, European Social Fund. We would like to thank Domen Marinčič, Rok Pilat, Boža Čveljković and Blaž Štrle for suggestions, discussions and help with the programming.

2nd Jožef Stefan International Postgraduate School Students Conference, May 27, 2010, Ljubljana, Slovenia

# Nadzor delovanja laboratorijske opreme

Blaž Mahnič<sup>1,2</sup>, Domen Marinčič<sup>1</sup>

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Nadzor nad hrambo vzorcev v laboratorijih je zelo pomemben, saj lahko že zelo majhna napaka povzroči veliko škode. Eden izmed ključnih elementov za optimalno delovanje laboratorija je stalen nadzor nad delovanjem laboratorijske opreme. Neprestano delovanje predstavlja za opremo (npr. hladilne skrinje) velik izziv. Poleg primarnega shranjevanja materialov je nujno tudi nadzorovanje delovanja opreme za hranjenje podatkov o vzorcih, zdravilih, pacientih in opremi. Meritve okoljskih parametrov v laboratorijih potekajo s pomočjo raznih merilnih naprav, ki v določenih časovnih intervalih zapisujejo podatke o izmerjenih vrednostih v podatkovno bazo.

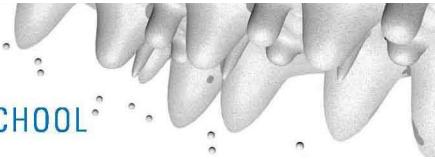
Za nadzor nad vrednostmi teh meritov smo razvili sistem iLab, ki temelji na uporabi teorije ekspertnih sistemov [1]. Znanje, ki je potrebno za pravilno delovanje ekspertnega sistema, je opisano v obliki množice pravil, katera uporabnik vnese v sistem s pomočjo uporabniškega vmesnika. Pravila opisujejo dovoljene oziroma zaželjene pogoje, ki morajo veljati za prostore, opremo, vzorce in delavce, na primer: temperatura v prostoru P ne sme preseči 15 °C. V primeru, da je eno od pravil kršeno, ekspertni sistem sproži alarm oziroma opozorilo ter poda opis trenutnega stanja uporabniku preko grafičnega vmesnika.

Rezultat našega dela je ekspertni sistem z uporabniku prijaznim uporabniškim vmesnikom. Sistem deluje tako, da uporabnika opozori o nepravilnostih delovanja opreme. V tesni povezavi z delovanjem opreme nadzoruje tudi področje analize in shranjevanja vzorcev. To pomeni, da v primeru ko oprema ne deluje dobro, lahko dvomimo v kakovost vzorcev in ne smemo zaupati rezultatom analiz.

Razvit prototip je primeren za uporabo v različnih laboratorijih [2], od zasebnih do javnih (v bolnišnicah, zdravstvenih domovih in veterinarskih postajah). Uporaba take aplikacije lahko bistveno zmanjša stroške hranjenja vzorcev in s skoraj optimalnim shranjevanjem zagotavlja in ohranja njihovo kakovost.

## Literatura:

- [1] J. C. Giarratano and G.D. Riley. *Expert Systems, Principles and Programming*. Thomson Course Technology, 2005.
- [2] J.E.H Stafford. *Advanced LIMS Technology, Case Studies and Business Opportunities*. Kluwer Academic Publishers, 1995.



## Nadzor delovanja laboratorijske opreme

### Blaž Mahnič

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MENTOR: dr. Domen Marinčič  
Inštitut Jožef Stefan, Jamova cesta 39, 1000 Ljubljana



#### Problem

- neustrezeno delovanje laboratorijske opreme
- odpis celotne serije zdravil, vzorcev, proizvodnih sestavin
- stalno spremljanje delovanja opreme
- neprekinjeno delovanje opreme pomeni velik izviv
- kakovost vzorcev močno odvisna od pravilnega delovanja opreme

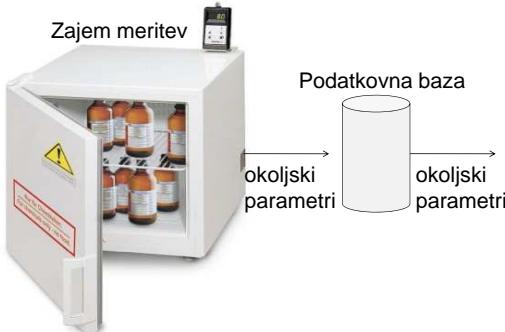


#### Opis rešitve

- izvajanje meritev okoljskih parametrov (oprema, prostori, vzorci)
- definiranje množice pravil s pomočjo uporabniškega vmesnika
- primer pravila: temperatura v prostoru  $P$  ne sme preseči  $15^{\circ}\text{C}$
- ekspertni sistem stalno preverja definirana pravila nad zajetimi okoljskimi parametri
- ob morebitnem kršenju pravila se sproži alarm, sistem opozori uporabnika



#### Zajem meritev



#### Ekspertni sistem *množica pravil* (preverjanje pravil)

opozorila, alarmi

#### Uporabniški vmesnik

Vložiti - Uporabniški vmesnik	
<input type="checkbox"/> Aktivni dogodek	<input type="checkbox"/> Neaktivni dogodek
<input type="checkbox"/> Potrjena opozorila	<input type="checkbox"/> Nepotrjena opozorila
<input type="checkbox"/> Potrjena in nepotrjena opozorila	
Datum OD:	Datum DO:
Izlan alarmi OD:	Izlan alarmi DO:
Potrjene alarmi OD:	Potrjene alarmi DO:
Pravilo ID: Podstrek Hrana	
Okupljeni parametri:	
Išči Podstrek filter Zadaj 30 zapored	
Zadaj aktivni izredčeni dogodek	
Zap. število Izredčeni dogodek Začetek Konec Opozorilo Kritičnost Čas potrditve	
403. 1 Kritično pravilo 2010-04-04 09:42... 2010-04-04 09:56... Preveriti mrežke Kritično 2010-04-13 18:31	
Vsi izredčeni dogodek	
Zap. število Izredčeni dogodek Začetek Konec Opozorilo Kritičnost Čas potrditve	
403. 1 Kritično pravilo 2010-04-04 09:42... 2010-04-04 09:56... Preveriti mrežke Kritično 2010-04-13 18:31	
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#### Cilji

- zmanjšanje stroškov hranjenja vzorcev
- povečanje zaloge vzorcev zaradi zmanjšanja pokvarljivosti le-teh
- zmanjšanje stroškov v zvezi s periodičnim fizičnim pregledovanjem opreme
- poslovna uspešnost, konkurenčna prednost, razvoj

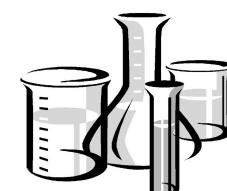


#### Uporaba

Uporaba take aplikacije lahko bistveno zmanjša stroške hranjenja vzorcev ter tako zmanjša proračunske odhodke . S skoraj optimalnim shranjevanjem zagotavlja in ohranja kakovost vzorcev.

#### Kje se lahko sistem uporabi?

- različni javni in zasebni laboratoriji
- bolnišnice, zdravstveni domovi, veterinarske postaje



# Learning Through Interaction

**Violeta Mirchevska<sup>1,3</sup>, Boštjan Kaluža<sup>2,3</sup>**

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This poster presents real-time learning through interaction. In sequential decision making domains and domains in which creating representative dataset is expensive and time consuming, learning through interaction is the only feasible way to train a system. Examples of such domains include system adaptation to particular user, control problems, learning to play games and similar.

Reinforcement learning is an approach for learning optimal action policy via experiencing, i.e. using observed reward in environment states. Reinforcement learning algorithms include adaptive dynamic programming, temporal difference learning and Q-learning[1]. Examples of successful applications of reinforcement learning are controller for sustained inverted flight on an autonomous helicopter [2] and learning to play the soccer game Keepaway[3].

We researched possibilities for adaptation of rule-based alarm detection system in the domain of remote elderly care using the CONFIDENCE system [4]. Experimental results show that reinforcement learning can be used for adaptation of the alarm detection system to the particular needs and preferences of the user.

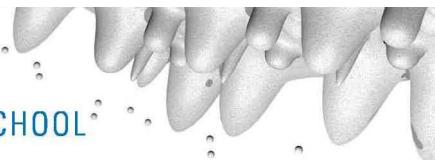
## References:

- [1] S. Russel and P. Norvig. *Artificial Intelligence: A Modern Approach, 2nd Edition*. Prentice Hall, 2003.
- [2] A. Y. Ng, A. Coates, M. Diel, V. Ganapathi, J. Schulte, B. Tse, E. Berger and E. Liang. Autonomous inverted helicopter flight via reinforcement learning. In *Proceedings of the International Symposium of Experimental Robotics*, pp. 363-372, 2004.
- [3] P. Stone, R. S. Sutton, and G. Kuhlmann. Reinforcement Learning for RoboCup-Soccer Keepaway. In *Adaptive Behavior*, 13(3), pp.165–188, 2005
- [4] CONFIDENCE Ubiquitous Care System to Support Independent Living - <http://www.confidence-eu.org/>



MEDNARODNA  
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JOŽEFA STEFANA

JOŽEF STEFAN  
INTERNATIONAL  
POSTGRADUATE SCHOOL



## LEARNING THROUGH INTERACTION



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MENTORS: prof. dr. Matjaž Gams, dr. Mitja Luštrek, Igor Korelič  
<sup>1</sup>RESULT d.o.o, <http://www.result.si>

<sup>2</sup>Department of Intelligent Systems, Jožef Stefan Institute, <http://dis.ijs.si>



*Imagine playing chess without any knowledge about the rules of the game. After hundred or so moves, your opponent says, "Yes, you loose!". How can you use this feedback in order to develop successful playing strategy?*

### LEARNING OPTIMAL BEHAVIOR THROUGH INTERACTION

Sequential decision making problems which are difficult to be represented with examples accurately and consistently

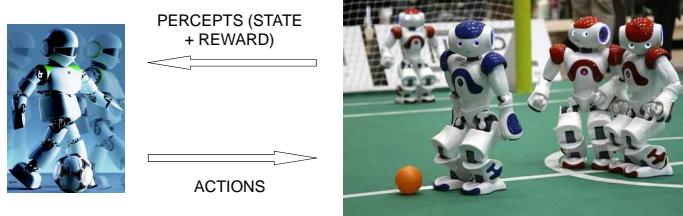
- System adaptation to user based on received feedback: user does not evaluate every low level action the system makes, but overall system performance
- Control: a traffic system can measure the delay of cars, however it is difficult to develop a strategy how to decrease the delay using this kind of data.
- Game playing: player knows whether it wins or loses, however this does not provide information how to move at each step.

### REINFORCEMENT LEARNING

*Learning from success and failure*

- Adaptive dynamic programming
- Temporal difference learning
- Q-learning

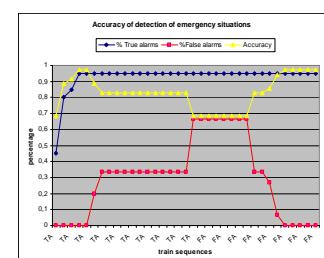
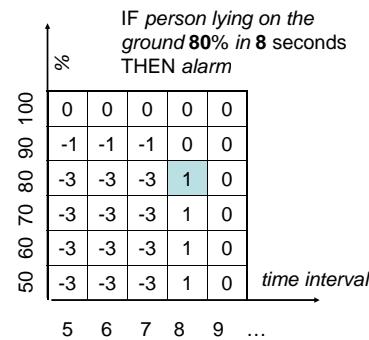
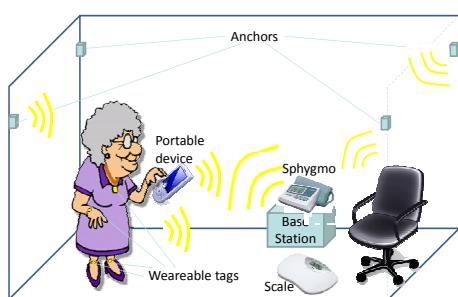
» EXPLORATION VS EXPLOITATION «



\* Peter Stone, Richard S. Sutton, and Gregory Kuhlmann.  
Reinforcement Learning for RoboCup-Soccer Keepaway.  
*Adaptive Behavior*, 13(3):165–188, 2005.

### APPLICATIONS

#### REMOTE HEALTH CARE – DETECTION OF EMERGENCY SITUATIONS



\* CONFIDENCE Ubiquitous Care System to Support Independent Living - <http://www.confidence-eu.org/>

**ACKNOWLEDGEMENTS:** The research of Violeta Mirchevska is partially financed by the European Union, European Social Fund. This work was supported partly by the Slovenian Research Agency under the Research Programme P2-0209 Artificial Intelligence and Intelligent Systems, and partly from the European Community's Framework Programme FP7/2007–2013 under grant agreement No. 214986. We would like to thank all colleagues at the Department of Intelligent Systems for suggestions, discussion and help with programming.

# Gaussian Processes for Machine Learning

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Gaussian process (GP) models form a new, emerging complementary method for nonlinear system identification. The GP model is a probabilistic nonparametric black-box model. It differs from most of the other frequently used black-box identification approaches as it does not try to approximate the modeled system by fitting the parameters of the selected basis functions, but rather searches for the relationship among measured data. Gaussian processes models are closely related to approaches such as Support Vector Machines, and specially Relevance Vector Machines [1]. Because GP model is a Bayesian model, the output of Gaussian process model is a normal distribution, expressed in terms of mean and variance. Mean value represents the most likely output and the variance can be viewed as the measure of its confidence. Obtained variance, which depends on amount of available training data, is important information distinguishing the GP models from other non-bayesian methods. Gaussian process can be used for model identification when data are heavily corrupted with noise, and when there are outliers or gaps in the training data. Another useful attribute of the GP model is the possibility to include various kinds of prior knowledge into the model, e.g. local models, static characteristic, etc.

A noticeable drawback of the system identification with Gaussian process models is computation time necessary for modeling. Gaussian process regression involves several matrix computations which load increases with the third power of the number of training data, such as matrix inversion and the calculation of the log-determinant of used covariance matrix. This computational greed restricts the number of training data, to at most a few thousand cases.

This limitation precludes usage of GP models for many real applications, usually dynamic systems, where the amount of data constantly rises. In these cases, the ability of online learning of GP models with constant time of an update is needed. This could be achieved with maintenance of a set of the most informative data. The size of a set should be small enough that an update could be completed before new data arrives. In many cases new data is much more important than old data. In these cases the feature of forgetting old data is used.

## References:

- [1] C. E. Rasmussen and C. K. I. Williams. *Gaussian Processes for Machine Learning*. The MIT Press, 2006
- [2] J. Kocijan, D. Petelin, V. Tanko, Identifikacija modelov črne skrinjice na podlagi Gaussovih procesov, IJS delovno poročilo, 2010
- [3] L. Csató and M. Opper. Sparse On-Line Gaussian Processes. Morgan Kaufmann, *Neural Computation*, 14(3):641-669, 2002.
- [4] D. Petelin. Sprotno učenje modelov na podlagi Gaussovih procesov. Diplomsko delo, 2009.



## GAUSSIAN PROCESSES FOR MACHINE LEARNING

Dejan Petelin, univ. dipl. inž. rač. in inf.

Study programme: Information and Communication Technologies,

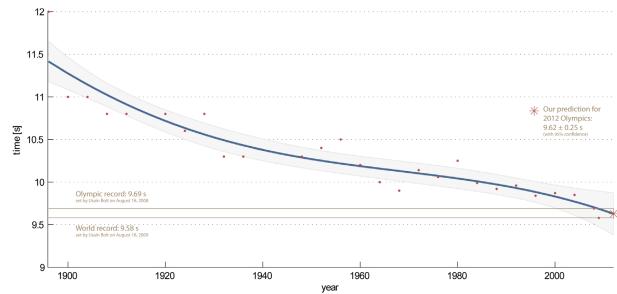
Jožef Stefan international postgraduate school

Mentor: prof. dr. Juš Kocijan

Institut Jožef Stefan, Jamova cesta 39, 1000 Ljubljana

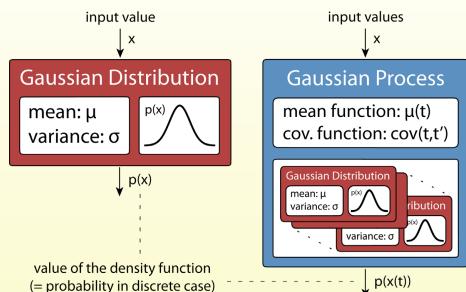


**Will the 100m  
sprint record  
be broken at the  
2012 Olympics?**



### BASIC INFORMATION

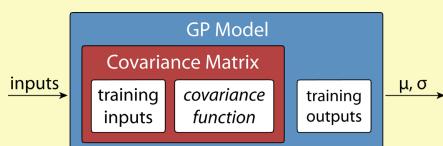
- GP model is non-parametric,
- probabilistic (Bayesian) method,
- it may be considered as a Black-box method while
- it searches relationships among data.
- It is a kernel method.



- It is easy to use,
- returns also a confidence in a prediction,
- is resistant to missing and noisy data and
- can't be overfitted (due to Bayesian nature).
- It has ability to include prior knowledge.

### MODELING

- GP model is fully specified with the data and a covariance matrix

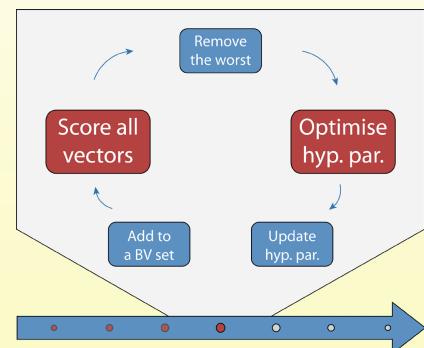


### COVARIANCE FUNCTION

- It reflects correlation between inputs,
- must generate semi positive-definite matrix.
- It is constructed out of a number of *hyperparameters*
- that may be used to adjust the properties of the GP prior

### ONLINE LEARNING

- Improving a model with every new data.
- Maintaining a subset of the most informative data (BV).
- Enables forgetting of old (irrelevant) data



### REAL APPLICATIONS



Wastewater systems



Weather (ozone, CO<sub>2</sub>, ...)



Robotics

- and many others

# Jezik matematičnih izrazov nad časovnimi vrstami z leksikalnim in sintaktičnim analizatorjem ter evaluatorjem

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V okviru opisanega dela je bil razvit jezik za zapis matematičnih izrazov nad časovnimi vrstami [4] ter programska oprema, ki omogoča leksikalno in sintaktično analizo ter evaluacijo izrazov, ki pripadajo opisanemu jeziku.

Jezik omogoča uporabo konstant, osnovnih matematičnih operacij (seštevanje, odštevanje, množenje, deljenje), potenciranja, trigonometričnih funkcij (sin, cos, tan), logaritmiranja in absolutne vrednosti. Na voljo so tudi primerjalni operatorji (enako, različno, večje, manjše, večje ali enako, manjše ali enako). V vlogi spremenljivk se uporablajo vrednosti časovnih vrst ob izbranih časih. Jezik omogoča tudi uporabo osnovnih funkcij nad intervali časovnih vrst, kot so minimum, maksimum in povprečna vrednost. Sintaksa izrazov je določena z gramatiko tipa LALR(1) [1].

Leksikalni analizator na vhodu sprejme niz znakov (ang. characters) sestavljen iz črk, desetiških cifer in ostalih znakov (+, -, \*, /, =, >, <). Če je sprejeti vhodni niz leksikalno pravilen, ga analizator pretvori v niz končnih simbolov (ang. tokens) gramatike jezika. V nasprotnem primeru analizator sporoči napako in zaporedno število znaka v izrazu, pri katerem je bila odkrita napaka. Leksikalni analizator, ki deluje kot deterministični končni avtomat (ang. deterministic finite state machine), je bil razvit s pomočjo orodja za generiranje učinkovitih leksikalnih analizatorjev Flex [3].

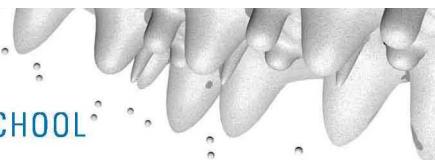
Sintaktični analizator na vhodu sprejme niz simbolov, ki je rezultat leksikalne analize. Če izraz pripada jeziku, ga pretvori v drevo izpeljave (ang. parse tree), sicer pa vrne sporočilo o napaki in mestu napake. Sintaktični analizator je bil razvit s pomočjo orodja CUP [2] in deluje kot skladovni avtomat (ang. pushdown automaton), kar mu omogoča časovno in pomnilniško učinkovitost.

Evaluator za izračun vrednosti izraza uporabi drevo izpeljave in funkcijo, ki jo zagotovi uporabnik, in na zahtevo vrača vrednosti časovnih vrst ob določenih časih. Evaluator je implementiran v okviru sintaktičnega analizatorja, tako da se izračun vrednosti izraza opravi že med izvajanjem sintaktične analize. Evaluacija izraza se po potrebi lahko izvaja tudi ločeno od sintaktične analize.

Jezik in razvita programska oprema sta primerna za uporabo v številnih aplikacijah v katerih je potrebna fleksibilna in uporabniku prijazna analiza časovnih vrst. Opisano delo smo npr. uporabili v projektu i-LAB, v katerem z ekspertnim sistemom nadzorujemo okoljske parametre v zdravstvenem laboratoriju in po kvaliteti primerjamo vzorce in reagente glede na pogoje hranja.

## References:

- [1] A. V. Aho, R. Sethi and J. D. Ullman. *Compilers: Principles, Techniques, and Tools*. Addison-Wesley, 1986.
- [2] CUP, LALR Parser Generator in Java. <http://www2.cs.tum.edu/projects/cup/>, 2010.
- [3] Flex: The Fast Lexical Analyzer. <http://flex.sourceforge.net/>, 2010.
- [4] G. Box, G. Jenkins. *Time series analysis: forecasting and control*. Holden-Day, 1976.



## JEZIK MATEMATIČNIH IZRAZOV NAD ČASOVNIMI VRSTAMI z leksikalnim in sintaktičnim analizatorjem ter evaluatorjem

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MENTOR: prof. dr. MATJAŽ GAMS

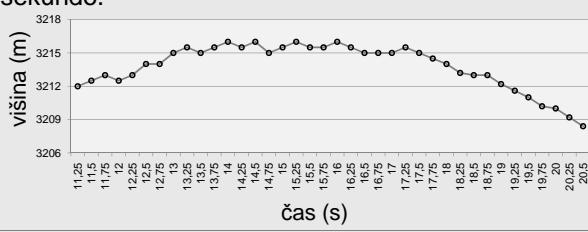
Inštitut Jožef Stefan, Jamova cesta 39, 1000 Ljubljana



**Časovna vrsta** (ang. time series) je zaporedje vrednosti določene spremenljivke v zaporednih časovnih intervalih.

### Primeri:

- Relativna zračna vlažnost v sušilnici izmerjena vsakih 5 minut.
- Število avtomobilov v parkirni hiši vsako minuto.
- Nadmorska višina letala izmerjena 4 kрат na sekundo.



**Matematični izraz** je beseda končne dolžine sestavljena iz znakov določene abecede in pripada nekemu jeziku besed. Znaki predstavljajo konstante, spremenljivke, operacije ali relacije.

### Primeri:

- $RH > 40$  (ali je trenutna vlažnost nad 40%)
- $315 - \max(N[1440-0])$  (najmanje število prostih mest v zadnjih 24 urah)
- $\text{abs}(h - h[8]) \geq 10$  (ali se je letalo v zadnjih dveh sekundah spustilo/dvignilo za več kot 10m)

**Gramatika jezika** je množica pravil, ki določajo, kako se iz simbolov določene abecede sestavijo izrazi, ki pripadajo jeziku, ki ga gramatika opisuje.

```

cond ::= expr = expr | expr != expr | expr > expr
       | expr < expr | expr >= expr | expr <= expr |
expr;
expr ::= expr + factor | expr - factor | factor;
factor ::= factor * term | factor / term | term;
term ::= ( expr ) | - term | SIN ( expr ) | COS ( expr )
      | TAN ( expr ) | ABS ( expr ) | SQRT ( expr )
      | POW ( expr , expr ) | LOG ( expr ) | num | var
      | MIN ( series ) | MAX ( series ) | AVR ( series );
num ::= REALNO_ST ;
var ::= SPREM | SPREM [ num ];
series ::= SPREM [ num - num ];

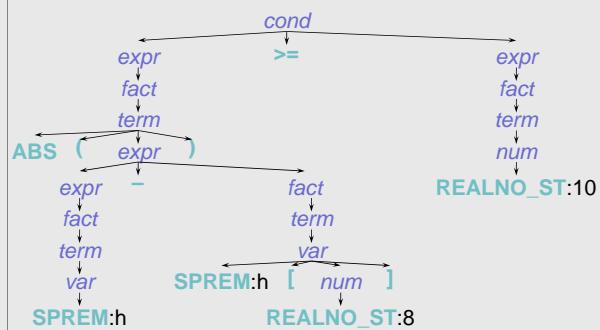
```

**Leksikalna analiza** (ang. lexical analysis) je proces pretvarjanja zaporedja znakov v zaporedje simbolov (ang. tokens).

**Primer:**  
 $\text{abs}(h - h[8]) \geq 10$  se po leksikalni analizi pretvori v:  
 $\text{ABS} ( ( \text{SPREM}:h | - | \text{SPREM}:h ) [ | \text{REALNO\_ST}:8 | ] ) |$   
 $\geq | \text{REALNO\_ST}:10 |$

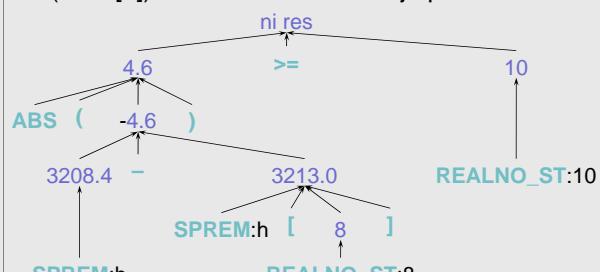
**Sintaksna analiza** (ang. parsing, syntactic analysis) je proces analiziranja teksta sestavljenega iz simbolov, ki ugotovi gramatično strukturo glede na dano formalno gramatiko (jezik).

**Primer:**  
 $\text{abs}(h - h[8]) \geq 10$  se po sintaksni analizi pretvori v:



**Evaluacija izraza** (ang. expression evaluation) pomeni izračun dejanske vrednosti izraza ob znanih vrednostih vseh spremenljivk, ki nastopajo v izrazu.

**Primer:**  
 $\text{abs}(h - h[8]) \geq 10$  se med evaluacijo pretvori tako::



**Uporaba:** jezik in razvita programska oprema sta primerna za aplikacije v katerih je potrebna analiza časovnih vrst.

Jezik smo uporabili v projektu i-LAB, v katerem z eksperimentarnim sistemom **nadzorujemo okoljske parametre** v zdravstvenem laboratoriju in **primerjamo vzorce in reagente po kvaliteti** glede na pogoje hranja.

# Reducing Power Consumption in a Network of iMote2/TinyOS Sensor Nodes

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Wireless sensor networks (WSNs) are one of the fastest changing ICT related areas both in industry and research fields, having a big impact on modern society. Nevertheless, designing a WSN requires considering a set of constraints and low energy is one of the most important of them [1]. From previous approaches we saw that the energy efficiency issue is addressed at different levels, including MAC and network protocols, physical layer communication, operating system, algorithms, etc. All these should be able to dynamically adapt in order to minimize power consumption [2]. Therefore, several optimizations have been proposed such as adaptive modulations and power, MAC protocols such as T-MAC, S-MAC, B-MAC, power aware routing algorithms like SPIN or LEACH, etc [2].

Our implementation is related to cross-layer design which is based on interaction between non-adjacent layers. Such approach can improve energy efficiency by joining design optimizations across hardware, link layer, MAC and routing protocols [2]. Our solution is based on accessing, from the application layer, the services provided by lower layers. These services are available as libraries and they perform power aware operations on the nodes without sacrificing the abstraction of low-level functionality. The power consumption is reduced using two methods: minimizing the communication process as it is one of the most consuming processes within the network, and periodically activating deep sleep mode for the nodes.

We used a WSN composed of two types of nodes: the sensing nodes for measuring environment data, and the gateway node through which the network is sending the data to a PC for storing and possible further processing. They transmit messages based on two types of communication: wireless communication between the nodes and the gateway, and wired communication between the gateway and the PC. The sensors located on the nodes are able to measure temperature, humidity, light and 3D acceleration. For developing the applications, few tools were used - namely .NET Micro Framework, Visual Studio 2005 and SQL Server. The application running on the sensor nodes periodically reads the sensor data and checks if the difference between the current value and the last sent value is above a threshold. If the difference is above, it saves these new values and sends a new message to the gateway. Otherwise, it discards the last sensed value. In both situations, the next step is activation of the deep sleep mode for a predefined timeslot. In this way, not only the power consumption is reduced but also the data redundancy. The node which acts as a gateway for the network performs the following tasks: receives the messages that are sent by the sensor nodes, converts them to the correct format and then sends them to the PC through serial port without looking in its content. The application running on the PC side executes the next operations for each new message received through the USB interface: message loading, identification of the actual information/fields in the message, computation of the real values from the sensor measurements and finally saving them into the database.

## References:

- [1] J. Yick, B. Mukherjee, and D. Ghosal, "Wireless sensor network survey," Computer Networks, vol. 52, 2008, pp. 2292-2330.
- [2] S. Rhee, D. Seetharam, S. Liu, "Techniques for minimizing power consumption in low data-rate wireless sensor networks".
- [3] G. Miao, N. Himayat, Y. Li, A. Swami, "Cross-layer optimization for energy-efficient wireless communications: A survey"



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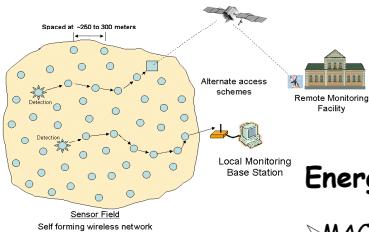
## REDUCING POWER CONSUMPTION IN A NETWORK OF iMOTE2/TINYOS SENSOR NODES

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CARMELA FORTUNA  
MENTOR: doc. dr. MIHAEL MOHORČIČ  
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### WSNs features and constraints

- Low energy
- Low cost
- Low data rate
- Short transmission range
- Limited hardware resources
- Interferences
- Heterogeneity
- Scalability



### Hardware

#### iMote2 Radio Processor Board (IPR2400)

- Intel XScale processor - PXA271
- 802.15.4 radio with an on-board antenna
- Wireless MMX coprocessor
- Multi-color status indicator LED
- Basic and advanced expansion connectors supporting: 3xUART, I2C, 2xSPI, SDIO, I2S, AC97, USB host, Camera I/F, GPIO, mini-USB port for direct PC connection



#### iMote2 Basic Sensor Board (ITS400)

- 3d accelerometer
- Temperature sensor
- Humidity sensor
- Light sensor
- 4-channel A/D



#### Interface Board (IIB2400)

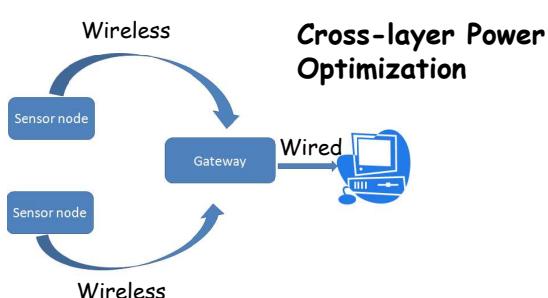
- code loading and debugging through JTAG interface



### Software

- TinyOS and nesC
- .NET MICRO Framework
- Visual Studio 2005
- SQL Server database

### Functionalities



Message=header (data  
about network, node  
and message type) +  
payload (sensor data)

#### Sensor node

- Periodically measures the environment
- Sends only when the variation is big enough
- **Minimize communication process**
- Enters deep sleep state

#### Gateway

- Receives the message from the sensor node
- Converts it to the correct format
- Sends it to the PC

#### PC side

- Reads messages from the USB interface
- Identifies and extracts the fields from the message
- Computes sensor data values
- Stores data into database

# Understanding the life of a knowledge worker

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This poster presents an implementation of data mining techniques to obtain a probabilistic process model from the low-level event log of the activity of a knowledge worker. In these settings, knowledge workers are often involved in numerous projects, that require accessing different data sources, interacting with different individuals, exchanging messages, browsing the web, etc. An individual's role may vary from project to project, and the relevance of different portions of the document will vary according to the project and the individual reading the document. From such events, we obtain dynamic models and demonstrate the process on real-world data collected from knowledge workers in a large telecom company. The goal is to aid the user with improved information delivery when we are provided with better understanding of the knowledge process [1].

We describe the situation as following: given a database, describing events in a business setting, such as e-mail messages and visited URLs, executed in different contexts, produce a probabilistic temporal model that best describes the action patterns appearing in the event log. We obtain this by solving three tasks: context mining, action mining and process mining.

*Context mining* is the task where we want to discover the different contexts that the knowledge worker is involved in. It is obtained by performing semi-supervised clustering of events, where each cluster represents a distinct context in which the knowledge worker is working. In most work environments, contexts are most often seen as projects or clients, such as "*Process mining research project*" or "*Proposal for client X*". In general, we distinguish between them by different content keywords, resources, and people involved in the events.

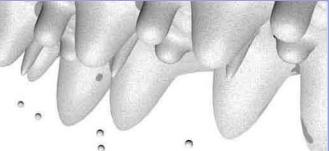
*Action Mining* is the task where we wish to look at the events in a context-free manner and identify more general atomic actions. It is performed by clustering [2] of a context-free representation of events. When events are stripped of context-describing features and given additional metadata, we are left with clusters, which describe generalized representations of events, such as "*Send e-mail to group of co-workers*" or "*View intranet website*", which may occur in multiple contexts.

*Process mining* shows us the dynamics of the knowledge process of either a particular knowledge worker or an aggregate process model of an entire team. It gives us the probabilistic model of transitions between actions within a context. It is done by learning probabilistic deterministic finite automata [3] (PDFAs) and reduces the full models to only statistically significant frequent sequences of actions in the data. This gives us a pruned process model which resists noise by only using statistically grounded transitions and is easier to interpret.

Demonstration on real data shows that we can interpret several patterns using this model. For instance, the transitions between project-related actions are more common than transitions to administration-related actions. Also, web browsing events tend to have longer homogeneous action sequences than e-mails.

## References:

- [1] J.M. Gomez-Perez, M. Grobelnik, C. Ruiz Moreno, M. Tilly, P. Warren. Using Task Context to Achieve Effective Information Delivery. *Workshop on Context, Information And Ontologies - CIAO at ESWC 2009*
- [2] B. Long, Z. Zhang, and P. S. Yu. A probabilistic framework for relational clustering. *In proceedings of the 13th ACM International Conference on Knowledge Discovery and Data Mining*, pages 470-479, 2007.
- [3] Jacquemont, S. and Jacquetin, F. and Sebban, M. Mining probabilistic automata: a statistical view of sequential pattern mining. *Machine Learning*, vol. 75, no. 1, pp. 91-127, Springer, 2009.



# **Understanding the life of a knowledge worker**

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<sup>2</sup> Jožef Stefan International Postgraduate School (ICT, 1st year)

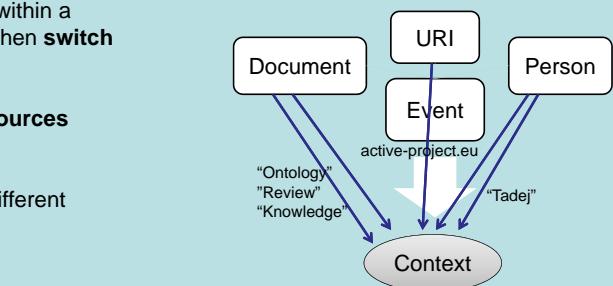
Supervisor: doc. dr. Dunja Mladenić

## Goal

- Fighting knowledge worker's **information overload** by enabling contextual information delivery
  - Knowledge workers are most often working within a single **context** for a given period of time and then **switch** to another context
  - While working, we are only interested in **resources within that particular context**
  - Example: Receiving too many emails from different contexts, **hard to manage**
  - Understanding the **dynamic** properties of a **knowledge process**
    - Given only basic productivity software and no big information systems, how can **we identify an informal knowledge process?**
    - Is there a bottleneck in the process?

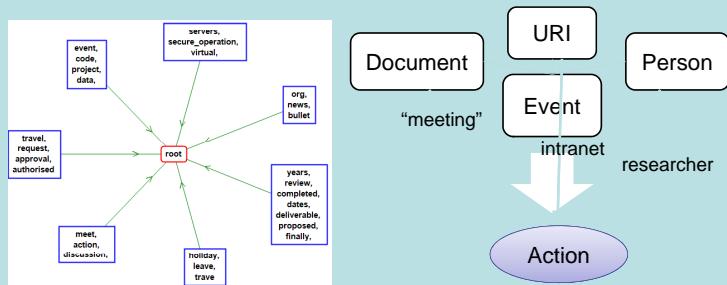
## Problem statement

- We need to solve the following:
    - Context discovery
    - Action discovery
    - Process discovery
  - Example - same process in different contexts:



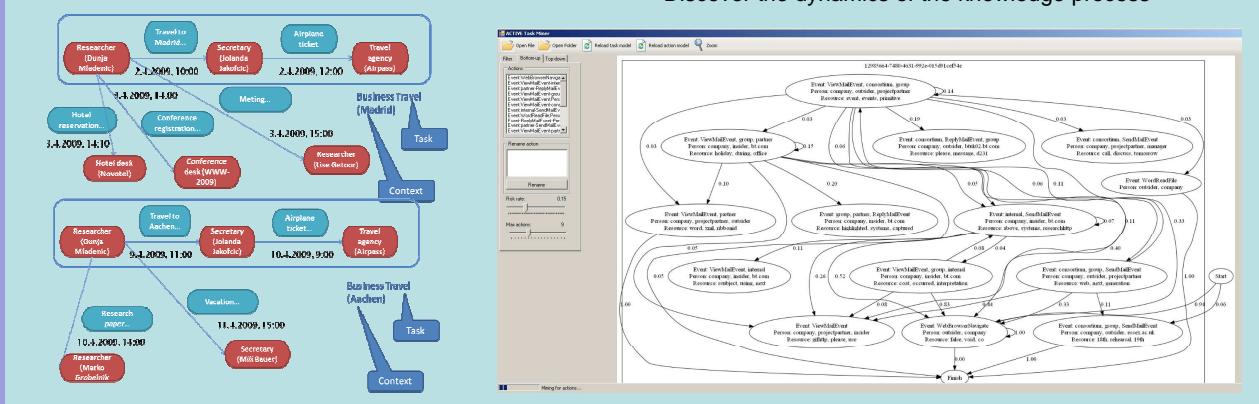
## Action Mining

- Discover the generalized actions the knowledge worker is doing in different contexts
  - Via clustering



## Process Mining

- Discover the dynamics of the knowledge process



# The use of agents in modeling human behavior

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The concept of agents is quite frequently used in computer science. Agents can be employed in a variety of applications and can be used to solve complex problems. This seemingly universal usability has brought the field of agents to a rapid growth. The most promising area of research that arrised in the last few years is human behavior modeling. The ultimate objective that researchers are trying to achieve is to make agents as capable and intuitive as humans are.

Before we start to address this problem, we have to define what an agent or an intelligent agent is. Unfortunately, there is no universally accepted definition of the term agent. However, most researchers would agree with the definition that was provided by Russell and Norvig [1]. An intelligent agent can be perceived as a computational entity that is able to sense and autonomously act upon its environment. There can be only one agent in the environment trying to solve some problem. Using only one agent may be suitable for some limited domains where there is no need for collaboration; however, such domains are rare in real life problems. Usually entities interact and collaborate with each other in order to attain certain objectives. In order to better collaborate with other agents in the environment, we need to know something about the other agents.

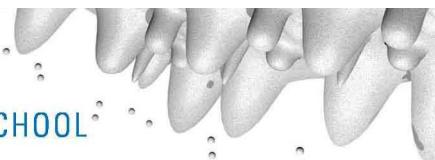
Learning about other entities in the environment is very helpful. In this way we can make good guesses of their expected behavior and act accordingly. A simple example could involve a computer program that is able to model the behavior, preferences and habits of the user and would be able to adjust itself in order to facilitate its use. Another example of the usefulness of behavior modeling is computer guided characters (bots) in video games that is able to learn from other players and imitate their behavior [2]. In time it would provide a much greater challenge to the human player, since it would be able to adapt and exploit the player's shortcomings.

Modeling a single agent or human is very useful in some domains, but a much greater challenge represents modeling a group of agents where complex interactions between entities have to be considered. Behavior modeling of crowds would allow the development of highly realistic and reusable models of human behavior that can be used for various tasks. For example, police officers would be able to simulate in a virtual environment various tactics that could be employed during riots or demonstrations and would result in a peaceful resolution of conflict.

The Multi-agent strategy discovering algorithm (MASDA) [3, 4] is able discover common agent strategy by tracking low-level behavior of a group of agents and using only basic domain knowledge. MASDA could be improved to generate behavior models for a larger group of interacting agents, where also the cognitive aspects of human decisions would have to be considered.

## References:

- [1] S. Russell and P. Norvig. Artificial Intelligence: A Modern Approach (2nd ed.), Upper Saddle River, New Jersey: Prentice Hall, ISBN 0-13-790395-2
- [2] C. Thurau, G. Sagerer and C. Bauckhage. Imitation learning at all levels of Game-AI. In Proceedings of the International Conference on Computer Games, Artificial Intelligence, 2004
- [3] A. Bežek and M. Gams. From Basic Behavior to Strategic Patterns in Robotic Soccer Domain. *Informatica*, 2:461-468, 2005
- [4] A. Bežek, M. Gams and I. Bratko. Multi-Agent Strategic Modeling in a Robotic Soccer Domain. In AA-MAS:457-464, 2006



## THE USE OF AGENTS IN MODELING HUMAN BEHAVIOR

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### INTELLIGENT AGENTS

An intelligent agent can be perceived as a computational entity, for example, a robot or software program, that is able to perceive and autonomously act upon its environment.

As mentioned an agent exists and operates in some environment, which is both computational and physical and may or may not contain other agents.

In a single-agent system only one agent is used to solve problems.

Using only one agent may be suitable for some limited domains where there is no need for collaboration, however, such domains are rare in real life problems. Usually entities interact and collaborate with each other in order to attain certain objectives. A single agent may not be capable enough or does not have the knowledge required to perform the task. Moreover, it may take too much time for a single agent to complete the assigned task. In such cases a multi-agent system is used.

### BEHAVIOR MODELLING

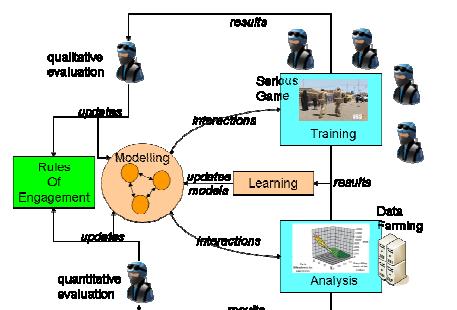
Learning about other agents in the environment is very helpful, this way we can make good guesses of their expected behavior and act accordingly (cooperate more effectively, for example). Imagine a computer program that would be able to model the preferences and habits of the user and would be able to adjust itself in order to facilitate

its use to the user. Computer guided characters (bots) in video games would pose a much greater challenge to a human player if they were able to learn from other players and imitate their behavior.

### CROWDS

Crowd behavior modelling involves modelling the behavior of a large group of people, such as crowds in a range from civilian to hostile.

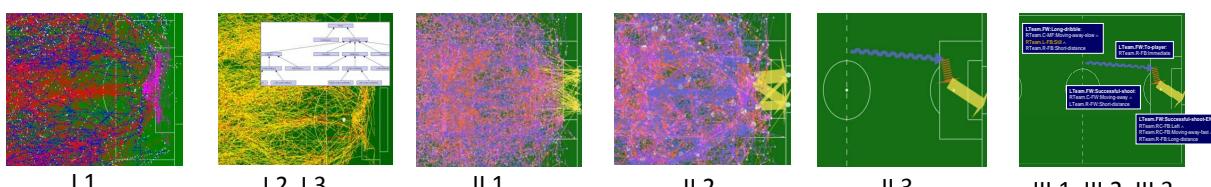
Behavior modelling would allow the development of highly realistic and reusable models of human behavior that can be used for various tasks (e.g. simulations, analysis, etc.)



### MULTI-AGENT STRATEGY DISCOVERING ALGORITHM

MASDA is able discover common agent strategy by tracking low-level behavior of a group of agents and using only basic domain knowledge.

- Observe elementary actions
- Merge elementary actions into
- Find similar actions occurring repeatedly
- Extract strategy from repeated actions, describe with rules and present them in a graphical and symbolic way



Numeric data (~3.000.000)	Symbolic data (~150.000)	Action graph (~6.500)	Abstract action graph (~1000)	Strategic action descriptions (~100)	Strategic concepts (~10)
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Increasing abstraction



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## **Nanoznanosti in nanotehnologije (Nanosciences and Nanotechnologies)**

# Hidrotermalna sinteza fotokatalitsko aktivnih alkalijskih titanatnih nanocevk

Ines Bračko<sup>1,2</sup>

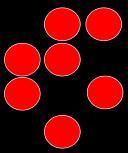
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Nanocevke na osnovi plastovitih titanatov, sintetizirane s hidrotermalno obdelavo TiO<sub>2</sub> v močno alkalnem okolju, imajo plastovito, lamelarno strukturo in značilno odprto, mezoporozno morfologijo, ki omogoča prenos ionov na površino nanocevk in med plasti v stenah večplastnih nanocevk. Nadalje je moč zmožnost ionske izmenjave nanocevk uporabiti za nalaganje nanodelcev različnih materialov (polprevodniški ali kovinski nanodelci) na negativno nabito površino nanocevk. Za takšno uporabo mora biti prekurzor za nanodelce v kationski obliki ali pa mora izkazovati močno afiniteto do titanatnih nanocevk. Primerni prekurzorji so kationi žlahtnih kovin in kationi prehodnih kovin. Glede na že raziskane in znane fotokatalitske lastnosti TiO<sub>2</sub> je v zadnjih letih veliko raziskav usmerjenih tudi v študij in prilagajanje lastnosti titanatnih nanocevk za uporabo v fotokatalitskih procesih. Vgrajevanje različnih specij (kationi alkalijskih, zemljoalkalijskih in prehodnih kovin, kovinski nanodelci) na površino nanocevk in v nanocevke omogočajo prilagajanje lastnosti titanatnih nanocevk in posledično njihovo morebitno uporabo v procesih fotokatalize, pri fotorazgradnji vode ter za shranjevanje in detekcijo vodika.

Hidrotermalno pripravljene nanocevke na osnovi plastovitih titanatov sem uporabila kot osnovni material (templat) za nadaljnjo ionsko izmenjavo s srebrom. Za izvedbo ionske izmenjave sem nanocevke v prisotnosti raztopine srebrnih kationov izpostavila hidrotermalnim pogojem ter nato katione srebra reducirala do nastanka kovinskih srebrnih nanodelcev. Morfologijo, sestavo in kristalno strukturo hidrotermalno pripravljenih produktov sem določila z uporabo rentgenske praškovne difracije in tehnik elektronske presevne mikroskopije. Za določitev specifične površine nanocevk sem uporabila Brunauer, Emmett, Teller (BET) metodo.



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## Hidrotermalna sinteza fotokatalitsko aktivnih alkalijskih titanatnih nanocevk

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Študijski program: Nanoznanosti in nanotehnologije

Mentor: prof. dr. Danilo Suvorov

Somentor: doc. dr. Boštjan Jančar

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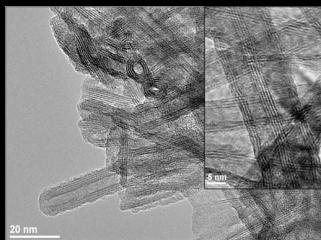


Nanocevke na osnovi  
plastovitih titanatov,  
sintetizirane s hidrotermalno  
obdelavo  $\text{TiO}_2$  v močno  
alkalnem okolju.

Hidrotermalna sinteza  
 $\text{TiO}_2$ ,  
10M NaOH  
165°C, 72 h

### NANOCEVKE

premer<sub>not</sub> ~ 5 nm  
premer<sub>zun</sub> ~ 10 nm  
dolžina več 100 nm  
visoka spec. površina



Nanocevke imajo  
plastovito, lamelarno  
strukturo in značilno  
odprto, mezoporozno  
morfologijo.

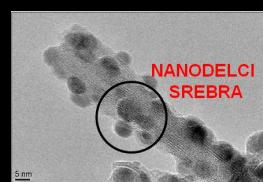
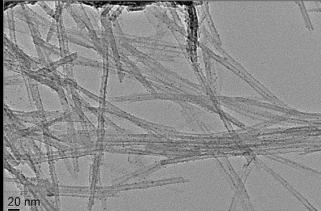
$$S_{\text{BET}} = 238 \text{ m}^2/\text{g}$$

Narava nanocevk omogoča prenos  
ionov na površino nanocevk in med  
plasti v stenah večplastnih nanocevk.

Hidrotermalna  
ionska izmenjava  
 $\text{AgNO}_3$   
100°C, 12h

### NANOCEVKE Z Ag NANODELCI

prekursor za nanodelce  
v kationski obliki



### Povzetek in možna uporaba

**Nanocevke** izkazujejo dobro zmožnost ionske izmenjave in imajo visoko specifično površino.

- ❖ Priprava kompozita med titanatnimi nanocevkami in nanodelci srebra omogoča izboljšanje fotokatalitske akvtinosti nanocevk v vidnem območju sončnega spektra.
- ❖ Fotokatalitsko aktivnost kompozita je moč uporabiti v procesih čiščenja odpadnih voda.

# Uporaba in funkcionalizacija magnetnih nanodelcev

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Z razvojem nanoznanosti in nanotehnologij, so bili odkriti tudi superparamagnetni nanodelci. Ti delci so pogosto iz železovih oksidov in imajo posebne lastnosti. Ob izpostavitvi zunanjemu magnetnemu polju, kažejo magnetne lastnosti, ko pa magnetno polje umaknemo, se delci ponovno porazdelijo po tekočini. Torej so njihove magnetne lastnosti izražene le ob prisotnosti magnetnega polja. Magnetni nanodelci so običajno reda velikosti 10 nm in njihovo obnašanje v magnetnem polju je enako kot obnašanje pri paramagnetičnih z ogromnim magnetnim momentom. Pogosta težava pri magnetnih nanodelcih je aglomeracija. Da se temu problemu izognemo, magnetne nanodelce pogosto oplaščimo. Oplaščimo jih lahko na različne načine; površino nabijemo, ali oplaščimo s polimeri, fosfolipid, silicijem dioksidom... Tako so delci bolje razporejeni, imajo večjo aktivno površino in kažejo superparamagnete lastnosti. Oplaščen nanodelc je tako stabilen in odporen na oksidacijo. Takšne je nato moč funkcionalizirati. Pri tem lahko kemijsko ali z adsorbcijo vežemo na površine delcev različne molekule ali funkcionalne skupine. Z vezavo protiteles na takšne delce lahko ločimo proteine iz komplikiranih suspenzij, kot je na primer krvna plazma. Uporaba nanodelcev v biomedicini je naredila velik korak k lažji separaciji in detekciji bioloških materialov. Poleg tega je znižala mejo koncentracije, ki je potrebna za detekcijo določenega proteina, saj ga magnetni nanodelci lahko poberejo po večjem volumnu in koncentrirajo na manjši volumen. Nanodelci se uporabljajo v medicini tudi za zdravljenje rakavih bolezni (s pomočjo hiperterije-lokalno segregiranje delcev ob izpostavitvi magnetnemu polju), kot kontrastno sredstvo pri magnetni resonanci ali kot transporterji zdravil v celice.

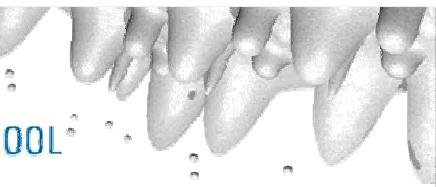
## Reference:

- [1] *What is nanomedicine?* Jr, Robert A. Freitas. 2-9, California : Nanomedicine: Nanotechnology, Biology and Medicine, 2005, Zv. 1.
- [2] *Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications.* Ajay Kumar Gupta, Mona Gupta. Scotland : Biomaterials, 2005, Izv. 26, 3995-4021.
- [3] *Medical application of functionalized magnetic nanoparticles.* Akira Ito, Masashige Shinkai, Hiroyuka Honda, and Takeshi Kobayashi. Nagoya : Journal of Bioscience and Bioengineering, 2005, Izv. 100, 1-11.
- [4] *Recent advances with liposomes as pharmaceutical carriers.* Torchilin, Vladimir P. 2005, Nature Reviews, str. 145-160. 10.1038/nrd1632
- [5] *Biotechnology of Magnet-Driven Liposome Preparations.* G. K. Ismailova, V. I. Efremenko and A. G. Kuregyan. 7 10.1007/s11094-005-0162-4, s.l. : Pharmaceutical Chemistry Journal, 2005, Zv. 39, str. 385-387.
- [6] *Liposomes in drug delivery: Progress and limitations.* Amarnath Sharma, Uma S. Sharma. 2, s.l. : International Journal of Pharmaceutics, 1997, Zv. 154, str. 123-140 . doi:10.1016/S0378-5173(97)00135-X
- [7] *Magnetic targeting of magnetoliposomes to solid tumors with MR imaging monitoring in mice: feasibility.* Fortin-Ripoche JP, Martina MS, Gazeau F, Ménager C, Wilhelm C, Bacri JC, Lesieur S, Clément O. 2, s.l. : Radiology, 2006, Zv. 239, str. 415-424. PMID: 16549622



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# Uporaba in funkcionalizacija magnetnih nanodelcev

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ŠTUDIJSKI PROGRAM: NANOZNANOSTI IN NANOTEHNOLOGIJE  
MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA  
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## TEORETIČNE OSNOVE

Magnetni nanodelci so delci reda velikosti okoli deset nm in njihovo obnašanje v magnetnem polju je enako kot obnašanje paramagnetov z ogromnim magnetnim momentom. Izven magnetnega polja ne kažejo magnetnih lastnosti, zato jih imenujemo superparamagneti delci.  $\text{Fe}_2\text{O}_3$  nanodelci so primer delcev katere lahko usmerjamo z mag. poljem. Nanje lahko vežemo različne komponente.

Funkcionalizirane magnetne nanodelce pripravljamo za detekcijo prionov v ELISA testih. Funkcionalizacija poteka preko vezave streptavidina na površino nanodelca, ki nato omogoča pripenjanje biotiniziranega protitelesa.



SEM slika: nano delci oplaščeni s polimerom

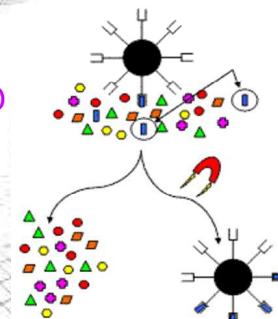
## APLIKATIVNOST

KONCENTRIRANJE VZORCA  
ČIŠČENJE TEKOČIN  
MEDICINSKE APLIKACIJE

Izolacija določene komponente  
(npr. zdravilnih učinkovin v farmaciji)

Uporabno, ko želimo na površino kemijsko vezati nanose  
(npr. vezava PDMS polimera)

Iz raztopin z magnetom izvlečemo strupene snovi  
(npr. za čiščenje odpadnih voda)



Vezava bioaktivnih učinkovin na magnetni nanodelc, separacija, magnetofekcija...

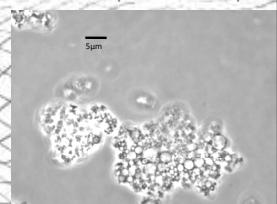
(npr. vezava protiteles za test ELISA)

Funkcionalizacija

Schematicni prikaz:  
Nanodelci oplaščeni z fosfolipidi



Optični mikroskop:  
nanodelci oplaščeni z fosfolipidi



► vezava streptavidina na površine magnetnih nanodelcev

► vezava protitelesa za detekcijo prionov

# Influence of processing conditions on dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ thin films

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$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  possesses one of the largest values of the effective dielectric permittivity in a large frequency and temperature range ever reported for a ceramic material, and is thus a very promising material for various electronic and electromechanical applications. The origin of such high permittivity has been attributed to ‘electrical’ heterogeneities in the microstructure [1-3]. By Chemical Solution Deposition, we have prepared  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  ceramic thin films under different conditions, trying to establish the influence of microstructure on their dielectric properties.

Dielectric permittivity of 2000 – 3000 at room temperature at frequencies lower than 1 kHz that drops rapidly for an order of amplitude at higher frequencies has been observed in developed  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  thin films. In order to shed some light on the nature of such dielectric behaviour, the dielectric response has been studied by high-resolution measurements in the temperature range of 100 K – 410 K and the frequency range of 1 Hz – 3 MHz on thin films with thicknesses in the range of 200 – 600 nm.

Experimental results and the analysis in terms of the equivalent circuit [3,4] revealed that each of the two constituents determines the dielectric behaviour of the thin film for different frequencies – insulating grain boundaries at lower and semiconducting bulk grains at higher frequencies. Consequently, the dielectric permittivity drop and its maximum value at a given temperature depend on the properties of grain boundaries and grains themselves. Thus the main influence on dielectric properties are the conditions under which the thin film was created – it drops at a lower temperature and has a higher maximum value for thicker films or films post-annealed at a lower oxygen partial pressure.

We suggest that such dielectric behaviour arises due to different distributions of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions (these have been shown to strongly influence the electrical properties of  $\text{ACu}_3\text{Ti}_4\text{O}_{12}$  systems [5]) within grains and grain boundaries after different annealing procedures. Ultimately, manipulating the conditions under which CCTO ceramic thin films are prepared enables us to control dielectric properties of these application compelling materials.

## References:

- [1] M. A. Subramanian, D. Li, N. Duan, B. A. Reisner and A. W. Sleight. High dielectric constant in  $\text{ACu}_3\text{Ti}_4\text{O}_{12}$  and  $\text{ACu}_3\text{Ti}_3\text{FeO}_{12}$  phases. *Journal of Solid State Chemistry*, 151: 323–325, 2000.
- [2] T. B. Adams, D. C. Sinclair and A. R. West. Characterization of grain boundary impedances in fine- and coarse-grained  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  ceramics. *Physical Review B*, 73: 094124, 2006.
- [3] P. Lunkenheimer, R. Frichtl, S. G. Ebbinghaus and A. Loidl. Nonintrinsic origin of the colossal dielectric constants in  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ . *Physical Review B*, 70: 172102, 2004.
- [4] V. Bobnar, P. Lunkenheimer, M. Paraskevopoulos and A. Loidl. Separation of grain boundary effects and intrinsic properties in perovskite-like  $\text{Gd}_{0.6}\text{Y}_{0.4}\text{BaCo}_2\text{O}_{5.5}$  using high-frequency dielectric spectroscopy. *Physical Review B*, 66: 184403, 2002.
- [5] J. Li, M. A. Subramanian, H. D. Rosenfeld, C. Y. Jones, B. H. Toby and A. W. Sleight. Clues to the giant dielectric constant of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  in the defect structure of ‘ $\text{SrCu}_3\text{Ti}_4\text{O}_{12}$ ’. *Chemistry of Materials*, 16: 5223–5225, 2004.



## Influence of processing conditions on dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ thin films

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Study programme: Nanosciences and Nanotechnologies

Supervisor: Asst. Prof. Vid Bobnar



### Aim of work

- ❖ Measurements of the dielectric response of various  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) ceramic thin films. CCTO namely possesses one of the largest values of the effective dielectric permittivity ever reported for a ceramic material in a large frequency and temperature range, and is thus a very promising material for various electronic and electromechanical applications.
- ❖ Separation of different dielectric contributions (bulk, grain boundaries, etc.).
- ❖ Investigations of the influence of processing conditions on dielectric properties of films.

### Temperature scans

The main  $\epsilon'$  'plateau' values and the temperature of their drop are strongly dependent on oxygen partial pressure in atmosphere during the post-annealing process.

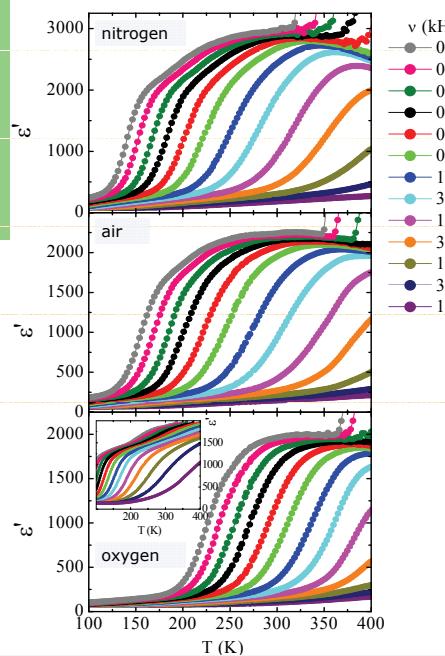


Fig. 2: 12-layer samples.

In 6-layer samples (see inset) the influence of surface layers is much more pronounced.

**Experimental results and the analysis in terms of the equivalent circuit reveal that each of the two constituents determines the dielectric behaviour of the CCTO thin film for different frequencies – insulating grain boundaries at lower and semiconducting grains at higher frequencies. The main influence on dielectric properties are the conditions under which the CCTO thin film was created.**

We suggest that such dielectric behaviour arises due to different distributions of  $\text{Cu}^+/\text{Cu}^{2+}$  ions (these have been shown to strongly influence electrical properties of  $\text{ACu}_3\text{Ti}_4\text{O}_{12}$  systems [5]) within grains and grain boundaries after different annealing procedures.

**Ultimately, manipulating the conditions under which CCTO ceramic thin films are prepared enables us to control dielectric properties of these applicatory compelling materials.**

### Materials preparation

Method of preparation: **Chemical Solution Deposition**

Conditions: 750°C, 15 min, air, RTA. Samples consist of 6 (260 nm) or 12 (540 nm) deposited layers and were post-annealed (750°C, 15 min) in nitrogen, air, or oxygen (low, medium, or high oxygen partial pressure, respectively).

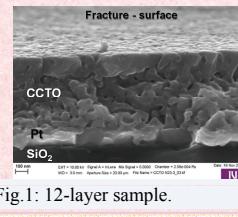


Fig.1: 12-layer sample.

### Frequency scans

#### Equivalent circuit model:

- ❖ leaky capacitor – insulating grain boundaries
- ❖ intrinsic response of semiconducting grains:
  - high frequency dielectric constant,
  - frequency dependent AC conductivity (UDR) and
  - DC conductivity.

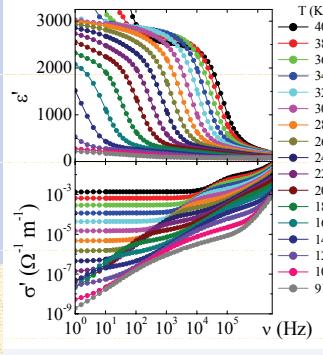


Fig.3: 12-layer sample (nitrogen).

The origin of high dielectric permittivity in CCTO ceramic thin films lies in 'electrical' heterogeneities in the microstructure [1-3]. We suggest that this is due to different distributions of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions within grains and grain boundaries.

### Analysis of results

Analysis in terms of equivalent circuit [3,4] reveals that post-annealing in lower oxygen partial pressure increases the conductance of both grains and grain boundaries.

In thin films it seems logical for variable range hopping to appear across the direction of space that represents the sample thickness. Variable range hopping model for 1D fully describes the charge transport behaviour in CCTO thin films.

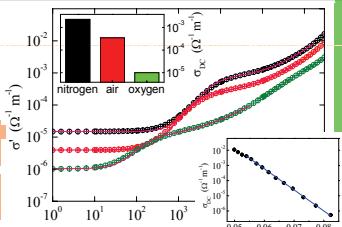


Fig.4: Analysis in terms of equivalent circuit.

### References:

- [1] M. A. Subramanian *et.al.*, J. Solid State Chem. **51** (2000).
- [2] T. B. Adams *et.al.*, Phys. Rev. B **73**, 094124 (2006).
- [3] P. Lunkenheimer *et.al.*, Phys. Rev. B **70**, 172102 (2004).
- [4] V. Bobnar *et.al.*, Phys. Rev. B **65**, 184403 (2002).
- [5] J. Li *et.al.*, Chem. Mater. **16**, (2004).

# Ferroelectric Thin Films for Tunable Microwave Applications

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Modern wireless communication systems are based on microwave technologies. Ferroelectric devices with the electric field dependent dielectric properties and low dielectric losses at microwave frequencies are very promising. Capacitance tunability  $n_c$ , defined as the ratio of the capacitance at zero applied bias voltage to the capacitance at some desired applied voltage, is the key functional property of ferroelectric materials. In order to avoid losses arising from the domain wall motion, these materials are mainly used in their paraelectric phase. [1]

Device electronics and thin film technology have in last years triggered intensive research activities in the field. Thin films enable usage of low bias voltages and therefore low energy consumption, miniaturization of microwave components, and integration into electronic circuits. Requirements for thin film varactors (variable capacitors) are: low dielectric losses  $\tan\delta$ , high tunability  $n_c$ , and the possibility of deposition on low-cost substrates. If all the requirements are fulfilled, ferroelectric thin films can be efficiently used as phase shifters, i.e. the active elements in electronically controlled antennas which are suitable for aerospace applications. [2]

The ferroelectric – paraelectric phase transition temperature of the  $K(Ta, Nb)O_3$  solid solution varies from 0 to 708 K, depending on the Ta / Nb ratio. In this respect it is analogous to the best known microwave ferroelectric material  $(Ba, Sr)TiO_3$ . However, literature reports on preparation and dielectric properties of this material in thin film form are scarce due to highly reactive reagents and demanding processing.

$K(Ta, Nb)O_3$  thin films on polycrystalline alumina were prepared by chemical solution deposition from potassium acetate and transition metal alkoxides in 2-methoxyethanol. The influence of the reflux time on microstructure and tunability of  $KTa_{0.6}Nb_{0.4}O_3$  films after heating at 900 °C was studied. The films, prepared from the 24-h refluxed solutions, have a homogeneous microstructure and the tunability, measured at room temperature and 1 MHz, equal to 2.6. The films, prepared from the 1 h-refluxed solutions, have heterogeneous microstructure and a lower tunability value, i.e. 1.9. [3]

Further more, the influence of the Ta / Nb ratio on dielectric properties of the  $K(Ta, Nb)O_3$  thin films, prepared from the 24 h refluxed solutions and heated at 900 °C, was studied. The tunability, measured at room temperature and 1 MHz, decreases with the increasing Ta / Nb ratio from 2.6 for the  $KTa_{0.6}Nb_{0.4}O_3$  films to only 1.01 for the  $KTaO_3$  films. On the other hand, dielectric losses at 9.7 GHz of  $KTa_{0.6}Nb_{0.4}O_3$  and  $KTaO_3$  decrease from 0.38 to 0.017, respectively.

## References:

- [1] S. Gevorgian. *Ferroelectrics in Microwave Devices, Circuits, and Systems: Physics, Modeling, Fabrication, and Measurements*. Springer, 2009.
- [2] P. Bao et al. Barium Strontium Titanate Thin Film Varactors for Room-temperature Microwave Device Applications. *Journal of Physics D: Applied Physics*, 41:063001, 2008.
- [3] S. Glinšek et al. Processing and Electric Field Dependent Dielectric Properties of  $KTa_{0.6}Nb_{0.4}O_3$  Thin Films on Alumina. *Ferroelectrics*, 387:112-117, 2009.



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## Ferroelectric Thin Films for Tunable Microwave Applications

Sebastjan Glinšek

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Jožef Stefan International Postgraduate School, program Nanosciences and Nanotechnologies

Mentor: Prof. Marija Kosec

Co-mentor: Ass. Prof. Barbara Malič

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### Technology Background

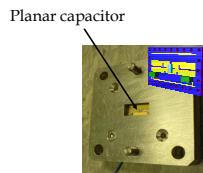
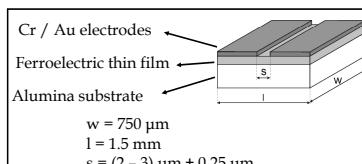
- ✖ Microwave technologies are the basis of modern wireless communication systems.
- ✖ Ferroelectrics are attractive for microwave devices due to:
  - strong electric field dependence of dielectric permittivity  $\epsilon'$
  - low microwave dielectric losses  $\tan \delta$
- ✖ Ferroelectric thin films technology offers advantages such as:
  - miniaturization of microwave components
  - low operating voltages
  - integration into electronic circuits

#### Key functional property

$$n_C = \frac{C(0)}{C(E_{max})}$$

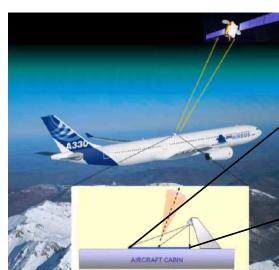
$n_C$ ...capacitance tunability  
 $C(0)$ ...capacitance at zero applied electric field  
 $C(E_{max})$ ...capacitance at selected electric field

Application: phase shifters in electronically steerable antennas\*



Planar capacitor based on ferroelectric thin film which is used as a phase shifter.

Phase shifter connected to the electronic circuit and mounted into metal housing.



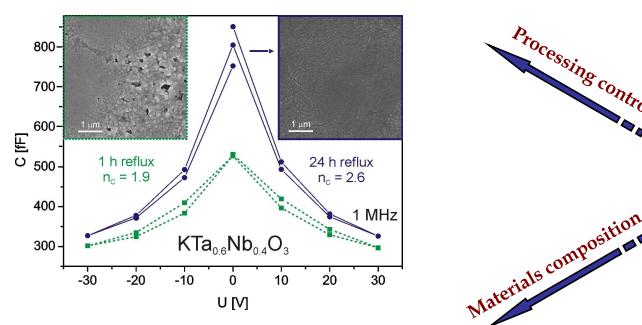
- ✖ Because of the geometry these antennas are convenient for aeronautical applications.

\*Developed in collaboration with Thales (France), EPFL (Switzerland), and HYB (Slovenia), RETINA (EC 6FP).

### Research Activities

Fast development of the communication systems stimulates the research of alternative materials.  $K(Ta, Nb)O_3$  solid solution is a promising candidate, however, scarce literature data on preparation and dielectric properties exist.

- ✖ Homogeneous microstructure and strongly enhanced tunability ( $n_C$ ) were obtained by prolonged reflux time.



Films prepared from the 24 h-refluxed sols.

Composition	$\epsilon'$ (1 MHz)	$n_C$ (1 MHz)	$\epsilon'$ (~9.7 GHz)	$\tan \delta$ (~9.7 GHz)
$KTa_{0.6}Nb_{0.4}O_3$	2200	2.6	675	0.38
$KTa_{0.8}Nb_{0.2}O_3$	375	1.25	690	0.033
$KTaO_3$	190	1.01	220	0.017

- ✖ Dielectric properties are tuned through the Ta/Nb ratio.

#### Chemical Solution Deposition of the Films

KOAc,  $Ta(OEt)_5$ , and  $Nb(OEt)_5$  were dissolved in 2-methoxyethanol.

Reactions were performed with different reflux times; by-products were removed by a distillation.

0.4 M sols were deposited on the alumina substrates by spin-coating.

App. 200 nm thick perovskite films were obtained after four sol depositions and heating at 900 °C for 15 min in an RTA furnace.

Research was supported by the Slovenian Research Agency (1000-07-310068, P2-0105)

# Infiltrati fotokatalitičnega TiO<sub>2</sub>

**Barbara Horvat<sup>1,2</sup>**

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TiO<sub>2</sub> je n-tip polprevodnika z energijsko vrzeljo 3,2 eV v primeru anataza oz. 3,0 eV v primeru rutila. Ker so najmanjši kristali rutila vedno večji od najmanjših kristalov anataza, je rutil kljub manjši energijski vrzeli slabši fotokatalizator.

Fotokataliza na anatazni modifikaciji TiO<sub>2</sub> poteče po vzbuditvi elektronov iz valenčnega v prevodni pas s fotoni valovne dolžine 387,5 nm ali manj, ko postane TiO<sub>2</sub> katalizator.

Izkazalo se je, da dodatek rutila anatazu, v ustremnem razmerju, poveča fotokatalitski učinek. Najbolj optimalno mešanico modifikacij predstavlja prah P25, kjer rutil omogoči vzbujenim elektronom anatazo kasnejšo rekombinacijo z vrzelmi.

Eden izmed možnih načinov ugotavljanja fotokatalitičnosti materiala je uporaba organskih barvil, ki jih fotoaktivni TiO<sub>2</sub> razgradi v drugo snov, ki je tudi druge barve. Tako gre moder resazurin v moder resorfin.

Fotoaktivni TiO<sub>2</sub> je aktivna snov v filtrih za čiščenje zraka v vinskih kleteh ter za čiščenje odpadnih voda. Uporablja se ga tudi za samočistilne površine kot so okna, strešniki, fasada ipd. Možna uporaba fotoaktivnega TiO<sub>2</sub> je tudi v tekstilni industriji za razgradnjo nečistoč na oblačilih kot so npr. madeži trave, zemlje, krvi kot tudi za preprečevanje vonja znoja.

Tkanino smo namakali v suspenziji P25 različne čase, del pustili nefiltriran s P25 za referenco, jo posušili, del obsevali 1 h na 20 °C z lučjo s sončevim spektrom brez UVC, del hrаниli v temi, tkanino sprali in nanjo kanili kapljico barvila resazurin. Polovico vzorcev smo dali v temo, drugo polovico pa obsevali še za 12 h.



## INFILTRATI FOTOKATALITIČNEGA $TiO_2$

BARBARA HORVAT, univ. dipl. fiz.

Študijski program: Nanozanosti in nanotehnologije, nanofizika

Mednarodna podiplomska šola Jožefa Stefana

MENTOR: doc. dr. GORAN DRAŽIĆ

Inštitut Jožef Stefan, Jamova cesta 39, 1000 Ljubljana

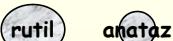


### FOTOKATALIZA in $TiO_2$

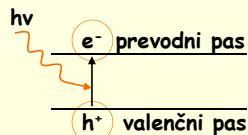
$TiO_2$  je n-tip polprevodnika z energijsko vrzeljo 3.2 eV v primeru anataza oz. 3.0 eV v primeru rutila.



Najmanjši kristali rutila so vedno večji od najmanjših kristalov anataza, zaradi česar ima anataz večjo specifično površino. Posledično je rutil kljub manjši energijski vrzelji slabši fotokatalizator.



Fotokataliza na anatazni modifikaciji  $TiO_2$  poteče po vzbuditvi elektronov iz valenčnega v prevodni pas s fotonimi valovne dolžine 387.5 nm ali manj, ko postane  $TiO_2$  fotokatalizator.



Izkazalo se je, da dodatek ustrezone količine rutila anatazu, poveča fotokatalitski učinek. Najbolj optimalno mešanico modifikacij predstavlja prah P25, kjer rutil omogoči vzbujenim elektronom anatazu kasnejšo rekombinacijo z vrzelmi.

Eden izmed možnih načinov ugotavljanja fotokatalitičnosti materiala je uporaba organskih barvil, ki jih fotoaktivni  $TiO_2$  razgradi, kar povzroči spremembo barve. Tako moder resazurin preide v rozo resorufin.



Fotokatalizator s 3 vrstami lučmi z različnimi spektri:

- UVC 264 nm,
- sončev spekter brez UVC spektra,
- Gaussov spekter z vrhom pri 380 nm.

### UPORABA

Fotoaktivni  $TiO_2$  je aktivna snov v filtrih za čiščenje zraka v vinskih kleteh ter za čiščenje odpadnih voda. Uporablja se tudi v obliki tankih plasti za samočistilne površine kot so okna, strešniki, fasada ipd.

Možna je tudi uporaba fotoaktivnega  $TiO_2$  je v tekstilni industriji za razgradnjo nečistoč na oblačilih kot so npr. madeži trave, zemlje, krvi in za preprečevanje vonja po znoju.

### ALI IMA $TiO_2$ POTENCIAL V TEKSTILSTVU?

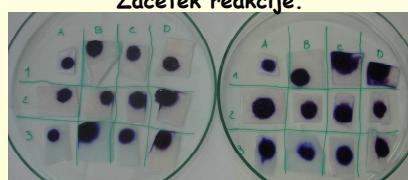
Tkanine smo različno dolgo namakali v suspenziji P25, jih posušili, del obsevali z lučjo s sončevim spektrom 1 h na 20 °C, del hranili v temi, vse tkanine sprali in nanje kapnili kapljice barvila resazurin. Polovico vzorcev smo dali v temo, drugo polovico pa obsevali še 12 h.



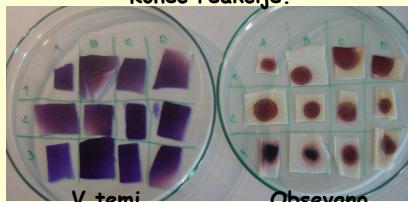
Na robovih široče se kapljice resazurina, kjer je bila koncentracija barvila najmanjša, se je v trenutku videla fotokatalitska reakcija.



Začetek reakcije.



Konec reakcije.



V temi.

Obsevano.

Vzorca 3A in 3B sta brez dodatka  $TiO_2$ . Ostali vzorci so bili različno dolgo v suspenziji prahu. Vzorci v stolpcih B in D so predhodno 1 uro izpostavljeni UV svetlobi, vzorci v stolpcih A in C pa ne.

Eksperimentalno smo prikazali, da je možna učinkovita uporaba fotokatalitičnih prahov v tekstilstvu ter da z uporabo organskega barvila lahko kvalitativno določimo fotokatalitičen efekt na tekstu. V kombinaciji z UV/Vis spektrofotometrom bi bilo moč fotokatalitski efekt tudi kvantificirati.

# Recent upgrades of the external beamline at MIC

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<sup>2</sup> Jožef Stefan International Postgraduate School (Nanoscience and nanotechnology, 3rd year)

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Microanalytical Centre at the Reactor center Brinje is hosting a 2MV (mega volt) ion accelerator of the type Tandetron. With a few MV ion beam, various analytical techniques can be practiced, all covered in the term "Ion Beam Analysis (IBA)". At the external beamline, there is a continuity of using PIXE and PIGE analysis methods (proton induced X-ray and gamma-ray emission). RBS (Rutherford back scattering) method was added recently [1]. The RBS method provides complementary information about the depth profile of a target. Layers of heavy (high Z) elements on the light substrate can easily be detected and their thicknesses determined. For all IBA methods the amount of protons hitting the target (proton dose) is a key parameter, since normalization to the proton dose is obligatory for quantitative results. Two possibilities of measuring proton dose are available, a chopper intersecting the proton beam and a metal wire charge collecting device. Both of them have been added in the last year. With these upgrades at external beamline at MIC accuracy of the measurements has been improved and additional information about sample structure is now available. Latest research includes measuring of textile fibres for forensic applications[2], measuring of meteorite, fallen on Mežakla in April 2009, and analysis of Roman sword, found in the river Ljubljanica.

## References:

- [1] D. Jezeršek, Ž. Šmit, P. Pelicon, External beamline setup for plated target investigation, Nucl. Instr. and Meth. B, [Print ed.], 2010, vol. 268, no. 11/12, pp. 2006-2009.
- [2] D. Jezeršek, S. Jakomin, Ž. Šmit, Analysis of textile fibers by in-air PIXE. Surf. interface anal., 2010, vol. 42, no. 5, pp. 423-428.



# Sintranje piezoelektričnih keramičnih materialov na osnovi alkalijskih niobatov

Jurij Koruza<sup>1,2</sup>, Barbara Malič<sup>1</sup>, Marija Kosec<sup>1</sup>

<sup>1</sup> Odsek za elektronsko keramiko, Inštitut Jožef Stefan, Ljubljana, Slovenija

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Piezoelektrični so materiali s sposobnostjo pretvorbe mehanske energije v električno in obratno. Ta lastnost jim omogoča široko uporabo v različnih senzorjih, aktuatorjih, pretvornikih, visokofrekvenčnih zakasnitvenih linijah v računalniški tehniki, sistemih za vbrizg goriva, piezoelektričnih motorjih, piezoelektričnih tiskalnikih, mikromanipulatorjih, sistemih za medicinsko diagnostiko in drugih [1].

Veliko skupino piezoelektrikov predstavljajo spojine ali trdne raztopine na osnovi svinčevih perovskitov. Njihove dobre piezoelektrične lastnosti so pogojene z velikim masnim deležem svinca, okoli 60 %, ki kot težka kovina predstavlja resen ekološki problem. Zato predvsem v zadnjem času veliko pozornosti posvečamo iskanju in razvoju alternativnih materialov, med katerimi so zelo obetavni keramični materiali na osnovi niobatov alkalijskih elementov, kot na primer trdna raztopina  $K_{0.5}Na_{0.5}NbO_3$  (KNN) ali  $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$  [2]. Keramika na osnovi KNN ima dobre piezoelektrične lastnosti, zaradi biokompatibilnosti [3] pa je primerna tudi za uporabo v medicini. Kljub številnim raziskavam piezoelektrični brez svinca na osnovi alkalijskih niobatov še niso komercialno dostopni, saj glavne probleme predstavljajo reaktivnost alkalijskih reagentov, sinteza keramičnih prahov, sintranje do velikih gostot, doseganje kemijske homogenosti in pojav sekundarnih faz, ki so večinoma občutljive na zračno vlago [4].

Da bi bolje razumeli proces sintranja trdne raztopine KNN, smo se odločili raziskati eno od mejnih spojin tega sistema - natrijev niobat ( $NaNbO_3$ ; NN). NN smo pripravili s sintezo v trdnem stanju iz izhodnih prahov  $Nb_2O_5$  in mehanokemijsko aktiviranega  $Na_2CO_3$ . Sintetizirani prah NN smo nadalje stisnili v tablete in sintrali na zraku pri temperaturah med 1250 °C in 1350 °C in različnih časih. Sintranim vzorcem smo izmerili gostoto, velikost in porazdelitev velikosti zrn ter natančno opazovali razvoj mikrostrukturnih elementov. Relativna gostota vzorcev po 5 minutah sintranja pri temperaturi 1350 °C je bila okoli 93 %, povprečna izmerjena velikost zrn pa okoli 2,7 µm. Ugotovili smo, da se s povečanjem časa sintranja gostota in povprečna velikost zrn povečuje do točke nasičenja, ki je dosežena po približno 15 minutah sintranja pri temperaturi 1350 °C. Relativna gostota teh vzorcev je bila okoli 97 %, velikost posameznih zrn pa je celo presegla 100 µm, kar je posledica izjemno hitre rasti zrn v relativno ozkem časovnem intervalu. Večina por je bila ujetih znotraj velikih zrn. Z nadaljnjam povečevanjem časa sintranja nismo dosegli bistvene spremembe mikrostrukture, relativna gostota vzorcev pa je bila celo nekoliko nižja (okoli 96 %).

## Reference:

- [1] J. Rödel, W. Jo, K. T. P. Seifert, E.-M. Anton, T. Granzow and D. Damjanovic. Perspective on the Development of Lead-free Piezoceramics. *Journal of the American Ceramic Society*, 92(6): 1153-1177, 2009.
- [2] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya and M. Nakamura. Lead-free piezoceramics. *Nature*, 432: 84-87, 2004.
- [3] K. Nilsson, J. Lidman, K. Ljungström and C. Kjellman. Biocompatible material for implants. WO Patent 99/54266, 1999.
- [4] B. Malič, A. Benčan, T. Rojac and M. Kosec. Lead-free Piezoelectrics Based on Alkaline Niobates: Synthesis, Sintering and Microstructure. *Acta Chimica Slovenica*, 55: 719-726, 2008.

# Sintranje piezoelektričnih keramičnih materialov na osnovi alkalijskih niobatov



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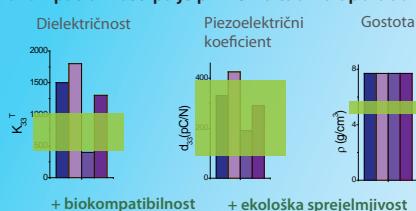
Jurij Koruza<sup>1,2</sup>, Barbara Malič<sup>1</sup>, Marija Kosec<sup>1</sup>

<sup>1</sup> Odsek za elektronsko keramiko, Institut Jožef Stefan, Ljubljana, Slovenija  
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## Uvod

Piezoelektrični so materiali s sposobnostjo pretvorbe mehanske energije v električno in obratno, kar jim omogoča uporabo v senzorjih, aktuatorjih, pretvornikih in številnih drugih aplikacijah.

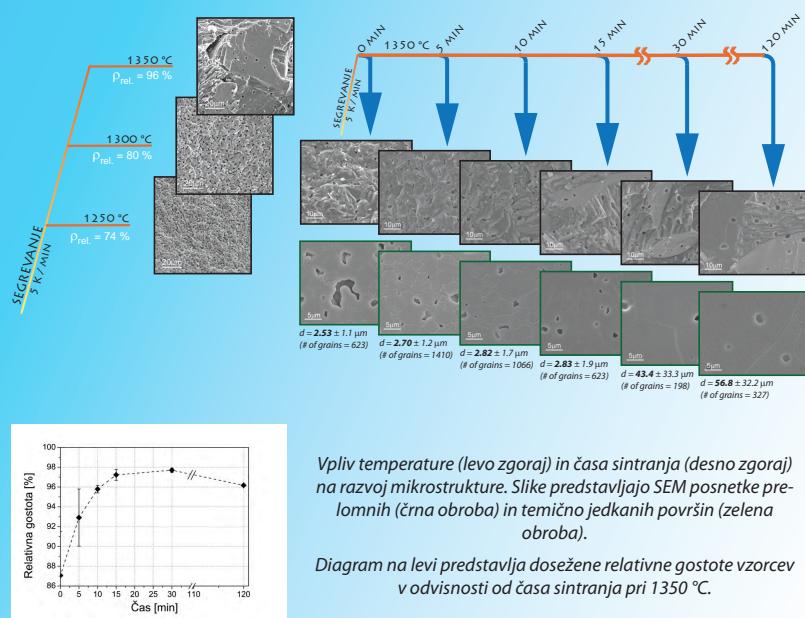
Veliko skupino piezoelektrikov predstavljajo kompleksni svinčevi perovskiti, v katerih velik masni delež svinca, okoli 60 %, predstavlja resen ekološki problem. Zato veliko pozornosti posvečamo iskanju in razvoju alternativnih materialov, med katerimi so zelo obetavni alkalijski niobati, kot na primer trdna raztopina  $K_{0.5}Na_{0.5}NbO_3$  (KNN). Ta ima dobre piezoelektrične lastnosti, zaradi biokompatibilnosti pa je primerena tudi za uporabo v medicini.



Primerjava lastnosti piezokeramike na osnovi svinca (vijolčna) in piezokeramike na osnovi alkalijskih niobatov (zelen).

## Preizkusi sintranja

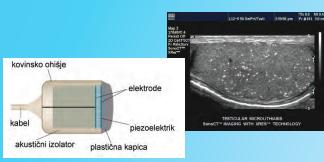
Sintranje do velikih gostot in kontrola mikrostrukture sta med ključnimi problemi priprave alkalijskih niobatov. Da bi bolje razumeli proces sintranja KNN, smo se odločili raziskati eno od mejnih spojin tega sistema -  $NaNbO_3$  (NN). NN smo pripravili s sintezo v trdnem stanju iz prahov  $Nb_2O_5$  in mehanokemijsko aktiviranega  $Na_2CO_3$ . Prah NN smo nadalje stisnili v tablete in sintrali na zraku pri temperaturah med 1250 °C in 1350 °C in različnih časih.



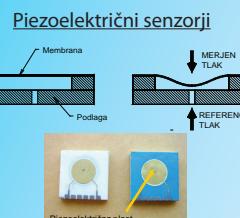
Relativna gostota vzorcev po 5 min sintranja pri temperaturi 1350 °C je bila okoli 93 % (povprečna velikost zrn d ~ 2,7 μm). Ugotovili smo, da se s povečanjem časa sintranja relativna gostota in povprečna velikost zrn povečujejo do točke nasičenja, ki je dosežena po približno 15 min sintranja pri temperaturi 1350 °C. Relativna gostota teh vzorcev je bila okoli 97 %, velikost posameznih zrn pa je celo presegla 100 μm, kar je nedvomno posledica izjemno hitre rasti zrn v relativno ozkem časovnem intervalu. Večina por je bila ujetih znotraj velikih zrn. Z nadaljnjim povečevanjem časa sintranja nismo dosegli bistvene spremembe mikrostrukture, relativna gostota pa se je celo nekoliko znižala.

## Možna področja uporabe

Medicinska diagnostika - ultrazvočni pretvorniki za slikanje z visoko ločljivostjo

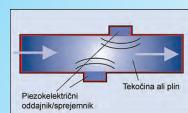


(Lethiec et al. Inform. MIDEM, 35 [4] 177 (2005))



(M. Santo Zarnik, D. Belavič. Int. J. Appl. Ceram. Technol., 6 [1] 9 (2009))

### Merilci pretoka



(www.picceramic.com)

### Mikro- in nano-manipulatorji



(www.physikinstrumente.com)

### Piezoelektrični motorji



(www.newscaledtech.com)

# Analiza domenske strukture v $K_{0,5}Bi_{0,5}TiO_3$ keramiki

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Perovskitni materiali na osnovi spojin  $K_{0,5}Bi_{0,5}TiO_3$  (KBT) so zaradi zanimivih in potencialno uporabnih feroelektričnih lastnosti v zadnjem času predmet številnih raziskav. Z dodajanjem KBT k spojinam kot sta na primer  $Na_{0,5}Bi_{0,5}TiO_3$  [1] in  $K_{0,5}Na_{0,5}NbO_3$  [2] nastajajo trdne raztopine, pri katerih se v določenem razmerju kationov pojavi morfotropna fazna meja. To je soobstoj dveh različnih struktur, ki omogočata več smeri polarizacije in s tem povečano elektromehansko sklopitev ter izboljšane piezoelektrične lastnosti.

Zaradi ključnega pomena strukture pri razumevanju električnih lastnosti keramik z vsebnostjo KBT sem se osredotočila na raziskave strukturnih lastnosti KBT kot ene izmed komponent v sistemih trdnih raztopin. KBT keramiko sem sintetizirala z reakcijo v trdnem. Z rentgensko praškovno difrakcijo (RTG) sem potrdila, da KBT kristalizira v tetragonalni  $P4mm$  strukturi, ki je polarna in značilna za feroelektrične materiale. Z ohlajanjem keramike s temperature sintranja ( $1030^\circ C$ ) se tvorijo feroelektrične domene, ki so posledica faznega prehoda iz kubične  $Pm\bar{3}m$  strukture v nižje simetrijsko tetragonalno strukturo pri temperaturi prehoda ( $T_{C(KBT)} = 380^\circ C$ ). Z visoko temperaturnim RTG sem ugotovila, da prehod poteka postopoma v širšem temperaturnem intervalu in ne sočasno po celotnem volumnu keramike pri  $T_C$ .

Za natančnejši vpogled v spremembe kristalne in domenske strukture KBT keramike na lokalni ravni sem vzorec analizirala s presevnim elektronskim mikroskopom in z elektronsko difrakcijo izbranega polja. Zrna kažejo lamelno domensko zgradbo, kjer vsaka lamela predstavlja domeno z enako usmerjenimi dipolnimi momenti, pri čemer so dipoli ene domene glede na drugo orientirani tako, da tvorijo kot približno  $90^\circ$ . Takšno orientacijo domen imenujemo  $90^\circ$  domene. Le-te so medsebojno ločene z domenskimi stenami, ki kristalografsko ustrezajo dvojčičnim ravninam (011) ali (101), značilnim za tetragonalne perovskite (npr.  $BaTiO_3$ ) [3]. Na podlagi vzorcev uklonov elektronske difrakcije z zajemom več posameznih domen sem lahko identificirala  $90^\circ$  domene, ki se kažejo kot cepitve uklonov vzdolž karakterističnih kristalografskih smeri. Domene lahko opišemo kot rotacijske dvojčke, kjer je simetrijska operacija, ki podaja relacijo med matrično domeno in dvojčkom, dvoštevna dvojčična os ( $180^\circ$  rotacija) pravokotna glede na dvojčično ravnino.

## Reference:

- [1] M. Otoničar, S. D. Škapin, M. Spreitzer and D. Suvorov. Compositional range and electrical properties of the morphotropic phase boundary in the  $Na_{0,5}Bi_{0,5}TiO_3-K_{0,5}Bi_{0,5}TiO_3$  system. *Journal of the European Ceramic Society*, 30(4):971-979, 2010.
- [2] R. Zuo, X. Fang and C. Ye. Phase Transitional Behavior and Piezoelectric Properties of Lead-Free ( $Na_{0,5}K_{0,5}NbO_3-(Bi_{0,5}K_{0,5})TiO_3$ ) Ceramics. *Journal of the American Ceramic Society*, 90(8):2424-2428, 2007.
- [3] S. Y. Cheng, N. J. Ho and H. Y. Lu. Transformation-Induced Twinning: The  $90^\circ$  and  $180^\circ$  Ferroelectric Domains in Tetragonal Barium Titanate. *Journal of the American Ceramic Society*, 89(7):2177-2187, 2006.

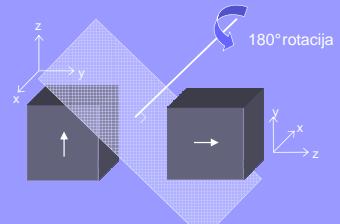
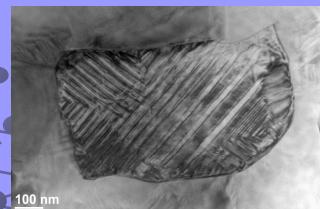


# Analiza domenske strukture v $K_{0,5}Bi_{0,5}TiO_3$ keramiki



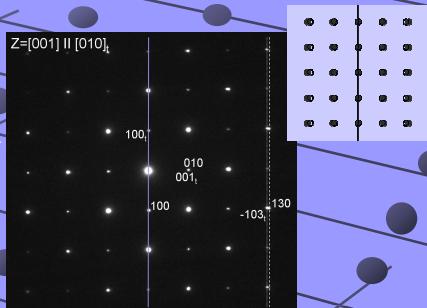
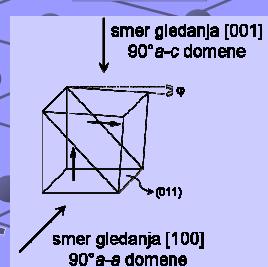
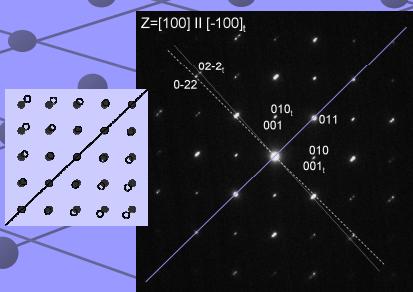
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Študijski program: Nanoznanosti in nanotehnologije  
Mentor: doc. dr. Srečo D. Škapin  
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$K_{0,5}Bi_{0,5}TiO_3$  keramika ima domensko zgradbo, ki kompenzira deformacije osnovnih celic zaradi spontane polarizacije materiala

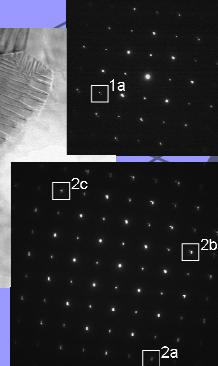
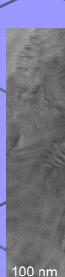


ROTACIJSKI DVOJČKI

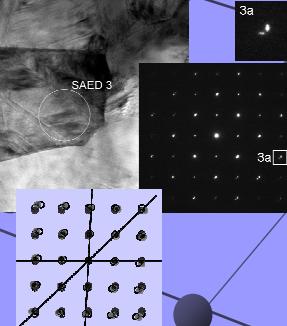
V tetragonalni strukturi nastanejo domene v obliki lamel; kot med dipolnimi momenti posameznih lamel je  $90^\circ$



Zrna s področji različno usmerjenih domen in vzorci elektronske difrakcije z večkratno cepitvijo uklonov:



- domena 1
- domena 2 ( $90^\circ$  a-c)
- domena 3 ( $90^\circ$  a-a)
- domena 4 ( $90^\circ$  a-c)



## ZAKLJUČKI

- >  $90^\circ$  domene:  $Z = [100]$  ali  $[010]$  —> cepitev uklon ov vz dolž  $[011]$  ali  $[101]$   
 $Z = [001]$  —> cepitev uklonov vz dolž  $[010]$  ali  $[100]$
- > dvojnične ravnine  $(011)$  ali  $(101)$
- > rotacijski dvojčki:  $180^\circ$  rotacija okoli dvoštevne dvojčne osi
- > smer polarizacije dvojčka pod kotom  $\approx 90^\circ$  glede na smer polarizacije matrične domene

Možnost uporabe:  
Kot piezoelektrični material, pri katerem pod vplivom električnega polja pride do mehanske deformacije materiala (motor) ali v primeru mehanske obremenitve do generacije električnega naboja (generator).

→ FEROELEKTRIČNE + FEROELASTIČNE DOMENE

# Barium Hexaferrite Thick Films for Microwave Absorbers and Circulators

Simona Ovtar<sup>1,2</sup>, Darja Lisjak<sup>1</sup>

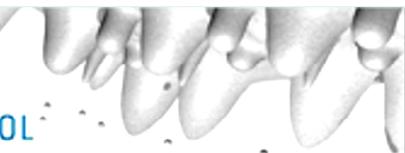
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Barium hexaferrite (BaHF) with the chemical formula  $\text{BaFe}_{12}\text{O}_{19}$  is a hard magnetic material and has high magnetic anisotropy field (MAF), 17 kOe. The easy direction of magnetization corresponds to the crystallographic c-axis and BaHF particles orient in this direction when are exposed to an external magnetic field. Because of the high MAF, a ferromagnetic resonant frequency appears from 45 to 50 GHz. For these reasons, BaHF can be used for electromagnetic absorbers (above 40 GHz) or for millimetre-wave non-reciprocal devices (i.e. circulators, isolators). Today, most of hexaferrites for microwave and millimetre-wave electronic components are prepared using ceramic technologies. To minimize the size of the electronic components, new techniques for thick-film deposition were developed. One of the simplest techniques is electrophoretic deposition (EPD). In the EPD process, the individually charged particles dispersed in a solvent are transported to the electrode of an opposite charge, where they agglomerate and form the deposit. The dispersed particles are one of the most important conditions for the preparation of homogeneous, dense and oriented deposits.

The stable magnetic suspensions of BaHF plate-like particles with diameter from 5–20 nm and 10–250 nm were prepared with surfactant dodecylbenzensulphonic acid in 1-butanol. The suspensions were deposited on the cathode ( $\text{Al}_2\text{O}_3$  coated with gold or platinum) by EPD. Different positions of electrodes were used. The randomly oriented deposits with thickness of 13  $\mu\text{m}$  were prepared from small BaHF plate particles with vertical position of electrodes. To prepare the oriented deposits from small particles, the magnetic field was applied parallel to the electric field. With applying magnetic field 2  $\mu\text{m}$  oriented thick films were prepared. In addition, the deposits with preferential orientation of the larger particles were prepared by using the horizontal position of electrodes, where the electric and the gravity fields were parallel to each other. Here, the 15  $\mu\text{m}$  thick oriented deposits were formed due to the shape anisotropy. The deposits were sintered at 950 °C for 10 hours or at 1300 °C for 3 hours to prepare films. The magnetic properties of the films were obtained with a vibration-sample magnetometer and the orientation was calculated from the XRD pattern. The high-frequency properties of the BaHF films were measured with a vector-network analyzer. Significant differences in the magnetic properties between the randomly oriented and magnetically-oriented films were shown. In case of magnetically-oriented films the remanent magnetization was higher when the magnetic field was applied perpendicular to the film plane. The orientation of particles in the deposit was also observed in the XRD pattern. The intensities of (00l) peaks were enlarged in the oriented film, because the easy direction of magnetization coincides with the crystallographic c-axis. We can conclude that the randomly oriented films of hard magnetic BaHF can be formed during EPD and that the oriented films can be prepared with or without an external magnetic field. The films show increased magnetic losses at 45-50 GHz, which makes this material interesting for microwave applications.



# Barium Hexaferrite Thick Films for Microwave Absorbers and Circulators

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## Introduction

1. Barium hexaferrite (BaHF) is a hard magnetic material with chemical formula  $\text{BaFe}_{12}\text{O}_{19}$ .
2. BaHF has high magnetic anisotropy field (17 kOe) and an easy direction of magnetization along (001) crystallographic axis.
3. Dispersed BaHF hard magnetic particles in suspension can be oriented with a gravity field or an external magnetic field.
4. Electrophoretic deposition (EPD) is a process where charged particles from suspension are transported to the conductive substrate, where they agglomerate and deposit.

## Experimental

1. Stabile magnetic suspensions from 5–20 nm and 10–250 nm BaHF plates were prepared with dodecylbenzensulphonic acid in 1-butanol.

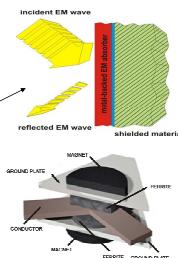
## Results

Orientation of particles	Randomly oriented	Oriented with gravity field	Oriented with magnetic field
Figure of EPD SEM image			
Film properties	Thickness: 13 μm	Thickness: 15 μm	Thickness: 2 μm
XRD pattern:	 $\text{orient} = \frac{\sum I_{00l} - \sum I_{00l}^o}{\sum I_{hkl} - \sum I_{hkl}^o} \times 100$	 $\text{orient} = \frac{\sum I_{00l} - \sum I_{00l}^o}{\sum I_{hkl} - \sum I_{hkl}^o} \times 100$	 $\text{orient} = \frac{\sum I_{00l} - \sum I_{00l}^o}{\sum I_{hkl} - \sum I_{hkl}^o} \times 100$
Magnetic measurements:	 $SQ = \frac{M_k}{M_s}$ $\text{Ideal oriented film } SQ_{\text{per}}=1$	 $SQ = \frac{M_k}{M_s}$	 $SQ = \frac{M_k}{M_s}$
Microwave measurements:	 $\text{orient} = 16\%$ $\text{Natural ferromagnetic resonance (0 Oe)} = 48 \text{ Gz}$		

Acknowledgement: This work was financially supported by ARRS

## Application

1. BaHF has high a magneto anisotropy field and can be used as a **permanent magnet**.
2. Thick films of BaHF can be used for **absorbers at high-frequency** (above 40 GHz).
3. Oriented films of BaHF can be used for **millimetre-wave non-reciprocal device**, i.e. circulators, isolators or gyrators.
4. Different positions of electrodes and external magnetic field were used.
5. Electric field 71 V/cm and deposition time 15 min
6. The films were prepared by sintering at 950 °C for 10 h or 1300 for 3 h.



## Conclusion

1. Higher density of oriented films, due to anisotropic grain growth.
2. The intensities of (001) peaks in oriented films were enlarged.
3. For oriented films the magnetic properties were different with measuring them parallel than perpendicular to the film plane.
4. The natural FMR for partly oriented film appears at 48GHz, which makes this material interesting for microwave applications.

Reference: 1. S.Ovtar, D. Lisjak, M. Drofenik, J. Colloid Interface Sci., 2009 (337), 456

2. S. Ovtar, D. Lisjak, M. Drofenik, Surf. Interface Anal., in press

# Biscuit – sintered zirconia ceramics for dental applications

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The available literature data suggest that the differences in the elastic moduli between zirconia and dentine result in stresses at their interface that increase the possibility of a marginal seal failure. As a consequence, this can lead to the development of secondary caries and/or periodontal disease.

**Objective:** In the present work we report on the development of moderately porous Y-TZP ceramics with a reduced elastic modulus ( $E$ ), while preserving its useful flexural strength ( $\sigma$ ).

**Methods:** The so-called core-shell concept was adopted for the preparation of the starting materials. This concept exploits homo-aggregation, which results in a uniform distribution of nanosized particles attached to the surface of the submicron-sized particles in the slurry. After the slip casting, the green pellets were biscuit-sintered at various temperatures in the ambient air in order to obtain moderately porous zirconia samples.

**Results:** In the temperature region from 1000°C to 1400°C the nanostructured ceramic exhibits a lower densification rate in comparison with the dry-pressed sub-micron sized Y-TZP powders. In contrast, the flexural strength of the biscuit-sintered nanostructured material rapidly increases with the fractional density, starting from 80MPa at 55% of TD and reaching a plateau of 670MPa at 70% of TD. The highest increase, from 200MPa to 450MPa, was observed for a minimal increase in densification from 58% TD to 60% TD. The calculated dependence of  $E$  on the relative density shows that at 70% of TD the value is reduced from an initial 210GPa at >99% of TD to 70GPa. The empirical equations used are a reasonably good fit with the measured values.

**Conclusion:** We believe that the remarkable increase in strength is related to the larger area of the inter-particle contacts. The addition of the nanoparticles enhances the formation of necks between the nanosized and/or the submicron-sized particles. At a TD of 70% the flexural strength almost doubles with respect to the conventionally used dry-pressed submicron-sized Y-TZP powder.



## Biscuit - sintered zirconia ceramics for dental applications

Background photograph shows dental posts made in Slovenia:

**SiPOST**

Sebastjan Perko

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### Introduction:

Yttria-stabilized tetragonal zirconia (Y-TZP) has become increasingly popular as an alternative high-toughness core material in dental restorations because of its biocompatibility, attractive mechanical properties and its superior natural appearance compared with metal - ceramic restorations. The available literature data suggest that the differences in the elastic moduli ( $E$ ) between zirconia and dentine result in stresses at their interface that increase the possibility of a marginal seal failure.<sup>1</sup> As a consequence, this can lead to the development of secondary caries and/or periodontal disease. For such applications, novel dental materials exhibiting lower elastic modulus than currently available are being developed.

### Objectives:

- to reduce elastic modulus of Y-TZP ceramic while preserving its useful flexural strength ( $\sigma$ )
- to evaluate mechanical properties of biscuit sintered nanostructured Y-TZP ceramics

### Methods:

The so-called core-shell concept was adopted for the preparation of the starting materials.<sup>2, 3</sup> This concept exploits homo-aggregation, which results in a uniform distribution of nanosized particles attached to the surface of the submicron-sized particles in the slurry. After the slip casting, the green pellets were biscuit-sintered at various temperatures in the ambient air in order to obtain moderately porous zirconia samples.

### Materials:

Y <sub>2</sub> O <sub>3</sub> mol%	BET, m <sup>2</sup> /g	crystallite size (nm)	pH	solids content (wt%)
TZ-3Y* (Toosh)	3	15.4	28	/ /
XZO 1350H* <sup>4</sup> (MEI, chemicals)	5	/	11	9.2 22-30



Figure 1: Dependence of the zeta potential on pH for a) the as-received nano- and micron-sized Y-TZP suspensions and b) for the combination of the surface-modified micron-sized Y-TZP and unchanged nano-sized Y-TZP suspensions. The vertical line indicates the pH at which the core-shell material was prepared.

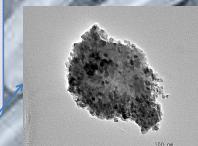


Figure 2: TEM micrograph of a single TZ-3Y core-particle coated with nano-sized zirconia particles.

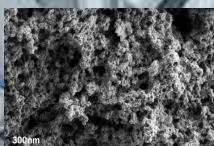


Figure 3: SEM analysis of the fractured surface of the slip casted pellet shows homogeneous distribution of shell particles through the whole thickness of the green sample.

### Results:

- densification and mechanical properties of biscuit-sintered nanostructured ceramics:

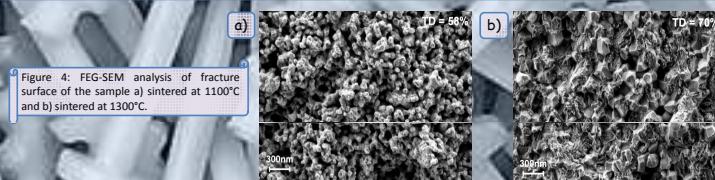


Figure 4: FESEM analysis of fracture surface of the sample a) sintered at 1100°C and b) sintered at 1300°C.

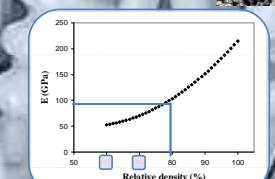


Figure 5: Calculated dependence of  $E$  vs. relative density.

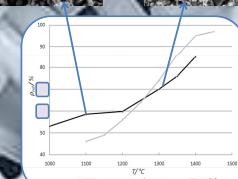


Figure 6: Dependence of relative density vs. temperature.

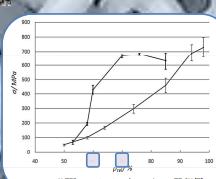


Figure 7: Biaxial flexural strength vs. theoretical density for nanostructured ceramics along with comparison curve of biscuit-sintered TZ-3Y powder.

### Characterization:

- ✓ zetapotential analysis
- ✓ fractional density
- ✓ biaxial flexural strength
- ✓ TEM and SEM analyses

### Conclusions:

The remarkable increase in strength is related to the larger area of the interparticle contacts.<sup>4</sup> The addition of the nanoparticles enhances the formation of necks between the nanosized and/or the submicron-sized particles. At a TD of 70% the flexural strength almost doubles with respect to the conventionally used dry-pressed submicron-sized Y-TZP powder.<sup>5</sup>

### References:

1. M. Guazzato, I. Ichim, M.V.Swain: IXth ECERS (2005), Book of abstracts, p.207
2. F. Caruso, Nanoengineering of particle surfaces, Nanengineering of particle surfaces, Adv. Mat., 13, No.1, (2001)
3. M. Carballeira, A. Videcoq, P. Abelaard, C. Pagnoux, F. Rossignol, R. Ferrando, Heteroaggregation between Al<sub>2</sub>O<sub>3</sub> submicrometer particles and SiO<sub>2</sub> nanoparticles: Experiment and simulation, Langmuir, 24, 3001-3008, (2008)
4. D. Hardy, D. J. Green, Mechanical properties of partially sintered alumina, J. Eur. Ceram. Soc., 15, 769-775, (1995)
5. S. Perko, A. Dakskobler, T. Kosmac, High performance porous nanostructured ceramics, In press, J. Am. Ceram. Soc. (2010)

# Oxide thermoelectrics

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Thermoelectrics are solid state devices with two basic modes of operation. The first mode, based on the Peltier Effect, involves the application of current through the module, absorbing heat from one side of the device and emitting it from the other side. The generation of cold and hot faces of the plate makes Peltier devices ideal for heating and cooling applications. Conversely, the Seebeck Effect, second mode of operation, can be used for power generation purposes. When a temperature gradient is applied across a TE module an electric current is produced [1].

The efficiency of a thermoelectric material depends on two conditions. The first is the Carnot efficiency (sets the limiting value on the fraction of the heat which can be used), which for all heat engines cannot be exceed. The second condition depends on the thermoelectric properties, Seebeck coefficient ( $S$ ), electrical resistivity ( $\rho$ ) and thermal conductivity ( $\kappa$ ). All these properties of material together are included in a dimensionless description of thermoelectric properties called Thermoelectric Figure of Merit ( $ZT$ ). For small temperature difference this efficiency is given by  $ZT = S^2 T / \rho \kappa$  [1].

Therefore the achievement of the highest possible thermoelectrical efficiency is a challenge owing to the conflicting combination of material traits that are required. Good thermoelectrics are therefore crystalline materials that manage to scatter phonons for reduced thermal conductivity without significantly disrupting the electrical conductivity. Thermoelectrics therefore require a rather unusual, so called a 'phonon-glass electron-crystal', (PGEC), type of material [2, 3].

Recently a new class of thermoelectric materials was introduced based on a metal oxide such as  $\text{Na}_2\text{CoO}_4$ ,  $\text{CaMnO}_3$ ,  $(\text{ZnO})(\text{In}_2\text{O}_3)$ ,  $\text{ZnO}$  and  $\text{CuAlO}_2$ . The listed oxide thermoelectric materials appear promising, since they are chemically stable at high temperatures and they have high oxidation resistance. They are also nontoxic [4]. Beside  $\text{ZnO}$  which is an outstandingly promising oxide n-type material as a high-temperature thermoelectric material above 973K, we shall also study p-type conductors  $\text{Na}_x\text{CoO}_2$ ,  $\text{Ca}_3\text{Co}_4\text{O}_9$  and their related systems, which exhibit thermoelectric anisotropy and fairly high thermoelectric performance due to the layered structure. We will study the synthesis of those thermoelectric materials and tailoring of their thermoelectric characteristics for the best thermoelectric efficiency via structure, microstructure and phase optimization, and with addition of various dopants. Finally, by constructing a new measuring system for thermoelectric characterization, we will be able to fully assess the thermoelectric properties of prepared materials in regard to their composition, structural and microstructural characteristics.

## References:

- [1] D.M. Rowe, *CRC Handbook of Thermoelectrics, Introduction*, (1995), 1-687
- [2] G. J. Snyder, Eric S. Toberer, Complex Thermoelectric Materials, *Nature Mater.*, 7, (2008), 105-114
- [3] G. J. Snyder, T. Ursell, Thermoelectric efficiency and compatibility, *Phys. Rev. Lett.*, 91, (2003) , 148-301
- [4] S. Sugiura, The Measurement of Thermoelectricity (Ch 14). *Materials for Energy Conversion Devices*, eds. Sorrell, C., Sugiura, S. & Nowotny J., Woodhead, Publishing in Materials, Cambridge, 2005, 359–364



## Oxide thermoelectrics

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**Thermoelectric materials DIRECTLY CONVERT HEAT INTO ELECTRICITY and vice versa.**

### Efficiency of thermoelectric materials

The efficiency of thermoelectric materials for both power generation and cooling is determined by its Thermoelectric Figure of Merit ( $ZT$ )

$$ZT = S^2 T / \rho k$$

Max.  $ZT$  depends on: **HIGH** Seebeck coefficient ( $S$ ), temperature ( $T$ ), **LOW** electrical resistivity ( $\rho$ ), and **LOW** thermal conductivity ( $k$ ).

### GOOD thermoelectric material

Electrons free to transport charge and heat  
Phonons disrupted from transporting heat

### Phonon-Glass Electron-Crystal material (PGEC)

Optimization of conflicting properties

### Oxide thermoelectrics

P-type:  $\text{Na}_4\text{CoO}_4$ ,  $\text{Ca}_3\text{Co}_4\text{O}_9$ , etc.

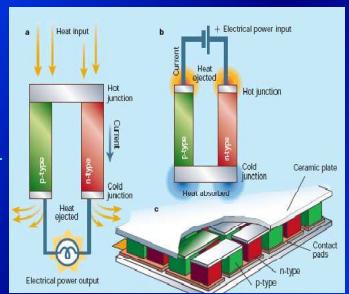
N-type:  $(\text{ZnO})(\text{In}_2\text{O}_3)$ ,  $\text{SrTiO}_3$ , Al doped  $\text{ZnO}$ , etc.

Advantages: - High durability against high temperature and oxidation  
- Chemical stability  
- Nontoxic  
- Light weight  
- Small thermal expansion

### Thermoelectric devices

Schematic presentation of typical thermoelectric applications (devices):

- a) power generation, and
- b) refrigeration device comprising of p-type and n-type semiconducting material.
- c) State of the art thermoelectric device containing several thermocouples.



### State of the art thermoelectric materials

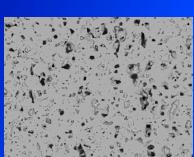
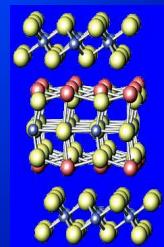
Conventional materials:  $\text{Bi}_2\text{Te}_3$ ,  $\text{Sb}_2\text{Te}_3$ ,  $\text{GeTe}$ ,  $\text{BiSb}$ ,  $\text{PbTe}$  alloy,  $\text{Zn}_3\text{Sb}_4$ , etc.

Limitations: - Poor chemical stability

- Brittle nature
- Toxic element
- Rare element
- Oxidation

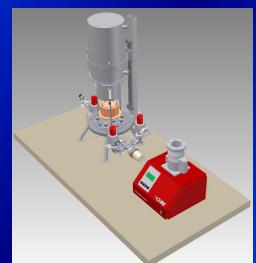
### Our work

- Synthesis of thermoelectric material ( $\text{Na}_x\text{CoO}_2$ ,  $\text{Ca}_3\text{Co}_4\text{O}_9$  and related systems, ceramics in  $\text{ZnO} - \text{In}_2\text{O}_3$  system doped with various dopants)
- Tailoring of thermoelectric characteristics for the best thermoelectric efficiency via:
  - structure
  - microstructure
  - phase optimization
  - with addition of various dopants



Structure of the  $\text{Ca}_3\text{Co}_4\text{O}_9$  phase and SEM image of the microstructure.

SEM image of the microstructure of  $\text{ZnO}-\text{In}_2\text{O}_3$  phase.



- Constructing a new measuring system for thermoelectric characterization

### Thermoelectric modules



### Applications

Thermoelectric cooling solutions for electronic telecommunication enclosures, computer cabinets, mini-fridges, and in other enclosed spaces that require specialized climate control.



NASA's Cassini Probe to Saturn and Jupiter



A radioisotope thermoelectric generator



Prototype projectors ; concepts:  
compactness,  
reduction of fans,  
and  
low noise.



# The giant electrocaloric effect: phenomenon for application in cooling and heating devices of new generation

**Brigita Rožič<sup>1,2</sup>, Zdravko Kutnjak<sup>1</sup>, Barbara Malič<sup>3</sup>, Hana Uršič<sup>3</sup>, Janez Holc<sup>3</sup>, Maja Kosec<sup>3</sup>, Raša Pirc<sup>4</sup>, Robert Blinc<sup>1</sup>**

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Electrocaloric effect (ECE) is a change in the temperature of electrocaloric material due to the applied electrical field under adiabatic conditions, and it generates great interest due its application in new generation cooling or heating devices, which would be friendlier for environment.

Recent predictions of the existence of the giant ECE in inorganic ferroelectrics are based solely on the indirect measurements of the electrical polarization and not on direct measurements of the ECE itself [1]. In our case, this effect was measured directly and the observed magnitude of ECE is consistent with recent predictions. We show direct measurements of ECE in PMN, PMN-30 PT, PMN-35 PT and in PLZT 8/65/35 ceramics [2]. Both bulk and thin films were measured.

The temperature dependence of ECE shows that the maximum ECE is achieved at the ferroelectric phase transition and the magnitude of ECE indicates that the giant ECE can be easily found in different classes of ferroelectric relaxors.

As we mentioned above, the ECE is very attractive phenomenon in a broad range of applications like actuators, sensors and also in heating and cooling devices, i.e. electrical refrigerator. Novel cooling elements could be made without moving parts and thus greatly simplifying the device configuration [2].

## Reference:

- [1] A. S. Mischenko, Q. Zhang, J. F. Scott, R. W. Whatmore, N. D. Mathur. Giant Electrocaloric Effect in Thin-Film PbZr<sub>0.95</sub>Ti<sub>0.05</sub>O<sub>3</sub>. *Science*, 311: 1270-1271, 2006.
- [2] B. Rožič, Sheng-Guo Lu, Z. Kutnjak, B. Malič, H. Uršič, J. Holc, M. Kosec, R. Pirc, R. Blinc, B. Neese, Minren Lin, E. Furman, Q. M. Zhang, poslano v objavo, 2010.



## THE GIANT ELECTROCALORIC EFFECT: phenomenon for application in cooling and heating devices of new generation

Brigita Rožič, prof. mat.

Jožef Stefan International Postgraduate School, Nanosciences and Nanotechnologies

MENTOR: prof. dr. Zdravko Kutnjak

CO-AUTHORS: dr. Barbara Malič, dr. Hana Uršič, dr. Janez Holc, dr. Marija Kosec,

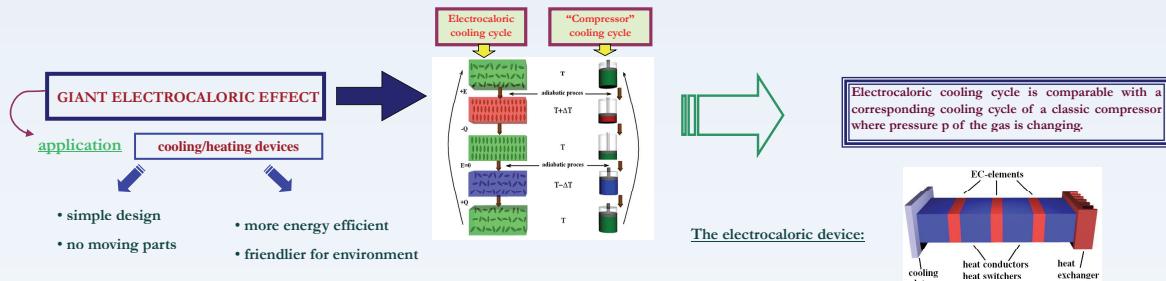
dr. Raša Pirc, dr. Robert Blinc

### Abstract

Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia

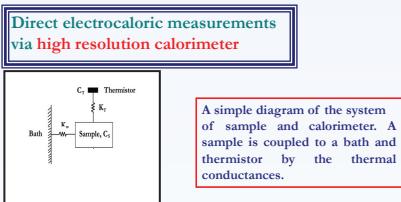


Electrocaloric effect (ECE) is a change in the temperature of material due to electric field under adiabatic conditions, and it generates great interest due to its application, for example in electrical refrigeration. A giant electrocaloric effect was observed in inorganic ferroelectrics [1]. These observations were based on the indirect measurements of the electrical polarization. We show direct measurements of ECE in PMN, PMN-30 PT, PMN-35 PT and in PLZT 8/65/35 ceramics. Both bulk samples and thin films were measured. The temperature dependence reveals that the maximum of ECE is obtained at the ferroelectric phase transition. The magnitude of ECE shows that the giant ECE can be easily found in different classes of relaxor ferroelectrics.

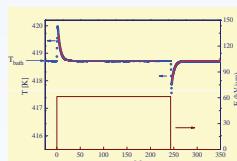


### Experimental method

### SAMPLES



#### Measurement:

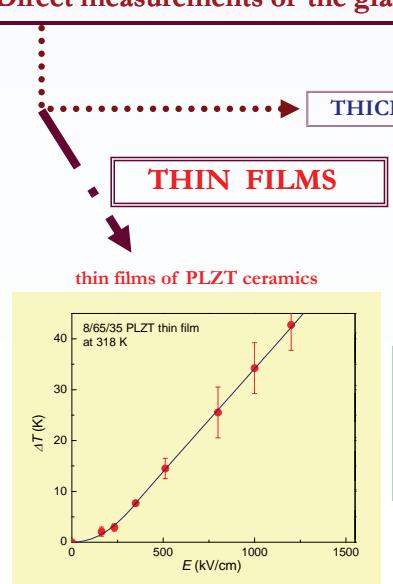


- step electrical signal used
- $\Delta T$  calculated from fits to the exponentially decaying wings
- resistive heating also taken into account

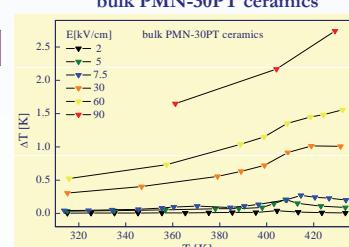


Produced by J. Holc, H. Uršič, M. Kosec, JSI

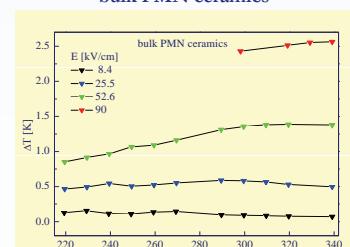
### Direct measurements of the giant electrocaloric effect



#### bulk PMN-30PT ceramics



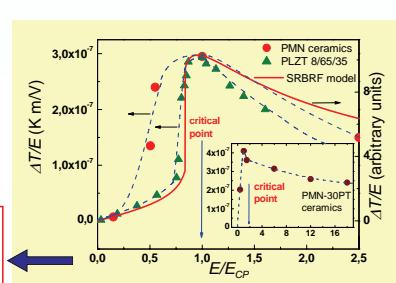
#### bulk PMN ceramics



### Conclusion

We can conclude that direct measurements confirm existence of the giant electrocaloric effect in different classes of relaxor ferroelectrics. The largest electrocaloric effect is observable in thin PLZT films.

$\Delta T/E$  as a function of the maximum of the amplitude of the electric-field pulses (in units of  $E_{CP}$ ) in bulk PMN, 8/65/35 PLZT and PMN-30PT ceramics (inset with same axis labels). Solid red line represents results of calculations of  $\Delta T/E$  based on a SRBRF model [2].



### References

- [1] A.S. Mischenko, Q. Zhang, J.F. Scott, R.W. Whatmore, N.D. Mathur, Science 311, 1270 (2006).
- [2] B. Rožič, Sheng-Guo Lu, Z. Kutnjak, B. Malič, H. Uršič, J. Holc, M. Kosec, R. Pirc, R. Blinc, B. Neese, M. Lin, E. Furman, Q. M. Zhang (postano v objavo, 2010)

# Control of phase composition in the hydrothermal synthesis of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$

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Sodium bismuth titanate,  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  (NBT), is a complex perovskite extensively studied over past years due to its interesting piezoelectric and ferroelectric properties. The relaxor ferroelectric behavior of the NBT material opens up the possibility for application as a voltage-tunable capacitor. The aim of work was preparation of nano-sized crystalline NBT particles which would be subsequently employed in the form of a thin film. In contrast to other more conventional techniques, the hydrothermal synthesis attracted considerable attention because it enables production of nanosized highly crystalline powders from a variety of inexpensive precursors under moderate temperature conditions.

Several papers reported the hydrothermal preparation of NBT. In addition, Lencka et al. [1] performed thermodynamic modelling, predicting the region of stability for pure NBT phase. Syntheses were based on proposed model and supporting experimental findings.

The hydrothermal synthesis of the NBT powder was performed in a strong alkaline medium.  $\text{TiO}_2$  (anatase) and  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  were used as the titanium and bismuth precursors and  $\text{NaOH}$  served as a source of sodium cations and to provide a highly basic environment. The influences of various alkaline conditions, the concentration of precursors, the reaction temperature and time on the formation of NBT were studied. The obtained powders were characterized by X-ray diffraction analysis and transmission electron microscopy.

Experimental results revealed that several parallel and consecutive reactions are proceeding in the reaction system, resulting in the formation of NBT along with secondary sodium titanate phases at the beginning of the reaction. Secondary phases arised also at lower alkali concentrations and mild temperature conditions. Both parameters significantly influence the solubility of precursors and the stability of NBT phase and therefore define the final phase composition obtained under chosen hydrothermal conditions. Secondary phase free composition was attained by employment of higher temperatures and stronger alkaline conditions. In addition, an excess of bismuth cations promoted the formation of phase pure product. Our experimental results led us to the conclusion that alkaline conditions ultimately define the crystallization process of NBT phase under hydrothermal treatment, mainly due to the significant contribution to the dissolution of precursors that enabled further recrystallization.

## References:

- [1] M. Lencka, M. Oledzka, and R.E. Riman, Hydrothermal Synthesis of Sodium and Potassium Bismuth Titanates, *Chem. Mater.*, 2000, 12 (5), 1323–1330



# Control of phase composition in the hydrothermal synthesis of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$



T. Šetinc

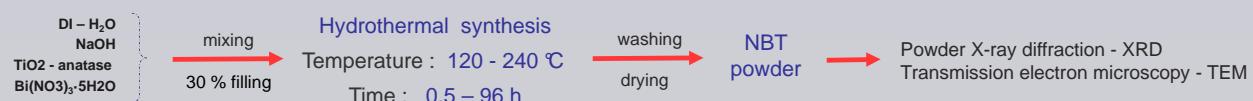
Study programme : Nanoscience and Nanotechnology, 2. year  
 Supervisor : D. Suvorov  
 Advanced Materials Department, Jožef Stefan Institute

$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  - a complex perovskite, interesting piezoelectric and ferroelectric properties

**Hydrothermal synthesis** - enables production of nanosized highly crystalline powders from a variety of inexpensive precursors under moderate temperature conditions

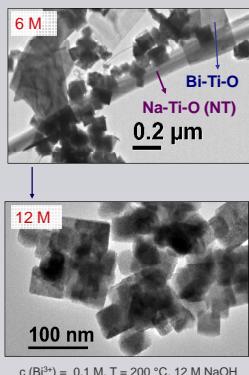
- Aim**
- study of reaction mechanisms
  - acquirement of the correlations between the chemical-thermodynamic parameters applied and the formation of NBT and secondary phases

## Experimental



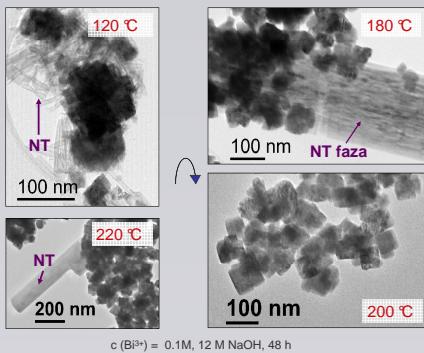
## Results

### NaOH concentration



$c(\text{Bi}^{3+}) = 0.1 \text{ M}, T = 200^\circ\text{C}, 12 \text{ M NaOH}$

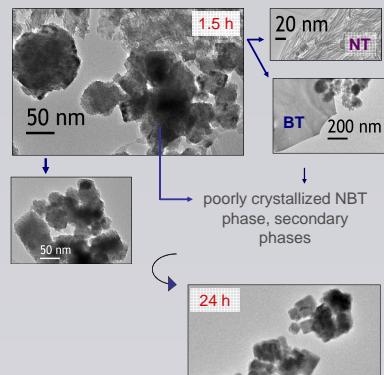
### Temperature



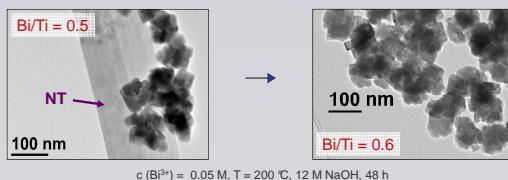
$c(\text{Bi}^{3+}) = 0.1 \text{ M}, 12 \text{ M NaOH, 48 h}$

### Characterization

### Reaction time



### Bi/Ti ratio



$c(\text{Bi}^{3+}) = 0.05 \text{ M}, T = 200^\circ\text{C}, 12 \text{ M NaOH, 48 h}$

## Summary

Control over the crystallization process and thus the final phase composition can be attained by managing parameters that ultimately define the solubility of chosen precursors and the stability of NBT phase under applied conditions.

### Future work

- synthesis of NBT-based solid solution
- employment of NBT/NBT-based ceramic particles in thin films through polymer-assisted assembly

### Final product

- lead-free piezoelectric powder materials
- NBT thin films, composite thin films, multicomponent systems

### Applications

- piezoelectric components  
sensors, resonators, transducers, actuators,...
- voltage-tunable capacitors, phase shifters, electronic components

# Comparison of the optically measured vaporization energy by ultrafast laser spectroscopy and condensation energy determined from specific heat measurements in superconducting cuprates

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Condensation energy can be thought as the difference in ground state energy between the normal state and the superconducting state in a superconductor. In a way to understand and prove theory for superconducting transition, an accurate measurement of the condensation energy is needed [1]. The most common method for determination of condensation energy is by measuring the thermodynamical critical field and alternatively, condensation energy can be found by integrating the difference in specific heats in the normal and superconducting states from  $T = 0$  to the superconducting transition temperature  $T_c$  [2,3]. With the use of femtosecond laser spectroscopy we can measure the absorbed light energy needed to destroy the superconducting condensate. The method relies on accurate measurement of the energy  $U_v$  needed to transform the superconducting state into the normal state (i.e. vaporize the condensate). By changing the laser pulse intensity, the superconducting state is destroyed, and the characteristic superconducting signal saturates, which can be determined very accurately. The accuracy of the deposited energy is thus limited only by the geometric factors related to the laser beam profile and optical absorption length  $\lambda_{op}$ . Recently, it was shown that the reflectivity of superconducting  $La_{2-x}Sr_xCuO_4$  ( $x = 0.1$ ,  $x = 0.15$ ) changes significantly when ultrashort intense laser pulses cause a transition from the superconducting state to a normal state [4]. The first measurements in  $La_{2-x}Sr_xCuO_4$  gave a vaporization energy  $U_v$  which was significantly higher than the condensation energy  $U_c$  determined from the specific heat measurements. Here we report on systematic measurements of the vaporization energy in a two different cuprates:  $YBa_2Cu_3O_{7-\delta}$  and  $La_{2-x}Sr_xCuO_4$  ranging from the underdoped to the overdoped region. It was found that the condensate vaporization energy  $U_v$  increases as a square power of  $T_c$  and it is approximately 16-18 times greater than condensation energy extracted from specific heat measurements, implying a significant heat capacity of the 'bosonic glue' responsible for its formation.

[1] E. Demler and S. Zhang, Nature 396, 733-735 (1998).

[2] J. W. Loram, J. L. Tallon and W. Y. Liang, Phys. Rev. B 69, 060502 (2004).

[3] M. Roulin, A. Junod and E. Walker, Physica C 296, 137-152 (1998).

[4] P. Kusar, V. V. Kabanov, J. Demsar, T. Mertelj, S. Sugai and D. Mihailovic, Phys. Rev. Lett. 101, 227001 (2008).



## Comparison of the optically measured vaporization energy by ultrafast laser spectroscopy and condensation energy determined from specific heat measurements in superconducting cuprates



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Tomaž Mertelj and Dragan Mihailović

Study program: Nanosciences and Nanotechnologies, Nanophysics

Jožef Stefan International Postgraduate School

Supervisor: prof. dr. Dragan Mihailović

Complex Matter Department

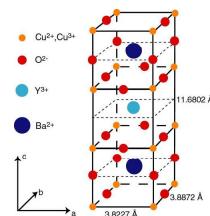
Jožef Stefan Institute, Jamova 39, Ljubljana, Slovenia

### Motivation

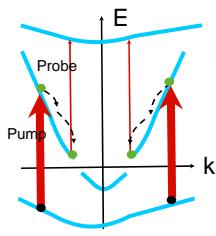
Our goal was determination of the energy needed to transform the superconducting state into the normal state (i. e. vaporize the condensate) and compare with calculated condensation energy in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

### Physical properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO) is high- $T_c$  superconducting cuprate with layered perovskite and highly anisotropic structure. An essential structural element is one or more copper oxide plane ( $\text{CuO}_2$ ), which is thought to contribute to the superconducting properties. Changing the oxygen stoichiometry in charge reservoirs planes (located above and below  $\text{CuO}_2$  planes), leads to change in electronic properties (change in  $T_c$ ).



Schematic structure of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . Unit cell consists of two  $\text{CuO}_2$  planes with Y ion in between. Charge reservoirs planes are  $\text{CuO}$  planes.

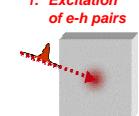


### How we can determine vaporization energy?

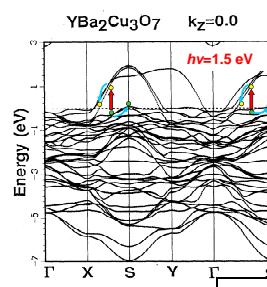
For studying quasiparticle relaxation dynamics we used femtosecond time-resolved pump-probe technique. The wavelength of the laser pulses was  $\lambda=800 \text{ nm}$  (~1.5 eV) and their pulselength was ~50 ps. The intensity ration of pump and probe beams was typically 100. To avoid any possible coherent effects, these two beams were perpendicular polarized.

Schematic of pump-probe technique. With the first beam - pump we excite the sample and with the second beam we probe the changes in reflectivity (transmission) as a function of time delay after the first pulse.

#### 1. Excitation of e-h pairs



#### 2. Intraband e-e scattering and thermalization with optic phonons $\tau \sim 10 - 40 \text{ fs}$



Representation for the energy band structure in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and excitation and relaxation processes.

By comparing measured vaporization energy and thermodynamically determined condensation energy, we found that certain amount of energy is stored by the glue boson.

Copper oxides superconductors (cuprates)

Iron-based superconductors (pnictides)

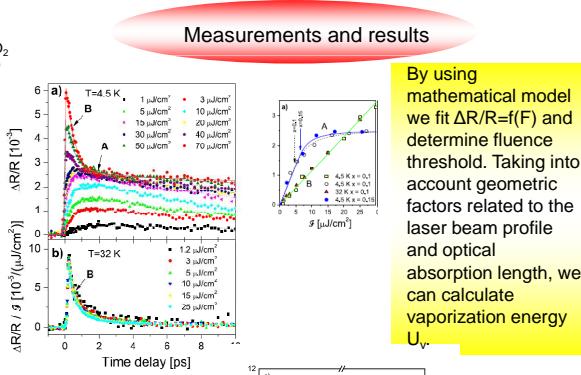
Conventional superconductors

Charge-density waves systems

Material	$T_c$ (K)	$U_v$	$U_c$	$U_v/U_c$
$\text{La}_2\text{Sr}_x\text{CuO}_4$ x=0.1	30	2-0.8 K/Cu	0.12 K/Cu	16.7
$\text{La}_2\text{Sr}_x\text{CuO}_4$ x=0.15	38	2.6-1 K/Cu	0.3 K/Cu	8.5
$\text{YBa}_2\text{Cu}_3\text{O}_7$	92	15.9-1.9 K/Cu	1.5 K/Cu	10.6
$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	63	7.5-0.7 K/Cu	0.77 K/Cu	9.7
$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	60	6.4-0.2 K/Cu	0.62 K/Cu	10.3
$\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ x=0.22, 0.45, 0.5	75	9.2±1 K/Cu	0.83 K/Cu	11.6
$\text{SmFeAsO}_1.0\text{F}_{0.9}$	49.5	1.8 K/Fe	1.7 K/Fe	~1
$\text{NbN}$	16	0.24 K/Nb	0.14 K/Nb	~1
$\text{TbTe}_3$	315	52 K/Tb	40.6 K/Tb	1.3
$(\text{TaSe}_4)_2\text{I}$	260	7.22-4.2 K/Ta	16.5-7.22 K/Ta	~1
$\text{K}_{0.3}\text{MoO}_3$	180	4.2 K/Mo	4.7 K/Mo	~1

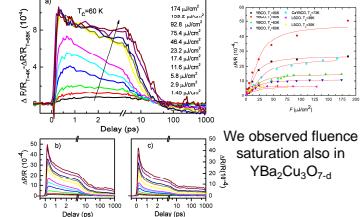
We annealed YBCO crystals in flowing oxygen at high temperatures from 400 to 900 °C for certain time and then quenching them by rapidly taking away from the oven. In this way we prepared samples with critical temperatures ranging from 60 to 90 K. Critical temperature was determined from magnetization measurements. At the end the surface was cleaved and all laser measurements have been performed on [a,b] plane.

### Sample preparation



By using mathematical model we fit  $\Delta R/R=f(F)$  and determine fluence threshold. Taking into account geometric factors related to the laser beam profile and optical absorption length, we can calculate vaporization energy  $U_v$ .

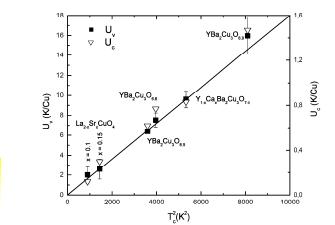
First measurements in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  showed that as we increase laser fluence, the amplitude of the signal first increases and then starts to saturate for certain value of the laser fluence.



We observed fluence saturation also in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

### Conclusions

Ratio  $U_v/U_c$  for cuprates is quite large compared to other superconductors and CDWs!



Vaporization vs condensation energy as a function of  $T_c^2$  for various doping level of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . Both, vaporization and condensation appear to follow square power law dependence on  $T_c$ .

# Application of Sonochemistry for Formation of Nanosized Silver and Silver/Hydroxyapatite Composite Particles

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Development of nanotechnology during last few decades gave significant contribution to different areas of research especially in biomedical sciences and improved characteristics of many biomaterials allowing their commercial application [1,2]. One of the representative examples is the development of nanomedicine, a new field of medical research which opened the possibility for interactions between nanomaterials and pathogens at the same scale of size [3]. This approach allowed development of nano-therapeutics, biosensors and point-of-care molecular diagnostic devices resulting in target, localized and more efficient medication [4]. So far, different techniques are applied for formation of these materials. Among them, sonochemical synthesis can be separated as a method based on the high temperature and pressure combined with intensive mixing induced by acoustic cavitation and micro jets. This method enables control over size, morphology and nano-/micro-structure of materials that are often unavailable by conventional methods [5].

The main goal of our work is application of the sonochemical synthesis method for preparation of nanosized particles of silver and silver composite with hydroxyapatite, as well-known bioactive and osteoconductive bioceramics for potential application in biomedicine as bone-defects filler with preventive anti-inflammatory properties. Urea, known as a homogeneous precipitation agent, was applied as capping agent of silver which allowed formation of silver complex able to be decomposed at 300°C and to form nanosized silver particles up to 20 nm in size. In the case of co-precipitation of silver with hydroxyapatite particles, after thermal decomposition of silver complex, hydroxyapatite/silver composite was obtained. At such conditions, uniform distribution of nanosized silver particles, with the size up to 10 nm, located onto the surface of hydroxyapatite submicrometre-sized rod-like particles, was obtained. These changes of the morphological properties of nano-silver, and its distribution, suggested a possible influence of hydroxyapatite surface on the mechanism of silver particles' growth. From the side of applicability, importance of obtained HA<sub>Ap</sub>/Ag composite morphology can be addressed to the well-known size-related dependence of antibacterial activity of metallic silver particles which showed significant improvement of this property of silver particle with the size in the range between 1 and 10 nm. This can be correlated to its possible application in orthopedics and dentistry.

## References:

- [1] M. Veerapandian, K. Yun. The state of the art in biomaterials as nanobiopharmaceuticals. *Digest Journal of Nanomaterials and Biostructures*, 4(2): 243-262, 2009
- [2] E. J. Harvey, J. E. Henderson. Nanotechnology and bone healing. *Journal of Orthopaedic Trauma*, 24(S): 25-30, 2010.
- [3] A. Surendiran, S. Sandhiya, S. C. Pradhan, C. Adithan. Novel applications of nanotechnology in medicine. *Indian Journal of Medical Research*, 130(6): 689-701, 2009
- [4] G. E. Marchant. Small is beautiful: What can nanotechnology do for personalized medicine? *Current Pharmacogenomics and Personalized Medicine*, 7(4): 231-237, 2009
- [5] J. H. Bang, K. S. Suslick. Application of ultrasound to the synthesis of nanostructured materials. *Advanced Materials*, 22(10): 1039-1059, 2010



## APPLICATION OF SONOCHEMISTRY FOR FORMATION OF NANOSIZED SILVER AND SILVER/HYDROXYAPATITE COMPOSITE PARTICLES

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Scientific program: Nanoscience and Nanotechnology

School: Jožef Stefan International Postgraduate school

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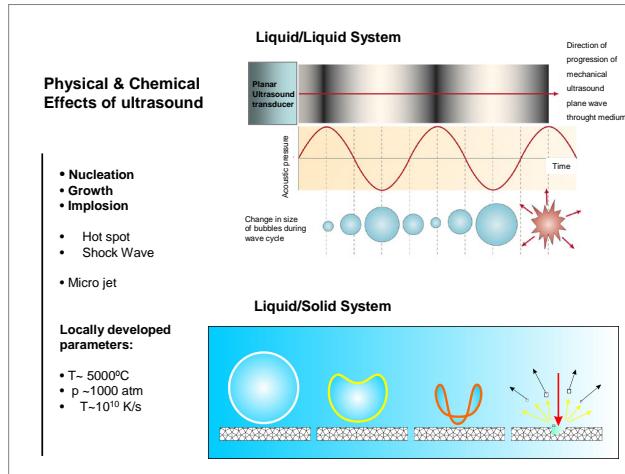
Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

Co-supervisor: Prof. Dr. Dragan Uskoković

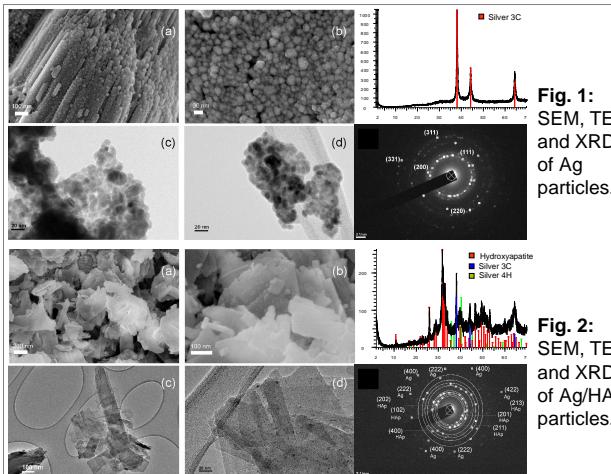
Institute of Technical Sciences, Knez Mihailova 35/4, 11000 Belgrade, Serbia



### Sonochemical synthesis



### Results



### Noble metals and hydroxyapatite properties

§ Nanosized silver is well-known antibacterial agent.

§ Hydroxyapatite is bioactive and osteoconductive bioceramics.

**The main goal of our work is:**

- Application of sonochemical synthesis method for preparation of nanosized silver particles and silver/hydroxyapatite composite for potential biomedical application.

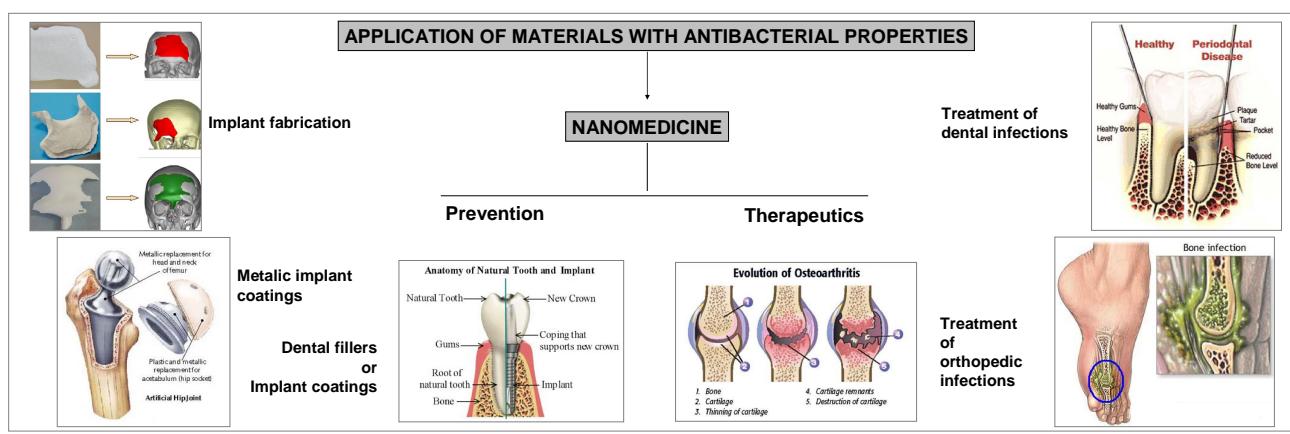
### Discussion & Conclusions

Obtained result show that:

- Monophase Ag with the structure of cubic silver (Ag 3C) and sphere-like morphology with particles up to 30 nm in size forms.
- In the case of HAp/Ag composite, Ag with the structure of cubic (3C) and hexagonal (6H) silver and sphere-like morphology with particles up to 10 nm in size attached to the surface of HAp rods was obtained.

**Morphology and structure of Ag particles within HAp/Ag composite can be influenced by the contribution of HAp surface to Ag particles growth.**

### Applications & Perspectives



# TiO<sub>2</sub> photocatalysis

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It is known that TiO<sub>2</sub> exhibits good photocatalytic properties which could be used in various commercial applications such as water and air purification or photo-induced biodegradation of microbes. TiO<sub>2</sub> occurs in nature in the form of three crystal polymorphs: anatase, brookite and rutile. For photocatalytic applications only anatase and rutile are of interest, however anatase shows greater photocatalytic activity. The ability to carry out photocatalytic reactions arises from TiO<sub>2</sub> band gap. When TiO<sub>2</sub> is irradiated with light of energy equal or higher to its band gap energy, an electron is promoted from the valence band to the conduction band leaving behind a positive hole. These photogenerated charge carriers can be trapped by surface adsorbed molecules, form strong radicals and oxidize organic compounds. However, a drawback in TiO<sub>2</sub> photocatalysis is that it absorbs mainly ultraviolet light. Therefore many efforts are made to prepare visible light-active TiO<sub>2</sub>.

Photocatalytic activity of titania (TiO<sub>2</sub>) depends on its crystal phase, crystallinity, particle size and/or specific surface area. High crystalline TiO<sub>2</sub> exhibits higher photocatalytic activity due to less bulk defects, which represent recombination centers for photogenerated charge carriers. On the other hand, high crystalline particles are usually large and the photogenerated electrons and holes undergo volume recombination before they can be trapped by surface adsorbed molecules and form radicals which are very important for photocatalytic activity. Powders consisting of small particles exhibit high specific surface area and offer more active sites for photocatalytic reactions [1], [2].

According to literature data, anatase with high specific surface area can be prepared by block copolymer templating sol-gel process. In order to achieve high crystalline anatase thermal treatment at higher temperature (300°-600°C) must be performed which leads to the collapse of organic templated structure supporting the TiO<sub>2</sub> framework and causes decrease of specific surface area. Thermal stability of TiO<sub>2</sub> can be improved by using phosphoric acid as a catalyst. The incorporation of phosphorus can stabilize TiO<sub>2</sub> framework by inhibiting particle growth and increase the specific surface area [3], [4].

It was reported that crystalline anatase can be prepared at low temperatures (90°C) by hydrothermal synthesis. At elevated temperature and pressure the conversion of amorphous TiO<sub>2</sub> into crystalline TiO<sub>2</sub> occurs [5].

Anatase powders with high crystallinity and high specific surface area were prepared by combined sol-gel and solvothermal synthesis followed by thermal treatment. Triblock copolymer P123 was used as a template and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) as a framework stabilizer. We can conclude that the use of P123 and H<sub>3</sub>PO<sub>4</sub> during the applied synthesis route leads to formation of crystalline anatase with high specific surface area (up to 296 m<sup>2</sup>/g) even after thermal treatment at high temperatures (at 500°C, up to 176 m<sup>2</sup>/g and at 600°C, up to 136 m<sup>2</sup>/g).

## References:

- [1] Z. Zhang, C.-C. Wang, R. Zakaria, J.Y. Ying, *The Journal of Physical Chemistry B* 102 (1998) 10871-10878
- [2] V. Puddu, H. Choi, D.D. Dionysiou, G. Li Puma, *Applied Catalysis B: Environmental* 94 (2010) 211-218
- [3] P. Yang, D. Zhao, D.I. Margolese, B.F. Chmelka, G.D. Stucky, *Chemistry of Materials* 11 (1999) 2813-2826
- [4] J.C. Yu, L. Zhang, Z. Zheng, J. Zhao, *Chemistry of Materials* 15 (2003) 2280-2286
- [5] D.S. Kim, S.-Y. Kwak, *Applied Catalysis A: General* 323 (2007) 110-118



## TiO<sub>2</sub> PHOTOCATALYSIS

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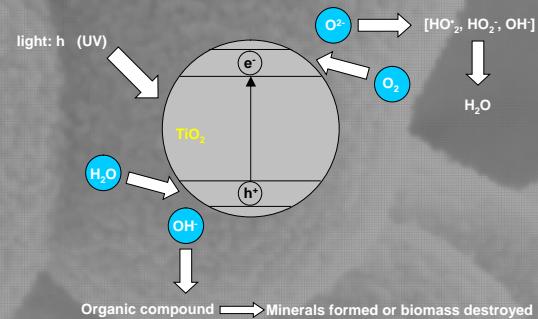
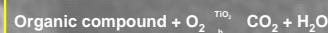
### Applications of TiO<sub>2</sub> photocatalysis:

- ✓ disinfection of surfaces and water from pathogenic organisms (bacteria, fungi, protozoa, algae)
- ✓ removal of organic and inorganic pollutants from waste water
- ✓ air purification

### Problem:

- ✓ TiO<sub>2</sub> absorbs mainly ultraviolet (UV) light

### Photocatalysis



### That is why most researches are oriented to:

- ✓ design of visible light responsive TiO<sub>2</sub> and
- ✓ increase of photoreactivity of TiO<sub>2</sub> in the near UV and visible region

### Photocatalytic activity of TiO<sub>2</sub> depends on:

- ✓ crystal phase (anatase or a mixture of anatase and rutile)
- ✓ crystallinity
- ✓ particle size and/or specific surface area

## Our research

Among the TiO<sub>2</sub> polymorphs (brookite, anatase, rutile) anatase is considered as the most photocatalytically active crystal phase and can be prepared by sol-gel synthesis followed by thermal treatment up to 300°C. Thermal treatment leads to particles growth and causes decrease of specific surface area. In sol gel synthesis amphiphilic copolymers can be used as templates supporting the 3D TiO<sub>2</sub> framework. The collapse of organic templated structure during thermal treatment can be prevented by phosphorous (P) incorporation as a TiO<sub>2</sub> framework stabilizer. On the other hand, high crystalline anatase with high specific surface area can be prepared by solvothermal synthesis at low temperatures.

### High crystallinity

Combination of sol-gel and solvothermal synthesis followed by thermal treatment (500°–700°C)

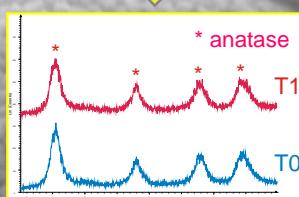


Figure 1: Crystal phases of the as prepared samples

### High specific surface area and small particle size

Use of amphiphilic triblock copolymer P123 as a TiO<sub>2</sub> framework template and incorporation of P from phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) as a TiO<sub>2</sub> framework stabilizer

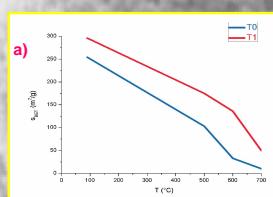
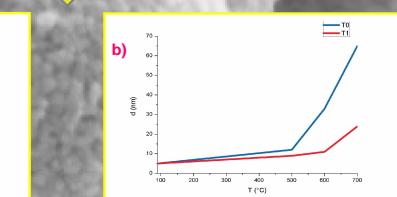


Figure 2: a) specific surface area of the as prepared samples and thermally treated samples b) particle size of the as prepared samples and thermally treated samples



Anatase powders with high specific surface area and high crystallinity were prepared by the combination of sol-gel and solvothermal synthesis.

Using triblock copolymer P123 as a TiO<sub>2</sub> framework template and phosphorous as a TiO<sub>2</sub> framework stabilizer it is possible to synthesize anatase powders with a high specific surface area (up to 296 m<sup>2</sup>/g) even after thermal treatment at high temperatures (at 500°C up to 176 m<sup>2</sup>/g and at 600°C up to 136 m<sup>2</sup>/g).

# Development of Materials for Industrial Applications

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Development of materials for industrial applications is associated with permanent increase in demands for: performance, effectiveness, toxicological and economical outcome of the final products. Therefore, our main goal is to improve the properties of industrially applicable materials with respect to: (i) better understanding of the basic processes and phenomena which occur in the matter, (ii) synthesis and processing of new materials and (iii) improvement of the materials' properties. Within that scope, three main groups of materials are being investigated: electroceramics, photocatalytic and biomedically applicable materials.

Photocatalytic properties of titanium dioxide ( $TiO_2$ ) could be taken as advantage in manufacturing of antibacterial coatings of the white goods. Among the  $TiO_2$  polymorphs, anatase exhibits the highest photocatalytic activity, mainly under ultraviolet irradiation. Photocatalytic efficiency of anatase depends on crystallinity, specific surface area and particle size. Therefore, our attempt was to improve these properties and to design a visible light responsive  $TiO_2$ . Nanocrystalline anatase with high specific surface area (up to  $335\text{ m}^2/\text{g}$ ) and small particle size (down to 5 nm) were prepared by the combination of sol-gel and solvothermal synthesis. Future research is aimed to achieve visible light activity of anatase by doping its' structure with small quantities of elements P, N, S and F.

Titanate-based nanotubes synthesized by the alkaline hydrothermal treatment of  $TiO_2$  are characterized as a layered, lamellar structure with mesoporous morphology. In our research, the ability of ion-exchange of hydrothermally synthesized titanate nanotubes has been utilized for the formation of Ag-titanate nanotube composite via incorporation of silver nanoparticles onto the surface of nanotubes. Intercalation of silver nanoparticles enables modification of titanate nanotubes resulting in an enhanced photocatalytic activity at visible wavelengths and makes such composites applicable in photocatalysis and photodecomposition of water.

Research on piezoelectric materials was focused on  $(Na_{1-x}K_x)_{0.5}Bi_{0.5}TiO_3$  (NBT-KBT) solid solutions and on the influence of their structure on the electrical properties. Upon cooling of sintered ceramics, the structure transforms from cubic to rhombohedral (NBT-rich) and tetragonal (KBT-rich) structure. At a  $Na/K = 4:1$  in the NBT-KBT, a morphotropic phase boundary is formed, where the tetragonal and the rhombohedral phases coexist. In this region the values of the dielectric constant, the remanent polarization and the piezoelectric coefficient are enhanced in comparison with the NBT and KBT end members.

Relaxor ferroelectric behavior of sodium bismuth titanate (NBT) opens a possibility for application as a voltage-tunable capacitor. Hydrothermal technique was employed for the preparation of NBT powder. Nanosized crystalline particles were prepared from inexpensive precursors under moderate temperature conditions. Subsequent employment of NBT particles in the form of thin film will enable preparation of composite thin films with desirable properties.

Sonochemical synthesis method is applied for the synthesis of silver and hydroxyapatite/silver composite particles. Using this approach resulted in the formation of nanometer-sized particles of silver which were attached onto the surface of rod-like, submicrometer-sized hydroxyapatite particles. Due to the development of the pathogens in implant's surroundings high percent of immune system rejections of biomaterials for bone replacement appears. Formation of HAp/Ag coatings on the surface of bone implants or its local usage as bone filler is a possible industrial application of this material.



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Supervisor : S.D. Skapin



**Marija Vukomanović**  
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**Ines Brácko**  
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Supervisor : D. Suvorov



**Moja Otoničar**  
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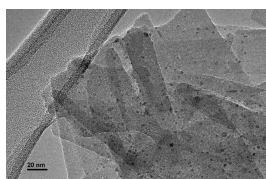


**Tina Šetinc**  
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Supervisor : D. Suvorov

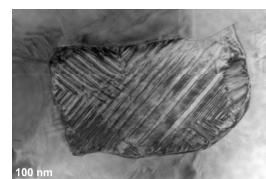
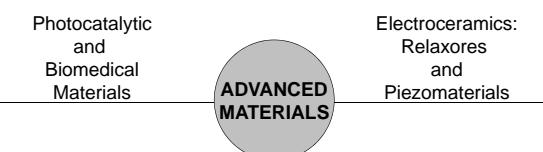
## Ph. D. Students at Advanced Materials Department

# Development of Materials for Industrial Applications

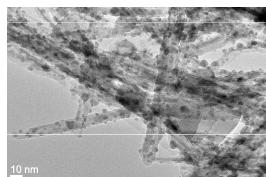
### Materials Research



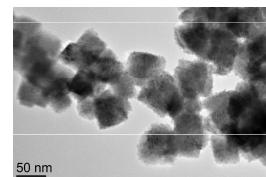
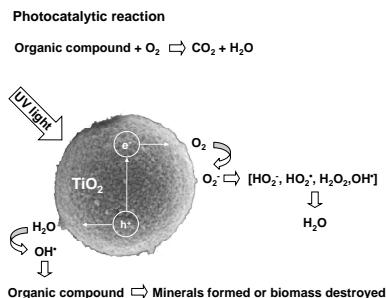
**Silver/hydroxyapatite composite particles**



**Domain structure in  $\text{Na}_{0.4}\text{K}_{0.1}\text{Bi}_{0.5}\text{TiO}_3$  ceramics**



**Ag/titanate nanotubes composite**



**Sodium bismuth titanate nanoparticles**

### Applications & Perspectives

#### APPLICATION OF ADVANCED MATERIALS



Implant fillers or coating against bone infections

Piezoelectric transducers



Antibacterial coatings



Biomedical, Photocatalytic Applications & Electrical Components



Piezoelectric motors



Tunable capacitor



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- Esotech, d.d.
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