

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

Andreja Eršte<sup>1,2</sup>, Brigita Kužnik<sup>3</sup>, Barbara Malič<sup>3</sup>, Marija Kosec<sup>3</sup> and Vid Bobnar<sup>1</sup>

<sup>1</sup> Condensed Matter Physics Department, Jožef Stefan Institute, Ljubljana, Slovenia

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

<sup>3</sup> Electronic Ceramics Department, Jožef Stefan Institute, Ljubljana, Slovenia

andreja.erste@ijs.si

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  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 applicatory 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.