Innovative Approach to Synthesis of $Pb(Mg_{1/3}Nb_{2/3})O_3$ Based Materials using Colloidal Interactions

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Abstract. A new approach to the synthesis of $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) based materials is presented. By manipulating the colloidal interactions, the designed self-assembled aggregates are formed, which enable the synthesis of PMN based materials in a single-annealing step. Furthermore the as prepared ceramics are sintered at 200 K lower temperatures compared to conventionally used methods and exhibit excellent electrical properties.

Keywords: PMN, synthesis, self-assembly, simulations, ceramics

1 Introduction

Lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and its solid solution with lead titanate $x Pb(Mg_{1/3}Nb_{2/3})O_3$-$(1-x)PbTiO_3$ (PMN-PT) belong to the group of relaxor ferroelectric materials and are the most studied materials of this group. They are known for large electrostrictive (strain ~0.1%) as well as large dielectric properties (ε_r ~ 15 000) at room temperature and are therefore used in actuator and high-dielectric-permittivity applications [1-4]. PMN based ceramics are usually prepared via solid-state synthesis. The general approach in the solid-state synthesis is to choose reactant compounds, typically inorganic compounds, composed of elements that are needed to make a particular multi-metal oxide. After mixing and heating at elevated temperatures the reaction starts at the contact of reactant powder particles and proceeds via diffusion. Therefore the starting compounds must consist of small particles and they have to be mixed homogenously to get fast reactions and homogenous product. This is true for two component systems, however not always

true, if we have more than two components. In a two component system a typical reaction is as follows A + B → AB. With reducing particle size and by homogenous mixing of A and B particles, the contact area between the A and B particles is increased, which is beneficial for the solid-state reaction. In the systems with more than two components multiple reactions may occur and all are not always wanted. A typical example of such problem is the PMN synthesis. This material is difficult to prepare in a pure perovskite form, due to the preferential reaction between lead and niobium oxide yielding secondary $Pb_xNb_yO_z$ pyrochlore phases. Therefore the final product is composed of a mixture of pyrochlore and perovskite PMN or PMN-PT phases. Pyrochlores are known to deteriorate dielectric properties of the PMN and PMN-PT ceramics. Therefore the pyrochlore phases should be avoided during the synthesis to produce high-quality electronic ceramics.

2 Idea

The columbite method is usually used for the preparation of pyrochlore-free materials. In this method the synthesis is composed of two steps, first the $MgNb_2O_6$ (columbite) is synthesized, and in the second reaction, the columbite reacts with PbO or PbO + TiO_2 to form the perovskite PMN or PMN-PT [5]. First step is needed to prevent the reaction between PbO and Nb_2O_5 to pyrochlore.

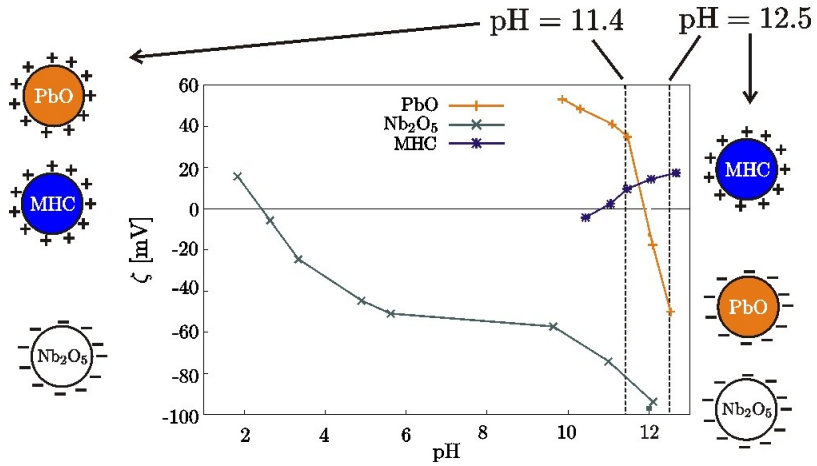

Figure 1: Zeta-potential measurements of the starting components as a function of pH. The dotted lines represent the pH values used for the synthesis of PMN.

In order to simplify the reaction to one-step method, we have to avoid the reaction between lead and niobium oxide in the reaction mixture of the starting compounds;

PbO, Nb_2O_5, $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ (MHC), and TiO_2. Our idea was to prevent contacts between PbO and Nb_2O_5 particles in the reaction mixture, and hence to slow down the reaction to the pyrochlore phase. This could be achieved by the directed self-assembly of the reactant particles in the suspensions. By changing the pH of the suspension, the zeta-potential of the particles is changing (see Fig. 1), and hence the interactions between the particles are changing. Therefore at different pH conditions aggregates with different type of contacts between particles should form. This was further investigated with the use of numerical modelling.

3 Simulation Study of Aggregate Formation

The Monte Carlo simulation method was used for modelling the aggregate formation in the suspension containing reactant particles for the PMN synthesis: PbO, Nb_2O_5, MHC. The method and the results are explained in detail in Ref. [6]; here the results are just briefly summarized. In Figure 2 the spatial distributions of reagent particles are shown for the suspensions with pH 11.4 and pH 12.5.

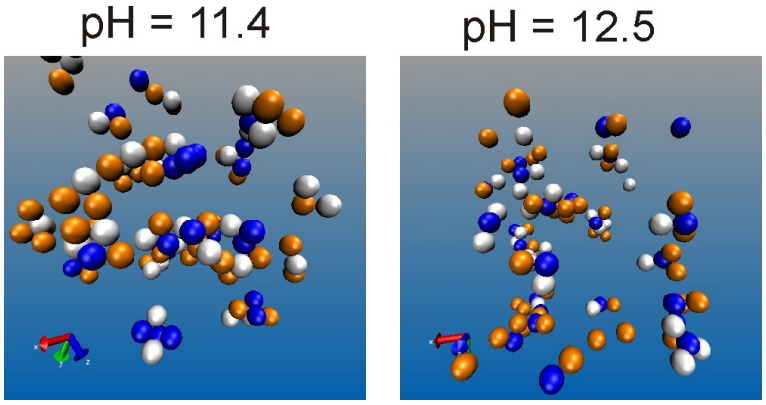

Figure 2: Snapshot of the formed aggregates in suspensions of PbO, Nb_2O_5 and MHC particles at pH 11.4 (left), and 12.5 (right). PbO – orange, Nb_2O_5 – white, MHC – blue.

At pH 11.4, a large population of aggregates with contacts between PbO and Nb_2O_5 is observed, whereas at pH 12.5, no such aggregates are formed. At lower pH, the charge of PbO and Nb_2O_5 is opposite and the two types of particles are attracted and form aggregates. At pH 12.5, PbO and Nb_2O_5 are both negatively charged, while MHC is positively charged, this situation leads to aggregates where MHC particles are effectively separating PbO and Nb_2O_5 particles. From the simulation results we can conclude that at the pH 12.5, the separation of PbO and

Nb_2O_5 should slow down the reaction to pyrochlores and therefore the conditions should be more favourable for synthesizing pyrochlore-free PMN.

4 Experimental Results

The starting powders for PMN and 0.65PMN-0.35PT synthesis, PbO, Nb_2O_5, MHC, and in the case of PMN-PT also TiO_2, were mixed in aqueous suspensions at pH 11.4 in the first case and at pH 12.5 in the second case. The suspensions were dried after milling and calcined at 900 °C for 5 h. The calcined powders were pressed to pellets and sintered as low as 950 °C. Then the electrical properties of the ceramics were measured. More detailed information on experimental procedures can be found in Ref. [7].

Based on the simulation results we have expected that the dried suspension of the starting compounds, prepared at pH 11.4, would react to the mixture of the perovskite and secondary pyrochlore phase after heating at 900 °C. On the contrary, the powder mixture, prepared at pH 12.5, should react to pure perovskite after the calcination at 900 °C. The XRD patterns of both calcined samples in the case of PMN synthesis confirm the simulation results. In addition to the perovskite phase also 5 mass% of secondary pyrochlore phase is detected in the pH 11.4 sample, while the pH 12.5 sample contains only the perovskite PMN phase. After sintering at 950 °C the pH 12.5 ceramic sample reaches 95 % of theoretical density (TD), while the pH 11.4 reaches only 85 % of TD.

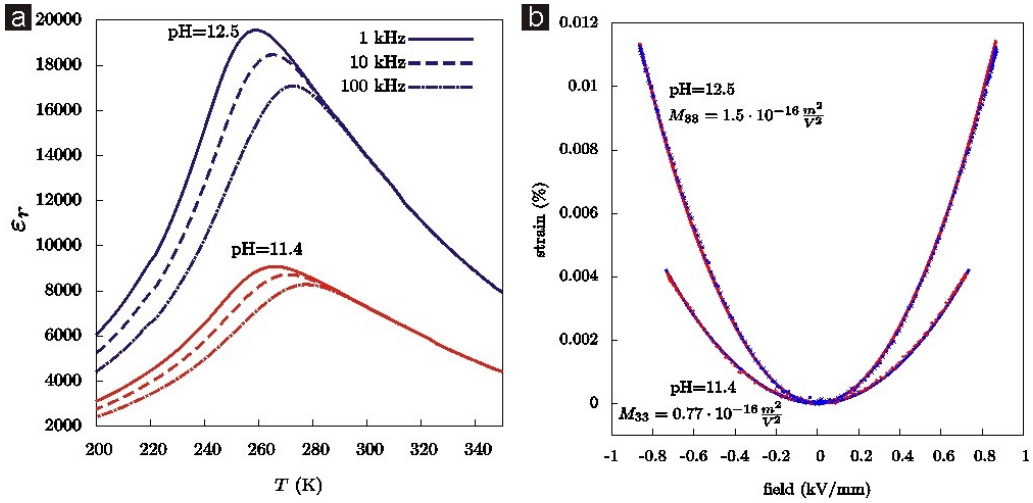

Figure 4: Electrical properties of the PMN ceramics prepared at pH 11.4 (red) and pH 12.5 (blue). a) Dielectric constant vs. temperature. b) Electrostrictive properties: strain vs. electric field.

Additionally the dielectric and electrostrictive properties were measured for both samples (see Figure 4). The pH 12.5 sample exhibits approx. two times higher dielectric constant in the measured temperature range as well as two times higher electrostriction coefficient M_{33} in comparison to the pH 11.4 sample. Clearly, the dielectric and electrostrictive properties of the pH 11.4 sample are deteriorated, due to the presence of the secondary pyrochlore phase and low density.

The same synthesis approach was tested on 0.65PMN-0.35PT system; here additionally TiO_2 particles are added into the reaction mixture. Again, the sample prepared at pH 11.4 and heated at 850 °C, contains in addition to the perovskite also a secondary pyrochlore phase, whereas in the pH 12.5 sample calcined at the same temperature, only the perovskite phase is detected. To further compare the two samples, ferroelectric and piezoelectric properties of the samples sintered at 950 °C were measured, see Figure 5.

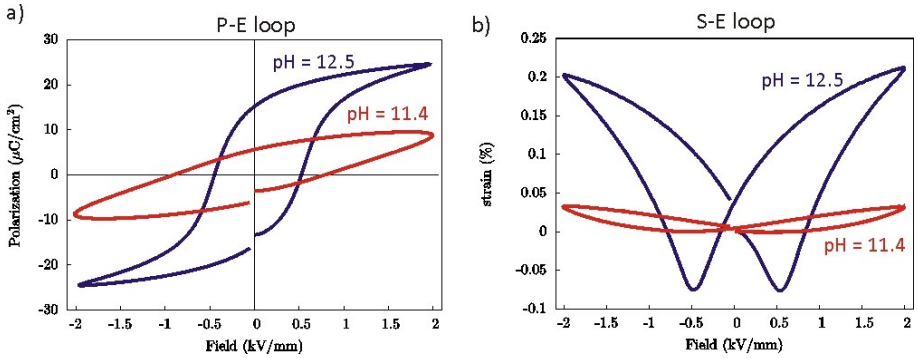

Figure 5: Electrical properties of the 0.65PMN-0.35PT ceramics prepared at pH 11.4 (red) and pH 12.5 (blue). a) Polarization vs. electric field. b) Strain vs. electric field.

The properties of the ceramics prepared from the pH 12.5 suspension are superior in comparison to the pH 11.4 sample also in the case of the PMN-PT synthesis.

5 Summary

By applying our new synthesis approach the phase-pure PMN and PMN-PT powders and high quality ceramics were prepared from simple materials in only one milling, one calcination, and one sintering step. We suppose that the presented approach is general and could be implemented for the synthesis of other complex perovskite materials.

References:

[1]G. H. Heartling. "Feroelectric ceramics: History and Technology". *J. Am. Ceram. Soc.*, 82(4):2341-2359, 1999.

[2]N. Setter. "Piezoelectric materials in devices", pages 1-27. EPFL, Lausanne, Switzerland, 2002.

[3]T. R. Shrout and A. Halliyal. "Preparation of Lead-Based Ferroelectric Relaxors for Capacitors". *Am. Ceram. Soc. Bull.*, 66(4):704-711, 1987.

[4]H. Uršič et al., "A large-displacement 65Pb($Mg_{1/3}Nb_{2/3}$)O_3-35PbTiO_3/Pt bimorph actuator prepared by screen printing. *Sens. Actuators, B.*, 133(2):699-704, 2008.

[5]S. L. Swartz and T. R. Shrout. "Fabrication of perovskite lead magnesium niobate". *Mat. Res. Bull.*, 17(10):1245-1250, 1982.

[6]G. Trefalt et al., "Formation of colloidal assemblies in suspensions for Pb($Mg_{1/3}Nb_{2/3}$)O_3 synthesis: Monte Carlo simulation study". *Soft Matter*, DOI: 10.1039/c1sm05228d.

[7]G. Trefalt et al., "Synthesis of Pb($Mg_{1/3}Nb_{2/3}$)O_3 by Self-Assembled Colloidal Aggregates". *J. Am. Ceram. Soc.*, 2011, DOI: 10.1111/j.1551-2916.2011.04443.x.

For wider interest

PMN and PMN-PT relaxor-ferroelectric materials are widely studied because their electrical properties (e.g. dielectric permittivity, electrostriction, piezoelectricity, ferroelectricity) enable their use in capacitor, actuator and sensor applications. Some of their typical applications are in actuators for precise positioning (piezo stages), sensors for force and pressure, ultrasonic transducers (medical imaging), and energy harvesting devices. It is hard to produce good quality ceramics from these materials, due to the formation of secondary pyrochlore phases during the synthesis. This work presents a new and simple approach to the synthesis of these materials with only one calcination step. This method has a potential to lower the production costs of these materials. A further advantage of this method is the use of environmentally friendly aqueous media and simple starting materials as well as simple and efficient processing techniques. Moreover, the method presented in this work is to our knowledge a new approach in the field of solid-state chemistry of complex multi-metal oxides. We supose that our approach of solid-state synthesis with designed heterogeneity could be used generally for the synthesis of materials with a complex chemical composition, which are of high technological importance.

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