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Influence of seed particle frequency on the phase formation and on the microstructure of 0.88 PZN–0.07 BT–0.05 PT ceramic

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Abstract

The Pechini method as well as the simultaneous addition of seeds particles and dopant solutions of $BaTiO_3$ (BT) and $PbTiO_3$ (PT) were used to prepare the perovskite phase 0.88 PZN–0.07 BT–0.05 PT. To study the influence of seed particle frequency on the synthesis of the PZN ceramic, two ranges of seed particle size were used: the range from 30 to 100 nm, termed small seed particles (frequency of 10^{15} particles/cm^3); and the range from 100 to 900 nm, termed large seed particles (frequency of 10^{13} particles/cm^3). The crystalline nuclei size influenced the calcining process, the sintering process and the microstructure. Samples prepared with lower seed frequency displayed more amount of pyroclore phase, need higher temperatures for sintering and showed a more heterogeneous microstructure with poor dielectric properties. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: C. Dielectric properties; PZN; Seed particles

1. Introduction

Zinc lead niobate (PZN) is a relaxor ferroelectric material with excellent dielectric, piezoelectric and eletrostrictive properties [1,2]. This material has been considered to use as dielectric for multilayer capacitors due to its high dielectric constant and high resistivity. However during synthesis of a stoichiometric PZN phase the formation of a low dielectric constant pyrochlore phase (k ranging from 130 to 200), that is more stable under the synthesis conditions ocurrs. The PZN phase, being unstable, is difficult to synthesize by conventional methods such as solid state reaction from oxide mixtures [3]. Under extreme conditions using high temperature and pressure, such as hot isostatic pressing (HIP), the pure PZN phase can be synthesized [4]. Using conventional chemical synthesis, the two phases, PZN and pyrochlore, occur in different relative amounts depending on the synthesis conditions. However, the pyrochlore phase leads to degradation in dielectric properties of PZN ceramics.

Several additives have been used to stabilize and increase the amount of PZN phase during synthesis. These additives, such as $PbTiO_3$ (PT), $BaTiO_3$ (BT) and $SrTiO_3$ (ST), showing perovskite structures are stable and have high dielectric constant and high transition temperature between ferroelectric and paraelectric states [2,5–7]. According to Halliayal [8] the BT phase has a high tolerance factor as well as accommodation to differences in electronegativity. These characteristics of BT make this compound an excellent additive to stabilize the PZN structure. An excess of PbO and ZnO has also been used to decrease the amount of pyrochlore phase formed during synthesis.

Another method used to control the microstructure and crystalline transformations in the ceramics consists of introducing so-called seed particles to the metastable phase. These seed particles have similar crystallographic structure to the desired final structure. Messing et al., [9,10] and Hennings [11] have proved the efficiency of such seed particles in the production of α-alumina from boehmite nucleated with α-alumina or Fe_2O_3. The pioneer work of Turnbull and Vonnegut [12] shows that the

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closer to similarity between lattice parameters of seed particles and the nucleating phase, the smaller was the nucleation barrier energy. Ravindranathan et al. [13] reported the effect of PMN seeds in lowering the crystallization temperature of PMN. Their data showed that seeding with as little as 1% of PMN nuclei lowered the formation temperature of perovskite phase and the higher seed concentration, the greater the amount of perovskite phase.

Seeding has not been applied to synthesis of PZN ceramics. If the nucleation and phase formation process can be controlled, the heterogeneous nucleation will have a great influence on the synthesis, properties and applications of this ceramic.

The objective of this research is to study the influence of seed particle frequency on the phase formation and microstructure of the 0.88 PZN–0.07 BT–0.05 PT ceramic synthesized by a polymeric precursor method and processed by the conventional sintering.

2. Experimental procedure

The synthesis of 0.88 PZN–0.07 BT–0.05 PT, based on the Pechini method [14], makes use of the capability of certain α-hydroxycarboxylic organic acids to form polybasic acid chelates with several cations. When mixing with a polyhydroxylic alcohol and heating, the chelate transforms into a polymer, maintaining the cations homogeneously distributed. The organic part is eliminated at low temperatures, forming reactive oxides with well-controlled stoichiometry.

Both additives, BT and PT, were added in form of 80% as particle seeds and 20% as ions (Ba^{2+} and Ti^{4+} referring to BT and Pb^{2+} and Ti^{4+} referring to PT). All samples were prepared with a 1 mol% excess of PbO to minimize the PbO loss by evaporation during sintering. To study the influence of seed particle frequency on the formation of stable PZN phase and on ceramic microstructure, two ranges of seed particles were considered: (a) the range from 30 to 100 nm, termed small seed particles (frequency of 10^{15} particles/cm^3); and (b) the range from 100 to 900 nm, termed large seed particles (frequency of 10^{13} particles/cm^3).

Appropriate amounts of metallic citrate solution and lead acetate were weighed and homogenized with stirring and heating (90°C to 110°C) until complete chelation of cations. At this state the seeds were deagglomerated by ultrasound, using DREW as a defloculant and then added to the metallic citrate solution. Next, the temperature was raised to 130°C for 2 h to polymerize the solution forming a glassy-like organic resin. This resin was decomposed by successive isothermal treatments: 3 h at 200°C, followed by 4 h at 300°C and by 4 h at 400°C. The resulting powders, decomposed at 400°C, were pulverized in a mortar and calcined at 800°C for 2 h or at 900°C for 1 h. After calcining the powders were ball milled for 6 h in isopropyl alcohol, dried and then submitted to XRD for phase determination. The powders were isostaticaly pressed (230 MPa) into pellets, using 2 wt% solution of polyvinyl alcohol (PVA) in water as a binder. Before sintering the pellets were heated at 500°C to eliminate the organic material.

Sintering was conducted inside a box furnace in a closed system containing 10 wt% of ($PbZnO_3$ + 5 wt% of PbO), relative to all mass of the pellets to generate a lead vapour atmosphere. The closed system was introduced into the furnace at 600°C and heated at 10°C/min to the sintering temperature (1100°C), holding at this

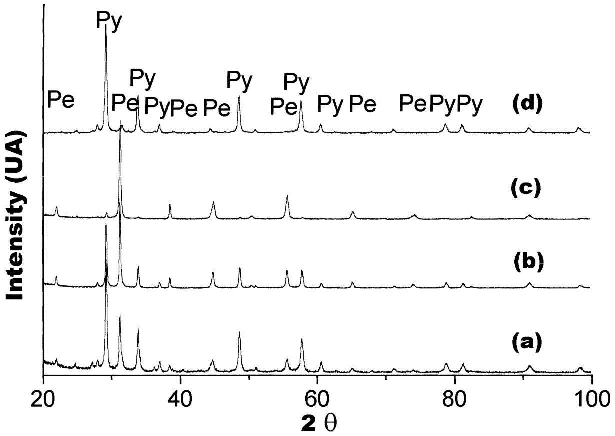

Fig. 1. X-ray diffractograms obtained from 0.88 PZN–0.07 BT–0.05 PT powders calcined in different conditions (radiation CuK_α): (a) and (c) refer to the powders prepared with small seed particles and calcined 800°C/2 h and 900°C/1 h, respectively, and (b) and (d) refer to the powders prepared with large seed particles and calcined 800°C/2 h and 900°C/1 h, respectively.

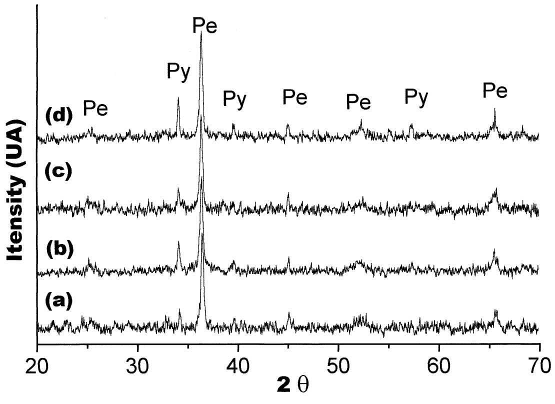

Fig. 2. X-ray diffractograms obtained from 0.88 PZN–0.07 BT–0.05 PT ceramic sintered at 1100°C for 1 h (radiation CoK_α), using the following precursors: (a) and (c) powders prepared with small seed particles and calcined 800°C/2 h and 900°C/1 h, respectively, and (b) and (d) powders prepared with large seed particles and calcined 800°C/2 h and 900°C/1 h, respectively.

temperature for 1 h. After sintering the furnace was cooled down to 850°C and the samples were taken out of the furnace and allowed to in air (quenched) to avoid the phase transformation from perovskite to pyrochlore. The phase formation in the ceramics was determined by XRD. The microstructures of samples were characterized by SEM observations. The dielectric constant as function of temperature and frequency were measured in the samples, after painting with silver electrodes, using an Impedance Analyzer HP 4192.

3. Results and discussions

X-ray diffractograms for calcined powders after different treatments are shown in Fig. 1. Characteristic peaks of the PZN perovskite phase (Pe) as well as peaks of the pyroclore ($Pb_{1.83}Nb_{1.71}Zn_{0.29}O_{6.39}$) phase (Py) are present. The amount of perovskite phase is higher for calcined samples at 900°C. For the same calcination condition, comparing the diffractograms obtained for samples prepared with small seed particles (frequency of 10^{15} particles/cm^3) with those prepared with large seed particles (frequency of 10^{13} particles/cm^3), the amount of perovskite phase is higher in samples prepared with higher seed frequency. This indicates that the seed frequency is a determinant factor for nucleation of perovskite PZN phase.

The powders calcined at 800°C for 2 h or at 900°C for 1 h were pressed in cylindrical shape and sintered at 1100°C for 1 h. After sintering, samples that were calcined at 800°C for 2 h reached 94% of PZN relative density and samples calcined at 900°C for 1 h reached 98% of PZN relative density.

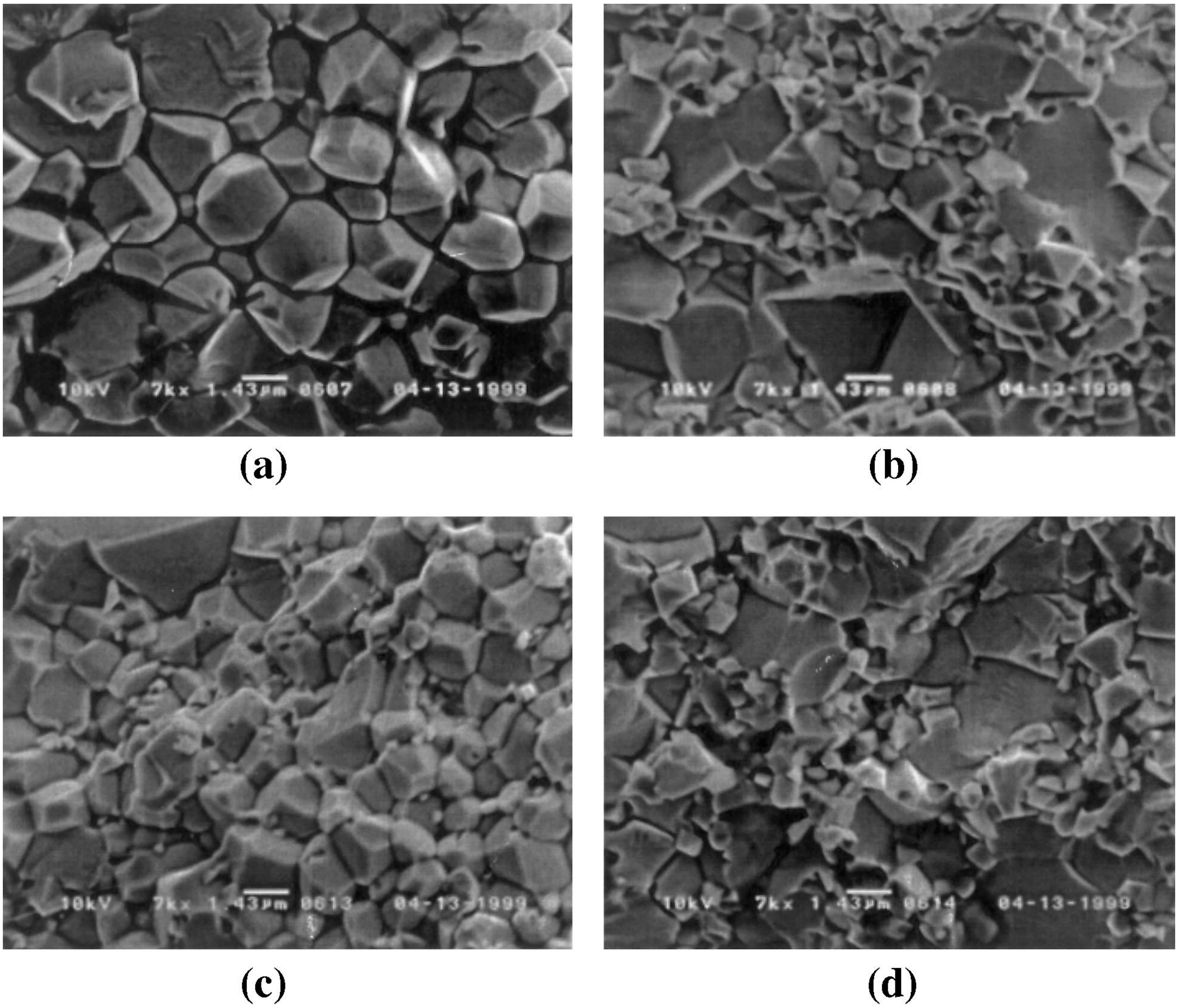

Fig. 3. SEM microstructure of fractured 0.88 PZN–0.07 BT–0.05 PT ceramic surface sintered at 1100°C/1h: (a) sample prepared with small seed particles and calcined 800°C/2 h; (b) sample prepared with large seed particles and calcined 800°C/2 h; (c) sample prepared with small seed particles and calcined 900°C/1 h; (d) sample prepared with large seed particles and calcined 900°C/1 h.

X-ray diffractions of sintered samples at 1100°C are shown in Fig. 2. Comparing the difractograms obtained after sintering with those for calcined powders (Fig. 1) indicate that the majority of samples exhibited transformation of pyrochlore into perovskite after sintering although there is still residual pyrochlore phase. However, the more perovskite phase remaining after calcination, the more perovskite was present after sintering. This indicates that the perovskite phase should be stabilized during calcination in order to obtain 100% perovskite phase after sintering.

In all micrograph obtained by SEM in fractured surface the remnant pyrochlore phase is identified by its pyramidal shape (Fig. 3). A secondary phase segregated at the grain boundary was also observed, probably with pyrochlore structure because of its pyramidal shape (Fig. 3). During the powder synthesis an excess of 1 mol% of PbO was added and during sintering this excess formed a liquid phase which is segregated at the grain boundary. The samples prepared with larger crystalline nuclei frequency, Figs. 3a and 3c, have the lower concentration of the secondary phase segregated at grain boundaries. The use of higher seed particle frequency to prepare the ceramic favors the formation of the perovskite phase and helps form a more homogeneous microstructure. However, a small amount of the secondary pyrochlore phase is still observed at the grain boundary of these samples.

The dielectric constant as function of temperature at 1 kHz for PZN samples sintered at 1100C for 1 h are shown in Fig. 4. The highest value for the dielectric constant was found to be 8500 at 115°C for samples prepared with higher seed particle frequency. The samples prepared with lower seed particle frequency showed dielectric constants smaler than 4000. In these samples the amount of pyrochlore phase is higher, the microstructure of the ceramics is heterogeneous and the grain size is smaller than 1.5 μm, thereby degrading the dielectric properties of these ceramics [15]; a crystalline nuclei frequency of 10^{13} particles/cm^3 is inadequate to obtain 0.88 PZN–0.07 BT–0.05 PT ceramic with perovskite phase and good dielectric properties.

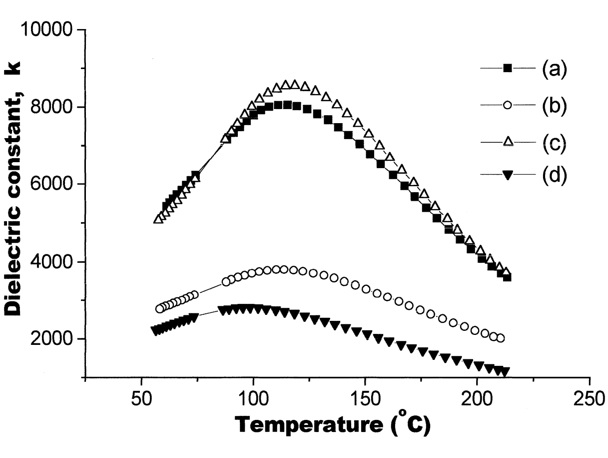

Fig. 4. Dielectric constant versus temperature at 1 kHz for 0.88 PZN–0.07 BT–0.05 PT ceramics sintered at 1100°C for 1 h: (a) sample prepared with small seed particles and calcined 800°C for 2 h; (b) sample prepared with large seed particles and calcined 800°C for 2 h; (c) sample prepared with small seed particles and calcined 900°C for 1 h; (d) sample prepared with large seed particles and calcined 900°C for 1 h.

4. Conclusions

The seed particle frequency influences the formation of perovskite phase and the microstructure and dielectric properties of 0.88 PZN–0.07 BT–0.05 PT ceramic. A crystalline nuclei frequency of 10^{15} particles/cm^3 stabilized the perovskite phase but a crystalline nuclei frequency of 10^{13} particles/cm^3 was inadequate. Therefore, it seems that the nuclei frequency for stabilization of PZN perovskite phase should be at least 10^{15} particles/cm^3.

The small amount of pyrochlore phase is precipitated at the PZN grain boundary, which degrades the dielectric constant. This phase should be eliminated in order to obtain better dielectric properties.

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