Grain growth in $Na_{0.5}Bi_{0.5}TiO_3$-based solid solutions

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ABSTRACT

This paper discusses effects of different dopants, sintering technique and parameters on microstructure and properties of pure and Yb, Er-doped $Na_{0.5}Bi_{0.5}TiO_3$ (NBT). All stoichiometric compositions follow the abnormal grain growth mechanism (AGG) and exhibit a bimodal grain size distribution. Bi over-stoichiometry, two step sintering and hot pressing are effective inhibitors of AGG. Microstructure of sintered NBT greatly influences such properties as dielectric permittivity and depolarization temperature.

ARTICLE HISTORY

Received

Accepted

KEYWORDS

Lead-free ferroelectrics; NBT; abnormal grain growth; solid-state sintering

1. Introduction

Lead-free ferroelectric ceramic materials with a perovskite structure, including $Na_{0.5}Bi_{0.5}TiO_3$ (NBT), are often considered as promising candidates for substitution of traditional manufacturing materials containing lead, such as PZT and PMN-PT. NBT ceramics are characterized by their high coercive field of 73 kV/cm and low depolarization temperature of 187 °C [1, 2]. NBT is frequently modified to improve its properties, however the influence of grain growth and grain size distribution on physical properties is studied less frequently. In this context, sintering plays a vital part in microstructural evolution during which transformations in grain size distribution occur. In the case of NBT and NBT-based solid solutions, anomalous grain growth (AGG) is a common grain growth mechanism, wherein only a small fraction of grains grow rapidly and the microstructure is characterized by a bimodal grain size distribution. AGG is often undesirable because the heterogenous microstructure is not reproducible and can deteriorate physical properties, e.g. hardness, but can also improve other properties, such as fracture toughness [3].

Normal grain growth occurs in systems with rough (atomically disordered) grain boundaries and is controlled by diffusion, while abnormal grain growth occurs in systems with faceted (atomically ordered) grain boundaries and is controlled by interface reactions and diffusion. The microstructural evolution principle can be developed based on these considerations, where different types of grain coarsening behavior can occur because of the reciprocal relation between the maximum driving force for growth of the largest grain in a system (Δg_{max}) and the critical driving force for appreciable migration of the grain boundary (Δg_c). According to this principle, stagnant, abnormal, pseudo-normal and normal grain coarsening can take place with a reduction of Δg_c for a given Δg_{max} [4–6].

This study is focused on effects of doping, non-stoichiometry, sintering technique (conventional, two-step sintering and hot pressing) and parameters on the microstructure and properties of $Na_{0.5}Bi_{0.5}TiO_3$ and lanthanide (Yb, Er)-modified $Na_{0.5}Bi_{0.5}TiO_3$ compositions.

2. Experimental details

$Na_{0.5}Bi_{0.5}TiO_3$, $Na_{0.5}Bi_{0.52}TiO_3$, $Na_{0.5}Bi_{0.5}Ln_xTiO_3$ and $Na_{0.5}Bi_{0.52-x}Ln_xTiO_3$ (Ln = Yb, Er) ceramic samples were prepared through the conventional ceramic route using reagent grade oxide and carbonate powders of Na_2CO_3, Bi_2O_3, TiO_2, Yb_2O_3, Er_2O_3 ("Sigma-Aldrich", "Acros Organics"). The raw materials were dried in an oven at 200 °C for 4 hours to remove any adsorbed moisture. Dried raw powders were then weighed according to calculated compositions, mixed and ball-milled for 24 hours using ethanol (99.8%) as medium. The slurry was dried in an oven at 200 °C for 4 hours. Powders were then crushed in a mortar and calcined in a corundum crucible at 850 °C for 2 hours. Calcined powders were crushed in a pestle and the ball-milling, drying and crushing processes were repeated. Second calcination was carried out at 970–1000 °C for 2 hours. X-ray diffraction of the calcined powders showed that the calcined powders are of a single perovskite phase. The obtained powders were crushed in a pestle and mixed with a 3% polyvinyl alcohol (PVA) binder and pressed using a hydraulic hand press under 32 MPa (sample diameter d = 17 mm, height h = 10 mm).

Individual samples were hot-pressed at 1120–1180 °C for 2 hours, while the remaining samples were put in a corundum crucible, on a Pt plate, covered with a corundum lid, and conventionally sintered at 1170–1235 °C for 2–12 hours in air with a heating rate of 3–4 °C/min. Some pressed pellets were two-step sintered, the process consisted of heating of the sample up to 1200–1250 °C followed by immediate cooling to 1100–1150 °C with a rate of 10 °C/min and holding at these temperatures for various times (10 min–12 hours). Crystallographic symmetry of dense ($\rho_{relat.} \geq 94\%$) $Na_{0.5}Bi_{0.5}TiO_3$-based samples was analysed using X-ray powder diffraction with CuKα radiation (XRD, "PANalytical X'Pert PRO") and exhibited a single perovskite phase. Microstructures were observed for polished and thermally etched (1020–1135 °C for 3–4 h) samples using a scanning electron microscope ("Phenom Pro"). Linear intercept method was used to determine average grain size, statistical analysis of grain size distribution was conducted for 1000 grains of each composition. Chemical analysis was carried out using energy dispersive spectroscopy ("EDAX/Ametek Eagle III microprobe" and "Tescan MIRA/LMU" SEM equipped with "Oxford 7378" EDS spectroscope). Dielectric measurements were carried out using an impedance analyzer ("HP4284A"). Depolarization temperatures were determined from the frequency independent maximum of tgδ for previously poled samples.

3. Results and discussion

3.1. Changes in grain growth behaviour depending on the sintering parameters

Grain growth at various sintering times. Average grain size of $Na_{0.5}Bi_{0.5}TiO_3$ sintered at 1180 °C has a tendency to decrease from 4.2 ± 2.0 μm (at 10 min) to 3.5 ± 1.8 μm (at 4 hours) upon increasing of sintering time at maximum temperature, while the fraction

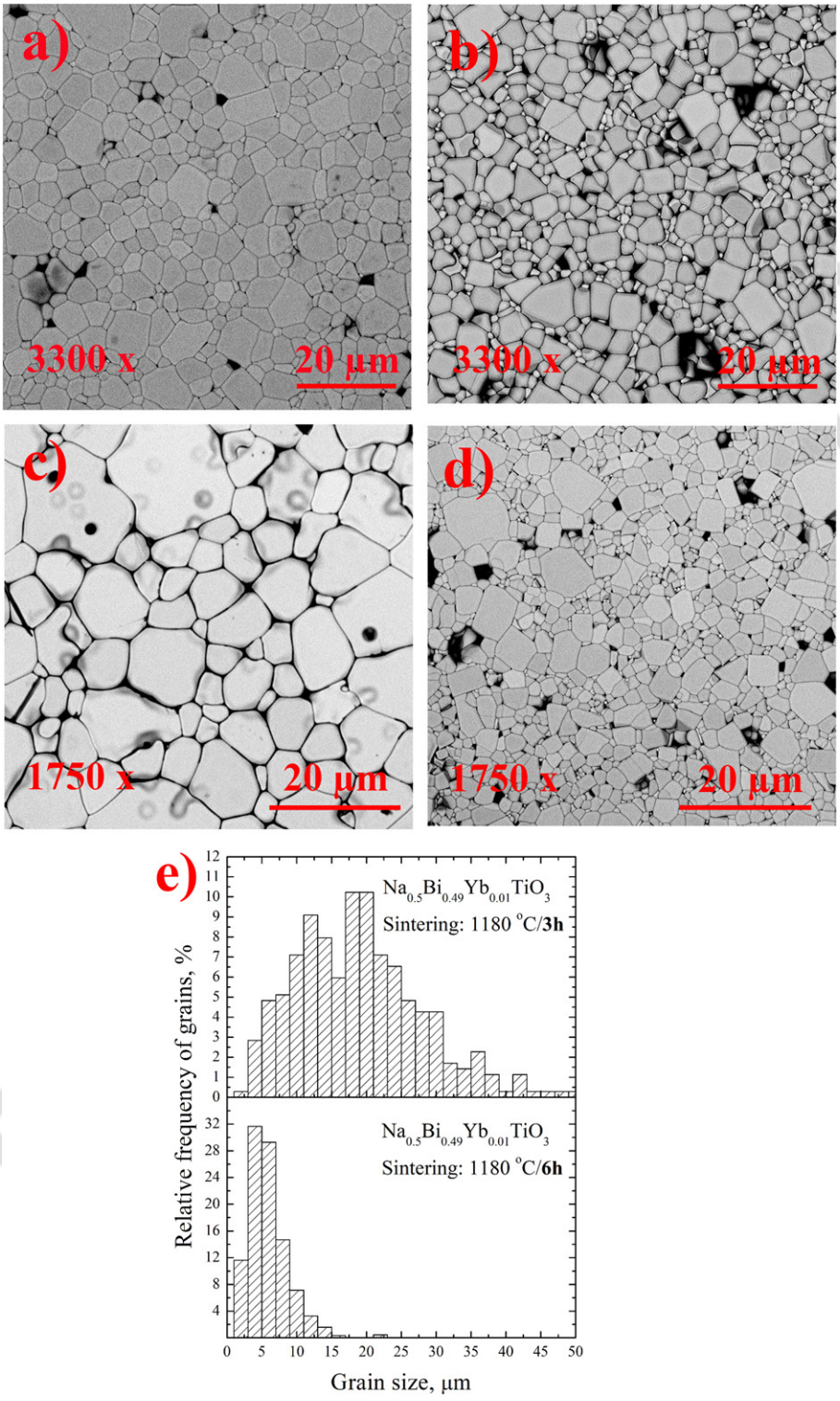

Figure 1. Micrographs of $Na_{0.5}Bi_{0.5}TiO_3$ sintered for a) 10 min; b) 4 h and of $Na_{0.5}Bi_{0.5}Yb_{0.01}TiO_3$ sintered for c) 3 hours; d) 6 hours and e) its grain size distribution

of faceted grains increases and bimodal grain size distribution becomes more pronounced (Figure 1a and b). Therefore, the critical driving force for appreciable grain boundary migration (Δg_c) increases as sintering time is increased. These are some of the key factors indicating AGG. The same correlation has also been identified in $Na_{0.5}Bi_{0.49}Yb_{0.01}TiO_3$, where grain size reduces from 18.0 ± 9.2 μm (at 3 hours) to 4.9 ± 2.9 μm (at 6 hours), grain size distribution becomes narrower and bimodality is more expressed (Figure 1c–e). A smaller fraction of abnormally large grains in a fine-grained matrix, observed at longer sintering times, does not outweigh the matrix of more uniformly distributed grains in terms of average grain size, therefore a reduction of average grain size with an increase in sintering time can be observed.

3.1.1. Grain growth at various sintering temperatures

Average grain size of A-site lanthanide substituted NBT, such as $Na_{0.5}Bi_{0.5-x}Yb_xTiO_3$ (x = 0.005–0.05), increases upon increasing of sintering temperature. In the case of $Na_{0.5}Bi_{0.49}Yb_{0.01}TiO_3$, as the sintering temperature is increased from 1170 °C to 1180 °C at a constant sintering time of 3 hours, grain size increases from 11.0 ± 7.2 μm to 18.0 ± 9.2 μm (Table 1). Grain boundaries are more faceted and grain size distribution is bimodal for samples sintered at 1170 °C, whereas at 1180 °C boundaries become rougher and the grain size distribution becomes more unimodal. This has been previously reported [6] – boundary structure is largely governed by the total vacancy concentration – faceted boundaries indicate a low vacancy concentration, whereas rough boundaries – high vacancy concentration. Evaporation of A-site ions, usually assumed to exist in NBT ceramics, induces a decrease in critical driving force Δg_c, leading to a transition from faceted to rough grain boundaries and inhibition of AGG. All stoichiometric $Na_{0.5}Bi_{0.5}TiO_3$ and lanthanide-doped $Na_{0.5}Bi_{0.5-x}Ln_xTiO_3$ (Ln = Yb, Er) compositions follow the AGG mechanism and exhibit a bimodal grain size distribution (Figure 1), independent of sintering time and temperature.

Energy dispersive spectroscopy (EDS) for A-site Er, Yb substituted NBT shows that as the intensity of ErL, YbL line increases, the bismuth line BiL decreases accordingly (Figure 2). This trend does not confirm previously considered presence of Bi vacancies (due to evaporation of Bi ions during sintering), because Er, Yb ions should occupy positions of Bi vacancies before they start replacing Bi therefore the content of Bi decreases. If A-site vacancies influence grain morphology, the average concentration of these vacancies should be vastly below 0.5 at.% [7].

Table 1. Average grain size in pure Er- and Yb-modified NBT compositions at different sintering temperatures.

$T_{sintering}$, °C	$t_{sintering}$, h	Composition	Average grain size, μm
1180	4	$Na_{0.5}Bi_{0.5}TiO_3$	3.6 ± 0.5
1170	3	$Na_{0.5}Bi_{0.49}Yb_{0.01}TiO_3$	11.0 ± 7.2
1180	3	$Na_{0.5}Bi_{0.49}Yb_{0.01}TiO_3$	18.0 ± 9.2
1180	3	$Na_{0.5}Bi_{0.51}Yb_{0.01}TiO_3$	3.0 ± 1.6
1180	4	$Na_{0.5}Bi_{0.492}Er_{0.008}TiO_3$	3.9 ± 0.6
1190	4	$Na_{0.5}Bi_{0.492}Er_{0.008}TiO_3$	4.2 ± 1.8
1180	4	$Na_{0.5}Bi_{0.512}Er_{0.008}TiO_3$	2.4 ± 1.2
1190	4	$Na_{0.5}Bi_{0.512}Er_{0.008}TiO_3$	3.2 ± 1.8

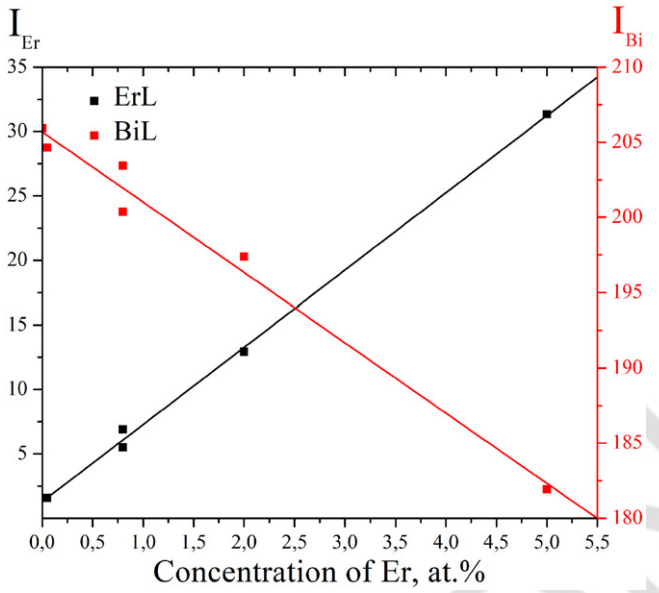

Figure 2. Bi and Er energy dispersive spectroscopy intensity dependence on concentration of erbium in $Na_{0.5}Bi_{0.5-x}Er_xTiO_3$ (x = 0–0.05) ceramics

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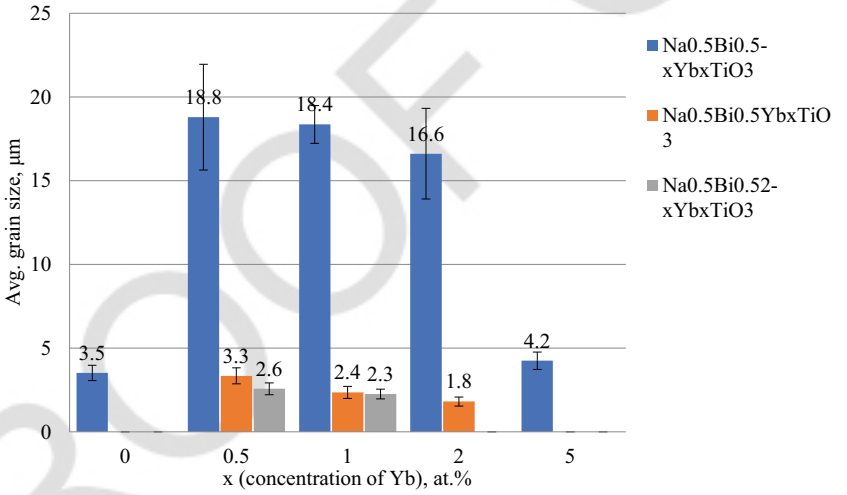

Figure 3. Average grain size of Yb-doped NBT ceramics

3.2. Grain growth behaviour in Bi-overstoichiometric samples

$Na_{0.5}Bi_{0.52}TiO_3$, $Na_{0.5}Bi_{0.52-x}Yb_xTiO_3$ and $Na_{0.5}Bi_{0.52-x}Er_xTiO_3$ over-stoichiometric compositions were sintered. Substantial reduction in average grain size in comparison with stoichiometric compositions is observed in all compositions (Figure 3). Apparently, over-stoichiometric amounts of Bi tend to decrease the energy required for grain growth. This can be attributed to the formation of a liquid phase in compositions with Bi over-stoichiometry. Nonetheless, these systems exhibit a bimodal grain size

distribution without the formation of abnormal grains. The larger grains are rough, while the smaller– faceted, therefore the presence of a liquid phase induces grain growth behaviour to change from abnormal to normal [8]. Bi-overstoichiometric samples also exhibit a correlation between concentrations of Bi and Er, Yb – the concentration of Bi decreases as concentration of Er, Yb increases.

3.3. Effect of two-step sintering and hot pressing

Two-step sintering was used for $Na_{0.5}Bi_{0.49}Yb_{0.01}TiO_3$ compositions, exhibiting larger grains compared to Er-containing compositions when sintered using the one-step conventional method. Sintering was carried out at two temperatures – after increasing the temperature up to 1200 °C, an immediate decrease to 1100 °C follows and this

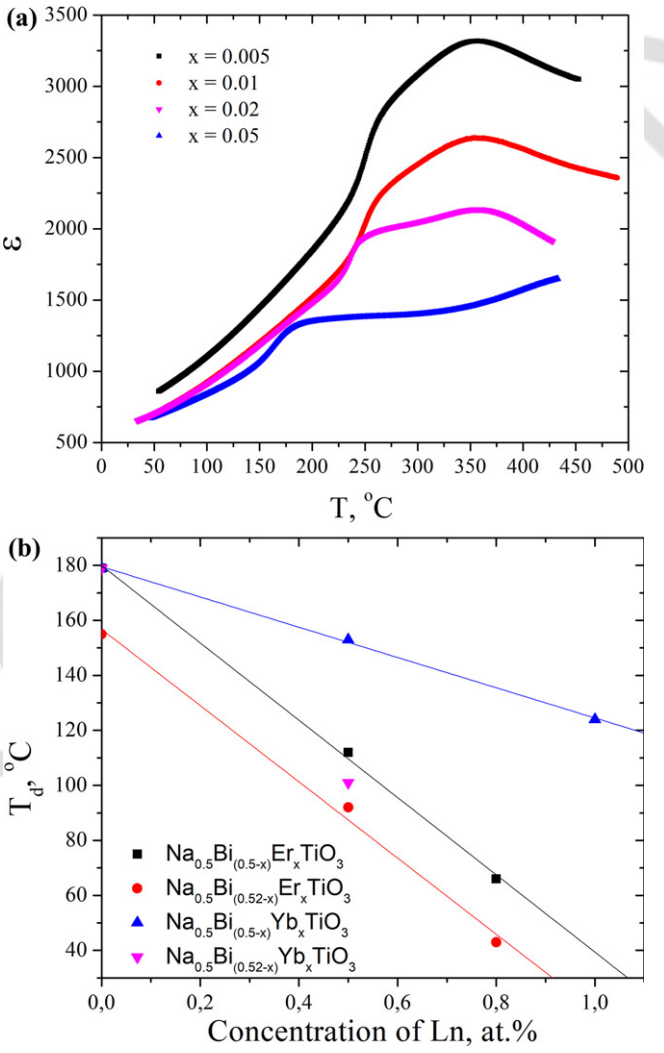

Figure 4. a) Dielectric permittivity dependence of temperature for $Na_{0.5}Bi_{0.5-x}Yb_xTiO_3$ at f = 1 kHz; b) depolarization temperature of Er, Yb-doped NBT as a function of concentration of Er/Yb

temperature is held constant for 10 min, 2 h, 6 h and 12 h. The minimum average grain size of 1.49 μm was obtained for the shortest sintering time (10 min), while the largest grain size of 2.4 μm – for 12 h sintering time at 1200 °C. Therefore, average grain size increases as sintering time is increased which is contrary to conventional one-step sintering.

Hot pressing was carried out at 1120 °C, 1170 °C and 1180 °C for 2 hours under the force of 15 kN. An increase in sintering temperature leads to an increase in average grain size and grain size distribution. In comparison with compositions sintered at atmospheric pressure, hot pressed samples have a narrower grain size distribution and average grain size (0.5 μm at $T_{sintering}$ = 1120 °C). Therefore, hot pressing inhibits the formation of abnormal grains and a wide grain size distribution.

3.4. Influence of microstructure on dielectric properties

Addition of lanthanide dopants to NBT leads to a decrease in the maximum of temperature dependence of dielectric permittivity and depolarization temperature (Figure 4), thus reflecting a reduction of stability of the ferroelectric state. In Bi over-stoichiometric compositions compared to stoichiometric compositions, depolarization temperature decreases, most notably in Yb containing ones. The depolarization temperature of $Na_{0.5}Bi_{0.5-x}Yb_xTiO_3$ is larger than in Bi over-stoichiometric, Er, Yb-containing compositions, which could be at least partly related to the larger grain size. Indeed, stoichiometric $Na_{0.5}Bi_{0.49}Yb_{0.01}TiO_3$ compositions, sintered at different times exhibit a reduction of T_d as the average grain size reduces.

4. Conclusions

One-step conventionally sintered $Na_{0.5}Bi_{0.5-x}Yb_xTiO_3$ compositions exhibit a substantial increase in average grain size at low concentrations of Yb (x = 0.005–0.02) and a pronounced bimodal grain size distribution in comparison with NBT, which points to AGG. For $Na_{0.5}Bi_{0.5-x}Er_xTiO_3$ the same mechanism applies, only the increase in average grain size compared to NBT is insignificant. Bi over-stoichiometry for both Yb and Er-modified NBT compositions lead to a reduction in average grain size and roughening of grain boundaries, interpreted as the reduction of critical driving force Δg_c, therefore inhibiting AGG. Bi over-stoichiometry may induce formation of a liquid phase that increases the path of diffusion, therefore reducing the rate of grain growth.

Average grain size in one-step sintered samples tends to decrease and bimodality of the grain size distribution becomes more pronounced with an increase in sintering time, whereas in two-step sintered samples the opposite is true. Two-step sintering tends to reduce broadening of the grain size distribution in comparison with one-step sintering, especially at short sintering times. This method can be used to effectively suppress grain growth. Depolarization temperature in Er, Yb-doped NBT reduces along with average grain size, which results in a reduction in stability of the ferroelectric state within grains.

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Institute of Solid State Physics, University of Latvia as the Center of Excellence has received funding from the European Union's Horizon 2020 Framework Programme H2020-WIDESPREAD-01-2016-2017-TeamingPhase2 under grant agreement No. 739508, project CAMART²