J Electroceram (2008) 21:637–640
DOI 10.1007/s10832-007-9279-z

Depth-dependence of electromechanical properties in a thick $0.7Pb(Mg_{1/3}(Nb_{0.9}Ta_{0.1})_{2/3})O_3$–0.3pbtio$_3$ ceramic disk

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Published online: 13 November 2007

Abstract A thick ceramic disk of $0.7Pb(Mg_{1/3}(Nb_{0.9}Ta_{0.1})_{2/3})O_3$–$0.3PbTiO_3$ (PMNT–PT) was prepared by columbite precursor method with PbO powder buffer surrounding the disk during the sintering process. The Electromechanical properties and the microstructure of PMNT–PT samples cut from the different depths of the disk are studied. Although the phase purity is homogenous in the whole disk, the middle sample has higher electric field induced strain. Electric field of 14 kV/cm induced strain 0.14% was found. It is believed that the prepared processes, especially the Pb volatilization is responsible for these results.

Keywords Pb volatilization · Dielectric constant · Electric field induced strain · Piezoelectric constant

1 Introduction

Relaxor ferroelectrics are intriguing materials for their electromechanical properties for applications in the areas of piezoelectric and electrostrictive actuators, acoustic sensors and pyroelectric detectors. The columbite precursor and sintering method is used to synthesize pyrochlore-free PMN–PT [1]. Pb can volatilize during the sintering and it leads to the formation of an unwanted pyrochlore secondary phase. To prepare a single phase perovskite $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ ceramic, James et al. [2] introduced a modified columbite precursor method with 10% excess PbO added to the specimen to compensate for Pb volatilization. Villegas et al. [3, 4] studied the effect of excess PbO in 0.9PMN–0.1PT on its densification, phase purity, microstructure and dielectric properties. Bidault et al. [5] prepared 0.9PMN–0.1PT ceramics with different lead vacancies by using different sintering times and found that a change in the polar cluster due to lead vacancy formation weakens the dipolar interaction and inhibits the spontaneous relaxor to ferroelectric phase transition. Our previous study shows that using an extra PbO buffer surrounding the samples during sintering improves phase purity and enhances dielectric properties better than adding extra PbO to the sample [6]. In this paper, we have designed a method to prepare perovskite $0.7Pb(Mg_{1/3}(Nb_{0.9}Ta_{0.1})_{2/3})O_3$–$0.3PbTiO_3$ samples in which Pb volatilization varies in different parts of the sample during the sintering, and then studied microstructure and electromechanical properties of them. The middle sample in this ceramics is found to have high electromechanical performances.

2 Experimental procedure

Regent grade chemical compounds MgO (98.6%), Nb_2O_5 (99.99%), and Ta_2O_5 (99.99%), were stoichiometrically mixed by ball-milling and calcined at 900 °C for 4 h to form the precursor $MgNb_{1.8}Ta_{0.2}O_6$. This precursor was then mixed by ball-milling with PbO (99.9%) and TiO_2 (99.99%) powders according to the formula $0.7Pb(Mg_{1/3}(Nb_{0.9}Ta_{0.1})_{2/3})O_3$–$0.3PbTiO_3$ (PMNT–PT), and the mixture was cold pressed into a thick disk (19 mm in diameter and 8 mm in depth) at 7,000 ψ. The disk was surrounded by extra PbO

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powder buffer and placed in double Al_2O_3 covered crucibles and sintered at 1250 °C for 4 h. After sintering, the thick disk was annealed at 900 °C for 6 h in a furnace with flowing oxygen. Then it was cut into seven thin slices shown in Fig. 1, and numbered as illustrated. The thickness of each sample is about 0.5 mm. After polishing, a Pt thin film was applied with a Cressington 108 auto Sputter Coater. Then, samples were fired at 600 °C for 10 min to ensure bonding of the electrodes to the sample surfaces. The electric field induced strain versus step electric fields were measured by Zygo interferometer system. A fracture surface at the center of the samples was examined using scanning electron microscopy (SEM). The element concentration was determined by X-ray energy dispersive spectroscopy (EDS). The crystal structure and the phase purity were determined by X-ray powder diffraction (XRD) pattern using a Rigaku D/Max 2100B, Cu Kα radiation.

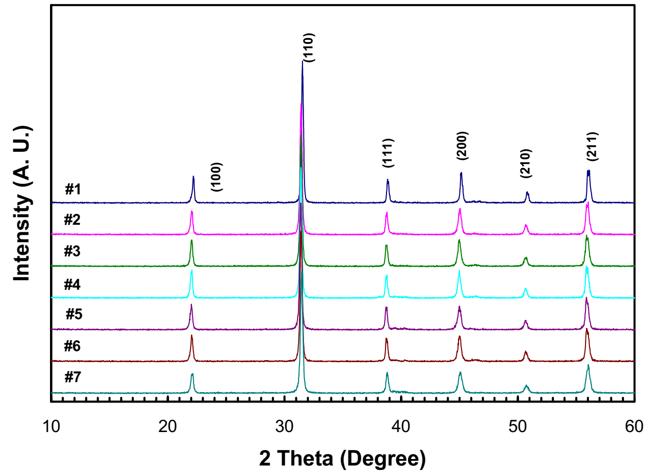

Fig. 2 X-ray diffraction patterns

3 Results

X-ray diffraction pattern (Fig. 2) proves all samples with a single perovskite phase, and SEM (Fig. 3) shows the shapes of grains are polygonal, and the fracture is mainly intergranular. However, the grain size and Pb content are different. Using the ImageJ software, we analyzed the granular properties of these samples by measuring the areas of 110 grains in SEM image. Assuming the shape of the grain was a circle, the corresponded diameter was calculated and shown in Table 1. The average atom percentage was measured by the EDS. The Pb atomic percentage is listed in Table 1 too. Pb is least abundant in the two end samples, while grain size is slight larger in the middle. These should be related to the prepared process, specially sintering. Pb volatilization during sintering occurs on the surface, and Pb atoms diffuse from the interior to the surface. Consequently, the Pb concentration on the surface (samples #1 and #7) will be lower than the interior region (sample #3, #4, #5). The top sample #1 faced open space during sintering while the bottom one #7 faced the crucible and was surrounded by extra PbO; hence, sample #7 has higher Pb concentration than sample #1. During sintering, Pb may form a liquid phase which can promote the growth of perovskite crystal grains as the mean grain diameter is larger where Pb concentration is higher. Samples #5 and #6 have higher Pb concentration and also have larger average grain size. On the contrary, sample #1 has lower Pb concentration and a smaller average grain size.

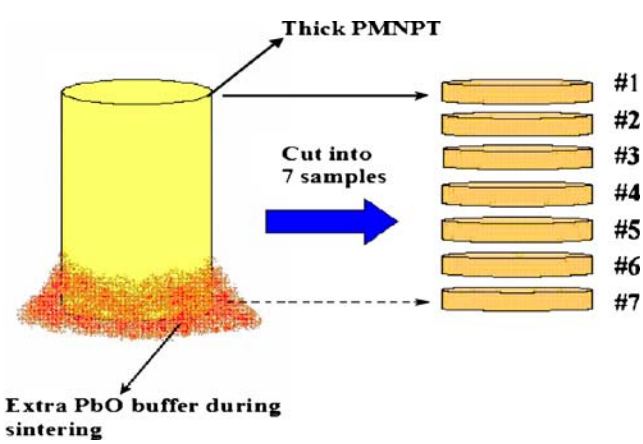

Fig. 1 Schema to cut the thick disk into seven samples

The relationship between the strain and the electric field is shown in Fig. 4. Sample #4 from the middle of the disk has the largest induced strain. The strains induced by step electric fields decrease with the location of the sample from the middle to both ends of the disk. The properties of samples cut from the bottom part are better than those cut from the upper of the disk. No strain data was available for sample #1 at 9.6 kV/cm because it broke down at a lower applied electric field. The tendency that the electric field induced strain changes with the depth is similar to the above grain size and Pb content result. We can explain it as following. Firstly, Pb volatilization creates Pb vacancies, and the lead vacancies can affect the dipole coupling and the domain formation. As reported by Dai et al. [7], the large number of lead vacancies induced by the substitution of La atom in a PLZT inhibits the long-range dipole coupling and promotes formation of polar nanodomains, while the small number of lead vacancies leads to the formation of the normal micro-sized domains. The difference in Pb volatilization within the

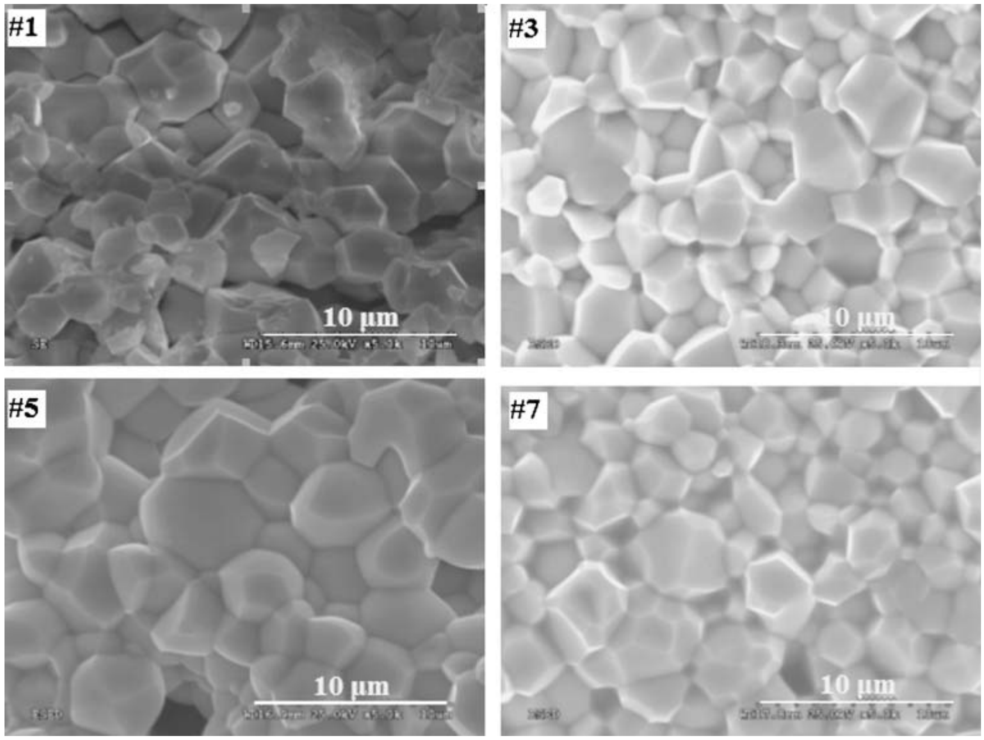

Fig. 3 SEM images of samples #1, #3, #5 and #7 at magnification 5 k

disk causes the variation of lead vacancies in our samples which, in turn, causes the change of electromechanical properties. Secondly, the granular characteristics are different within the thick disk due to Pb volatilization. The mechanical interaction between the grains leads to a high level of compressive pressure inside a small grain, while a mean stress value (or the stress in the center of the grain) remains relatively low for a large grain. The growth and reorientation of polar clusters under an external electric field bias may be considerably restricted in smaller grains via the stronger coupling between local strain and polarization. Shvartsman [8] found that relatively high piezoelectric activity and more pronounced hysteresis are characteristics of a larger grain and d_{33} is, therefore, a function of the grain size. It is consistent with our results.

Table 1 Grain size and Pb content of different samples.

Sample label	#1	#2	#3	#4	#5	#6	#7
Average grain size (µm)	1.866	2.289	2.283	2.260	2.631	2.431	2.264
Pb atomic percentage (%)	22.69	24.3	24.74	24.55	25.60	25.98	24.06

4 Conclusion

The Pb volatilization during sintering in the columbite precursor method affects the microstructure and electromechanical properties of $0.7Pb(Mg_{1/3}(Nb_{0.9}Ta_{0.1})_{2/3})O_3$–$0.3PbTiO_3$ ceramics. The samples have larger grain size if they undergo less Pb volatilization, and it has larger electric field induced strain. The strain induced by electric field 14 kV/cm is 0.14% for the middle sample while about 0.06% for end samples.

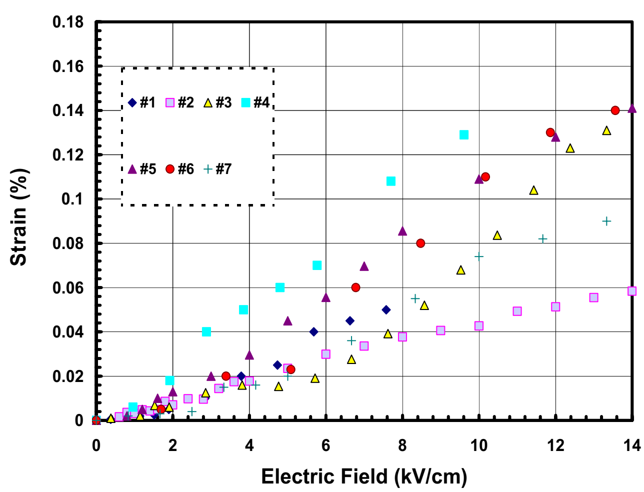

Fig. 4 Strain as a function of step electric field

Acknowledgements This work is supported by Office of Naval Research, US Navy, research grant N00014-02-1-0275.

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