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Annealing of Sintered $Pb_{0.9175}La_{0.055}Zr_{0.975}Ti_{0.025}O_3$ in Air

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Annealing of a sintered pellet of $Pb_{0.9175}La_{0.055}Zr_{0.975}Ti_{0.025}O_3$ in air without any precautions against PbO evaporation results in a core–shell microstructure with a solid PLZT core and a porous ZrO_2-rich shell.

I. Introduction

Antiferroelectric (Pb,La)(Zr,Ti)O_3 PLZT with a 5.5/97.5/2.5 composition was previously studied to investigate sintering in the presence of PbO powder. The effects of sintering temperature and time on the microstructure of a PLZT composition were reported.[1]

Attempts have been made to anneal a sintered lead zirconate structure by heating in air for a short time and at a temperature just high enough to remove free PbO in the grain boundaries.[2,3] The intention was to evaporate the free PbO and thereby allow the perovskite grains to grow together with a grain boundary that is close to being "clean." An increase in the dielectric loss can occur if PbO is left in the grain boundaries after the sintering. Therefore, it is critical that both the sintering and the annealing processes are carried out in an optimized manner.

During sintering, it is important that the temperature is just high enough to allow the free PbO to evaporate without losing PbO from the PZT structure.[2,3] However, in an effort to prevent PbO loss, sometimes, the PbO vapor pressure in the surrounding atmosphere during sintering can be too high. This was pointed out by Xia and Yao,[2] and by Kingon and Clark.[4,5] They found lower densities in PZT structures when using a high PbO vapor pressure in the sintering atmosphere. The annealing process has mainly been used for rapid annealing of thin films of ferroelectric PLZT compositions.[3,6] These compositions contain more Ti than the antiferroelectric PLZT, and therefore the melting point of the PbO-rich grain boundary phase will be lower and the solubility of PLZT material in the PbO phase will be increased.[7–9] Thus, it will be easier for the creation of a PbO-free "clean" PLZT grain boundary phase in the titanium-rich PLZT compositions.

II. Experimental Procedure

It is important to investigate which reactions occur when annealing sintered samples of Zr-rich antiferroelectric PLZT. The present study comprises both short-time (2.5 min) and long-time (1 h) annealing of a sintered antiferroelectric PLZT pellet in a preheated furnace at 1000°C, in still air, without any precautions against PbO evaporation. The PLZT pellets (2 mm × 12.5 mm) were sintered at 1300°C for 2 h, with PbO powder to protect against PbO evaporation, as described earlier.[1] Surface morphology and element identification and distribution of a fractured cross section were carried out using scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy (EDS) techniques (HITACHI S-3500N-PGT-EDS, Tokyo, Japan). Phase determination on the face of a pellet annealed for 1 h was carried out using an automated X-ray powder diffractometer (PAD V, Scintag, Santa Clara, CA) using Cu$K\alpha$ radiation and $\lambda = 1.54056$ Å and a scan of 10°–80° 2Θ with a speed of 2°/min.

III. Results and Discussions

Figure 1 shows an intergranular fractured surface of a sintered pellet before annealing. Annealing a sintered pellet for 1 h resulted in the formation of a well-defined outer layer. The pellet was fractured and the interior and the surface layers were studied using SEM/EDS. The interior showed an intergranular fracture similar to that found for an unannealed sample. The outer layer was on the order of 6-μm thick (Fig. 2) and had a surplus of Zr and a deficiency of Pb as shown in the EDS element X-ray map (Fig. 3). Figure 4 shows that the layer is very porous with 50–100 nm-sized grains of ZrO_2. The composition was determined by X-ray diffraction. The ZrO_2 X-ray peaks were broader than the peaks found for the very fine-grained ZrO_2 raw material used for fabrication of PLZT pellets. This relates well with the nm grain size of the formed ZrO_2 as observed in the SEM of the outer surface.

Annealing for 1 h creates a sharp boundary between unaltered PLZT and the ZrO_2-rich layer. This suggests that the first part of the removal of the PbO from the PLZT is a fast process as PbO vapor is transported through the porous material. The

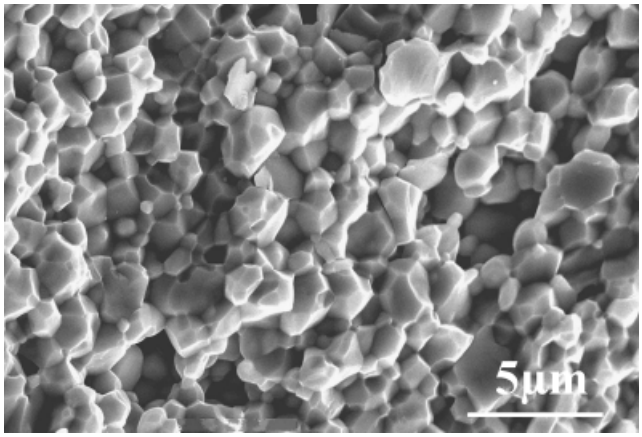

Fig. 1. Scanning electron microscopy image of a fractured surface of sintered un-annealed PLZT 5.5/97.5/2.5.

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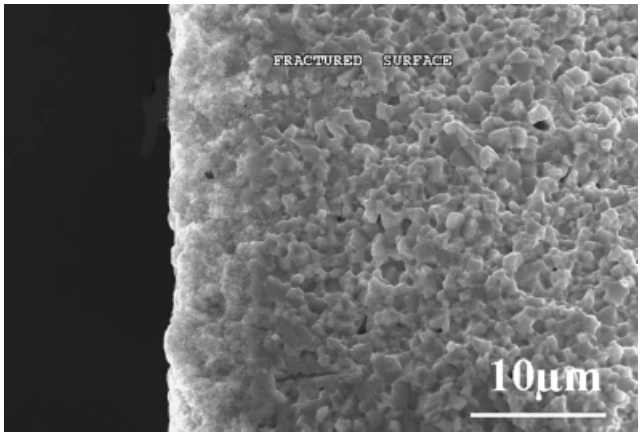

Fig. 2. Scanning electron microscopy image of a fractured surface of a sintered PLZT 5.5/97.5/2.5 after 1 h annealing at 1000°C in air. The image shows the top surface to the left.

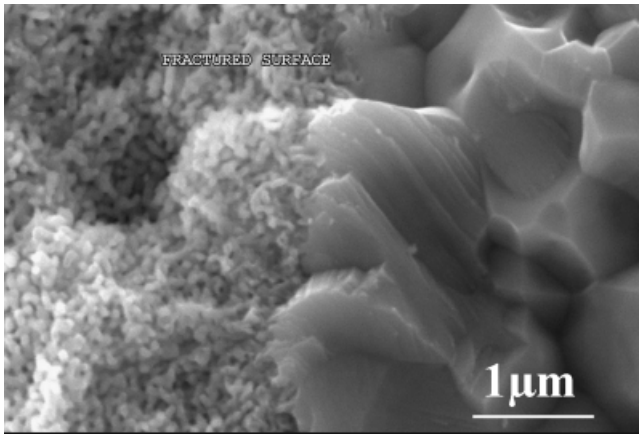

Fig. 4. Close-up of the region seen in Fig. 2. There is a sharp boundary between the sintered PLZT material and the fine-grained ZrO_2-rich, PbO-depleted surface material.

second process is a bulk material diffusion of PbO along the grain boundaries through the condensed material in the grain boundaries. Even though, at 1000°C, PbO is above its nominal melting temperature, the diffusion is much slower than the gaseous diffusion, and some of the PbO in the grain boundary phase may remain in place. The fracture surface of the interior (Fig. 2) is intergranular and appears similar to the fractured surface of an unannealed sample (Fig. 1), suggesting that there may still be free PbO left in the grain boundaries after the annealing.[2] Only with further PbO depletion, as explained earlier,[1] will the PbO grain boundary phase completely disappear, resulting in an intragranular fracture.

The short-time annealing process was studied with an experiment similar to the 1-h annealing, but was heated for only 2.5 min. In order to ensure a fresh PLZT surface a fractured piece was used. Figure 5 shows that some small grains, presumably ZrO_2, were formed. The grains are of the order of 50–100 nm, and the thickness of the layer cannot be determined, as only a few new grains have nucleated on the surface.

These results show that, when a sintered antiferroelectric PLZT pellet is annealed in a preheated furnace at 1000°C in air, and without any precautions against PbO evaporation, the first process is a rapid diffusion of PbO into the air. This results in the formation of a porous PbO depleted outer layer that consists of nonometer-sized ZrO_2. There were no detectable changes in the interior. These results suggest the much slower process of diffusion of free PbO in the interior through solid material toward the outer surface or the porous outer layer.

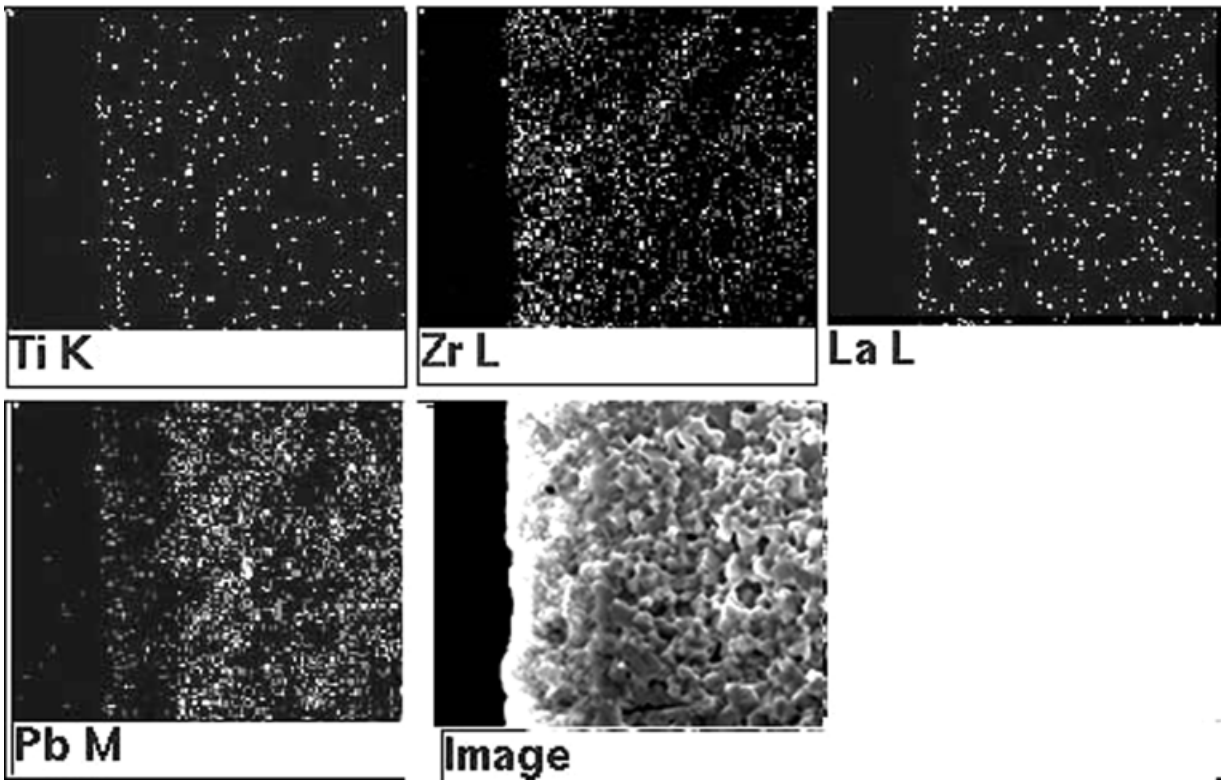

Fig. 3. Sintered PLZT 5.5/97.5/2.5 after 1 h annealing at 1000°C in air. Element X-ray dot-map from the area seen in Fig. 2. The surface layer is Zr rich and Pb deficient.

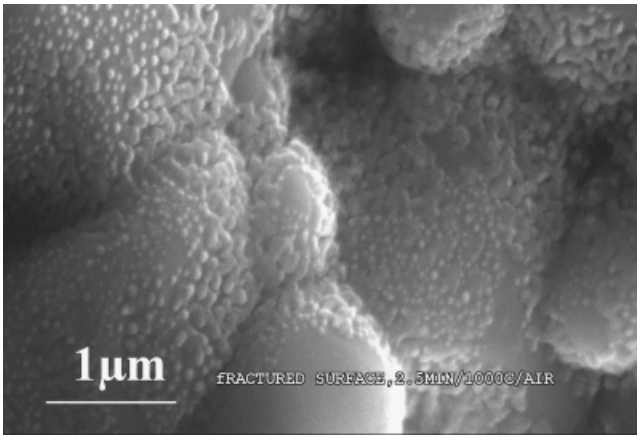

Fig. 5. Scanning electron microscopy image of PLZT annealed at 1000°C in air for 2.5 min. The surface shows the growth of new nm grains that is likely ZrO_2.

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