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Effect of excess PbO and sintering temperature on the templated grain growth of $Pb(Mg_{1/3}Nb_{2/3})_{0.67}Ti_{0.33}O_3$ polycrystals

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The effect of excess lead oxide and sintering temperature on the microstructure evolution in the templated grain growth (TGG) of the $Pb(Mg_{1/3}Nb_{2/3})_{0.67}Ti_{0.33}O_3$ (PMNT67/33) polycrystals was investigated. By adding excess PbO in the precursor of PMNT ceramics, the textured structure of PMNT polycrystals was obtained near $SrTiO_3$ (ST) template by the conventional ceramic technique. The texture profiles developed progressively with increasing the concentration of excess PbO. A suitable sintering temperature is also very essential to grow a thick textured layer and avoid a second phase. Furthermore, the through-thickness of the PMNT textured layer is strongly influenced by the uniaxial compact-pressure of preparing the ST seeded PMNT specimen.

1. Introduction

Recently, great interest has been focused on the growth of relaxor-based ferroelectric single crystals due to their high piezoelectric properties. ⟨001⟩-oriented lead magnesium niobate-lead titanate (PMNT) single crystal near the morphotropic phase boundary (MPB) is a promising candidate for improved transducers and actuators [1, 2]. But the superior properties of single crystals are not observed in ceramics with an equivalent composition because they are averaged out and clamped in polycrystalline samples in which each grain has a different crystallographic orientation. However, scientists and engineers still pay attention to ceramics because compared with the ceramics the growth of relaxor ferroelectric single crystal is much more expensive, time-consuming and difficult to reproduce.

Grain orientation is one of the effective methods to enhance the piezoelectric property of a polycrystalline ceramics. The abnormal grain growth is a typical method to get oriented polycrystalline materials, and the growth of grains is by an Ostwald ripening-type process [3]. Based on this, recently, a process named as Templated Grain Growth (TGG) has been reported to produce single crystals and textured ceramics, such as Al_2O_3, $Sr_{0.53}Ba_{0.47}Nb_2O_6$, $Bi_4Ti_3O_{12}$, and so on [4–7]. Many techniques (e.g. tape-casting, hot pressing and hot forging, etc.) are reported to be effective to align the anisotropic templates [8–13]. However, in order to improve the quality of textured polycrystalline material and simplify the fabrication procedure, further studies should be done to investigate the factors affecting on the oriented layer of grain growth.

In this study, the $Pb(Mg_{1/3}Nb_{2/3})_{0.67}Ti_{0.33}O_3$ (abbreviated as PMNT67/33) textured polycrystals were prepared by a templated grain growth method. ⟨001⟩-$SrTiO_3$ (abbreviated as ST) template crystal embedded in the PMNT matrix is applied as a crystal nucleus for oriented grain growth. Particularly, we carried out this TGG fabrication processing by the conventional ceramic technique. The effect of excess PbO concentrations, sintering temperatures and uniaxial compact-pressures of ST seeded specimen on the textured polycrystals in PMNT67/33 ceramics are discussed.

2. Experimental procedure

Analytical grade PbO (99%, Shanghai First Chemical Factory, Shanghai, China), Nb_2O_5 (99.5%, Jiujiang Rare Earth Factory, Jiangxi, China), MgO (98%, Tianjin Haizhong Chemical Factory, Tianjin, China) and TiO_2 (98.5%, Beijing Chemical Factory, Beijing, China) were used as raw materials. The PMNT67/33 powders were prepared using the columbite process [14]. The PMNT67/33 powder was mixed with PbO

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in a ball mill for 12 h to obtain powder compositions containing 0, 5, 10, 15 and 20 wt% excess PbO, using ethanol as a medium. After drying the slurries, Polyvinyl Alcohol (PVA) binder was added in the powder to granulate and press to form green compacts. The uniaxial pressure of 100 MPa/700 MPa was used to form them. After that, the green compacts were heated at 500°C for 1 h for binder burnout. For sintering and growth experiments, samples surrounding by $PbZrO_3$ atmosphere powders in a covered crucible were heated in a muffle furnace at various predefined temperatures of 1050, 1100, 1150, 1200 and 1250°C for 10 h.

The crystalline phases were determined by X-ray diffraction (XRD) (Model D/max-3c, Rigaku Co., Tokyo, Japan) using a Cu Kα radiation and a graphite monochromator with a 2θ range of 20 to 60°. The compositions of ceramic matrix were analyzed by X-ray fluorescence (XRF) (Model RIX-2100, Rigaku Co., Tokyo, Japan). Cross sections of the sintered compacts were studied by scanning electron microscopy (SEM) (Model JSM-5800, JEOL, Tokyo, Japan). For SEM observation, samples were cut perpendicular to the pellet face, polished to 0.5 μm, and then thermally etched to reveal grain boundaries. In order to analyze the reaction mechanism and detect the lead loss in the heating process, thermal analysis was performed by a thermogravimetry (TG) (Model SDT2960, TA Instruments, USA). PMNT solid-solution precursors of about 30 mg each were put in Pt pans, heated from the room temperature to 1400°C at a rate of 20°C min^{-1} in air atmosphere.

3. Results and discussion

3.1. Effect of excess PbO concentration in the PMNT matrix

Fig. 1a–d show the SEM microstructure of specimens sintered at 1050°C from the PMNT precursors with different excess PbO. Near the strontium titanate single crystal, a grown grains layer with textured structure can be clearly discerned although they are thin. With increasing the concentration of excess PbO, the thickness of the textured layer increases evidently. Especially for the specimen obtained from the precursors with 20% excess PbO, the thickness is about 37.4 μm. As we know, the melting point of pure PbO is about 880°C. It suggests that the nucleation and growth process in our experiments is mainly controlled by the dissolution/precipitation mechanism. According to the dissolution/precipitation mechanism, appropriate liquid phase is useful to diffuse. In our experiment, more excess lead oxide led to easier diffusion among PMNT grains around template. That is, the grains began to grow at temperature lower than 1050°C. The morphology of textured structure in Fig. 1 supports this argument. In the presence of PbO-rich liquid phase, the diffusion process is so facilitative that grains grow rapidly. Near the ST, larger grains appear with increasing excess PbO concentration. That is, when there is sufficient PbO, PMNT67/33 perovskite grains at (001) ST surface preferentially nucleate and grow orientedly during the thermal treatment. Furthermore, the oriented PMNT67/33 polycrystals grow slow if the matrix compositions are in stoichiometric ratio and the sintering temperature is not high enough. When the PbO is

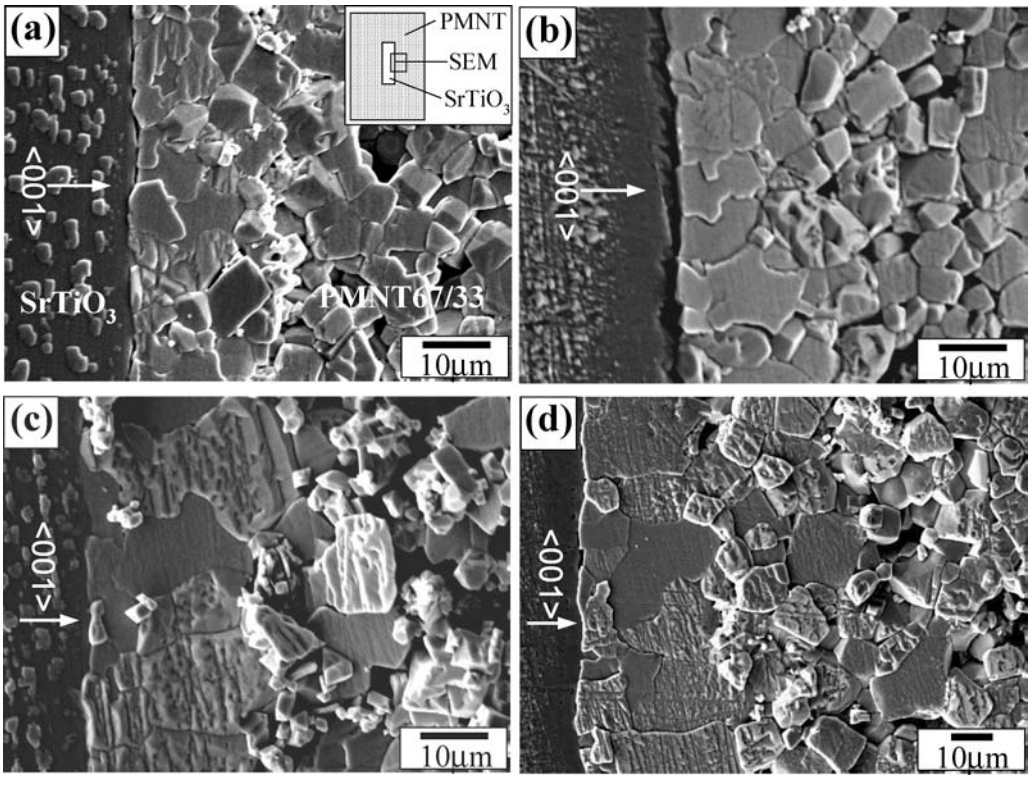

Figure 1 SEM micrographs of the specimens sintered at 1050°C for 10 h from the precursors with (a) 5% PbO, (b) 10% PbO, (c) 15% PbO, and (d) 20% excess PbO. Inserted figure in (a) showing the schematic depiction of the section of sintered specimens.

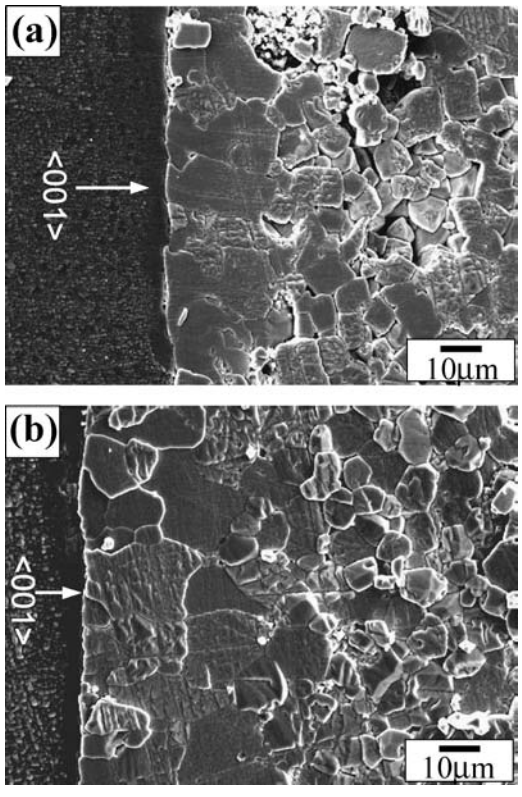

Figure 2 SEM micrographs of the specimens from the precursors with 10% excess PbO sintered at (a) 1100°C and (b) 1250°C for 10 h.

deficient, the perovskite phase is metastable. The PMNT perovskite decomposes to the pyrochlore and the magnesium oxide [15, 16].

3.2. Effect of sintering temperature

The textured layer also grows thicker with increasing the sintering temperature. The SEM micrographs of specimens sintered at 1100 and 1250°C for 10 h from the precursors with 10% excess PbO are shown in the Fig. 2a and b. With increasing the sintering temperature, the through-thickness of the textured layer increases notably. Fig. 3 displays the effect of temperature and

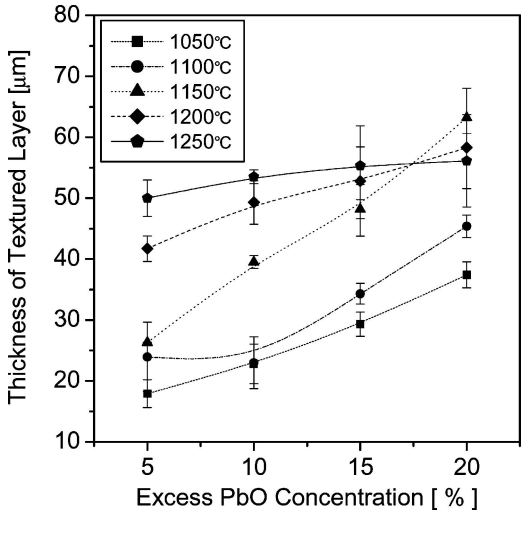

Figure 3 Effect of excess PbO concentration and sintering temperature on the thickness of textured layer.

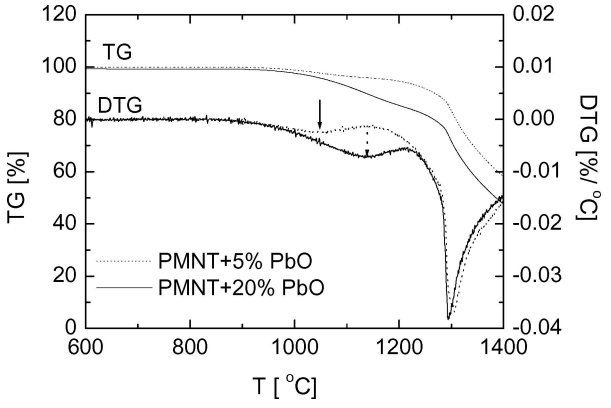

Figure 4 Thermal analysis TG/DTG curves for the PMNT precursors with 5 and 20% excess PbO.

excess PbO concentration on the thickness of textured layer in more detail. It should be noted that there is a cross at the point that the excess PbO concentration is ∼17% in Fig. 3. When the concentration of excess PbO in PMNT precursors is less than 17%, increasing the sintering temperature is effective to improve the extent of textured layer. However, when the concentration of excess PbO is more than 17% and the sintering temperature is above 1100°C, the through-thickness of the textured layer reduced with increasing sintering temperature. The cross about 17% excess PbO concentration, in the Fig. 3, implies that the same thickness of the textured layer could be obtained at the sintering temperature 1150, 1200 or 1250°C. Thermal analysis results for the PMNT precursors with 5 and 20% excess PbO are shown in Fig. 4. In the DTG curve, a broaden peak appears at about 1050°C for the sample with 5% excess PbO and at 1150°C for the sample with 20% excess PbO, respectively. These peaks seem to be related to the PbO evaporation. In the sample with 20% excess PbO, there is sufficient liquid phase when the sintering temperature is less than 1150°C; and near the ST template, the oriented growth of PMNT polycrystals takes place. The through-thickness of the textured layer increased dramatically with increasing the sintering temperature until 1150°C. However, when the sintering temperature is too high (at 1200 and 1250°C), there is no sufficient liquid phase in the PMNT matrix due to PbO evaporation. For all samples, it is very obvious that 1050 and 1100°C is too low to get a thick textured layer. Both the liquid phase and the high temperature promote the diffusion of PMNT. Although excess PbO, to some extent, is in favor of the diffusion of PMNT, the evaporation of PbO is stronger and stronger with increasing the sintering temperature. Higher sintering temperature is prone to resulting in decomposition/phase separations, because the melting point of the PMNT67/33 crystals is ∼1270°C, which is corresponding to the sharp peak in Fig. 4. Above it PMNT67/33 decomposes violently due to the evaporation of PbO and the volatilization of the molten parts. Therefore, there must be a best temperature range for the development of the textured structure. For a thick textured layer, 1150°C or so may be the proper sintering temperature.

To investigate the effect of PbO addition on the compositions of ceramic matrix, the ceramic matrix was

TABLE I The XRF results of different specimens sintered at 1150°C for 10 h

The PbO content in different PMNT specimens			
Theoretical value in PMNT67/33	XRF value from the specimen with 0% PbO excess	XRF value from the specimen with 5% PbO excess	XRF value from the specimen with 20% PbO excess
70.2%	70.5%	70.3%	70.8%

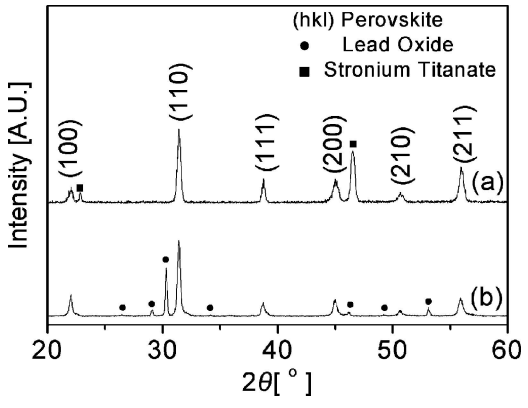

Figure 5 XRD patterns of the PMNT specimens: (a) the fracture surface of ST seeded PMNT bulk ceramics and (b) PMNT solid-solution precursors with 20% excess PbO.

analyzed by XRF. The PbO concentrations in the powders of ceramic matrix are shown in Table I. The addition of excess PbO hardly affected the composition of ceramics because most of the PbO in the ceramic matrix evaporated during the sintering above 1100°C. The crystalline phases in the ceramics were determined by XRD. Fig. 5 displays the XRD patterns of PMNT specimens including precursors and ST seeded PMNT bulk ceramics sintered at 1150°C from the solid solution with 20% excess PbO. Fig. 5a shows the XRD patterns of the fracture surface of PMNT bulk ceramics, which include the PMNT perovskite phase and the ⟨001⟩-oriented ST phase. The excess PbO disappeared after sintering from the precursor with 20% excess PbO, of which strong PbO peak was detected in Fig. 5b. The XRD patterns support the XRF results.

3.3. Effect of the uniaxial compact-pressure

As the abnormal grain growth takes place by an Ostwald ripening-type process, we also investigated the effect of uniaxial compact-pressure on the textured structure. 100 MPa or 700 MPa was used to form green compacts, followed by sintering under normal pressure conditions. The cross sections of seeded PMNT67/33 specimens sintered at 1250°C for 10 h are shown in Fig. 6. Fig. 6a presents the microstructure of sintered specimen prepared by 100 MPa uniaxial compact-pressure from the precursor with 20% excess PbO. Fig. 6b displays a cross section of the sintered specimen prepared by 700 MPa uniaxial compact-pressure from the precursor with 20% excess PbO. The difference in through-thickness of textured layer can be seen distinctly. Compared with Fig. 6a, the textured layer in Fig. 6b exhibited a thicker

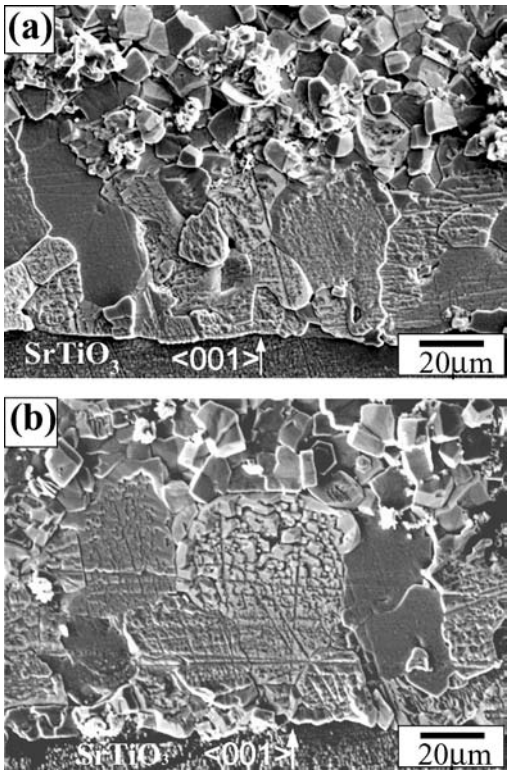

Figure 6 SEM micrographs of the sintered specimens prepared by different compact-pressure: (a) 100 MPa and (b) 700 MPa.

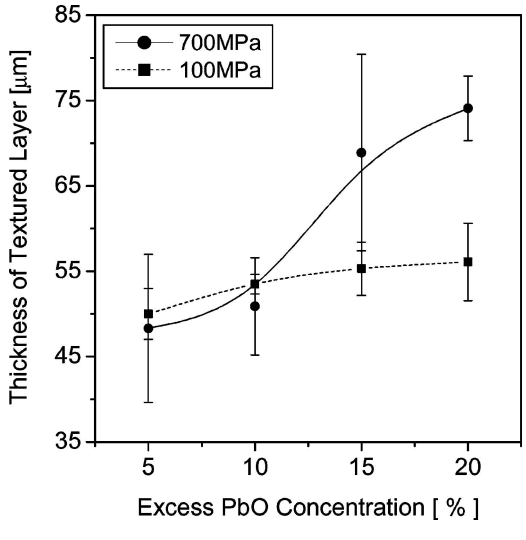

Figure 7 The thickness of the textured-layer of sintered specimens prepared by different uniaxial compact-pressure from precursors with different excess PbO.

morphology, whose thickness is ∼75 μm. More results are shown in Fig. 7. It is obvious that the thickness of textured layer is related to the concentration and the evaporation of PbO in the matrix. When the concentration of excess PbO is below 10% in the matrix, the effect of uniaxial pressure on the textured layer thickness is not evident because 1250°C is so high that most of the PbO evaporated rapidly during very short sintering time. However, when the concentration of excess PbO is above 10% in the precursors, the thickness of textured layers are improved significantly with increasing the uniaxial compact-pressure because longer time is needed for the PbO evaporation. More liquid phase was supplied during the sintering time in per volume

matrix when increasing the uniaxial compact-pressure. Therefore, high quality textured structure may be prepared by using higher compact-pressure.

4. Summary and conclusions

Textured layer of PMNT polycrystals is grown using the TGG method at suitable sintering temperature and excess PbO in PMNT solid-solution precursors. Excess PbO was found to be the primary factor controlling the textured structure in TGG method. The through-thickness of the textured layer increases with increasing the excess PbO concentration and the pressure of forming the green seeded disk. At the same time, the suitable sintering temperature was very essential to prepare the textured structure. 1150°C or so was the proper sintering temperature for preparing the PMNT67/33 textured structure. The development of PMNT textured structure is controlled mainly by the dissolution/precipitation mechanism in ST seeded PMNT matrix.

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