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Synthesis of High-Aspect-Ratio $BaTiO_3$ Platelets by Topochemical Conversion and Fabrication of Textured $Pb(Mg_{1/3}Nb_{2/3})O_3$-32.5$PbTiO_3$ Ceramics

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Perovskite structured barium titanate particles ($BaTiO_3$) platelets were synthesized by molten salt synthesis and topochemical microcrystal conversion. As the precursors of $BaTiO_3$, plate-like $BaBi_4Ti_4O_{15}$ particles were first synthesized by the reaction of $Bi_4Ti_3O_{12}$, $BaCO_3$, and TiO_2 at 1080 °C for 3 h in $BaCl_2$-KCl molten salt. After the topochemical reactions, layer-structured $BaBi_4Ti_4O_{15}$ particles transformed to the perovskite $BaTiO_3$ platelets. $BaTiO_3$ particles with thickness of approximately 0.5 μm and a length of 10-15 μm retained the morphology feature of the $BaBi_4Ti_4O_{15}$ precursor. For <001> $Pb(Mg_{1/3}Nb_{2/3})O_3$-32.5$PbTiO_3$ (PMNT)-5 wt % PbO piezoelectric ceramics textured with 5 vol % of $BaTiO_3$ templates, the Lotgering factor reached 0.82, and d_{33} was 870 pC/N.

Key Words : Grain growth, Topochemical microcrystal conversion, Piezoelectric properties, Perovskites

Introduction

Templated grain growth (TGG) is one of the effective methods to enhance the physical and mechanical properties of the ceramics with anisotropic properties. It has been widely used to prepare textured polycrystalline ceramics.[1] During TGG process, plate-like or needle-like shaped particles were aligned in matrix powders as nucleation site for oriented growth during heat treatment. The characters of the template particles, including structure, morphology and size, have strong influences on the microstructure and the properties of the resulting ceramics.

TGG has been used to produce single crystal Al_2O_3, ferrites, $BaTiO_3$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$-32.5$PbTiO_3$ (PMNT).[2,3] In most cases crystals were grown by a homoepitaxial TGG, which means the growing matrix has the same composition and crystal structure as the template material. However, anisotropic morphology is generally not expected to result from unconstrained growth for perovskite crystals with a cubic or pseudo-cubic structure. Since plate-like PMNT is difficult to synthesize, and the TGG method requires anisometric particles with a proper lattice match and the designed stability, $BaTiO_3$ with a good stability in PMNT matrix and strong epitaxial relationship to the crystal structure of the matrix composition could be used as the template of PMNT ceramics. $BaTiO_3$ prepared firstly by Remeika[4] method have been used to obtain textured PMNT ceramics. However, it showed approximately equiaxed morphology which cannot fit the requirements for template in TGG process.

Topochemical microcrystal conversion method is a very favorite method to prepare anisotropic particles. It involves replacing or modifying the interlayer cations while retaining the morphological and structural features of plate-like layered-perovskite precursors by topochemical reaction at low temperatures. Using topochemical reactions, it is possible to design the aimed product with desired shape and structure from multistep sequence of low-temperature reactions. Although topochemical conversion method has been used by Liu *et al.* and Messing *et al.*,[5,6] the as-synthesized $BaTiO_3$ templates have not been used effectively to templated PMNT ceramics. In this work, a two-step method to synthesize plate-like $BaTiO_3$ with perovskite structure and nearly perfect size for TGG has been designed. Aurivillius structured $BaBi_4Ti_4O_{15}$ (BBT) precursor was first synthesized as the precursor. Then plate-like $BaTiO_3$ was synthesized through a topochemical process from this precursor. The textured PMNT ceramics with high Logtering factor have been obtained by using high aspect ratio $BaTiO_3$ templates.

Experimental Procedure

The plate-like BBT particles were synthesized by the molten salt method from plate-like $Bi_4Ti_3O_{12}$ (BiT, synthesized according to ref. 7) firstly. BiT particles were reacted with $BaCO_3$ and TiO_2 in a ration of 1:1:1 mol. Equal weights of $BaCl_2$-KCl (1:2 mol) were added as salts. These raw materials were mixed by magnetic stirring in ethanol medium. After drying, the reactants were reacted at 1080 °C for 1 h. BBT grains were separated from the salts by washing with de-ionized water. In the second step, BBT platelets and $BaCO_3$ were mixed in a ration of 1:3.1 mol, and an equal weight of KCl salt was added. The slurry was dried and subsequently heated at 950 °C for 3 h. $BaTiO_3$ platelets retaining the morphology of the BBT precursor were separated from the salts by washing with hot deionized water and ethanol. The corresponding chemical reaction is as follows:

$$Bi_4Ti_3O_{12} + BaCO_3 + 4TiO_2 \rightarrow BaBi_4Ti_4O_{15} + CO_2 \quad (1)$$

$$BaBi_4Ti_4O_{15} + 3BaCO_3 \rightarrow 4BaTiO_3 + 2Bi_2O_3 + CO_2 \quad (2)$$

Textured PMNT ceramics were fabricated by the TGG method using plate-like $BaTiO_3$ particles as template. Because the driving force for the TGG is the surface free energy difference between the template and the matrix, on the basis of the size of $BaTiO_3$ and the presintered PMNT matrix, the fraction of the $BaTiO_3$ was nominated as 5 vol %. The template powder and presintered PMNT matrix powder were mixed in a solvent (45 vol % ethanol and 55 vol % toluene), binder (polyvinyl butyral), and plasticizer (dibutyl phthalate) to form a slurry. The slurry was tape-cast using a doctor blade machine. After drying, a single-layer sheet with a thickness of approximately 100 μm was cut, stacked, and laminated at 80 °C and 10 MPa to fabricate a 2 mm-thick green compact. The green compacts were first heated at 600 °C for 1 h to remove organic substances prior to sintering, and were fired at 1200 °C for 4 h in O_2.

SEM (model JEOS 6470) was used to determine the microstructure. The crystalline phases were determined by X-ray diffraction (model Rigaku 2500). The piezoelectric constant d_{33} was measured by a ZJ-3A (Beijing, China) quasistatic d_{33} meter.

Results and Discussion

Figure 1 shows the micrographs of particles of BiT, BBT and $BaTiO_3$. These particles had a plate-like shape. Figure 1(a) is the image of BiT as judged from the XRD pattern (Fig. 2(a)), which can be easily obtained from molten salt method, and the aspect ratio of BiT can be controlled by the different soaking time. The average size of BiT platelets is about 10 μm (length), and 0.5 μm (thickness). Crystalline phase of the particles as shown in Figure 1(b) is layered-perovskite $BaBi_4Ti_4O_{15}$ (BBT), BBT shows a microstructure of plate-like morphology with a length of 10-15 μm and a thickness of 0.5 μm. As determined by the XRD pattern shown in Figure 2(b), all of the diffraction peaks are assigned to JCPDS No. 35-0757 $BaBi_4Ti_4O_{15}$ (BBT), the strong intensities of (0010) and (0018) peaks indicate that the surface of the BBT platelet was parallel to (00l), and suggest that the BBT particles are of very high degree of orientation. Figure 1(c) shows the SEM micrographs of $BaTiO_3$ templates prepared from BBT particles by the topochemical reaction at 950 ºC for 3 h. Similar to the BBT particles, most of the $BaTiO_3$ particles are of plate-like shape with an average length of 15 μm and a thickness of 0.5 μm. The XRD pattern of $BaTiO_3$ is shown in Figure 2(c), it can be seen that the $BaTiO_3$ platelets exhibit a single-phase perovskite structure, the split of (200) and (002) peaks near 45º indicates that the $BaTiO_3$ particles have a tetragonal structure rather than cubic. From the topochemical reaction, the layer-structured BBT platelets have been transformed into perovskite $BaTiO_3$, and the plate-like shape was pre-

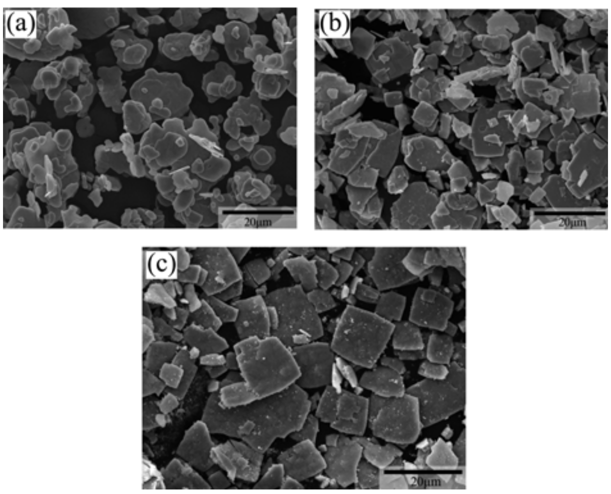

Figure 1. SEM images of (a) $Bi_4Ti_3O_{12}$, (b) $BaBi_4Ti_4O_{15}$, and (c) $BaTiO_3$.

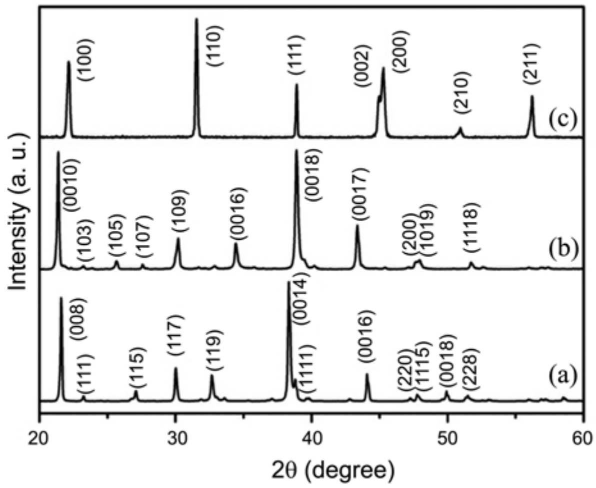

Figure 2. XRD patterns (a) $Bi_4Ti_3O_{12}$, (b) $BaBi_4Ti_4O_{15}$, and (c) $BaTiO_3$.

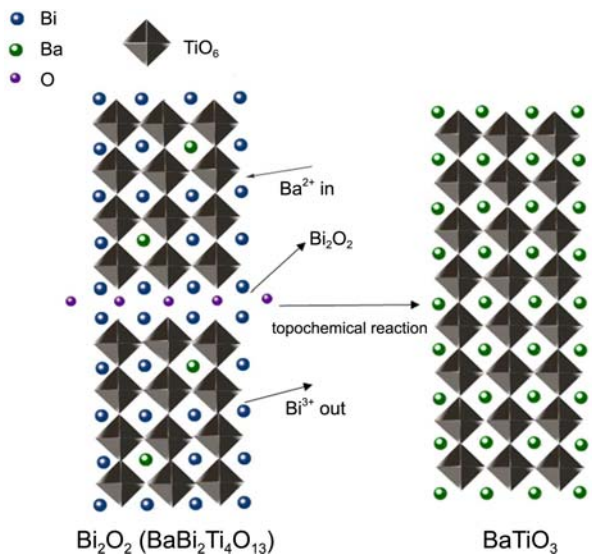

Figure 3. Crystal structures: Layer-structured $BaBi_4Ti_4O_{15}$ and perovskite-structured $BaTiO_3$.

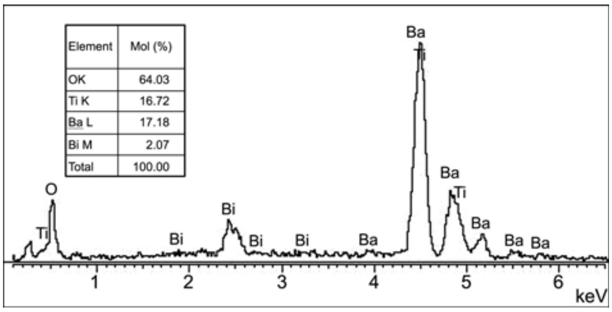

Figure 4. EDX pattern of $BaTiO_3$.

served.

The entire process of the topochemical conversion from layered perovskite BiT and BBT to perovskite $BaTiO_3$ is illustrated in Figure 3. The transformation may contain two processes: one is the decomposition of $(Bi_2O_2)^{2+}$ fluorite layers. BBT belonging to Aurivillius families with a formula of $Bi_2O_2(A_{n-2}B_nO_{3n+1})$ have a structure of $[Bi_2O_2]$ interlayer and perovskite sub-lattice,[8,9] and the network between the two-dimensional perovskite slabs are weak covalent, so the $[Bi_2O_2]$ slabs are easily to be removed during high temperature treatment; the other is the diffuseness of Ba^{2+} into the perovskite lattices and the substitution of Ba^{2+} with Bi^{3+}. Because three-dimensional atomic arrangement in the pseudo perovskite block is closely packed in the space, Bi atoms in the pseudo TiO_6 octahedron perovskite block cannot be replaced by Ba atoms easily. So, proper sintering temperature and soaking time are necessary for this replacement. In this work, $BaTiO_3$ platelets had been obtained by sintering at 950 ºC for 3 h.

To evaluate the atomic conversion ratio from Bi atoms to Ba atoms in the crystalline particles, the EDX analysis of $BaTiO_3$ particle synthesized by the topchemical method from $BaBi_4Ti_4O_{15}$ precursor particles had been done (see Fig. 4). It had shown that Ba:Ti:O:Bi atomic ratio is 16.7: 17.2:64.0:2, this ratio is in good agreement with chemical formula of $BaTiO_3$. It is clear that the Ba atoms replaced 97.1% Bi atoms in the A-site positions, and 1.2% of Bi atoms remained in crystalline lattice. However, the residual Bi that hard to remove completely had no major effect on the TGG process.[6,10]

Figure 5 shows the XRD and SEM image of PMNT textured ceramics templated by 5 vol % $BaTiO_3$ platelets, the textured materials sintered at 1200 ºC for 4 h in O_2 with PbO (5 wt % of PMNT) as sintering aids. It can be observed that compared to the random one, the textured materials shows strong intensity in <00l> direction, and the textured PMNT are dense and brick-like, the calculated Lotgering factor of the {100} orientation had been calculated as high as 82% (indicating a high degree of grain orientation). By comparison with the random sample (d_{33} ~ 530 pC/N), the d_{33} value of the textured PMNT reached 870 pC/N. These values also suggest that the $BaTiO_3$ templates were efficient in inducing grain orientation in the PMNT ceramics, and because the structure of $BaTiO_3$ templates is stable and similar to PMNT, only a few templates (5 vol % in this work) will lead to a high degree of texture, and the textured ceramics will be well-sintered and much denser than those composed of more templates.

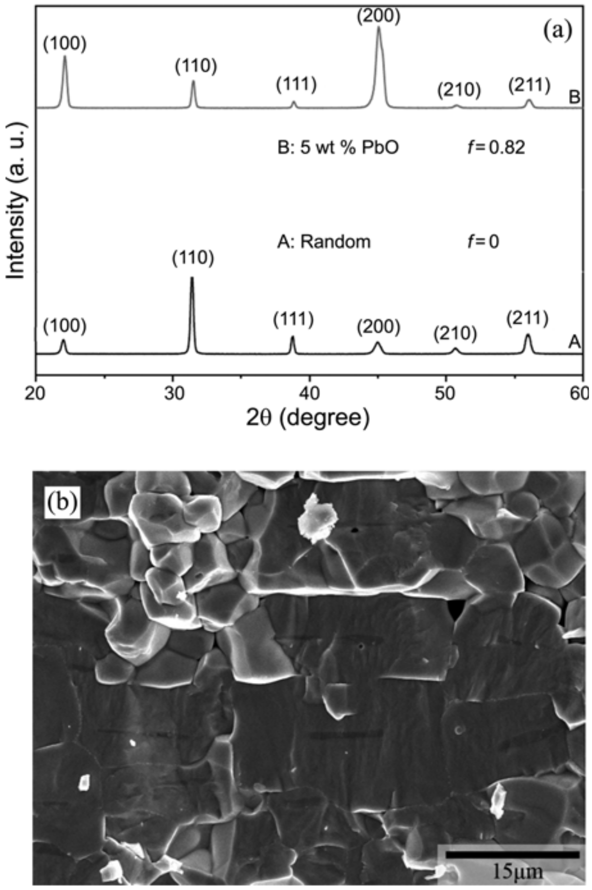

Figure 5. Characterization of PMNT textured ceramics templated by $BaTiO_3$ platelets (a) XRD patterns and (b) SEM image.

Conclusions

Plate-like $BaTiO_3$ particles were synthesized by the topochemical microcrystal conversion method from layer-structured $BaBi_4Ti_4O_{15}$ precursor particles. SEM and XRD analysis indicated that the $BaTiO_3$ particles had an average size of 15 μm and a thickness of 0.5 μm. They were perovskite structure and retained the morphological features of the $BaBi_4Ti_4O_{15}$ platelets. Using the $BaTiO_3$ platelets as templates in templated grain growth process, <001> grain-oriented PMNT-5 wt % PbO ceramics had been prepared. The result shows the plate-like $BaTiO_3$ particles were available in the templated grain growth process. And the topochemical method designed to prepare plate-like templates with perovskite structure will be used to synthesize the other perovskite-structured templates for texturing various ceramic materials.

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