Dispersion of barium titanate and strontium titanate nanocubes and their selective accumulations

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Barium titanate (BaTiO₃, BT) and strontium titanate (SrTiO₃, ST) nanocube particles were prepared by a solvothermal method. The prepared particles were collected by a centrifugal separator. The X-ray diffraction (XRD) measurement and a transmittance electron microscope (TEM) observation confirmed the formation of perovskite BT and ST nanocube particles with sizes of around 17 nm. These nanocube particles were monodistributed in hexane with tri-n-butylphosphine oxide (TBPO) as dispersant, separately, and then, the accumulations composed of the BT and ST nanocubes were built up using a selective catalytic reaction between 3-bromopropylphosphonic acid (BP) and aminomethylphosphonic acid (AM) as smart glue. The TEM observation confirmed that a part of accumulations showed a hetrointerface connection between BT and ST.

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1. Introduction

To create future materials with new and enhanced properties, nano-controlled structure is a key issue. Recently, enhanced piezoelectric and dielectric properties were reported for the materials with the nano-controlled structures. The lead zirconium titanate [Pb(Zr,Ti)O₃, PZT] ceramics has excellent piezoelectric and dielectric properties owing to the coexistence region of two different ferroelectric phases, i.e., a morphotropic phase boundary (MPB).¹⁾ For this enhancement, the polarization rotation mechanism (PRM) is responsible, reported by Ishibashi and Iwata²⁾ and Fu and Cohen.³⁾ Thus, a structure-gradient region in a hetrointerface between two phases can be considered as region with polar directions rotated between [111] and [100], and this should be origin of the enhanced properties. Recently, it was reported that the ferroelectric non-180° domain wall region had significant piezoelectric and dielectric properties.⁴⁾ It was considered that the non-180° domain wall region might be the region with polar directions rotated between [100] and [110], and the PRM can contribute to these enhancements. Moreover, for barium titanate (BaTiO₃, BT) and strontium titanate (SrTiO₃, ST) artificial superlattice films, enhanced dielectric properties were reported by Harigai et al.⁵⁾ Jiang et al. reported that the crystal structure of BT/ST artificial superlattice film was assigned to orthorhombic phase with polar direction along [110],⁶ while Johnston et al. also reported that in an interface boundary between BT and ST layers, a gradient change of polar direction from [100] in BT layer to [110] in ST layer was estimated using the first principle calculation.⁷⁾ This interface can be considered as the structure-gradient region. For BT nanoparticles, the excellent dielectric properties were reported by Wada et al.⁸⁾ For BT nanoparticles, there were mesoscopic particle structures, i.e., surface cubic layer, bulk tetragonal layer, and structuregradient region between surface and bulk, and this structuregradient region can have the enhanced dielectric properties owing to the polar vector rotated from [100] in bulk to [110] in surface. Therefore, to enhance properties, the polarization rotated region, i.e., structure-gradient region, must be required, and to induce this region into materials, nano-controlled structure with the steeper hetrointerface must be an important issue.

Thus, to induce the structure-gradient region into ceramics, conventional sintering cannot be applied because of no steeper hetrointerface by fast diffusion at high temperature. For future ceramics processing, there should be no sintering to induce nano-ordered structures. No sintering means that there is no diffusion of chemical spices between two phase. Moreover, if dense ceramics is required, we must control size and shape of nanoparticles, and so, nanocubes with a narrow size distribution could be required. Recently, the BT nanocube particles with sizes of 20 nm were successfully prepared using by a solvothermal method.⁹⁾ Moreover, Nozawa et al. reported a preparation of 2-dimentional artificial superlattice accumulations using the BT and ST nanocube particles with tri-n-octylphosphine oxide (TOPO) as dispersant and DNA basic pair as smart glue.¹⁰⁾ However, this method exhibited two problems as follows, i.e., (1) difficulty of removal of TOPO by heat treatment owing to large molecular weight of 386.64 g/mol, and (2) high cost of DNA basic pair. Thus, in this study, the first objective is proposal of new dispersant with smaller molecular weight than TOPO, and the second objective is proposal of new smart glue with lower cost than DNA basic pair. Finally, the BT/ST accumulations were also prepared using the new dispersant and smart glue with molecular recognition.

2. Experimental procedure

The BT and ST nanocubes were prepared by a solvothermal method.¹⁰⁾ A mixture of ethanol and 2-metoxy-ethanol was used as the solvent, while TiO_2 (Ishihara Sangyo Kaisha LTD.,

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>99.9%, size: 7 nm), Ba(OH)₂ (Strem Chemicals, >99.9%), and Sr(OH)₂ (Ube Materials Industries Co., LTD., >99.9%) were used as raw materials. The obtained powders were collected by a centrifugal separator. The crystal structures and crystallite sizes were investigated by a conventional X-ray diffraction (XRD) (Rigaku RINT2000, Cu K α , 50 kV, 30 mA). Average particle size and shape were investigated by a transmission electron microscope (TEM).

Using the above BT and ST nanocube particles, the accumulations with hetrointerface was prepared. To prepare this accumulation, monodispersed nanocubes and smart glue for selective binding between BT and ST nanocubes must be required. For these purposes, TOPO, tri-n-butylphosphine oxide (TBPO), and triphenylphosphine oxide as typical phosphine oxide compounds, 3-mercaptopropaonic acid as typical thiol compounds, several phosphate compounds, and several carboxyl compounds were used as new dispersants, while a selective catalytic reaction between 3-bromopropylphosphonic acid (BP) and aminomethylphosphonic acid (AM) was used as smart glue with molecular recognition. This detail will be described later. Finally, microstructure of the obtained accumulation body was observed using a scanning electron microscope (SEM) and TEM.

Results and discussion

3.1 Proposal of new dispersant for BT and ST nanocube particles

The BT nanocube particles were prepared at Ba/Ti atomic ratio of 1.1, Ti concentration of 0.04 mol/l and 240°C, and treated using diluted acetic acid solution. The XRD measurement of the obtained BT nanocube particles revealed that a crystallite size was estimated at 16.5 nm using Scherer's equation using 111 plane. The crystal structure of the particles was assigned to $Pm\bar{3}m$ with *a*-axis of 402.68 pm. TEM observation also indicated that those particles were cubic-shape with sharp edge and corner and sizes of around 17 nm. On the other hand, The ST nanocube particles were prepared at Sr/Ti atomic ratio of 1.5, Ti concentration of 0.04 mol/l and 260°C, and treated using diluted acetic acid solution. The XRD measurement of the obtained ST nanocube particles revealed that a crystallite size was estimated at 17.0 nm using Scherer's equation using 111 plane. The crystal structure of the particles was assigned to $Pm\bar{3}m$ with *a*-axis of 391.94 pm. TEM observation also indicated that those particles were cubic-shape with sharp edge and corner and sizes of around 17 nm.

The screening of the optimum dispersants was performed for excellent dispersion of the BT nanocube particles in hexane at 70°C. The 0.15 mmol of BT nanocube particles were added into hexane of 20 ml under ultrasonic radiation for 3 min, and then, the 3.75 mmol of dispersant was added into the hexane with BT nanocube particles under ultrasonic radiation for 3 min. After 24 h, a dispersion state was judged on the basis of observation of Tyndall effect for all of dispersants. As the results, no Tyndall effect was observed for thiol compounds, phosphate compounds and carboxyl compounds, while only for phosphine oxide compounds such as TOPO and TBPO, Tyndall effect was clearly observed. Therefore, dispersion mechanism using phosphine oxide compounds was discussed.

Typical phosphine oxide had three functional group branches. When the branch of phosphine oxide compounds was changed from normal chain alkyl group to aromatic compound such as phenyl group, no Tyndall effect was observed. Moreover, when the branch of phosphine oxide compounds was changed from butyl group to propyl group, no Tyndall effect was also observed.



Fig. 1. Tyndall effects of BT nanocubes dispersed using (a) TBPO and (b) TOPO in hexane.



Fig. 2. TG curves of (a) TBPO and (b) TOPO.

It should be noted that a length of phenyl group is 466 pm while a length of butyl group is 754 pm. The above results indicated that a length of three functional group branches over 754 pm was the most important factor for dispersion of BT nanocube particles in hexane, which suggested that this dispersion mechanism was originated from a sterific hindrance by three functional group branches. Thus, on the basis of this mechanism, the most suitable dispersant in this study was concluded as TBPO with a molecular weight of 218.32 g/mol. It should be noted that the molecular weight of TBPO is almost half of TOPO. Figure 1 shows the Tyndall effects of BT nanocube particles dispersed using (a) TBPO and (b) TOPO in hexane. From Fig. 1, laser light was much clearly observed for BT nanocube particles slurry with TBPO as compared to that with TOPO. Moreover, a thermogravimetric (TG) analysis of TBPO and TOPO was investigated at a heating rate of 3.0°C/min in air. Figure 2 shows TG curves of (a) TBPO and (b) TOPO. From Fig. 2, TBPO was completely decomposed at almost 200°C, while TOPO was completely decomposed at almost 300°C, which revealed that a thermal decomposition temperature of TBPO was lower by 100°C as compared to that of TOPO. The above results clarified that for dispersion of BT nanocube particles in hexane, TOBO was one of the promising dispersants.

3.2 Preparation of BT/ST accumulations using the selective catalytic reaction

To prepare 3-dementional artificial superlattice accumulations, smart glue must be required for selective binding between BT and ST nanocubes. In this study, the selective catalytic reaction between BP and AM under excess AM¹¹ was chosen as smart



Fig. 3. Schematic scheme of the selective catalytic reaction between BP and AM



Fig. 4. SEM image of the BT/ST accumulations.

glue. Figure 3 shows a schematic scheme of the selective catalytic reaction between BP and AM. Under excess AM, this reaction can proceed to selective polymerization of BP and AM with a formation of HBr and N–C bonding. Thus, if BP-added BT and AM-added ST nanocube particles were mixed under excess AM, it can be expected to form 3-dementional BT/ST artificial superlattice accumulations.

First, the BT or ST nanocube particles were distributed in hexane using TBPO at 70°C, separately. TEM observation revealed that almost monodispersion state was achieved for both nanocube solutions. Then, the BP for TBPO-modified BT nanocubes or the AM for TBPO-modified ST nanocubes was added at 70°C, respectively. The BT and ST nanocube solutions were mixed at room temperature, and held stationary for 24 h. Then, a part of supernatant was dried, and then, annealed in atmosphere at 200°C to remove organic compounds such as TBPO. Finally, a structure of the accumulations was observed using both SEM and TEM.

Figure 4 shows SEM image of the BT/ST accumulations. From SEM observation, most of accumulations were composed of two or three nanocube particles with preferential crystallographic orientation. From TEM observation of each BT and ST nanocube particle, surface of nanocube was assigned to $\{100\}$ planes.¹⁰ Thus, these nanocube accumulations had interface boundary of $\{100\}$. In this study, our objective is a formation of BT/ST accumulations with hetrointerface. To confirm a formation of hetrointerface, TEM observation was performed for



Fig. 5. TEM bright-field image of the accumulations.

the several accumulations. **Figure 5** shows TEM bright-field image of a 2-dimentional regulated arrangement. Since these nanocubes were covered by organic molecules, chemical composition analysis was not applied. Thus, on the basis of different characteristic microstructure between BT (elastically strained structure) and ST (no strained structure) nanocubes,¹⁰) each nanocube in Fig. 5 were assigned to BT and ST. From Fig. 5, it was confirmed that the BT and ST nanocubes were connected on hetrointerface of {100} planes.

Summary

The BT and ST nanocube particles with sizes of around 17 nm were prepared by a solvothermal method. These nanocube particles were monodistributed in hexane with TBPO, separately, and then, the BT/ST accumulations were built up using the selective catalytic reaction between BP and AM under excess AM as smart glue. Finally, TEM observation confirmed that a part of accumulations had a hetrointerface between BT and ST nanocubes.

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