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SYNTHESIS OF (Ba,Pb)TiO_3 SOLID SOLUTION HAVING NO COMPOSITIONAL FLUCTUATION

Kazuyuki KAKEGAWA[+*], Jun-ichi MOHRI[+], Hiroyuki ISHIGURO[+], Koichiro TAKAHASHI[++],
and Shin-ichi SHIRASAKI[++]
[+] Faculty of Engineering, Chiba University; Yayoi-Cho, Chiba-Shi 260
[++]National Institute for Research in Inorganic Materials; Sakura-Mura,
Niihari-Gun, Ibaraki 305

A solid solution of (Ba,Pb)TiO_3 without compositional fluctuation has not been obtained by an ordinary solid-solid reaction of $BaCO_3$, PbO and TiO_2. This was confirmed through the measurements of Δd/d using X-ray diffraction. A new method of preparing (Ba,Pb)TiO_3 without compositional fluctuation was developed.

A number of compounds with perovskite structure exhibit ferroelectricity. They are widely used for various electric devices. Barium titanate, one of the most important ferroelectric materials for applications, has relatively low Curie temperature (120°C). To shift the Curie point to higher temperatures, $PbTiO_3$ is added, yielding (Ba,Pb)TiO_3 solid solutions(BPT). Generally solid solution tends to have a compositional fluctuation. Sometimes the compositional fluctuation is harmful because of causing a diffuse ferroelectric-paraelectric phase transition. In addition, the compositional fluctuation complicates a morphotropic phase boundary[1-2]. A chemical preparation in liquid phase is effective to eliminate the compositional fluctuation. But only a few perovskite compounds can be prepared by a simultaneous precipitation because it is often difficult to find a common condition precipitating all the constitute cations. Most A-site cations are hard to be precipitated by a simple hydroxidation. Moreover, some anion (like Cl^-) in a stable solution of cations (ex. Ti^{4+},Zr^{4+}) makes certain cation (like Pb^{2+}) insoluble. For example, it is impossible to make a mixed solution of $TiCl_4$ and $Pb(CH_3COO)_2$. Consequently there can be a difficulty in making a solution consisting of all the constituent cations. Let us note the following two facts: (A) A solid-solid reaction of PbO (A-site component) and TiO_2 (B-site component) forms $PbTiO_3$ having no compositional fluctuation[3-4]. (B) Pb(Zr,Ti)O_3 prepared by a solid-solid reaction among PbO, TiO_2, and ZrO_2 has a compositional fluctuation[5-6]. Considering these facts, it is interesting to examine the compositional fluctuation of a solid solution prepared by a solid-solid reaction between a coprecipitate of A-site constituents and that of B-site constituents. If a solid solution having no compositional fluctuation be obtained by this method, it will be very useful because we need not coprecipitate all the constituent cations. We have already examined a particular case[1], i.e. a reaction between PbO (A-site component) and a coprecipitate of Zr^{4+} and Ti^{4+} (B-site constituents). Pb(Zr,Ti)O_3 prepared by this method has no compositional fluctuation. This example is a B-site substituted solid solution. Effectiveness of the method of solid-solid reaction between a coprecipitate of A-site constituents and a B-site component has been left unexamined. Consequently, $(A_I,A_{II})BO_3$ having no compositional fluctuation has not been obtained thus far. To get $(Ba,Pb)TiO_3$ having no compositional fluctuation is important not only for a preparation of excellent dielectrics but for investigating an effect of vaporization of Pb on the compositional fluctuation. It was difficult to precipitate Pb^{2+} and Ba^{2+} simultaneously and homogeneously. Actually we tried to precipitate them as an oxalate, but failed in obtaining a homogeneous precipitate[7]. We wish to report on a new method of preparing $(Ba,Pb)TiO_3$ solid solution having no compositional fluctuation.

Table 1 Chemical analysis of the co-precipitates

Sample	Pb/(Pb+Ba) desired	Pb/(Pb+Ba) analysed
A	0.7	0.703
B	0.7	0.696
C	0.7	0.696

$BaCO_3$ (99.999%, Johnson Matthey Chemicals Ltd.), PbO (99%, Junsei Chemical Co. Ltd.) and TiO_2 (99.98%, TP-3, Fuji Titanium Co. Ltd.) were thoroughly mixed in a mortar with a pestle. The mixture was pressed into a powder compact, placed in a alumina crucible and fired at desired temperature. In this procedure the specimen was covered with another smaller alumina crucible and a powder of the same composition as the sample was packed over the latter crucible to supply PbO vapor around the sample.

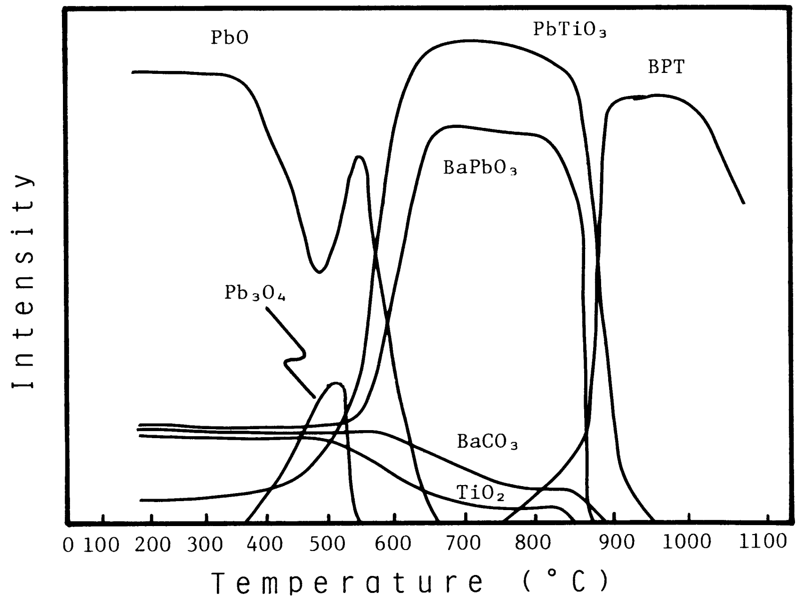

Fig. 1 Reaction processes for BPT prepared by a wet-dry combination technique.
scanning region: 23-25° and 25-35°
heating rate: 5°C/min

A different method was undertaken to get the solid solution. A mixed aqueous solution of $Pb(CH_3COO)_2 \cdot 3H_2O$ (Guaranteed reagent, Wako Pure Chemical Industries. Ltd.) and that of $Ba(CH_3COO)_2 \cdot H_2O$ (Guaranteed reagent, Kanto Chemical Co. Ltd.) were prepared, dropped into a solution of 6M $(NH_4)_2CO_3$ (Guaranteed reagent, Kanto Chemical Co. Ltd.), to get a white precipitate. This was washed and dried at 200°C. The X-ray diffraction pattern showed the dried material to be a single phase of $(Ba,Pb)CO_3$ (aragonite structure). The mole ratio of Pb/Ba for typical 3 specimens was determined by fluorescence X-ray analysis (Rigaku Denki Co. Ltd., Type-3064), and compared with that of the starting powders (Table 1). The resultant values are very close to the desired ones indicating that the foregoing chemical precipitation proceeded quantitatively. The precipitate was fired at 700°C for 1 h and then mixed dry with TiO_2. Experimentally, this firing temperature and period was the most favorable condition. Details on this condition will be reported near future. The resultant mixture was fired at a desired temperature to get a BPT solid solution. This procedure is hereafter called "wet-dry combination technique". A high temperature X-ray diffractometer (JEOL) was used for tracing the formation process of the material (Fig. 1). The characteristic peaks of interest were scanned by oscillating in the ranges of 2θ=25-35° and 23-25° with the radiation of CuKα and a temperature elevation speed of 5°C/min. The starting materials were PbO, $BaCO_3$, $BaPbO_3$ and TiO_2 where PbO and $BaCO_3$ were formed as a result of the decomposition of $(Ba,Pb)CO_3$ at 700°C firing. After PbO transformed into Pb_3O_4 in the vicinity of 380°C, the resultant Pb_3O_4 converted again to PbO in the vicinity of 500°C[8]. Above 550°C, $BaPbO_3$ was formed by the reaction between these PbO and $BaCO_3$, and at the same time $PbTiO_3$ appeared in accordance with disappearance of TiO_2. BPT appeared rapidly at about 900°C, and at the same time $PbTiO_3$, $BaPbO_3$ and TiO_2 disappeared. It is thought that a gradual decrease of the BPT peak intensity with temperature above 1000°C corresponds to an evapolation of PbO in the material, since the reaction was carried out in an open atmosphere. This fact indicates that samples should be fired in a PbO vapor atmosphere to get a stoichiometric material as were actually done in the preparation of BPT.

The system of $BaTiO_3$-$PbTiO_3$ makes a complete solid solution over a whole range, and exhibits a tetragonal crystal system. As reported elsewhere[9], the axis ratio, c/a, of $PbTiO_3$ is largest among the compounds with perovskite structure. With an increase in x of $(Ba_xPb_{1-x})TiO_3$, the c-axis decreased and the a-axis increased, while c/a decreased. The compositional parameter x dependence of c-axis was somewhat larger than that of a-axis. The fluctuation of lattice spacing of a material is generally determined from the slope of the plots of $\beta\cdot\cos\theta$ vs. $\sin\theta$[10], where β is the net X-ray diffraction line broadening originating from the material only. The plots of $\beta\cdot\cos\theta$ vs. $\sin\theta$ for $(Ba_{0.3}Pb_{0.7})TiO_3$ prepared by the solid-solid reaction (1200°C, 1 h) are shown

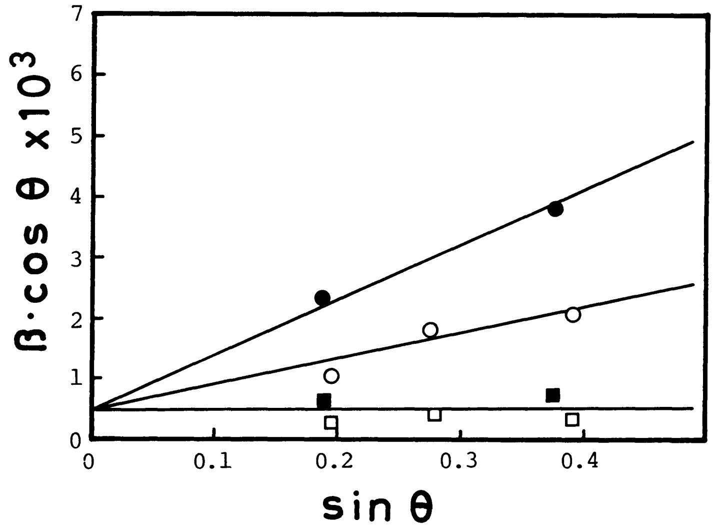

Fig. 2

Plots of $\beta\cdot\cos\theta$ vs $\sin\theta$ for $(Ba_{0.3}Pb_{0.7})TiO_3$

For sample prepared by a solid-solid reaction

○:hk0 diffraction

●:00ℓ diffraction

For sample prepared by a wet-dry combination technique

□:hk0 diffraction

■:00ℓ diffraction

for hk0 and 00ℓ diffraction of the material in Fig. 2. As seen there, both slopes for hk0 and 00ℓ peaks were positive and the slope for the diffraction of the latter was larger than that for the former. These slopes is interpreted in terms of compositional fluctuation of the material. Remarks is necessary that the same type of plots for pure $BaTiO_3$ and $PbTiO_3$ prepared by the ordinary dry method gave zero gradients, from which one can not expect the compositional fluctuation. The plots of $\beta \cdot \cos\theta$ vs. $\sin\theta$ for $(Ba_{0.3}Ti_{0.7})O_3$ prepared by the wet-dry combination technique are also shown in Fig. 2. Both slopes for hk0 and 00ℓ diffractions are zero, indicating that the material has no compositional fluctuation. The lack of the compositional fluctuation in this material may be originated from their homogeneous distribution in the mixed solution of Pb^{2+} and Ba^{2+}. As mentioned before, the result of high temperature diffraction suggests the formation of $BaPbO_3$ and $PbTiO_3$ as intermediate products. It is noted that such a coexistence of $PbTiO_3$ and $BaTiO_3$ can eventually go to homogenization of Pb^{2+} and Ba^{2+}; this implies that the two by-products were homogeneously-mixed considerably. It is concluded that the method of obtaining A-site substituted solid solution by a solid-solid reaction between a coprecipitate of A-site constituents and a B-site component is successful. The ferroelectric material prepared by this method may be very useful in their applications. It would provides a preliminary step to get $(A_I,A_{II})(B_I,B_{II})O_3$ type perovskite compound without compositional fluctuation by a similar method.

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