Preparation of Homogeneous $Pb(Zr_xTi_{1-x})O_3$ by Rapid-Quenching Technique and Its Compositional Fluctuation

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Abstract

The effect of the Rapid-quenching technique on the elimination of the compositional fluctuation was investigated for the solid solution of a $PbZrO_3$-$PbTiO_3$ system (PZT). A mixture of ZrO_2 and TiO_2 was rapidly quenched. The rapidly quenched materials were mixed with PbO and heated. PZT was formed without intermediate compounds. By using the Williamson-Hall method, it is found that PZT prepared by using the Rapid-quenching technique had almost no compositional fluctuation.

Key words: PZT, rapid-quenching technique, homogeneous solid solution, compositional fluctuation

1. Introduction

Solid solutions tend to have compositional fluctuation. It affects many electrical properties [1-4], and also causes incorrect interpretations of measured values [3, 4]. In order to know the intrinsic electrical properties and transformation behavior, it is essential to obtain solid solutions having no compositional fluctuation. We have developed a method to estimate the width of the compositional fluctuation [5-9]. Specifically, compositional fluctuations of solid solutions of $PbTiO_3$-$PbZrO_3$ system (PZT) prepared by solid-state reaction [8], wet-dry combination method [10], freeze dry method [11], spray decomposition method [12], alcoxide method [13], and chelate method [14] were investigated.

Generally, wet methods are effective to obtain homogeneous solid solutions, (*i.e.* solid solutions having no or very small compositional fluctuations). Wet methods consist of a preparation of a feed solution, which contains all the constituent cations, and the simultaneous precipitation of compounds of the constituent cations. There are many systems in which wet methods are difficult to use. For example, fabrication of a solid solution of $PbTiO_3$-$PbZrO_3$ system (PZT) has both problems. Preparation of a mixed solution of Pb^{2+}, Zr^{4+} and Ti^{4+} needs a complex process. Stable forms of water soluble compounds of zirconium and titanium are $ZrOCl_2 \cdot 8H_2O$ and $TiCl_4$. Pb^{2+} precipitates, when Cl^- coexists. So zirconium oxychloride and titanium chloride should be converted into nitrides. Simultaneous precipitation of all the constituent cations is also difficult in this system. Strict pH control is required to precipitate Pb^{2+}, Zr^{4+} and Ti^{4+}. McNamara *et al.* [15] used a controlled bubbling of CO_2 and NH_3 gases for the simultaneous precipitation of the cations.

Melting oxides of constituent cations of the solid solutions is considered to be a homogeneous distribution of ions. If it is cooled, oxides of different cations precipitate separately, causing an inhomogeneous distribution of oxides. Rapid quenching of the melt may maintain in liquid phase. This method may be applied to systems, in which the wet method can hardly be applied.

In the Wet-dry combination method, the wet method should be applied to only a part of the constituent cations for the preparation of solid solutions having no compositional fluctuation [10]. In a PZT system, the wet method is to be applied to the precipitation of Zr^{4+} and Ti^{4+}. Pb^{2+} is not required to be precipitated.

In this paper, the effect of rapid quenching on compositional fluctuations was evaluated for the PZT system, in which the behavior of compositional fluctuation has well been studied and compared with the dry method.

2. Experimental Procedures

2.1 Rapid-quenching technique

The process called the *Rapid-quenching method* is shown in Figure 1(A). In order to confirm the effect of rapid quenching, a process without rapid quenching was performed. The sintered rod was ground without rapid quenching. It was mixed with equimolar PbO and sintered in the same manner as the case of rapid quenching process, called the *Dry method* as shown in Figure 1(B).

A mixture of powders of ZrO_2 and TiO_2 was pressed into a rod-shaped powder compact and sintered at 1000^oC for 1 h. One end of the sintered rod was put into a flame of arc discharge [16]. The melt at the end of the rod dropped into a gap of rotating aluminum rollers, forming a film of rapid quenched material. The film was ground and mixed with equimolar PbO using an agate mortar and pestle. Then the mixed powder was pressed into a disk, 12 mm in diameter and about 1.5 mm in thickness under pressure of 75 MPa and then sintered at 1100^oC for 1h.

2.2 Measuring compositional distribution

Kakegawa *et al.* have developed a method to determine the compositional fluctuation [9]. The observed width of an X-ray diffraction peak consists of resolving power of the equipment and the net width, , of the sample itself. After the resolving power was removed from the observed value, plots of cos versus sin were performed (Williamson-Hall method). Plots of diffraction peaks for equivalent planes are theoretically on the same line. The slope of those plots gives a value of fluctuation of lattice spacing, and the section at sin =0 crystallite size. The equivalent diffraction peaks are those from the lattice planes, which have the same fluctuation in spacing by the compositional fluctuation. In tetragonal perovskite-type solid solution, the dependence of the lengths of the a-axis and c-axis on the composition is different. For the determination, only *hk*0 diffractions were used. Compositional fluctuation leads to a fluctuation of the length of a-spacing. Lattice spacings of (*hk*0) planes are fixed only by the a-axis. So, the slope of plots of *hk*0 diffractions corresponds to *a*/*a*. From the measurement of *a*/*a*, *a* is converted to x, using a relation between the lattice constant (a) and composition.

3. Results and Discussion

3.1 Comparison of formation process of PZT

For comparison, the formation process without rapid quenching, *Dry method*, was examined.

From the XRD patterns of materials from the product of Fig. 1(B), at 600^{o}C, lead titanate (PT) peaks as an intermediate compound appeared, which is common for the formation process of PZT. At 800^{o}C, the ultimate compound, PZT began to form. Above 900^{o}C, the peak of lead zirconate (PZ) disappeared and single phase of PZT was obtained, and the peaks of TiO_2 (rutile) and $PbTiO_4$ phases were weak or overlapped with other peaks. Figure 2 shows that the variation of peak heights of PbO(Yellow) (111), PbO(Red) (101), $PbTiO_3$ (110) and PZT (101) were plotted with the firing temperatures in the *Dry method*. However, their change was almost parallel with that of PbO and the change in the amount of raw materials was traced by plotting the heights of PbO peaks. Fig. 2 also shows the change of phase compositions during the PZT formation process. Around 500^{o}C, the intensity of PbO(Red) slightly increased and that of PbO(Yellow) decreased. This is due to a partial transformation of PbO(Yellow) into PbO(Red) phase. Then $PbTiO_3$ was formed as an intermediate compound. It began to decrease above 700^{o}C and the ultimate compound, PZT, was formed. Above 900^{o}C, single phase PZT was obtained.

From the XRD patterns of materials processed with the *Rapid-quenching method*, there was no lead titanate (PT) peak detected during the sintering temperatures. This is very different from the *Dry method*. PZT peaks appeared above 800^{o}C, and confirmed PZT at 900^{o}C. Figure 3 shows the change of phase compositions during the PZT formation process with the *Rapid-quenching method*. The first appearance of the PZT was at 800^{o}C, which is identical to the dry method. It is noteworthy that PZT forms directly by the *Rapid-quenching method* without any intermediate compounds. This may be attributed to a homogeneous distribution of Zr^{4+} and Ti^{4+} from the starting materials and/or rapidly quenching the materials.

3.2 Evaluation of compositional fluctuation

The width of the compositional fluctuation of PZT prepared with the *Dry method* and the *Rapid-quenching method* was evaluated by the reported method. The results were plotted in Figure 4 as a function of sintering temperature. When processed with the dry method(○), the width of the compositional fluctuation was very large (*x*=0.2). The width decreased gradually as the firing temperature increased. Thus, it has a large compositional fluctuation, even fired up to 1200^{o}C, near the melting point.

The width of the compositional fluctuation for PZT, prepared with the *Rapid-quenching method* as shown in Fig. 4 (●), is much smaller than that processed by the *Dry method*. The PZT processed with the *Rapid-quenching method* fired at 900^{o}C has a small compositional fluctuation (*x*=0.02). Even fired above 950^{o}C, the compositional fluctuation width was almost zero. The previous study [17, 18] showed that homogenization could be accomplished by two methods: by mixing in the starting materials or diffusion during firing. By mechanically mixing in the starting materials, it is impossible to obtain the finished product below the size of aggregation. The homogenization during firing is effective for a smaller size in raw materials. Generally, products processed by the *Dry method* (mechanical mixing + firing) have a gap in size, which neither mechanical mixing nor diffusion is effective and leads to the compositional fluctuation. It is revealed that mixing at a smaller size than a few microns is important for the starting materials in order to obtain compositionally homogeneous solid solutions. The mixture of ZrO_2 and TiO_2 processed with rapid quenching is assumed well mixed to a smaller micron size.

3.3 Detail examination of compositional fluctuation

Figure 5 is a simplified phase diagram of the PZT system. At room temperature there is a phase boundary between tetragonal and rhombohedral at x=0.535 in $Pb(Zr_xTi_{1-x})O_3$. This phase boundary is called the Morphotropic Phase Boundary, or "MPB". The PZT is formed at high temperatures, and there is no discontinuous point in the composition. The inhomogeneity of the sample may be like a Gaussian distribution indicated as a relation between *f* (the distribution function) and the composition shown in the upper position of Fig. 5. In this case, the sample can be regarded to have a compositional distribution width shown as a line with arrows ( ). When the sample with such compositional fluctuation is cooled below the reaction temperature, the two phases form in tetragonal and rhombohedral [19, 20].

The sample near the MPB will exhibit a mixture of tetragonal phase and rhombohedral phase, even having a small compositional fluctuation. Thus, the XRD patterns near the MPB were examined both for the *Dry method* and the *Rapid-quenching method*. Figure 6-1 shows the XRD pattern of $Pb(Zr_{0.53}Ti_{0.47})O_3$, processed with the *Dry method* (A) and the *Rapid-quenching method* (B). This composition belongs to the tetragonal region. Thus, if the sample has no compositional fluctuation, it would exhibit a single phase of the tetragonal pattern. If the sample has a compositional fluctuation, rhombohedral phase peaks will appear in addition to the tetragonal phase peaks. If a sample has a large compositional fluctuation, the intensity of rhombohedral phase peaks will be comparable with that of tetragonal phase peaks. Generally, tetragonal phase peaks and rhombohedral phase peaks are very close each other, sometimes overlapping. It is distinguishable by looking at peaks around 100 to 200 diffractions. In Fig. 6-1, the arbitrary peaks marked by ( ) are rhombohedral, and ( ) are tetragonal. From the sample processed with the *Dry method* (A), considerable intensity of rhombohedral phase peaks was observed. This means that the PZT processed by the *Dry method* exhibits a significant compositional fluctuation. For the sample processed with the *Rapid-quenching method* (B), weak intensity of rhombohedral phase peaks was observed. This means that the *Rapid-quenching method* experienced less compositional fluctuation, which had not been detected by the measurement using values.

Figure 6-2 shows XRD patterns of $Pb(Zr_{0.54}Ti_{0.48})O_3$, processed with the *Dry method* (A) and the *Rapid-quenching method* (B). This composition belongs to the rhombohedral region. Thus, if the sample experienced no compositional fluctuation, it would exhibit a rhombohedral single-phase pattern. If the sample experienced a compositional fluctuation, the tetragonal phase would coexist in addition to the rhombohedral phase. If the sample has a large compositional fluctuation, the intensity of tetragonal phase peaks will be comparable with the rhombohedral phase peaks. From that processed by the *Dry method* (A), considerable intensity of tetragonal peaks was observed. This means that the PZT processed with the *Dry method* has significant compositional fluctuation. Conversely, from that processed with the *Rapid-quenching method* (B), weak intensity of tetragonal peaks was observed. This means that the PZT processed with the *Rapid-quenching method* has less compositional fluctuation, which had not been detected by the measurement using values [21].

It was confirmed that the *Rapid-quenching method* is effective for a preparation of homogeneous solid solutions. This method can be extended and applied to other systems in which the wet methods are difficult to employ.

4. Summary

(1) In $Pb(Zr_{0.3}Ti_{0.7})O_3$ processed with the *Rapid-quenching method*, the width of the compositional fluctuation was almost zero in upper 950°C and the PZT was much more homogeneous than that was processed with the *Dry method*.
(2) Observation of coexisting behavior for the PZT prepared with the *Rapid-quenching method* revealed a very little compositional fluctuation and the degree of the compositional fluctuation was much smaller than that by the *Dry method*.
(3) The *Rapid-quenching method* can be extended and applied to solid solutions in which the wet methods are difficult to be employed.

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Figure captions

Figure 1. Process of a preparation of PZT

(A) Process of *Rapid-quenching method*

(B) Process of *Dry method*

Figure 2. Change in phases of materials by *Dry method* with sintering temperature

■: PbO(Red) □: PbO(Yellow) ●: $PbTiO_3$ ○:PZT

Figure 3. Change in phases of materials by *Rapid-quenching method* with sintering temperature

■: PbO(Red) □: PbO(Yellow) ○:PZT

Figure 4. Change in the compositional fluctuation with sintering temperature

●: *Rapid-quenching method* ○: *Dry method*

Figure 5. Phase diagram of PZT system and compositional fluctuation in a sample near the morphotropic phase boundary

Figure 6-1 and 2. XRD patterns of $Pb(Zr_{0.53}Ti_{0.47})O_3$ and $Pb(Zr_{0.54}Ti_{0.46})O_3$

(A) by *Dry method* (B) By *Rapid-quenching method*

: rhombohedral

: tetragonal