JOURNAL OF MATERIALS SCIENCE **36** (2001) 1039–1042

Determination of compositional fluctuation region in solid solution of lanthanum-modified lead zirconate titanate

Y. ABE
Graduate School of Science and Technology, Chiba University, Yayoi-cho Inage-ku Chiba-shi 263-8522, Japan

S. TANEDA, K. KAKEGAWA, Y. SASAKI
Faculty of Engineering, Chiba University, Yayoi-cho Inage-ku Chiba-shi 263-8522, Japan

A method was developed to determine a compositional fluctuation region in $Pb_{1-y}La_y(Zr_xTi_{1-x})_{1-(y/4)}O_3$ (PLZT) solid solution in the tetragonal region. The compositional fluctuation in PLZT extends two-dimensionally on the phase diagram. The method described in this paper utilized the fact that the compositional fluctuation region extends to the composition lines whose lattice spacing corresponds to the higher or lower fluctuation limit. The fluctuation limits of the lattice spacings were estimated from X-ray diffraction analysis. This method revealed that the compositional fluctuation in PLZT is difficult to be eliminated by using a conventional dry method (mixed oxide method). The shape of the region indicated that homogenization of Zr^{4+} and Ti^{4+} was more difficult as compared with that of Pb^{2+} and La^{3+}.

1. Introduction

Perovskite-type (ABO_3) solid solution of lanthanum-modified lead zirconate titanate, $Pb_{1-y}La_y(Zr_xTi_{1-x})_{1-(y/4)}O_3$ (PLZT), has attracted great attention of many researchers because of its interesting and excellent properties [1, 2]. The phase diagram for PLZT was studied in details by G. H. Haertling [1]. The addition of lanthanum to the lead zirconate-lead titanate solid solution system lowers Curie temperature and brings about the diffuse phase transition. Electromechanical coupling coefficient shows a maximum when the composition approach the phase boundary between the rhombohedral ferroelectric phase and the tetragonal ferroelectric phase. Three types of electrooptic birefringence characteristics (e.g., linear, memory, and quadratic electrooptic behaviors) are observed in the corresponding compositional regions.

Solid solutions tend to have a compositional inhomogeneity (compositional fluctuation) [3–5]. In the case of the solid solution having two compositional parameters, the compositional fluctuation is represented as a two-dimensional region on the phase diagram. The size and shape of the region depend on the conditions of synthesis such as particle size, mixing level of raw-powders, firing temperature and period, and so on. If the solid solution has a large dependence of property on the composition, the property depends both on the compositional fluctuation region. Though it is essential to establish methods to determine the compositional fluctuation region in solid solutions, such method for PLZT system has not been studied well.

We have studied methods for the determination of the compositional fluctuation region in the ternary perovskite-type solid solutions of $Pb(Zr_xTi_{1-x})_{1-y}(Mg_{1/3}Ta_{2/3})_yO_3$ [6], $Pb(Zr_xTi_{1-x})_{1-y}(Mg_{1/3}Nb_{2/3})_yO_3$ [7], $Pb(Zr_xTi_{1-x})_{1-y}(Mg_{1/2}W_{1/2})_yO_3$ [8], and $Pb(Zr_xTi_{1-x})_{1-y}(Co_{1/3}Nb_{2/3})_yO_3$ [9]. The methods revealed that these solid solutions have a compositional fluctuation when they were fabricated using a conventional dry method (mixed-oxide method). The methods also clarified that the compositional fluctuation affected the temperature dependence of dielectric constant [10].

In PLZT, many properties significantly depend on the composition as mentioned above. To obtain the excellent properties of PLZT, the compositional fluctuation is one of the most important factors. In this paper, we present a method to determine the compositional fluctuation region in PLZT and discussions of characteristics of its compositional fluctuation estimated by the method.

2. Experimental procedure

2.1. Sample preparation

Samples were prepared by the conventional dry method. Reagent-grade powders of PbO, La_2O_3, ZrO_2, and TiO_2 were carefully blended in appropriate proportions and mixed thoroughly with an agate mortar and pestle. The mixture was pressed into powder compacts. The powder compacts were sintered in a double closed magnesia crucible [7] with a pellet of equimolar

mixture of PbO and ZrO_2 as a source of PbO vapor. For a measurement of the lattice constants the powder compacts were calcined at 1200° C for 2 h and sintered at 1200° C for 2 h. In this paper, the sintered sample is abbreviated as PLZT- (x, y), where x and y indicate the intended composition in $Pb_{1-y}La_y(Zr_xTi_{1-x})_{1-(y/4)}O_3$.

2.2. X-ray diffraction analysis

The powder X-ray diffraction data for the fired samples were obtained with Ni filtered Cu K_α radiation. In order to determine the lattice constants of tetragonal PLZT, the 002 and 200 diffraction lines were chosen and pure Si powder (99.99%) was used as an internal standard to calibrate the systematic errors in the peak position.

The fluctuation of lattice spacings were determined for the widths of the 00l, hk0, h0h, hhh, and 311 diffraction peaks. These peak profiles were fitted to the following equation using the least-squares analysis:

$$I(2\theta) = \frac{A}{\{1 + B(2\theta - C)^2\}} + \frac{0.5A}{\{1 + B(2\theta - C - \delta)^2\}}$$

where $I(2\theta)$ is the intensity at an angle 2θ, δ is the line splitting by the doublet of Cu K_{α_1} and K_{α_2}, and A, B and C are constants. By means of this fit, widths at half maximum intensity (WHI) for an X-ray of single wavelength of K_{α_1} were obtained. From this method WHIs of Si were determined. The WHI of Si can be seen as a width establishing the resolving power of the apparatus. These values were plotted against 2θ in order to obtain the resolution width at any angle. The resolution width at the diffraction angle of the sample was subtracted from the WHI of the sample, resulting in a value β [11], which is the net width of the sample.

3. Method

In general, lattice constants of solid solutions vary with composition. The equal lattice spacing line on a ternary diagram for any lattice planes can be estimated from the relation between the composition and the lattice constants. Many tetragonal solid solutions that contain PZT have the equal lattice spacing lines whose shapes differ from lattice plane to lattice plane. This is due to the different dependencies of the length of a- and c-axes on the composition. So, the fluctuation of each lattice plane is differently affected by the compositional fluctuation.

The fluctuation of the lattice spacings can be determined from the value of β. The plots of $\beta \cos\theta$ vs. $\sin\theta$ (where θ is the Bragg angle) for diffractions from a certain plane and its higher order diffractions must theoretically be fitted on a straight line [12]. The slope of this line corresponds to the fluctuation of the lattice spacing, $\Delta d/d$. The higher limit of fluctuation of the lattice spacing can be assumed to be $d_0 + (\Delta d/2)$ and the lower $d_0 - (\Delta d/2)$, where d_0 is the average lattice spacing. The compositions whose lattice spacing corresponds to the higher fluctuation limit or lower one are on a curve on the phase diagram.

The compositional fluctuation obeys the normal distribution curve generally. So the shape of the compositional fluctuation region can be assumed to be an ellipse. The ellipse area should extend to the lines of composition that have higher or lower limit of the lattice spacing. When the lines for several planes whose equal lattice spacing lines have various shapes are drawn, the ellipse region that touches all of these lines will be limited. The compositional fluctuation region can be regarded as this ellipse region.

4. Application of the method

The relation between the lattice constants and composition for tetragonal $Pb_{1-y}La_y(Zr_xTi_{1-x})_{1-(y/4)}O_3$ is shown in Fig. 1. From this relation, equal lattice spacing lines were obtained on the diagram (Figs 2–6). It is obvious that the shape of these lines differ from lattice plane to lattice plane. Thus, the compositional fluctuation region can be determined from the measurement of β of these lattice planes.

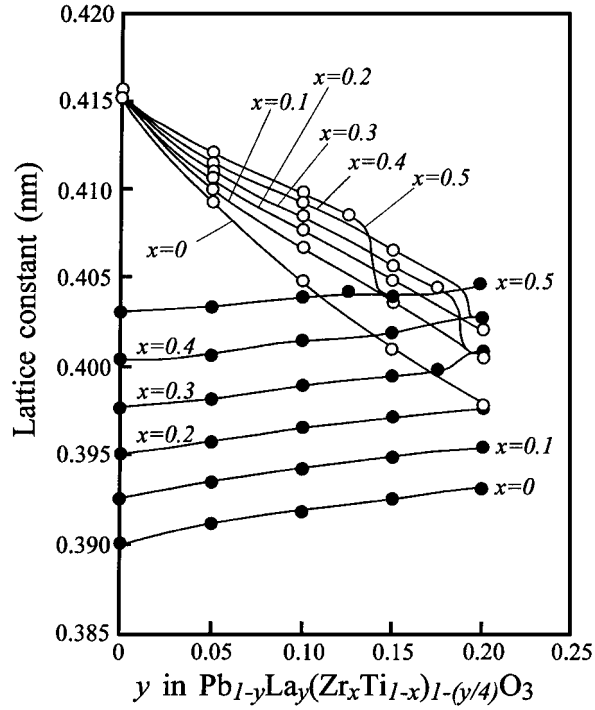

Figure 1 Relation between lattice constants and composition for $Pb_{1-y}La_y(Zr_xTi_{1-x})_{1-(y/4)}O_3$. (●):a-axis, (○):c-axis.

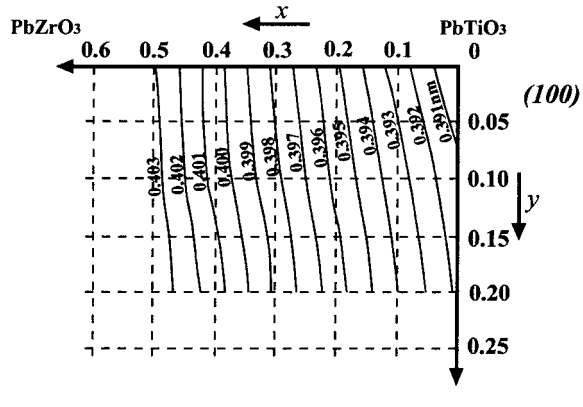

Figure 2 Equal lattice spacing lines for (100) plane of PLZT.

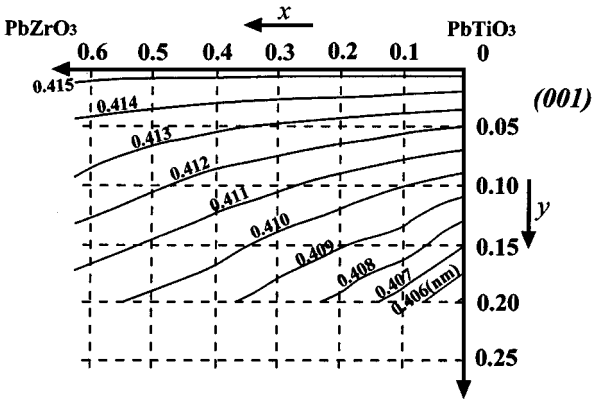

Figure 3 Equal lattice spacing lines for (001) plane of PLZT.

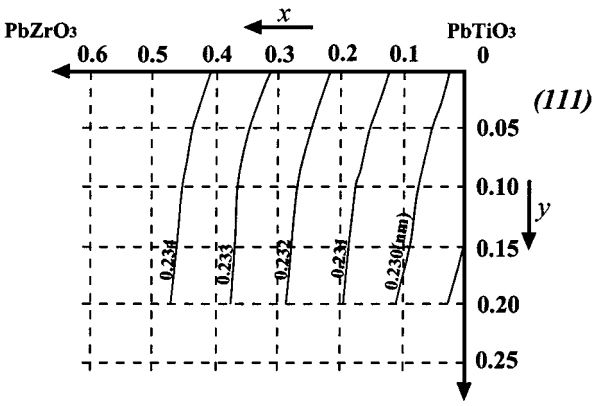

Figure 4 Equal lattice spacing lines for (111) plane of PLZT.

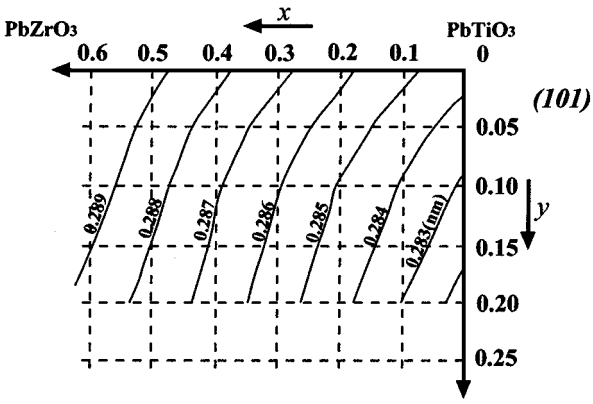

Figure 5 Equal lattice spacing lines for (101) plane of PLZT.

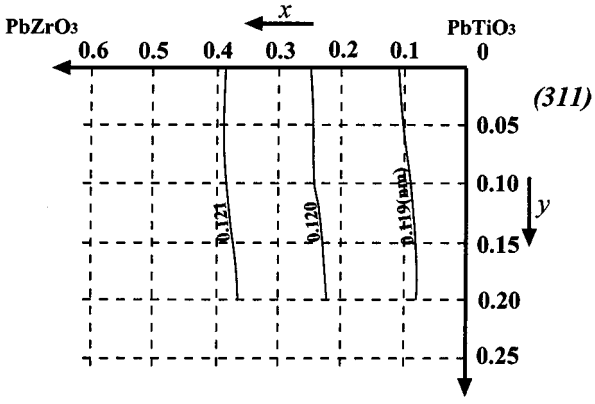

Figure 6 Equal lattice spacing lines for (311) plane of PLZT.

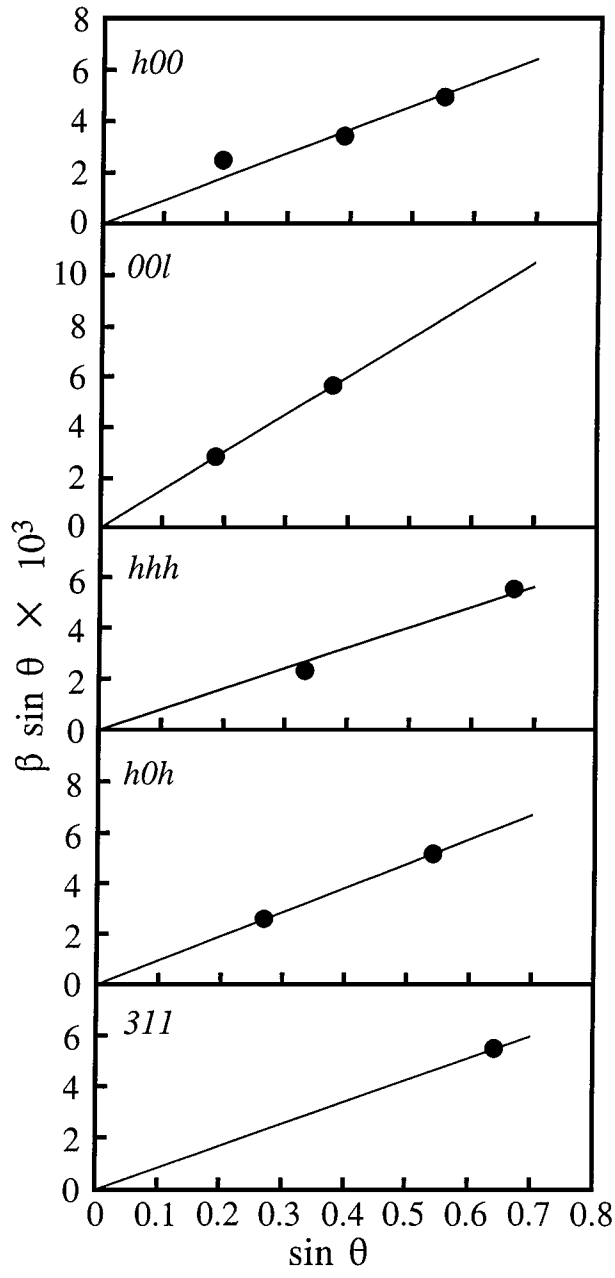

Figure 7 Plots of $\beta \cos\theta$ vs. $\sin\theta$ for PLZT-(0.2, 0.05) prepared by the dry method with the conditions of calcining at 1200° C for 2 h and sintering at 1200 °C for 2 h.

Fig. 7 shows the plots of $\beta \cos\theta$ vs. $\sin\theta$ for the $h00$, $00l$, hhh, $h0h$, and 311 diffraction peaks of PLZT-(0.2,0.05) prepared by the dry method with conditions of calcining at 1200° C for 2 h and sintering at 1200° C for 2 h. The plots of $h00$, $00l$, hhh, and $h0h$ diffractions were fitted on straight lines, so that the slopes were estimated. The intercepts of the lines at $\sin\theta = 0$ for all the diffractions must be theoretically the same, which depends on the crystallite size of the sample. The plots of ($3n$ n n) diffraction peaks ($n \geqq 2$) could not be obtained because of difficulty of the measurement. Thus the plot of (311) planes was linearly connected with the intercept mentioned above, and then the slope was estimated. Fig. 8 shows the lines of compositions corresponding to the fluctuation limits of lattice spacings and the compositional fluctuation region ellipse estimated from these curves. It was obvious from Fig. 8 that the compositional fluctuation region was considerably

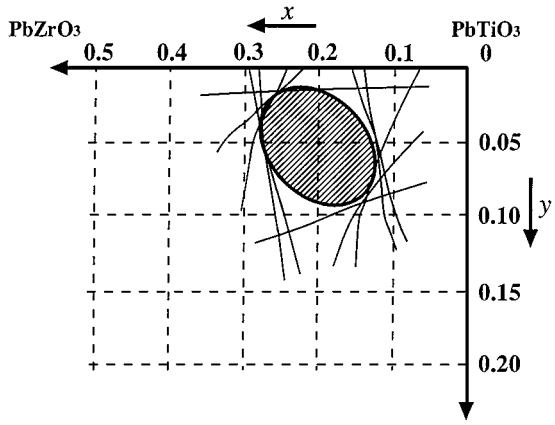

Figure 8 Compositional lines corresponding to higher and lower fluctuation limits of lattice spacings and compositional fluctuation region estimated for PLZT-(0.2, 0.05) prepared by the dry method with the conditions of calcining at 1200° C for 2 h and sintering at 1200°C for 2 h.

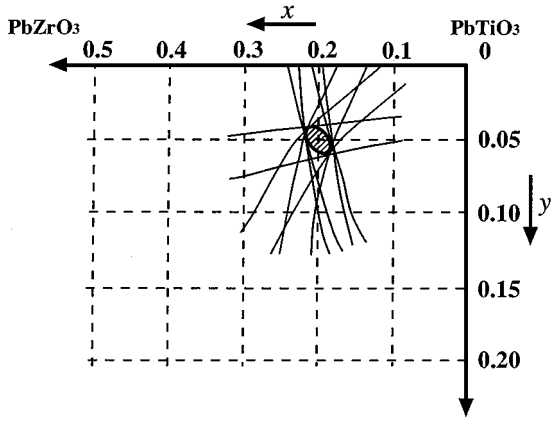

Figure 9 Compositional lines corresponding to higher and lower fluctuation limits of lattice spacings and compositional fluctuation region estimated for PLZT-(0.2, 0.05) prepared by the dry method with the conditions of calcining at 1000° C for 1 h and sintering at 1300°C for 40 h.

large. The widths of the ellipse region were 16% in the direction of x and 8% in the direction of y. This means that homogenization of Zr^{4+} and Ti^{4+} in B-site was more difficult than that of Pb^{2+} and La^{3+} in A-site.

To obtain transparent PLZT ceramics, the sintering is often performed with conditions of a high temperature and a long period. We attempted to determine the compositional fluctuation in PLZT prepared by such conditions. Fig. 9 shows the compositional fluctuation region in PLZT-(0.2,0.05) prepared by the conventional dry method with the conditions of calcining at 1000° C for 1 h and sintering at 1300° C for 40 h. The compositional fluctuation region was smaller as compared with that shown in Fig. 8. However, the compositional fluctuation could not be eliminated. It can be said that the compositionally homogeneous PLZT is difficult to be prepared by the conventional dry method.

In the case of PLZT, many properties (e.g., dielectric constant, electromechanical coupling coefficient, electrooptic birefringence and hysteresis loop) have large dependence on the composition [1, 2]. This means that these properties must be affected greatly by the compositional fluctuation. To obtain the excellent properties from PLZT, or to study the structure and the properties of PLZT, it is necessary to prepare the sintered body having no compositional fluctuation.

5. Conclusions

In this study, we developed the method for the determination of the compositional fluctuation region in $Pb_{1-y}La_y(Zr_xTi_{1-x})_{1-(y/4)}O_3$ by using X-ray diffraction analysis. The shape of the equal lattice spacing lines for tetragonal PLZT on the phase diagram differed from lattice plane to lattice plane. The compositional fluctuation region could be determined by measurements of higher and lower fluctuation limits of several lattice spacings. This method revealed that PLZT prepared by the conventional dry method had the compositional fluctuation in both A-site cations and B-site cations. The shape of the compositional fluctuation indicated that homogenization of B-site cations was more difficult than that of A-site cations. Elimination of the compositional fluctuation was difficult even if the sample was sintered with conditions of a high temperature and a long period.

References

1. G. H. HAERTLING and C. E. LAND, *J. Amer. Ceram. Soc.* **54** (1971) 1.
2. G. H. HAERTLING, *ibid.* **54** (1971) 303.
3. K. KAKEGAWA, J. MOHRI, S. SHIRASAKI and K. TAKAHASHI, *ibid.* **65** (1982) 515.
4. K. KAKEGAWA, K. WATANABE, J. MOHRI, H. YAMAMURA and S. SHIRASAKI, *J. Chem. Soc. Jpn.* (1975) 413.
5. K. KAKEGAWA, J. MOHRI, T. TAKAHASHI, H. YAMAMURA and S. SHIRASAKI, *Solid State Commun.* **24** (1977) 769.
6. K. KAKEGAWA, M. KAWAKAMI and Y. SASAKI, *J. Amer. Ceram. Soc.* **71** (1988) C-444.
7. K. KAKEGAWA, K. MAKIGAKI and Y. SASAKI, *J. Ceram. Soc. Jpn.* **96** (1988) 681.
8. Y. ABE, K. KAKEGAWA and Y. SASAKI, *Solid State Commun.* **72** (1989) 1071.
9. Y. ABE, I. TANAKA, K. KAKEGAWA and Y. SASAKI, *J. Euro. Ceram. Soc.* **18** (1998) 1609.
10. Y. ABE, K. KAKEGAWA and Y. SASAKI, *J. Chem. Soc. Jpn.* (1992) 361.
11. H. P. KIUG and L. ALEXANDER, in "X-ray Diffraction Procedures" (Wiley, New York, 1954) p. 500.
12. G. K. WILLIAMSON and W. H. HALL, *Acta Metall.* **1** (1953) 22.

Received 5 January
and accepted 22 July 1999