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Observations and Analyses on the Thermal Stability of $(1 - x)$Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$−xPbTiO$_3$ Thin Films

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Relaxor ferroelectric $(1 - x)$Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$−xPbTiO$_3$ ($(1 - x)$PZN-xPT) thin films with $x = 0.1−0.6$ were prepared on (001)-oriented single-crystal LaAlO$_3$ (LAO) substrates using a poly(ethylene glycol) (PEG)-modified sol−gel method. The films of the different compositions were annealed at different temperatures with varied duration. The evolution of the crystalline structure of the films with different heating conditions was analyzed using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and micro-Raman spectra. Our experimental results showed that the thermal stability of the $(1 - x)$PZN-xPT perovskite phase degraded with reducing the PT amount and increasing annealing temperature and duration. A bond valence method for analyzing perovskite structural stability was developed with corrected bond lengths at the high annealing temperature. The observed thermal stability of the perovskite phase in the $(1 - x)$PZN-xPT system could be well explained accordingly.

1. Introduction

Perovskite relaxor ferroelectric lead zinc niobate−lead titanate ($(1 - x)$PZN-xPT) solid solution has attracted strong interest for device applications because of its extraordinary electromechanical properties. Its perovskite single crystal with a composition near the morphotropic phase boundary (MPB; $x \sim 0.1$) exhibits a very high dielectric permittivity ($\epsilon_r > 3000$), high electromechanical coupling coefficient ($k_{33} > 90\%$), and high piezoelectric coefficient ($d_{33} > 1500$ pC/N) along the [001] direction.[1−6] A $(1 - x)$PZN-xPT thin film with the MPB composition is promising for microelectronic or micro-electromechanical device applications, such as capacitors, ferroelectric random access memories, and electromechanical transducers. Its superior piezoelectric properties may even make it potentially replace the currently dominant piezoelectric lead zirconate titanate (PZT) films. However, synthesizing single phase perovskite $(1 - x)$PZN-xPT thin films has been extremely difficult because of the preferential formation of the pyrochlore phase.[7−10]

Recently, with a poly(ethylene glycol) (PEG) modified sol−gel method, we have made significant progress in synthesizing perovskite $(1 - x)$PZN-xPT thin films with $x = 0.1−0.7$ on LaAlO$_3$ (LAO) single-crystal substrates.[11] With PEG added in the sol precursor, the formation of the perovskite phase was promoted and the pyrochlore phase was suppressed dramatically. In this paper, the dependences of the thermal stability of the perovskite phase in the $(1 - x)$PZN-xPT thin films on the PT amount, annealing temperature, and duration were experimentally examined. Because $(1 - x)$PZN-xPT has the most unstable perosvkite phase among all the reported ferroelectric materials with the general ABO$_3$ formulas, it is interesting to investigate its thermal stability theoretically. Here we proposed for the first time that the theoretical analysis on the phase stability should take into account the difference in the parameter factors between processing temperature and room temperature. On the basis of this general point, a bond valence theory was developed with corrected bond length at the high annealing temperatures, and the experimental results on the structure stability of the perovskite phase $(1 - x)$PZN-xPT at various temperatures was quantitatively discussed.

2. Experimental Section

The preparation of the $(1 - x)$PZN-xPT thin films followed our previous work.[11] PEG with a molecular weight of 200 (PEG200) was used to modify the sol precursor. The amount of PEG was 60% based on the weight of the metal oxides in the precursor. The $(1 - x)$PZN-xPT thin films with $x = 0.1−0.6$ were deposited on the (001)-oriented single-crystal LaAlO$_3$ (LAO) substrates. The thickness of the films was 0.25 μm. The films were preannealed at 580 °C for 10 min, followed by a final annealing at a higher temperature. X-ray diffraction (XRD; Bruker GADDS, D8-ADVANCED) was carried out to determine the structures of all the films annealed at different temperatures. The morphology of the samples was examined using field emission scanning electron

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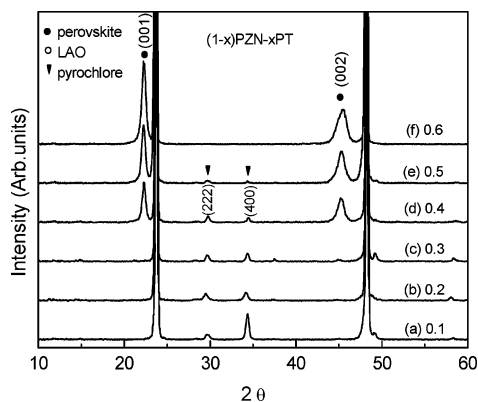(10) Yu, S.; Yao, K.; Tay, F. E. H. *Chem. Mater.* **2004**, *16*, 346.
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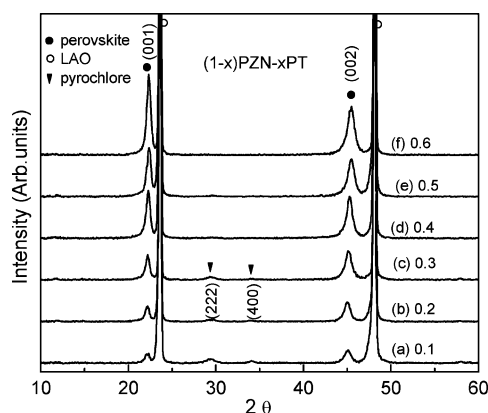
Figure 1. XRD patterns of $(1 - x)$PZN-xPT films on LAO substrates with $x = 0.1-0.6$. Films were preannealed at 580 °C for 10 min.
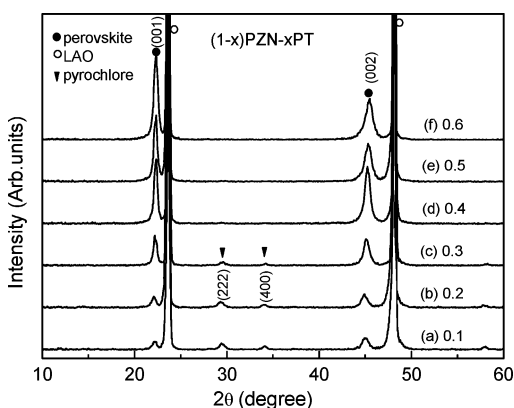
Figure 2. XRD patterns of $(1 - x)$PZN-xPT films on LAO substrates with $x = 0.1-0.6$. Films were annealed at 700 °C for 30 min.

Figure 3. XRD patterns of $(1 - x)$PZN-xPT films on LAO substrates with $x = 0.1-0.6$. Films annealed at 800 °C for 30 min.

microscopy (FESEM, JSM-6700F). Micro-Raman spectra were obtained at room temperature using a Raman spectrometer (Spex T64000, Jobin Yvon, France) with the 514.5 nm line of an argon laser.

3. Results

3.1. Crystalline Structure of the $(1 - x)$PZN-xPT Films. Figures 1–3 present the XRD patterns of the $(1 - x)$PZN-xPT films annealed at 580 °C, 700 °C, and 800 °C, respectively.

As shown in Figure 1, for the films annealed at 580 °C, $(1 - x)$PZN-xPT films with $x \geq 0.4$ exhibit only perovskite phase, with no pyrochlore phase being detected. All the films are (001)-oriented. The pyrochlore phase appears in the films

with $x < 0.4$ and increases with reduced PT amount. The intensity of the XRD peaks of the perovskite phase increases with PT amount. Although the pyrochlore phase is not detectable in the films with $x \geq 0.4$, the intensity of the peaks of the perovskite phase in 0.6PZN-0.4PT and 0.5PZN-0.5PT is substantially lower than that in the 0.4PZN-0.6PT film. The decreased intensity of the XRD peaks of perovskite phase with reduced PT amount may indicate small grains and/or poor crystallinity. The results clearly indicate that the stability of the perovskite phase increases with PT amount in the $(1 - x)$PZN-xPT films.

For the films annealed at 700 °C (Figure 2), the pyrochlore phase in 0.9PZN-0.1PT, 0.8PZN-0.2PT, and 0.7PZN-0.3PT films does not transform into the perovskite phase but slightly increases, while the content of the perovskite phase decreases in the 0.9PZN-0.1PT and 0.8PZN-0.2PT films. This indicates that formation of the pyrochlore phase is more favored at this temperature for those compositions. The perovskite phase in the $(1 - x)$PZN-xPT films with $x \geq 0.4$ is still stable at this temperature. Therefore, with the decrease of the PT content in the $(1 - x)$PZN-xPT, the perovskite phase becomes unstable and tends to transform into the pyrochlore phase at a higher temperature.

For the films annealed at 800 °C for 30 min as shown in Figure 3, all of the perovskite phase in the $(1 - x)$PZN-xPT films with $x = 0.1$, 0.2, and 0.3 transforms into the pyrochlore phase. The pyrochlore phase even appears in the films with $x = 0.4$ and 0.5. The film with $x = 0.6$ still shows a single perovskite phase. The results imply that when PT content is adequately low, the perovskite phase formed at a lower temperature can completely transform into pyrochlore phase at a higher temperature.

The above results show that although perovskite phase forms in the $(1 - x)$PZN-xPT thin films with $x \leq 0.3$ with the aid of PEG, the perovskite phase is thermally unstable compared with the pyrochlore phase. This finding is consistent with the previous report on the PZN bulk single crystal.[12] PZN single crystals can be prepared in the perovskite form by the flux method. However, on reheating the crystal, the perosvkite structure converts to pyrochlore structure at ~600 °C, indicating that the perovskite structure in PZN is in the metastable condition. As our thin films are deposited on the perovskite LAO substrate, the transformation from pyrochlore to perovskite phase may only take place at a higher temperature than 600 °C.

Our experimental results also show that a long time annealing duration is not favorable for the existence of the perovskite phase in the $(1 - x)$PZN-xPT films. For example, when the annealing time was increased to 1 h, the pyrochlore phase appeared in the 0.6PZN-0.4PT film and the percentage of the pyrochlore phase in the films with $x < 0.4$ increased. The results indicate that a transformation from the perovskite phase to pyrochlore phase happens with an extended annealing duration.

3.2. Raman Spectra. The Raman spectra of the samples annealed at 700 °C for 30 min are shown in Figure 4. The

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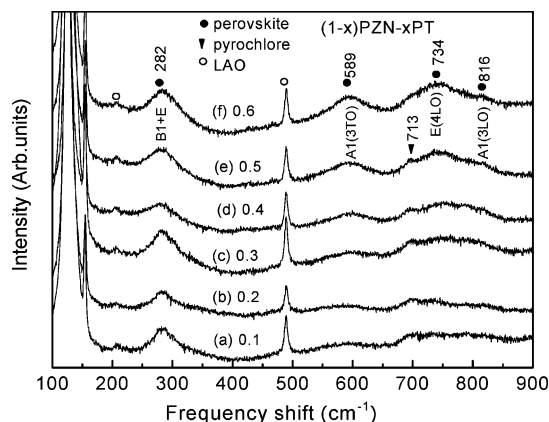
Figure 4. Room-temperature Raman spectra of $(1 − x)$PZN-xPT thin films on LAO substrate. Films were annealed at 700 °C for 30 min.

peaks at about 282, 589, 734, and 816 cm^{-1} are assigned to the perovskite phase, corresponding to the B1 + E(3TO + 2LO), A1(3TO), E(4LO), and A1(3LO) modes, respectively.[13–15] The peak at 713 cm^{-1} is attributed to pyrochlore phase, and it is detectable when $x = 0.5$. According to the XRD results as shown in Figure 2, the pyrochlore phase is not detected in the films with $x = 0.4$ and 0.5. It implies that Raman is more sensitive than XRD in detecting the pyrochlore phase because a Raman spectrum does not require correlation lengths as large as those for XRD.[13]

3.3. SEM Morphology. Figure 5 presents the FESEM images of the surfaces of the $(1 − x)$PZN-xPT films with $x = 0.1-0.6$ annealed at 700 °C for 30 min. The grain size is a few tens of nanometers, and there are some larger second phase grains on the film surface. However, the amount of the larger grains decreases with the increase of PT amount. Only a few can be found when x reaches 0.4, and none are found in the 0.4PZN-0.6PT film. The larger and long-shaped grains are the pyrochlore phase according to the XRD results (Figure 2). The perovskite grains in the 0.4PZN-0.6PT films are large (100 nm) and uniform, which is consistent with the high XRD intensity result (Figure 2f).

4. Discussion on the Thermal Stability with Bond Valence Theory

Although the pyrochlore phase is a metastable phase and transforms into the perovskite phase in many perovskite ABO$_3$ materials such as PZT, it does not in the PZN-PT system with low PT content, as observed in this study. The intensity of the pyrochlore phase in the $(1 − x)$PZN-xPT films with low content of PT has increased with increasing annealing temperature. No any evidence has shown that the pyrochlore phase transforms into perovskite phase once it has formed. The result indicates that the pyrochore phase is thermally more stable than the perovskite phase in the $(1 − x)$PZN-xPT films with low PT amount. It is well-known that PZN ceramics or films cannot be synthesized under atmospheric pressure with the columbite method[16] or the sol−gel[17] method. Pure PZN can be synthesized only under high

pressure[18] or as a single crystal in an excess PbO flux.[19] Under atmospheric pressure, PZN can be stabilized by addition of some perovskite-type compounds to form solid state solution.

Furukawa et al. and Halliyal et al.[20−22] believed that the stable ABO$_3$ perovskite compounds should have a tolerance factor $t ≈ 1$ (0.88−1.09) and a high electronegativity difference between cations and anions ($X_{M−O}$). The values of t and $X_{M−O}$ for PZN are 0.985 and 1.80, respectively, which indicates that the perovskite structure should be favorable for PZN compounds, but it is actually not. It is found that there are many perovskite compounds with smaller tolerance factors and lower electronegativity difference than PZN can form perovskite structure with conventional methods.[21] This indicates that neither t nor $X_{M−O}$ is able to explain the stability of the perovskite structure effectively.

Another concept to estimate the stability of a crystal structure is bond valence theory.[23,24] The bond valence of a cation or anion in a crystal is determined by its coordination number and bond length between cations and anions. In bond valence theory, the valence v_{ij} of a bond between two atoms i and j is defined so that the sum of all the valences from a given atom i with valence V_i obeys

$$V_i = \sum_j v_{ij} \tag{1}$$

The most commonly adopted empirical expression for the variation of the length d_{ij} of a bond with valence is

$$v_{ij} = \exp[(R_{ij} − d_{ij})/b] \tag{2}$$

where R_{ij} is the bond valence parameter, d_{ij} is the length of a bond between two atoms i and j, and b is commonly taken to be a "universal" constant equal to 0.37 Å.[23]

Wakiya et al.[25] estimated the stability of various perovskite-type compounds with bond valence. They found that the absolute value of the bond valence sum of oxygen, $|V_O|$ of PZN, is the smallest in the reported Pb-contained perovskite-type compounds, which corresponds to the fact that it is most difficult to synthesize PZN under atmospheric pressure. However, these calculations are based on the lattice parameters of materials at room temperature and cannot explain the thermal stability of $(1 − x)$PZN-xPT with low PT content at various temperatures.

As described below, here we calculated the $|V_O|$ of the $(1 − x)$PZN-xPT system under various temperatures.

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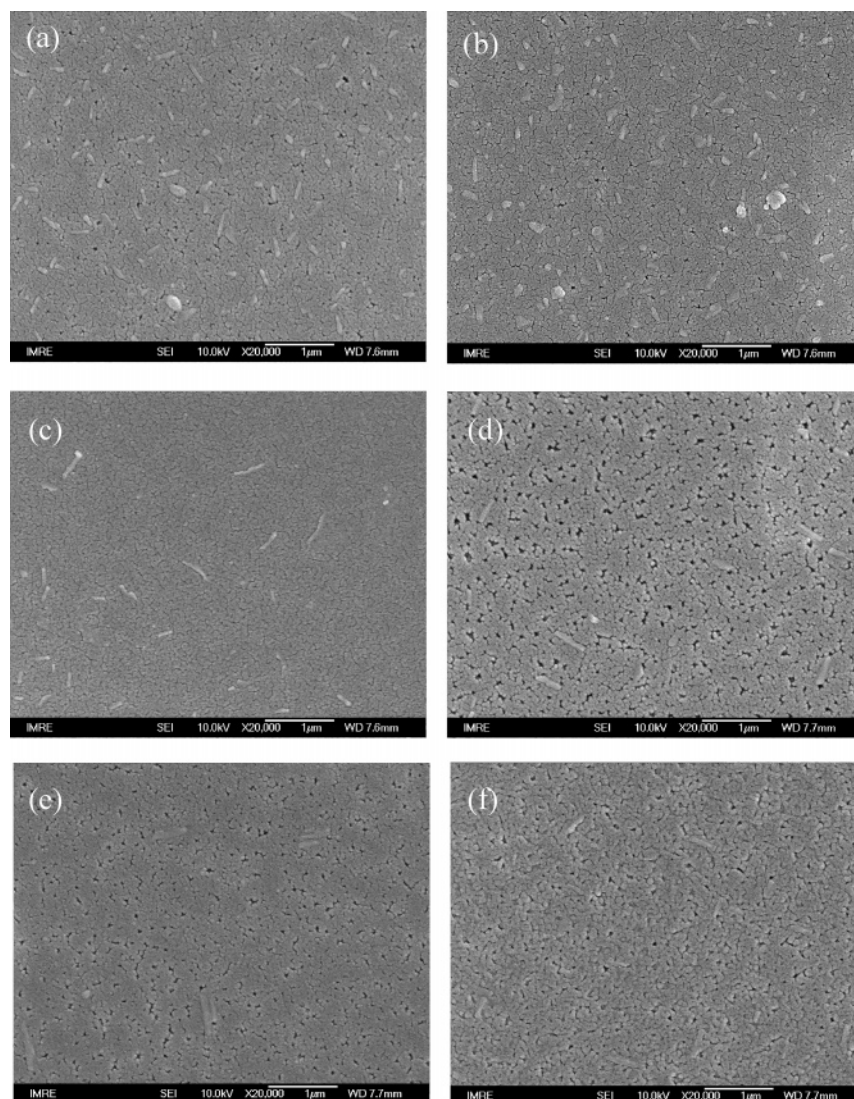
Figure 5. FESEM images of the $(1 - x)$PZN-xPT films on LAO substrates with $x =$ (a) 0.1; (b) 0.2; (c) 0.3; (d) 0.4; (e) 0.5; and (f) 0.6. Films were annealed at 700 °C for 30 min.

Bond valence sums of A, B, and O sites, V_A, V_B, and $|V_O|$, respectively, are calculated for PZN, PT, and $(1 - x)$PZN-xPT compounds with $x = 0.1-0.6$. $|V_O|$ of Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN), which has difficulty forming perovskite phase but can be synthesized with the columbite method,[26] is calculated for comparison. To calculate bond valence sums, interatomic distances between cations and anions are needed. The values are estimated from lattice parameters as follows:

$$d(A-O) = a/\sqrt{2} \qquad (3)$$

$$d(B-O) = a/2 \qquad (4)$$

where $d(A-O)$ and $d(B-O)$ are the distances between A and O and between B and O atoms, respectively, and a is the lattice parameter. If the symmetry of a perovskite-type compound is not cubic, the cube root of the cell volume per formula is used. For calculation of the bond valence at room temperature, lattice parameter data reported in powder diffraction data in JCPDS-ICDD were used.

For the bond valence of the materials at the annealing temperatures of 580 °C, 700 °C, and 800 °C, respectively, the lattice parameters are calculated with the equation

$$a_2 = \alpha a_1(T_2 - T_1) + a_1 \qquad (5)$$

where α is the coefficient of thermal expansion. Because abnormal change in the lattice structure takes place around the Curie temperature (T_c),[27,28] α derived above T_c (140 °C and 490 °C for PZN and PT, respectively) is adopted in this calculation. Reports of both PZN and PT show that the lattice parameter increases linearly with temperature above T_c.[27,28] In eq 5, a_1 is the lattice parameter at temperature T_1 which is above T_c.

The lattice parameters of $(1 - x)$PZN-xPT at a certain temperature T can be obtained from

$$a = (1 - x)a_T(\text{PZN}) + xa_T(\text{PT}) \qquad (6)$$

In the ABO$_3$ perovskite structure, the coordination numbers of A and B sites are 12 and 6, respectively. As a result,

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$$V_A = v_{A-O} \times 12 \qquad (7)$$

$$V_B = v_{B-O} \times 6 \qquad (8)$$

and there are three oxygens in one unit cell, therefore,

$$|V_O| = (V_A + V_B)/3 \qquad (9)$$

We believe that the bond valences calculated with the method described above can be used to evaluate the stability of PZN-PT in single crystal, ceramics, and thin films.

The calculated bond valences of PT, PMN, and PZN at room temperature are 1.902, 1.787, and 1.752, respectively. Table 1 lists the calculated $|V_O|$ values of the $(1 − x)$PZN-xPT system at various temperatures from room temperature to 800 °C. The percentages of perovskite phase relative to pyrochlore in the thin films derived in this study after annealing at different temperatures are also provided. The relative amounts of pyrochlore and perovskite phases in the thin films are determined by comparing the intensity of the (001) peak for perovskite and (222) for pyrochlore. The percentage of perovskite phase is calculated using the following equation:

$$\% \text{ perovskite} = I_{\text{perovskite(001)}}/(I_{\text{perovskite(001)}} + I_{\text{pyrochlore(222)}}) \qquad (10)$$

As shown in Table 1, $|V_O|$ increases with PT amount but decreases with increasing temperature. At room temperature, only $|V_O|$ of 0.9PZN-0.1PT and 0.8PZN-0.2PT is less than that of PMN (1.787), corresponding to the experimental results that the pyrochlore phase is difficult to remove for the two compositions. The calculated values can also explain the reported data on PZN-PT bulk ceramic synthesis,[24] in which at least 20 mol % of PT is needed to stabilize PZN.

At high annealing temperatures, the crystal lattice dilates as a result of thermal expansion, leading to the decrease of $|V_O|$, as indicated in the table. At the temperatures of both 580 °C and 700 °C, the $|V_O|$ values of $(1 − x)$PZN-xPT with $x = 0.1-0.3$ are less than that of PMN (1.787), consistent with the XRD results that the pyrochlore phase is detected in these films. When the temperature reaches 800 °C, $|V_O|$ decreases further. The value of $|V_O|$ of 0.6PZN-0.4PT becomes smaller than 1.787, and $|V_O|$ of 0.5PZN-0.5PT is close to 1.787, which is consistent with the experimental results that the pyrochlore phase appears in the two samples after annealing at 800 °C. When x reaches 0.6, no significant transformation from the perovskite to the pyrochlore phase is observed, as a result of the large $|V_O|$ of 1.801 even at 800 °C.

The discussion above indicates that the analysis on bond valence values corresponding to high annealing temperature

Table 1. Calculated Bond Valence Values ($|V_O|$) and Percentages of Perovskite Phase for $(1 − x)$PZN-xPT

	RT[a]	580 °C		700 °C		800 °C	
material	$|V_O|$	$|V_O|$	%Pe[b]	$|V_O|$	%Pe	$|V_O|$	%Pe
0.9PZN-0.1PT	1.766	1.756	66.5	1.752	55.8	1.749	0.3
0.8PZN-0.2PT	1.781	1.769	86.3	1.764	65.0	1.759	0.7
0.7PZN-0.3PT	1.796	1.782	88.9	1.775	88.2	1.770	2.9
0.6PZN-0.4PT	1.810	1.795	96.8	1.787	98.0	1.780	85.8
0.5PZN-0.5PT	1.825	1.808	96.4	1.798	98.3	1.791	94.8
0.4PZN-0.6PT	1.840	1.821	99.5	1.810	99.8	1.801	99.8

a RT: room temperature. *b* %Pe: percentage of perovskite phase.

can well explain the thermal stability of the perovskite phase in $(1 − x)$PZN-xPT. Because materials are generally much more active for chemical reactions or phase transitions at the high annealing temperatures than at room temperature, the analysis on thermodynamic phase stability should be based on the parameters at the annealing temperature rather than room temperature. Therefore, the bond valence analysis method with the corrected bond lengths at the high annealing temperature as proposed in this paper is more reasonable to analyze the stability of the ABO$_3$ perovskite phase. We believe this point is also generally applicable to theoretical analysis on phase stability on the basis of geometric factor, chemical valence, and so forth, in which the difference in the parameters between processing temperatures and room temperature is suggested to be taken into account.

5. Conclusions

The dependence of the structural stability of the perovskite phase in $(1 − x)$PZN-xPT ($x = 0.1-0.6$) thin films on compositions and annealing conditions were investigated. Our experimental results showed that the thermal stability of the $(1 − x)$PZN-xPT perovskite phase degraded with reducing the PT amount, and the pyrochlore phase could not be completely eliminated when the PT amount was below 30 mol % in our present preparation process. When the PT amount was low, it was observed that the perovskite phase formed at a lower temperature was transformed into pyrochlore phase at an elevated temperature. An extended annealing duration also favored the transformation from perovskite to pyrochlore. A bond valence method was developed with corrected bond lengths at the high annealing temperature that could well explain the observed thermal structural stability of the perovskite phase in the $(1 − x)$-PZN-xPT system. We believe the proposed theoretical strategy here is also generally applicable to many other phase stability analyses on the basis of geometric factor, chemical valence, and so forth, in which the difference in the parameters between processing temperature and room temperature are suggested to be taken into account.