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Phase transition behaviors of (1–x)Pb($Yb_{1/2}Nb_{1/2}$) O_3–xBa($Yb_{1/2}Nb_{1/2}$)O_3 ceramics

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Abstract

The phase transition behaviors of (1–x)Pb($Yb_{1/2}Nb_{1/2}$)O_{3-x}Ba($Yb_{1/2}Nb_{1/2}$)O_3 (PBYN) solid solution system ($0 \leqslant x \leqslant 0.30$) have been investigated by X-ray diffraction, permittivity and E–P hysteresis loop measurements. In the solid solution, for $x \leqslant 0.10$, the transition shows a normal first-order paraelectric (PE)–antiferroelectric (AFE) behavior and its AFE crystal structure is orthorhombic. The transition temperature gradually decreases with the increasing Ba^{2+} concentration. On the composition range $0.16 \leqslant x \leqslant 0.30$, a typical relaxor behavior is displayed. The low temperature crystal structure is pseudocubic in this composition range. © 2001 Published by Elsevier Science Ltd.

Keywords: Dielectric properties; Ferroelectric properties; Perovskite; Relaxor; X-ray method

1. Introduction

The B-site ordered lead based complex perovskites, Pb(B′B″)O_3, and especially several modifications of these perovskites in the form of solid solutions have been studied extensively because of their variety of physical properties and wide range of industrial applications.[1] Several A-site substituted solid solution systems have been studied for the same reason. The so-called relaxor behavior having the broad dielectric maximum and frequency dispersion has been observed in these oxide.[2] In La substituted $PbZr_{1-x}Ti_xO_3$,[3] vacancy appears in A-sites due to charge imbalance and the vacancy was reported to be responsible for the relaxor behavior. Ba-substituted $PbMg_{1/3}Nb_{2/3}O_3$ and $PbZr_{1-x}Ti_xO_3$ also display relaxor behavior due in part to the Pb and Ba compositional fluctuatuation.[4,5]

The aforementioned relaxors are either ferroelectrics or ferroelectric solid solutions. In the present work, we will investigate the dielectric behaviors of the Ba-substituted antiferroelectric Pb($Yb_{1/2}Nb_{1/2}$)O_3 solid solution, $Pb_{1-x}Ba_x$($Yb_{1/2}Nb_{1/2}$)O_3 (PBYN), as a function of Ba concentration x. On this sold solution, a Ba^{+2} ion replaces a smaller Pb^{+2} ion on substitution. The ionic size difference as well as the polarizability difference will apparently alter the PYN phase transition behavior on Ba substitution. We will pay particular attention to how the intrinsic antiferroeletricity of PYN changes as a function of Ba concentration through X-ray diffraction, dielectric constant and E–P hysteresis loop measurements.

2. Experimental

Ceramic samples with the chemical formula of $Pb_{1-x}Ba_x$($Yb_{1/2}Nb_{1/2}$)O_3 (PBYN) ($0 \leqslant x \leqslant 0.30$) were prepared by reacting the stoichiometric proportions of high purity (99.9%) PbO, Yb_2O_3, Nb_2O_5 and $BaCO_3$ powders. The mixtures were ball-milled in acetone, dried and then calcined at 950°C. The calcined powders were reground, pressed and sintered at 1000–1280°C for 1 h in an MgO crucible.

X-ray diffraction experiments were carried out on a two-circle Rigaku Rotaflex X-ray diffractometer (D/max-RB). The specimens for dielectric investigations were electroded with silver paste (Dupont No. 7075) by firing at 590°C for 5 min. The dielectric constant was

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measured at several frequencies between 1 kHz and 1 MHz using a Hewlett Packard 4194A impedance/gain phase analyzer on heating at a constant rate of 3°/min. Temperature was measured by a platinum resistance thermometer using a HP3478A multimeter. The hysteresis loops were measured on a Sawyer–Tower hysteresis analyzer at a frequency of 60 Hz.

3. Results and discussion

PYN is an antiferroelectric perovskite which has basically a B-site ordered complex perovskite structure. At 302°, it undergoes a paraelectric-to-antiferroelectric phase transition. Its space group symmetry of high temperature phase is Fm3m, and that of low-symmetry phase is Pbmn.[6]

The X-ray diffraction patterns of the solid solution at room temperature at different Ba compositions are shown in Fig. 1. The low temperature phase PYN has two kinds of superstructure: Pb ion antiparallel modulation displacement and B-site ordering. Its orthorhombic structure changes with Ba substitution. With increasing Ba substitution, the intensity of modulation superlattice lines in the AFE phase becomes gradually weaker, and then disappears altogether for $x \geqslant 0.15$. This disappearance means that the AFE phase gives way. However, the B-site ordering is maintained beyond $x = 0.15$ because Ba substitution seems to have no effect on the Yb and Nb B-site arrangement. In the mean time, the initially split fundamental lines merge into single lines for $x \geqslant 0.15$. This line merging indicates that the room temperature phase of PBYN becomes pseudocubic for the composition range.

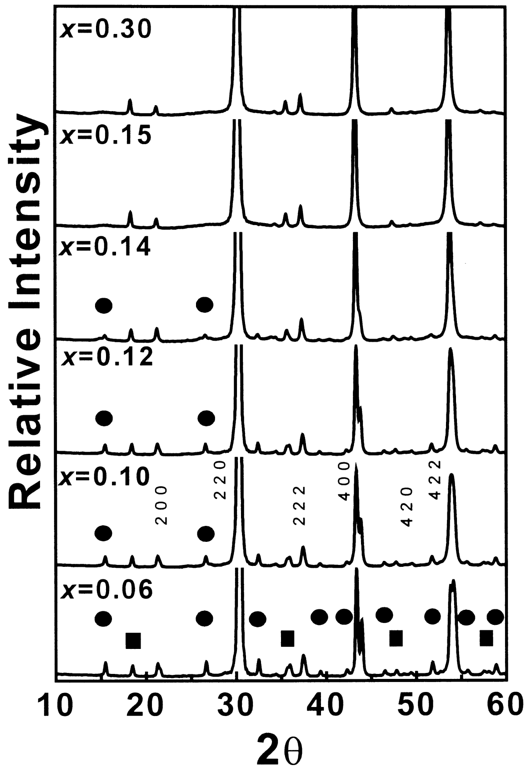

Fig. 1. X-ray powder diffraction patterns of the PBYN ($0 \leqslant x \leqslant 0.30$) at room temperature: ●, superstructure reflection due to the antiparallel cation displacement; ■, F-reflection due to the B-site ordering.

Fig. 2 shows the temperature dependence of the dielectric constant in PBYN ($0 \leqslant x \leqslant 0.30$). In the PYN rich region ($x \leqslant 0.10$), the phase transition behaves similarly to that of PYN, while the transition temperature, T_m, having the maximum of the dielectric constant gradually decreases. With increasing Ba concentration, the diffuse phase transition (DPT) behavior having the broad maximum and frequency dispersion becomes more self-evident. This DPT behavior is closely connected with the relaxor behavior as exhibited by other solid solutions[4,5,7] as shown in Fig. 3. The relaxor behavior becomes pronounced in the concentration range $x \geqslant 0.14$.

The E–P hysteresis loop was measured at temperatures lower than the phase transition for PBYN. As $x \leqslant 0.10$, the E–P curves is a linear line [Fig. 4(a)]. Here PBYN is AFE up to this composition. As $x = 0.12$, it exhibits a very small polarization [Fig. 4(b)], and eventually it establishes a quite square hysteresis loop at $x = 0.14$ [Fig. 4(c)]. This observed evolutionary change from the antiferroelectric (AFE) to the ferroelectric (FE) induced by Ba substitution of Pb has been quite unexpected since the electronic polarizability of Pb is larger than that of Ba. One reason which could explain this change may be coined to the ionic size difference between Ba^{2+} and Pb^{2+}. On Ba substitution, the antiparallel modulated displacement of Pb is broken due to the effect of size difference between Ba^{2+} and Pb^{2+} ion as we can see in the disappearance of the modulation

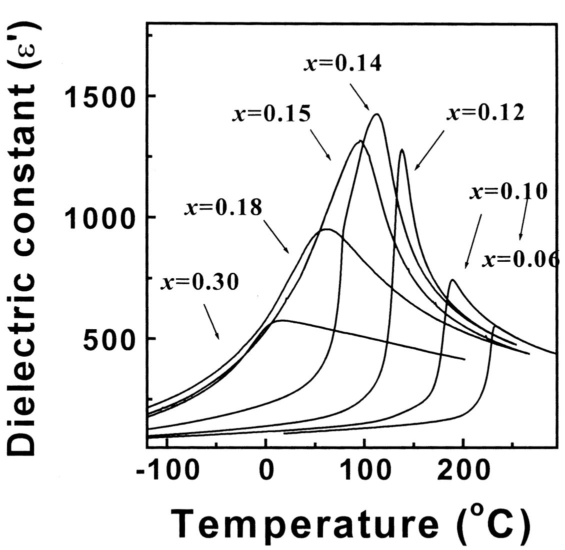

Fig. 2. Temperature dependence of the dielectric constant at 1 kHz on heating conditions for PBYN ($0 \leqslant x \leqslant 0.30$).

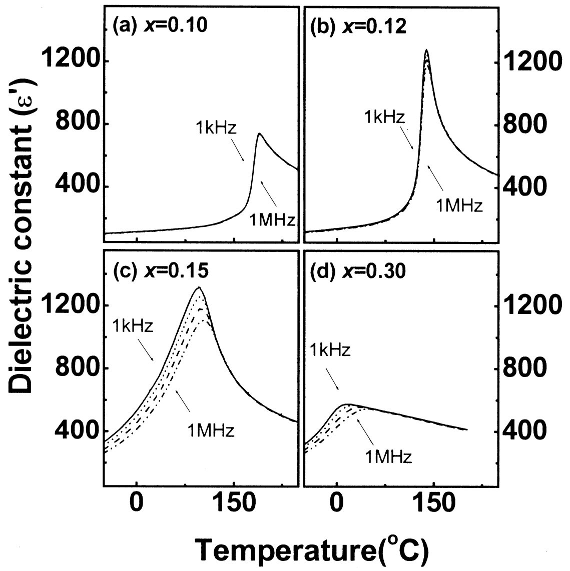

Fig. 3. Temperature dependence of the dielectric constant at various frequencies (1 kHz, 10 kHz, 100 kHz and 1 MHz) in heating for the PBYN: (a) $x=0.10$; (b) $x=0.12$; (c) $x=0.15$; (d) $x=0.30$.

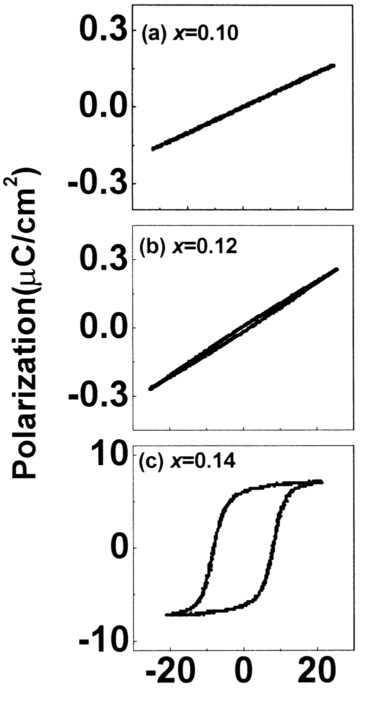

Fig. 4. E–P hysteresis loops at the various compositions of PBYN: (a) $x=0.10$; (b) $x=0.12$; (c) $x=0.14$.

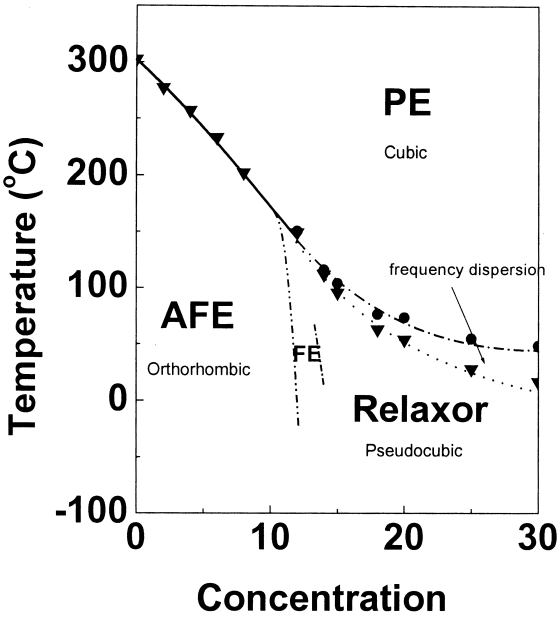

Fig. 5. Phase diagram for PBYN determined from the dielectric measurements. The 1 kHz data points are marked by filled triangles and 1 MHz data points are marked by filled circles.

lines in Fig. 1 for $x \geqslant 0.14$. The emergence of FE phase coincides with the Pb modulation disappearance. The FE phase tends to consolidate on farther Ba substitution.

Fig. 5 is the phase diagram of the $Pb_{1-x}Ba_x(Yb_{1/2}Nb_{1/2})O_3$ solution we have obtained from the experimental results. As the Ba concentration increases, the low temperature phase changes from the AFE to relaxor phase with an intervening FE phase. The extent of the relaxor transition temperature difference is also indicated.

4. Conclusion

The dielectric properties and crystal structures of $Pb_{1-x}Ba_x(Yb_{1/2}Nb_{1/2})O_3$ ($0 \leqslant x \leqslant 0.30$) solid solution have been investigated. With increasing Ba concentration, the crystal structure is changed from the orthorhombic to the pseudocubic. The AFE phase disappears for $x \geqslant 0.15$. The sharp normal phase transition behavior in the PYN rich region changes the DPT having the broad dielectric maximum and frequency dependent. Finally, the phase diagram of $Pb_{1-x}Ba_x(Yb_{1/2}Nb_{1/2})O_3$ has been determined.

Acknowledgements

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