Journal of the European Ceramic Society 21 (2001) 1669–1672
www.elsevier.com/locate/jeurceramsoc

X-ray and dielectric studies of $Pb(Mg_{1/2}W_{1/2})O_3$ substituted $Pb(Yb_{1/2}Nb_{1/2})O_3$ ceramics

J.-H. Kim [a,*], K.S. Koh [b], H.-S. Han [c], W.K. Choo [a]

[a]Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology,
373-1 Gusong-Dong, Yusong-Gu, Taejon, South Korea
[b]Department of Chemistry, Chungang University, 221 Heuksuk-Dong, Tongjak-Gu, Seoul, South Korea
[c]FED Team, Cooperate R&D Center, Samsung SDI Co., Ltd., 575 Shin-Dong, Paldal-Gu, Suwon, Kyungki-Do, South Korea

Received 4 September 2000; accepted 5 November 2000

Abstract

The crystal structure and dielectric properties of the antiferroelectric solid solution of (1–x)$Pb(Yb_{1/2}Nb_{1/2})O_3$–x$Pb(Mg_{1/2}W_{1/2})O_3$ ($PYN_{1-x}PMW_x$) ($0 \leqslant x \leqslant 0.30$) have been studied. The crystal structure is shown to become pseudocubic from the PYN's orthothombic structure with increasing x. In the PYN-rich composition range ($0 \leqslant x < 0.28$), the paraelectric (PE)–antiferroelectric (AFE) phase transition occurs sharply and is independent of the applied frequency. However, in the higher PMW concentration ($x = 0.30$), the dielectric constant vs. temperature curve becomes gradually broader and the solid solution becomes relaxor. © 2001 Published by Elsevier Science Ltd.

Keywords: Calcination; Dielectric properties; Perovskite; X-ray methods

1. Introduction

Lead based complex perovskites, $Pb(B'_{1/2}B''_{1/2})O_3$, have different phase transition behaviors dependent on the degree of the B-site cation ordering.[1] In the highly ordered compounds such as $Pb(Co_{1/2}W_{1/2})O_3$ and $Pb(Mg_{1/2}W_{1/2})O_3$, a sharp phase transition takes place at a well-defined temperature. When the B-site ions are disordered such as in disordered $Pb(Sc_{1/2}Ta_{1/2})O_3$,[2] and $Pb(Sc_{1/2}Nb_{1/2})O_3$,[3] a diffuse phase transition (DPT) behavior characterized by the frequency dependence of the transition temperature and a broadly distributed transition temperature in the measured dielectric constant curve are observed. The DPT has often been explained by the presence of dipole inhomogeneity, which is ascribed to the compositional fluctuation,[4] to the glassy dipolar arrangement[5] or to the fluctuation in chemical ordering.[2] The DPT behavior is observed often in the solid solution systems[6,7] and in disordered crystalline perovskites.[8]

PYN belongs to a subgroup of complex perovskites with a highly B-site cation chemical order. It undergoes the PE–AFE phase transition near 302°C.[9,10] Although it is known that the DPT behavior can be induced by the structural or compositional disorder, there is no complete correlation between the degree of order and the on-set of DPT in solid solutions.[7]

In this study, the solid solution behavior of ordered AFE PYN and PMW has been examined. Structural analysis, dielectric constant and P–E hysteresis loop measurements were performed to investigate the phase transition phenomena in the $PYN_{1-x}PMW_x$ ceramics solid solutions.

2. Experimental

Ceramic samples with a chemical formula of (1–x) $Pb(Yb_{1/2}Nb_{1/2})O_3$–x$Pb(Mg_{1/2}W_{1/2})O_3$ ($PYN_{1-x}PMW_x$) ($0 \leqslant x \leqslant 0.30$) were prepared by reacting stoichiometric proportions of high purity (99.9%) PbO, Yb_2O_3, Nb_2O_5, MgO and WO_3 powders. The mixtures were ball-milled in acetone, dried and then calcined at 850–900°C. The calcined powders were reground, pressed and sintered at 1000–1050°C for 1 h in MgO crucibles.

X-ray diffraction experiments were carried out on a two-circle Rigaku Rotaflex X-ray diffractometer. The specimens for dielectric investigations were electroded with silver paste by firing at 590°C for 5 min. The dielectric constant was measured at several frequencies between

---

* Corresponding author. Tel.: +82-42-869-4253; fax: +82–42-869-4273.
E-mail address: s-k2@cais.kaist.ac.kr (J.-H. Kim).

0955-2219/01/$ - see front matter © 2001 Published by Elsevier Science Ltd.
PII: S0955-2219(01)00089-9

1 kHz and 1 MHz using a Hewlett Packard 4194A impedance/gain phase analyzer interfaced with a personal computer. The hysteresis loops were measured on a Sawyer–Tower hysteresis analyzer.

3. Results and discussion

3.1. X-ray measurement

Fig. 1 shows the X-ray diffraction patterns of $PYN_{1-x}PMW_x$ at several PMW concentrations at room temperature. For pure PYN ($x=0$), two sets of superlattice reflection are observed; the first is associated with the AFE lattice modulation and the other, with the B-site cation ordering, marked by the solid circles and squares respectively. With the substitution of PMW ($0<x\leqslant 0.25$), the intensity of the superlattice lines gradually decreases and finally disappears at $x=0.28$. The intensity reduction of the diffraction lines from the B-site order may be associated with replacement of the Mg and W ions breaking the long range order of the Yb^{3+} and Nb^{5+} ions. In this composition range, the AFE phase on the room temperature indicates that the on-going transition is one of PE–AFE transition types. The splitting of fundamental lines begins to disappear between $x=0.25$ and $x=0.28$, giving rise to a pseudocubic phase beyond $x=0.28$.

3.2. Dielectric constant measurement

Fig. 2 shows the dielectric constant vs. temperature curves at different applied frequencies between 1 kHz and 1 MHz of the solid solution at concentrations on the heating cycle are given. It has already been reported that PYN follows the Curie–Weiss law well above the phase transition temperature.[10] The $PYN_{1-x}PMW_x$ ($0<x\leqslant 0.25$) undergoes the similar tendency of pure PYNs phase transition, while the AFE–PE phase transition temperature gradually decreases with concentration. In the PMW concentration range ($x\geqslant 0.30$), the DPT behavior having the broad maxima and the frequency-dependent transition appears. The solid solution is definitely a relaxor judging from these behaviors. At $x=0.28$, which separates the composition boundary between the PE–AFE and the relaxor transition, a unique frequency–dependent dielectric constant behavior suddenly shows up at a temperature point on the heating cycle from the low temperature frequency independent one. It may be called a normal-to-relaxor phase transition because the phenomenon occurs on the heating cycle, however, the relaxor-to-normal transition may be coined to the terminology more appropriately.

The relaxors are often interpreted as a dipole glass obeying the Vögel–Fulcher relation.[11,12] Then the frequency ω dependence of the temperature of the broad dielectric permittivity maximum of $PYN_{1-x}PMW_x$ can be fitted with the following relation

$$\omega = \omega_0 \exp[-E_{\mathrm{act}}/k\mathrm{B}(T_{\mathrm{a}} - T_{\mathrm{f}})], \qquad (1)$$

where ω_0, E_{act} and T_{f} and T_{a} are the pre-exponential factor, activation energy, freezing temperature and the temperature of the dielectric constant maximum respectively. The parameters in Eq. (1) for $PYN_{0.72}PMW_{0.28}$ obtained after the optimal numerical fitting are $\omega_0=2.415\times 10^{10}$ Hz, $E_{\mathrm{act}}=0.0379$ eV and $T_{\mathrm{f}}=289.3$ K (16.3°C). The optimally fit curve is shown in Fig. 3. The T_{f} derived from the Vögel–Fulcher relation agrees with

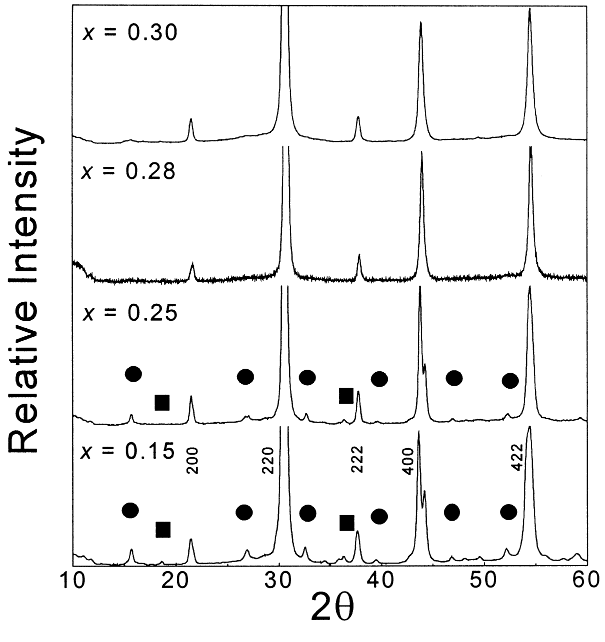

Fig. 1. X-ray diffraction patterns of $PYN_{1-x}PMW_x$ solid solution at room temperature: solid squares are attributed to the B-site atomic ordering and the solid circles, to the antiparallel Pb^{2+} cation shifts.

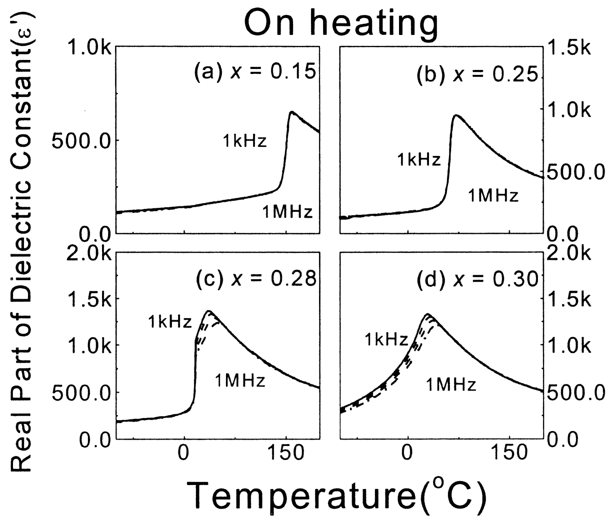

Fig. 2. The dielectric constant vs. temperature curve at various frequencies (1 kHz, 10 kHz, 100 kHz and 1 MHz) of $PYN_{1-x}PMW_x$.

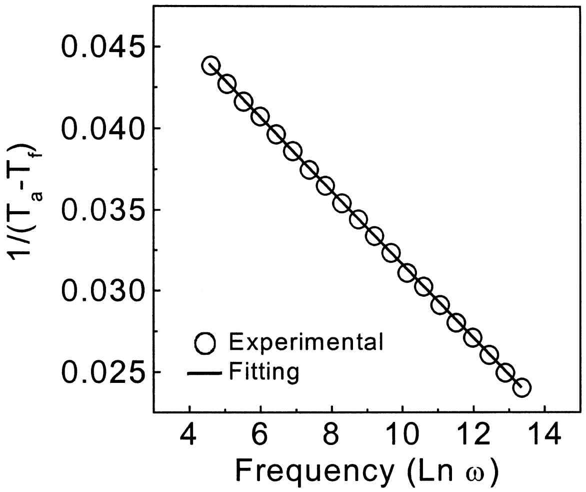

Fig. 3. The inverse of permittivity maximum as a function of logarithmic frequency for $PYN_{0.72}PMW_{0.28}$.

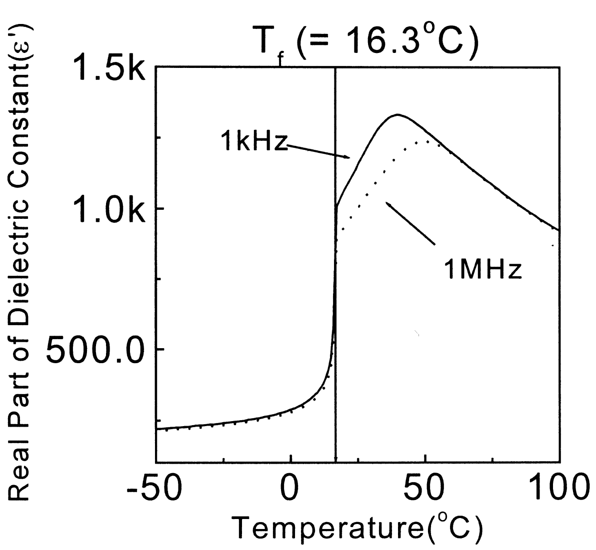

Fig. 4. The real part of the dielectric constant of $PYN_{0.72}PMW_{0.28}$ as a function of temperature on cooling and heating at 1 kHz and 1 MHz.

the lower converging point of the dielectric constant curve as shown in Fig. 4. The origins of the relaxor behavior are interpreted differently depending on the ferroelectrics so far studied. The relaxor transition behavior of 12% La substituted PZT (PLZT) was linked to the micro–macro domain switching as temperature is changed.[13] On the other hand, Pb-ion vacancies were reported to give rise to the relaxor behavior in PST[3,14]. In $PYN_{0.72}PMW_{0.28}$, however, from the agreement with the Vögel–Fulcher relation, the relaxor behavior may be interpreted to originate from the sudden increase in the dipole fluctuation and then this gives rise to an abrupt increasing in the dielectric constant at T_f.

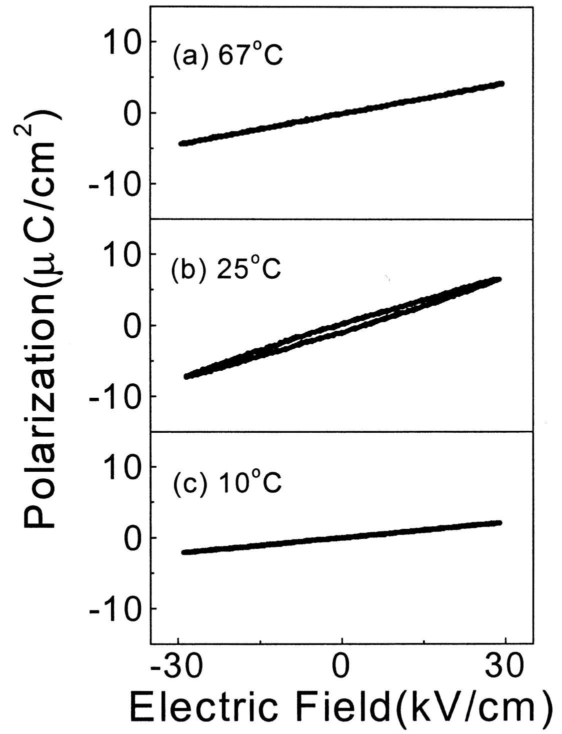

Fig. 5. Hysteresis loop curve at different temperatures for $PYN_{0.72}PMW_{0.28}$: (a) 67°C, (b) 25°C; (c) 10°C.

Fig. 5 shows the P–E hysteresis curves of $PYN_{0.72}PMW_{0.28}$ at several temperatures, 67, 25 and 10°C in which the linear P–E relation shows that $PYN_{0.72}PMW_{0.28}$ is paraelectric above T_a. In the temperature range $T_f < T < T_a$, a weak slim loop appears indicating the existence of a weak ferroelectric relaxor phase. In the lower temperature region ($T < T_f$), the remanent polarization disappears as shown in Fig. 5(c).

4. Conclusion

The crystal structure of $PYN_{1-x}PMW_x$ solid solution changes from the orthorhombic to the pseudocubic structure at room temperature as the PMW content increases. A typical DPT behavior exhibiting the broad maxima and the frequency-dependent transition shows up for $x \leqslant 0.30$, while the frequency-independent sharp transition is predominant for $x \leqslant 0.25$. At an intervening relaxor composition $x = 0.28$, the relaxor-to-normal AFE transition can be interpreted by the Vögel–Fulcher relation. At this composition, a successive phase transition occurs from the PE to the AFE state via a relaxor phase.

Acknowledgements

This work was supported in part by the Korea First Co., Ltd., under contract No. 98-G-06-02-A-16. The authors deeply appreciate this support.

References

1. Randall, C. A., Bhalla, A. S., Shrout, T. R. and Cross, L. E., Classification and consequences of complex lead perovskite ferroelectrics with regard to B-site cation order. *J. Mater. Res.*, 1990, **5**, 829–834.

2. Setter, N. and Cross, L. E., The role of B-site cation disorder in diffuse phase transition behavior of perovskite ferroelectrics. *J. Appl. Phys.*, 1980, **51**, 4356–4360.
3. Chu, F., Reany, I. M. and Setter, N., Spontaneous (xero-field) relaxor-to-ferroelectric-phase transition in disordered Pb $(Sc_{1/2}Nb_{1/2})O_3$. *J. Appl. Phys.*, 1995, **77**, 1671–1676.
4. Smolensky, G. A., Physical phenomena in ferroelectrics with diffused phase transition. *J. Phys. Soc. Jpn. Suppl.*, 1970, **28**, 26.
5. Burns, G., Dirty displacive ferroelectrics. *Phys. Rev. B*, 1976, **13**, 215–226.
6. Furuya, M., Mori, T., Ochi, A., Saito, S. and Takahashi, S., Dielectric properties and crystal structure in ternary system $Pb(Mg_{1/2}W_{1/2})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ ceramics. *Jpn. J. Appl. Phys.*, 1992, **31**, 3139–3143.
7. Chen, I., Li, P. and Wang, Y., Structural original of relaxor perovskites. *J. Phys. Chem. Solids*, 1996, **57**, 1525–1536.
8. Salje, E. and Bismayer, U., Order parameter behavior in the relaxor ferroelastic lead scandium tantalite. *J. Phys. Condens. Matter*, 1989, **1**, 6967–6976.
9. Tomashpol'skii, YuYa and Venevtsev, Yu.N., X-ray and electrical investigations of the system $Pb(Co_{1/2}W_{1/2})O_3$–$Pb(Yb_{1/2}Nb_{1/2})O_3$. *Sov. Phys.-Solid State*, 1965, **6**, 2388–2392.
10. Kwon, J. R. and Choo, W. K., Antiferroelectric crystal structure of highly ordered complex perovskite $Pb(Yb_{1/2}Nb_{1/2})O_3$. *J. Phys. Condens. Matter*, 1991, **3**, 2147–2155.
11. Viehland, D., Jang, J., Cross, L. E. and Wutting, M., Dipolar-glass model for lead magnesium niobate. *Phys. Rev. B*, 1991, **43**, 8316–8320.
12. Viehland, D., Jang, J., Cross, L. E. and Wutting, M., Freezing of the polarization fluctuation in lead magnesium niobate relaxors. *J. Appl. Phys.*, 1990, **68**, 2916–2921.
13. Dai, X., Xu, Z. and Viehland, D., The spontaneous relaxor to normal ferroelectric transformation in La-modified lead zirconate titanate. *Philos. Mag.*, 1994, **B70**, 33–48.
14. Chu, F. Setter, N and Tagantsev, AK (The spontaneous relaxor-ferroelectric transition of $Pb(Sc_{1/2}Ta_{1/2})O_3$). *J. Appl. Phys.*, 1993, **74**, 5129–5134.