Effect of A Site Substitution on Order–Disorder Transition in $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN) and $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (PST)

Yoshihiro FUJII, Naoki WAKIYA, Jin-Ho LIM*, Osamu SAKURAI,
Kazuo SHINOZAKI and Nobuyasu MIZUTANI

Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152

*Department of Inorganic Materials Engineering, Kyungpook National University, 1370, Sankyuk Dong, Pukku, Taegu 702-701, Korea

$\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN)及び $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (PST)における 秩序–無秩序転移に及ぼす A サイト置換効果

藤井義博・脇谷尚樹・林 進浩*・桜井 修・篠崎和夫・水谷惟恭

東京工業大学工学部無機材料工学科, 152 東京都目黒区大岡山 2-12-1

*慶北大学校工科大学無機材料工学科, 702-701 大韓民国大邱広域市北区山格洞 1370

The effect of A site substitution of $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN) and $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (PST) with Na or La on the order–disorder transition and dielectric characteristics was examined. It was clarified that the degree of ordering at the B site did not change by the substitution though it has been reported that in case of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN), the degree of ordering can be controlled by the A site substitution. The reason may be due to the difference in cation size ratio of B site, that is, Mg: Nb = 1 : 2 for PMN and Fe: Nb and Sc: Ta = 1 : 1 for PFN and PST. By partial substitution of A site by La or Na, the dielectric characteristics of PFN and PST drastically changed from normal ferroelectric to “relaxor ferroelectric”. This indicates that “relaxor ferroelectrics” can not be necessarily derived from the order–disorder state at the B site sublattice as understood so far. The “relaxor ferroelectric” property of Na or La doped PST and PFN would be classified into the same group of (Pb, La) (Zr, Ti) O_3 (PLZT) and La doped (Sr, Ba) Nb_2O_6 (SBN).

[Received March 29, 1996; Accepted May 15, 1996]

Key-words : Lead iron niobium oxide, PFN, Lead scandium tantalum oxide, PST, Order–disorder transition, A site substitution

1. Introduction

Lead containing perovskite type compounds with general formula, $\text{Pb}(\text{B}'\text{B}'')\text{O}_3$, have been widely used as dielectric materials. Some of these materials show normal ferroelectric or anti-ferroelectric characteristics. And some of these materials show “relaxor-type” behavior which is characterized by a diffuse and dispersive phase transition. It has been believed that the dielectric properties can be classified by the degree of ordering of B' and B'' cations at the B site sublattice¹⁾ as following. Compounds whose B site sublattices are disordered such as $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN) or long range ordered such as $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (PST) show normal ferroelectric properties. On the other hand, compounds whose B site sublattices are short range ordered such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) show “relaxor-type” properties. For PST, it was also reported that the degree of ordering at the B site sublattice can be changed by heat treatment.^{2)–5)} That is, quenching from high temperature causes short range ordering and its dielectric property is “relaxor-type”, on the other hand, annealing at low temperature causes long range ordering and its dielectric property is normal ferroelectric.

For PMN, it was reported that the degree of ordering at the B site can be changed by the partially substitution of Pb^{2+} by hetero valent cations,^{6)–8)} that is, substitution of Pb^{2+} with La^{3+} enhances the degree of ordering and substitution of Pb^{2+} with Na^+ suppresses the degree of ordering. Wang et al. calculated Madelung energies for $\text{A}^{2+}(\text{B}_{1/3}^{2+}\text{B}_{2/3}^{5+})\text{O}_3$ and $\text{A}^{2+}(\text{B}_{2/3}^{3+}\text{B}_{1/3}^{6+})\text{O}_3$ systems for different dopants at the A site.⁹⁾ As the theoretical result, they reported that substitution of A site cation by higher-valence cation enhances the ordering at the B site for $\text{A}^{2+}(\text{B}_{1/3}^{2+}\text{B}_{2/3}^{5+})\text{O}_3$ whereas substitution by lower-valence cation promotes ordering at the B site for $\text{A}^{2+}(\text{B}_{2/3}^{3+}\text{B}_{1/3}^{6+})\text{O}_3$.

However it is still unknown if it is possible to be changed the degree of ordering for $\text{A}^{2+}(\text{B}_{1/2}^{3+}\text{B}_{1/2}^{5+})\text{O}_3$ by doping different valence cations at the A site. In this work, the effect of A site substitution on the degree of ordering was examined for $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN) and $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (PST). Moreover in this work relationship between the degree of ordering at the B site and the dielectric properties was also examined.

2. Experimental procedure

The specimens were prepared by conventional solid-state reaction using ball-milling in ethanol with zirconia balls for 22h. The compositions of the samples were shown as following.

First powder mixtures of Fe_2O_3 and Nb_2O_5 or Sc_2O_3 and Ta_2O_5 were calcined at 900°C for 2h to prepare FeNbO_4 or ScTaO_4 . Then the powders of PbO , La_2O_3 , Na_2CO_3 and FeNbO_4 or ScTaO_4 were mixed for the second calcination at 800°C for 2h. The powders were pressed into pellets and embedded in the powder with the same composition in a magnesia crucible with an alumina lid and sintered at 1000°C for 2h for PFN and 1500°C for 20 min for PST. After sintering, the samples were cooled in the furnace with cooling rate around 300°C/h.

Lattice parameters were determined from powder X-ray diffraction data with silicone as an internal standard using the program RLC-3.¹⁰⁾ In this work, order parameter S for a particular sample was defined by comparing the ratio of the observed superlattice reflection to the base lattice reflection for that sample with the calculated intensities for per-

fect ordering.

$$S = \frac{(I(111)/I(220))_{\text{obs}}}{(I(111)/I(220))_{\text{cal}}} \times 100$$

where $I(111)$ and $I(220)$ denoted the intensity of superlattice reflection and base lattice reflections of perovskite type compound respectively (indices refer to the double-cell unit cell). The intensities for perfect ordering were calculated using the program RIETAN.¹¹⁾

The relative amount of the perovskite to the pyrochlore type compound was calculated using following equation.

$$\text{perovskite}\% = \frac{I_{\text{perovskite}}(110)}{I_{\text{perovskite}}(110) + I_{\text{pyrochlore}}(222)}$$

where $I_{\text{perovskite}}(110)$ and $I_{\text{pyrochlore}}(222)$ were the major X-ray peak intensities for perovskite and pyrochlore type compounds respectively.

Dielectric properties were measured with an HP4192A impedance analyzer and the data were collected every 1°C at various frequencies between 1 kHz and 1000 kHz.

TEM specimens were prepared by crushing and observed using JEM-200CX electron microscope.

3. Results

3.1 La-doped PFN

Perovskite% of pure PFN and La-doped PFN was shown in Table 1. As shown in Table 1, the perovskite% was more than 97%. Figure 1 shows the relationship between the lattice parameter and La content. In Fig. 1, change of lattice parameter with La content was compared with that of calculated one. The calculate lattice parameter " a (calculation)" was derived using following equation.

$$a(\text{calculation}) = \frac{\sqrt{2}(r_A + r_O) + 2(r_B + r_O)}{2}$$

where r_A , r_B and r_O represented the ionic radii of A, B and O ions, respectively. Since it is difficult to calculate the accurate lattice parameter using ionic radii, the calculated lattice parameter is not consistent with measured one. However Fig. 1 shows that the tendency of the change of the lattice parameter with La content agrees with calculat-

Table 1. Change of Perovskite% with La Content for PFN

La content mol%	Perovskite%
0	97
5	97
10	98

Fig. 1 Relationship between lattice parameter and La content X in $(\text{Pb}_{1-X}\text{La}_X)(\text{Fe}_{(1+X)/2}\text{Nb}_{(1-X)/2})\text{O}_3$.

ed one and the figure shows that the lattice parameter linearly changes with La content, which suggests that Pb^{2+} cation at A site is actually substituted by doped La^{3+} cation.

Many authors reported that short range ordering at the B site causes superlattice reflection of $(1/2 \ 1/2 \ 1/2)$ in $\langle 110 \rangle$ zone axis pattern,^{1),4),6)–8)} however as shown in Fig. 2, such superlattice reflection was not detected for $(\text{Pb}_{0.95}\text{La}_{0.05})(\text{Fe}_{0.525}\text{Nb}_{0.475})\text{O}_3$. This result suggests that donor doping does not bring about ordering at the B site. In addition, slight beam split can be observed in Fig. 2(b). The reason is uncertain but it can be thought that the split might suggest the ferroelectric phase.

Figure 3 shows the temperature dependence of dielectric constant for the pure and La-doped PFN. This figure shows that no frequency dependence of the maximum value in the dielectric constant is perceived for pure PFN and the fre-

Fig. 2 (a) Bright-field image and (b) diffraction pattern of $(\text{Pb}_{0.95}\text{La}_{0.05})(\text{Fe}_{0.525}\text{Nb}_{0.475})\text{O}_3$.

Fig. 3 Temperature dependence of dielectric constant for pure and La doped PFN measured at 1, 10, 100 and 1000 kHz.

quency dependence is detected for 5 and 10% La-doped PFN. This result indicates that the dielectric property changes from normal ferroelectric to "relaxor-type" by La doping without formation of short range ordering at the B site.

3.2 Na-doped and La-doped PST

The perovskite% of pure, Na-doped and La-doped PST was shown in Table 2. As shown in Table 2, no pyrochlore type compound coexisted with the perovskite type compound except for La 10% doped PST (perovskite% = 99%).

Figure 4 shows the change of the lattice parameter and the order parameter with the amount of dopants. As well as in the case of PFN, the lattice parameter linearly changes with the amount of dopant and the tendency is in good agreement with calculated ones. From Fig. 4, it was clarified that the order parameter slightly increased with La content, however the parameter was almost constant against Na content. As well as the result of X-ray diffraction, the superlattice reflection of $(1/2\ 1/2\ 1/2)$ in $\langle 110 \rangle$ zone axis pattern was clearly observed in Na doped PST. This result indicates that the substitution of A site cation by hetero valence cation does not affect the degree of ordering at the B site. It was reported that the degree of ordering can be changed easily by cooling condition. However in this experiment to examine the net effect of doping on the degree of ordering, all specimens were prepared by slowly cooling in the furnace.

Figure 5 shows the temperature dependence of dielectric

Table 2. Change of Perovskite% with La or Na Content for PST

La content mol%	Perovskite%	Na content mol%	Perovskite%
0	97	0	97
5	97	5	97
10	98	10	98

Fig. 4 Change of lattice parameter and ordering parameter S with Na or La content X in $(\text{Pb}_{1-X}\text{Na}_X)(\text{Sc}_{(1-X)/2}\text{Ta}_{(1+X)/2})\text{O}_3$ or $(\text{Pb}_{1-X}\text{La}_X)(\text{Sc}_{(1+X)/2}\text{Ta}_{(1-X)/2})\text{O}_3$.

Fig. 5 Temperature dependence of dielectric constant for pure, La doped and Na doped PST (Slow cooling) measured at 1, 10, 100 and 1000 kHz.

constant for the undoped and La or Na doped PST. Since the relative density of sintered pellets was between 72 and 84% of theoretical density, the maximum value of dielectric constant is about 1 order of magnitude lower than the reported value.⁵⁾ As well as in the case of PFN, no frequency dependence of the maximum value in the dielectric constant is perceived for pure PST and the frequency dependence is detected for 5 and 10% La or Na doped PST. This result indicates that the dielectric property changes from normal ferroelectric to "relaxor-type" by La or Na doping without formation of the short range ordering at the B site.

4. Discussions

4.1 Effect of doping on the degree of ordering

Since the Mg/Nb ratio for PMN is 1 : 2, La doping increases the Mg/Nb ratio toward 1 : 1. It is reported that this is the reason why La doping increases the degree of ordering at the B site. On the other hand, for PST, the Sc/Ta ratio is originally 1 : 1 and La or Na doping causes the departure from the ratio. Therefore in PST it was expected that La or Na doping would suppress the degree of ordering. However as shown in Fig. 2, ordering parameters were almost constant against the dopant content. It must be noted that the degree of ordering is not 100% but 50% level. That is, around half of PST is the ordering state and half is the disorder state. Consequently to understand our result, it is presumed that the dopants were preferentially incorporated into the lattice of disorder state. For PFN, Fe and Nb cations are disorder state, therefore, it was expected that La or Na doping does not affect the degree of ordering, which is in good agreement with experimental result.

4.2 Effect of doping on the dielectric properties

As shown in Figs. 3 and 5, the dielectric characteristics of PST and PFN changed from normal ferroelectric into "relaxor-type" by La or Na doping though the degree of B site ordering did not change by the doping. Randall and Bhalla¹⁾ classified the dielectric characteristics of many $\text{Pb}(\text{B}'\text{B}'')\text{O}_3$ type perovskite type compounds according to the degree of ordering at the B site, and attributed the "relaxor" characteristics to the short range ordering at the B site. However our results show that their classification is not enough. Therefore the dielectric characteristics may be due to the formation of random ferroelectric cluster around impurity cation as well as in the case of La doped $(\text{Sr}, \text{Ba})\text{Nb}_2\text{O}_6$ (SBN)¹²⁾, La doped $(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3$ (PLZT)¹³⁾ and Nb doped KTaO_3 (KTN).¹⁴⁾⁻¹⁶⁾

5. Conclusions

The effect of A site substitution of PST and PFN with Na or La was examined. Consequently, it was clarified that the degree of ordering at the B site was not changed by the substitution though it has been reported that in case of PMN, the degree of ordering can be controlled by the A site substitution. The reason may be due to the difference of cation ratio of B site, that is, Mg: Nb = 1 : 2 for PMN and Sc: Ta, Fe: Nb = 1 : 1 for PST and PFN.

On the other hand, the dielectric characteristics drastically changed from normal ferroelectric to "relaxor ferroelectric" by A site substitution for PST and PFN. This indicates that "relaxor ferroelectrics" can not be necessarily derived by the order-disorder state at the B site sublattice as understood so far. And the "relaxor ferroelectric" property of Na or La doped PST and PFN would be classified into the same group of PLZT and La doped SBN.

Acknowledgment The authors gratefully thank Prof. T. Takenaka of Science University of Tokyo and Dr. M. Yonezawa of NEC Corporation for helpful discussions.

References

- 1) C. A. Randall and A. S. Bhalla, *Jpn. J. Appl. Phys.*, **29**, 327-33 (1990).
- 2) C. F. G. Stenger, F. L. Scholten and A. R. Burggraf, *Solid State Commun.*, **32**, 989-92 (1979).
- 3) N. Setter and L. E. Cross, *J. Mater. Sci.*, **15**, 2478-82 (1980).
- 4) Y. J. Chang and Z. L. Chen, *Ferroelectrics Lett.*, **4**, 13-18 (1985).
- 5) L. E. Cross, *Ferroelectrics*, **76**, 241-67 (1987).
- 6) J. Chen, H. M. Chan and M. P. Harmer, *J. Am. Ceram. Soc.*, **72**, 593-98 (1989).
- 7) M. P. Harmer, J. Chen, P. Peng, H. M. Chan and D. M. Smyth, *Ferroelectrics*, **97**, 263-74 (1989).
- 8) L. Yinmei, S. Chengyu and W. Baosong, IEEE CH3416-5 226-28 (1995).
- 9) Q. Wang, H. Rushan and Z. Z. Gan, *J. Am. Ceram. Soc.*, **75**, 2881-82 (1992).
- 10) T. Sakurai, Universal Program System for Crystallographic Computation, Crystallographic Society of Japan (1967).
- 11) F. Izumi, *Kobutsugaku Zasshi*, **17**, 37 (1985).
- 12) R. R. Neurgaonkar, J. R. Oliver and W. K. Cory, *J. Cryst. Growth*, **89**, 463-70 (1988).
- 13) F. Fang and X. Zhang, *J. Mater. Res.*, **10**, 1582-84 (1995).
- 14) G. A. Samara, *Phys. Rev.*, **53**, 298-301 (1984).
- 15) W. Kleemann, F. J. Schäfer and D. Rytz, *Phys. Rev. Lett.*, **54**, 2038-41 (1985).
- 16) M. D. Fontana, M. Maglione and U. T. Höhli, *J. Phys.: Condens. Mater.*, **5**, 1895-900 (1993).