

XAFS Study of Relaxor $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$

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Pb L_{III} -edge absorption spectra of ordered and disordered $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PIN) were analyzed. The absorption edges of both the ordered and disordered PIN were shifted depending on the thermal condition of post-annealing. A clear edge shift was observed between the ordered and disordered PIN crystals. The local environments of the Pb atoms were different in these PIN crystals. The edge shift can be interpreted by introducing disarrangement of B-site atoms. Disorder of B-site atoms did not influence the environment of B-site atoms though was in Pb environment.

Key words; $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$, relaxor, x-ray absorption fine structure, structure analysis

1. INTRODUCTION

Lead indium niobate ($\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$), usually abbreviated PIN, belongs to the complex lead-based perovskite-type ferroelectric materials $\text{Pb}(\text{B},\text{B}')\text{O}_3$. PIN crystals show different ferroelectric features depending on the thermal treatments applied. Different treatments result in an ordered PIN exhibits an antiferroelectricity, or else a disordered PIN exhibits relaxor behavior [4,5].

Previous XAFS investigations of the ordered and disordered PIN have shown that changes of macroscopic symmetry have surprisingly little effect on the local environment of atoms and that the local structure remains highly distorted even in the cubic phase. The local structure model was also confirmed by pulsed neutron scattering pair-distribution function analysis [6-8].

In the previous report, the ordered and disordered PIN was distinguished by In/Nb chemical ordering. The In/Nb chemical order parameter for these crystals were determined by comparing the ratio of the observed superlattice reflection of the In/Nb arrangement at B-site to the base lattice reflection [4]. However, it was found that in $\text{Pb}(\text{Mg}_{0.3}\text{Ta}_{0.6}\text{Zr}_{0.1})\text{O}_3$ (PMT-PZ) the relaxor behavior is retained even after long range chemical ordering develops [9]. This observation strongly suggests the ordering fluctuation of the B-site atoms is not essential condition for relaxor system. We have shown that the highly ordered and disordered PIN can be selected by thermal analysis. In this study, we re-examined the XANES spectra of ordered and disordered PIN and discussed the origin of the relaxor ferroelectricity.

2. EXPERIMENTAL SETUP

PIN single crystals were flux-grown from a $\text{PbO}-\text{In}_2\text{O}_3-\text{Nb}_2\text{O}_5$ system in a temperature range from

1200 to 950°C at a crystallization rate of 3°C/h, followed by cooling from 950 to 750°C at a rate of 7°C/h. The ordered PIN crystals were prepared by annealing the as-grown PIN crystals at 923°C for 20h. The disordered PIN crystals were prepared by quenching the as-grown crystals from 950°C to room temperature, utilizing a rapid thermal processing technique [10]. These crystals were cubic in shape with a pseudo-cubic (100) plane crystal habit and 1-2 mm on a side.

The x-ray diffraction patterns obtained from the ordered and disordered PIN were consistent with the orthorhombic and the cubic perovskite structure, respectively, and did not show the presence of any additional phases.

The ordered and disordered PIN samples were annealed for several times and the post-annealing process was monitored by differential thermal analysis (DTA, Rigaku, DSC8230D, Japan).

XAFS measurements were carried out at Pb L_{III} and In K absorption edges. The samples were carefully ground and mixed with BN. Then, they were pressed to form pellets about 0.3 mm thick. Measurements were performed in transmission at Synchrotron Radiation Source (SPring-8) at BL14B1, which is a bending-magnet beamline equipped with Si(111) double-crystal monochromator. The x-ray beam was focused to 3 mm at the sample position by a sagittal focus bender [11,12]. All the XAFS spectra were taken at room temperature.

3. EXPERIMENTAL RESULTS

3-1. Pre-edge structure of Pb L_{III} edge

Figure 1(a) shows the DSC results of post-annealing process of the ordered PIN, which has been reported in Ref. 5. Clear thermal anomalies were observed around 200°C, those show an antiferroelectric phase transition.

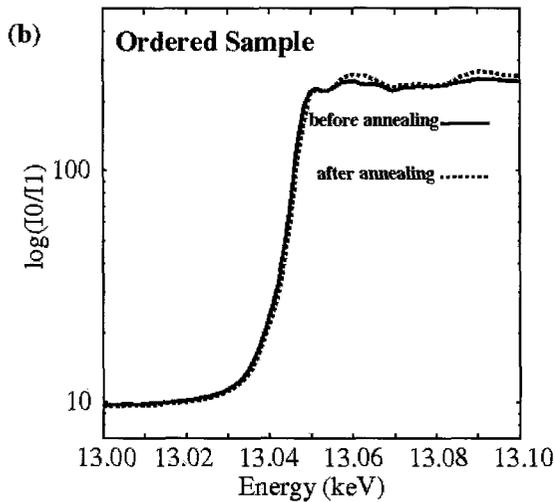
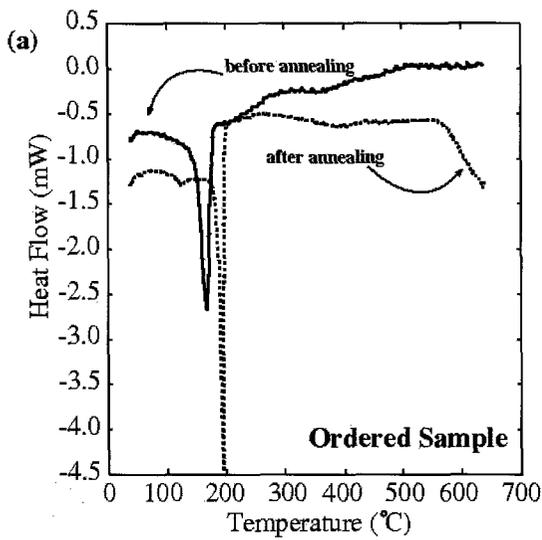


Fig. 1 (a) DSC curves of ordered sample before and after post annealing. (The same data as Fig. 2(a) of Ref. 5.) (b) Pb L_{III} near-edge spectra of corresponding ordered sample.

Although the order parameter values of the In/Nb arrangements did not change through the heat treatment, the transition temperature of the post-annealed sample was slightly different. Figure 1(b) shows the Pb L_{III} XANES spectra of the ordered sample before and after the post-annealing. The absorption edge of the ordered sample with the higher transition temperature tended to shift toward higher energy.

Figure 2(a) shows the DSC results of post-annealing process of the disordered PIN, which has been also reported in Ref. 5. The disordered sample with the In/Nb order parameter ≈ 0.0 shows no thermal anomaly within the measured temperature range. However, after the post-annealing, the disordered sample of the In/Nb order parameter was 0.05 and a weak anomaly appeared around 200°C. Figure 2(b) shows the Pb L_{III} XANES spectra of the disordered sample before and after the post-annealing. The absorption edge of the post-annealed disordered sample, which showed the

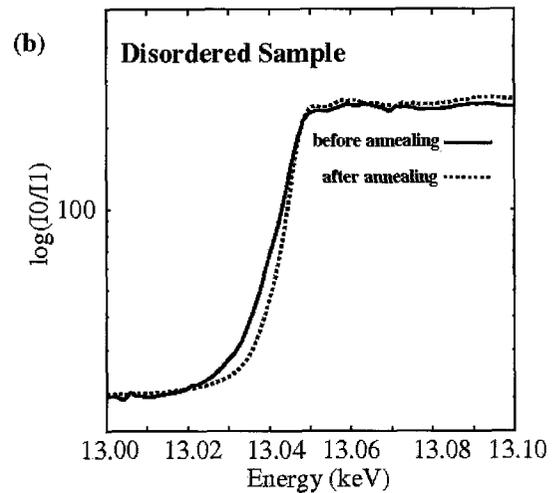
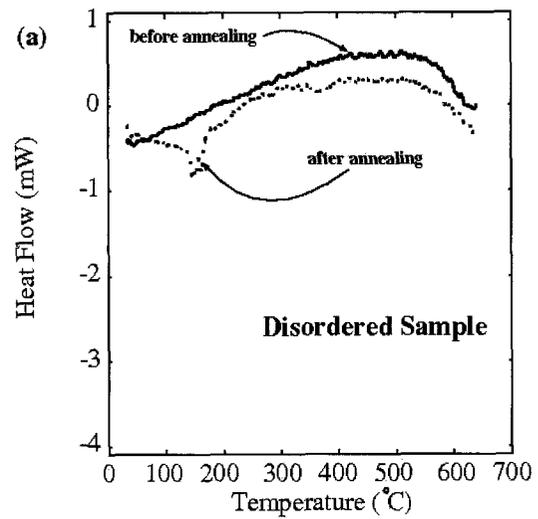


Fig. 2 (a) DSC curves of ordered sample before and after post annealing. (The same data as Fig. 2(a) of Ref. 5.) (b) Pb L_{III} near-edge spectra of corresponding disordered sample.

weak thermal anomaly shifted to higher energy comparing to that of the disordered sample before the post-annealing that showed no thermal anomaly.

Figure 3 shows the Pb L_{III} XANES spectra of the ordered and disordered samples. The ordered PIN was the sample that showed the higher transition temperature. The disordered PIN was the sample that showed no thermal anomaly. A clear absorption edge shift was observed between the ordered and disordered PIN crystals. In the ordered PIN, the absorption edge tended to shift toward higher temperature owing to the rigid Pb environments. On the other hand, the absorption edge shifted to lower energy in the disordered PIN indicating a large fluctuation around the Pb environments.

In order to explain the thermal properties of the ordered and disordered PIN, we have already suggested a defect model [5] and we showed the local environment of the Pb atom of disordered PIN is different from that of ordered PIN [13]. The shift of the antiferroelectric phase transition temperature in the ordered PIN as well

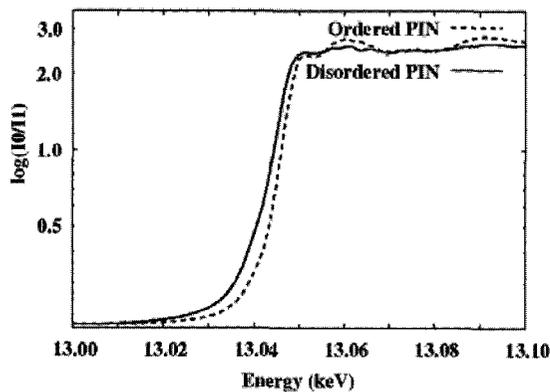


Fig. 3 Pb L_{III} near-edge spectra of ordered and disordered PIN crystals.

as the absence in the disordered PIN can be illustrated by the defect density. The defect behavior should be caused by the disarrangement of the B-site atoms. The disarrangement of the In/Nb atoms causes a random field, and the random field causes the large fluctuation around the Pb atoms. The Pb atoms should be influenced by the ordering fluctuation of the B-site atoms like $Pb(Zr_{1-x}Ti_x)O_3$ system [14]. The disarrangement of the B-site atoms also caused an electric disproportion, and the oxygen deficiency may be caused so that it makes amends for the electric disproportion. Since the $(In_{0.5}Nb_{0.5})O_6$ octahedron consists of rigid covalent

bonds, the disorder feature is effective for the bond distribution of Pb-O rather than that of In-O and Nb-O. Both local environment and electric configuration around the Pb atoms fluctuated due to the electric disproportion of the B-site atoms and the oxygen deficiency. This electric fluctuation appeared as the lower shift of the absorption energy. Since the long-range order structure cannot grow with the disarrangement of the B-site atoms, the superlattice peak was absent and the In/Nb ordering parameter was almost equal to zero in the disordered PIN. Furthermore, the neighborhood of the In/Nb disarrangement, the Pb atomic positions were also fluctuated. We concluded that the order fluctuation of the B-site atoms and the positional fluctuation of Pb atoms are essential condition for relaxor behavior.

3-2. EXAFS of In K -edge

Since the L -edge EXAFS spectra are generally difficult to use for EXAFS analysis, we performed EXAFS measurements using the In K -edge absorption edge. Figure 4(a) shows the XAFS spectra of ordered and disordered PIN samples. The K -edge XANES spectra of these samples are very similar, as shown in Fig. 4(b). The similarity of these samples are also seen in the XAFS function and bond distribution around the In atom, as shown in Fig 4(c) and (d), respectively. The local structure around the B-site atoms does not change even if B-site atomic arrangement is ordered or disordered. The nearest bond distribution around In atom

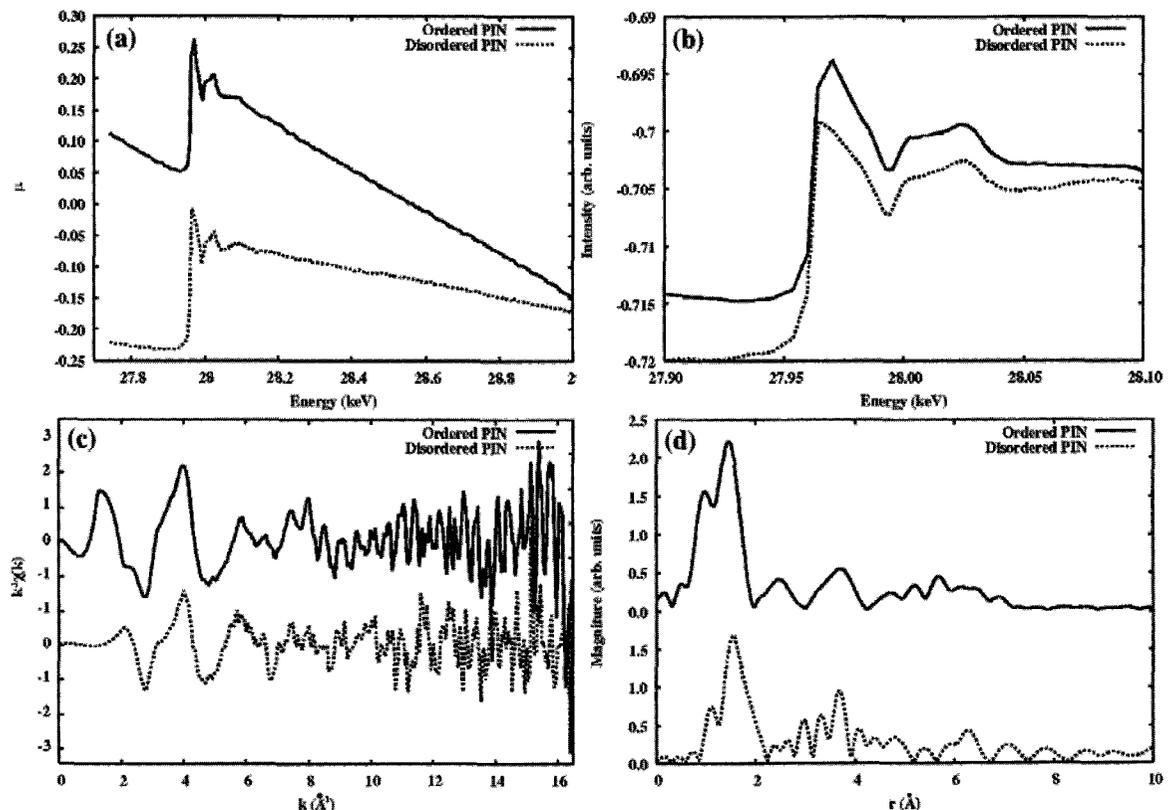


Fig.4 (a) Observed In K -edge XAFS spectra of ordered and disordered PIN. Corresponding (b) XANES, (c) XAFS spectra, and (d) Fourier transforms of the XAFS spectra

is not sensitive to In/Nb arrangement owing to the rigid and covalent In-O bonding. Shuvaeva and coworkers have been found the similarity of Nb-O bond distribution using the Nb *K*-edge EXAFS [1].

4. SUMMARY

As a result of the XANES study of the ordered and disordered PIN crystals, the absorption edge is closely connected with the ferroelectric feature of the PIN crystals. The edge shift showed the large fluctuation around the Pb atoms and it was caused by the disarrangement of the B-site atoms.

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REFERENCES

- [1] V. A. Shuvaeva, I. Pirog, Y. Azuma, K. Yagi, K. Sakaue, H. Terauchi, I. P. Raevskii, K. Zhuchkov and M. Y. Antipin, *J. Phys.: Condens. Matter*, **15**, 2413 (2003).
- [2] V. A. Shuvaeva, D. Zekria, A. M. Glazer, Q. Jiang, S. M. Webber, P. Bhattacharya and P. A. Thomas, *Phys. Rev. B*, **71**, 174114 (2005).
- [3] V. Shuvaeva, Y. Azuma, I. Raevski, K. Yagi, K. Sakaue, H. Terauchi, *Ferroelectrics*, **299**, 103 (2004).
- [4] K. Nomura, T. Shingai, N. Yasuda, H. Ohwa and H. Terauchi, *Ferroelectrics*, **128**, 69 (1998).
- [5] Y. Yoneda, N. Matsumoto, H. Terauchi and N. Yasuda, *J. Phys.: Condens. Matter*, **15**, 467 (2003).
- [6] T. Egami and S. J. L. Billinge, *Underneath the Bragg Peaks: Structural Analysis of Complex Materials*, Oxford: Pergamon/Elsevier, (2003).
- [7] T. Egami, *Ferroelectrics*, **222**, 183 (1999).
- [8] T. Egami, *Ferroelectrics*, **267**, 101 (2002).
- [9] M. Akbas and P. K. Davies, *Commun. Amer. Ceram. Soc.*, **80**, 2933 (1997).
- [10] N. Yasuda, H. Inagaki and S. Imamura, *Jpn. J. Appl. Phys.*, **31**, L574 (1992).
- [11] Y. Yoneda, N. Matsumoto, Y. Furukawa and T. Ishikawa, *J. Synchrotron Rad.*, **8**, 18 (2001).
- [12] Y. Yoneda, N. Matsumoto, Y. Furukawa and T. Ishikawa, *Nuclear Instruments and Method in Physics Research A*, **467-468**, 370 (2001).
- [13] Y. Yoneda, K. Suzuya, J. Mizuki and S. Kohara, *J. Appl. Phys.*, **100**, 093521 (2006).
- [14] S. Teslic, T. Egami and D. Fiehland, *J. Phys. Chem Solids*, **57**, 1537 (1996).

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