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# Defect-induced phase separation in relaxor $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ crystals

Y Yoneda<sup>1</sup>, N Matsumoto<sup>1</sup>, H Terauchi<sup>2</sup> and N Yasuda<sup>3</sup>

<sup>1</sup> Synchrotron Radiation Research Centre, Japan Atomic Energy Research Institute, Sayo-gun, Hyogo 679-5148, Japan

<sup>2</sup> Department of Physics, Kwansai-Gakuin University, Sanda, Hyogo 669-1337, Japan

<sup>3</sup> Electrical and Electronic Engineering Department, Gifu University, Gifu 501-1193, Japan

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## Abstract

Thermal properties of ordered and disordered  $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PIN) single crystals were investigated. For the ordered PIN, typical thermal anomalies were observed at the antiferroelectric transition temperature. These anomalies were degraded and disorder appeared during heating processes. The defect-induced phase separation provided a good account of the instability of the relaxor and antiferroelectric states of the PIN crystals.

## 1. Introduction

Complex lead-based perovskite-type ferroelectric materials  $\text{Pb}(\text{B}, \text{B}')\text{O}_3$  with ordered and disordered cation (B, B') arrangements in the octahedral lattice positions have been of fundamental and practical interest for several years [1–4]. As for the compositional fluctuation, it was reported that the chemical ordering of B-site cations can be controlled by relevant thermal treatment for some relaxors such as  $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PIN),  $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PSN), and  $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$  (PST) [5–8]. In general, the phase transitions in PIN crystals depend on the In/Nb arrangements on B-sites (chemical ordering,  $S$ ) in perovskite structures. Ordered PIN,  $S \geq 0.8$ , is isostructural with antiferroelectric  $\text{PbZrO}_3$  at room temperature [9] and shows antiferroelectric behaviour, while disordered PIN,  $S \leq 0.2$ , shows relaxor behaviour [10]. It is known that the difference between ordered and disordered PIN is governed by the degree of chemical order at the B-site. The structure of the disordered PIN at room temperature is rhombohedral ( $R3m$ ) and a rounded unsaturated  $P$ – $E$  hysteresis loop remains above  $T_m = 12^\circ\text{C}$ , around which the dielectric permittivity shows a diffuse maximum [11, 12]. On the other hand, the structure of the ordered PIN at room temperature is orthorhombic ( $Pbam$ ), and it shows a normal antiferroelectric phase transition [13]. The degree of chemical order was reported to be controlled by isothermal annealing at a suitable high temperature. However, the phase separation or phase transition between the disordered PIN and the ordered PIN has not been well understood.

There have been various models of relaxor materials: the compositional heterogeneity model [14, 15], the superparaelectric model [16], the Raman-field Potts model [17–19], and so on. These models explain the mechanism giving rise to the glassy and diffuse nature of the relaxors. In PIN crystals, the non-relaxor state ( $S \geq 0.2$ ) shows antiferroelectric properties, but the phase transition disappears in relaxor PINs. It is important to clarify the stability of relaxor and non-relaxor PINs from the standpoint of the disappearance of the antiferroelectric phase transition.

The stability of relaxor PIN has been investigated by x-ray diffraction [20] and dielectric measurements [11], and these show that the relaxor PINs can change into non-relaxor PIN at 0.4 GPa. On the other hand, the antiferroelectric phase transition of non-relaxor PIN has also been investigated by optical microscopy [21]; it was demonstrated that the phase transition occurs separately in each domain. The stability of relaxor materials should bear a relation to domains but little attention has been given to this point, which offers a key to understanding the relationships between domains and structure and between domains and phase transitions.

In this paper, we performed differential scanning calorimeter (DSC) measurements over and over again with PIN single crystals. As a result, we observed that the transition temperature shifted and the diffuseness grew as the number of repetition times increased. These observations suggest that the domain size is important for understanding the glassy nature of PIN crystals.

## 2. Experimental details

PIN single crystals were flux-grown from the  $\text{PbO-In}_2\text{O}_3\text{-Nb}_2\text{O}_5$  system in the temperature range from 1200 to 950 °C at a crystallization rate of 3 °C h<sup>-1</sup>; this was followed by cooling from 950 to 750 °C at a rate of 7 °C h<sup>-1</sup>. The as-grown samples are of the disordered type. The ordered crystals were prepared by annealing disordered crystals at 923 °C for 20 h. These crystals were cubic in shape with the perovskite-unit (100) plane.

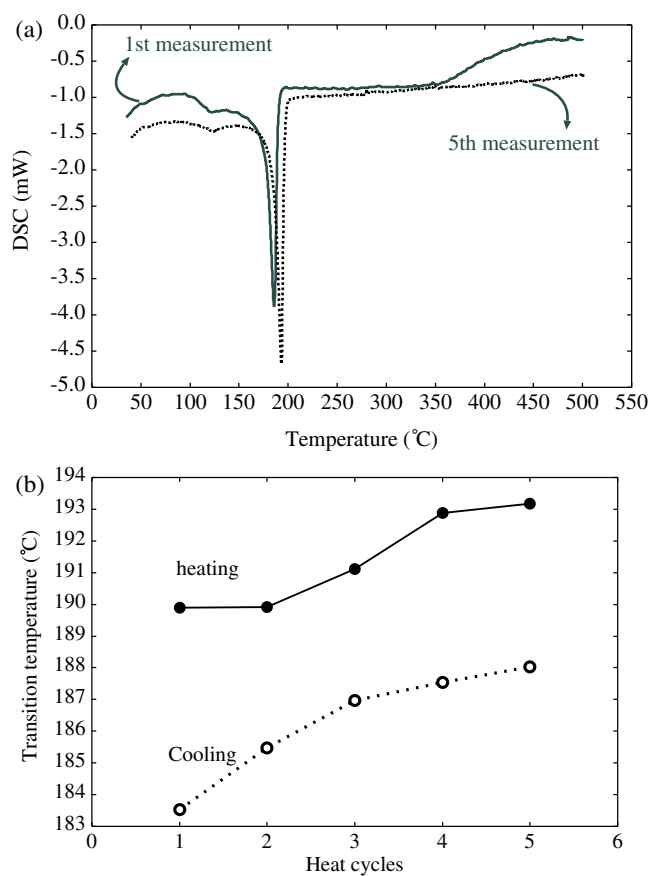
The chemical order parameter ( $S$ ) was calculated from (0.5 0.5 0.5) reflections of x-ray diffraction profiles. The estimated values for ordered and disordered PIN crystals were  $S = 0.8$  and 0.2, respectively.

Differential scanning calorimeter (DSC, Rigaku Model DSC8230D, Japan) analysis was performed in order to characterize the antiferroelectric phase transition of the PIN crystals.

## 3. Results and discussion

The thermal behaviours of the disordered and ordered PINs with the same chemical composition were characterized by DSC. First, we performed the DSC measurement with an ordered (antiferroelectric) PIN single crystal. Figure 1(a) shows the DSC curves obtained during the first and fifth heating processes. In the first measurement, the PIN sample was heated up to 500 °C and the same measurement was repeated five times. In the DSC curve of the first heating process, a clear heat anomaly at 189.9 °C which corresponds to the antiferroelectric phase transition, was observed. On the other hand, in the fifth heating process, the heat anomaly was observed at 193.0 °C. The heat anomaly shifted to higher temperature compared to the first measurement. The antiferroelectric transition temperature was shifted higher gradually, as the measurement was repeated, as shown in figure 1(b).

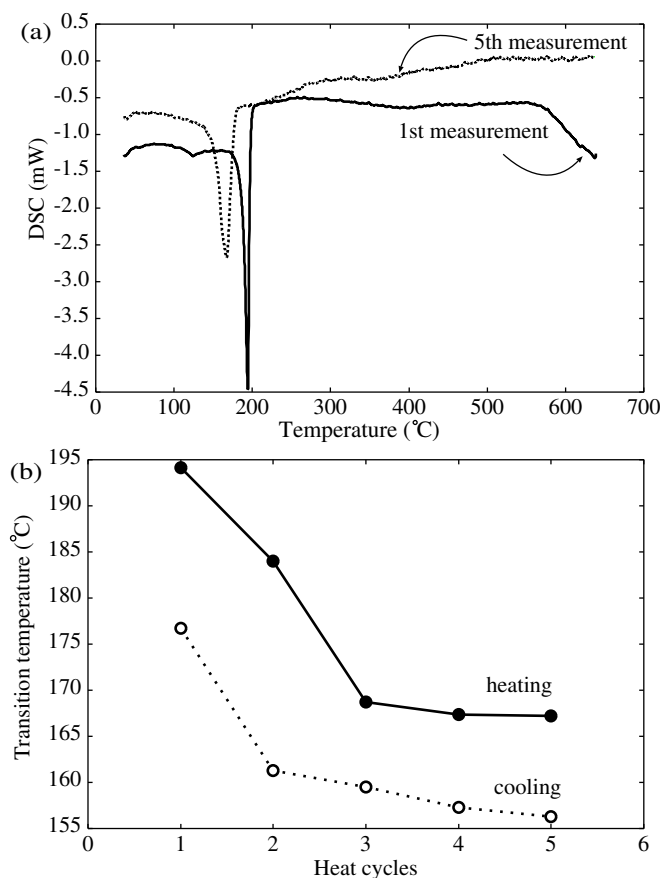
Then, we continued with the DSC measurement with the same ordered PIN single crystal. In the next five DSC measurements, the sample was heated up to 650 °C. Figure 2(a) shows the DSC curves of the first and fifth measurements. The DSC curve of the fifth measurement is



**Figure 1.** (a) DSC curves for an ordered PIN single crystal in the first (solid curve) and fifth (broken curve) measurements. (b) Antiferroelectric phase transition temperature versus measurement cycle for the sample heated to 500 °C. The open and closed circles are the transition temperatures of the heating process and that of the cooling process, respectively.

broader and the peak amplitude is smaller than those of the first measurement. This broadening was never observed when the PIN crystal was heated up to 500 °C. The sharp antiferroelectric phase transition of the ordered PIN crystal was changed to a diffuse and glassy phase transition through heating up to 650 °C. Moreover, the shift of the transition temperature was also different from that of the 500 °C heated measurements. Figure 2(b) shows the transition temperature dependence of the measurement cycles. In the previous measurements with heatings to 500 °C, the transition temperature was increasing, but in these measurements at 650 °C, the transition temperature was decreasing.

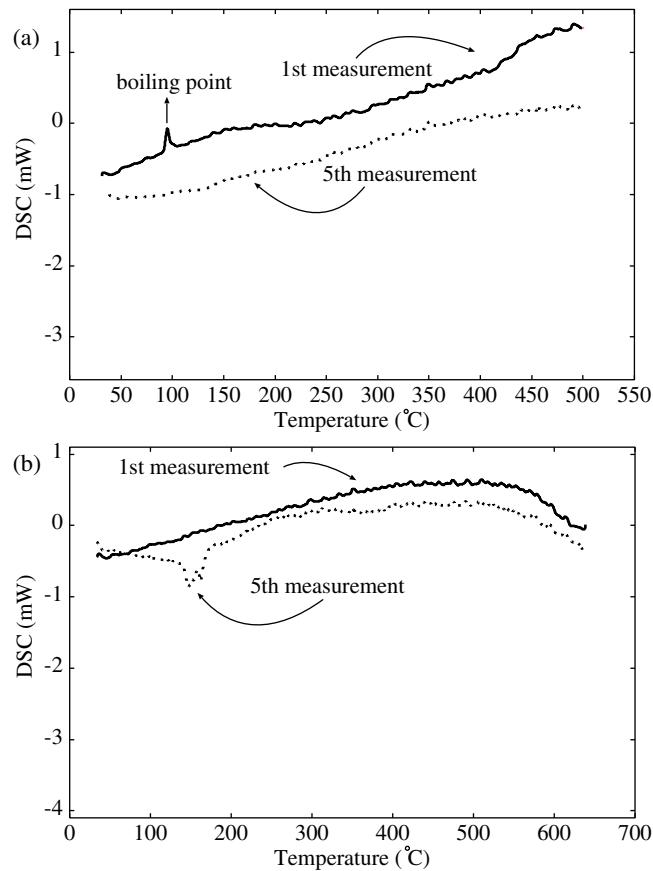
We attempted to extend the observation to a disordered PIN single crystal. The disordered PIN shows relaxor properties; therefore, the antiferroelectric phase transition around 200 °C is absent. The heat anomaly of the antiferroelectric phase transition was not observed, except a small anomaly that is the boiling point of water, as shown in figure 3(a). The disordered PIN did not seem to change in these heating processes up to 500 °C. Next, the DSC measurements were performed in the temperature range from RT to 650 °C. No anomaly was observed in the measurements from the first to the third heating processes up to 650 °C, but clear split anomalies of antiferroelectric phase transitions were observed in the fourth and the fifth heating



**Figure 2.** (a) DSC curves for an ordered PIN single crystal in the first (solid curve) and fifth (broken curve) measurements. (b) Antiferroelectric phase transition temperature versus measurement cycle for the sample heated to 650 °C. The open and closed circles are the transition temperatures of the heating process and that of the cooling process, respectively.

processes, as shown in figure 3(b). A difference in behaviour was also observed between the measurements up to 500 °C and those up to 650 °C even in the disordered PIN crystal. There is something of a transition point around 650 °C for both ordered and disordered PIN crystals.

There is sufficient evidence for a diffuse phase transition to show that the DSC curves of the ordered PIN were broadened and those of the disordered PIN were split. It follows from what has been said that the antiferroelectric phase transition occurred separately in each domain. The diffuse behaviour should be explained by the domain size. Large strains exist around the domain boundary to compensate different lattice parameters. As the domain size becomes smaller, the number of domain walls increases and lattice strain is also increased. Since the antiferroelectric PIN crystal is free from large strains, the phase transition occurs at lower temperatures. Therefore, the antiferroelectric phase transition temperature lowers as the domain size gets smaller, and the phase transition shows diffuse behaviour. The domain size rule helps to account for the result of the DSC measurements. For example, the transition temperature of the ordered PIN in the temperature range below 500 °C was shifted higher as the measured cycle increased, as shown in figure 1(b). The domain size grew bigger in this

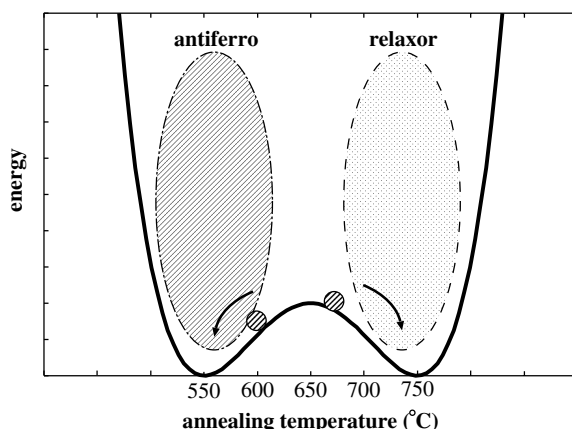


**Figure 3.** DSC curves of disordered PIN single crystal. The temperature range of the measurement is (a) from RT to 500 °C and (b) from RT to 650 °C. The solid curves and broken curves show the first heating process and the fifth heating process, respectively.

process. When the antiferroelectric domain size was larger, the heat anomaly was sharper and the transition temperature was higher. The same observation applies to the DSC measurements of ordered PIN in the temperature range below 650 °C. In this process, the domain size was reduced. As a result, the domain size was smaller, the heat anomaly was broader, and the transition temperature was lower, as shown in figure 2(b).

The behaviours of DSC curves depended on the measured temperature. Both ordered and disordered PIN crystals showed differences in behaviour between the measurements up to 500 °C and those up to 650 °C. It is likely that a transition point exists around 650 °C. We can represent the transition diagrammatically, as shown in figure 4. The PIN crystals have two states: one is the antiferroelectric state and the other is the relaxor state. These states are divided by an energy barrier around 650 °C. When the annealing temperature is below 650 °C, the energy barrier cannot be got over and the antiferroelectric PIN crystal cannot change to the relaxor state, and vice versa.

Judging from the above, there is some domain reconstruction around 650 °C. We would like to focus attention on what controls the domain size. The most likely explanation is the defects. The size of ferroelectric and antiferroelectric domains depends on defect density and defect distribution. When defect density is large and the defects spread uniformly, the domain



**Figure 4.** The coordinate diagram of PIN crystals. The two-state configurations are distinguished by a small energy barrier, that corresponds to 650 °C. When PIN crystal is annealed around 650 °C, the crystal shows mixed properties: part of the crystal shows antiferroelectric properties and the other part shows relaxor properties.

cannot grow larger but remains small. In contrast, the domain can grow larger with unbalanced distribution. Since the relaxor PIN crystal is obtained by a rapid quench, the defect density should be larger and the defects should spread uniformly according to defect theory [22]. On the other hand, the defect density should be small and the defects should not spread uniformly in the antiferroelectric PIN crystal, because the PIN is obtained through slow cooling. From this viewpoint, one may say that the domain size of PIN crystals was controlled by defect formation. The defect distribution should be changed because of defect migration around 650 °C. The energy barrier around 650 °C in figure 4 is the migration energy of defects which is determined by defect mobility. It would be possible to argue for frequency dispersion around  $T_m$ . Since the relaxor PIN consists of small multi-domains, the dielectric constants depend on the size of the domains. This domain size dependence will lead to the dielectric dispersion that is peculiar to relaxor materials.

If the relaxor and antiferroelectric states of PIN crystals depend on the domain size, this helps to explain their structure. At the domain boundary, the perovskite lattice is strained to compensate for the different lattice parameters and they would become the average. The smaller the domain size, the greater the domain boundary increase. As a result, the lattice parameters of the tetragonal structure are expected to be equalized, and the crystal structure changes to pseudo-cubic. Indeed, the cell parameters of the perovskite unit in the antiferroelectric phase are  $a = b = 4.116 \text{ \AA}$ ,  $c = 4.115 \text{ \AA}$ , and that in the relaxor phase is  $a = 4.113 \text{ \AA}$ ; the cell parameter of the pseudo-cubic phase is very close to the average of tetragonal cell parameters. This model makes it possible to interpret the order parameter  $S$  of PIN crystals. Since the long-range order structure cannot grow with a large defect density, the superlattice peak is hardly observed and the order parameter  $S$  is almost equal to zero. In contrast, the intensity of the superlattice peak is large and  $S \simeq 1$ , since the long-range order grows with slight defects. When the structure is transformed to pseudo-cubic because of equalization of cell parameters, the antiferroelectric phase no longer exists. That is, the antiferroelectric phase transition disappears.

There is scope for further investigation of the defect-induced structure in PIN crystals. Usually, defect analysis is performed by diffuse x-ray scattering investigation. For ferroelectric and antiferroelectric materials, the diffuse x-ray scattering is very complicated, because it is

sensitive not only to defects but also to lattice strain from the domain boundary. It is difficult to obtain enough defect-origin diffuse scattering to allow analysis of the defect structure. Many structure analyses on relaxor materials have been performed by using x-ray [23–25] and neutron diffractions [26]. It is widely accepted that relaxor ferroelectrics are composed of two-state ferroelectric (antiferroelectric) and paraelectric materials, but there is still room for a considerable measure of disagreement regarding the detail of each structure. The averaged structure is concealed by defects, strain, and domains. If the relaxor consists of micro-domains, structure analysis should not be performed on long-range order but on short- and intermediate-range order. We are now trying to perform a pair distribution function analysis [27, 28] by using high-energy x-ray diffraction to determine the intermediate-range order structure of the PIN crystal. The results will be reported in the near future.

#### 4. Conclusions

We performed DSC measurements using ordered and disordered PIN single crystals. We observed the transition around  $650^\circ\text{C}$  from the ordered (antiferroelectric) state to the disordered (relaxor) state, and vice versa. This behaviour can be explained by defect migration. This model also explains various relaxor properties such as the structure of relaxor PINs, the disappearance of the antiferroelectric phase transition, and the glassy nature of the relaxor state. All of this amounts to saying that defects induce phase separation of relaxor and antiferroelectric states.

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