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Structural study of the intermediate phase of the ferroelastic $Pb_3(PO_4)_2$ crystal

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Mechanical measurements showed that the structural anomalous region of $Pb_3(PO_4)_2$ exists in the range between 175 and 195 °C. It was shown that the intermediate phase has a different mechanical behavior from both the paraelastic and ferroelastic phases, and has a strong bias-stress dependence. In this region, no domain structure could be observed by using a polarizing microscope, but it had a still switching behavior according to mechanical measurements. This suggests that there microdomains of a smaller size than several hundred nm still exist in the rhombohedral paraelastic phase.

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I. INTRODUCTION

The precursor phenomena have attracted considerable attention in the recent years, particularly in connection with martensitic transformations in metals. The incompleteness of the lattice instability leads to the first-order nature of the phase transition. Various kinds of pretransitional phenomena around the martensitic transformation have been reported.[1–4]

One of the precursor phenomena is the appearance of anomalous satellite reflections at noncommensurate positions as observed in diffraction experiments. Salamon, Meichle, and Wayman observed satellites at the commensurate reciprocal lattice points of the low-temperature phase in the high-temperature phase of TiNi, and they called this reciprocal lattice a "ghost lattice."[5] Fuchizaki and Yamada discussed the anomalous instability in the diffraction pattern observed as a precursor of first-order phase transitions on a phenomenological basis and reported that the anomaly is characterized by the incommensurability that is dependent on the reference Brillouin zone.[6]

Lead phosphate, $Pb_3(PO_4)_2$, was first observed to be ferroelastic by Brixner *et al.*[7] This material was considered a prototype of ferroelastics and much research concentrated on elucidation of the physical origin of its ferroelasticity. This crystal undergoes a first-order ferroelastic phase transition at $T_c = 180\,^\circ\mathrm{C}$. Salje *et al.* had discussed the intermediate phase between 180.4°C and 300 °C for the first time.[8,9] And Salje and co-workers suggested that the low-temperature monoclinic phase of $Pb_3(PO_4)_2$ coexists with a high-temperature rhombohedral phase between 180 and 300°C.[10–12] And they had studied the critical exponents of specific heat for pure $Pb_3(PO_4)_2$ and the isostructural mixed crystals $Pb_3(P_{1-x}As_xO_4)_2$.[10] In their result, they have reported not only the pure crystal but also shows the anomaly near 257 °C, from a slight change in the slope of the specific heat (C_p). The added small arsenic, As, changed the anomaly temperature and induced an additional anomaly at near 300 °C.

Kiat *et al.* reported such an effect as a precursor effect in the nonmetallic material lead phosphate.[13] Their investigation provided the observation of an anomalous incommensurability in the temperature range between 180 and 300 °C of lead phosphate. They had reported that the symmetry of lead phosphate is in fact $C2$.[13] But contradictory results also exist regarding the structure. Bleser *et al.* reported the the real symmetry is $C2/c$ and the $C2$ structure could be induced by the defect.[14] So up to now the structural situation is not clear. This study reveals the existence of monoclinic microdomains of $Pb_3(PO_4)_2$ above T_c in rhombohedral structure through a mechanical measurement and neutron diffraction experiment.

II. EXPERIMENTS AND DISCUSSION

Figure 1(a) is a schematic diagram of the thermomechanical analysis system for the measurement of the strain under stress (TMA/SS). The lead phosphate samples were prepared in the form of a rod parallel to the (100) plane, and both ends of the samples were fixed inside the temperature-controlled chamber with a temperature precision of 10 mK in the TMA/SS system. To measure the temperature of the sample, the Pt-Rh thermocouple was located as close to the sample as possible. The sample geometry for the mechanical measurement is presented in Fig. 1(b) and the dimension of the specimen is 15 mm×3.5 mm×1 mm. The lead phosphate crystal has three permissible orientation states, but the samples generally included domains of two orientation states.[15] Accord-

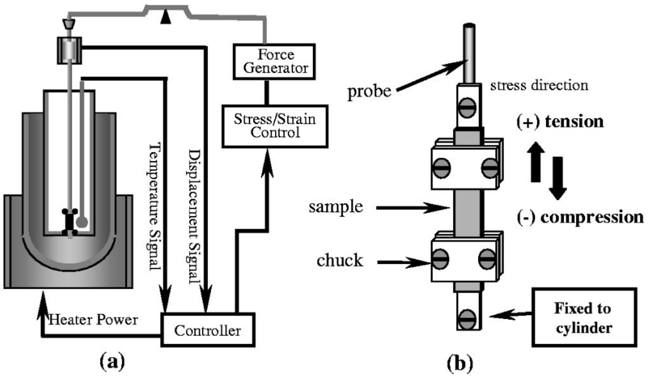

FIG. 1. (a) The schematic diagram of the thermomechanical analysis system for the measurement of the strain under stress. (b) The sample geometry of the thermal expansion and hysteresis loop measurements.

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ing to the preparation conditions, a sample could be mainly oriented to the *b* axis or *c* axis, and it can be switched to the other orientation under external stress.[16,17] In the thermal expansion coefficient measurements, static stress was used. But for a hysteresis loop measurement, periodic sinusoidal stress whose frequency and amplitude are 0.02 Hz and 0.6 MPa, respectively, was used in all measurements. The stress was applied to probe connected with the end of sample by stainless steel chucks. The other end of sample was fixed in the cylinder also by a stainless chuck. As shown Fig. 1(b), a tensile stress corresponds to the positive direction and a compressive corresponds to the negative one. The resolution of stress and strain is 0.01 gf and 0.02 μm, respectively. It is possible to obtain typical ferroelastic hysteresis loops directly because the sinusoidal stress could make domains full switching by tensile (positive) stress and compressive (negative) stress. For the switching by only a stress, it is important to minimize the effect of thermal strain attributed by any temperature difference between the start and stop points in the loops. In hysteresis loop measurements, the heating rate was 0.3 °C/min and the temperature during per one cycle was 0.24 °C. This difference did not affect the total change of strain during one stress cycle; we could obtain typical stress-strain hysteresis loops in the result.

To investigate the structural details of the anomalous region above T_c of lead phosphate, a high-resolution powder diffractometer (HRPD) by neutron scattering in HANARO (High-Flux Advanced Neutron Application Reactor) at KAERI (Korea Atomic Energy Research Institute) was used. The measurements were carried out at 12 different temperatures using a thermal neutron beam of wavelength 1.8347 Å obtained from 90° reflection of a Ge(331) monochrometer. Thirty-two $_3$He multidetectors were used in 12 ranges for the detection. From the neutron scattering, more information could be obtained about the relatively small atoms such as P and O in comparison with Pb than through x-ray diffraction measurements.

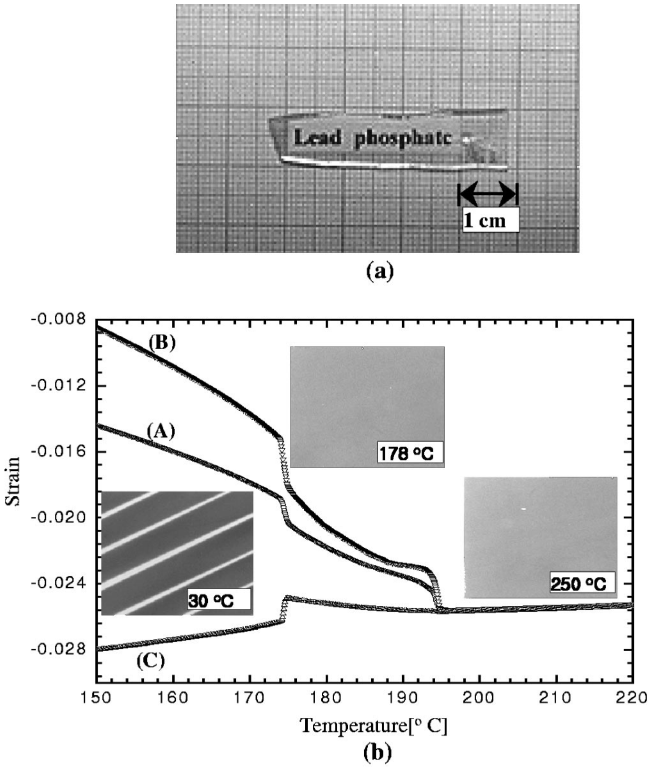

FIG. 2. (a) Photograph of the grown Pb3$(PO_4)_2$. (b) The thermal expansion in the function of the temperature under (A) zero, (B) 0.8 MPa, and (C) −0.8 MPa external bias stress and the polarizing microscope images of sample at several temperatures.

A. mechanical study using a thermomechanical analysis system

The lead phosphate crystals were grown by the by the Czochralski method. The photograph of crystal was shown in Fig. 2(a).[16,17] The crystal growing process was repeated with a new seed crystal of improved quality. Figure 2 presents the strain change of samples as a function of the temperature. Curve (A) shows the thermal expansion under zero bias external stress. Curves (B) and (C) show the changes in the thermal expansion through the switching under external stresses of 0.8 MPa and −0.8 MPa, respectively. To obtain curve (B), the sample was cooled by applying the positive bias external stress of +0.8 MPa at 300 °C and, at room temperature, removing the bias stress and then continuously measuring curve (B). Curve (C) was also measured after undergoing the process of cooling under applying a negative bias stress of −0.8 MPa at 300 °C and removing it at room temperature. Curve (B) shows that the sample was more distinctively switched to the *b* axis than at curve (A), and the negative thermal expansion of the *b* axis was also presented by the x-ray diffraction (XRD) measurement.[13] On the other hand, curve (C) shows that the sample was switched to the *c* axis, and the positive thermal expansion of the *c* axis was compared with the XRD results. The anomaly at 175 °C corresponds to the known ferroelastic phase transition temperature T_{c} and is observed at temperatures lower than 180 °C, which was investigated by other measurements such as the polarizing microscope and differential scanning calorimetery (DSC). The temperature difference was caused by the structure of the measurement system. The nonlinear behavior of the thermal expansions below T_{c} is due to the switching of the ferroelastic domains. Compared to curve (A), curve (B) shows the larger strain change and is analogous to the temperature dependence of the lattice parameter *b* with the negative thermal expansion coefficient.[11,13] Curve (C) shows the same positive thermal expansion as the lattice parameter *c*, meaning that the domains of curve (B) are oriented more to the *b* axis by the positive bias stress and those of curve (C) are oriented more to the *c* axis by the negative bias stress. The thermal expansions above 195 °C showed exactly linear behaviors and it was shown that the sample had a high-temperature rhombohedral phase above 195 °C. In the temperature range between T_{c} and 195 °C, anomalous thermal expansion behavior could be observed. The magnitudes of the thermal expansions were reduced distinctly, but still showed nonlinear and different temperature dependences than those below T_{c}. To reveal the details of this anomalous region, the mechanical measurements and optical observations were conducted using a polarizing microscope. The best way to prove the existence of a domain is to measure the stress dependence of the sample because domains must have a certain stress dependence such as domain switching.

The photographs of domains in each phase are shown in Fig. 2(b). In our direct observation using the polarizing microscope, no domains could be found in the temperature range of the anomalous region, meaning that the size of domains must be smaller than several hundred nm in the phase. The high-temperature normal phase should not show any stress dependence by domain switching under applied stress. In other words, if one observes no stress dependence of the domain, the phase must be a paraelastic phase. All responses found by several mechanical measurements were linear, and no stress dependence was found above 195 °C. In contrast, the stress dependence in the range between T_c and 195 °C differed in some ways from that in the ferroelastic phase.

To prove the existence and behavior of the microdomains in the region between T_c and 195 °C, the temperature dependence of thermal expansion coefficients, $\alpha = d\varepsilon/dT$, was investigated under various bias stresses. Here ε is strain. Figure 3(a) shows the results of thermal expansion coefficients under various levels of positive bias stress. The temperature dependence of the thermal expansion coefficient under 0 Pa is the same as the temperature derivative of the thermal expansion. As shown in Fig. 3(a), the peaks at 177 and 195 °C correspond to the anomalies at T_c and 195 °C in Fig. 2, respectively. The extrapolated line from the curve above 195 °C can be assume as a zero basis. The deviation from the extrapolated line denotes the nonlinear behavior of the thermal expansion. Under 0 Pa of the bias stress, the spreading of the curve in the ferroelastic phase below T_c is somewhat larger than that of the paraelastic phase above 195 °C, indicating that continuous domain growth exists through domain switching in the ferroelastic phase.

The data points in the outlying area of the main curve are assumed to be due to an abrupt strain change caused by discontinuous domain switching. The curve in the temperature range between T_c and 195 °C also shows a spread, but it is somewhat smaller than that of the ferroelastic phase, suggesting that a domainlike behavior also exists in this range.

With increasing bias stress, the spread of the curve in the ferroelastic phase became larger, and the spread of the curve increase proportionally to the bias stress. From these results, it can be seen that the bias stress promotes domain growth and discontinuous domain switching.

With increasing bias stress, the curve in the ferroelastic phase deviates much more from the extrapolated line in the high-temperature rhombohedral phase, and the nonlinear behavior of the thermal expansion in the ferroelastic phase increases distinctly with increasing bias stress.

The most striking feature in $Pb_3(PO_4)_2$ is the bias stress dependence of the thermal expansion coefficient above T_c. Under zero bias stress, a small anomaly T_{pin} could be observed around 180 °C, just above T_c. With increasing bias stress, the anomaly at T_{pin} increased distinctly and shifted to a higher temperature.

In the temperature range between T_c and 195 °C, it was found that the higher the bias stress, the larger the spread of the curve. Under a bias stress of 1.2 MPa, the spread of the curve become very large in the temperature range between 175 and 182 °C. This suggests that in the temperature range between T_c and T_{pin}, the domains existing in this region have a bias stress-sensitive switching mechanism and, at T_{pin}, the domains seem to be pinned. Approaching 195 °C from T_{pin}, the nonlinear behavior decreases. In this temperature range, the growth and switchings of the domains are strongly reduced and the domains are assumed to be constricted by the stabilization of the high-temperature rhombohedral structure with increasing temperature. Finally, the nonlinear behavior disappears at 195 °C. The disappearance of the nonlinear behavior indicates the disappearance of the domains and that the phase above 195 °C has a completely high-temperature rhombohedral structure.

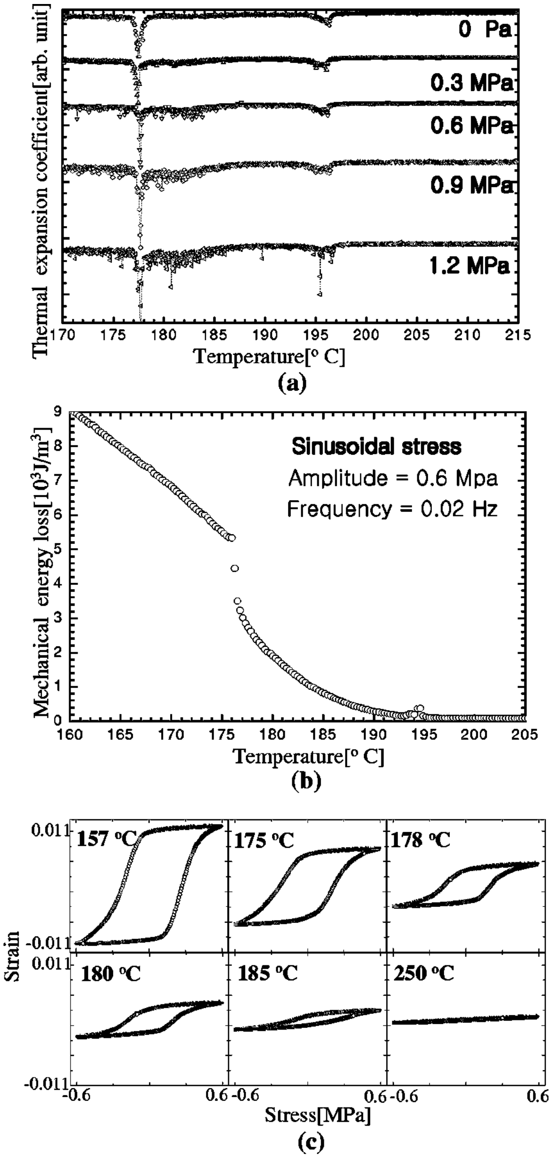

FIG. 3. (a) The temperature dependence of the thermal expansion coefficients under various positive bias stresses on heating. (b) The temperature dependence of the mechanical loss energy. (c) Ferroelastic stress-strain hysteresis loops at several temperatures.

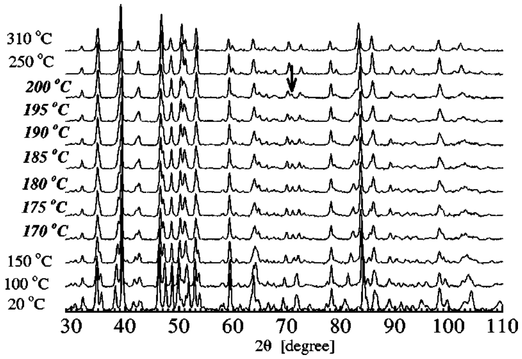

FIG. 4. The temperature dependence of the high-resolution powder diffraction pattern (HRPD) by the neutron scattering.

Figure 3(b) represents the change of mechanical energy loss, $W=\oint_{cycle}\sigma\, d\varepsilon$, calculated from the area of hysteresis loops at each temperature. Here σ is the applied stress. A hysteresis loop measured in this study could not show the absolute values of strain and stress, but only the relative comparison of the magnitude of the strain at some different temperatures. The energy loss abruptly decrease at 175 °C and gradually decreased up to the second anomaly about 195 °C. The several hysteresis loops are also shown in Fig. 3(c). The loop at 157 °C showed the typical shape of a ferroelastic phase and that of 250 °C showed the line shape which means a paraelastic phase. The amplitude and area of hysteresis loops gradually decrease in the range between T_c and 195 °C. This could clearly reveal the existence micodomain having switching properties similar with domain of the ferroelastic phase in this region. But in the range between T_c and 195 °C, the temperature dependences of the hysteresis loops were different from that below T_c.

Such a mechanical anomalous region in $Pb_3(PO_4)_2$ was found in other ferroelastic materials such as $RbMnCl_3$, $KMnCl_3$, $LiCsSO_4$, and K_2ZnCl_4, even though their physical behavior and structure are not exactly the same.[18,19] A new dielectric anomaly was also found at 250 °C above the ferroelastic phase transition at 145 K in K_2ZnCl_4 and was distinguished from other new dielectric anomalies T_x at around 280 °C in the commensurate phase caused by a stabilization process of discommensurations.[18]

B. Neutron scattering study of lead phosphate single crystal

Figure 4 presents the neutron diffraction pattern measured at various temperatures, and the figure shows a distinct difference in the anomalous region, not only from the low-temperature ferroelastic phase, but also from the high-temperature rhombohedral phase. The diffraction patterns between 175 and 195 °C correspond to the mechanical anomalous region. The peak of the marked position is the ghost peak, which is possible only in a monoclinic structure, persisted up to nearly 200 °C.

Figure 5 shows the results obtained by the Rietvelt refinement method for the ferroelastic monoclinic phase at 20 °C, the high-temperature rhombohedral phase at 310 °C, and the structural anomalous region at 190 °C. The dotted line is the observed data, the solid line is the calculated value, the bars are the Bragg positions shown in the low field, and the curve at the bottom denotes the difference between the observed data and the calculated value. The results at 20 °C [Fig. 5(a)] show that the crystal has a monoclinic structure with lattice parameters of $a=13.8069$ Å, $b=5.6944$ Å, $c=9.4276$ Å, and $\beta=102.36°$, and the observed data agree well with the calculated Bragg positions. The phase at 310 °C [Fig. 5(b)] corresponds to the high-temperature rhombohedral structure with lattice parameters of $a=5.5535$ Å and $\beta=102.36°$, and the observed data also agree well with the calculated values. However, the results at 190 °C [Fig. 5(c)] did not fit well with any single phase of the high- or low-temperature phase, but fitted only with both structures of the high- and low-temperature phases. This suggests that the structure in the anomalous region is neither the monoclinic single phase nor

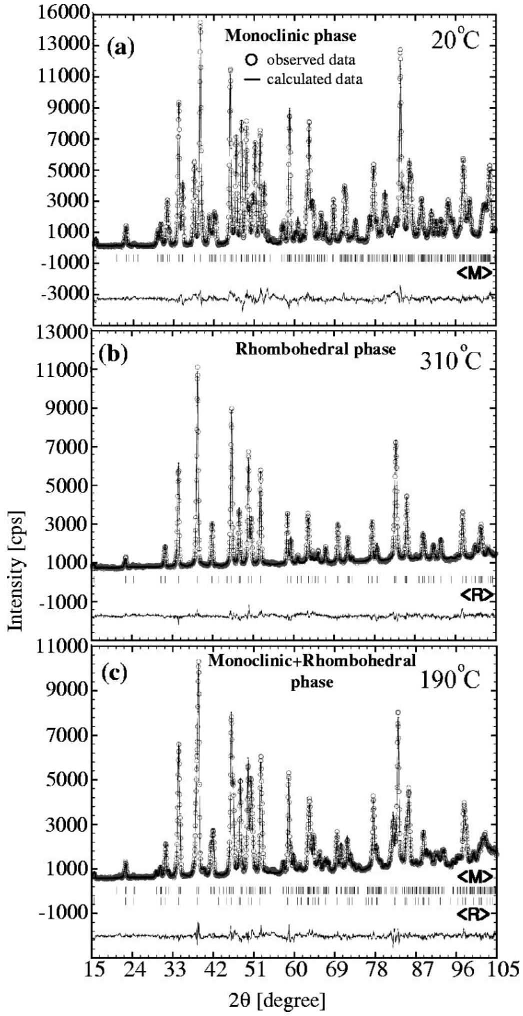

FIG. 5. The results of the refinement of the neutron diffraction pattern of (a) the ferroelastic monoclinic phase at 20 °C, (b) the high-temperature rhombohedral phase at 310 °C, and (c) the anomalous region at 190 °C. [The observed intensity data are plotted in the upper field. The calculated patterns shown in the same field as a solid-line curve. The difference observed minus the calculation, is shown in the low field. The short vertical bars in the middle field indicate the possible Bragg positions of monoclinic (a), rhombohedral (b), and both monoclinic and rhombohedral (c).]

the rhombohedral single phase, but a mixture of the monoclinic and rhombohedral phases.

No distinct domain structure could be observed through the polarizing microscope in this region, but in the mechanical measurements, the anomalous region still showed ferroelasticity, meaning that the region between T_c and 195 °C can have domains of invisible size. The results of neutron scattering revealed the coexistence of the monoclinic and rhombohedral phases, supporting strongly the belief that in this region, the monoclinic structure exists in the form of microdomains with a size below a few hundred nm in the rhombohedral phase.

III. CONCLUSION

This study investigated the temperature dependence of the mechanical properties of $\mathrm{Pb_3(PO_4)_2}$. It was found that the region have both monoclinic microdomain and rhombohedral structures coexist in the temperature range between 175 and 195 °C. The nonlinear behavior of the thermal expansion in anomalous region between 175 and 195 °C was clearly different not only from that of the paraelastic phase, but also that of the ferroelastic phase, indicating that domain switching still exists in this region.

The structural study through neutron scattering confirmed that the high-temperature phase and low-temperature phase coexist in this region. The neutron diffraction pattern could be systematically reproduced by assuming that the satellite precursor peaks prepare the low-temperature structure and are sitting at the commensurate position of the low-temperature lattice, whereas the fundamental Bragg reflections construct the high-temperature reciprocal lattice. This behavior of the diffraction pattern is a ghost lattice effect and is considered to be a signature of the premartensitic regime. This results indicate that the ghost lattice distorts strongly the rhombohedral matrix and the structural deformation is due to monoclinic precursor effect.[10,13]

Based on the results of an observation using a polarizing microscope, mechanical measurements, and a structural study using neutron scattering, we suggest the possibility that in the structural and mechanical anomalous regions, the monoclinic microdomains with smaller sizes than several hundred nm exist within the rhombohedral high-temperature phase and disappear with increasing temperature from 195 °C.

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