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# X-Ray Topographic Study of $NaNO_2$ near the Curie Temperature

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The domain structure of $NaNO_2$ near the Curie point, $T_c$, was studied by X-ray topography. The topographs were obtained above and below $T_c$ using 011 and 042 reflections. The hysteresis phenomenon of the domain structure for heating and cooling process was observed. The 042 surface reflection topographs gave the domain structure near the specimen surface in ferroelectric phase and the satellite reflection in anti-ferroelectric phase. The change in crystalline state near the surface was detected in the range of 10°C below $T_c$. The mechanism of the polarization reversal by the external electric field was also studied at just below $T_c$.

The ferroelectric $NaNO_2$ crystal has body-centered orthorhombic structure $C_{2v}^{20}$-$Im2m$ below the Curie temperature $T_C = 163°C$. The cell parameters are $a = 3.560$, $b = 5.563$ and $c = 5.384$ Å at room temepraturе.[1] The crystal takes sheet-like antiparallel domains with boundaries parallel to $a$-plane. The previous X-ray topographic study[2] has shown the domain walls of the order of one micron thick with a definite crystal structure. In order to see the behaviour of $NaNO_2$ crystal near $T_C$, X-ray topographs from a specimen set in a small electric furnace were examined. The $NaNO_2$ crystal was grown from the melt by slow cooling method at the cooling rate of 20°C per day. A good part of the crystal block was selected and sliced by wet thread saw. Plate-like specimens with dimensions of about 10, 0.6 and 4 mm in $a$, $b$ and $c$ directions respectively were used. X-ray source was fine focus X-ray tube with Cu target worked at 45 kV and 3 mA. The apparent focus size was $0.1 \times 0.1$ mm$^2$. The electric furnace was made of nichrome wires which were installed in a brass capsule. The furnace was mounted on the goniometer head of Lang camera. The atomospheric temperature stabilized by a controller was detected by chromel-alumel thermocouple. There was a temperature gradient of $0.3 \sim 0.8$°C/mm in the specimen in vertical direction ($a$-axis). The local temperature in the specimen was determined by detecting the transition temperature of 042 reflection whose intensity showed very sharp temperature dependence near $T_C$. The initial stage of the specimens were consisted of a large number of 180 domains whose average thickness was a few tens of microns. The 180 domains at room temperature were revealed as dark and light bands in 011 topographs owing to the anomalous dispersion effect as was shown in the previous paper[2] and in Fig. 1(b). The contrast of the domain wall itself is not seen in this reflection. In 042 topograph, however, only the domain walls are revealed as horizontal white lines as shown in Fig. 3(a). The X-ray diffraction topography has shown the hysteresis phenomenon of the domain structure in the heating and cooling processes and the change in the crystalline state of the specimen surface in the range of 10°C below $T_C$.

*Heating process*

Figure 1(a) shows the temperature dependence of 011 intensity near $T_C$. When the specimen was heated above room temperature, the domain structure remained substantially same unless the temperature approaches close to the transition point. If narrow domains exist at room temperature, the coalescence of such narrow domains to the adjacent wider domains was observed at a few degrees below $T_C$. Figure 1(c) is an 011 topograph taken at $T_C - 3$°C from the corresponding part of Fig. 1(b) which was taken at 23°C. These topographs clearly show the coalescence of the narrow domains near $T_C$. The coalescence was also observed in 042 surface reflection topographs as a fact that the distances between the neighbouring white lines (domain walls) became larger near $T_C$ compared with

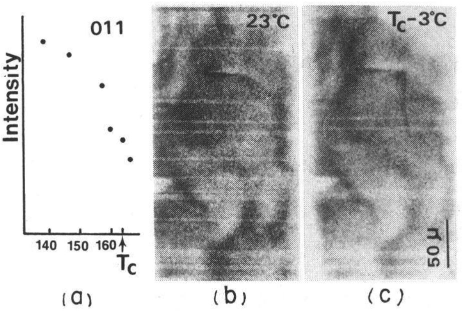


Fig. 1. (a) Temperature dependence of Cu 011 reflection, 011 topographs taken at (b) 23°C and (c) $T_c-3$°C.

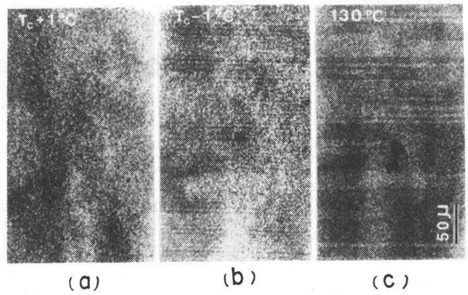


Fig. 2. Cu 011 topographs taken at (a) $T_c+1$°C, (b) $T_c-1$°C and (c) 130°C.

those at room temperature. On heating, the 011 diffracted intensity changed gradually around $T_C$ (Fig. 1(a)) and the domain contrast has disappeared completely above $T_C$ giving only the uniform image (Fig. 2(a)). No anomaly of the image contrast was detected at around the Néel temperature, $T_N=164.5$°C. The 042 diffracted intensity showed very steep change near $T_C$ (Fig. 4(a)) and the image disappeared at above $T_C$.

*Cooling process*

When the specimen temperature was lowered from above $T_C$, quite remarkable change in the domain structure was observed. A large number of narrow domain-like contrast of a few microns thick have appeared at just below $T_C$ (Fig. 2(b)). The sharp image in Fig. 2(b) means that the narrow patterns were stable during the exposure time of about ten hours. They have lasted for longer than a week during this experiment. Such narrow domains were also observed in 042 topographs as white lines with narrow spacings. They have changed into the ordinary wide domain pattern below $T_C-10$°C. Such narrow patterns did not appear in the heating process. This hysteresis phenomenon was repeatedly observed in several heating and cooling cycles. In Fig. 2 are compared the section patterns taken at $T_C+1$°C (Fig. 2(a)), at $T_C-1$°C in the cooling process (Fig. 2(b)) and at 130°C (Fig. 2(c)).

*Surface state*

In 042 surface reflection topographs which gives mainly the image from the region near the specimen surface, the band-like domain structure was observed in the temperature range of about 10°C below $T_C$ (Fig. 3(b)). It looks similar to the domain pattern in 011 topograph at room temperature whose contrast was due to the anomalous dispersion effect. However the band-like contrast was not observed in 042 transmission topograph of separately prepared specimen which was taken to see the interior of the specimen by 042 reflection. The band-like contrast was changed by rapid temperature change of about 10°C per hour (Fig. 3(c)) and wall parts are seen as dark lines there. And it went back again to the smooth band when the specimen temperature was kept at a few degrees below $T_C$ for a few days. The origin of the band-like contrast is not clear at this moment. But the topographs show that the crystalline state of the specimen surface sensitively changes with the temperature.

*Intermediate state*

In Fig. 4(a) is shown the temperature dependence of 042 intensity. The 042 surface reflection topograph taken at just $T_C$ at cooling process is shown in Fig. 4(b) where the upper part is in antiferroelectric (A. F.) phase and the lower part is in ferroelectric (F) phase. Black and white band are seen near the F. and A. F. phase boundary. The width of the white region

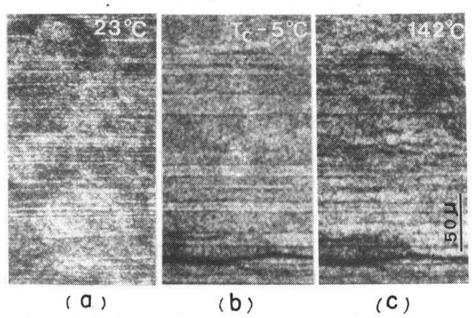


Fig. 3. Cu 042 surface reflection topographs taken at (a) 23°C, (b) $T_c-5$°C and (c) 142°C.

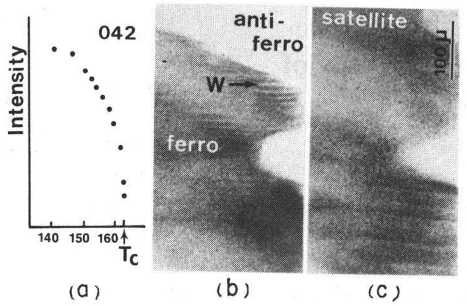


Fig. 4. (a) Temperature dependence of 042 reflection, (b) 042 surface reflection topograph taken at $T_c$ and (c) $\frac{1}{8}$ 42 satellite topograph.

W in Fig. 4(b) become narrower at lower temperature region, namely, at the region far from the phase boundary. These white bands have the thickness of several microns near the phase boundary, and shrink into the narrow white lines at lower temperature region. These white regions will correspond to the intermediate state regions, that is, the expanded domain walls. This suggests that the structure of the domain wall plays an important role in the A.F. to F. phase transition.

*Satellite topograph*

In Fig. 4(c) is shown a topograph taken at about $T_C+0.5°C$ from the corresponding part of Fig. 4(b) using satellite reflection $\frac{1}{8}42$.[3] There is some intensity modulation which was not observed in ferroelectric state. The origin of the satellite contrast is not made clear yet. But the detailed study of such satellite topograph will give further information on the crystalline state of A.F. phase.

*Polarization reversal*

An external d.c. electric field of 100 V/mm was applied normal to the surface of the polydomain specimen for several seconds at a few degrees below $T_C$. And the regions outside of the electrodes were observed. It was found that the domain structure has started to be destructed from the surface near negative side of the electrodes. The boundary region between polydomain and single domain regions is not clear, because there is intermediate state region which would have the domain wall structure. The kinetics of the poling was similar to that at room temperature.[4] The crystal takes a metastable structure as an intermediate state before completing the polarization reversal.

In conclusion, X-ray topography has shown the hysteresis phenomenon of the domain structure, surface state at just below $T_C$, satellite topograph and polarization reversal process. The topographic study can give many information on the change in the secondary structure, especially on the important role of the domain wall. The details of the study will be reported soon.

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