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X-ray diffraction study on the phase transitions of $(CH_3NH_3)_3Bi_2Br_9$ crystal

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X-ray scattering experiments of methylammonium nonabromobismuthate, $(CH_3NH_3)_3Bi_2Br_9$ were carried out in order to study of the nature of the phase transitions. Temperature dependences of lattice parameters and x-ray profiles were obtained, indicating the domain structure in low temperature phases. Discontinuous changes of lattice parameters corresponding to the first order phase transitions of I-II, II-III, III-IV were observed. In the phase III, the volume of the unit cell was larger than that of adjacent phases II and IV. The relation of $\Delta\gamma$ and spontaneous strain in ferroelastic phases (II, III and IV) and the symmetry of phase II are discussed .

1. INTRODUCTION

The alkyl-ammonium halogenometallic group compounds [$(CH_3NH_3)_5M_2X_{11}$, $(CH_3NH_3)_3M_2X_9$ (M=Sb,Bi; X=Cl,Br,I)] have attracted much interest, because they show a variety of phase transitions and ferroelectric and ferroelastic properties[1-12]. It was considered that these successive phase transitions were related to freezing of reorientational motion of methyl-ammonium cations. Methylammonium nona-bromobismuthate; $(CH_3NH_3)_3Bi_2Br_9$ (abbreviated to MABB) is one of the above compounds and undergoes successive phase transitions. At room temperature (phase I), MABB shows "plastic-like" properties[6,10]. A crystal structure of MABB at room temperature was considered to belong a trigonal system with space group of $P\bar{3}m1$ and to be isomorphous with $Cs_3Bi_2Br_9$[13]. Methylammonium cations occupy the vacancies inside a corrugated layer of $(Bi_2Br_9^{3-})_n$ polyanions. One methylammonium cation is situated at the positions of $\bar{3}m$ symmetry in the layer of polyanions and others are situated at the positions of 3m symmetry between the layers. These cations have a large freedom of rotation motion possessing dynamically spherical symmetry[14]. With decreasing temperature, MABB undergoes three first-order phase transitions to phases II, III and IV at T_1=188K, T_2=140K and T_3=102K respectively[10]. These three phase transitions were related to the freezing process of the methyl ammonium cations, but the details were not clear. From the measurements of dielectric permittivity under hydrostatic pressure, it was found that the region of the phase III became narrower with increasing pressure and vanished at the triple point of 50MPa and 128K[11]. From the observation of domain structure and the pyroelectric measure-ment, it was reported that the phases II, III and IV showed ferroelasticity and the phase IV showed ferroelectricity[12]. There were no structural data of MABB crystal of low temperature phases, for instance temperature dependence of lattice parameters and space group etc. The purpose of this study is to examine the structural nature at each phase transition in $(CH_3NH_3)_3Bi_2Br_9$. We carried out x-ray scattering experiments of MABB using a single crystal.

2. EXPERIMENTAL

The single crystals of MABB were grown by the slow evaporation method at 30°C from the aqueous solution of stoichiometric mixture of CH_3NH_3Br and $BiBr_3$ with great excess of HBr(about 40%). The evaporation rate was adjusted so that crystals of centimeter size were formed in a period of several weeks. As-grown crystals were yellowish in color and had a perfect cleavage plane which is perpendicular to the trigonal unique axis. The specimen was cut out from mono-domain single crystal and its shape was nearly spherical with diameter of 0.38mm.

X-ray diffraction measurements were carried out by using an automatic four-circle diffractometer with a large χ -cradle, Rigaku AFC off-center type, with MoKα radiation (50kV,240mA) monochromatized by PG(002). A scintillation counter was used for a detector. The specimen was attached to a copper sample holder mounted in the cryostat. The specimen temperature was controlled within $\pm$ 0.1K , using a closed-cycle He-gas refrigerator and monitored with Au+0.07% Fe-chromel thermocouple.

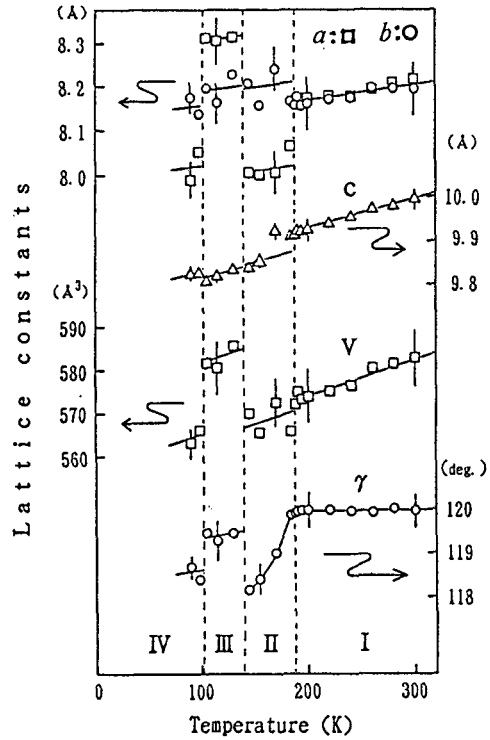

Fig.1 The temperature dependences of trigonal lattice parameters: a, b, c, γ and the volume of unit cell V

3. RESULTS AND DISCUSSION

X-ray diffraction data were collected for the temperature range of 300K to 90K. At each temperature the lattice constants were determined by least square method using the 15～24 Bragg reflections. Temperature dependences of lattice parameters are shown in Fig.1. At 300K (phase I), the value of the lattice parameter a was same as the lattice parameter b and the angle γ was 120° , indicating that the phase I belonged to the trigonal symmetry. This result was agreed with the result of Jakubas et al[10]. With decreasing temperature in the phase I , the lattice parameter a, b and c monotonously decreased and the angle γ remained the value of 120° . At 188K, the lattice parameter a decreased, while the lattice parameter b increased drastically, and the angle γ deviated from 120° . This drastic change indicated breaking of the trigonal symmetry due to the transformation from the high symmetry phase I to the low symmetry phase II. Further at 140K, the lattice parameters had a discontinuous change. The lattice parameter a increased and its value became larger than the lattice parameter b. The angle γ also changed and that value was near 120° Therefore, the volume of the unit cell of the phase III became about 3% larger. Finally at 102K, the discontinuous change of the lattice parameters occurred and the lattice parameter a decreased more than the lattice parameter b. As a result the volume of the phase IV became about

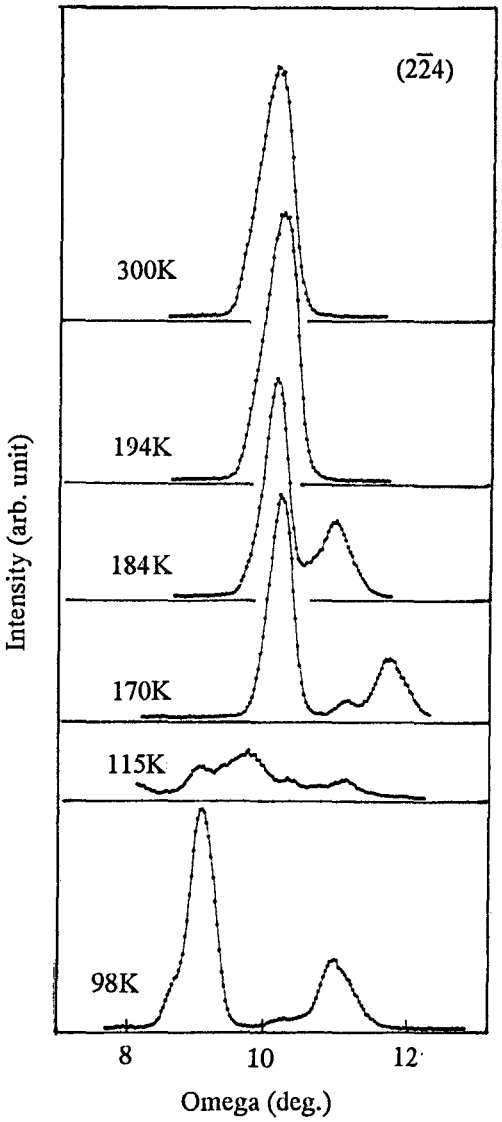

Fig.2 The rocking curves of (2$\bar{2}$4) Bragg reflection in the phase I (300K,194K), the phase I (184,170K), phase III (115K) and phase IV (98K). In phase III, the Bragg reflection was not observed at the (2$\bar{2}$4) of the reciprocal lattice point. In phase II and IV, three peaks were observed indicating the existence of the three kinds of domain structure.

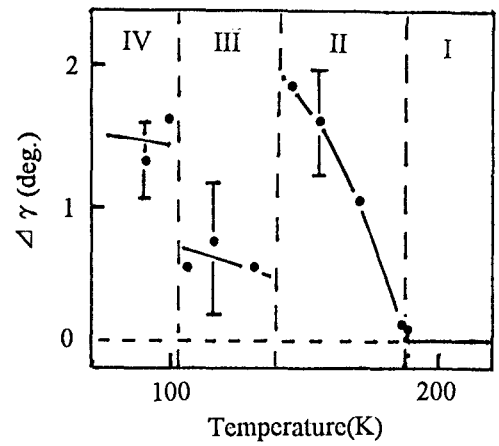

Fig. 3 The temperature dependence of the $\Delta\gamma$. This was component of the spontaneous strain.

3% smaller. These changes of the lattice parameters corresponded to the phase transitions of I-II, II-III and III-IV in MABB crystal. All of these phase transitions were first order transitions. The various rocking curves of the Bragg reflection of (2$\bar{2}$4) are shown in Fig.2 as a function of temperature. In the phase I (T > 188K), a single peak was observed. After the transformation from the phase I to the phase II (90K < T < 188K), it was considered that three kinds of domain related by the symmetry of three-fold rotation axis in the phase I were appeared. The profile at 170K in Fig.2 showed the appearance of the above three domain regions in MABB crystal. With decreasing temperature in the phase II, three peaks indicating the domain structure were separated by each other. This corresponds to the deviation of the angle γ from 120° . At 115K (phase III), these Bragg reflections suddenly disappeared. We could not observe this Bragg reflection any more. Below 102 K, however , the Bragg reflection of the (2$\bar{2}$4) appeared again. The observed reflection indicated the existence of three kinds of domain at least. From the results of the anomalous

behavior of the lattice parameters and the disappearance of the Bragg reflection of the $(2\bar{2}4)$ in the phase III, it was considered that the phase III in MABB was unstable phase. The disappearance of the phase III at the triple point was due to the above reason.

From the group theoretical consideration[12], if the I-II transition is induced at Γ-point and the phase II is nonpolar, the point group of the phase II is 2/m or $\bar{1}$. According to Aizu[15], in the case of 2/m the deviations from the trigonal angles $\Delta\gamma$, and either $\Delta\alpha$ ($=\alpha$-90°) or $\Delta\beta$ ($=\beta$-90°) are possible components of spontaneous strain while in the case of $\bar{1}$ all deviations are possible components of spontaneous strain. Therefore the $\Delta\gamma$ is a component of spontaneous strain, and the temperature dependence of the $\Delta\gamma$ is shown in Fig.3. In the phase II, the $\Delta\gamma$ appeared and increased with decreasing temperature. We could not observe the appearance of the $\Delta\alpha$ and $\Delta\beta$ within experimental error. In fact Iwata et al. observed that the diagonal element of elastic constant C_{66}(corresponding to $\Delta\gamma$) decreased to vanish toward T_1 and that C_{44} is almost independent of temperature in the phase I. Our results are consistent with this situation and we expect that the phase II has 2/m symmetry because of the existence of the lower temperature phases III and IV.

4. CONCLUSION

We have carried out x-ray diffraction experiments of MABB using a single crystal and obtained the temperature dependences of lattice parameters and diffraction patterns. It was revealed that low temperature phases are ferroelastic phases and $\Delta\gamma$ is spontaneous strain. The point group of the phase II is considered to be 2/m. In the phase III the volume of the unit cell was larger than that in the adjacent phases II and IV.

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