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Structures and Phase Transitions in Rb_2MoO_4 and Rb_2WO_4

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Abstract

The structural phase transitions of Rb_2MoO_4 and Rb_2WO_4 have been reinvestigated with the use of heat capacity measurement and synchrotron X-ray and neutron scattering techniques. In Rb_2MoO_4, the existence of polymorphous structures has been confirmed. These crystal structures at 290 K are a monoclinic β-K_2MoO_4 type one and an orthorhombic β-K_2SO_4 type one. In an annealed sample, two typical first-order-type anomalies were observed at 783 and 752 K. Furthermore, new λ-type anomaly equivalent to the second normal-incommensurate phase transition in A_2BO_4-type ferroelectrics was observed at 223 K. On the other hand, the crystal structure at 290 K of Rb_2WO_4 was a monoclinic β-K_2MoO_4 type one and no phase transition was detected down to 8 K.

Key word: Rb_2MoO_4, Rb_2WO_4, structural phase transition, structural analysis

I. Introduction

Many of the A_2BO_4-type crystals have the β-K_2SO_4 type structure (space group *Pnam*). Since the subgroup $Pna2_1$ is polar, the family of crystal has been investigated widely as a candidate of ferroelectrics. However, these crystals have not necessarily the same succession of the phase transition. According to an empirical rule about the ratio the ionic radius of A^+ to the average bond length B-O in the BO_4^{2-} tetrahedron, $r(A)/r(BO)$ [1], A_2BO_4-type crystals can be loosely classified into two main groups. When the ratio is less than 1.3 beyond 0.93 (group I), all compounds transform from the parent high-symmetry hexagonal phase (phase I, α-K_2SO_4 type, space group $P6_3/mmc$) to the orthorhombic phase (phase II, β-K_2SO_4 type, *Pnam*, normal, Z=4, a_0, b_0, c_0) at high temperatures ($T_{\text{I-II}}$ = 700 ~ 1100 K), for example A_2CrO_4, A_2SO_4, Rb_2SeO_4, Cs_2SeO_4 and Cs_2MoO_4 (A=K, Rb and Cs) [2]. When the ratio is under 0.93 (group II), there is another intermediate high-temperature incommensurate phase between phases I (α-K_2SO_4 type, $P6_3/mmc$) and II' (β-K_2MoO_4 type, $C2/m$), for example K_2WO_4 and K_2MoO_4 [3]. Although it is reported that Rb_2MoO_4 and Rb_2WO_4 have the monoclinic β-K_2MoO_4 type structures at room temperature and some phase transitions, at 503 and 773 K for Rb_2MoO_4 and at 568, 663 and 738 K for Rb_2WO_4, it has not clarified fully yet [4, 5].

Among the A_2BO_4-type crystals belonging to the group I, the low-temperature normal-incommensurate (N-INC) phase was observed only in K_2SeO_4. As temperature decreases K_2SeO_4 transforms from phase I to phase II and to a low-temperature incommensurate phase (phase III, ~$3a_0$, b_0, c_0), which is followed by a ferroelectric phase (phase IV, $Pna2_1$, Z=12, $3a_0$, b_0, c_0) [6]. In the case of K_2CrO_4 and Rb_2SeO_4, the calculated dispersion curves contain an unstable Σ_2 phonon branch [7], which is similar to those obtained for the prototype incommensurate material K_2SeO_4. But no transition is detected down to 0 K in K_2CrO_4 and Rb_2SeO_4. The calculated temperatures of hypothetical phase transitions are 4 K and -7 K for K_2CrO_4 and Rb_2SeO_4, respectively. However, a softening tendency of the Σ_2 phonon branch around 0.7a^* was observed in K_2CrO_4 [8] and Rb_2SeO_4 [2].

We have been studying the mechanism of normal-incommensurate phase transition and hypothetical one in A_2BO_4-type crystals. In Rb_2MoO_4 and Rb_2WO_4, because the value of $r(A)/r(BO)$ is nearly identical to 0.93, it was expected that the N-INC phase transition exists as similar to K_2SeO_4. In order to obtain additional information about structures and structural phase transitions in Rb_2MoO_4 and Rb_2WO_4, we performed heat capacity measurement, and synchrotron X-ray and neutron scattering experiments. The observed results and discussions are presented in the following.

II. Experimental

Powder samples of Rb_2MoO_4 and Rb_2WO_4 were prepared by the solid-state reaction method in air at 900 K for 24 hours using Rb_2CO_3, MoO_3 and WO_3 as starting materials. Furthermore, single crystals of Rb_2MoO_4 were grown by a slow evaporation method from a saturated ammonium solution of Rb_2CO_3 and MoO_3 at 310 K. By a preliminary X-ray diffraction analysis, crystal systems for powder samples and single crystal samples in Rb_2MoO_4 were confirmed orthorhombic and monoclinic, respectively. Single crystal samples were annealed in air at 500 K for 4 hours before measurements in order to get the orthorhombic morphotype.

A heat capacity measurement was carried out by using a heat capacity measurement module, Quantum Design PPMS, in the temperature range from 2 to 300 K. Above 300 K, different scanning calorimeter (DSC) measurement was carried out on a SEIKO DSC220 at a heating rate 5 $\mathrm{Kmin^{-1}}$. The heat capacity of the empty calorimeter in DSC was calibrated by the use of sapphire as a standard sample.

X-ray powder diffraction measurements with a large Debye-Scherrer camera were performed using the synchrotron radiation source at the BL15XU beam line of SPring-8 [9]. Incident beam was monochromatized at λ = 0.65297 Å. Neutron powder diffraction experiments were also performed by using the Kinken powder diffractometer for high efficiency and high resolution measurements, HERMES, of Institute for Materials Research, Tohoku University, installed at the JRR-3M reactor in Japan Atomic Energy Research Institute (JAERI), Tokai [10]. Neutrons with a wavelength of 1.8196 Å were obtained by the 331 reflection of a Ge monochromator. These diffraction data were analyzed using the Rietveld method (RIETAN-FP) [11].

III. Results and discussion

Figure 1 shows X-ray powder diffraction patterns of annealed Rb_2MoO_4 at 290 K. Although the crystal structure of non-annealed sample is the monoclinic β-K_2MoO_4 type, the crystal structure of annealed sample is orthorhombic (β-K_2SeO_4 type structure, space group *Pnam*). The orthorhombic structural parameters were refined by least-squared calculations, and final results are given in Table 1. The R-factors R_{wp} (weighted pattern R-factor), R_p (pattern R-factor) and R_e (expected R-factor) are 6.65 %, 4.78 % and 0.27 %, respectively. The value of $r(A)/r(BO)$ is determined as 0.943, with using the ionic radius of A^+ (8-coordinated site) 1.61 Å and A^+ (11-coordinated site) 1.69 Å [12], and the bond lengths B-O in the tetrahedral BO_4^{2-} ion 1.724(5), 1.735(5), 1.771(8) and 1.771(8) Å. Below T_3 (about 230 K) the superlattice reflections appeared at the position ($\sim h/3$, k, l), where h, k and l denote the Miller indices in the normal phase ($T_3 < T < T_2$), similar to K_2SeO_4 (group I). Therefore, the low-temperature phase transition at T_3 is a N-INC phase one. Among A_2BO_4 crystals, annealed Rb_2MoO_4 is the second example that possesses the N-INC phase transition. At 290 K, it has been confirmed that the crystal prepared by the solid-state reaction method is orthorhombic β-K_2SO_4 type structure.

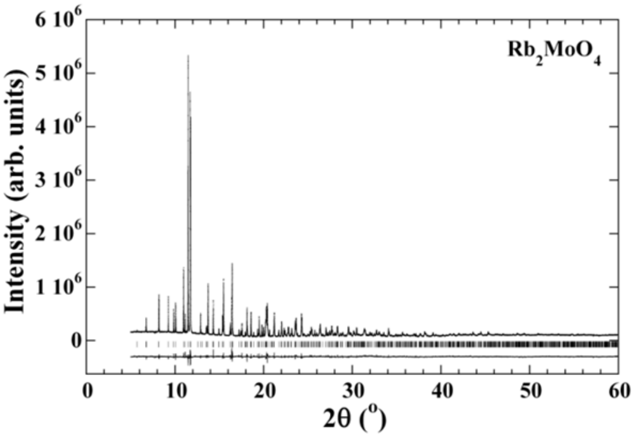

Fig. 1 X-ray powder diffraction patterns of annealed Rb_2MoO_4 at 290 K. The positions shown by dot-marks represent observed diffraction data. The continuous solid-line is the calculated profile from Rietveld refinement, and small vertical markers show the positions of all the allowed Bragg reflections in the *Pnam* space group of Rb_2MoO_4. The lower curve represents the difference between the observed and the calculated profiles.

Figure 2 shows the molar heat capacity measured in the annealed sample of Rb_2MoO_4. Two anomalies due to the high-temperature phase transitions are observed at T_1 = 783 and T_2 = 752 K, such as K_2WO_4

and K_2MoO_4 (group II), which are very sharp and of first-order nature. The entropies of transition ΔS_1 and ΔS_2, and the enthalpies of transition ΔH_1 and ΔH_2 are estimated to be 4.11 $Jmol^{-1}K^{-1}$, 3.88 $Jmol^{-1}K^{-1}$, 3.22 $kJmol^{-1}$ and 2.92 $kJmol^{-1}$, respectively. Furthermore, λ-type anomaly was also observed at $T_3 = 223$ K ($\Delta S_3 =$ 1.043 $Jmol^{-1}K^{-1}$, $\Delta H_3 =$ 0.229 $kJmol^{-1}$). The transition points reported around 503 and 773 K was not confirmed by our study both crystals grown by the solid-state reaction method and the slow evaporation method.

Table 1 Final positional parameters and isotropic atomic displacement parameters of annealed Rb_2MoO_4 at 290 K: Space group; *Pnam*. a_0 = 8.0926(1) Å, b_0 = 11.0998(1) Å, c_0 = 6.3739(1) Å and V = 572.536(9) $Å^3$.

Atom	x	y	z	B($Å^2$)
Rb1	0.6687(1)	0.4198(1)	0.25	2.21(4)
Rb2	0.9987(2)	0.7104(1)	0.25	2.13(4)
Mo	0.2185(1)	0.4210(2)	0.25	1.22(3)
O1	0.0058(8)	0.4297(7)	0.25	4.32(20)
O2	0.3130(9)	0.5613(7)	0.25	2.99(18)
O3	0.2830(6)	0.3442(6)	0.0206(10)	3.35(20)

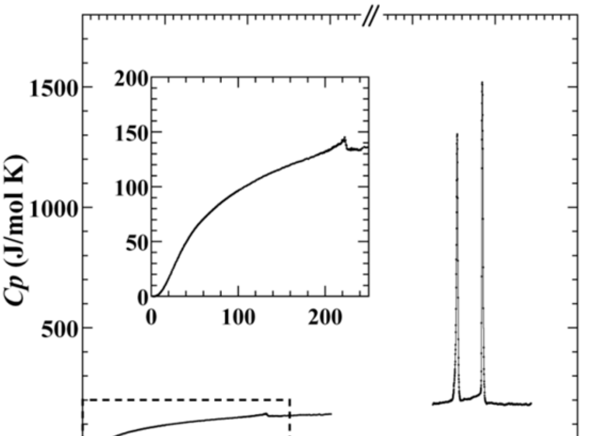

Fig. 2 Molar heat capacity measured in annealed Rb_2MoO_4.

On the other hand, at room temperature Rb_2WO_4 takes monoclinic *β*-K_2MoO_4 structure (space group *C*2/*m*), which retains down to 8 K. The *R*-factors at 290 K obtained were as follows; R_{wp} 5.37 %, R_p 4.15 %, and R_e 3.34 %, respectively. The value of *r*(A)/*r*(BO) in determined as 0.926. Neutron powder diffraction patterns and the final structural parameters are shown in Figure 3 and Table 2, respectively.

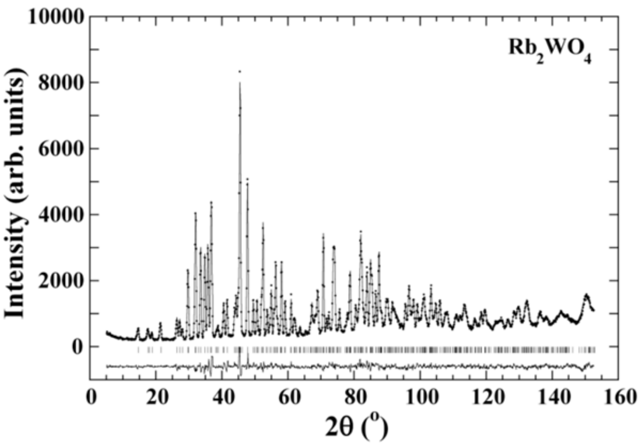

Fig. 3 Neutron powder diffraction patterns of Rb_2WO_4 at 290 K. The positions shown by dot-marks represent observed diffraction data. The continuous solid-line is the calculated profile from Rietveld refinement, and small vertical markers show the positions of all the allowed Bragg reflections in the *C*2/*m* space group of Rb_2WO_4. The lower curve represents the difference between the observed and the calculated profiles.

Table 2 Final positional parameters and isotropic atomic displacement parameters of Rb_2WO_4 at 290 K: Space group; *C*2/*m*. *a* = 12.8338(5) Å, *b* = 6.2827(2) Å, *c* = 7.8505(3) Å, *β* = 115.794(2) and V = 569.92(77).

Atom	x	y	z	B($Å^2$)
Rb1	0.5088(3)	0	0.2367(4)	1.56(8)
Rb2	0.8442(3)	0	0.2572(4)	2.04(8)
W	0.1761(4)	0	0.2256(6)	1.56(11)
O1	0.3255(3)	0	0.3760(5)	2.19(10)
O2	0.0903(3)	0	0.3533(5)	2.15(9)
O3	0.1429(2)	0.2312(4)	0.0807(3)	1.88(8)

Here, lattice parameters ratio a_0/c_0 in the *β*-K_2SO_4 type structure are adopted as an additional parameters for the group I, where the *a*-axis is a pseudo-hexagonal axis and $b_0 \cong \sqrt{3}c_0$. In fact, the value of a_0/c_0 for our annealed Rb_2MoO_4 are determined as 1.270. According to the rigid body motion analysis and Brown theory [13, 14], A(1) (11-coordinated site) ion is the main one that produces the different type of transitions, and the rotation of the tetrahedral BO_4^{2-} ion around the *c*-axis is important to remain the orthorhombic *β*-K_2SO_4 type structure. The rotation contributes to change the lattice parameter ratios a_0/c_0 ($\cong \sqrt{3}a_0/b_0$) and a_0/b_0. Figure 4 shows the relationship between lattice parameter ratios a_0/c_0 and phase transition temperatures of representative A_2BO_4-type crystals, which belong to the group I. The values obtained for a_0/c_0 and T_3 are 1.270 and 223 K in annealed Rb_2MoO_4, 1.277 and 131 K in K_2SeO_4, 1.297 and 4 K in K_2CrO_4, 1.292 and -7 K in Rb_2SeO_4, and 1.302 and -111 K in Ce_2SeO_4, respectively. The N-INC phase transition temperature increases loosely with decreasing lattice parameter ratio a_0/c_0.

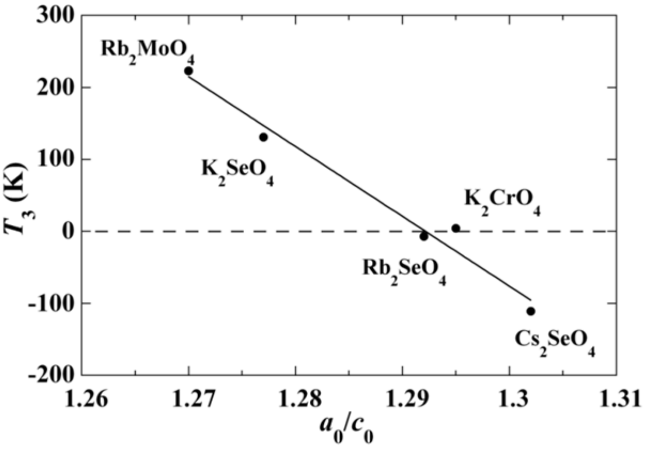

Fig. 4 The relationship between the lattice parameter ratios a_0/c_0 and the N-INC phase transition temperatures of some A_2BO_4-type crystals belonging to the group I. Here, the temperature 4 K for K_2CrO_4, -7 K for Rb_2SeO_4 and -111 K for Cs_2SeO_4 are calculated values in ref 7. The existence of the transition in K_2CrO_4 was not confirmed by experimental studies in ref 8.

In conclusion, A_2BO_4-type crystals can be classified by both ratios of $r(A)/r(BO)$ and a_0/c_0 . Annealed Rb_2MoO_4 has both characters of groups I and II and is expected to undergo the succession of phase transition: the high-symmetry hexagonal phase (α-K_2SO_4 type) – intermediate high-temperature incommensurate phase – orthorhombic phase (β-K_2SO_4 type) – low-temperature incommensurate phase. Unfortunately, it is not clear the connection between another room temperature phase (monoclinic β-K_2MoO_4 type) and the suggested successive phase transition. In annealed Rb_2MoO_4, the new phase transition at T_3 is considered as a displacive-type transition with a typical soft phonon mode. Furthermore, the existence of a lock-in transition below T_3 can be expected, so the inelastic neutron scattering and X-ray scattering studies are now in progress.

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