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# STRUCTURES AND PHASE TRANSITIONS IN $(K_{1-x}Rb_x)_2SeO_4$

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The phase diagram of the mixed crystal $(K_{1-x}Rb_x)_2SeO_4$ was determined by means of thermal analysis and neutron scattering experiments. The hexagonal to orthorhombic phase transition line exists for any *x*. The normal-incommensurate phase transition temperature decreases continuously with increasing Rb content. However, the incommensurate–commensurate phase transition was not observed except for $K_2SeO_4$. According to the clear softening of the $\Sigma_2$–$\Sigma_3$ phonon branches and the finite frequency at 0 K for x>0.34, an existence of the hypothetical phase transition was confirmed.

***Keywords:*** *DSC, heat capacity, $K_2SeO_4$, neutron scattering, $Rb_2SeO_4$, structural phase transition*

## Introduction

$Rb_2SeO_4$ and $K_2SeO_4$ belong to a family of $A_2BX_4$-type (*X*=Br, Cl and O) crystals with the β-$K_2SO_4$-type structure. As temperature decreases, $Rb_2SeO_4$ transforms from a high-temperature hexagonal phase I (space group $P6_3/mmc$) to an orthorhombic phase II (space group *Pnam*) at $T_{I\text{-}II}$=821 K [1]. No phase transition exists at lower temperatures and the melting point is observed at $T_m$=1233 K. On the other hand, in $K_2SeO_4$ three phase transitions and melting occur at temperatures of $T_{I\text{-}II}$=745 K, $T_i$ =127.7 K, $T_C$=95.1 K and $T_m$=~1270 K [2, 3]. The four phases are summarized as follows: phase I ($T>T_{I\text{-}II}$, space group $P6_3/mmc$), phase II ($T_{I\text{-}II}>T>T_i$, *Pnam*, *Z*=4, $a_0$, $b_0$, $c_0$), phase III ($T_i>T>T_C$, incommensurate, ~3$a_0$, $b_0$, $c_0$) and phase IV ($T_C>T$ , $Pna2_1$, *Z*=12, 3$a_0$, $b_0$, $c_0$), where $a_0$, $b_0$ and $c_0$ are unit cell parameters of phase II. Among a lot of $A_2BX_4$-type crystals, a typical soft phonon mode was clearly observed in $K_2SeO_4$ both above and below the normal-incommensurate (N-INC) phase transition point, $T_i$, by neutron scattering [4, 5]. That is to say, the transition in $K_2SeO_4$ is interpreted as displacive type one. On the other hand, since the soft mode above N-INC transition point in $Rb_2ZnBr_4$, $Rb_2ZnCl_4$, and $K_2ZnCl_4$,was not observed, it was thought that their transition type was order-disorder one. For many $A_2BO_4$-type crystals such as $K_2SO_4$, $K_2CrO_4$, $Rb_2SeO_4$ and $Cs_2SeO_4$, the N-INC transition has never been reported. However, in the case of $K_2CrO_4$, and $Rb_2SeO_4$, the calculated dispersion curves contain an unstable $\Sigma_2$ phonon branch [6], whose qualitative and quantitative features are similar to those obtained for the prototype incommensurate material $K_2SeO_4$. Furthermore, the calculated hypothetical transitions for many $A_2BO_4$-type crystals are shown in [6]. Indeed, a softening tendency of the $\Sigma_2$ phonon branch was observed in $Rb_2SeO_4$ [1].

In order to get further information about the successive phase transitions in $A_2BX_4$-type crystals, especially to determine the phase diagram and to investigate the existence of the hypothetical phase transition, we have performed heat capacity and neutron scattering experiments in $(K_{1-x}Rb_x)_2SeO_4$.

## Experimental

Single crystals of $(K_{1-x}Rb_x)_2SeO_4$ (*x*=0, 0.12, 0.23, 0.34, 0.42, 0.54, 0.62, 0.72, 0.82, 0.90 and 1.00) were grown by a slow evaporation method from a saturated aqueous solution containing the salts $K_2SeO_4$ and $Rb_2SeO_4$ in different molar ratios at 310 K. About four months were needed to grow large single crystals. The obtained crystals were colorless and transparent. Samples were annealed in air 400 K for five hours before an experiment to avoid an influence of water contamination. K and Rb content were determined using inductively coupled plasma atomic emission spectrometry. As a results of phase analysis by X-ray diffraction, it was confirmed that all samples of the general formula $(K_{1-x}Rb_x)_2SeO_4$ have a single phase with the orthorhombic (space group *Pnam*) symmetry at room temperature.

A heat capacity measurement was carried out using a Quantum Design PPMS heat capacity measure-

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ment module in the temperature range from 2 to 200 K. The single-crystal specimens were used and the mass was from 2 to 5 mg. Above 200 K differential scanning calorimetry (DSC) measurements were carried out using a Seiko DSC220 at a heating rate of 10 K min$^{-1}$. The phase transition point was determined from the temperature at which the DSC curve began to change. For $(K_{1-x}Rb_x)_2SeO_4$ ($x$=0.12, 0.34 and 0.54), neutron scattering experiments were performed by use of the triple-axis spectrometers (4G, T1-1 and C1-1) at JRR-3M reactor of the Japan Atomic Energy Research Institute. In the 4G spectrometer, a fixed incident neutron beam of $k_i$=2.5790 Å$^{-1}$ was used for measuring high-energy excitation and high-angle reflections. A PG filter and the beam collimation 40'–40'–40'–40' were employed. On the other hand, the T1-1 and C1-1 spectrometers were used for requiring a high energy resolution. The used conditions were following: PG filter, $k_i$=2.555 Å$^{-1}$ and open–40'–40'–40' collimation for T1-1, and Be filter, $k_i$=1.544 Å$^{-1}$ and 80'–80'–80'–80' collimation for C1-1. In all spectrometers, a crystal with a size greater than 5.0 cm$^3$ was mounted in an aluminum can filled with pure helium gas and set in a closed-cycle refrigerator which was cooled by cryogenics in the temperature range 8 to 300 K. The data collections were carried out in the ($a^*$, $c^*$) scattering plane and the measurements of phonon dispersion were performed along the line 002–202 for C1-1 and the line 004–204 for 4G and T1-1.

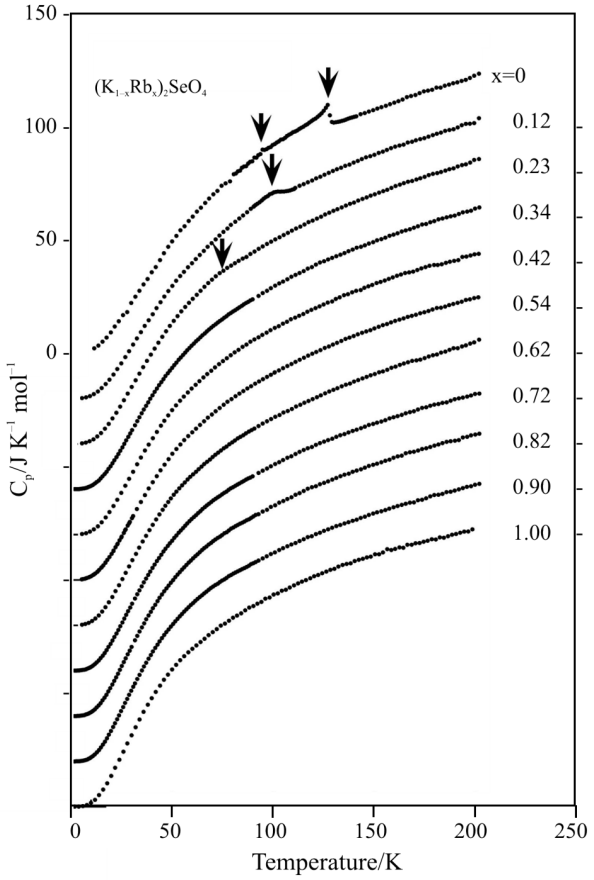


**Fig. 1** Measured molar heat capacity of $(K_{1-x}Rb_x)_2SeO_4$. Anomalous peaks are indicated by arrows

## Results and discussion

Figure 1 shows the measured molar heat capacity. Anomalies due to the phase transitions were observed at 128 and 95 K for $K_2SeO_4$, at 101 K for $(K_{0.88}Rb_{0.12})_2SeO_4$ and at ~75 K for $(K_{0.77}Rb_{0.23})_2SeO_4$. The N-INC transition temperature decreases continuously with increasing Rb content. On the other hand, phase transition was not observed at $T_C$ except for $K_2SeO_4$. The excess heat capacities due to the transition were estimated by subtracting the normal portion of the heat capacity [2]. In $K_2SeO_4$, the heat-capacity anomaly due to the phase III-to-IV transition is very sharp and very small. Furthermore, it sits on the tail of the heat-capacity anomaly due to the N-INC phase transition. Therefore, the excess heat capacity due to the two transitions was estimated with no distinction. In $K_2SeO_4$, our experimental values are in fair agreement with the already reported results [2], and the total entropy of transitions $\Delta S$ and the total enthalpy $\Delta H$ are estimated to be 1.01 J mol$^{-1}$K$^{-1}$ and 0.116 kJ mol$^{-1}$, respectively. For $(K_{0.88}Rb_{0.12})_2SeO_4$, we obtained $\Delta S$=0.68 J mol$^{-1}$ K$^{-1}$ and $\Delta H$=0.063 kJ mol$^{-1}$. For $(K_{0.77}Rb_{0.23})_2SeO_4$, it was difficult to estimate the entropy and the enthalpy because the anomalous peak was very broad.

DSC signals are shown as a function of temperature in Fig. 2. All anomalies due to the phase I (space group $P6_3/mmc$)-phase II ($Pnam$) transition are observed in the temperature range of 740 to 830 K. At $x$<0.54, the transition temperature $T_{I\text{-}II}$ and the magnitude of the anomalous peaks are almost equivalent. On the other hand, at $x$>0.54, the peak intensities and the phase transition at $T_{I\text{-}II}$ increase continuously with increasing Rb content.

The acoustic branch makes anticrossing with the optical branch, and the optical (lowest $\Sigma_2$–$S_3$ phonon) branch becomes soft with decreasing temperature. Figure 3 shows the phonon dispersion curves of the lowest $\Sigma_2$–$\Sigma_3$ phonons along the ($\xi$ 0 0) line below room temperature. An important result of the lattice dynamics calculations is that in $A_2BO_4$-type crystals the unstable phonon branch is either optical or acoustic, but anticrossed with an optical branch [6, 7]. Indeed, in the case of $K_2SeO_4$, the clear softening of the $\Sigma_2$ branch originates in the anticrossing of the acoustic branch with an optical one; the unstable branch is the prolongation of the lowest $\Sigma_2$–$\Sigma_3$ optical

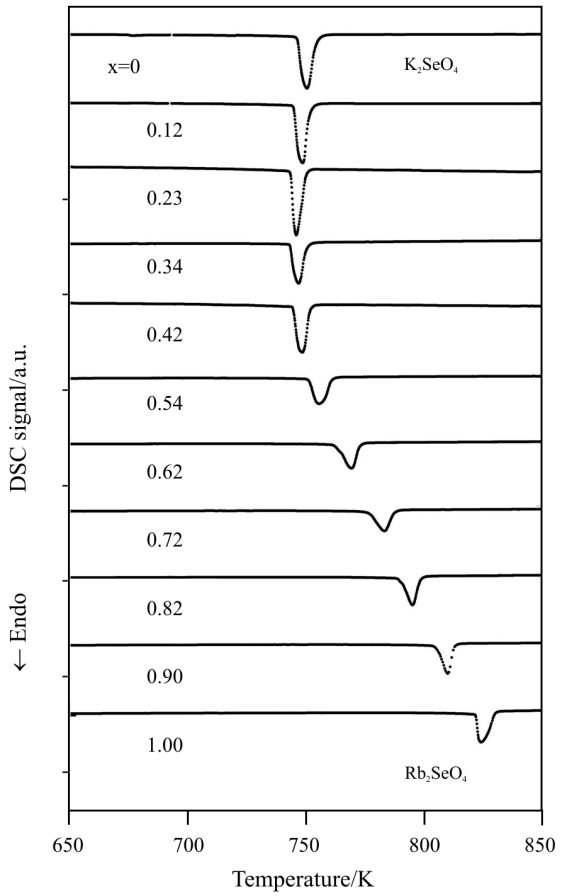


**Fig. 2** Temperature dependence of the DSC signals on heating

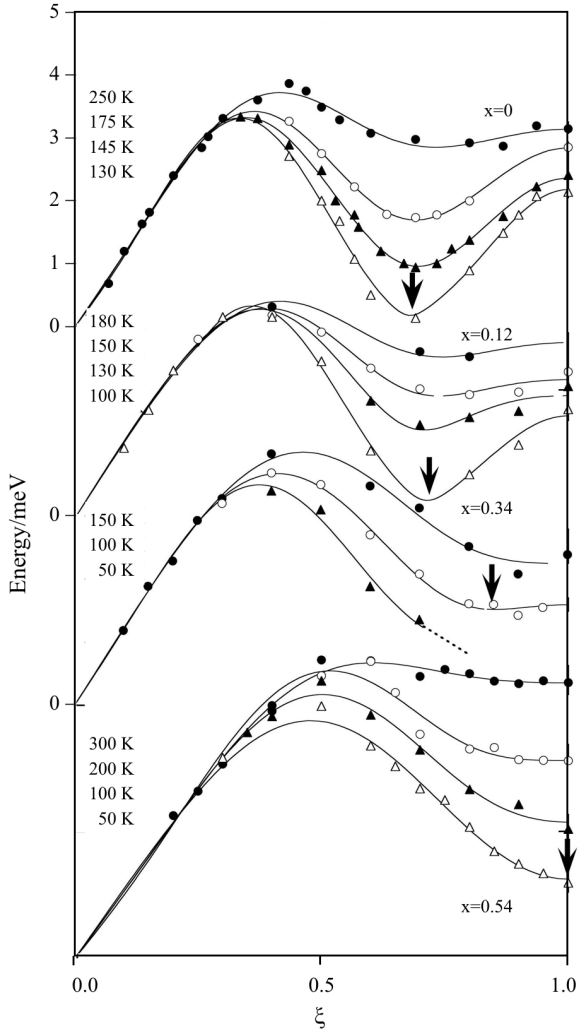


**Fig. 3** Phonon dispersion curves in an extended-zone scheme on the (ξ 0 0) for $(K_{1-x}Rb_x)_2SeO_4$ ($x$=0, 0.12, 0.34 and 0.54). The data for $x$=0 show the phonon dispersion curves in [4]. The minimum positions of the $\Sigma_2$ branch are indicated by arrows

branch in essence [4, 5]. Furthermore, we show that the behavior of the lowest $\Sigma_2$–$\Sigma_3$ optical branch for $(K_{1-x}Rb_x)_2SeO_4$ ($x$=0.12, 0.34, 0.54) is similar to those for $K_2SeO_4$ as the results of our study. Incidentally, the mode softening or the anticrossing has not been observed in non-oxide $A_2BX_4$-type crystals [8–10]. In a case of $K_2SeO_4$, the prolongation of the acoustic branch has its minimum around $0.7a^*$ and the crystal transforms into an incommensurate phase at $T_i$=127.7 K [3]. With increasing Rb content, the modulation wave number at $T_i$ decreases. In $(K_{1-x}Rb_x)_2SeO_4$ ($x$=0.12, 0.23 and 0.34), N-INC phase transitions were observed at 101 K ($x$=0.12, $q$~(5/18)$a^*$), at 75 K ($x$=0.23, $q$~(4/17)$a^*$) and at 8 K ($x$=0.34, $q$~(1/6)$a^*$). The diffraction profiles are shown in Fig. 4. Thermal analysis and structure analysis showed no phase transition in $(K_{1-x}Rb_x)_2SeO_4$ ($x$>0.34) and they retain the orthorhombic structure (space group *Pnam*) down to 2 K. The obtained phase diagram is summarized in Fig. 5.

It is clear that the $\Sigma_2$–$\Sigma_3$ phonon branch softens in the vicinity of ξ=1 in $(K_{0.46}Rb_{0.54})_2SeO_4$ with decreasing temperature. The square of the soft frequency at ξ=1 *vs*. temperature shows a linear dependence. Though the frequency remains finite at 0 K, the extrapolation will give the hypothetical transition temperature at the cross point with the temperature

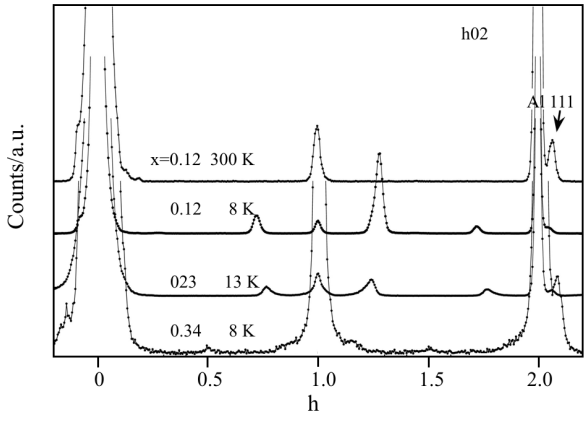


**Fig. 4** The typical diffraction profiles for $(K_{1-x}Rb_x)_2SeO_4$ ($x$=0.12, 0.23 and 0.34). The profiles of 8 or 13 K are the lowest temperature measured. The intensity at h=1 and ~2.05 are caused from multiple scattering and sample-holder aluminum 111 reflection, respectively

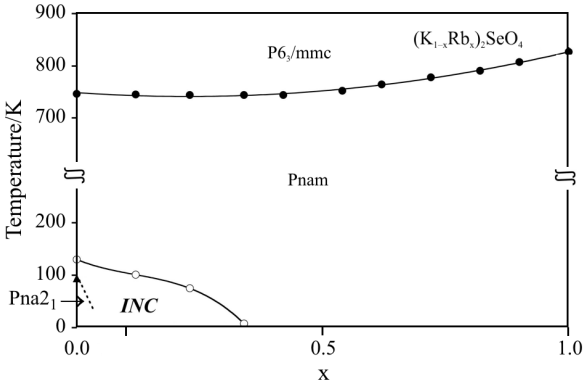


**Fig. 5** Phase diagram of $(K_{1-x}Rb_x)_2SeO_4$

axis. The estimated hypothetical temperature is –16±5 K, which is lower than the calculated hypothetical temperature, –7 K, for $Rb_2SeO_4$ [6]. Thus the existence of the hypothetical phase transition is supported by our experiments.

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