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Neutron powder diffraction study on the high-temperature phase of $K_3H(SeO_4)_2$

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Abstract

Neutron powder diffraction measurements were carried out on $K_3H(SeO_4)_2$ at 413 K in the protonic conducting phase (phase I) and at 298 K in the room-temperature phase (phase II) using a time-of-flight (TOF) neutron diffractometer VEGA. The crystal structures and nuclear density distribution maps were obtained by the Rietveld method and maximum entropy method (MEM). In the phase I, a proton in the hydrogen bond is disordered and SeO_4 tetrahedron is rotationally displaced. The structure in the phase II locally remains even in the phase I. The amount of the proton in the hydrogen bond region varies from 87% for the phase II to 21% for the phase I. In the phase I, the proton densities were also obtained in the inter SeO_4 layers space with the amount of 13%.

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$M_3X(YO_4)_2$ (M: K, Rb, Cs or NH_4; X: H or D; Y: S or Se) type hydrogen-bonded materials have been the subjects of investigations owing to many interesting phenomena. Most of the materials undergo phase transition in the high temperature region. In the high temperature phases, the materials exhibit high electric conductivities which are over 100 times higher than those at the room-temperature [1,2]. It is considered that the higher conductivities were due to the proton transfer. Therefore, these materials have attracted much attention as the solid electrolytes for fuel cells in recent years. The crystal structures in the room-temperature phase are characterized by isolated YO_4–X–YO_4 dimer including a hydrogen bond [3]. The layered structures consist of dimers related with pseudo-$\bar{3}$ axis (a^*-axis). The layers exist parallel to the monoclinic *bc*-plane. In the high-temperature phase, a YO_4 tetrahedron is linked to one of the nearest three equivalent YO_4 tetrahedra by destruction and reconstruction of the hydrogen bond. The situation is closely related with the mechanism of proton transfer at the inside of the layer [4]. Actually, the materials show the highest conductivities in the direction along the monoclinic *c*- or *b*-axis [1]. Many models based on the proton transfer at the inside of the layer accompanied by reconstruction of the hydrogen bond [4,5]. However, the model requires the defects of protons in the layer. The electric conductivity in a direction perpendicular to the layer (a^*-axis) has similar temperature dependence in spite of it has an order of magnitude lower than the other two axes [2]. Little attention has been given to those facts, and it has made the mechanism of protonic conductivity unclear. We, therefore, investigated the

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mechanism of phase transition and proton conductivity by means of neutron structural analysis to clarify the structural change, and using maximum entropy method (MEM) to visualize the proton densities.

$K_3H(SeO_4)_2$ (abbreviated as TKHSe) undergoes two successive phase transitions at 390 and 20 K. The phases are denoted as I, II and III in decreasing order of temperatures. The crystal exhibits the protonic conductivity in the phase I, the ferroelastic in the phase II and antiferroelectric in the phase III. The space group is $R\bar{3}m$ in the phase I and C2/c in the phase II. C2, Cc or $P2_1/c$ were reported as the space group in the phase III [3]. Single crystals of TKHSe were prepared at 313 K by slow evaporation method from an aqueous solution. The crystals were powdered conscientiously and 3.89 g of them were put into a vanadium cell. Neutron powder diffraction data were collected using a time-of-flight (TOF) neutron diffractometer, VEGA, at KENS pulsed spallation neutron facility. Rietveld analyses were performed by RIETAN-2001T modified for VEGA. Prior to the MEM, we needed to estimate the integrated intensities I and their standard deviations σ_I. Assuming that the reflections overlap as $Y_{\mathrm{obs}} = y_a + y_b + \cdots + B$, the integrated intensity for y_a is estimated from following equations:

$$I_a = \sum_i \frac{y_{ai}}{Y_{\mathrm{calc}\,i} - B_i + \varepsilon}(Y_{\mathrm{obs}\,i} - B_i), \tag{1}$$

where Y_{obs} and Y_{calc} are observed and calculated total intensity including back-ground; B back-ground estimated from analysis; ε a small number to avoid Eq. (1) equal to 0/0. Then, the standard deviations caused by measurements are led from Eq. (1) as

$$\sigma_{\mathrm{obs}} = \sqrt{\sum_i \frac{y_{a\,i}}{Y_{\mathrm{calc}\,i} - B_i + \varepsilon}(Y_{\mathrm{obs}\,i} + B_i)}. \tag{2}$$

In addition to Eq. (2) we introduced the standard deviations caused by the analysis

$$\sigma_{\mathrm{ana}} = \sqrt{\sum_i \frac{y_{ai}}{Y_{\mathrm{calc}\,i} - B_i + \varepsilon}\frac{(Y_{\mathrm{obs}\,i} - Y_{\mathrm{calc}\,i})^2}{N}}. \tag{3}$$

Then the σ_I is represented as

$$\sigma_{Ia} = \sqrt{\sigma_{\mathrm{obs}}^2 + \sigma_{\mathrm{ana}}^2}. \tag{4}$$

Thus, we obtained the structure factors $|F|$ and standard deviation σ_F using Eqs. (1), (4), scale factor s and its standard deviation σ_s. The calculations of MEM were carried out by PRIMA using 935 reflections for phase II and 227 reflections for phase I.

Fig. 1(a) and (b) show the Rietveld diffraction fitting of TKHSE at 298 and 413 K, respectively. Good agreements between the observed and calculated patterns were obtained with the agreement factors and goodness-of-fit (GOF) indicator of $R_{\mathrm{wp}} = 0.010$, $R_I = 0.004$, and $S = 1.23$ for phase II, and $R_{\mathrm{wp}} = 0.014$, $R_I = 0.019$, and $S = 1.77$ for phase I. The rhombohedral lattice parameters at 413 K in the phase I are obtained as: $a = 8.0297(1)$ Å and $\alpha = 43.1944(7)°$. The crystal structures of TKHSE in the phase II and phase I are illustrated in Figs. 2(a) and 3(a), respectively. The occupancies of the oxygen atoms are $\frac{1}{3}$ in the phase I. The occupancy of hydrogen atom is $\frac{1}{6}$ in the phase I, and $\frac{1}{2}$ in the phase II. As shown in Fig. 3(a), in the

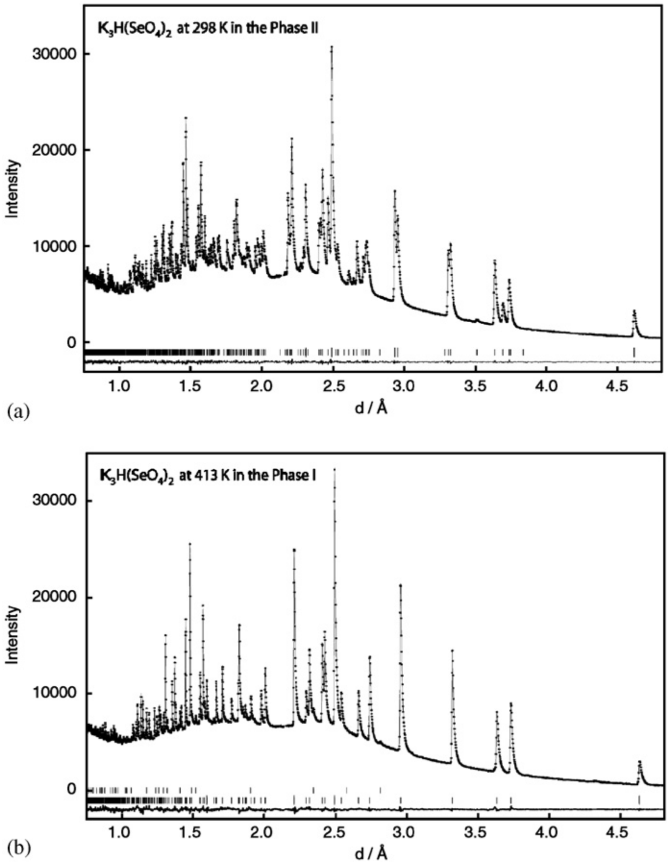

Fig. 1. The observed diffraction patterns and results of Rietveld analysis for $K_3H(SeO_4)_2$: (a) at 298 K and (b) at 413 K.

Table 1
Interatomic distances (Å) and bond angles (°) of $K_3H(SeO_4)_2$ at 298 and 413 K, with the standard deviations in parentheses

	Phase II (298 K)	Phase I (413 K)
Hydrogen bond		
O1–O1^a	2.522(2)	2.595(9)
O1 ··· O1^b	3.738(2)	3.822(9)
O1–H1	1.021(7)	0.89(2)
H1 ··· O1^a	1.501(7)	1.74(1)
H1 ··· H1^a	0.48(1)	0.94(3)
O1–H1 ··· O1^a	177.9(5)	160.7(9)
SeO_4 *tetrahedron*		
Se1–O1	1.683(1)	1.683(7)
–O2(O21)	1.624(2)	1.511(9)
–O3(O22)	1.620(1)	1.668(6)
–O4	1.615(2)	
Mean distance excepted O1	1.620(3)	1.616(12)

Symmetry codes: (a) $1 - x,\ 1 - y,\ 1 - z$ (b) $1 - x,\ y,\ \frac{3}{2} - z$ for phase II, (a) $-x,\ -z + 1,\ -y + 1$ (b) $-z + 1,\ -y + 1,\ -x + 1$ for phase I.