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Electron Densities Distribution on Protonic Conductor $K_3H(SeO_4)_2$

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Introduction

$K_3H(SeO_4)_2$. (abbreviate as TKHSe) undergoes phase transition at 390 K (T_C) The crystal shows remarkable high electric conductivity in its high temperature phase in spite of the dielectric, that is, the high conductivity is caused by the protons transfer. The crystal structure in the room-temperature (Phase II) is characterized by isolated SeO_4-H-SeO_4 dimers. In the high temperature phase (Phase I), a SeO_4 tetrahedron is linked to on of the nearest three equivalent SeO_4 tetrahedra with the probability of 1/3 by disconnections and reconstructions of the hydrogen bond. This situation is closely relate to the mechanism of proton transfer, and many advocated models had been based on such mechanism.[1]

Recently, we had carried out neutron powder diffraction measurements at varied temperature.[2] Rietveld analyses and maximum entropy method (MEM) were performed The results show that two SeO_4 tetrahedra are connected by a hydrogen bond even in the phase I, and the structure in the phase II remain locally. MEM results show that proton is distributed all over the unit cell in the phase I, and the density was obtained in the inter layer space where no hydrogen bond exists in the phase II. In additional to the experiment, we also carried out incoherent quasi elastic neutron scattering measurements[3]. Diffusion constants of proton were obtained as the order of 10^{-10} m^2/s , and electric conductivities are estimated as the order of 10^{-3} S/cm using proton densities obtained from MEM. The results are good agreement with those obtained from macroscopic measurements, and suggest that the proton in the inter-layer space is the conduction proton.

However, the details of proton transfer mechanism are still unknown. To understand electron distribution will be give us intrinsic information about proton transfer as the charged particle. We, therefore, carried out X-ray diffraction measurement using synchrotron radiation and performed MEM.

Results and Discussion

A minute single crystal of TKHSe was used for measurement. 120 pictures were taken by a imaging plate diffractometer, and 14459 point of Bragg reflections were measured with the maximum 2θ=120 degrees. Independent 5679 reflections were observed and the refinement was based on F^2 using 3277 reflections ($I>3+\sigma$). 64 parameters were refined with the agreement factor R=0.036 and S=1.01.

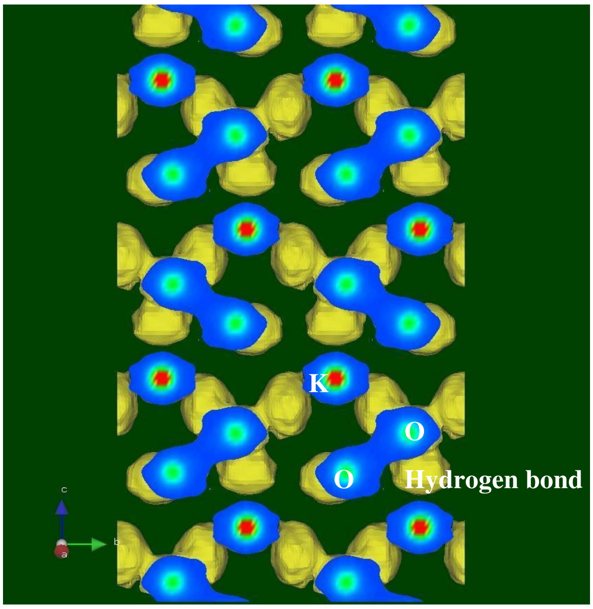

Figure 1 Electron density distribution map of $K_3H(SeO_4)_2$ at 298 K obtained from MEM.

Figure 1 is electron density map at 298 K projected from crystallographic *a**. The hydrogen bonds in the dimers can be clearly seen as the blue herringbone pattern. Most of the hydrogen atoms are localized in the hydrogen bonds in the dimers at this temperature. The hydrogen bond distance is obtained as 2.541(3) Å. The Se-O covalent bond can see as the yellow mass of electron densities. On the other hand, no electron densities is observed between potassium and SeO_4-H-SeO_4 dimer, but the electron distributions of potassium are not exactly spherical. The result shows that asymmetrical electrical potential lays in the crystal, and the ionic bonds between potassium and dimers or between dimers are complicate.

As mentioned above, we can know the bond state in the crystal by using MEM. High temperature measurement will clear up the mechanism of proton transfer.

References

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