

Diffuse Scattering Measurement on Protonic Conductor $K_3H(SeO_4)_2$

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Much attention has been paid to some hydrogen bonded dielectric materials as the electrolytes for fuel cells which function above the boiling temperature of water. $K_3H(SeO_4)_2$ undergoes 1st order phase transition at 390 K (T_C). The material shows remarkable high electric conductivities above T_C (Phase I) and ferroelastic below T_C (Phase II). From the structural analyses by means of neutron diffraction, it developed that the slight deform of potassium lattice determine the hydrogen bonds orientation in the phase II, and alternate rotational displacements of SeO_4 tetrahedra which explained as zone boundary phonon mode correspond with the crystal structure in the phase II. [1, 2] We, therefore, have carried out inelastic neutron scattering (INS) experiments to clarify the mechanism of protonic conductivities and ferroelastic phase transition. No soft mode was obtained both of acoustic and zone boundary optical modes, however, diffusive spectra were obtained near the 0 meV at the L-point (0.5 2 0) above T_C . The results suggest that the rotational phonon mode of tetrahedra is to exist as over dumped phonon.

INS measurements were carried out using a high energy resolution triple axis spectrometer (C1-1 HER) installed at JRR-3M reactor, JAEA, Tokai, Japan. The energy scans were performed at zone boundary L-point with the energy transfer range from -2 meV to 4 meV. Final momentum vector k_f was fixed at 1.555 \AA^{-1} . The h-scans from (0.25 2 0) to (0.75 2 0) were also performed to confirm that the INS spectra is obtained at only L-point.

Figure 1 shows INS spectra measured on the L-point by constant-Q mode at varied temperatures near T_C . Lorentzian shape spectrum increases with decreasing

the temperature as shown in the figure. The result is close to the spectra of over dumped phonon of $CsPbCl_3$ due to the M_3 mode tilts of $PbCl_4$ octahedra. [3] It shows that the rotational mode of SeO_4 tetrahedra drives the improper ferroelastic phase transition, and plays an important role to the mechanism of proton conductivity in the phase I. It naturally expected that tilted tetrahedra form the hydrogen bonds locally even in the phase I, and the rotational mode over-dumped by the formation of hydrogen bonds. It developed that the hydrogen bonds disconnect and reconstruct due to the rotational tetrahedra mode in the phase I. It suggested that the rotational mode assists in the protons jumping to the inter-layer space in the metastable state.

References

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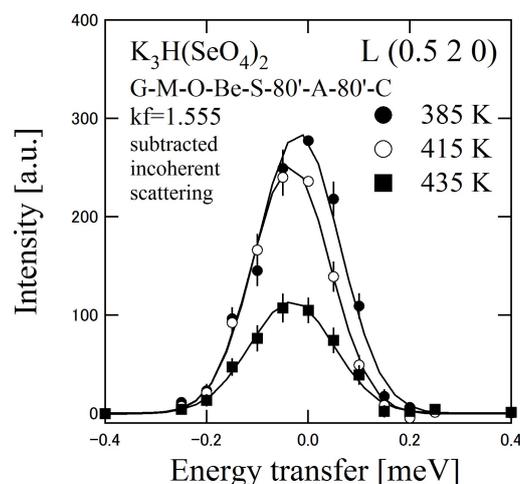


Fig. 1. INS spectra of $K_3H(SeO_4)_2$ at L-point