Proc. Int. Symposium on Advances in Neutron Scattering Research, Tokai, 2000
J. Phys. Soc. Jpn. **70** (2001) Suppl. A pp. 386–388

Neutron Scattering Study of Protonated and Deuterated Potassium Phosphate Glasses

Osamu YAMAMURO, Yasushi MADOKORO, Hideki OBARA, Kouji HARABE, Takasuke MATSUO, Takashi KAMIYAMA[1], Hiroshi FUKAZAWA[2] and Susumu IKEDA[2]

Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan
[1] *Graduate School of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan*
[2] *Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK) Oho 1-1, Tsukuba, Ibaraki 305-0801, Japan*

The incoherent inelastic neutron scattering from protonated potassium phosphate glass was measured on CAT at KENS and AGNES at ISSP (JRR-3M) over a wide energy range of 0.1-300 meV. The measurement of coherent inelastic scattering was also performed for the deuterated analogue in the energy range 3-90 meV and momentum transfer range 1-13 $Å^{-1}$ by using MARI at ISIS. We have found a boson peak at around 4 meV and some interesting features of the acoustic and localized vibrations characteristic to the amorphous structure of the present materials.

KEYWORDS: glass, hydrogen bond, neutron scattering, boson peak

§1. Introduction

KH_2PO_4 (KDP) is a well-known hydrogen-bonded crystal which has a ferroelectric phase transition at T_c = 123 K.[1)] The ferroelectricity of KDP is due to the ordering of protons on O-H···O hydrogen bonds. A number of studies have been done to investigate interesting properties of the transition such as the large isotope effect (T_c (DKDP) = 213 K). The isotope effect was explained by a model proposed by Sugimoto and Ikeda [2)] and Ikeda *et al.*[3)]

Recently we found that the glassy state of KDP can be obtained by quenching KDP melt. The composition was changed to $KH_{1.34}PO_{3.67}$ due to partial dehydration of the sample on heating. In this paper, we designate this material glassy KDP for simplicity. Our calorimetric study showed that the ferroelectric transition completely disappeared, and a glass transition with a large heat capacity jump occurred at 323 K.[4)] Glassy KDP may have one-dimensional chain or ring structure from the analogy of alkali meta-phosphate glasses (MPO_3). Investigation of glassy KDP and DKDP is important in relation to the current research interest in various aspects of amorphous materials such as the dispersion relation and the boson peak as well as for further deepening of our understanding of ferroelectricity and hydrogen bonds.

In this study, we have measured the inelastic neutron scattering of glassy KDP by using CAT at KENS and AGNES at ISSP (JRR-3M) over wide energy range 0.1-300 meV. The observed data were dominated by incoherent scattering from hydrogen atoms. A preliminary experiment of the coherent scattering of DKDP was also performed using MARI at ISIS.

§2. Experimental

KDP (Wako Pure Chemical Industries, Ltd.) and DKDP (Aldrich Chemical Company, Inc., 98 D-atom %) crystals were melted (T_{fus} = 550 K) and then press-cooled between a pair of copper slabes at room temperature. The obtained sample was transparent plate with thickness of ca. 1 mm. Complete formation of the glassy state (no remaining crystalline phases) was confirmed by X-ray powder diffraction. The compositions of the glassy samples were determined to be $KH_{1.34}PO_{3.67}$ and $KD_{1.40}PO_{3.70}$ by thermogravimetry.

For the CAT experiment, the plate of glassy KDP were used as they were obtained by the press cooling since CAT is a time-focusing spectrometer requiring a flat plain sample. The sample plate were crushed into smaller pieces and confined in a concentric double-cylinder aluminum can sealed with an indium gasket for AGNES and MARI experiments. The sample height (h), diameter (d) and thickness (t) are as follows: h = 40 mm, d = 14 mm, t = 2 mm for AGNES (KDP) and h = 50 mm, d = 40 mm, t = 5 mm for MARI (DKDP). The transmission of neutron beam considering the packing factor was about 93 % for CAT, 94 % for AGNES and 90 % for MARI.

CAT[5)] is a time-focusing spectrometer installed at a pulse neutron source at KEK, Tsukuba, Japan. The energy resolution is 2-3 % over wide energy range E < 300 meV. The measurement on CAT was performed at 20 K both for glassy and crystalline KDP.

AGNES[6)] is a direct geometry TOF spectrometer belonging to Institute for Solid State Physics, the University of Tokyo. It is installed at the cold neutron guide (C3-1) of JRR-3M (Tokai, Japan). The energy resolution for elastic scattering was 0.1 meV and the energy window was smaller than 20 meV on the side of neutron energy gain. The momentum transfer region was 0.23-2.70 $Å^{-1}$ for elastic scattering. The measurement on AGNES was performed at room temperature (298 K).

MARI[7)] is a direct geometry chopper-type TOF spectrometer installed at the pulse neutron source of ISIS, Rutherford Appleton Laboratory, UK. It is advantageous of this spectrometer that wide energy and momentum transfer ranges can be covered by using various incident

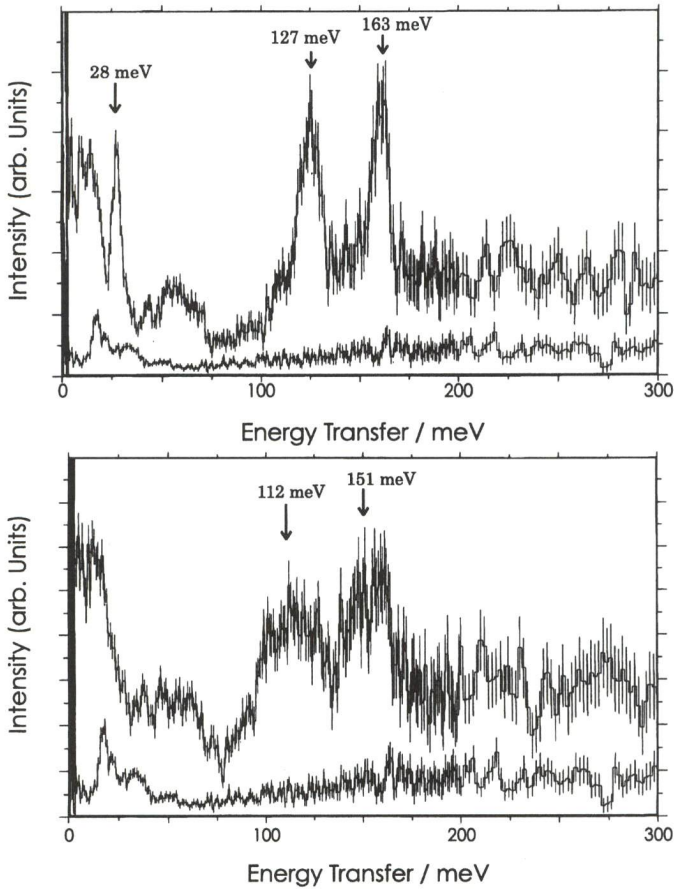

Fig. 1. Neutron scattering spectra of crystalline (upper) and glassy (lower) KDP obtained by CAT at 20 K. The lower curves represent the background.

neutron energy and wide area of detector bank (2θ = 3-135). The energy resolution can be changed by choosing chopper type and frequency. We chose the incident energy of 100 meV using a S chopper (with the strongest intensity and poorest resolution) with frequencies of 400 Hz. The energy resolution was 3-5 % and the covered Q range was 0.5-13 $Å^{-1}$. The measurement was performed at 120 K.

§3. Results and Discussion

Figures 1 shows the neutron scattering spectra of crystalline (upper) and glassy (lower) KDP measured by CAT. For the crystalline KDP, the peaks at 127 and 163 meV are attributed to the bending modes of protons on the O-H···O hydrogen bonds. The sharp peak at 28 meV is due to the librational motion of PO_4^{3-} group with hydrogen-bonded protons and appears only in the ferroelectric phase.[8–10] In the glassy KDP, the peaks for the bending modes became broader and slightly shifted to the low-energy side while the PO_4^{3-} mode disappeared completely. The present data shows that the O-H···O hydrogen bonds were not changed much whether they were in the crystalline or glassy KDP but the ferroelectric ordering of the hydrogen-bond network of $H_2PO_4^-$ had been lost in the glassy state. This is consistent with our structural model that glassy KDP have one-dimensional chain or ring structure of O-P-O covalent bonds.

Figure 2 shows the $S(Q, E)$ spectra of glassy KDP obtained by AGNES. The data of glycerol,[11] which is a typical hydrogen-bonded glass, were also plotted for comparison. These spectra were obtained by summing up the data from the counters positioned at scattering angles of 89-120; the average Q value for elastic scattering was 2.35 $Å^{-1}$. For comparison of intensity, both data were divided by the integrated intensity of each spectrum and the data of glassy KDP measured at 298 K was bose-scaled to 180 K where glycerol was measured. A boson peak was found at about 4 meV in glassy KDP. The boson peak intensity of glassy KDP was much smaller than that of glassy glycerol which is known to be smaller in the family of alcohol glasses .[11]

As has been described above, glassy KDP may have a chain or ring structure of phosphate groups by the analogy with alkali meta-phosphate glasses. The hydrogen bonds may interconnect such chains. Glassy glycerol has a network structure formed by intermolecular hydrogen bonds which are much weaker than O-P-O covalent bonds. Hence the network structure in glassy KDP (formed by O-P-O and O-H···O bonds) can be regarded to be stronger than that in glassy glycerol. The present result is consistent with our experimental results for the hydrogen-bonded glasses[11] as well as the Nakayama model for network glasses;[12,13] the stronger the network connectivity is (or equivalently, the fewer the dangling bonds are), the weaker the boson peak intensity becomes.

Figure 3 shows the intensity map in the Q-E plane obtained by MARI. The intensity was multiplied by E and divided by Q to give a quantity corresponding to density of states. The intensity is strong in the white region. The curve below the intensity map gives the Q dependence of the integrated elastic intensity $I(Q)$, corresponding to the static structure factor $S(Q)$. In the energy region below 30 meV, there are stripes of intensity with maxima at Q values of 2.5, 5.5 and 7.9 Å^{-1}. These stripes may be due to the acoustic phonons. There are also intensity bands of optical phonons at around 50 and 65 meV corresponding to O-P-O bending vibrations (52 and 70 meV in PO_4^{3-} ions). The Q dependence of the intensity is small but there is a small maximum at about 6.5 Å^{-1}. It is noteworthy that the Q values of the stripes below 30 meV correspond to the peaks of $I(Q)$ and the Q value at the maximum energy of the optical bands to the valley of $I(Q)$.

It is a recent important finding that dispersion relations of acoustic phonons appeared in the similar MARI data of glassy SiO_2[14] and $Ni_{67}Zr_{33}$,[15] which are both 3-dimensional network glasses. The present data show the Q-dependent intensity of the acoustic phonons but they are not like dispersion curves. This may be due to the 1-dimensional network structure of amorphous DKDP and/or the fact that the network structure is disturbed by the hydrogen bonds. For further clarification of the phonon dispersion in glasses, it is desirable to study systems whose network dimensionality and connectivity can be changed as experimental parameters. We are planning to measure glassy KPO_3 which has a similar 1-dimensional network structure to glassy DKDP but is not modified by hydrogen bonds.

Acknowledgements

The experiment of CAT was supported by Mr. Akira Sakaguchi (Hiroshima University), AGNES by Professor Kajitani and members of his group (Tohoku University), and MARI by Drs. Steve Bennington and Oleg Petrenko (ISIS). The authors are grateful to them. This work was financially supported by Nippon Sheet Glass Foundation for Materials Science and Engineering.

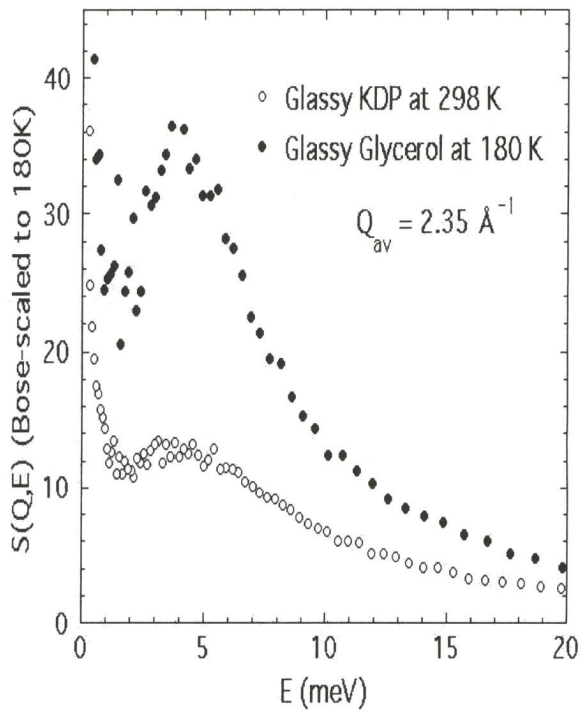

Fig. 2. Dynamic structure factor of glassy KDP (open circles) and glycerol (closed circles) measured by AGNES. The data of the glassy KDP at 298 K was Bose-scaled to 180 K where glycerol was measured.

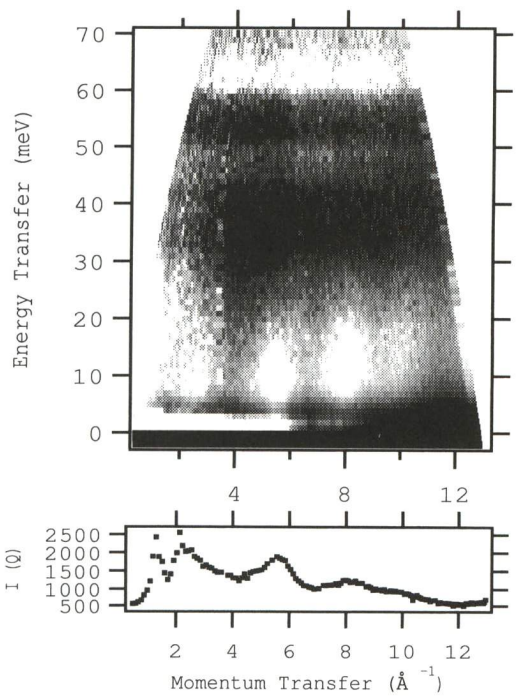

Fig. 3. Intensity map (multiplied by E/Q) of glassy DKDP in the Q-E plane obtained by MARI ($Ei = 100$ meV, $T = 120$ K). The lower curve is the Q-dependence of integrated elastic intensity.

1) B. A. Strukov and A. P. Levanyuk: "Ferroelectric Phenomena in Crystals", Springer (Berlin) (1997).
2) H. Sugimoto and S. Ikeda: Phys. Rev. Lett. **67** (1991) 1306.
3) S. Ikeda, H. Sugimoto and Y. Yamada: Phys. Rev. Lett. **81** (1998) 5449.
4) H. Obara O. Yamamuro and T. Matsuo: J. Korean Phys. Soc. **32** (1998) S821.
5) S. Ikeda and N. Watanabe: Nucl. Instrum. Method **221** (1984) 571.
6) T. Kajitani, K. Shibata, S. Ikeda, M. Kohgi, H. Yoshizawa, K. Nemoto and K. Suzuki: Physica B **213-214** (1995) 872.
7) M. Arai, A. D. Taylor, S. M. Bennington and Z. A. Bowden: "Recent Development in Physics of Fluids", Adam Hilger (Bristol), p. F321 (1992).
8) H. Sugimoto, J. Phys.: Condens. Matter **6** (1994) 5561.
9) S. Ikeda and Y. Yamada, Physica B: **213-214** (1995) 652.
10) I. Tamura, Y. Noda and S. Ikeda, Physica B: **219-220** (1996) 608.
11) O. Yamamuro, K. Harabe, T. Matsuo, K. Takeda, I. Tsukushi and T. Kanaya: J. Phys.: Condens. Matter **12** (2000) 5143.
12) T. Nakayama and N. Sato: J. Phys.: Condens. Matter **10** (1998) L41.
13) T. Nakayama: Phys. Rev. Lett. **80** (1998) 1244.
14) M. Arai, Y. Inamura, T. Otomo, N. Kitamura, S. M. Bennington and A. C. Hannon: Physica B **263-264** (1999) 268.
15) T. Otomo, M. Arai, Y. Inamura, J. -B. Suck, S. M. Bennington and K. Suzuki,: Non-Cryst. Solids **232-234** (1998) 613.