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Temperature and pressure studies of Raman peaks related to hydrogen modes in KDP

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Abstract

Raman scattering spectra of a KH_2PO_4 (KDP) single crystal have been obtained under various temperature and pressure conditions. It was observed that (i) the peak around 1310 cm^{-1} is not a single peak as reported previously but consists of two components and (ii) in the ferroelectric phase the 1013, 1306 and 1315 cm^{-1} peaks become obscure near the ferroelectric–paraelectric phase boundary. Furthermore, they show positive pressure shifts and the pressure coefficients are obtained. An interpretation is proposed for the origins of these Raman peaks.

1. Introduction

KH_2PO_4 (KDP) is a hydrogen-bonded ferroelectric compound, and a ferroelectric–paraelectric phase transition occurs at $T_c = 123\text{ K}$. It is well known that the Curie temperature T_c increases from 123 to 218 K by deuteration (i.e. in DKDP). This drastic isotope effect has stimulated many researchers and huge numbers of experimental [1–15] and theoretical [16–20] works have been performed previously. Since the main point at issue in this phenomenon is a relation between the ferroelectric phase transition and the proton tunnelling, it is most important to reveal the proton dynamics. In 2003, Tominaga *et al* [21] studied KDP/DKDP mixed crystals by Raman scattering. They observed new Raman peaks (1012, 1312, 1856, 2400 and 2680 cm^{-1} in KDP and 725, 973, 1381, 1758 and 1962 cm^{-1} in DKDP) in $Z(XY)$ – Z geometry and showed that (1) the high frequency Raman spectra of KDP/DKDP mixed crystals can be well reproduced through the simple addition of KDP and DKDP spectra, (2) the frequency ratio of all of these peaks is 1/1.37, which coincides with the ratio of the square root of the reduced mass of O–D and O–H and (3) their frequencies are almost unchanged between $T > T_c$ and $T < T_c$. Since non-shifted modes between KDP and DKDP can be assigned to the molecular vibrations of PO_4 tetrahedrons [7], the authors thought these modes in KDP and DKDP to be

ordinary local vibrations of hydrogen bond. Since it is very important for studying the proton dynamics of this system to identify the Raman peaks strongly affected by the hydrogen motions, further studies must be carried out. We performed Raman scattering under various temperature and pressure conditions and obtained new experimental results.

2. Experimental details

Raman scattering measurements were performed on KDP single crystals. Generally, the signal intensity from the sample in the high pressure cell is very weak because the specimen is very thin and small, and moreover the existence of the anvil reduces the intensity. Therefore two plate samples aligned with the *c*-axis perpendicular to the face were prepared: (1) a large sample with the dimensions of $10 \times 10 \times 2 \text{ mm}^3$ for ambient pressure study and (2) a small sample with the dimensions of $0.2 \times 0.2 \times 0.1 \text{ mm}^3$ for high pressure study. The samples were polished carefully to avoid mechanical strain. The small one was placed in the gasket hole with a diameter of 0.4 mm. In order to avoid the disturbance due to the strong Raman signal from the anvil around 1330 cm^{-1} , a sapphire anvil was used instead of the conventional diamond anvil. Ethanol was used for the pressure medium. Applied pressure was monitored by the frequency shift of the fluorescent line R_1 of ruby chips. The specimen was compressed up to 1.6 GPa. Raman scattering spectra were obtained by a Jobin–Yvon T-64000 triple spectrometer and a Jobin–Yvon Spex Spectrum-one CCD (charge coupled device) system. The exciting light source was the 514.5 nm line from an argon-ion laser with a power of 200 mW. The measurements were carried out in the back-scattering geometry $Z (XY)–Z$. Here Z is the normal to the *c*-plane and X and Y are taken in the directions of the crystallographic *a*- and *b*-axes of the paraelectric ($T > 123 \text{ K}$) phase. The specimen was cooled using an Iwatani CryoMini model CRT-006-0000 cooling system and the temperature was controlled using an Iwatani TCU-4 digital program temperature controller.

3. Results and discussion

As mentioned above, Tominaga *et al* observed five characteristic Raman peaks at 1012 (labelled A), 1312 (labelled B), 1856, 2400 and 2680 cm^{-1} in KDP. However, the latter three peaks were unable to be assigned in the small specimen in the high pressure anvil cell because of their broadness and weakness. Therefore, we restricted our study to the former two sharp peaks A and B.

Figure 1 shows a Raman spectrum obtained in $Z (XY)–Z$ geometry under 20 K and ambient pressure conditions. We can see sharp peaks at 910 (labelled ν_1), 1013, 1306 and 1315 cm^{-1} . The 1013 cm^{-1} peak is A; however, it must be pointed out that peak B located around 1310 cm^{-1} is not a single peak reported previously [21] but consists of two components (labelled B1 and B2, respectively). We suppose that the nearness of B1 and B2 in frequency suggests the direct or indirect interaction between their oscillators. In the incoherent inelastic neutron scattering study on KDP, three strong peaks of hydrogen modes were observed at 126 and 159 meV in $Q \parallel c$ geometry and 161 meV in $Q \parallel a$ geometry and the former two peaks were assigned to be two bending modes of the O–H–O bond and the last one was assigned to be an O–H stretching mode, respectively [22]. Note that their peak positions are very near our three Raman peaks A (126 meV), B1 (162 meV) and B2 (163 meV), respectively.

Figure 2 shows the temperature dependence of the Raman spectra. The peaks A, B1 and B2 broaden with temperature and we cannot distinguish B1 and B2 when the temperature is greater than 118 K. The three peaks were analysed by combined Gaussian–Lorentzian fitting and the temperature dependences of peak positions and full widths at half maximum (FWHMs) are illustrated in figures 3 and 4, respectively. It is clear that the peak position is nearly independent

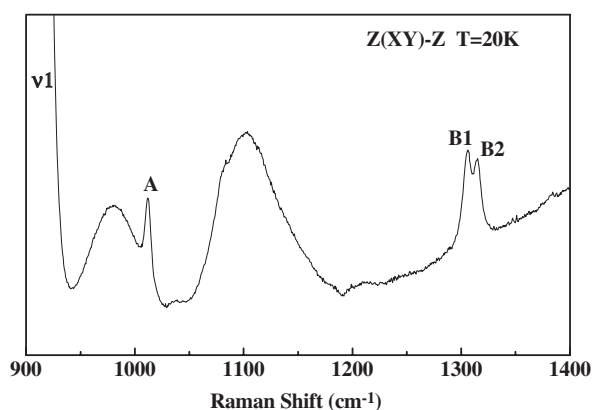


Figure 1. Raman spectrum of KDP obtained in $Z(XY)-Z$ geometry at ambient pressure.

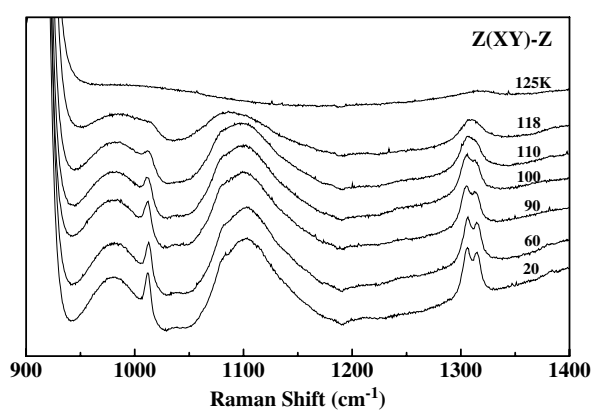


Figure 2. Raman spectra at various temperatures.

of temperature; on the other hand, the width shows very interesting temperature dependence. All the peaks broaden gradually with temperature and the broadening becomes excessive around 100 K. Since the Boltzmann factor at an excited state located around 1000 cm^{-1} above its ground state is less than 10^{-6} at 100 K, most of their oscillators populated in the ground states. Moreover, the ν_1 peak does not show such a drastic phenomenon. Therefore, the abrupt broadening of the three peaks from 100 K is not an ordinary thermal effect due to the population increasing of the excited states, but it seems that the inner strain around the A, B1 and B2 oscillators becomes highly inhomogeneous. However, they seem to have no direct relation to the phase transition itself, because the peak frequencies of the three peaks do not show a clear change near the transition temperature, 123 K. Agui *et al* performed the neutron scattering studies on RbH_2PO_4 , which is an isomorphic substance of KDP, and observed that the widths of the scattering peaks by hydrogen modes located at 124 and 159 meV increase drastically at paraelectric phase without peak shifts [23]. They suggest that this occurs due to the large fluctuation of the hydrogen potential affected by the disorder of PO_4 tetrahedrons. Considering the similarities between the neutron scattering peaks and Raman ones in peak positions and in the broadening phenomenon, we conclude that the origins of the A and B1 peaks are two bending modes of the O–H–O bond, and B2 is an O–H stretching mode.

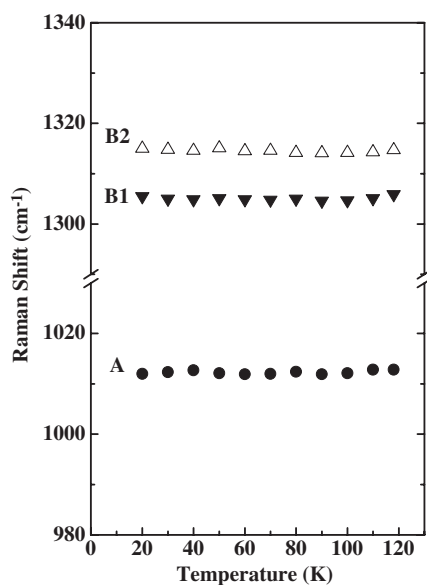


Figure 3. Temperature dependence of the A, B1 and B2 peak positions.

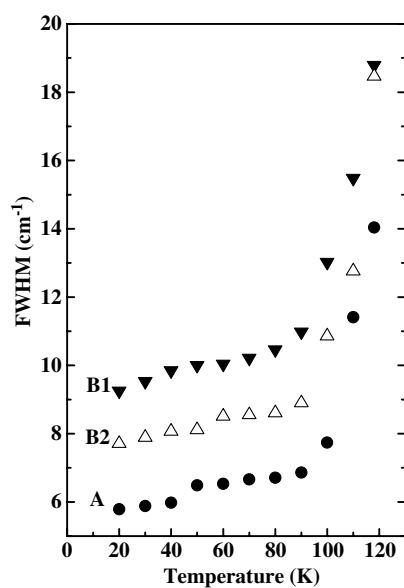


Figure 4. Temperature dependence of the width of A, B1 and B2.

The peaks A, B1 and B2 become obscure at the paraelectric phase even in a bare and large sample, so that we could not observe them at $T > T_c$ in a high pressure study. Figure 5 shows the Raman spectra in $Z(XY)-Z$ geometry obtained under the pressure of 0.01, 0.6, 0.9 and 1.6 GPa at 50 K. It is observed that the peaks A and B (i.e. B1 + B2) marked by arrows shift toward the higher energy side and the width broadens remarkably with increasing pressure. Around 0.9 GPa the peaks are merged into the background. At 50 K the ferroelectric–

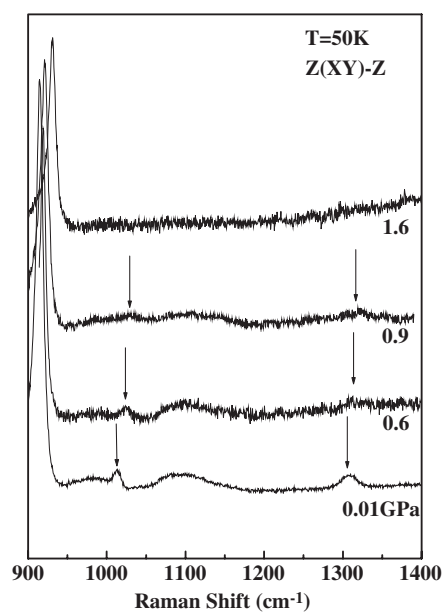


Figure 5. Pressure dependence of A and B peaks at 50 K.

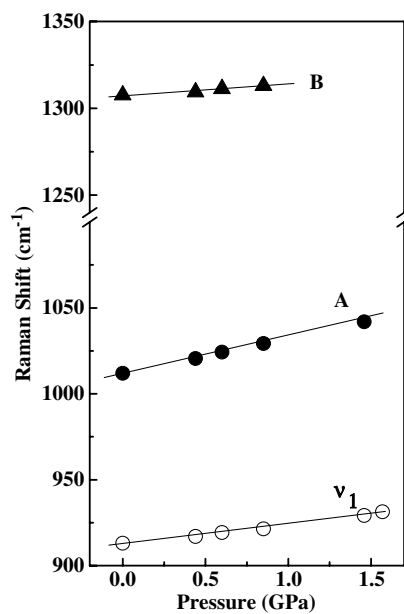


Figure 6. Pressure dependence of the position of three Raman peaks ν_1 (○), A (●) and B (▲).

paraelectric phase transition occurs around 1.3 GPa [4]. As mentioned above, from figure 5 the A and B peaks are merged into the background near the paraelectric phase with increasing temperature. These results on pressure and temperature dependences indicate that the pressure-induced indistinctness of the A and B peaks is related to the disorder of PO_4 tetrahedrons. The pressure dependences of the ν_1 (○), A (●) and B (▲) peak positions are shown in figure 6

and their pressure coefficients are obtained to be 11.1, 20.6 and 6.4 $\text{cm}^{-1} \text{GPa}^{-1}$, respectively.

4. Conclusion

We studied the 1013 cm^{-1} (A), 1306 cm^{-1} (B1) and 1315 cm^{-1} (B2) Raman Peaks of KDP under various temperature and pressure conditions. It has been observed that in ferroelectric phase with increasing pressure these peaks shift toward to the higher energy sides with remarkable broadening and become difficult to observe in the paraelectric phase. Their peak obscuration in the paraelectric phase was also observed in a temperature study at ambient pressure. The peak broadening suggests that the inner strain around their oscillators becomes highly inhomogeneous in the paraelectric phase. From these results and those of the neutron scattering study, we conclude that the origins of the A and B1 peaks are two bending modes of the O–H–O bond, and B2 is an O–H stretching mode. The disorder of PO_4 tetrahedrons becomes remarkable from 100 K. The pressure coefficients of the ν_1 , A and B peaks are obtained to be 11.1, 20.6 and 6.4 $\text{cm}^{-1} \text{GPa}^{-1}$, respectively.

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