High Pressure Raman Study and Phase Transitions of KIO_3 Non-Linear Optical Single Crystals

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Potassium iodate KIO_3 single crystal samples have been studied under pressure up to 35 GPa at room temperature. Drastic spectral changes and phase transitions were observed. The first phase transition occurs at 5.0 GPa characterised by major spectral changes in the Raman bands belonging to the ν_1 , ν_2 , and ν_4 modes. The other phase transitions were found at 8.7, 15 and 22 GPa. The ν_1 modes soften with pressure up to 15 GPa. The phase that is stable between 15-22 GPa has a higher symmetry than the phases in the lower pressures. The IO_3 pyramidal ions may have lost their identity and changed to IO_6 octahedra above 22 GPa, as indicated by the changes in the Raman bands of the ν_1 modes and the new bands in the spectral region between 500-600 cm^{-1} . [KIO₃, high pressure, micro-Raman, phase transitions, ferroelectric]

1. Introduction

Potassium iodate (KIO_3) single crystals are non-linear materials having the largest non-linear optical coefficient among all the iodate crystals. Single crystals with good thermal stability can be obtained by cooling from aqueous solution [1], which makes it potentially a very useful material with a wide working temperature range. At atmospheric pressure, potassium iodate undergoes several phase transitions with temperature. On cooling, it transforms from the rhombohedral phase I (space group $R3m$) to the monoclinic phase II (space group Cm) at 485 K, and then to the triclinic phase III (space group $P1$) at 343 K [2-4]. Below room temperature, two more phase transitions exist, phase III to phase IV transition at 255 K, and IV to V at 83 K [5]. Phase I is paraelectric while all the other phases are ferroelectric. Based on neutron diffraction data, Lucas [6] argued that phases IV and V have essentially the same atomic arrangement as that of phase III and that the marked differences in the ferroelectric behaviour are originated from domain- and twin-scale changes within the sample. No high pressure work has been reported in the literature for KIO_3 .

2. Experimental

The KIO_3 single crystal samples used in the experiment were grown from cooling of aqueous solution and the crystals obtained in this way are multi-domain and twinned [1]. Raman measurements were performed using the Renishaw Ramascope 2000 micro-Raman system, with a diode laser operating at 782 nm as the excitation source. The spectral resolution is 2 cm^{-1} . High pressure was generated by a gasketed diamond anvil cell (DAC) with 4:1 mixture of methanol-ethanol as pressure medium. A 20X super-long working distance microscope objective lens was used (with numerical aperture $NA = 0.35$) to collect the Raman signal from DAC. Pressure was calibrated using the well-known ruby fluorescence technique, using 782 nm laser excitation and checked using 488 laser excitation. The ruby fluorescence process using 782 nm excitation involves two-

photon absorption of the NIR laser, and the detailed description will be presented elsewhere. The pressures that were calculated from data obtained using both lasers agree well.

Table 1. The observed Raman bands under ambient conditions and their assignments, together with the wavenumber dependence with pressure in phase III.

Wavenumber cm^{-1}	$d\nu/dp$ $\text{cm}^{-1}/\text{GPa}$	Assignment
161.4	-1.4	ν_4
164.9	4.1	
179.5	4.4	
303.1	2.5	ν_2
324.3	3.6	
348.2	3.6	
366.8	4.4	
730.5	-3.9	ν_1
747.8	-2.0	
765.5	0.5	ν_3
778.5	5.2	
805.6	3.6	

Note (1) The assignment was done based on the IO_3 pyramidal ion rather than the IO_6 octahedron normally found for ABO_3 -type ferroelectric materials. (2) The two Raman bands belonging to the ν_1 mode soften with increasing pressure.

3. Results and Discussion

Under ambient conditions, KIO_3 belongs to the triclinic space group $P1$, with the following crystal parameters: $a=0.7436$, $b=7.7183$, $c=7.7328$ nm, $\alpha=108.986^\circ$, $\beta=109.449^\circ$.

$\gamma=109.209^\circ$, and with four molecular units per unit cell $Z=4$. Unlike most other ABO_3 type ferroelectric materials which have the typical perovskite structure and the B atoms are surrounded by six O atoms to form BO_6 octahedron, the iodine atom has three nearest O atoms to form a severely distorted pyramidal IO_3 ion [6]. An isolated XY_3 unit belongs to the C_{3v} point group and has four internal vibrational modes: $\nu_1(A_1)$, $\nu_2(A_1)$, $\nu_3(E)$, $\nu_4(E)$. All the modes are active in both Raman and infrared. Consequently, there are 4 Raman bands expected for the ν_1 and ν_2 vibrational modes, and 8 Raman bands for the ν_3 and ν_4 modes in the crystal.

Fig.1. Representative Raman spectra in the wavenumber region below 600 cm^{-1} . The numbers in the parentheses indicate respective phases. Note the scale in this figure is expanded by 8 times relative the spectra shown in Fig. 2.

The observed Raman bands and their assignments are given in Table 1. All the bands can be assigned to the vibrational modes of the IO_3 pyramid: the bands between $150 - 200\text{ cm}^{-1}$ to the ν_4 modes, the $300 - 400\text{ cm}^{-1}$ region to the ν_2 modes, the bands at $730, 750$ and 765 cm^{-1} to ν_1 , and those at 783 and 807 cm^{-1} to ν_3 . The ν_1 modes are by far the strongest bands in the spectra, about 20 times stronger than the other bands. The number of observed bands are smaller than expected from the group theory predictions, especially for the ν_3 and ν_4 bands. This can be contributed to the low intensity of some Raman bands and the expected overlapping at room temperature which makes it very difficult to resolve closely spaced bands. Polarized Raman

work with good quality crystals may detect more bands. No bands were assigned to the translational modes of the K^+ ions since these bands are expected to be below 100 cm^{-1} and cannot be measured due to the cut-off of the holographic notch filters used in the experiment (see latter section).

Fig.2. Representative Raman spectra in the wavenumber region above 600 cm^{-1} .

Figures 1 and 2 show typical high pressure Raman spectra up to 35 GPa, together with the proposed phase transitions inferred from this work. It is immediately clear that a rich variety and drastic spectral changes occur in KIO_3 and very different structures exist in the pressure range studied.

Below 5.0 GPa, the wavenumbers of the ν_1 modes at 730.5 and 747.8 cm^{-1} decrease under compression. The lowest wavenumber Raman band observable in this experiment at 161.4 cm^{-1} also decreases with increasing pressure, while the other bands show the expected stiffening. In fact there are some subtle changes in the 0-5 GPa pressure range, which may indicate phase transitions. For example, the ν_3 and ν_4 Raman bands at 3.6 GPa look quite different from those at ambient pressure. However we cannot rule out the possibility that these relatively small changes are due to the relative orientation of the laser polarization direction and that of the single crystal sample. Another possibility is related to the multi-domain nature of the sample and the fact that it is not guaranteed that the laser

will hit the same spot (about 1 μm diameter) of the sample all the time.

Drastic spectral changes occur for all the modes at the ambient pressure phase III to the high pressure phase HPI transition at 5.0 GPa. The ν_4 modes, at 161.4, 164.9 and 179.5 cm^{-1} at ambient pressure, are replaced by a new set of bands. The most striking difference is that the four ν_2 bands disappear and two stronger bands appear. In the high this phase transition, the ν_1 bands become broader and the two low wavenumber bands below 200 cm^{-1} merge into one band. In the spectrum at 10.4 GPa in Fig. 1, there is a strong band at 144.8 cm^{-1} which is not present in the spectra at lower pressures. This band actually exists at lower pressure, but at lower wavenumber. It could not be recorded in our experiment because the holographic notch filters used in the micro-Raman spectrometer blocks any bands below about 125 cm^{-1} . It becomes visible in our experiment at higher pressure as its wavenumber increases under compression. Above 10 GPa, the pressure deviates from truly hydrostatic and this causes band broadening which is expected to be more pronounced for the low wavenumber modes.

We propose another phase transition (HPII to HPIII) at 15 GPa. In phase HPIII, the two high wavenumber Raman bands of the ν_1 mode merge into one which starts to stiffen under further compression, while the other ν_1 band continues to soften though at a slower rate. The low wavenumber bands around 200 cm^{-1} are replaced by a complete new set of bands in phase HPIII. HPIII may have a higher symmetry than the two lower pressure phases as indicated by the simpler ν_1 bands and the IO_3 pyramid may be more regular. This transition is first order with a large pressure hysteresis as seen from the continuous evolution of the low wavenumber bands in HPIII.

Major spectral changes also happen at the HPIII/HPIV phase transition at 22 GPa, where the ν_1 bands are replaced by a completely new set of bands. At least five bands can be discerned in the ν_1 mode region. Some new bands also appear in the 500-600 cm^{-1} region, which cannot be assigned to either of the vibrational modes of the IO_3 pyramidal ion. It is quite clear that this transition involves drastic structural changes of the sample. The IO_3 pyramids may have lost their identity in HPIV and the iodine atom has a coordination number different from 3 to accommodate the same number of molecular units in a much smaller volume.

We speculate that the iodine ions have coordination number 6 and form IO_6 octahedra like most other ABO_3 ferroelectric materials. The HPIII/HPIV transition is deep into the pressure region where the pressure is highly inhomogeneous using the ethanol-methanol pressure medium. It is worth noting that two Raman spectra recorded at 33 GPa at a 24-hour interval are nearly identical and the pressure dropped by only 2 GPa. Therefore we suggest that the drastic change in the Raman spectra observed at 22 GPa signifies a structural phase transition, rather than mere spectral changes brought about by the inhomogeneity of the pressure. However it is not clear what is the role played by the stress in causing this phase transition.

wavenumber region, the two strong ν_1 bands at 730.5 and 747.8 cm^{-1} split into three bands. The two stronger ν_3 bands are also replaced by two new bands. In phase HPI, the Raman bands belonging to the ν_1 modes continue to soften with increasing pressure, while all the other bands show the expected increase in wavenumber with pressure.

The HPI to HPII phase transition occurs at 8.7 GPa, involving relatively subtle spectral changes. At

In our high pressure studies of ferroelectric materials [7-9], we have found that the wavenumber of the ν_1 mode often decreases with increasing pressure and there seems to be a correlation between the softening mode and structural instability at high pressure. However the other ABO_3 type ferroelectric materials we studied all belong to the perovskite structure.

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