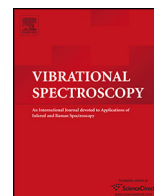




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journal homepage: www.elsevier.com/locate/vibspecPressure dependent Raman studies in the $K_2Mo_2O_7 \cdot H_2O$ crystalG.D. Saraiva^{a,*}, J.A. Lima Jr^b, F.F. de Sousa^c, J.H. da Silva^d, V.O. Sousa Neto^a,
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ABSTRACT

The pressure dependent Raman scattering in the potassium molybdenum oxide hydrate crystal, $K_2Mo_2O_7 \cdot H_2O$, was measured. The high pressure Raman study showed, that the compound remains in the triclinic structure within the 0.0–3.81 GPa range and undergoes a structural phase transition between 3.81 and 4.13 GPa. This particular phase transition is most likely connected with changes in the Raman spectrum, in which the number of modes associated originally with the stretching vibrations in the MoO_5 and MoO_6 units is increased. However, the phase at atmospheric pressure shows bands due to the presence of only one equivalent site, while in the high-pressure phase, two bands are associated with the stretching modes. Continuing the pressure evolution up to 17.04 GPa, two further phase transitions occurred in this crystal in the 6.3–8.1 GPa and the 12.3–14.0 GPa range, respectively. The Raman spectra measured at about 17.04 GPa presented a crystal structure, which experienced a pre-amorphization with a total loss of all lattice modes. This particular result is indicative that this material may have undergone a complete amorphization at pressures larger than 17.04 GPa. Then, the reversible character in the triclinic $P-1$ (C_2^1) structure was recovered after releasing the pressure.

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1. Introduction

In this research, the vibrational properties of hydrated potassium molybdate have been studied as a function of the hydrostatic pressure. The compound potassium dimolybdate hydrate, $K_2Mo_2O_7 \cdot H_2O$, belongs to the triclinic system with the space group ($P-1$), with two formulae per unit cell ($z=2$). The lattice cell dimensions are as follows: $a=7.635(4) \text{ \AA}$, $b=8.906(4) \text{ \AA}$, $c=7.647(4) \text{ \AA}$, $\alpha=109.44(7)^\circ$, $\beta=95.73(6)^\circ$, $\gamma=119.20(7)^\circ$. The chain structure in the edge shared the octahedron MoO_6 and the trigonal pyramids MoO_5 , approximately parallel to the “a” axis in the crystal [1,2]. Fig. 1 shows a schematic unit cell of the hydrated potassium dimolybdate viewed along the axes “b”, in agreement with Ref. [1]. The potassium ions and water molecules are found in inter chain positions [1,2].

The molybdate compounds reported in the literature exhibit interesting physical properties, such as rich phase transition sequences [3], highly disordered phase, conformational changes, an amorphization process (induced by high pressure) [4] and an

amorphous–crystalline transition [5], which makes this material a good prototype in order to establish new concepts on the physics underlying the phase transitions [6,7], as well as their technological applications [8] in the field of catalysis [9,10] and quantum electronics [7]. Furthermore, from the point of view of vibrational spectroscopy (Raman and infrared) [11,12] and X-ray diffraction [9,1], many studies have been performed for hydrate molybdate crystals. Raman spectroscopy measurements in the polycrystalline $K_2Mo_2O_7 \cdot H_2O$ compound, combined with hydrostatic pressure, are powerful techniques allowing us to monitor special vibrational effects that occur with the translational, stretching and bending vibrations of the MoO_5 and MoO_6 units, as a function of pressure. For instance, these combined techniques were important to investigate the vibrational behavior in the hydrated material for the occurrence of soft mode and conformational changes, connected with water libration modes under hydrostatic pressure [3].

The hydrate molybdates reported in this study exhibited three phase transformations. The first and second phase transition occurs in a hydrostatic regime. As reported with previous data [13], the increase in the ruby R1 line width remains below 1 cm^{-1} up to 8 GPa and reaches 10 cm^{-1} at 20 GPa [14,15]. Furthermore, the

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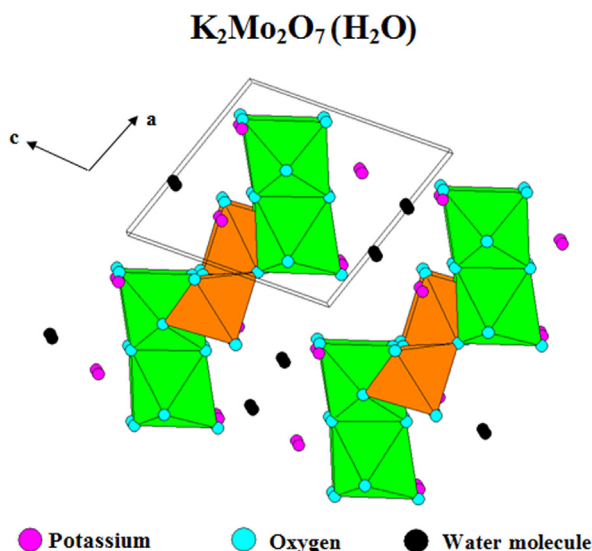


Fig. 1. Unit cells of the $K_2Mo_2O_7 \cdot H_2O$ crystal in the triclinic phase (C_1 space group). The structure is viewed along the “*b*” axis.

requirement on hydrostatics depends considerably on the type of measurement and the sample under investigation. The third phase transformation occurs at non-hydrostaticity, while occurring in these media under pressure [16–18].

2. Experimental

A powder sample of dipotassium molybdate $K_2Mo_2O_7 \cdot H_2O$ was obtained from K_2MoO_4 and MoO_3 , which were mixed

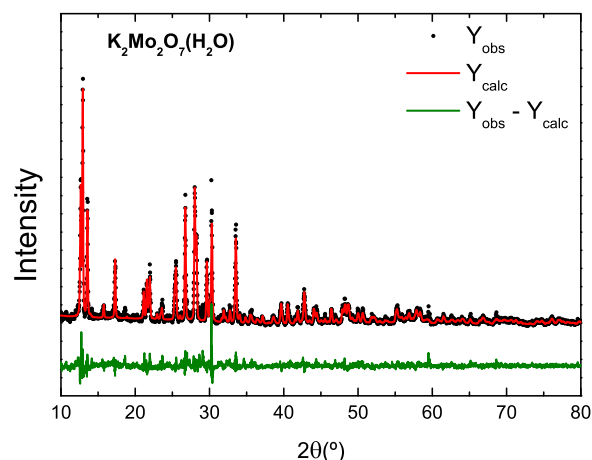


Fig. 2. Rietveld refinement of X-ray diffraction pattern $K_2Mo_2O_7 \cdot H_2O$ crystals measured at ambient conditions.

homogeneously in 1:1 molar ratio. This mixture was heated in ceramic boats and aired up to 800 °C during 2 h. The melting was cooled down to room temperature for 24 h. The formation of the product (crystalline phase) and its structural characterization were confirmed by X-ray diffraction (XRD) measurements, using a Bruker D-8 Advance XRD diffractometer with the $CuK\alpha$ radiation of $\lambda = 1.54 \text{ \AA}$ in the 2θ range from 5° to 60°. Fig. 2 shows the structural refinement, which was done using the Rietveld method along with the GSAS program, which confirmed a triclinic structure (ICSD No. 202392) without any secondary phase with the following structural refinement details: $\chi^2 = 2.51$ is the square of goodness-of-fit indicator and the $R_{WPF} = 0.19$ is the refinement quality

Table 1
Observed Raman modes for the $K_2Mo_2O_7 \cdot H_2O$ system, together with their tentative assignment for the triclinic phase with ω_{obs} (cm^{-1}) for observed bands.

Raman (Triclinic Phase) ω_{obs} (cm^{-1})	Calculations from Ref. [23]	Mode assignments adapted from Ref. [23]
934	945	Mo—O stretching
907	895	Mo—O stretching
887	890	Mo—O stretching
857	839	Mo—O stretching
772	819	Mo—O stretching
734	767	Mo—O stretching
710	746	Mo—O stretching
581	516	Bending(oct)
475	477	Bending(oct)
418	415	Bending(oct)
381	380	Bending(oct) + bending(pyr)
360	370	Bending(oct) + bending(pyr)
348	356	Bending(oct) + bending(pyr)
332	318	Bending(oct) + bending(pyr)
295	288	Bending(oct) + bending(pyr)
284	284	Bending(oct) + bending(pyr)
252	254	Bending(oct) + bending(pyr)
226	223	Bending(oct) + bending(pyr)
211	211	Bending(oct) + bending(pyr)
191	195	MoO ₅ and MoO ₆ units motions
169	182	MoO ₅ and MoO ₆ units motions
164	161	MoO ₅ and MoO ₆ units motions
146	153	MoO ₅ and MoO ₆ units motions
140	145	Pyr + K trans
123	127	Pyr + K trans
113	112	Pyr + K trans
106	104	Pyr + K trans
98	101	Pyr + K trans
82	84	Pyr + K trans
65	73	trans (oct + K) + trans (pyr)
58	51	trans (oct + K) + trans (pyr)

oct.: octahedron; pyr.: pyramidal; trans.: translation.

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