

High-pressure Raman scattering of MgMoO_4

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ABSTRACT

In this paper, we present results of high-pressure Raman scattering studies in $\beta\text{-MgMoO}_4$ from atmospheric to 8.5 GPa. The experiments were carried out using methanol–ethanol as pressure medium. By analyzing the pressure dependence of the Raman data (change in the number of lattice modes, splitting of bands and wavenumber discontinuities) we were able to observe a phase transition undergone by the $\beta\text{-MgMoO}_4$ at 1.4 GPa, which is only completed at ~ 5 GPa. The transition was observed to be irreversible and the modifications in the Raman spectra were attributed to the changes in coordination of Mo ions from tetrahedral to octahedral. The transition possibly changes the original $C2/m$ symmetry to $C2/m$ or to $P2/c$. Implication on the phase transition for similar molybdate structures, such as $\alpha\text{-MnMoO}_4$, is also highlighted.

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1. Introduction

Molybdate and tungstate crystals belong to a class of compounds with interesting physical and chemical characteristics, thus leading them to be used in several technological applications [1], including hydrogen batteries [2,3], equipments for ionizing radiation detectors and scintillators for use in cryogenic experiments in particle physics [4–6], tunable lasers [7], optoelectronic devices [8,9], among others. Furthermore, some molybdates and tungstates exhibit negative thermal expansion in wide temperature range, a phenomenon which has been exploited in view of producing certain devices [10–12].

When submitted to extreme pressure conditions, molybdates and tungstates exhibit several lattice instabilities giving rise to a rich polymorphism, which will depend on the original structure as well as type of ions present in a compound [1]. It is known that BWO_4 wolframites (B = divalent ion) are much harder than the scheelite-type tungstates, thus leading pressure-induced phase transitions at wolframites to occur at much higher pressure values as compared to scheelite [13]. Under high pressure it was also possible to observe a scheelite-to-wolframite phase transition in cadmium molybdate, CdMoO_4 , and a scheelite-to-fergusonite

phase transition in BaWO_4 , PbWO_4 , SrWO_4 and CaWO_4 [14]. In another hand, wolframite-type structures such as MgWO_4 , MnWO_4 , CoWO_4 , NiWO_4 , ZnWO_4 and CdWO_4 show no phonon softening upon compression [15] while scheelite structures like BaWO_4 present bands with soft-mode characteristics [16].

Among the molybdates, MgMoO_4 has recently received attention due to its potential application as a tunable solid-state laser crystal [7]. Moreover, Yb^{3+} doped MgMoO_4 was also reported as a cryogenic photon-scintillation detector [9]. Two polymorphs of MgMoO_4 are known to exist, α and β . The $\alpha\text{-MgMoO}_4$ crystallizes in the cuproscheelite-type structure (space group $P-1$), similar to CuMoO_4 , and it is isostructural to $\alpha\text{-ZnMoO}_4$ [17,18]. The $\beta\text{-MgMoO}_4$ crystallizes in a monoclinic structure in the $C2/m$ (C_{2h}^3) space group with cell parameters $a = 10.273 \text{ \AA}$, $b = 9.288 \text{ \AA}$, $c = 7.025 \text{ \AA}$, $\beta = 106.96^\circ$, $Z = 8$ [18,19]. This phase is isostructural to the high-temperature phases of $\alpha\text{-MnMoO}_4$, $\beta\text{-NiMoO}_4$, $\beta\text{-FeMoO}_4$ and $\beta\text{-CoMoO}_4$. According to Ref. [20] the primitive cell contains four Mo atoms (two of them in sites with C_2 symmetry and the other two in sites with C_2 and C_s symmetry) surrounded by slightly distorted oxygen tetrahedra. Temperature-dependent Raman study showed that the monoclinic phase is stable from 293 K to 640 K. However, at higher temperatures the crystal undergoes two structural phase transitions changing from monoclinic to an incommensurate phase at 640 K and from the incommensurate state to a hexagonal phase at 770 K [21].

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In this paper we investigate β -MgMoO₄ (hereafter MgMoO₄) under high pressure conditions for pressures in the range 0.0–8.5 GPa. We report the occurrence of a phase transition as well as a discussion about the new crystal phase.

2. Experimental

MgMoO₄ salt was furnished by Aldrich Chemicals, being used without further purification. X-ray diffraction measurements confirmed that the room temperature and atmospheric phase of the material is β -MgMoO₄. The pressure-dependent Raman spectra were obtained with a triple-grating spectrometer T64000 from Jobin-Yvon equipped with a N₂-cooled charge coupled device detector system. The excitation was the 514.5 nm line of an argon laser and the spectrometer slits were set for a resolution of 2 cm⁻¹. The high pressure was reached with the samples loaded into a diamond anvil cell from EasyLab with diamond of 0.5 mm of culets. A stainless steel gasket with a thickness of 200 μ m was pre-indented to 45 μ m. A hole with 120 μ m diameter was drilled in the center of the indentation by using an electric discharge machine from EasyLab. The transmitting media utilized was the methanol–ethanol 4:1 mixture and the pressure was calibrated from the shifts of the ruby R₁ and R₂ fluorescence lines [22].

3. Results and discussion

At room temperature and atmospheric pressure, MgMoO₄ crystallizes in a monoclinic structure, space group $C2/m$ (C_{2h}^3), with 8 molecules per unit cell [18,19]. Group theory analysis predicts that the optical modes are distributed among the irreducible representations of the factor group C_{2h} in the Γ point as $19A_g + 17B_g + 14A_u + 19B_u$. The internal modes of the MoO₄²⁻ tetrahedra are distributed as $11A_g + 7B_g + 8A_u + 10B_u$, where $2A_g + 1A_u + 1B_u$ are due to symmetric stretching ν_1 modes, $3A_g + 3B_g + 2A_u + 4B_u$ are due to anti-symmetric stretching ν_3 modes, $3A_g + 1B_g + 3A_u + 1B_u$ are due to symmetric bending ν_2 and $3A_g + 3B_g + 2A_u + 4B_u$ comes from anti-symmetric bending ν_4 modes. The external lattice modes are distributed as $8A_g + 10B_g + 6A_u + 9B_u$. The selection rules state that modes with A_g and B_g are Raman active while modes with A_u and B_u symmetry are infrared active.

Fig. 1 presents the Raman spectra of MgMoO₄ taken at different pressures in the spectral range 550–50 cm⁻¹. Most of the bands appearing in this plot for wavenumbers lower than 250 cm⁻¹ are assigned to lattice vibrations following the model of Ref. [20]. It is worth to mention that because we have recorded the unpolarized Raman spectra, the vibrational modes with A_g and B_g symmetries were observed. The modes above 250 cm⁻¹ are assigned as internal modes of MoO₄ units, although some bending modes are mixed with some lattice modes as discussed in Ref. [20]. By further increasing pressure, we observe that Raman spectra remain qualitatively the same up to 1.1 GPa. However, the spectrum recorded at 1.4 GPa shows a very different profile from that obtained at 1.1 GPa, with the emergence of six new bands at about 143, 150, 172 and 237 cm⁻¹, splitting of some bands and wavenumber change of various vibrational modes. The main changes observed in the spectra can be better understood by analyzing the wavenumber (ω) vs. pressure (P) plot shown in Fig. 2. This figure indicates clearly that the material experiences a structural modification at $P \sim 1.4$ GPa. The wavenumber vs. pressure data are well fit with a linear function $\omega(P) = \omega_0 + \alpha P$. The experimental wavenumber (ω_{obs}), the pressure intercept ω_0 and the pressure coefficient α , as well as the assignment of the bands are listed in Table 1. As far as the assignment is concerned, it is important to remember that some of the lattice modes couple with bending (ν_2 and ν_4) modes; and this is the

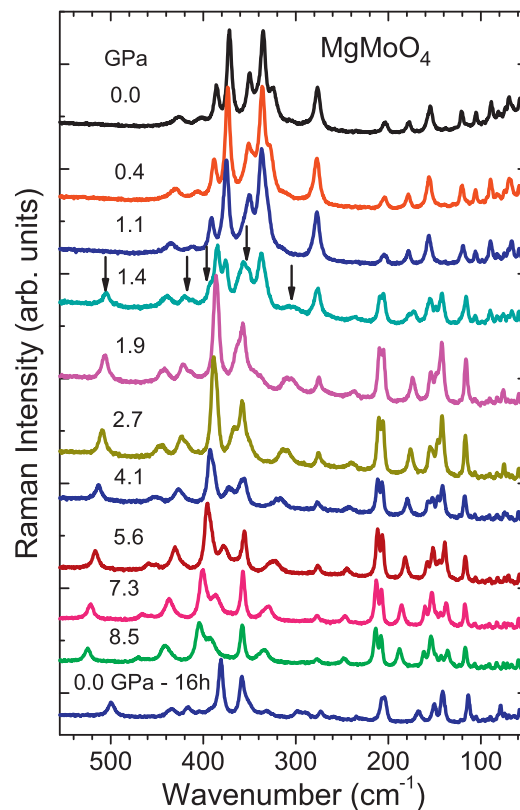


Fig. 1. Room-temperature Raman scattering spectra of MgMoO₄ up to 8.5 GPa in the wavenumber range 550–50 cm⁻¹.

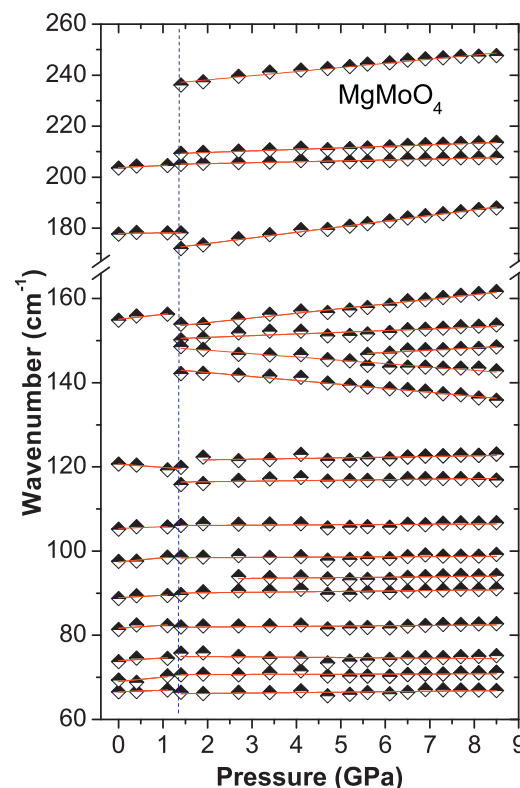


Fig. 2. Pressure dependence of the experimental Raman mode wavenumbers of the MgMoO₄. The solid lines (red) correspond to fits to the experimental data and the dashed vertical line corresponds to the boundary between the atmospheric phase and the high pressure phase. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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