

Ag₂Mo₃O₁₀·1.8H₂O Nanowires Under High Pressure: In Situ Raman Spectroscopy

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Introduction

Silver molybdates, a group of important inorganic materials, have attracted growing attention in photoluminescence, antibacterial, anode material for batteries and photocatalysis applications. Among the molybdates, the silver trimolybdate - Ag₂Mo₃O₁₀·1.8H₂O - stands out for presenting a band gap of 2.8 eV, turned out to be a material with a great significance due to its visible-light photocatalytic properties [1]. In this work, we present a pressure-dependent behavior of silver trimolybdate nanowires using *in situ* Raman scattering. The Ag₂Mo₃O₁₀·1.8H₂O nanowires was obtained by hydrothermal method at 140 °C for 6 h. The structural and morphological characterization of the sample has been done by X-ray diffraction (XRD) and scanning electron microscopy (SEM). A membrane diamond-anvil cell (MDAC) was used to investigate the effect of high pressure in Ag₂Mo₃O₁₀·1.8H₂O nanowires.

Results and Discussion

At ambient conditions, the silver trimolybdate crystallizes in orthorhombic structure (*Pnma* space group; Z=4; lattice parameters of a=13.201(2) Å, b=7.593(1) Å, c=9.754(1) Å). The as-prepared material presented straight wire-like structures with high morphology homogeneity, without any impurity particles, amorphous materials or aggregates. Pressure-dependent studies of Raman scattering were performed on Ag₂Mo₃O₁₀·1.8H₂O nanowires up to 5.0 GPa. The vibrational spectra of the Ag₂Mo₃O₁₀·1.8H₂O nanowires under high pressure showed overlaps of some bands and appearance of some peaks above 0.8 GPa and 3.4 GPa, which were attributed to the structural phase transformations associated with deformations of the polyhedral into a unit cell (See Figure 1). Another feature to highlight is that the lowest frequency mode at 56 cm⁻¹ (translational mode) is found to soften with pressure between 1 atm and 0.5 GPa (Phase I – Ambient phase). The same happens with the vibrational mode at 67 cm⁻¹ between 0.8 GPa and 2.7 GPa (Phase II). The intrinsic dynamic instability of the phases I and II in Ag₂Mo₃O₁₀·1.8H₂O nanowires is supported by the presence of an external soft mode, leading to

structural phase transitions. The reversibility of structural transitions was observed during the decompression experiment. It is worth noting that generally the transformations driven by soft modes are expected to be reversible [2].

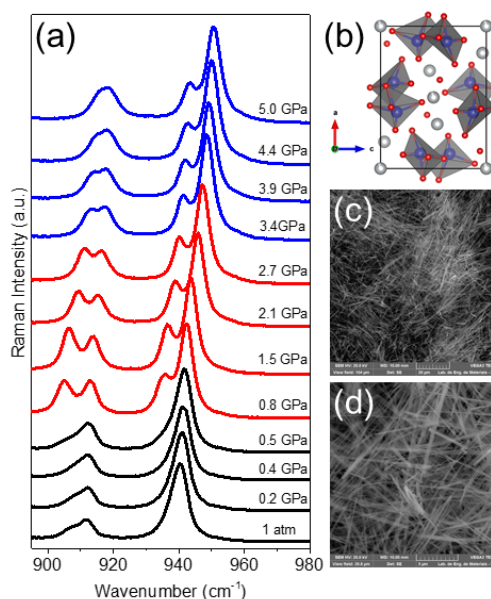


Figure 1. (a) Selection of Raman spectra collected under compression up to 5.0 GPa. (b) Unit cell of Ag₂Mo₃O₁₀·1.8H₂O crystal. (c) SEM images of the as-prepared silver trimolybdate nanowires.

Conclusions

This study described the effects of the pressure-dependent Raman scattering in the vibrational and the structural properties of Ag₂Mo₃O₁₀·1.8H₂O nanowires obtained by a hydrothermal method. The reversible phase transformations under pressure was observed in this material: Phase I - Ambient phase (1 atm - 0.5 GPa) → Phase II (0.8 GPa - 2.7 GPa) → Phase III (3.4 GPa - 5.0 GPa).

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¹ X. Chen *et al.* Ag₂Mo₃O₁₀ Nanorods Decorated with Ag₂S Nanoparticles: Visible Light Photocatalytic Activity, Photostability, and Charge Transfer, Chem. Eur. J., 21, 2015, pp. 18711–18716.

² N. Gang *et al.* Phase transitions in Sc₂(WO₄)₃ under high pressure Physical Review B, 72, 2005, pp. 064106.