

Raman-scattering studies of MoO₃ polymorphs under extreme conditions.

Jose V. Silveira^{1,*}, Adrya J. P. Cordeiro², Francisco F. Ferreira², Cleanio L. Lima³, Paulo T. C. Freire⁴, Antonio G. Souza Filho⁴.

¹Laboratório de Síntese e Engenharia de Nanomateriais (LSE Nano), Universidade Federal do Ceará, Sobral, Brazil.

²Programa de Pós-Graduação em Física, Universidade Federal do Pará, Belém, Brazil.

³Departamento de Física, Universidade Federal do Piauí, Teresina, Brazil.

⁴Departamento de Física, Universidade Federal do Ceará, Fortaleza, Brazil.

*jvaldenirs@fisica.ufc.br.

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Introduction

Molybdenum oxide-based materials are an attractive materials class due to their ability to produce multiple valence states and exhibit rich chemistry, such as oxide, suboxides, hydroxides, and crystalline hydrate¹. Particularly, MoO₃ oxide exhibits a wide variety of crystalline phases and has attracted the interest of many research groups over time. At ambient conditions, MoO₃ present five known polymorphs. Under extreme conditions, the MoO₃ presents structural phase transitions or amorphization. This makes MoO₃ an interesting material from the scientific point of view.

Here, we present high-pressure and high-temperature Raman spectroscopy studies of different MoO₃ polymorphs. In addition, we will also present results related to obtaining a new MoO₃ polymorph, synthesized under high-pressure conditions.

Results and Discussion

Under high-pressure conditions (up to 22 GPa), the Raman spectra of nanoribbons in the orthorhombic phase (α -MoO₃) show slight modifications, indicating the occurrence of a phase transition accompanied by changes in morphology (nanoribbons fracture). On the other hand, under high-temperature conditions (up to 750 °C) spectral changes have occurred due to the change in nanoribbons morphology (coalescence).

Temperature-dependent Raman spectroscopy in both the monoclinic (β -MoO₃) and hexagonal (h -MoO₃) metastable phases confirms a phase transition in the 400–450 °C temperature range to orthorhombic phase. Raman data analysis of the hexagonal phase unveiled that the wavenumber difference between two particular lower frequency modes can be used as a temperature gauge for h -MoO₃ nanorods in the 300–690K temperature range.

Under high-pressure conditions, we have observed that h -MoO₃ nanorods present an irreversible pressure-induced amorphization at 16.8 GPa. Monoclinic β -MoO₃ microcrystals investigated by *in situ* Raman scattering up to 10 GPa show a pressure-induced structural phase transition

occurred between 1.3 and 3.7 GPa. Moreover, we observed that the new crystalline phase has remained on decompression, and it has never been observed before.

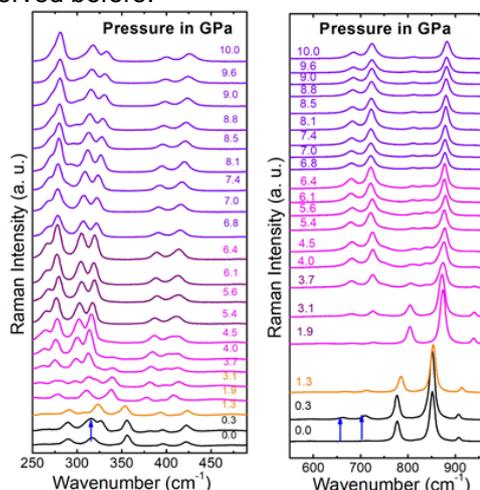


Figure 1. Pressure-dependent Raman spectra of the β -MoO₃ with the spectral range (a) 250-490 cm⁻¹ and (b) 550-970 cm⁻¹.

Conclusions

Raman spectra of the MoO₃ polymorphs are dependent on the crystalline phase and very sensitive to structural changes. Raman data, such as wavenumber, relative intensities, and linewidth of the active Raman bands of MoO₃ polymorphs carry detailed information about sizes, shapes and crystalline phases of the material. This technique is a powerful tool to study MoO₃ polymorphs and is of fundamental significance in understanding crystal packing and the origin of lattice instabilities in such structures.

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