

Pressure-induced phase transitions in $\text{Al}_2(\text{WO}_4)_3$

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Abstract

The high pressure behavior of aluminum tungstate [$\text{Al}_2(\text{WO}_4)_3$] has been investigated up to ~ 18 GPa with the help of Raman scattering studies. Our results confirm the recent observations of two reversible phase transitions below 3 GPa. In addition, we find that this compound undergoes two more phase transitions at ~ 5.3 and ~ 6 GPa before transforming irreversibly to an amorphous phase at ~ 14 GPa.

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1. Introduction

In recent years, several compounds of the family $A_2(\text{BO}_4)_3$ ($A = \text{Al}, \text{Sc}, \text{Zr}, \text{Y}, \text{Cr}$, etc. and $B = \text{Mo}$ and W) have been investigated due to their interesting physical and chemical properties. While some of these show ferroelastic phase transitions at low temperatures [1,2] others do not [3]. Also many of these show negative thermal expansion (NTE), low pressure phase transformations as well as amorphization at high pressures [4–13]. Aluminum tungstate, which is a member of this family, crystallizes in the orthorhombic phase and shows a phase transition from orthorhombic to monoclinic symmetry at low temperatures [1]. However, the NTE behavior of $\text{Al}_2(\text{WO}_4)_3$ is a bit controversial as the dilatometry measurements suggest that it has NTE whereas, the X-ray diffraction experiments show that it has an anisotropic NTE and that its overall thermal expansion is positive [4]. The behavior of this compound has also been investigated under pressure in several studies [5,8,14,15]. A Raman scattering investigation on $\text{Al}_2(\text{WO}_4)_3$ suggested a reversible symmetry lowering phase transition at ~ 0.1 GPa [5]. At pressures higher

than 7 GPa, it evolved irreversibly into a disordered phase. Subsequent resistivity and compressibility studies, using a piston–cylinder device, also indicated a phase transformation at 0.6 GPa [14]. An X-ray diffraction study on the recovered samples of $\text{Al}_2(\text{WO}_4)_3$, pressurized up to 8 GPa, showed the absence of any irreversible change [16]. An electrical conductivity study by Liu et al. [15] indicated pressure-induced valence change of $\text{W}^{6+} \rightarrow \text{W}^{5+}$ at 0.9 GPa, 400 °C. They also reported an orthorhombic to tetragonal structural phase transition at 400 °C, 2.8 GPa. Recent Raman investigations have shown the existence of two reversible phase transformations at 0.28 and 2.8 GPa [8]. As most of these studies are at low pressures, we have investigated the behavior of $\text{Al}_2(\text{WO}_4)_3$ at higher pressures (~ 18 GPa) with the help of Raman scattering studies.

2. Experimental

Polycrystalline sample of aluminum tungstate was prepared by the conventional solid-state reaction of Al_2O_3 and WO_3 respectively [16]. The high-pressure experiments were carried out using a Mao Bell type of diamond anvil cell. A finely ground powder of the

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sample and a ruby chip were loaded in a 150 μm hole of a steel gasket, pre-indented to a thickness of 70 μm . Methanol–ethanol mixture in the ratio of 4:1 was used as pressure transmitting medium for the quasi-hydrostatic studies. To avoid non-hydrostatic stresses due to sample bridging the diamonds, experiments were repeated several times with varying amount of sample in the gasket. Only those data are presented for which the pressure is reasonably hydrostatic up to ~ 12 GPa. Pressure was monitored using the shift of ruby R-lines [17].

Unpolarized Raman scattering data at high pressures were collected in the 45° geometry, with the help of a CCD-based single stage spectrograph. 532 nm line of a solid-state diode laser was used as an excitation source. An appropriate super-notch filter was used to cut off the Rayleigh scattering, because of which the Raman modes below ~ 200 cm^{-1} could not be recorded. Raman spectra were recorded in finer pressure steps up to 7 GPa and beyond that the pressure was raised up to 18 GPa in somewhat coarser steps. Reasonably good quality Raman data could be obtained with typical collection times of 30–100 s.

3. Results and discussion

At ambient conditions, $\text{Al}_2(\text{WO}_4)_3$ exists in the orthorhombic structure in which AlO_6 octahedra and WO_4^{2-} tetrahedra are corner linked. In this structure (space group $Pnca$, $Z = 4$, 68 atoms per unit cell) Al^{3+} ions occupy the general site '8d' having C_1 symmetry while W occupies '8d' and '4c' sites such that WO_4^{2-} tetrahedra have C_1 and C_2 symmetry [18]. The factor group analysis of Maczka et al. [8] suggests 102 Raman active modes. The unpolarized Raman spectra, recorded by us at room temperature, is shown in Fig. 1(a). As in Ref. [8], the number of observed modes are far less than expected because of the unresolved factor group splittings. However, the observed modes are in agreement with the earlier observations [1,8] and hence we would use the assignments given in Ref. [1]. Accordingly the modes observed between 1010 and 1050 cm^{-1} are identified to be the symmetric stretch modes of WO_4^{2-} tetrahedra, the modes between 800 and 1000 cm^{-1} are assigned to the asymmetric stretch vibrations and the bending modes are between 300 and 500 cm^{-1} . The two modes observed below 300 cm^{-1} are essentially the translational modes.

Figs. 1(a) and (b) show the background subtracted Raman spectra of Aluminum tungstate at different pressures. The observed pressure dependence of the frequencies of Raman modes is presented in Fig. 2. Our results indicate that below ~ 0.4 GPa, $\text{Al}_2(\text{WO}_4)_3$ continues to exist in the initial orthorhombic phase. Beyond 0.4 GPa, the observed splitting of a few modes indicate a

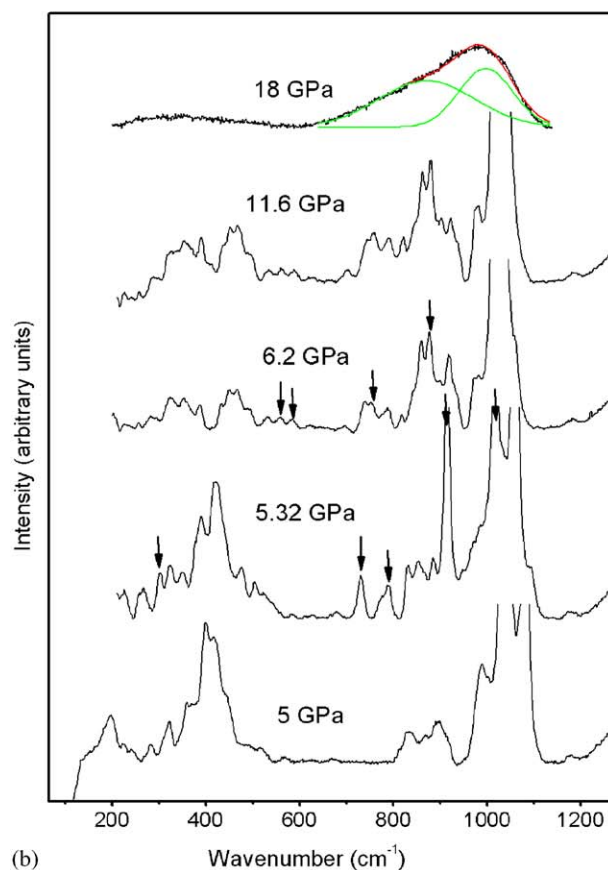
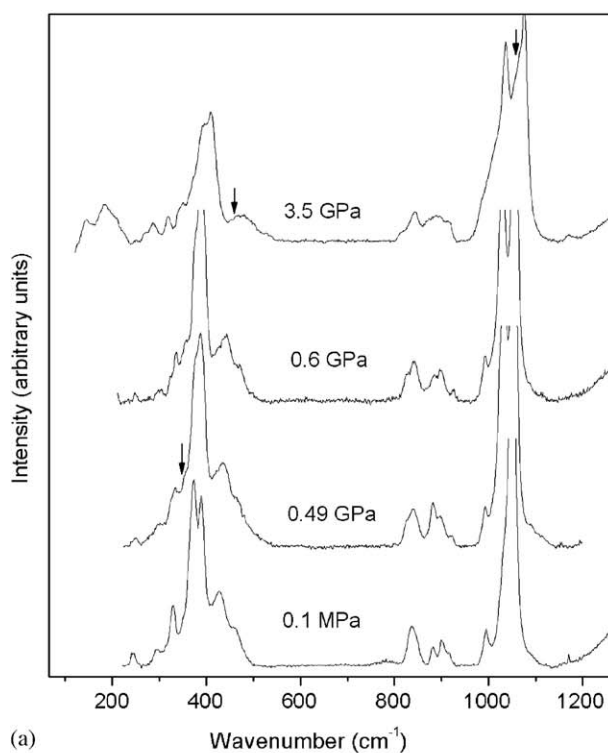


Fig. 1. (a) Raman spectra of $\text{Al}_2(\text{WO}_4)_3$ up to 3.5 GPa. (b) Raman spectra of $\text{Al}_2(\text{WO}_4)_3$ between 5 and 18 GPa. The arrows indicate some of the new Raman modes, and the gray lines indicate the fit to the Raman spectra at 18 GPa.

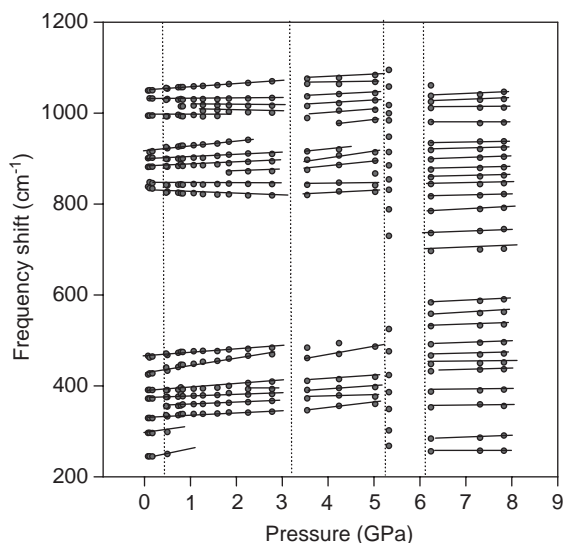


Fig. 2. Frequency shift of the observed Raman modes as a function of pressure. The solid lines are a guide to the eye. The vertical dotted lines indicate the pressures of transformation.

phase transition to a lower symmetry phase. Moreover, as shown in Fig. 2, some weak modes (at 354, 869, 1005 and 1015 cm^{-1}) become observable only at somewhat higher pressures. These new modes are a subset of the new modes observed recently by Maczka et al. at ~ 0.3 GPa. As the measurements in the single crystals have better signal-to-noise ratio [8] not all the weak modes observed with a single crystal could be seen in our powder samples. Furthermore, none of the observed modes show a discontinuity either in frequencies or in slopes [$d\nu/dP$] at 0.4 GPa. This feature implies that the new phase may be closely related to the parent phase and has earlier been suggested to be the same as the low temperature monoclinic phase (due to the similarity of the Raman spectra). We also note that even in the isostructural $\text{Sc}_2(\text{MO}_4)_3$, a phase transformation at 0.29 GPa has been ascribed to a low temperature monoclinic structure (space group $P2_1/a$) [6]. In addition, Figs. 1 and 2 show that beyond ~ 3 GPa, several modes change slope and the FWHM of some of the peaks increases (e.g., for the modes at 366 and 410 cm^{-1} , FWHM increases to 1.5 times while for 1016 cm^{-1} it becomes almost three times). These results imply another phase transition at ~ 3 GPa. Further, the Raman spectra recorded on release of pressure from 3.8 GPa (Fig. 3(a)), confirm the reversible nature of these two phase transitions. The observations of these two reversible phase transitions in our powder samples confirm the results of single crystal study of Maczka et al. [5,8].

On further increase of pressure, beyond 5 GPa the Raman spectrum again shows several changes. Figs. 1(b) and 2 show that new modes emerge between

300–500 and 700–900 cm^{-1} . The Raman mode at 900 cm^{-1} becomes quite intense and sharp and the other modes of this phase are also more clearly resolved than in the previous phase. On further increase of pressure the emergence of several more new Raman peaks beyond ~ 6 GPa, indicates the existence of another phase transition. The observation of several new modes in the region of 600–800 cm^{-1} implies modifications in the interactions of the WO_4^{2-} tetrahedra, as in other compounds of this family, such as $\text{Sc}_2(\text{MO}_4)_3$ [6]. At still higher pressures the Raman modes gradually broaden indicating increasing disorder in the structure. At ~ 14 GPa, the Raman modes merge into broad bands centered at 400 and 1000 cm^{-1} . Raman spectra continues to show these two bands up to the highest recorded pressure of 18 GPa. The observed separation of 14.4 cm^{-1} in R_1 – R_2 lines of ruby at ~ 12 GPa implies that the pressure is reasonably hydrostatic when the structural disorder sets in. Therefore, the emergence of the amorphous phase is not entirely due to non-hydrostatic stresses, in agreement with the similar observations in this family of compounds [13]. Moreover, on release of pressure from 18 GPa (Fig. 3(a)) we observe that these two broad bands continue to exist even at 0.01 MPa indicating an irreversible transformation to an amorphous state. To further characterize the nature of the disordered state, we have also recorded the angle dispersive X-ray diffraction patterns at ambient conditions, at 16.4 GPa and on release of pressure from 16.4 GPa.¹ In the diffraction patterns, shown in Fig. 3(b), all the Bragg peaks of the crystalline $\text{Al}_2(\text{WO}_4)_3$ vanish at 16.4 GPa, implying that this compound turns amorphous by 16 GPa. Non-emergence of any of the Bragg peaks on release of pressure confirms the irreversible nature of this transformation.

Fig. 3(a) shows one broad band around 950 cm^{-1} at 18 GPa, which can be analyzed in terms of two broad bands at 870 and 995 cm^{-1} . On release of pressure, these bands shift to the values 825 and 985 cm^{-1} , respectively, and appear as two separate bands due to lesser broadening. Even at 18 GPa, the centroid of the higher frequency band is red shifted compared to the symmetric stretch modes of the structure prior to amorphization.² These results are common to several compounds of this family [5,6,13]. An explanation of these results in the high-pressure amorphous phase as well as in the recovered samples requires the knowledge of underlying structural arrangements such as changes in tetrahedral nature etc. In the absence of any structural information available in these compounds in the amorphous phase,

¹These measurements were made by a MoK_α line ($= 0.71069 \text{ \AA}$) of the laboratory X-ray source and the diffractions patterns were recorded on an imaging plate kept at a distance of ~ 20 cm. One-dimensional diffraction profiles were obtained through FIT2D [19].

²Asymmetric stretch modes seem to be less sensitive to the local internal strain than the symmetric stretch modes, see for example [20].

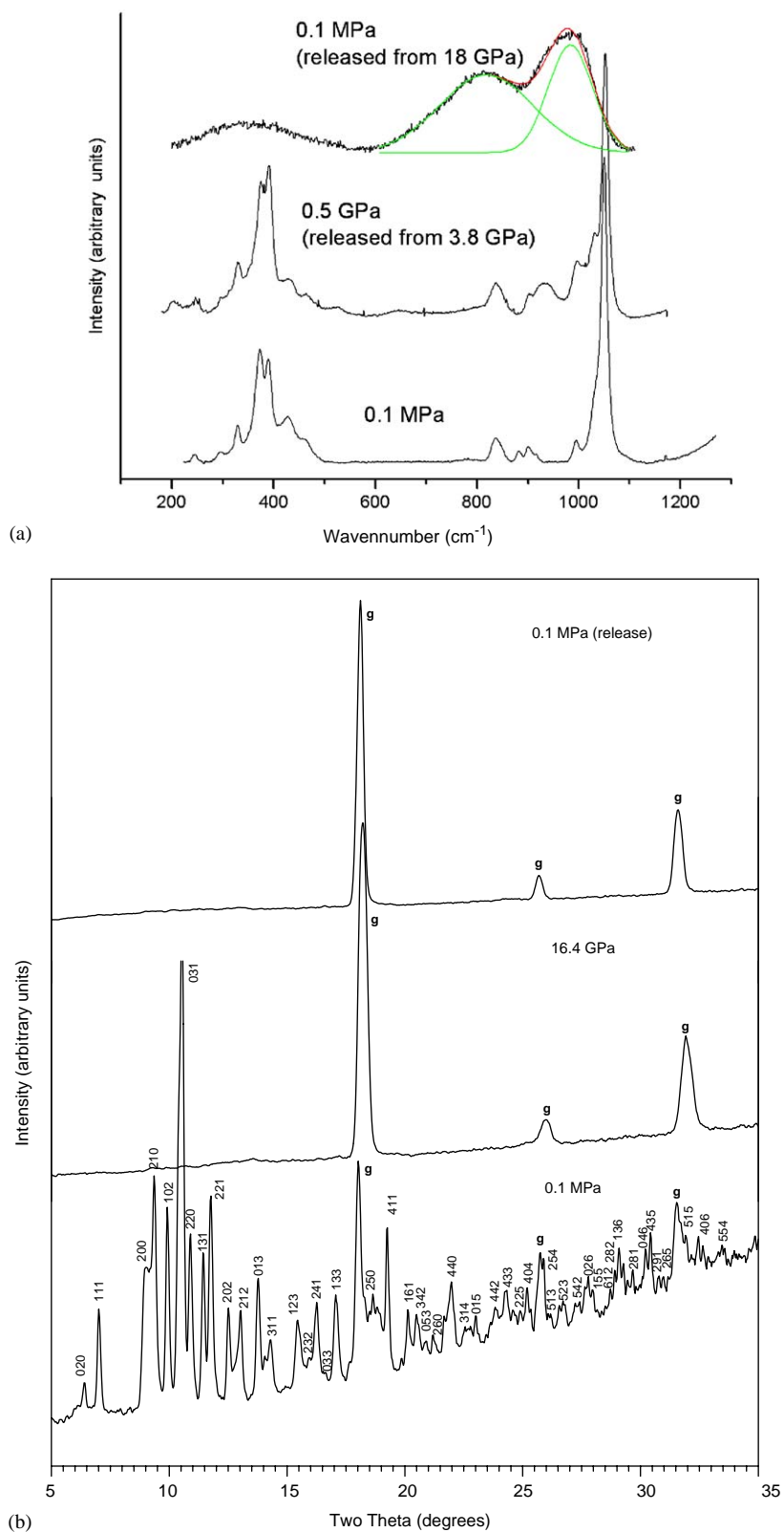


Fig. 3. (a) Raman spectra of $\text{Al}_2(\text{WO}_4)_3$ on release of pressure from 3.8 and 18 GPa. The gray lines indicate the fit to the Raman peaks at 0.1 MPa, on release from 18 GPa. (b) X-ray diffraction patterns of $\text{Al}_2(\text{WO}_4)_3$ at 0.1 MPa, 16.4 GPa and on release of pressure. The tungsten gasket peaks are marked as g.

one can only speculate about the cause of these observations. In a broader sense, at high pressures, the red shift of the centroid (mentioned above) may be due to somewhat larger W–O bond length. This may be due to the approach of oxygen atoms from the neighboring polyhedra, reflecting an effective higher W–O coordination [21]. A slight red shift on release of pressure may be due to the removal of the compressive strain, without any significant structural rearrangements. Essentially, the irreversible nature of amorphization implies that polyhedra not only deform and interconnect probably differently, but also the structural changes are significantly large to hinder the reversal of nature of deformations on release of pressure. A clearer insight may emerge if one has high-pressure EXAFS data and these results may also encourage theoretical simulations.

4. Conclusions

High-pressure Raman studies of aluminum tungstate confirm the reversible pressure-induced phase transitions in this compound around ~ 0.4 and ~ 3 GPa [5,8]. In addition, $\text{Al}_2(\text{WO}_4)_3$ undergoes two more phase transitions at ~ 5.3 and ~ 6 GPa before transforming irreversibly to an amorphous phase at ~ 14 GPa. The irreversible nature of the amorphous phase, characterized by the bands close to the bending and stretching modes of WO_4^{2-} tetrahedra, should encourage X-ray absorption and theoretical studies on this family of compounds.

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