Proceedings of the Symposium A of the European Materials Research, Warsaw, September 2008

# High-Pressure Study of $Gd_2(MoO_4)_3$ by Raman Scattering and *Ab Initio* Calculations

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High-pressure induced phase transitions in a single crystal of gadolinium molybdate,  $Gd_2(MoO_4)_3$  were studied by the Raman spectroscopy and *ab initio* calculations. The amorphization of the sample takes place at about 6 GPa in a mixture of alcohol as a pressure transmitting medium and begins as soon as 3 GPa in argon. In both media, the amorphization is irreversible in the 0–9 GPa investigated pressure range. The joint *ab initio* and Raman results allowed us to conclude that rotations of MoO<sub>4</sub> tetrahedra are the primary structural changes involved in the first phase transition (at about 2 GPa) explaining the softening of the low frequency modes at about 50 cm<sup>-1</sup>. In addition, a progressive distortion of tetrahedra followed by a coordination change (IV–VI) of Mo atoms is observed through the five structural transitions including amorphization. This mechanism based on the steric hindrance of polyhedra is believed to be the most relevant for explaining the amorphization of  $Gd_2(MoO_4)_3$ .

PACS numbers: 61.50.Ks, 64.70.K-, 71.15.Mb, 78.30.-j

#### 1. Introduction

Gadolinium molybdate,  $Gd_2(MoO_4)_3$ , noted GdMo hereafter, is a compound undergoing a pressure-induced amorphization (PIA) [1]. At ambient conditions, it exists in its metastable ferroelastic-ferroelectric  $\beta'$  phase  $(C_{2v}^8)$ space group [2]), instead of the stable denser  $\alpha$  (C2/c) phase. Actually, for GdMo, the high-pressure crystalline form observed by X-ray diffraction (XRD) is a monoclinic or triclinic  $\delta$  form appearing at about 2 GPa and different from the expected  $\alpha$  phase. The disappearance of the diffraction pattern at high pressure is the indication of an amorphization process. This transformation is irreversible and takes place between 6 and 9 GPa depending on the hydrostaticity conditions [3]. Jayamaran et al. monitored the amorphization of polycrystalline GdMo by Raman spectroscopy [4] and found that it takes place near 6 GPa and is preceded by a phase transition at about 2 GPa. Recently  $Eu^{3+}$  fluorescence spectroscopy [5] have given some insight in the amorphization mechanism of the isostructural compound EuMo. Five spectral changes in the fluorescence spectra of Eu<sup>3+</sup> ions preceding the crystal amorphization were observed (Table I). Preliminary results showed that these pressure-induced phase transitions could be observed by the Raman spectroscopy on single crystals [6]. At last, Ganguly et al. [7] have submitted a crystal of GdMo to a uniaxial pressure along the [100] axis at about 140°C, and observed an increase of the band maximum and of the halfwidth of the unstable  $A_1$  TO mode at about 50 cm<sup>-1</sup> with pressure increase. Among the possible amorphization mechanisms the chemical decomposition of GdMo into components Gd<sub>2</sub>O<sub>3</sub> and 3 MoO<sub>3</sub> is favored by the fact that these components occupy a smaller volume than the parent crystal. However, the steric constraint model mentioned for explaining PIA of Zr(WO<sub>4</sub>)<sub>2</sub> [8] could be relevant to GdMo.

In the ferroelectric phase, all of the 201 optic phonons are Raman active. However, at room temperature, the number of observed bands is smaller and it is possible in first approximation to consider the tetragonal symmetry of the paraelectric form which gives rise to 76 Raman active modes. The complete vibrational analysis in the orthorhombic and in the tetragonal factor groups is given in [9], where the vibrations are described in terms of internal and external modes (librations and translations) of the different types of  $(MoO_4)^{2-}$  tetrahedra and of rare-earth ions translations. Table II summarizes the expected  $A_1$  and  $A_2$  vibrations at high (700–1000 cm<sup>-1</sup>) and low (10–600 cm<sup>-1</sup>) wave numbers, respectively.

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#### TABLE I

Expected vibrations in YY, ZZ and XY spectra for orthorhombic and tetragonal phases.  $\nu_1$  to  $\nu_4$ : tetrahedra internal vibrations, R librations, T translation. Only vibrations active in  $\beta$  phase are expected to be intense in  $\beta'$  phase. Two of the symmetry coordinates of librational motions of tetrahedra  $T_{II,III}$  and  $T_I$  in the tetragonal  $D_{2d}$  factor group are reported.

Spectral range $[cm^{-1}]$	Vibrations	Tetrahedra types	$\beta'$ orthorhombic phase $C_{2v}$	$\beta$ tetragonal phase $D_{2d}$				
1000-700								
	$ u_1 $	$MoO_4 T_I$	$A_1 + A_2$	$A_1$				
		$MoO_4 T_{II,III}$	$2A_1 + 2A_2$	$A_1$				
	$\nu_3$	$MoO_4 T_I$	$3A_1 + 3A_2$	$B_1$				
		$MoO_4 T_{II,III}$	$6A_1 + 6A_2$	$2A_1 + B_1$				
600 - 250								
	$\nu_2$	$MoO_4 T_I$	$2A_1 + 2A_2$	$A_1 + B_1$				
		$MoO_4 T_{II,III}$	$4A_1 + 4A_2$	$A_1 + B_1$				
	$ u_4$	$MoO_4 T_I$	$3A_1 + 3A_2$	$B_1$				
		$MoO_4 T_{II,III}$	$6A_1 + 6A_2$	$2A_1 + B_1$				
250 - 10	Т	$MoO_4 T_I$	$3A_1 + 3A_2$	$B_1$				
		$MoO_4 T_{II,III}$	$6A_1 + 6A_2$	$2A_1 + B_1$				
	Т	Gd	$6A_1 + 6A_2$	$2A_1 + B_1$				
	R	$MoO_4 T_I$	$3A_1 + 3A_2$	$A_1$				
		$MoO_4 T_{II,III}$	$6A_1 + 6A_2$	$A_1 + 2B_1$				
Raman activity			XY	XY				
			YY	YY				
			ZZ	ZZ				
$S_{Ry}^{E} = (1/2)(R_{1}y - R_{3}y - R_{2}x - R_{4}x)$ for tetrahedra I								

 $\frac{S_{Ry}}{S_{Ry}^{E}} = (1/2)(R_{1}y - R_{3}y + R_{2}x + R_{4}x)$  $\frac{R_{1}}{S_{Ry}^{E}} = (1/2)(R_{1}x - R_{1}y - R_{2}x - R_{2}y) \quad \text{for tetrahedra II and III}$  $= (1/2)(R_{1}x - R_{1}y + R_{2}x - R_{2}y)$ 

# TABLE II

Transition pressures and observed phases in various experiments.

Experiment	Transition pressures [GPa]								
	P1	P2	P3	P4	P5	P6			
Fluorescence [8]	2.08	2.4	3.5	4.2	5.8	7			
Raman alcohol	$2.00\pm0.1$	2.35	$2.9\pm0.3$	$4.12 \pm 0.4$	$4.75\pm0.2$	6.2			
Phases	I I	I III		V V	V VI		VII		
	$C_{2v}^{8}$	(	$C_{2h}^2$ (	$\mathcal{C}^4_{2h}$	(	$\mathcal{C}^6_{2h}$	(A)		
	Z = 4	Z = 8			2	Z = 8			
Raman argon	2.45			$4.1 \pm 0.4$	$5.02\pm0.2$				
Phases	Ι			1	4+ 2	$4^{+}$	VII		
	$C_{2v}^{8}$	Ι	V + A	I	V V	VI	(A)		
	Z = 4								

# 2. Experimental conditions

# 2.1. Raman measurements

Raman measurements were made on single crystal grown from the melt by Czochralski method. Samples were cut and polished into a parallelepiped  $1 \times 0.5 \times$  $0.5 \text{ cm}^3$ , with orientations  $\{100\}$ ,  $\{010\}$  and  $\{001\}$  of the orthorhombic cell. Monodomain fragments (20  $\times$  20  $\times$ 

20  $\mu$ m<sup>3</sup>) oriented in the (a, c) and (a, b) planes, respectively, were placed in a diamond anvil cell (DAC). A mixture of ethanol-methanol (4:1 volume ratio) on one hand and argon on the other hand were used as pressure transmitting medium (PTM). Pressure was monitored by ruby fluorescence from 1 atm up to 9 GPa [10]. The polarized Raman spectra of  $Gd_2(MoO_4)_3$  single crystal were recorded in the backscattering geometry. The 514.5 nm

line from an Ar ion laser was used as excitation source. Y(ZZ)Y, Z(YY)Z, and Z(XY)Z spectra were recorded in ethanol-methanol mixture, Y(ZZ)Y spectra were also obtained in argon.

## 2.2. Ab initio calculations

We performed the calculations on the orthorhombic  $\beta'$ phase. A unit cell consisting of 8 Eu, 12 Mo, and 48 oxygen ions was considered (Fig. 1). The system was confined in a monoclinic box without symmetry constraints. All first-principles calculations were performed using the projector augmented wave (PAW) method [11, 12] as implemented in the Vienna Ab-initio Simulation Package (VASP) program [13, 14]. The Vosko, Wilk and Nusair interpolation [15] for the exchange-correlation potential is used within the local density approximation (LDA). The cell volume was varied from 1200 to 900 Å<sup>3</sup> in order to reproduce the investigated pressure range. To optimize the geometry of the cells, we performed internal relaxation of the atomic positions for various volumes.



Fig. 1. Relation between tetragonal and orthorhombic cells. Curved arrows represent Rx and Ry librations around X and Y axes.

#### 3. Phase transitions and soft modes

Polarized spectra, YY, ZZ, XY of GdMo in alcohol are shown in Fig. 2. Five spectral discontinuities (number of bands, halfwidths, intensities) are observed between 1 atm and 6 GPa. The last change is observed above 6 GPa and appears abruptly in the high wave number part of the spectra, which becomes structureless within a pressure increment of 0.5 GPa. The following sequence of transition pressures can be proposed:  $P_1 = 2.07 \pm 0.08$ ,  $P_2 = 2.3 \pm 0.05$ ,  $P_3 = 2.9 \pm 0.3$ ,  $P_4 = 4.12 \pm 0.5$ ,  $P_5 = 5.5 \pm 0.2$ , and  $P_6 = 6.5 \pm 1$  GPa. The last transition corresponds to the amorphization of the compound. Except for  $P_3$  and  $P_4$  which are not clearly identified in all experiments, the transition pressures deduced from spectra recorded in alcohol are close to those reported in fluorescence experiments [5]. It is important to note that the transitions  $I \rightarrow II$  and  $II \rightarrow III$  are reversible. At last, let us note that the amorphization is complete only after pressure release. In argon (Fig. 2d) the first transition takes place at about  $P_1 = 2.4$  GPa. Actually the phase which is formed exhibits a spectrum close to that of phase IV in alcohol as if phases II and III could not form in argon. Only  $P_4$  and  $P_5$  are identified, and bands of phases V and VI are smeared out under a background associated to the amorphous phase which appears as soon as 3 GPa.

Polarizations are preserved up to 2.3 GPa for alcohol experiments. Above  $P_2 = 2.35$  GPa, the Z(YY)Z and Z(XY)Z spectra are no more distinct (Fig. 2). However, the ZZ spectra remaining distinct from the other spectra, one may conclude that a change of optical axis orientation takes place in the XY plane. Beyond 2.55 GPa, ZZ high frequency spectra begin to be similar to other polarizations.

The total energy of the system versus the volume of the simulation cell is displayed in Fig. 3. For the early stages of the compression (p < 1.96 GPa), the major effect of reducing the volume cell is to force the tetrahedra to change their relative orientation in order to minimize the oxygen–oxygen repulsions. For p < 3.13 GPa, the system undergoes a series of structural changes that only involve rotations of the MoO<sub>4</sub> tetrahedra. Despite the rotation of the tetrahedra, the total energy of the cell increases with pressure.

Above 3.13 GPa, the system evolves towards a new phase. The minimum of energy corresponds to the amorphous state since the associated structure appears as a broad and disordered distribution of various polyhedra and corresponds to a renormalized pressure of 10 GPa. For these smaller volumes, the tetrahedra are so close that most of them share a vertex and the average coordination number around Mo atoms evolves to 5 and 6. Let us note that this trend of coordination increase under pressure is often observed in minerals [16].

Thus, the system displays two stable phases and the intermediate structural states observed in the Raman spectra are metastable phases which for giving a subminimum or a plateau in the curve E = f(P) would require more points of calculation.

The frequency lowering of the  $\nu_1$  (955 cm<sup>-1</sup>) and  $\nu_3$  (825 cm<sup>-1</sup>) bands results mainly from the first I–II transition. Despite they increase with pressure in the intermediate phases II–IV, they remain below their original value. This general behavior is also quite clear for the argon medium spectra (Fig. 2). This negative frequency shift at the transition I–II can be due to a slight coordination increase. As observed by *ab initio* calculations the Mo atoms share an extra oxygen atom with a neighboring tetrahedron as soon as 3 GPa.



Fig. 2. Spectra (a), (b) and (c) represent  $A_1$  TO and LO and  $A_2$  stretching modes obtained with the Y(ZZ)Y, Z(YY)Z and Z(XY)Z geometries in alcohol. Spectra (d) represent the Y(ZZ)Y spectra obtained in argon. Pressures (in GPa) are indicated for each spectrum. Transition pressures  $P_i$  and phases (latin numbers) are also indicated.

Excepted at the first transition, all the stretching and bending modes of the tetrahedra, in the existence domain of each of the six high-pressure phases, behave regularly, and undergo a frequency increase with pressure. Up to 2.15 GPa the spectra are characteristic of the orthorhombic  $\beta'$  structure Pba2  $(C_{2v}^8)$  Z = 4 noted phase I in Table I. Above this pressure, in alcohol, the phase II is formed and XX and XY spectra are drastically modified. The increase of the number of bands suggests that the cell multiplicity increases. The number of bands in the 200–600  $\text{cm}^{-1}$  range (Fig. 4) varies from 6 in phase I to 11 in phase II, this number is kept in the sequence of transitions, Z = 8 might explain these new bands. The existence domain of this phase is very narrow because a second spectral change is observed at  $P_2 = 2.3$  GPa. The number of bands does not increase but the intensities and the halfwidths vary when crossing the  $P_3$  and  $P_4$  transition pressures. In phase VI, a decrease in the number of bands of high frequency spectra is observed suggesting that Z could decrease to four, in agreement with what was observed in fluorescence for EuMo.

All the low frequency bands which undergo a frequency decrease when pressure increases are assigned to librations of polyhedra. This assignment is based on *ab initio* results which report that the main effect of the pressure increase in phase I is to induce reorientation of tetrahedra II, III, and I, successively. This behaviour is the indication that the corresponding potential is rather flat and thus can explain the softening of the modes involving the same degree of freedom and their occurrence at low frequency.

The bands (Fig. 4) measured at about 50 cm<sup>-1</sup> in YYand  $ZZ A_1$  spectra and in  $XY A_2$  spectra undergo a frequency decrease in phase I. Actually, for ZZ spectra, the initial band is a superimposition of several components that evolve differently with pressure and are clearly separate above 1.4 GPa. Two of these components continue to soften when pressure increases while the two others harden up to 55 cm<sup>-1</sup>. At  $P_1$  these bands disappear and are replaced by new bands below 40 cm<sup>-1</sup>. These new bands continue to soften and are observed in phases II and III. For argon, a band at about 40 cm<sup>-1</sup> is still observed in phase IV although the remaining of the low frequency spectrum is structureless and characteristic of an amorphous state. Let us note that this mode continues to soften in these phases.

As stated above, for alcohol experiments, the preservation of XX and XY polarizations in phase II up to 2.30 GPa means that optical axes of phases I and II are quite close and that the loss of polarization in the



Fig. 3. Total energy curve of the completely unconstrained cell of the molybdate. Some of the corresponding crystallographic structures, viewed along the [001] axis are represented. Tetrahedra T<sub>I</sub> rotate abruptly at very low pressure (0.92 GPa), while T<sub>II</sub> and T<sub>III</sub> rotate gradually from zero to 3.14 GPa. At p = 3.14 GPa, some tetrahedra T<sub>I</sub> start to share oxygen atoms with neighbours so that the coordination around some Mo evolves to 5. Around p = 4.46 GPa, the change in coordination number also affects tetrahedra T<sub>II,III</sub>. However, a certain symmetry is still observed. Above this pressure, all the tetrahedra are converted into pentahedra, and an increasing deformation of the oxygen cage is obtained as pressure is increased. No symmetry remains and an amorphous state is reached.

phase III above 2.30 GPa is due to the rotation of the optical axis in the XY plane. Such a rotation could be associated with the cell doubling which accompanies the transition towards  $C_{2h}^2$  and  $C_{2h}^4$  space groups proposed for interpreting fluorescence spectra of EuMo [5] between 2 and 5.8 GPa. Above 2.55 GPa, high frequency ZZ spectra begin also to be similar to the other spectra and it may be concluded that it is due to pretransitional effects of the phase IV, the polarization of high frequency spectra being completely lost only above 3.5 GPa. Let us note that *ab initio* results show that tetrahedra are strongly distorted and form non-regular polyhedra, thus it is impossible to consider symmetric and antisymmetric motions and it is not surprising to lose any polarization for stretching modes.

# 4. Effect of the transmitting pressure medium

In argon, the sequence of transitions is altered compared to alcoholic medium: the first drastic spectral

change occurs between 2.28 and 2.6 GPa in argon instead of 2.05 in alcohol. In phase IV, the Mo–O stretching bands at about 900  $\rm cm^{-1}$  are much broader than in alcohol. This could be related to the fact that argon is solid (above 1.3 GPa) and that the crystal cannot accomodate its new structure as easily as in alcohol which solidifies only above 9 GPa [17]. The transition pressures  $P_2$ ,  $P_3$  and  $P_4$  are not identified in argon medium, phase VI observed above  $P_5$  is similar to that observed in alcohol experiments but the bands are much broader and phase VI coexists with the amorphous phase. For instance, the three maxima at 960, 925 and 900  $\rm cm^{-1}$ in argon at 5.25 GPa show a similitude with the well--defined bands at 970, 950 and 925  $\mathrm{cm}^{-1}$  characteristic of phase VI in alcohol at 6.03 GPa. Thus it seems that the amorphization process starts sooner with argon and that the amorphous phase appears in coexistence with high pressure phases IV and VI above 3 and 5 GPa, respectively.

The difference in the band broadening in argon above 2.5 GPa, as compared to alcohol, means that argon is responsible for disorder in the different structures preceding amorphization and that this disorder could accelerate the transitions leading to amorphization. At 293 K argon remains in a liquid state up to 1.3 GPa and crystallizes in a face centered cubic structure above this pressure [18]. Solid argon has a large elastic anisotropy [19] and different portions of the crystal experience different stresses and radial strains. These non-hydrostatic stresses, through coupling to the spontaneous strain of the crystal, can also promote/suppress ferroelastic phase transitions to normal thermodynamic stable or metastable phases whose degree of crystallization depends on the hydrostatic conditions provided by the PTM as observed for  $\alpha$ -SiO<sub>2</sub> quartz [20], GeO<sub>2</sub> [21] or  $ABO_4$  (A = Al, Ga, Fe, B = P, As) berlinites [22]. As far as the amorphization is concerned, the above results provide two pieces of information. ¿From a thermodynamic point of view, the volume change associated to chemical decomposition should appear at the same pressure in both media. This is not the case and the chemical decomposition mechanism must be rejected. Moreover, it appears also that phases II and III are not necessary for amorphization to take place and thus polymorphism mechanism must also be rejected.

#### 5. Conclusion

Polarized Raman spectra of single crystals of molybdate,  $Gd_2(MoO_4)_3$ , were obtained between 0.1 and 8 GPa. Using a mixture of alcohol as a transmitting medium, YY, ZZ, XY spectra were measured. The ZZ spectra were also obtained in argon. In alcohol, the six clear spectral changes observed at about 2.05, 2.25, 3.5, 4.2, and 5.0 GPa are associated to five phase transitions preceding the amorphization taking place at about 6.5 GPa. In argon the first transition takes place at 2.45 GPa instead of 2.05 GPa in alcohol. Above this



Fig. 4. Low frequency Raman spectra (a), (c), (d) for the Z(XY)Z and Y(ZZ)Y and geometries in alcohol. Inset: changes in the frequency of the 50 cm<sup>-1</sup> band component which softens and becomes the 30 cm<sup>-1</sup> band in phase II. (b) Spectra for Y(ZZ)Y in argon.

pressure, bands are much broader and it is difficult to identify intermediate transitions. Amorphization takes place sooner in argon than in alcohol and the amorphous phase coexists with phases IV and V up to 5 GPa and with phase VI above this pressure. The shearing elastic modulus of argon is likely responsible for disorder in the different structures preceding amorphization and this disorder could accelerate the transitions leading to amorphization. This disorder is quite well reproduced by *ab initio* calculations, for high pressures one obtains a distribution of bond-lengths and bond-angles of polyatomic units which prevents to keep trying to retrieve specific polyhedra and which could explain the broadening of internal modes across amorphization.

The  $A_1$  LO and TO low frequencies spectra, although different in intensity distribution, behave quite similarly under the effect of the pressure: the 50 cm<sup>-1</sup> band decreases in frequency and splits progressively into two components, at the first transition these bands are replaced by one band at about 35 cm<sup>-1</sup> in YY spectra and by a doublet in the ZZ spectra. The softening of these modes, probably due to librations of tetrahedra, is related to the orientation change of tetrahedra observed by *ab initio* calculations when the volume cell is decreased. Symmetry coordinates for these modes are identical to cooperative orientation changes observed in *ab initio* results. These orientation changes can explain the frequency decrease of Mo–O stretching modes above 2 GPa, which indicates an increase of Mo coordination.

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