Pressure-induced amorphization of $Gd_2(MoO_4)_3$: A high pressure Raman investigation

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Abstract. High pressure Raman spectroscopic studies on $Gd_2(MoO_4)_3$(GMO) have been carried out at ambient temperature in the diamond cell to 10 GPa hydrostatic pressure. These experiments have revealed pressure-induced phase transitions in GMO near 2 GPa and 6·0 GPa. The first transition is from Pba2(β') phase to another undetermined crystalline phase, designated as phase II, and the second transition is to an amorphized state. On releasing pressure there is a partial reversion to the crystalline state. The Raman data indicate that the amorphization is due to disordering of the MoO_4 tetrahedral units. Further, it is inferred from the nature of the Raman bands in the amorphized material that the Mo–O bond lengths and bond angles have a range of values, instead of a few set values. The results of the present study as well as previous high pressure–high temperature quenching experiments strongly support that pressure-induced amorphization in GMO is a consequence of the kinetically impeded β to α phase transition. The system in frustration becomes disordered. The rare earth trimolybdates crystallizing in the β' structure are all expected to undergo similar pressure-induced amorphization.

Keywords. High pressure Raman spectroscopy; pressure-induced amorphization; gadolinium trimolybdate; terbium trimolybdate.

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1. Introduction

The rare earth trimolybdates $R_2(MoO_4)_3$ are an interesting class of materials crystallizing in four different crystal structures: monoclinic C2/c(α), orthorhombic Pba2(β'), tetragonal $P\bar{4}_12m(\beta)$, and cubic Pnca(γ). Of these, the α is the thermodynamically stable phase for the compounds from Pr to the Ho, but it is bypassed and the (β) form is obtained metastably, upon cooling from the melt. Compounds from Er to Lu crystallize in the (γ) form, which is the only stable phase for them.

The most interesting members of the group are the Pr to Ho molybdates, for they undergo a phase transformation from β to the β'-form upon cooling, in which they exhibit ferroelectric and ferroelastic behavior. The T_c for the paraelectric to the ferroelectric–ferroelastic phase decreases continuously from 235°C for Pr to 121°C in the Ho compound, and hence they are all ferroelectric at room temperature. Among them, the gadolinium trimolybdate (GMO) and the terbium trimolybdate (TMO) are the best studied materials by X-ray [2], neutron scattering [3], Raman [4], Brillouin and infrared absorption spectroscopic [5] methods, because of the interest in elucidating the mechanism of the paraelectric to the ferroelectric–ferroelastic phase transition, as well as their vibrational properties [6].

Also, the large difference in the density between the α-phase and the metastable β-phase (5·647 g/cc for the (α)-phase against 4·555 g/cc for the (β)-phase) prompted some high pressure–high temperature studies on GMO [7] in the hope that high pressure would favor the α-phase. Accordingly Brixner [7, 1] found that the β-phase transformed to the α-phase when GMO was subjected to high pressure and high temperature (3 GPa and 555°C), but turned amorphous when pressure was applied at temperatures below 400°C. These findings were based on an X-ray diffraction study of the quenched product.

We were motivated to study GMO by high pressure Raman technique to gain insight into the pressure-induced amorphization transition. We have also carried out a high pressure Raman infrared absorption and X-ray studies on TMO (to be published elsewhere). We believe that GMO and TMO are the archtypical for the group and their behavior would set the trend for the whole series. In this paper we will present and discuss the results on GMO.

2. Experiments and results

Samples of GMO were from AT & T Bell Labs stock, in the form of large single crystal platelets. Small unoriented chips from these were used as samples for high
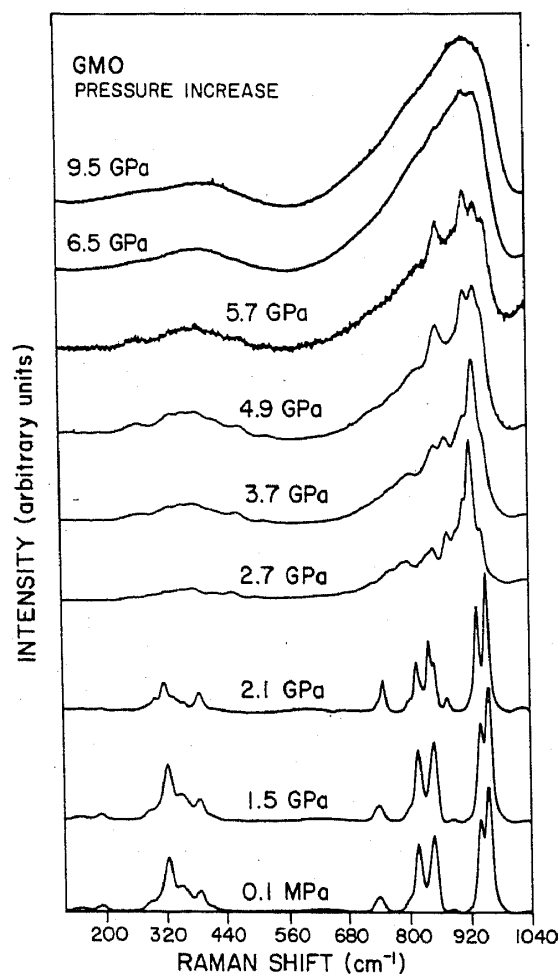

Figure 1. Raman spectra of TMO recorded at several pressures in the diamond cell on the increasing pressure cycle, with 488·0 nm line of the argon ion laser, at power levels around 10–20 mW. See text for explanation.

pressure Raman experiments. Pressure was generated using the gasketed diamond anvil cell of the Mao–Bell type. In Raman studies a 4:1 methanol–ethanol mixture was used as a pressure medium. Pressure was calibrated by the well-known ruby fluorescence technique [8]. Raman spectra were recorded with a Spex Triplemate instrument equipped with a CCD detector. For Raman excitation the 488·0 nm line of the argon laser was employed and unpolarized Raman spectra were obtained at ambient temperature.

In figure 1 spectra taken at nine different pressures are shown. The lowest pressure spectrum obtained at about 0·1 MPa is characteristic of the ferroelectric β' phase. In the spectrum taken at 2·7 GPa, a pressure-induced phase transition is evident from the dramatic changes in the peak frequencies and number. New peaks appear and the old ones are nearly gone. This transition actually occurs near 2 GPa, as judged from the Raman features, as well as from optical observation of the sample. When the sample is viewed under a microscope it shows numerous darklines within the body, evidently due to optical inhomogeneities introduced by the pressure-induced phase transition. Also, the sample had turned light brown in color. We have labelled the new phase as phase II (see figures 3 and 4). At pressures above 6 GPa all the sharp Raman peaks disappear and only two very broad bands in the region of the v_1, v_3 and $v_2 + v_4$ of the internal modes of the MoO_4 tetrahedra are seen (see the 8th and 9th spectra from the bottom in figure 1). We believe that this change is due to pressure-induced amorphization in GMO. Further increase of pressure results in some shifting and broadening of the bands. On releasing the pressure (figure 2) the broad band feature persists almost down to ambient pressure. However, the two broad bands observed in the amorphized phase shows a narrowing in the v_1, v_3 region and consequent splitting. In figure 3 the observed Raman spectrum of phase II (middle spectrum) and the spectrum of the β' phase (bottom) are shown. On the top of figure 3
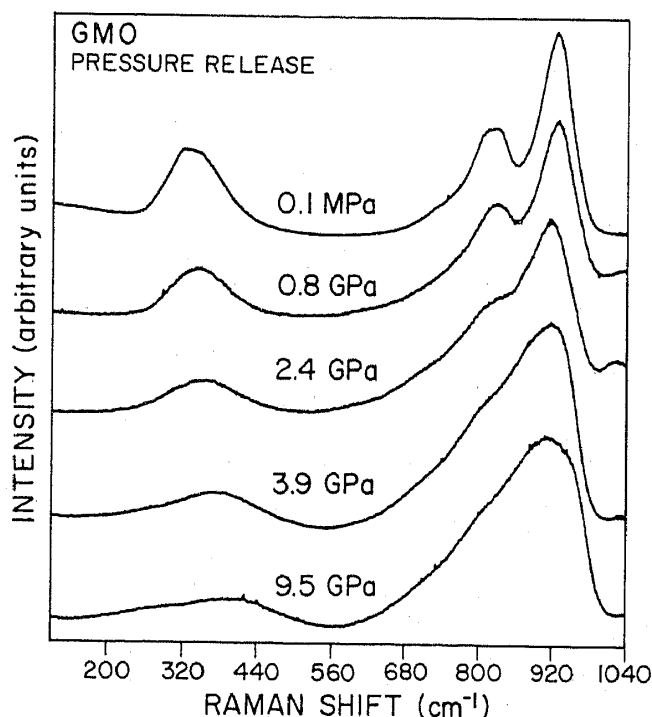

Figure 2. Raman spectra of GMO recorded on the decreasing pressure cycle from the amorphized phase, which demonstrate a small degree of reversibility.
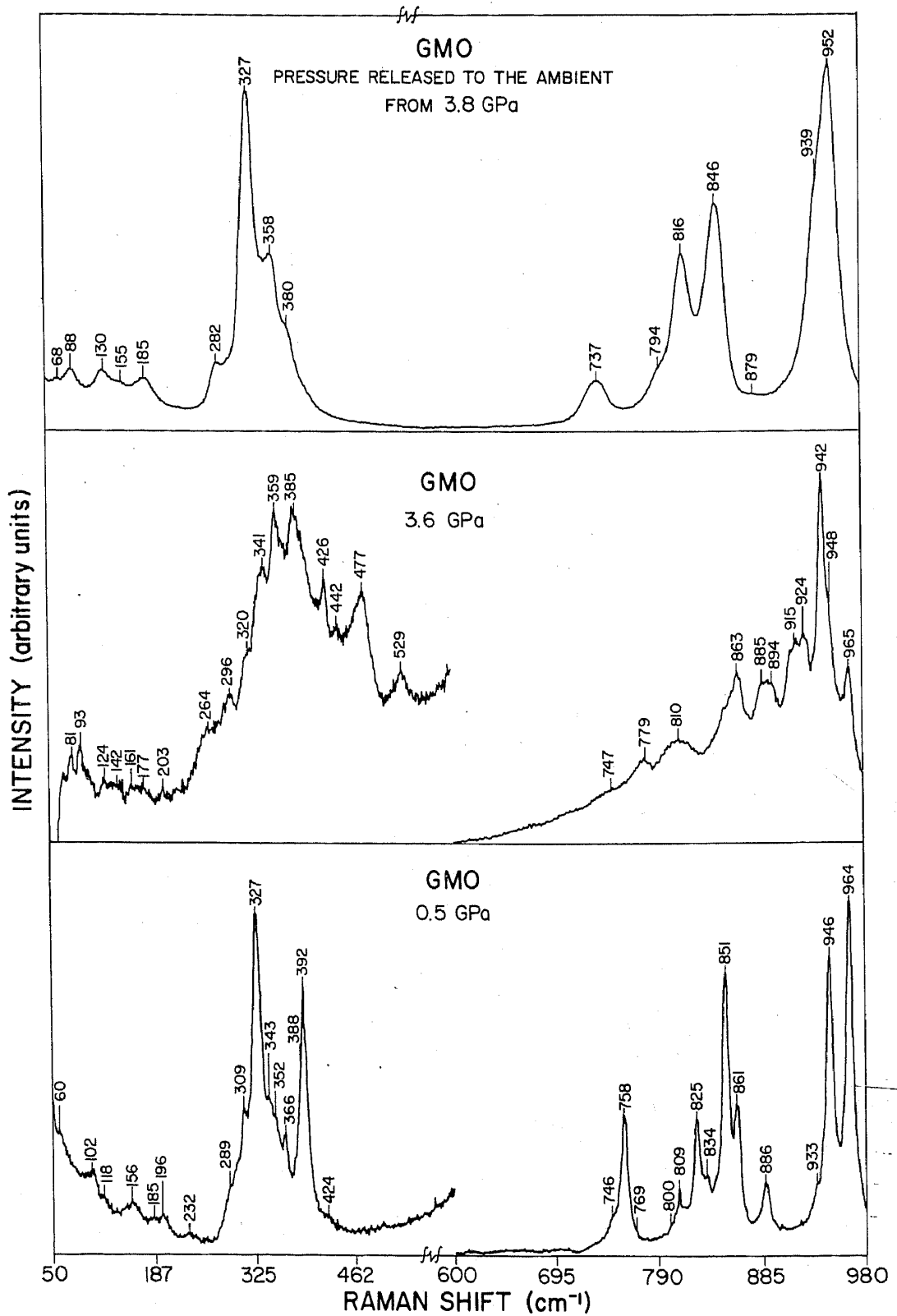
Figure 3. Raman spectra of the β phase at ambient pressure (bottom), phase II at 3·8 GPa (middle) and pressure released sample (top) from the phase II region demonstrating the reversibility of the phase transition.
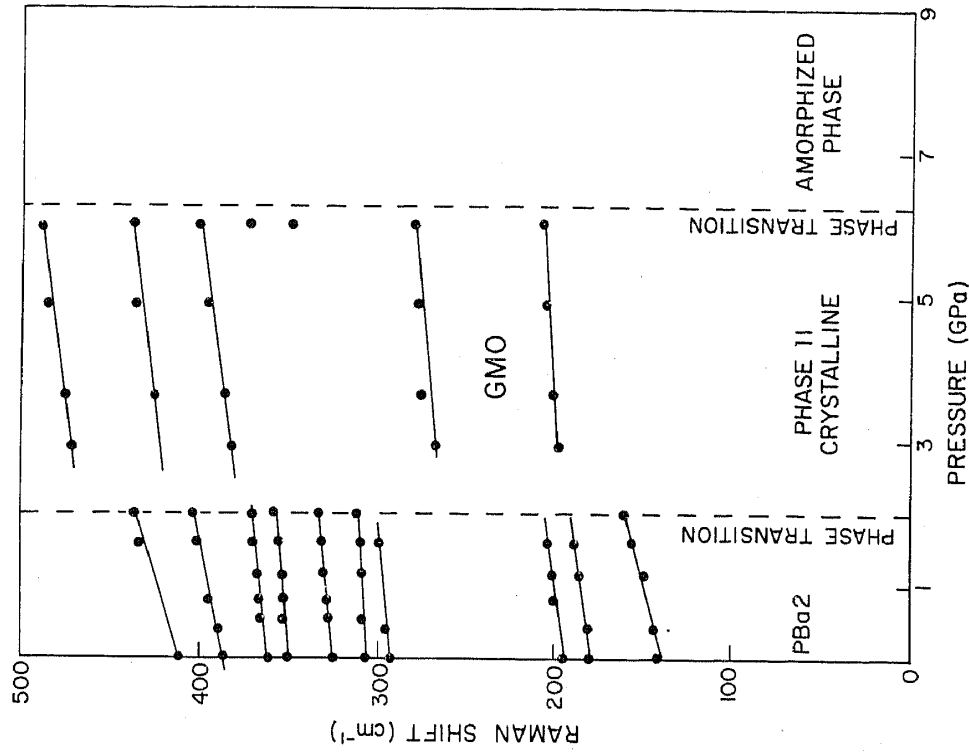
Figure 5. Pressure dependence of the Raman peaks, low frequency region. Dashed lines mark the transition pressures, as noted on the increasing pressure cycle.
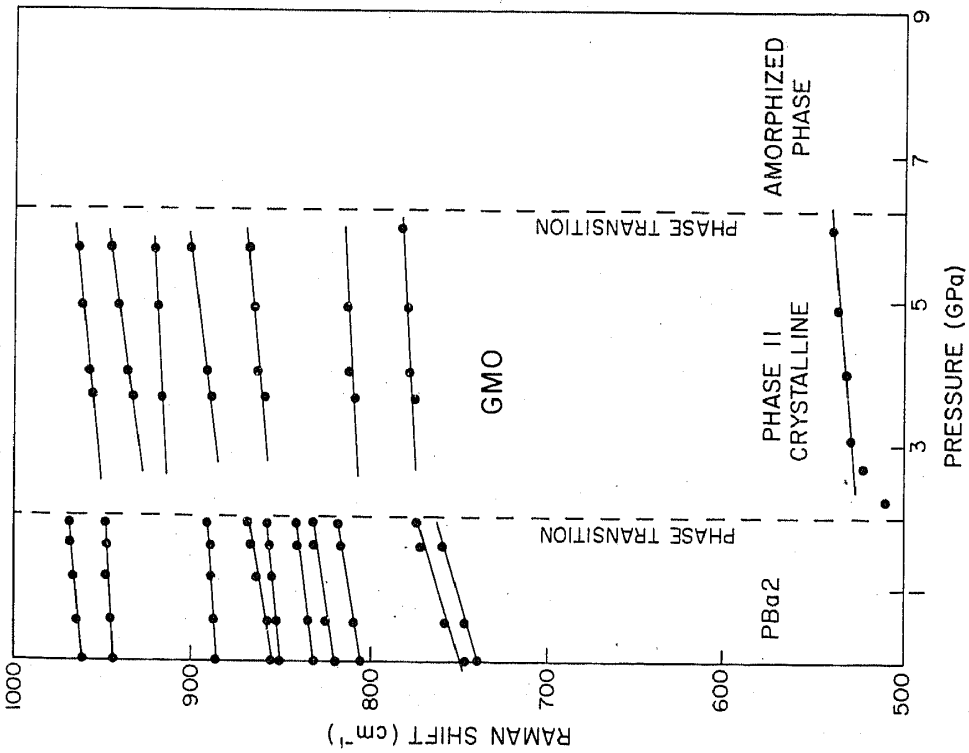

Figure 4. Pressure dependence of the observed Raman peaks in GMO, high frequency region. The dashed lines mark the transition pressure noted on the increasing pressure cycle.

Table 1. Observed Raman peaks in GMO, their pressure dependance and mode Grüneisen parameter γ*.

	Frequency (cm^{-1})	dv/dP(cm^{-1}/GPa)	γ	Phase II at 3·6 GPa
v_1	961 vs	4	0·1	965 m
	945 vs	3	0·1	942 vs
				924 m
v_3	887 w	3	0·1	917 m
	857 s	8	0·3	890 m
	849 s	4	0·2	863 m
	829 m	6	0·3	810 w
	821 s	6	0·3	778 w
	802 w	7	0·3	742 vw
	748 m	15	0·7	
	738 m	13	0·6	
				477 w
$v_2 + v_4$	409 w	12	1	444 w
	386 w	9	0·9	426 w
	356 m	4	0·5	387 w
	324 s	4	0·5	360 w
	301 w	2	0·2	341 vw
	288 w	5	0·6	296 vw
External modes of	195 vw	6	1·1	
MoO$_4$ and RE ions	140 vw	7	2	93 vw
	115 vw	10	3	81 vw

*To calculate γ, the bulk modulus of GMO was obtained from the elastic constants [18]. K = 35·5 GPa was used for the purpose.
vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

is shown the spectrum of the sample after release of pressure from 3·8 GPa. It is clear that the sample has partially reverted to the parent phase. In figures 4 and 5 the pressure dependence of the Raman peaks are presented. The dashed vertical lines mark the pressure-induced phase transitions observed on the increasing pressure cycle. The Raman peaks of the β' phase are listed in table 1 and their origin indicated. The observed peak frequencies are in very good agreement with the published data [4, 5]. The designation v_1, v_2, v_3, and v_4 modes of the MoO$_4$ ion is according to the earlier assignments [4, 5].

3. Discussion

Pressure-induced amorphization has been reported in a number of materials, in recent years; α-quartz [9], AlPO$_4$[10], LiKSO$_4$[11], Ca(OH)$_2$[12], T–Nb$_2$O$_5$[13], Ca(NO$_3$)$_2$/NaNO$_3$[14], as for instance. Several mechanisms have been proposed for the cause of such crystal to amorphous transitions: Kruger and Jeanloz [10] have suggested that a pressure-induced amorphization may result from an impeded phase transition. Winters et al [14] have proposed that the formation of polytetrahedral units under pressure leads to noncrystallographic packing and hence to amorphization, in solids which have only nondirectional bonding among their basic structural units. Adams et al [15] have suggested that pressure-induced amorphization could result

from a kinetically inaccessible high pressure crystalline phase. Recently Sikka and Sharma [16] have proposed that the steric hindrance coupled with the tendency to attain close-packing may be the driving force in pressure-induced amorphization. According to them, "when the basic packing unit cannot tolerate further steric constraints, the amorphization sets in due to frustration resulting from unfavorable kinetics to achieve a better coordination in the crystalline form. This fact seems independant of the type of bonding in the constituents". The common feature underlying most of the suggestions appears to be that the system, in its frustration to reach a dense crystalline phase goes into an amorphous state.

The pressure-induced amorphization in GMO seems to be a clear case of an impeded phase transition for the following reason. As mentioned earlier the α-phase (C2/c) is the stable phase below 857°C for GMO, but this is bypassed in favor of the less dense β phase upon cooling through the β-α transformation boundary. The density of the α-phase is about 20% higher compared to the β-β' phase ($\beta' = 4.555$ g/cc, $\alpha = 5.647$ g/cc). Therefore, from thermodynamics we can expect that the application of pressure on the β-phase would strongly favor the formation of the α-phase. In fact this has been shown to be the case by Brixner [17], who treated β'-GMO to 3 GPa at 550°C and found a complete transformation to the α-phase, in the quenched material. Also, Brixner *et al* [7] subsequently reported that β'-GMO when treated to 6.5 GPa became amorphous, when the temperature was 400°C and lower. Further, they found that the glassy phase when heated to 700°C converted to pure α-GMO. These experiments clearly establish that high pressure favors the formation of the α-phase but the β' to α-phase transition is kinetically impeded at temperatures below 400°C. The β' to α transition undoubtedly involves a drastic structural rearrangement including higher coordination for the cations and therefore it is not surprising that there is a large energy barrier for the transition. The behavior of TMO closely follows that of GMO, as is expected from the strong similarities between the two. We therefore have a system in GMO and TMO wherein the pressure-induced amorphization is directly attributable to a kinetically impeded phase transition, namely the β to α phase transition.

We believe, that a microscopic picture of the amorphous state is the following: The MoO_4 tetrahedral units which are the backbone of the structure (see figure 6) become completely disordered in the process of amorphization. Further, they are closer-packed than in phase II and phase I, because of the thermodynamic principle that pressure always would favor the denser phase. The bond lengths and bond angles of the MoO_4 tetrahedral units in a randomly oriented situation may be expected to take a range of values, since there is no structural constraint in the amorphized state. This is well supported by the Raman results. In the amorphized GMO two broad bands are observed in the internal mode region corresponding to v_1, v_2, v_3, v_4 of the MoO_4 tetrahedra, and the bands are quite broad. This is indicative of a broad distribution of bond lengths and bond angles for the MoO_4 units. Further, the observed decrease in the frequency of the totally symmetric stretching frequency v_1 (see figure 1) in going from phase I to II and then into the amorphized phase is consistent with tighter packing, in that order.

It is an interesting question whether the α-phase when subjected to pressure would be amorphized. Our guess is that such a scenario is unlikely for the α-phase, because it is a high density phase already and there may not be a pressure-induced phase transition to a higher density phase. However, at this point this is an open question, whether there will be a pressure-induced crystalline to crystalline phase transition in
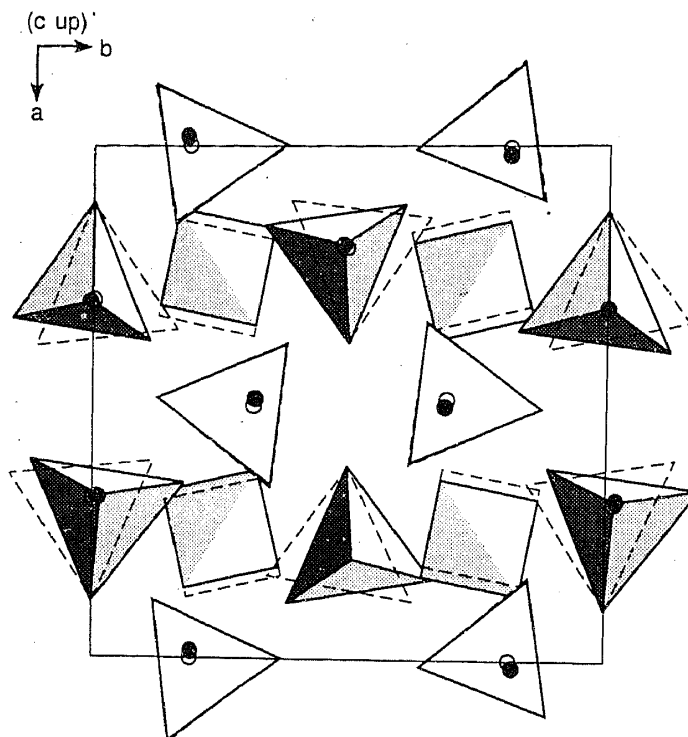
Figure 6. The arrangement of the MoO_4 tetrahedra in the β' phase of GMO, from reference 5. These tetrahedra become disordered in the amorphized phase. The dashed tetrahedra are for the C-down orientation. There are three crystallographically nonequivalent MoO_4 in the unit cell, which form successive layers along the C-axis.

the α-phase or not. Pressure investigations on the α-phase would be really of interest, which we hope to undertake in the near future. We also believe that all RMO that crystallize in the β' structure, would undergo similar crystal to crystal and to amorphous phase tranformations that we find in GMO and TMO. Whether the size of the rare earth ion has any effect on the phase transition pressure is something to be investigated.

From the Raman data alone, we are unable to comment upon the structure of Phase II. Unfortunately our X-ray diffraction data on TMO were not good enough to carry out further analysis. Since phases I to II and to the amorphous state transitions take place well within hydrostatic limit, in both GMO and TMO, a detailed and precise X-ray diffraction study may be rewarding.

4. Summary and conclusions

High pressure Raman and infrared absorption studies on GMO have revealed that the open crystalline packing arrangement of the β phase collapses under pressure to an amorphous phase. The amorphization is due to the kinetically impeded β to α phase transitions and the system in frustration becomes disordered. The Raman results indicate that disordering and bond length–bond angle changes occur in the MoO_4 structural units and further the system must be densely packed. We believe that a high pressure X-ray diffraction study would be rewarding.

The pressure behavior of TMO and GMO closely follows each other, transforming from β' to phase II near 2 GPa and from the latter to an amorphized phase near

6 GPa. All the rare earth trimolybdates crystallizing in the β-form should undergo similar pressure-induced amorphization and thus opens up a whole lot of compounds for pressure studies.

Acknowledgements

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