

## Pressure-induced structural and electronic transition in $\text{KTb}(\text{MoO}_4)_2$ through Raman and optical studies

A JAYARAMAN, S K SHARMA, S Y WANG, S R SHIEH, L C MING and S-W CHEONG\*

University of Hawaii at Manoa, Hawaii Institute of Geophysics and Planetology, Honolulu, HI 96822, USA

\*Lucent Technology, Murray Hill, NJ 07974, USA

MS received 22 March 1996

**Abstract.** Raman and optical absorption studies under pressure have been conducted on  $\text{KTb}(\text{MoO}_4)_2$  up to 35.5 GPa. A phase transformation occurs at 2.7 GPa when the crystal is pressurized at ambient temperature in a hydrostatic pressure medium. The sample changes to a deep yellow color at the transition and visibly contracts in the *a*-axis direction. The color shifts to red on further pressure increase. The Raman spectral features and the X-ray powder pattern change abruptly at the transition indicating a structural change. The pressure-induced transition appears to be a property of the layer-type alkali rare earth dimolybdates. However, the color change at the transition in  $\text{KTb}(\text{MoO}_4)_2$  is rather unusual and is attributed to a valence change in Tb initiated by the structural transition and consequent intervalence charge transfer between Tb and Mo. *In situ* high pressure X-ray diffraction data suggest that phase II could be orthorhombic with a unit cell having 3 to 4% smaller volume than that of phase I.

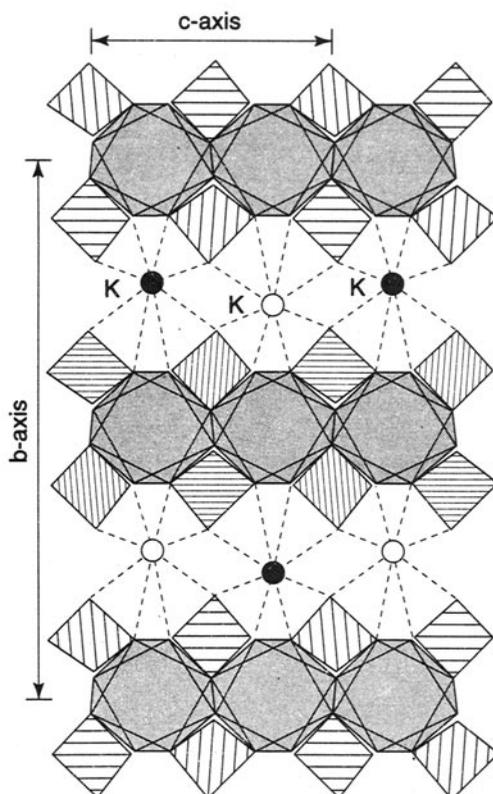
**Keywords.** High pressure Raman spectroscopy; optical spectroscopy; potassium terbium molybdate; electronic transition; phase transition.

PACS Nos 62·50; 64·70; 70·30; 78·20

### 1. Introduction

The alkali-rare earth double molybdates  $\text{M}^{1+}\text{Ln}^{3+}(\text{MoO}_4)_2^{4-}$  have been of considerable interest from a crystal chemistry point of view, and their structural properties have been extensively investigated, in particular by the Russian group [1–4]. The compounds crystallize either in the scheelite or in the distorted scheelite structures having orthorhombic, monoclinic, or triclinic symmetry. The tetrahedral coordination of Mo with respect to the oxygens ( $\text{MoO}_4$ ) [4] is preserved, however. It has been found that the members of the heavier alkali metal and rare earths are stable in a layer-type orthorhombic structure in which the rare earth and ( $\text{MoO}_4$ ) group are in the layer, with the alkali metal ion sandwiched between the layers [4] (see figure 1).

The vibrational properties of the orthorhombic layer-type  $\text{KLn}(\text{MoO}_4)_2$ ,  $\text{Ln} = \text{Y, Dy to Lu}$  [5, 6], as well as some Cs [7, 8] and Rb [9] members have been reported in the literature. Further, some high pressure-high temperature quenching experiments [10] have reported the occurrence of new pressure-induced denser phases in many  $\text{MLn}(\text{MoO}_4)_2$  systems, as revealed by X-ray powder diffraction studies on quenched products.



**Figure 1.** The layer structure of  $\text{KLn}(\text{MoO}_4)_2$  following ref. [4]. The  $\text{LnMo}_2\text{O}_8$  constitute the layers parallel to the  $a$ - $c$  plane. The  $\text{LnO}_8$  polyhedra are linked and form a chain. The  $\text{K}^+$  ions act as links between the layers.

We have a continuing interest in the high pressure behaviour of molybdate systems of different complexity and have reported pressure-induced phase transformations including amorphization in  $\text{Tb}_2(\text{MoO}_4)_3$  [11],  $\text{Gd}_2(\text{MoO}_4)_3$  [12] and more recently in  $\text{NaLa}(\text{MoO}_4)_2$  [13] using high pressure Raman, IR and X-ray diffraction studies. We were motivated to study the layer-type double molybdates, exemplified in the potassium based heavy Ln double molybdate  $\text{KTb}(\text{MoO}_4)_2$  (KTMO), for possible pressure-induced phase transitions and their effect on the physical properties. Our choice of  $\text{KTb}(\text{MoO}_4)_2$  was because of its ready availability. Further, the vibrational properties of the isostructural  $\text{KY}(\text{MoO}_4)_2$  [14] and  $\text{KDy}(\text{MoO}_4)_2$  [15] at ambient pressure have been thoroughly investigated by polarized Raman scattering and IR absorption measurements, thus providing a standard for comparison.

We have conducted high pressure Raman scattering measurements up to 35 GPa on KTMO in the diamond cell. Optical microscopic observations as well as some qualitative optical absorption studies were made under high pressure. Some preliminary high pressure X-ray diffraction studies in the diamond cell were also conducted. We have found a rather spectacular pressure-induced phase transition near 2.7 GPa at

ambient temperature, in which the crystal sample abruptly turns deep yellow in color, with a totally different Raman spectrum from that of the starting orthorhombic phase (Pbcn,  $D_{2h}^{14}$ ). The X-ray diffraction pattern also changes at this pressure. At higher pressures the sample color turns progressively toward orange, then red and finally black near 35 GPa. The sudden change to yellow color at the transition near 2.7 GPa must be the result of an electronic structure change, possibly a change in the valence state of  $Tb^{3+}$  to the  $Tb^{4+}$  state, and consequent charge transfer between the Tb and Mo metal *d*-orbitals. The crystal structure change is apparent in the Raman spectrum, as well as in X-ray diffraction. These results will be presented and discussed in this paper.

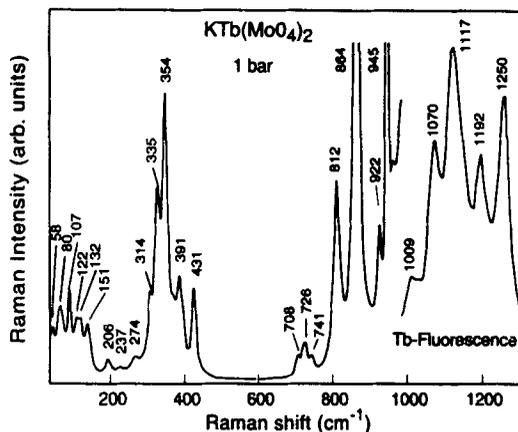
## 2. Experiments and results

High-pressure Raman scattering measurements were performed using a gasketed Mao–Bell-type diamond anvil cell. For the pressure medium, either the standard 4:1 methanol-ethanol mixture or argon was used. Argon filling into the diamond cell was accomplished in a specially fabricated 2-kilobar high-pressure gas system. In some experiments the sample powder was packed into the hole drilled in the gasket and resurized directly without any medium. The pressure was calibrated using the well-known ruby fluorescence technique [16] in all cases. The gaskets were from hardened 301 stainless steel, and typically the hole was 200  $\mu\text{m}$  wide and 70–100  $\mu\text{m}$  thick.

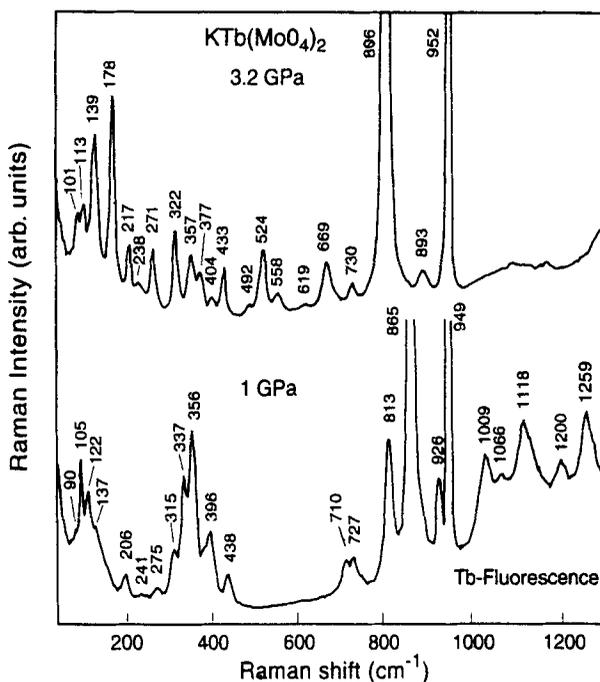
Raman measurements were carried out using a Spex Triple spectrometer equipped with a liquid  $N_2$  cooled CCD detector. Spectra were excited using mainly the 514.5 nm line of the argon laser. The power levels were generally in the range of 30–60 mW.

Large flaky crystals of KTMO grown in AT&T Bell laboratories many years ago for possible application as laser hosts were available to us. The crystals were colorless and transparent and could be cleaved very easily in the layer plane (*a-c* plane). The lattice parameters were checked by X-ray powder diffraction and were found to be consistent with the published data [10] ( $a = 5.098 \pm 0.004 \text{ \AA}$ ,  $b = 18.17 \pm 0.03 \text{ \AA}$ ,  $c = 8.027 \pm 0.003 \text{ \AA}$ ). The crystals were Eu doped with half atomic per cent Eu substituting for Tb, and the sample was highly fluorescent in the yellow green and red region. However, there was no interference from fluorescence with the Raman spectrum when the 514.5 nm line of the argon laser was used for Raman excitation. In figure 2, the Raman spectrum of a crystal plate of KTMO recorded with the 514.5 nm line is shown. The peaks appearing above  $1000 \text{ cm}^{-1}$  are the fluorescence peaks from Tb. The Raman spectra recorded at 1 and 3.2 GPa with the sample in the diamond cell are shown in figure 3. The spectrum of the sample abruptly changes near 2.7 GPa and is completely different from that at lower pressures (as shown in figure 3), signifying a pressure-induced phase change. Another interesting fact is that the fluorescence peaks vanish in the high-pressure phase. Upon further increase in pressure the Raman peaks shift to higher wavenumbers but the spectral features do not change up to 22 GPa, the highest pressure reached in the experiment with methanol/ethanol as a pressure medium. On pressure release the high pressure phase was stable down to 0.3–0.2 GPa, as judged by the Raman spectrum, and reverted completely on the release of the pressure to the ambient. When argon was used as the pressure-medium very similar behaviour of the sample was observed.

Optical observation of the sample under a microscope revealed that at the 2.7 GPa phase transition the color of the sample abruptly turns yellow in transmitted light. Also,



**Figure 2.** The Raman spectrum of  $\text{KTb}(\text{MoO}_4)_2$  recorded at ambient pressure with 514.5 nm line of the argon laser. The Tb-fluorescence peaks are at the extreme right and they are very strong. Hence they are scaled down by a factor of two compared to the Raman peaks. The latter are listed in table 1.



**Figure 3.** The Raman spectra of  $\text{KTb}(\text{MoO}_4)_2$  single crystal samples recorded at 1 and 3.2 GPa. The lower spectrum is that of the normal orthorhombic  $Pbcn$  phase. The upper spectrum is quite different, due to a pressure-induced phase transition. The Tb fluorescence peaks are almost gone in the new phase.

the sample visibly shrinks along the *a*-axis of the orthorhombic crystal, and the single crystal nature is preserved. On pressure release the sample color continues to be yellow down to 0.3 GPa and then develops striation due to retransformation.

In a different experiment, the powdered sample (synthesized from high purity  $K_2MoO_4$  and  $Tb_2(MoO_4)_3$  by heating to 950°C) was pressurized directly without any pressure medium. The Raman spectrum of the powder was identical to that of the crystal. The spectral features changed near 3 GPa; the spectra recorded between 3 and 6 GPa showed Raman peaks of the low pressure as well as the high pressure phases. From the behavior of the stronger high frequency peaks it was clear that the high-pressure phase was growing at the expense of the low-pressure phase in the 3–6 GPa range. Above 6 GPa and up to 30 GPa the Raman spectral features remained more or less the same. The highest pressure reached in the powder run was 35.5 GPa, and only two high-frequency, broad Raman peaks could be seen. There was also a broad background. When pressure was released down to ambient pressure, the sample completely reverted to the original starting phase.

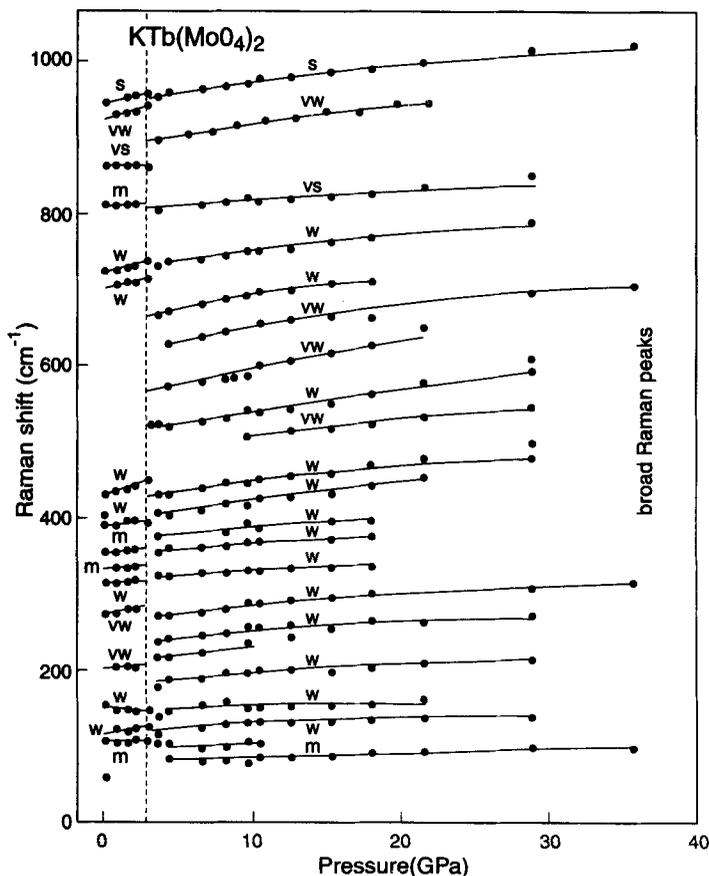
Optical observations on the powder sample revealed a color change near 3 GPa; the powder distinctly turned yellow. The color deepened with pressure, progressively turning orange, red and black. In a microphotograph taken at 35.5 GPa the sample appeared yellow on the outer edge, then orange, red and black in moving toward the center; apparently the result of a large pressure gradient over the sample area. The deepening of the yellow color after the transition and shift toward orange was very clear in single crystal sample runs with methanol/ethanol or argon as the pressure medium in which the maximum pressures reached were lower.

The pressure dependence of the observed Raman peaks is presented in figure 4. The dotted vertical line marks the phase transition pressure. The Raman data for the starting orthorhombic phase are given in table 1 with the assignments from ref. [14]. The Raman peaks observed in the high-pressure phase (phase II) are also listed both near the transition pressure as well as at ambient pressure, the latter obtained from pressure release data and extrapolation.

### 3. Discussion

The orthorhombic KTMO belongs to the space group  $D_{2h}^{14}$  Pbcn with  $Z = 4$  and is isostructural with  $KY(MoO_4)_2$  (KYMO) [4] and  $KDy(MoO_4)_2$  (KDMO) [15]. Polarized Raman and IR absorption measurements on single crystals of the latter two compounds have been reported by Hanuza and Labuda [14]. They assigned the observed infrared and Raman peaks to vibrational modes obtained from a group theoretical analysis for the space group and polarization studies. Following their work [14] we have labeled the Raman peaks of the orthorhombic KTMO in table 1.

Based on the structural features and the number of bands observed in the IR and Raman spectra of KYMO and KDMO, Hanuza and Labuda [14] have proposed a dimer formation ( $Mo_2O_8$ ) in the compounds, with two oxygens bridging adjacent  $MoO_4$  tetrahedra. The large spread in the internal stretching mode frequencies of  $280\text{ cm}^{-1}$  (from  $950\text{ cm}^{-1}$  to  $670\text{ cm}^{-1}$ ) is unusual for the isolated  $MoO_4$  group and is believed to be the result of additional interaction between the molybdate ions in the unit cell. However, the dimer formation has been questioned by Fomichev and



**Figure 4.** The pressure dependence of the observed Raman peaks in  $\text{KTb}(\text{MoO}_4)_2$  up to 35 GPa. The phase transition at 2.7 GPa is marked by the dashed vertical line. The intensities of the peaks are indicated. At the highest pressure the observed Raman features are broad.

Kondratov [7] who investigated  $\text{CsPr}(\text{MoO}_4)_2$  and compared it with  $\text{KDy}(\text{MoO}_4)_2$ . They have calculated the force constants for a number of alkali double molybdates and, in particular, the latter two and arrive at the following conclusions: (1) the interaction between  $\text{MoO}_4$  species through “long” bonds affects the nature of the spectra, and (2) the Mo atoms are not purely in tetrahedral coordination with O, and remote O atoms interact to form complicated systems that are intermediate between a structure with discrete tetrahedral anions and condensed systems of complex oxide-polyhedra.

#### *The 2.7 GPa phase transition*

Our main objective is to discuss the high-pressure behaviour and, in particular, the pressure-induced phase transitions. The Raman data and optical observations unambiguously reveal that a phase transition in KTMO occurs near 2.7 GPa (see figure 3). In the transition, the highest frequency mode which is normally the symmetric stretching

**Table 1.** Observed Raman peaks in  $\text{KTb}(\text{MoO}_4)_2$  of phase I and high pressure phase II and their pressure dependence

Mode	Phase I ( $\text{cm}^{-1}$ )	$d\omega/dP$ ( $\text{cm}^{-1}$ GPa) (PI) <sup>a</sup>	(PII) <sup>b</sup>	Phase II (3.2 GPa)	PII(amb.) ( $\text{cm}^{-1}$ )
$\nu_1$	$A_g$ 945 s <sup>†</sup>	2.5	3	952 s	942
	$B_g$ 922 vw	4	5	893 vw	878
$\nu_3$	$A_g$ 864 vs	0	2	806 vs	799
$\nu_{\text{br}}$	$A_g$ 812 m	0	5	730 vw	715
	$B_g$ 741 vw	2.5	5	669 w	652
	$B_g$ 726 vw	1.2	n.d. <sup>c</sup>	619 vw	
	$B_g$ 708 vw	n.d.	5	558 vw	544
$\nu_2 - \nu_4$	$A_g$ 431 w	6.5	5	524 w	508
	$A_g$ 404 vw	0	6	492 vw	474
	$A_g$ 391 w	3.3	3	433 w	420
	$A_g$ 354 m	2.5	3	404 vw	392
	$A_g$ 335 w	1	3	377 w	367
	$A_g$ 314 vw	1	5	357 w	340
	$A_g$ 274 vw	4.5	3	322 w	312
	T and R		2.5	3	271 w
K-K-T mode	$A_g$ 206 vw	-1	5	238 vvw	223
Y-T mode	$A_g$ 151 w	-2.5	5	217 w	202
	$B_g$ 132 w	n.d.		n.d.	n.d.
	122 w	n.d.		n.d.	n.d.
MoO <sub>4</sub> , T-mode	$A_g$ 107 w	-1.3	2.5	178 m	170
R-mode	80	n.d.	3	139 m	132
	58 w	n.d.	2	113, 101 w	104, 96

<sup>a</sup>PI, Phase I; <sup>b</sup>PII, Phase II; <sup>c</sup>n.d., not determined.

<sup>†</sup>s, strong; m, medium; w, weak; vw very weak; vvw, very very weak.

of  $\text{MoO}_4$  ( $\nu_1$ ) is only slightly affected (shifts downward by a few  $\text{cm}^{-1}$ ), whereas the antisymmetric stretching mode ( $\nu_3$ ) decreases in frequency by about  $60 \text{ cm}^{-1}$  in the high pressure phase. Also, the number of modes in the bending region ( $\nu_2$  and  $\nu_4$ ) fills the entire range from  $700 \text{ cm}^{-1}$  to  $270 \text{ cm}^{-1}$ . Further, there are more Raman peaks in the translational and rotational region, suggestive of a transition to a lower symmetry phase. The small shift of ( $\nu_1$ ) frequency is an indication that the tetrahedral coordination for Mo is essentially preserved in the high-pressure phase. The  $60 \text{ cm}^{-1}$  downward shift of the ( $\nu_3$ ) may be attributed to the small adjustments of the Mo-O bond lengths in the layer, in response to the observed abrupt shrinkage of the structure parallel to the *a*-axis.

In the layer-type materials, maximum compression will take place along a direction perpendicular to the layer, which in the present case is the *b*-axis of the orthorhombic  $D_{2h}^{14}$  phase (see figure 1). At some critical interlayer distance the  $\text{MoO}_4$  tetrahedra apparently readjust within the layer to overcome the increase in the electrostatic repulsion energy between the oxygens of adjacent layers. We find from pressure Raman studies on isostructural KYMO and KDMO that an analogous pressure-induced

phase transition occurs in the vicinity of 2–3 GPa [17]. Their lattice parameters are very nearly the same as that of KTMO. This similarity indicates that the structural instability is a common behavior for the layer-type alkali rare earth molybdates, and the instability is mainly determined by the interlayer distance and ( $\text{MoO}_4$ ) interactions. For a more detailed understanding, the exact nature of the structural rearrangement in the high-pressure phase would have to be determined.

#### 4. X-ray diffraction results

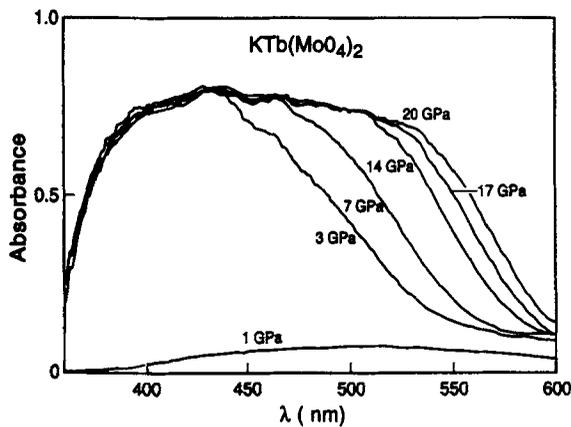
An earlier study has indicated that potassium RE double molybdates as well as several other alkali RE double molybdates transform under high-pressure and high-temperature treatment (in the range of 2.5–8 GPa and 700–1000°C) to denser phases. In these studies the product quenched to ambient conditions [10] was examined by high pressure X-ray diffraction and was reported to have the  $\beta$ -KY( $\text{WO}_4$ )<sub>2</sub> structure (C2/c) with a volume 13% smaller for the formula unit compared with the original phase in a dozen compounds including KTMO, KYMO and KDMO. The high-pressure phase that we have found in room-temperature compression experiments is not quenchable, and our *in situ* X-ray diffraction data cannot be indexed on the basis of the lattice parameters reported for the quenched phase [10]. Further, the Mo-O coordination is given as 6 for the quenched phase, but there is no Raman evidence [18] for such a coordination increase in our high pressure phase. These considerations lead us to believe that our high pressure phase is different from the above mentioned quenched materials.

Our *in situ* high-pressure X-ray diffraction data on the high-pressure phase (phase II) can be indexed on the basis of an orthorhombic cell. At 2 GPa we find that the new orthorhombic cell has  $a = 9.58 \text{ \AA}$ ,  $b = 8.90 \text{ \AA}$  and  $c = 8.03 \text{ \AA}$ , with 4 formula units; the corresponding volume ( $v$ ) per formula unit calculates to  $103.2 \text{ cm}^3/\text{mol}$ , compared with the  $107.5 \text{ cm}^3/\text{mol}$  at 2 GPa for the orthorhombic cell of phase I. Because the compressibilities of phase I and II are very different, the  $\Delta v$  evaluation would depend on the pressure. At the transition pressure of 2.7 GPa, the  $\Delta v$  would be about  $\sim 3\%$ , whereas it would be about 7% when evaluated at ambient pressure. This difference in  $\Delta v$  explains our optical observations on the sample during pressurization and pressure release. When the transition (phase I to II) occurs near 2.7 GPa on the increasing pressure cycle, the crystal visibly contracts in the  $a$ -direction but remains as a single crystal. On the other hand, the reverse transition which occurs almost near the ambient pressure on pressure release breaks up the crystal, because of the large expansion ( $\sim 7\%$ ) associated with the II to I transition. First, parallel lines coincident with the  $c$ -axis appear in the sample as pressure decreases to 0.2 GPa, followed by breaking up of the crystal when the pressure is completely off.

A complete structure analysis of phase II based on single crystal diffraction data is needed to determine the exact nature of the atomic arrangement and what exactly happens to the  $\text{MoO}_4$  and the cationic polyhedra.

#### *The color of the high-pressure phase and its origin*

The most spectacular aspect of the 2.7 GPa transition in KTMO is the abrupt change in the color of the sample to a deep yellow color in transmitted light [19]. This strongly



**Figure 5.** Shows optical absorption by the sample (single crystal) at different pressures. At the 2.7 GPa transition the sample abruptly turns yellow in color, as reflected in the curve for 3 GPa. At higher pressures the absorption shifts toward red (see text for explanation).

suggests a change in the electronic structure in the high-pressure phase. The color deepens and shifts to longer wavelengths with increasing pressure (see figure 5). It is of interest to note that no such color change is seen in the case of KYMO and KDMO, although the same structural phase transition occurs [17] (as deduced from the Raman and X-ray powder diffraction data). Therefore, we believe that the color change is something special to KTMO and attribute this to a charge transfer absorption ( $4f-5d$ ) originating from a change in the valence state of Tb from  $3^+$  to the  $4^+$  state. That Tb can exist in these two valence states is well-known. As the material is still an insulator in the high pressure phase, a valence change in Tb must be compensated by a change in the valence state of Mo to the  $5^+$  state to preserve charge neutrality. This would, then, be a case of intervalence charge transfer between Tb and Mo from  $Tb^{3+}-Mo^{6+} \rightarrow Tb^{4+}-Mo^{5+}$ . An analogous charge transfer mechanism between Tl and Re has been proposed for the 10 GPa phase transition observed in  $TlReO_4$  [20], in which the colorless sample turned to a dark red color in the high-pressure phase. Our scenario for KTMO is that at the structural transition near 2.7 GPa the oxygens surrounding the Tb ion move closer to the terbium, causing an abrupt increase in the crystal field splitting of the  $5d$  state of Tb. This increased splitting brings down the  $5d$  energy and facilitates electron transfer from  $4f$  into the  $5d$ . To preserve charge neutrality the promoted electron transfers into the Mo- $4d$  band through the ligand. In the case of Y and Dy compounds the question of valence change does not arise and hence no color change is expected in them, as is actually the case. It must be noted that the phase transition in KTMO is not driven by the electronic instability in Tb but rather the structure change is the one that causes the electronic change. Our experiments on KYMO and KDiMO are proof of this contention.

The Tb fluorescence peaks are almost gone when the 2.7 GPa phase transition takes place (see figure 2). This we believe is another significant evidence that the electronic structure of terbium has changed at the phase transition. An interesting question that

comes up here is, whether the valence state of Tb can be described in terms of an interconfiguration fluctuation leading to a mixed valence state. It is possible that magnetic susceptibility measurements on the high pressure phase could throw some light on the question.

## 5. Summary and conclusions

The alkali rare earth dimolybdate  $\text{KTb}(\text{MoO}_4)_2$  undergoes a pressure-induced phase transition near 2.7 GPa when pressurized at room temperature in a hydrostatic pressure medium. The phase transition involves a structural rearrangement which is abrupt. The crystal sample contracts visibly in the  $a$ -axis direction and simultaneously acquires a strong yellow color. The color deepens with further increase in pressure and shifts toward red. The reverse transition occurs at pressures near 0.3 GPa on pressure release, thus exhibiting a large hysteresis. The structural transition is the property of layered alkali-rare earth dimolybdates, but we believe the color change in KTMO is caused by a change in the valence state of Tb from  $\text{Tb}^{3+}$  to  $\text{Tb}^{4+}$  and consequent charge transfer to the Mo- $d$  state ( $\text{Tb}^{3+}-\text{Mo}^{6+} \rightarrow \text{Tb}^{4+}-\text{Mo}^{5+}$ ). The electronic transition is triggered by the lowered  $d$ -state of terbium caused by an abrupt increase of the crystal field (ligand field) splitting because of a shorter Tb-O distance in the high-pressure phase.

## Acknowledgement

This work was supported by a grant from the National Science Foundation, Division of Materials Research. This is a contribution from SOEST (No. 4107) and HIGP (No. 898).

## References

- [1] V K Trunov, V A Fremov and Yu A Velikodnyi, *The crystal chemistry and properties of double molybdates and tungstates*, in Russian (Nauka, Leningrad, 1986) pp. 137
- [2] B M Sokolovski, A A Jevdokimov and V K Turnov, *Zh. Neorg. Khim.* **22**, 1499 (1977)  
A Vielidodny and V K Turnov, *Zh. Neorg. Khim.* **22**, 1496 (1976)  
N N Bushuyev and V K Turnov, *Kristallografiya* **21**, 69 (1976)
- [3] R F Klevtsova, L P Kozyeva and P V Klevtsova, *Kristallografiya* **19**, 89 (1974)  
R F Klevtsova, *Kristallografiya* **20**, 746 (1975)  
P V Klevtsov, W A Winokurov and R F Klevtsova, *Kristallografiya* **18**, 1192 (1973)  
P V Klevtsov and L P Kozyeva, *Kristallografiya* **21**, 316 (1976)  
P V Klevtsov, L P Kozyeva and A A Pavluk, *Kristallografiya* **20**, 1216 (1975)
- [4] R F Klevtsova and S V Borisov, *Dokl. Akad. Nauk. SSSR* **177**, 1334 (1967)
- [5] J Hanuza and L Macalik, *Spectrochim. Acta*, **A38**, 61 (1982)
- [6] J Hanuza and M Maczka, *Vibrational Spectrosc.* **1**, 85-96 (1994)
- [7] V V Fomichev and O I Kondratov, *Russ. J. Inorg. Chem.* **37**, 587 (1992)
- [8] V P Gnezdilov, V V Eremenko, N M Neoterenko and V I Fomin, *Optical Spectrosc.* (USSR) **68**, 324 (1990)
- [9] O I Kondratov, D D Baldanova, V V Fomichev, K I Petrov and I I Olikov, *Russ. J. Inorg. Chem.* **31**, 1152 (1986)
- [10] B M Sokolovski, A A Evdokimov and V K Trunov, *Russ. J. Inorg. Chem.* **22**, 816 (1977)  
A A Evdokimov, V K Trunov and B M Sokolovskii, *Russ. J. Inorg. Chem.* **25**, 389 (1980)

*Pressure-induced structural and electronic transition*

- [11] A Jayaraman, S K Sharma, Z Wang, S Y Wang, L C Ming and M Manghnani, *J. Phys. Chem. Solids* **54**, 827 (1993)
- [12] A Jayaraman, S K Sharma and S Y Wang, *Pramana – J. Phys.* **40**, 357 (1993)
- [13] A Jayaraman, S Y Wang and S K Sharma, *Solid State Commun.* **93**, 885 (1995)  
S R Shieh, L C Ming and A Jayaraman, *J. Phys. Chem. Solids* **57**, 247 (1996)
- [14] J Hanuza and L Labuda, *J. Raman Spectrosc.* **11**, 231 (1981)
- [15] J Hanuza and V V Fomitzev, *J. Mol. Struct.* **66**, 1 (1980)
- [16] J D Barnett, S Block and G J Piermarini, *Rev. Sci. Instrum.* **44**, 1 (1973)
- [17] A Jayaraman, S K Sharma, S Y Wang, S R Shieh, L C Ming and S-W Cheong, *J. Raman Spectrosc.* (in press)
- [18] A Jayaraman, S Y Wang and S K Sharma, *Curr. Sci.* **69**, 44 (1995)
- [19] A Jayaraman, S Y Wang, S K Sharma, and S-W Cheong, *Curr. Sci.* **70**, 232 (1996)
- [20] A Jayaraman, G A Kourouklis and L G Van Uitert, *Phys. Rev.* **B36**, 8547 (1987)