Joint 20th AIRAPT – 43th EHPRG, June 27 – July 1, Karlsruhe/Germany 2005

Phase transitions and optical absorption of $BaMoO_4$ under pressure

D. Christofilos[a], *J. Arvanitidis*[a,b], *E. Kampasakali*[a,c], *K. Papagelis*[d], *S. Ves*[b] *and G. A. Kourouklis*[a,*]

[a]*Physics Division, School of Technology, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece*

[b]*Physics Department, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece*

[c]*Chemistry Department, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece*

[d]*Material Science Department, University of Patras, 26504 Patras, Greece*

**corresponding author: e-mail: gak@gen.auth.gr*

Summary

Optical absorption spectra of polycrystalline $BaMoO_4$ powder have been recorded in the range of 9 up to 19 GPa, along with Raman spectra. The absorption edge lies outside the optical region (>3.1 eV) for pressures below 9 GPa, whereas for higher pressures it becomes observable exhibiting a pressure induced red shift of ~21 meV/GPa. As a result, the sample turns progressively from white to light yellow at the highest pressure. The appearance of the absorption edge in the optical region coincides with changes in the Raman spectra indicating the onset of a pressure induced phase transition, which seems to be the reason for the observed behaviour of the gap.

Introduction

Tungstates and molybdates with the scheelite ($CaWO_4$) structure, apart from being used as host materials of rare earth ions in solid state lasers e.g. (Faure 1996), emerge into today's technological focus as candidates for applications like Raman lasers (Brenier 2004, Pask 2003, Kaminskii 2000) as well as scintillators (Sulc 2005, Mikhailik 2004). Raman spectroscopy has been used extensively for the study of their structural stability and phase transitions under high pressure e.g. $BaMoO_4$ (Christofilos 2004), $SrWO_4$ (Christofilos 2002), $CaWO_4$ (Christofilos 1996), $CaMoO_4$ (Christofilos 1995), $SrMoO_4$ (Jayaraman 1995a), $CdMoO_4$ (Jayaraman 1995b), $PbMoO_4$ and $PbWO_4$ (Jayaraman 1985), $BaWO_4$ (Jayaraman 1983). The interest in their electronic properties has stimulated detailed theoretical studies of their band structures and optical properties (Hizhnyi 2005, Abraham 2000, Zhang 1998), whereas synchrotron x-ray scattering studies allowed the clarification of the high-pressure phase in several members of the family; $CaMoO_4$ (Crichton 2004), $BaWO_4$ (Panchal 2004), $CaWO_4$ (Grzechnik 2003, Errandonea 2003), $CdMoO_4$ (Shieh 1996). In the case of $BaMoO_4$, optical and luminescence studies indicate a band gap at ~4.2 eV at low temperature (Spassky 2004). However, with the exception of $PbMoO_4$ (Jayaraman 1985), no information exists about the behavior of the band gap of these materials as a function of pressure.

In this report we present our results on the band gap behaviour of $BaMoO_4$ under high hydrostatic pressure. At ambient conditions and even after the first, reversible, pressure-induced phase transition at 5.8 GPa (Christofilos 2004) the absorption edge remains outside the optical window. The sudden appearance of the band gap at ~9.1 GPa in combination with changes observed in the Raman spectra indicate a new high-pressure phase of $BaMoO_4$.

Experimental Method

High pressure was generated using a diamond anvil cell of the Mao and Bell type. The ~150 μm diameter hole of a hard steel gasket was completely filled with polycrystalline $BaMoO_4$

powder. Ruby chips, for the determination of pressure, and a mixture 4:1 methanol-ethanol, as hydrostatic pressure-transmitting medium were also placed inside the hole.

A Jobin Yvon THR1000, single grating monochromator system, equipped with a liquid nitrogen cooled CCD was used for the acquisition of extinction spectra. For the illumination, a 40 μm pinhole, illuminated by a 150W xenon lamp, was imaged on the sample with the help of a 60 mm achromate (1:1 magnification). The collected light was further spatially filtered by means of an adjustable iris in the intermediary focal plane of a non-standard design Jobin Yvon microscope, fiber-coupled to the spectrometer. The transmission spectra are normalized to their low energy side where the spectral profile remains unaffected by pressure. For the determination of the optical density, the spectrum of the pressure-transmitting medium was independently measured and used as a reference.

Raman spectra were acquired by a DILOR XY triple grating, micro-Raman system, equipped with a Wright cryogenic CCD detector. The 647.1 nm line of a Kr+ laser was used for excitation with a laser power of ~5 mW, measured before the high-pressure cell.

Results

The optical density is depicted in figure 1 for several pressures. The absorption edge lies initially outside the recorded window (visible region) as indicated by the spectrum at 7.5 GPa. At a pressure of ~9 GPa, the absorption edge moves inside the recorded window and displays a red shift with increasing pressure. In the inset of figure 1, the absorption edge, determined as the intercept of the background line to that of the edge, is illustrated as a function of pressure.

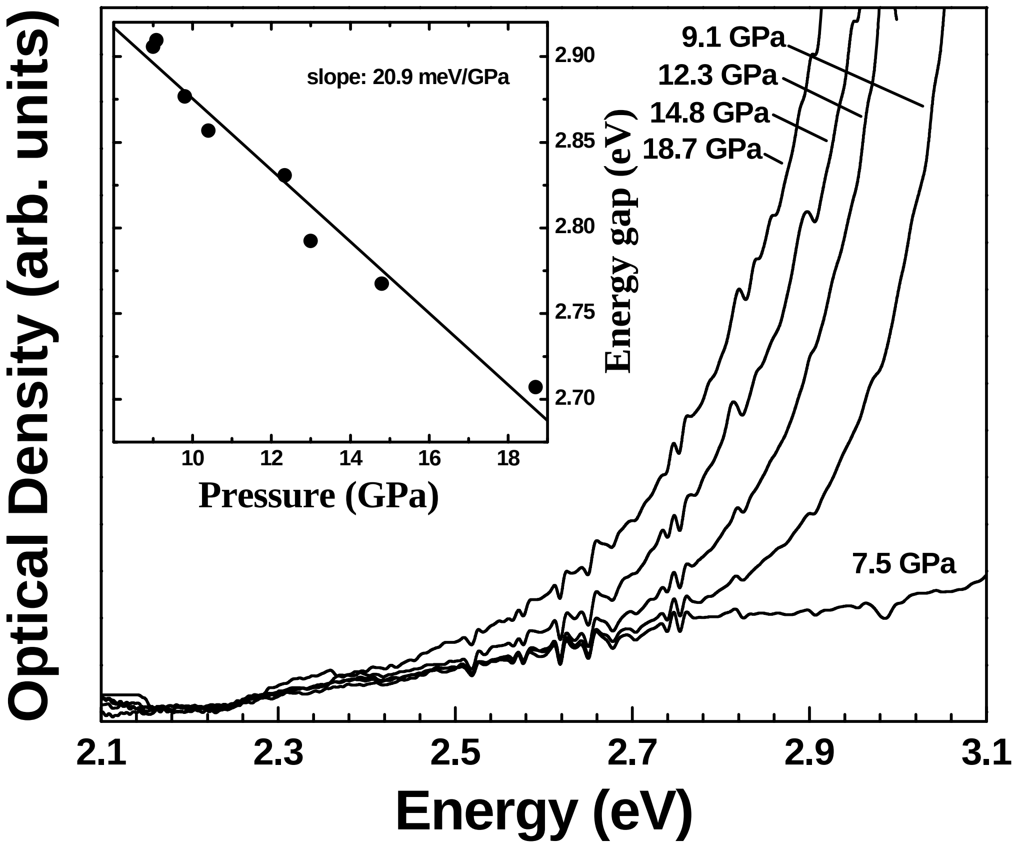

Figure 1: Optical extinction spectra of $BaMoO_4$ powder for several pressures. The inset shows the dependence of the absorption edge upon increasing pressure.

The reduction of the gap appears to be almost linear with pressure, closing at a rate of ~21meV/GPa. Extrapolation to ambient pressure yields a value of ~3.1 eV at normal conditions.

In order to connect the structural changes of the material with the observed behavior of the optical gap, indicative Raman spectra at three different pressures of the current study are presented in figure 2. They correspond to three different phases of $BaMoO_4$.

Discussion

$BaMoO_4$ is known to undergo a reversible pressure induced phase transition at 5.8 GPa. Above this pressure its structure remains stable at least up to ~8.5 GPa (Christofilos 2004). The two spectra at 4.4 and 7.6 GPa, in figure 2, correspond to the ambient pressure scheelite phase of the material and the first high-pressure phase (HPP I), respectively. For the HPP I, the Raman spectra clearly reveal that the MoO_4 units of the scheelite structure undergo considerable changes. Numerous new lines appear in the high and low frequency regions of the internal (MoO_4) modes. We point out that the total number of the Raman peaks (including shoulder features) is larger than that anticipated for a fergusonite, wolframite or other similar centrosymmetic structures with two chemical units in the primitive cell. In those structures, only 18 Raman active modes are expected because of the splitting of the E_g modes of the scheelite structure into A_g and B_g modes, since the degeneracy due to the tetragonal symmetry is removed.

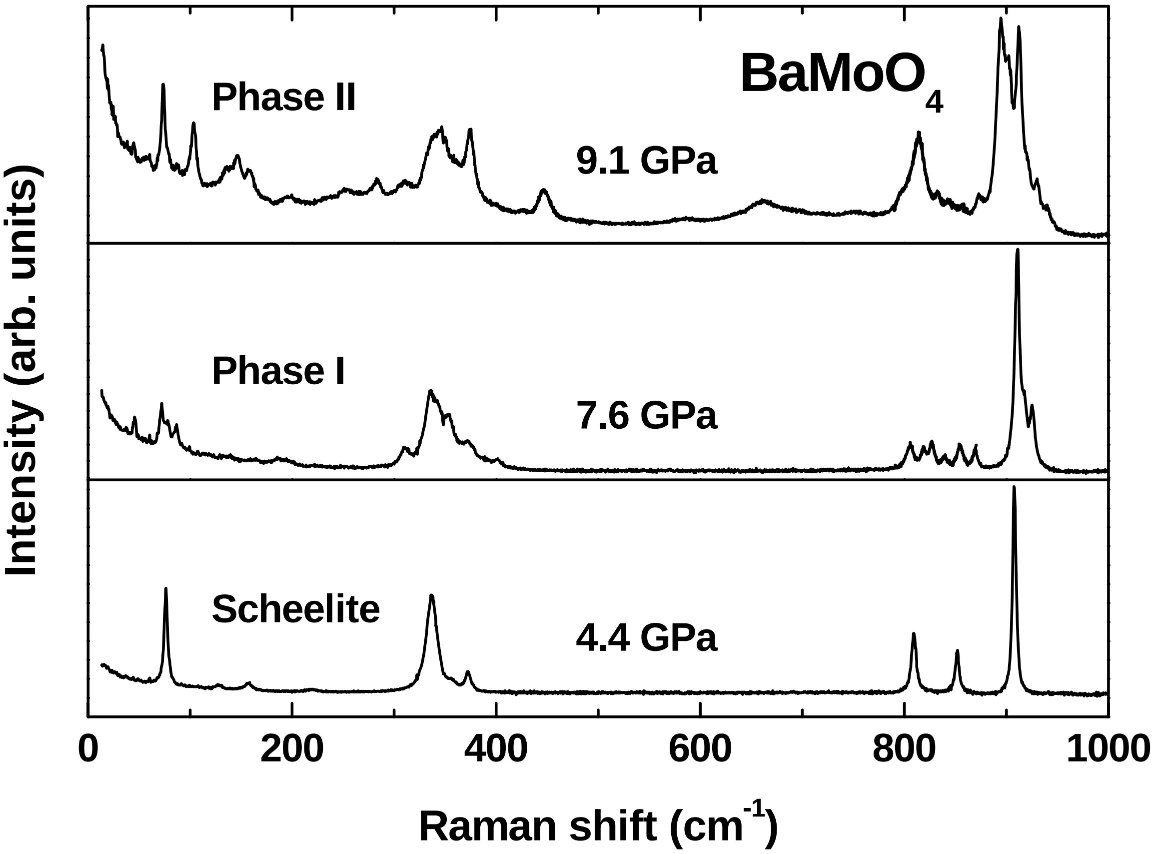

Figure 2: Raman spectra of $BaMoO_4$ powder corresponding to ambient and different high-pressure phases.

It must be noted, however, that although the Raman spectra of $CaWO_4$ and $BaWO_4$ exhibit distinct differences in their pressure induced phase transformations, high pressure X-ray diffraction studies on these materials suggest the same fergusonite-like phase as the high pressure phase. In our case, if we assume that the HPP I is that of fergusonite, a possible explanation would be the co-existence of the two phases (scheelite-fergusonite). The slightly different environment of the different crystallites in the polycrystalline material under investigation, resulting to an increased number of peaks, could offer an alternative explanation. In any case, if we assume that the HPP I is that of fergusonite for all these materials, then the differences in their respective Raman response remains unclear and an open subject for clarification. Let us, however, stress that the conservation of the tetrahedral character of the MoO_4 units in HPP I, although deformed and interacting with each other is supported by the fact that, the new peaks in the internal mode frequency range, span, more or less, the same frequency range with those of the scheelite structure.

The third spectrum at 9.1 GPa, displays dramatic changes in comparison with that of HPP I. Our ongoing detailed Raman investigations (Christofilos 2005), support the consistency of the observed spectra, signifying beyond doubt the onset of a second high pressure phase (HPP II) which, in addition, is sluggish and completes at ~10 GPa. Numerous new peaks appear all over the whole Raman spectra including peaks in the “phonon gap” region of the scheelite and HPP I (450 – 800 cm^{-1}). Note that in tungstate compounds of the wolframite ($NiWO_4$) structure the more closely octahedral-like coordination of the W cation results in the appearance of peaks in the “phonon gap” region mentioned above (e.g. $CdWO_4$ (Jayaraman 1995c)). In this respect, we expect that in HPP II, the tetrahedral character of the cation in the initial MoO_4 units of the scheelite structure, strongly interacting and deformed in the case of HPP I, is now better described as octahedral.

Let us now turn to the origin of the band gap in alkaline earth or lead molybdate and tungstate scheelites. Electronic and optical properties for many of the members of this family have been calculated in the framework of density-functional theory (Abraham 2000, Zhang 1998). The almost tetrahedral geometry in the vicinity of the Mo ions splits their 4d states in e- and t_2-like states while in the case of oxygen, the crystal field effect due to the Mo ions results in the splitting of the atomic-like 2p wavefunctions of oxygen in σ and π contributions. The bottom of the conduction band is dominated by the 4d (especially e-like) states of Mo while the top of the valence band is mainly populated by the 2p oxygen states (especially π-like contributions). The alkaline earth cation contributions in the mentioned region are negligible. Thus, in a simplified view, the observed band gap in these materials is mainly attributed to the BO_4 tetrahedra (B=Mo, W), and the corresponding dominant optical transitions from the 2p O states to the 4d (or 5d for tungstates) states of the B cation. In the case of $PbMoO_4$ and $PbWO_4$, the lead cation, due to the different electronic structure, contributes to the top of the valence band comparably with the oxygen so the above scheme is not accurate. Under these considerations any pressure-induced changes of the structure should be directly reflected in the band gap of the material, especially if it leads to the increase of the cation’s coordination.

In the case of tungstate and molybdate scheelites the band gap at ambient pressure lies in the range of 3.5-4.5 eV. For $BaMoO_4$, the corresponding value lies at ~4.2 eV, determined by reflectance measurements at low temperatures (Spassky 2004). The extrapolation of our high pressure absorption data at ambient pressure yields a value of 3.1 eV, smaller than 4 eV. In a detailed work concerning the band gap properties of double perovskite structured molybdates and tungstates (Eng 2003), including alkaline earth members of the family (e.g. Sr_2CaMoO_6), the optical gap of the purely octahedrally coordinated Mo ion (MoO_6) is nearly identical for all of the examined materials at ~2.7 eV. Moreover, the closing rate of the band gap of 21meV/GPa, is almost half of that in $PbMoO_4$, ~50 meV/GPa, observed by Jayaraman (1985) for the scheelite structure.

Thus the observed band gap of HPP II (~2.9 eV) at the onset of this phase at 9 GPa and the smaller band gap slope of –21 meV/GPa compared to that of $PbMoO_4$ scheelite phase, are compatible with a high pressure phase of $BaMoO_4$ where the Mo cation is better described as octahedrally coordinated in agreement with the Raman spectra of this phase.

Conclusions

High-pressure absorption studies in combination with Raman spectroscopy, reveal a second high-pressure phase of polycrystalline $BaMoO_4$ above ~9 GPa. Due to the phase transition the absorption edge of the material appears in the optical region and continues to close up to ~19 GPa. Results are compatible with a phase where the Mo cation exhibits an octahedral coordination.

REFERENCES

ABRAHAM Y., HOLZWARTH N.A.W., WILLIAMS R.T., 2000. Electronic structure and optical properties of $CdMoO_4$ and $CdWO_4$. *Physical Review B*, 62 (3), 1733-1741

BRENIER A., JIA G.H., TU C.Y., 2004. Raman lasers at 1.171 and 1.517 pm with self-frequency conversion in SrWO4: Nd3+ crystal. *Journal of Physics-Condensed Matter,* 16 (49), 9103-9108

CRICHTON W.A., GRZECHNIK A., 2004, Crystal structure of calcium molybdate, $CaMoO_4$, a scheelite-type to fergusonite-type transition in powellite at P>15 GPa. *Zeitschrift fur Kristallographie-New Crystal structures,* 219 (4), 337-338

CHRISTOFILOS D., ARVANITIDIS J., KAMPASAKALI E., PAPAGELIS K., VES S., KOUROUKLIS G.A., 2005. to be published

CHRISTOFILOS D., ARVANITIDIS J., KAMPASAKALI E., PAPAGELIS K., VES S., KOUROUKLIS G.A., 2004. High pressure Raman study of $BaMoO_4$. *Physica Status solidi B-Basic Research,* 241 (14), 3155-3160

CHRISTOFILOS D., PAPAGELIS K., VES S., KOUROUKLIS G.A., RAPTIS C., 2002. High-pressure Raman study and lattice dynamical calculations for $SrWO_4$. *Journal of Physics-Condensed Matter,* 14 (47), 12641-12650

CHRISTOFILOS D., VES S., KOUROUKLIS G.A., 1996. Pressure induced phase transitions in alkaline earth Tungstates. *Physica Status Solidi B-Basic Research,* 198 (1), 539-544

CHRISTOFILOS D., KOUROUKLIS G.A., VES S., 1995. A high pressure Raman study of Calcium Molybdate. *Journal of Physics and Chemistry of Solids,* 56 (8), 1125-1129

ENG H.W., BARNES P.W., AUER B.M., WOODWARD P.M., 2003. Investigations of the electronic structure of d^0 transition metal oxides belonging to the perovskite family. *Journal of Solid State Chemistry,* 175 (1): 94-109

ERRANDONEA D., SOMAYAZULU M., HAUSERMANN D., 2003. Phase transitions and amorphization of $CaWO_4$ at high pressure. *Physica Status Solidi B-Basic Research,* 235 (1): 162-169

FAURE N., BOREL C., COUCHAUD M., BASSET G., TEMPLIER R., WYON C., 1996. Optical properties and laser performance of neodymium doped scheelites $CaWO_4$ and $NaGd(WO_4)_2$. *Applied Physics B-Lasers and Optics,* 63 (6), 593-598

GRZECHNIK A., CRICHTON W.A., HANFLAND M., VAN SMAALEN S., 2003. Scheelite $CaWO_4$ at high pressures, *Journal of Physics-Condensed Matter,*15 (43), 7261-7270

HIZHNYI Y.A., NEDILKO S.G., NIKOLAENKO T.N., 2005. Theoretical investigation of the luminescence centres in $PbWO_4$ and $CdWO_4$ crystals, *Nuclear Instruments & Methods in Physics Research Section A-Accelerators Spectrometers and associated equipment,* 537 (1-2), 36-39

JAYARAMAN A., WANG S.Y., SHIEH S.R., SHARMA S.K., MING L.C., 1995, High pressure Raman study of $SrMoO_4$ up to 37 GPa and pressure induced phase transformations. *Journal of Raman Spectroscopy,* 26 (6): 451-455 JUN

JAYARAMAN A., WANG S.Y., SHARMA S.K., 1995. High pressure Raman investigation on $CdMoO_4$ and pressure induced phase transformations. *Physical Review B,* 52 (14), 9886-9889

JAYARAMAN A., WANG S.Y., SHARMA S.K., 1995. New pressure induced phase changes in $CdWO_4$ from Raman spectroscopic and optical microscopic studies. *Current Science,* 69 (1), 44-48

JAYARAMAN A., BATLOGG B., VANUITERT L.G., 1985. Effect of high pressure on the Raman and electronic absorption spectra of $PbMoO_4$ and $PbWO_4$. *Physical Review B,* 31 (8), 5423-5427

JAYARAMAN A., BATLOGG B., VANUITERT L.G., 1983. High pressure Raman study of alkaline earth Tungstates and a new pressure-induced phase transition in $BaWO_4$. *Physical Review B,* 28 (8), 4774-4777

KAMINSKII A.A., MCCRAY C.L., LEE H.R., LEE S.W., TEMPLE D.A., CHYBA T.H., MARSH W.D., BARNES J.C., ANNANENKOV A.N., LEGUN V.D., EICHLER H.J., GAD G.M.A, UEDA K., 2000. High efficiency nanosecond Raman lasers based on tetragonal $PbWO_4$ crystals. *Optics communications,* 183 (1-4), 277-287

MIKHAILIK V.B., BAILIFF I.K., KRAUS H., RODNYI P.A., NINKOVIC J., 2004. Two-photon excitation and luminescence of a CaWO4 scintillator. *Radiation Measurements,* 38 (4-6): 585-588

PANCHAL V., GARG N., CHAUHAN A.K., SANGEETA B., SHARMA S.M., 2004. High pressure phase transitions in $BaWO_4$. *Solid State Communications,* 130 (3-4), 203-208

PASK H.M., 2003. The design and operation of solid-state Raman lasers, *Progress in Quantum Electronics,* 27 (1), 3-56

SHIEH S.R., MING L.C., JAYARAMAN A., 1996. Pressure-induced phase transitions in $CdMoO_4$: An in-situ high pressure X-ray diffraction study up to 52 GPa. *Journal of Physics and Chemistry of Solids,* 57 (2): 205-209

SULC M., NIKL M., VOGNAR M., BOHACEK P., MIKES P., KOBAYASHI M., USUKI Y., 2005. On-line measurement of gamma radiation-induced absorption in A^{3+}-codoped $PbWO_4$: Mo crystals, *Nuclear Instruments & Methods in Physics Research Section A-Accelerators Spectrometers and associated equipment,* 537 (1-2), 446-448

SPASSKY D.A., IVANOV S.N., KOLOBANOV V.N., MIKHAILIN V.V., ZEMSKOV V.N., ZADNEPROVSKI B.I., POTKIN L.I., 2004. Optical and luminescent properties of the lead and barium molybdates, *Radiation Measurements,* 38 (4-6), 607-610

ZHANG Y., HOLZWARTH N.A.W., WILLIAMS R.T., 1998. Electronic band structures of the scheelite materials $CaMoO_4$, $CaWO_4$, $PbMoO_4$, and $PbWO_4$. *Physical Review B*, 57 (20), 12738-12750