High pressure theoretical and experimental analysis of the bandgap of BaMoO$_4$, PbMoO$_4$ and CdMoO$_4$

V. Monteseguro,$^1$ J. Ruiz-Fuertes,$^2$ J. Contreras-García,$^3$ P. Rodríguez-Hernández,$^4$ A. Muñoz,$^2$ and D. Errandonea$^1$

$^1$Departamento de Física Aplicada-ICMUV, Universitat de València, Calle Dr. Moliner 50, 46100 Burjassot, Spain
$^2$DCITIMAC, Universidad de Cantabria, Avenida de los Castros 48, 39005 Santander, Spain
$^3$CNRS, Laboratoire de Chimie Théorique, LCT, Sorbonne Université, F. 75005 Paris, France
$^4$Instituto de Materiales y Nanotecnología, Departamento de Física, Universidad de La Laguna, La Laguna, 38205 Tenerife, Spain

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We have investigated the origin of the bandgap of the BaMoO$_4$, PbMoO$_4$, and CdMoO$_4$ crystals on the basis of optical absorption spectroscopy experiments and *ab initio* electronic band structure, density of states, and electronic localization function calculations under high pressure. Our study provides an accurate determination of the bandgaps $E_g$ and their pressure derivatives $dE_g/dP$ for BaMoO$_4$ (4.43 eV, -4.4 meV/GPa), PbMoO$_4$ (3.45 eV, -53.8 meV/GPa), and CdMoO$_4$ (3.71 eV, -3.3 meV/GPa). The absorption edges were fitted with the Urbach exponential model which we demonstrate to be the most appropriate on thick crystals with direct bandgaps. So far, the narrowing of the bandgap of distinct PbMoO$_4$ had been qualitatively explained considering only the presence of the Pb 6$s$ levels at the top of its valence band. Its fast pressure dependent redshift and the occurrence of its direct bandgap away from $\Gamma$ in contrast to the other scheelites had remained unsolved. Here we show that contrary to what had been proposed and differently to the other scheelites, in PbMoO$_4$ the band gap takes place between the Pb 6$s$ levels at the top of the valence band and the antibonding O 2$p$ levels at the bottom of the conduction band. For this reason the direct bandgap is pushed away from zone center in order to allow $s$ – $p$ mixing. Its pressure dependence is one order of magnitude faster than in the other scheelites due to two effects: its delocalized character and the higher compressibility of dodecahedral units, PbO$_8$, compared to tetrahedral units, MoO$_4$. This is one order of magnitude faster than for the remaining studied scheelites, i.e. the bandgap of CaWO$_4$ varies at $-2.1$ meV/GPa [7]. Such a different response to pressure between lead-bearing and non-lead-bearing scheelites has been tentatively attributed to the influence of the Pb 6$s$ states located at the top of the valence band overlapping with the O 2$p$ states [5, 8]. Although the presence of the Pb 6$s$ levels at the top of the valence band must have an effect on the strong redshift of the bandgap in PbWO$_4$ and PbMoO$_4$, what particular effect it is has never been explained.

Furthermore, differently to scheelite-type tungstates, an accurate determination in the case of scheelite-type molybdates at ambient pressure is still missing. It is known [7, 10] that the absorption edge of scheelites must be explained according to Urbach’s law [10] and an inappropriate $(\alpha h\nu)^2$ analysis can lead to different values depending on the maximum absorption coefficient $\alpha$ measured in the experiment. In fact, a rapid search in the literature provides an enormous dispersion of the bandgap values of scheelite-type molybdates. For example, in PbMoO$_4$ we find experimental bandgaps that range from 3.1 to 3.6 eV [1, 9], for BaMoO$_4$ from 3.2 to 4.1 eV [11, 12], and for CdMoO$_4$ from 3.3 to 4 eV [13, 14]. This indicates that the bandgap of scheelite-type molybdates cannot be regarded as being accurately determined.

In this letter we shall determine the bandgap of BaMoO$_4$, CdMoO$_4$, and PbMoO$_4$ by employing Urbach’s law and we shall also get a deeper insight into the consequences of the presence of Pb 6$s$ electrons at the top of the valence band. We shall present optical absorption measurements on scheelite-type BaMoO$_4$, CdMoO$_4$, and PbMoO$_4$ scintillators under compression and pressure dependent electronic band structure, electronic density of states (DOS) and electron localiza-

*Electronic address: Virginia.Monteseguro@uv.es*
The electronic band structure and electron charge density calculations at different pressures have been performed within the framework of DFT [17] with the Vienna ab initio simulation package (VASP) [18–21]. Projector augmented wave (PAW) [22] pseudopotentials were used and the set of plane waves were extended up to a cutoff of 520 eV. The exchange-correlation energy was described with a generalized gradient approximation (GGA) within the PBEsol prescription [23].

The integrations over the Brillouin zone (BZ) of the scheelite structures were carried out with a dense grid of special \( k \)-points (4 × 4 × 4) employing the Monkhorst-Pack method [24]. The convergence achieved was 1.2 meV per formula unit in the total energy, the forces on the atoms were almost negligible (smaller than 0.005 eV/\( \AA \)) and the deviations of the stress tensor from its diagonal hydrostatic form minimal (lower than 0.1 GPa). In order to analyze the electronic structure, we have resorted to quantum topology. We have used the electron density and its critical points, noticeable the first order critical points, also known as bond critical points (bcp)s within the Quantum Theory of Atoms in Molecules.[25] The delocalization and sharing of electrons was evaluated thanks to the Electron Localization Function (ELF) [26, 27]. The ELF enables to highlight the change in kinetic energy density due to the Pauli principle, thus providing a picture in terms of electron pairs. Data were obtained from the numerical analysis of the respective VASP output files (ELFCAR and CHGCAR) with the CRITIC code [28, 29].

The optical absorption experiments were performed on \( \sim 80 \times 80 \mu m^2 \) crystals platelets with a thickness of \( \sim 10 \mu m \) obtained from large single crystals grown by the Czochralski method [15]. The optical setup consisted on a confocal system with a deuterium lamp, a fused silica lens, and two Cassegrain objectives for focusing on the sample and collecting the transmitted light. The beam spot size was 50 \( \mu m \) and the spectrometer employed was an UV-VIS OCEAN HR4000. The samples were loaded together with a ruby chip for pressure determination [16] and a mixture of methanol-ethanol-water (16:4:1) as pressure transmitting medium (PTM) in the 250 \( \mu m \) hole of a 40 \( \mu m \) thick stainless-steel gasket placed between the two 500 \( \mu m \) diamonds of a membrane-type diamond anvil cell (DAC).

The optical absorption edges of \( \alpha \) BaMoO\(_4\), \( \alpha \) CdMoO\(_4\), and \( \alpha \) PbMoO\(_4\) from ambient pressure to 6.2, 9.9, and 9.9 GPa, respectively. The arrows indicate the direction in which the spectra move under compression. In the insets, the linear fits of the \( \ln(\alpha) \) in a semilogarithmic plot of the three compounds at 1 atm and high pressure are represented.
FIG. 2: Pressure dependence of the bandgap $E_g$ of BaMoO$_4$, CdMoO$_4$, and PbMoO$_4$ (filled circles) as obtained from the fits to our spectra.

slope of the semilogarithmic plot (Fig. 1). To perform the fits, we followed the strategy used before in other type of compounds [35, 36], obtaining an estimate value of $A_0 = 1200$ cm$^{-1}$ for the three compounds which was assumed to be constant with pressure as observed before [7]. We fitted all the spectra, including the one at ambient pressure, fixing $A_0 = 1200$ cm$^{-1}$ and leaving $E_U$ and $E_g$ free. For $E_U$, we found with pressure almost constant values of 0.06 eV for BaMoO$_4$, 0.04 eV for CdMoO$_4$ and PbMoO$_4$; in the order of the $E_U$ values previously obtained for scheelite type tungstates [7] and indicative of the steepness of the spectra. Our fits at ambient pressure yield bandgap values for the three compounds of 4.43 eV (BaMoO$_4$), 3.71 eV (CdMoO$_4$), and 3.45 eV (PbMoO$_4$). Larger than those reported before for BaMoO$_4$ [11, 12] and PbMoO$_4$ [9]. The pressure dependence of the bandgaps of the three compounds is shown in Fig. 2. As already observed in Fig. 1, under pressure the bandgap of the three compounds redshifts but while it barely moves with pressure for BaMoO$_4$ (−4.4 meV/GPa) and CdMoO$_4$ (−3.3 meV/GPa), it redshifts at −53.8 meV/GPa for PbMoO$_4$ in good agreement with Jayaraman et al. [9] that found a value of −50 meV/GPa.

The contribution of the atomic orbitals in the band-structure through the partial density of states (pDOS) is shown in Fig. 3. In BaMoO$_4$ and CdMoO$_4$, the valence (VB) and conduction (CB) bands can be mostly understood by considering the (MoO$_2$)$^{2+}$ ions alone. The top of the VB is dominated by the O$^{2-}$ 2$p$ states, while the bottom of the CB consists of the Mo$^{6+}$ 4$d$ states [5]. In the case of PbMoO$_4$, the top of VB is also dominated by the 6$s$ orbitals of Pb atoms, which overlap with the O−2$p$ states, and the Pb$^{2+}$ 6$p$ states are present at the bottom of the CB.

The electronic band-structures of BaMoO$_4$, CdMoO$_4$, and PbMoO$_4$ at ambient pressure and 6 GPa can be seen in Fig. 4. BaMoO$_4$ has a direct bandgap of 3.88 eV located at $\Gamma$ at ambient pressure, which compares very well with the experimental one mentioned above. According to the calculations its bandgap becomes indirect, from $\Gamma$ to Z, beyond 4 GPa, although the direct bandgap is the one observed experimentally. In the CdMoO$_4$, the bandgap, of 2.21 eV at 0 GPa, is indirect from $\Gamma$ to the direction ($\Gamma$Z) in the whole range. However, the direct bandgap, the experimentally accessible one, is found at $\Gamma$ and it is of 2.27 eV at 0 GPa. Finally, the bandgap of PbMoO$_4$ is indirect at all pressure points, going from the direction $\Delta$ to $\Gamma$ and taking a value of 2.67 eV at 0 GPa. Experimentally, the bandgap observed is the direct one, located at the direction $\Delta$, and it is of 2.71 eV at ambient pressure. In CdMoO$_4$ and PbMoO$_4$, the theoretical bandgap energy is underestimated if we compare it with the experimental values, probably due to the influence of the d orbitals of Cd and Pb atoms at the VB, which do not contribute much to the experimental bandgap. However, the theoretical pressure evolution of the bandgap is in good agreement with our experiments in the three cases. For BaMoO$_4$ and CdMoO$_4$, the bandgaps redshift at −1.1 meV/GPa and −5.8 meV/GPa, respectively. As was noticed experimentally, in the case of PbMoO$_4$, the bandgap decreases abruptly at −70 meV/GPa.

FIG. 3: Electronic partial density of states of BaMoO$_4$ (a) at 0 GPa and (b) at 6 GPa, of PbMoO$_4$ (c) at 0 GPa and (d) at 6 GPa and of CdMoO$_4$ (e) at 0 GPa and (f) at 6 GPa. The 2$p$ orbitals of O are represented by red line, the 4$d$ orbitals of Mo by blue line, the 5$p$ orbitals of Ba by orange line, the 6$s$ (6$p$) orbitals of Pb by green (black) line and the 4$d$ (5$s$) orbitals of Cd by pink (violet) line.

The analysis of the electron density and related scalar fields is shown in Fig. 5. The Laplacian of the electron density at the bcp (electron density saddle point) gives an idea of the ionicity ($\nabla^2 \rho > 0$) vs covalency ($\nabla^2 \rho < 0$) of a system. When the Laplacian is close to zero, densities are typically very flat (weak bonds or metals). As can be seen in Figure 5 (a), Cd−O interactions are rather ionic ($\nabla^2 \rho = 0.17$ a.u.) whereas the Laplacian at Pb-O and Ba-O interactions ($\nabla^2 \rho \approx 0.1$ a.u.) identifies a rather delocalized interaction. Moreover, looking at the electron density of these two interactions [Fig. 5 (b)], we can see that the interaction in Ba−O is weaker ($\rho = 0.026$ a.u.) than that of Pb ($\rho = 0.036$ a.u.). Hence, the interactions in the compounds can be relatively classified as ionic for Cd, weak for Ba, and more delocalized for Pb. This interpretation is confirmed by the ELF values at the bcps [Fig. 5 (c)], which are higher for the two stronger compounds (Cd and Pb). In conclusion, in the case of PbMoO$_4$ compound, we describe a delocalized Pb−O bond, due to a high ELF value,
FIG. 5: Pressure evolution at the O–X (X = Cd,Pb,Ba) bond critical points (bcps) of (a) the Laplacian of the electron density, (b) the electron density and (c) the ELF at the bond critical points. The black, red and blue curves correspond to BaMoO₄, PbMoO₄ and CdMoO₄, respectively. The two lines per compound are due the presence of two non-equivalent O–X bcps in the unit cell.

The delocalized densities are associated with the top of the bands, in agreement with the DOS analysis. Moreover, they are more compressible and more reactive (bigger $\partial E/\partial V$), what explain the steeper evolution of the top of the band with pressure. Our DOS and ELF analysis open a new interpretation of the origin of the bandgap of PbMoO₄: the charge transfer band in PbMoO₄ is most probably taking place between the Pb 6s and O 2p levels instead of between the O 2p and the Mo 4d levels as in the rest of free lead molybdates. Such an explanation is also based in the fact that the band gap of these compounds is associated with the behaviour of the local structure of the scheelites under compression. In the scheelite-type molybdate structure, $\Delta$MoO₄, the compressibility is ruled by the dodecahedral AO₈ units since the tetrahedral MoO₄ units are almost incompressible [37, 38]. Therefore, the fast decrease of the bandgap in the PbMoO₄ with respect to the other scheelites can be understood considering the energy transition to be from Pb–6s to O–2p bands within the PbO₈ dodecahedra, which is more sensitive to the increase of the pressure than the O–2p to Mo–4d transition, constrained to the MoO₄ tetrahedra, as in BaMoO₄ and CdMoO₄. Furthermore, taking into account that the crystal structure of scheelites (space group $I4_1/a$) is centrosymmetric and the $s - p$ mixing is forbidden at zone center, this would explain why the direct bandgap of PbMoO₄ takes place at $\Delta$ instead of at zone center as in BaMoO₄ and CdMoO₄.

In conclusion, we have accurately determined the bandgaps and pressure derivatives of BaMoO₄, PbMoO₄, and CdMoO₄ crystals by means of the linear fit of their absorption edges to Urbach’s law finding that the bandgap of PbMoO₄ reacts one order of magnitude faster than in the lead-free molybdates. Such a feature is well explained if we consider that the transition occurs between Pb–6s levels in VB and O–2p levels in CB. Such a transition is more sensitive to compression changes due to its high electron delocalization and the high compressibility of dodecahedral PbO₈ units in the scheelite-type tetragonal structure. This charge transfer band is confirmed by the $ab$ initio DOS and ELF calculations and it is allowed since it fulfills the electric dipole selection rules. This transition explains that the bandgap occurs in the direction $\Delta$ instead of the zone center as expected in a centrosymmetric structure in which $s - p$ mixing is not allowed at zone center. Finally, our results can be directly extended to BaWO₄, PbWO₄ and CdWO₄ which show an identical electronic band structure.

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