

Unveiling the effect of the Pb 6s electronic levels in distinct PbMoO₄ under high pressure

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Lead molybdate (PbMoO₄) belongs to a family of scintillating crystals in which the understanding of the nature of their bandgaps is crucial to tune their luminescent properties. However, questions as why PbMoO₄ has a direct bandgap extremely sensitive to compression (-50 meV/GPa), why its location is at Σ , away from zone center and why it is considerably narrower than its scheelite-type counterparts, remain unsolved.

According to electronic band structure calculations [1], in PbMoO₄, the narrowing of the bandgap has its origin on the considerable density of Pb 6s levels that exists at the top of its valence band. This qualitative explanation was already proposed in the first optical absorption study of the bandgap of PbMoO₄ by Jayaraman et al. [2] back in 1985. In such an explanation, the electronic transition is still considered from the occupied O 2p at the top of the valence band to the empty Mo 4d levels at the bottom of the conduction band. However, why the direct bandgap of PbMoO₄ takes place away from the zone center differently to the other scheelite-type molybdates or why its value changes with pressure one order of magnitude faster than in lead-free molybdates cannot be understood simply considering the presence of Pb 6s levels.

In this work, we employ optical absorption spectroscopy, *ab initio* electronic band structure and electronic localization function calculations under high pressure to unveil, for the first time since 1985, the real origin of the bandgap of PbMoO₄. Moreover, we determine the exact bandgap value of PbMoO₄, BaMoO₄, and CdMoO₄ which requires a fit to Urbach's law. Under the light of our theoretical *ab initio* calculations at different pressures, we conclude that the bandgap of PbMoO₄ is the result of a *sp* mixing involving the filled Pb 6s valence bands and the empty O 2p levels at the conduction band instead of the O 2p to Mo 4d frame of the lead-free scheelite-type molybdates. This result, which directly explains why the direct bandgap of PbMoO₄ is pushed out of the zone center, also clarifies why the bandgap of PbMoO₄ is one order of magnitude more sensitive to pressure than in the other scheelite-type molybdates.

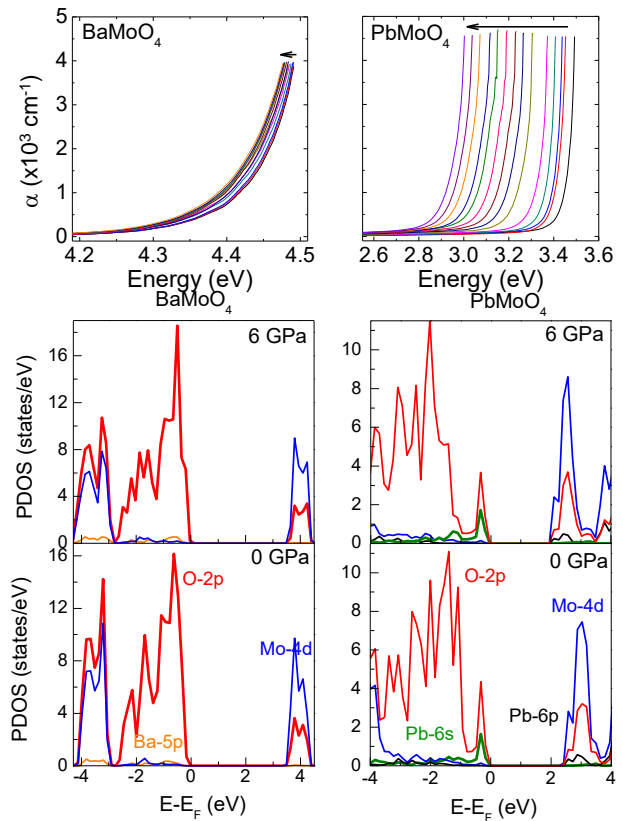


Figure 1. (top) Absorption spectra of BaMoO₄ and PbMoO₄ up to ~8 GPa showing the strong pressure dependence of the bandgap of PbMoO₄. (bottom) Partial density of states for BaMoO₄ and PbMoO₄ showing the distinctive presence of Pb 6s levels at the top of the valence band.

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