

High-pressure study of PbCrO₄ by single-crystal X-ray diffraction and *ab initio* simulations. Structural and vibrational properties

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The high-pressure behavior of chromates with formula ACrO_4 has been object of experimental and theoretical efforts in Material and Earth Sciences during the last decade. The previous experimental studies were carried out by powder X-Ray diffraction and Raman. Although the existence of large regions of phase coexistence is commonly observed in HP powder XRD experiments, however HP single-crystal XRD experiments have shown that there are cases where phase coexistence is not of intrinsic origin being triggered by stress between grains of the powder sample.

In order to improve the knowledge about the high-pressure behavior of lead chromate, PbCrO_4 , under pressure, we have investigated it using single-crystal X-Ray diffraction and *ab initio* simulations. In particular, we have probed the existence of a structural transition under high pressure at 4.5 GPa and that the structural sequence of PbCrO_4 is different than the one previously determined. We have established that PbCrO_4 displays under pressure a monoclinic to tetragonal phase transition, with no intermediate phases between the low-pressure monoclinic monazite structure (space group $P2_1/n$) and the high-pressure tetragonal structure.

The crystal structure of the high-pressure polymorph as been by the first time undoubtedly determined to be a tetragonal scheelite-type structure (space group $I4_1/a$) with

unit-cell parameters $a = 5.1102(3) \text{ \AA}$ and $c = 12.213(3) \text{ \AA}$. These findings have been used for a reinterpretation of previously published Raman and optical-absorption results. In this work, information of the calculated infrared-active phonons and their theoretical pressure dependence will be also provided by the first time for both polymorphs.

In addition, the pressure dependence of the unit-cell parameters, atomic positions, bond distances, and polyhedral coordination are discussed. An equation of state was established for the two polymorphs and the tensor of compressibility determined. The softest and stiffest direction of compression for monazite-type PbCrO_4 are also reported.

Calculations contribute to the understanding of the electronic properties of monazite- and scheelite-type PbCrO_4 and support that the band-gap collapse can be correlated to the phase transition.

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