

Study of the PbSO_4 Anglesite under high pressure

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In this work we present synchrotron X-ray diffraction experiments and *ab initio* simulations to study the behavior of the lead sulfate under high pressure [1]. PbSO_4 , mineral name anglesite, adopts the barite-type structure, space group $Pnma$, at ambient conditions.

The angle-dispersive X-ray diffraction experiments were carried out at the I15 beam line of Diamond Light Source using monochromatic radiation of $\lambda = 0.4246 \text{ \AA}$. The sample was placed in a rhenium gasket cavity inside a LeToullec-type membrane DAC loaded with He as pressure transmitting medium. Diffraction patterns were collected using a large MAR345 image-plate detector. The high pressure experiments were performed up to 67 GPa.

Ab initio total-energy simulations were carried out using density functional theory (DFT) with the Vienna *Ab initio* Simulation Package, VASP. The projector-augmented wave (PAW) scheme was used and the basis set of plane waves was extended up to a cutoff energy of 520 eV. The exchange-correlation energy was described with the Perdew-Burke-Ernzerhof prescription for solids of the generalized gradient approximation, GGA. A dense sampling of *k*-special points was employed to perform the Brillouin zone integrations. All the structures were optimized using the typical convergence criteria to achieve forces over the ions lower than 0.003 eV/Å and differences in the stress tensor diagonal lower than 0.02 GPa.

Our combined study shows that the compression of PbSO_4 anglesite induces a phase transition from the $Pnma$ barite-type structure to the $P2_12_12_1$ post-barite-type structure at pressures above 27 GPa. This phase transition is of first-order. The phase transition involves a volume collapse of 2.4% and a relative displacement of the Pb and S atoms of approximately 0.8 Å, with an increase of the number of neighbors in the second coordination sphere from 7 to 8 and a tilting of the $[\text{SO}_4]$ groups. The axial and the bulk moduli of both polymorphs have also been determined.

The post-barite-type phase seems to be the thermodynamically stable high pressure phase for ABO_4 ternary oxides with large *A* (Pb, Ba, NH_4 , or La) and small *B* (S, Cr, Cl, or P) atoms

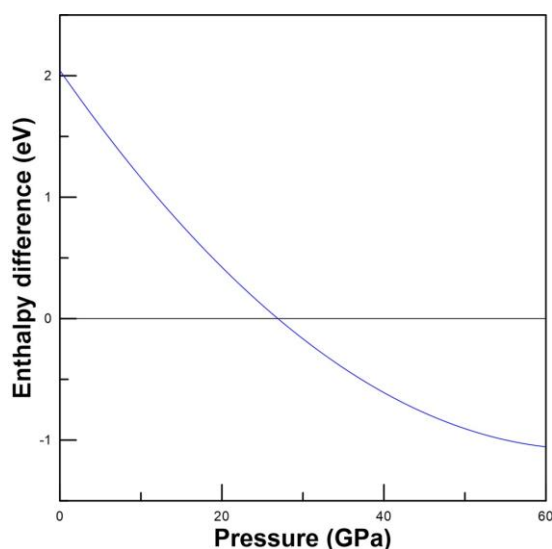


Figure 1. Enthalpy variation versus pressure for both PbSO_4 polymorphs (low-pressure $Pnma$ and high-pressure $P2_12_12_1$ (blue) phases), taking the initial $Pnma$ structure as reference.

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[1] D. Santamaria-Pérez, R. Chulia-Jordan, D. Daisenberger, P. Rodríguez-Hernández, and A. Muñoz, *Inorg. Chem.* 2019, **58**, 2708.