High-pressure behavior of AO$_2$ (A = Sn, Pb, Hf) compounds beyond 2 Mbars

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Abstract

There is widespread interest in the high-pressure behavior of metal dioxides, AO$_2$, where A includes group 14 and 15 cations like Si, Ge, Sn, Pb, Ti, Zr, Hf. These materials show extensive polymorphism under pressure and exhibit a variety of complex transformation pathways$^1$. SiO$_2$, has been extensively studied because of its geophysical importance. The other group 14 and 15 oxides have been investigated due to their wide range of technological applications and as analogues for SiO$_2$ as they show similar sequences of phase transitions as silica, but at lower pressures. Theoretical calculations based on density functional theory (DFT) predict the nine-coordinated cotunnite-type structure (space group: Pnam) occurs in SiO$_2$ at ~750 GPa$^2$. The cotunnite-type structure is stable in SnO$_2$, PbO$_2$ and HfO$_2$ at pressures < 75 GPa$^3$–$^5$. In this study, we have studied the possible post-cotunnite phases in SnO$_2$, PbO$_2$ and HfO$_2$ using laser-heated diamond anvil cell experiments and DFT calculations.

Our experiments showed that the cotunnite-type phase was stable up to the peak pressure (~2Mbars) in SnO$_2$ and PbO$_2$, while the Fe$_2$P-type was observed in HfO$_2$ at pressures > 1.2 Mbars. From theoretical calculations, the eleven coordinated Ni$_2$In-type phase is found to be the stable phase in HfO$_2$ at P > ~400 GPa. The 10-coordinated I4/mmm phase reported to be the post-Fe$_2$P-type phase in SiO$_2$ and TiO$_2$ was not found to be stable in any of the studied materials at least up to 600 GPa. The transition sequences predicted in these oxides are consistent among three different exchange-correlation functionals and can be explained by the energetic competition of stationary electronic flat bands and a pressure-induced shift of electronic states to lower energies.

References