

High-pressure behavior of AO₂ (A = Sn, Pb, Hf) compounds beyond 2 Mbars

R. Dutta^{1*}, B. Kiefer², V. B. Prakapenka³ and T. S. Duffy¹

¹Department of Geosciences, Princeton University, NJ 08544, USA.

²Department of Physics, New Mexico State University, Las Cruces, New Mexico 88011, USA

³Center for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637, USA.

Abstract

There is widespread interest in the high-pressure behavior of metal dioxides, AO₂, 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 pathways¹. SiO₂ 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 SiO₂ 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 SiO₂ at ~750 GPa². The cotunnite-type structure is stable in SnO₂, PbO₂ and HfO₂ at pressures < 75 GPa³⁻⁵. In this study, we have studied the possible post-cotunnite phases in SnO₂, PbO₂ and HfO₂ 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 SnO₂ and PbO₂, while the Fe₂P-type was observed in HfO₂ at pressures > 1.2 Mbars. From theoretical calculations, the eleven coordinated Ni₂In-type phase is found to be the stable phase in HfO₂ at P > ~400 GPa. The 10-coordinated *I4/mmm* phase reported to be the post-Fe₂P-type phase in SiO₂ and TiO₂ 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

- 1 J.M. Leger and J. Haines, Eur. J. Solid State Inorg. Chem 37, 785 (1997).
- 2 A.R. Oganov, M.J. Gillan, and G.D. Price, Phys. Rev. B 71, 064104 (2005).
- 3 S.R. Shieh, A. Kubo, T.S. Duffy, V.B. Prakapenka, and G. Shen, Phys. Rev. B 73, 014105 (2006).
- 4 B. Grocholski, S.-H. Shim, E. Cottrell, and V.B. Prakapenka, American Mineralogist 99, 170 (2014).
- 5 Y. Al-Khatatbeh, K.K.M. Lee, and B. Kiefer, Phys. Rev. B 79, 134114 (2009).