New High-Pressure Forms of the Negative Thermal Expansion Materials Cubic $ZrMo_2O_8$ and $HfMo_2O_8$

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Abstract No. Lind1334
Beamline(s): **X17B1**

Introduction: Negative thermal expansion **(**NTE**)** materials are of considerable scientific and technological interest. Their use in composites may facilitate the control of thermal expansion and allow the attainment of zero expansion. The high-pressure behavior of NTE materials is relevant to their application, as the NTE material will experience compression both during processing and use from the surrounding matrix material when used as a filler in a composite. Phase changes that occur under pressure such as that seen in cubic ZrW_2O_8 **(**transformation to an orthorhombic phase at 0.21 GPa**)** are thus undesirable, as the original expansion properties are lost.

Methods and Materials: We have investigated the high-pressure behavior of the NTE materials cubic $ZrMo_2O_8$ and cubic $HfMo_2O_8$ in a high-pressure cell using synchrotron radiation for in situ observation. Experiments were carried out at pressures up to 8.6 GPa and at temperatures up to 600 **º**C with both white and monochromatic radiation. The influence of hydrostatic versus non-hydrostatic pressure was investigated.

Results: Quasi-hydrostatic experiments on cubic AMo_2O_8 **(**A = Zr, Hf**)** have shown that the materials undergo a first order phase transition involving an 11 \% volume decrease between 0.7 and 1.5 GPa. The transition is reversible upon decompression, but shows considerable hysteresis. Under non-hydrostatic conditions, the cubic materials start to amorphize above 0.3 GPa and can be converted to the monoclinic polymorphs when heated under pressure. This is the first time that monoclinic $HfMo_2O_8$ has been observed.

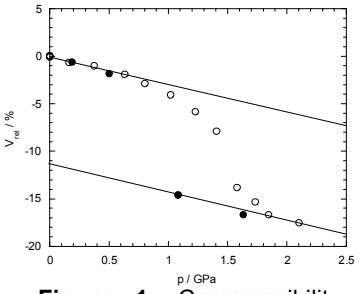

Figure 1. Compressibility of cubic $ZrMo_2O_8$ in a fluorinert pressure transmitting medium. Open symbols represent data collected during compression, filled symbols during decompression.

Conclusions: The complete reversibility and high onset pressure of the phase transition in cubic AMo_2O_8 could offer advantages over ZrW_2O_8. However, the onset of amorphization at pressures as low as 0.3 GPa under non-hydrostatic conditions may place severe limitations on the use of these materials. The different behavior observed under hydrostatic and non-hydrostatic conditions suggests that the stress state of NTE fillers in composite materials needs to be carefully controlled.

Acknowledgments: This work was supported by the NSF under grant EAR 89-20239 to the Center for High Pressure Research, and by the DOE under contract number DE-AC02-98CH10886 to the NSLS.

The work performed at the Georgia Institute of Technology was supported by both the NSF through grant DMR-9623890 and by the ONR through the Molecular Design Institute at the Georgia Institute of Technology, which is supported under ONR contract N00014-95-1-1116. CL is grateful for travel support from the German National Merit Foundation.