New High-Pressure Form of the Negative Thermal Expansion Materials Zirconium Molybdate and Hafnium Molybdate

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Received September 29, 2000. Revised Manuscript Received November 23, 2000

High-pressure X-ray diffraction experiments on cubic $ZrMo_2O_8$ have shown that the material undergoes a first-order phase transition involving an 11% volume decrease between 0.7 and 2.0 GPa under quasi-hydrostatic conditions. The transition is reversible upon decompression, but shows considerable hysteresis. Similar behavior was observed for cubic $HfMo_2O_8$. Under nonhydrostatic 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 $HfMo_2O_8$ was observed.

Introduction

Cubic ZrW_2O_8[1,2] and $ZrMo_2O_8$[3] have received considerable attention since they were shown to exhibit isotropic negative thermal expansion (NTE) over a large temperature range (0.3−1050 and 11−573 K, respectively). It has been proposed that the negative thermal expansion of these materials is due to the presence of low-frequency phonon modes.[1,4−6] Direct evidence for these rigid unit modes has been obtained from heat capacity[7] and phonon density of states measurements[8] and their contribution to the NTE has been demonstrated by David et al.[9,10] The high-pressure behavior of these materials has also been explored experimentally and theoretically.[11−16]

NTE materials are interesting candidates for use as fillers in composites with designed thermal expansion properties. Control of bulk thermal expansion is often needed as mismatches between system components can lead to failure. Additionally, the production of materials with zero thermal expansion is desirable for applications in optics, electronics, and other fields where the exact positioning of parts is crucial. The fabrication and use of controlled thermal expansion composites can result in the filler experiencing high pressures either during the initial processing of the material or due to the expansion of the surrounding matrix during use. As negative thermal expansion is only observed in materials with open framework structures,[17−20] phase transitions under pressure are likely. Cubic ZrW_2O_8 undergoes a transformation to an orthorhombic structure at pressures as low as 0.21 GPa[11] and amorphizes between 1.5 and 3.5 GPa.[12] Both phases can be quenched and are metastable with respect to the cubic structure to which they reconvert upon heating to 393 and 923 K at ambient pressure, respectively. Orthorhombic γ-ZrW_2O_8 shows negative thermal expansion only below room temperature, and its NTE is both anisotropic and an order of magnitude smaller than that of the cubic material.[13,15] Recent work on the preparation of copper−ZrW_2O_8 composites has illustrated the problems associated with the formation of orthorhombic ZrW_2O_8 during processing.[21,22] As pressure-induced phase transformations are likely to degrade the performance of composites, it is desirable to fully characterize the high-

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pressure behavior of NTE materials. A good understanding can only be gained by in situ studies.

Previous neutron diffraction studies using a helium gas cell at pressures of up to 0.6 GPa[3,11] have demonstrated that cubic ZrW_2O_8 and $ZrMo_2O_8$ behave differently upon compression. While cubic ZrW_2O_8 (192 Å³/formula unit) transforms to γ-ZrW_2O_8 (182 Å³/formula unit at ambient pressure, 95% of cubic) at 0.21 GPa, no structural changes were observed for cubic $ZrMo_2O_8$ up to 0.6 GPa. There are two other known ambient pressure polymorphs of $ZrMo_2O_8$, trigonal[23] (174 Å³/formula unit, 92% of cubic) and monoclinic[24] (143 Å³/formula unit, 75% of cubic), which are both denser than the cubic form (190 Å³/formula unit). Furthermore, trigonal $ZrMo_2O_8$ converts to new monoclinic (extrapolation to ambient pressure: 164 Å³/formula unit, 86% of cubic) and triclinic structures (extrapolation to ambient pressure: 141 Å³/formula unit, 74% of cubic) at pressure of 1.06–1.11 and 2.0–2.5 GPa, respectively.[25] Consequently, we anticipated that the cubic phase would undergo at least one transformation at pressures above 0.6 GPa.
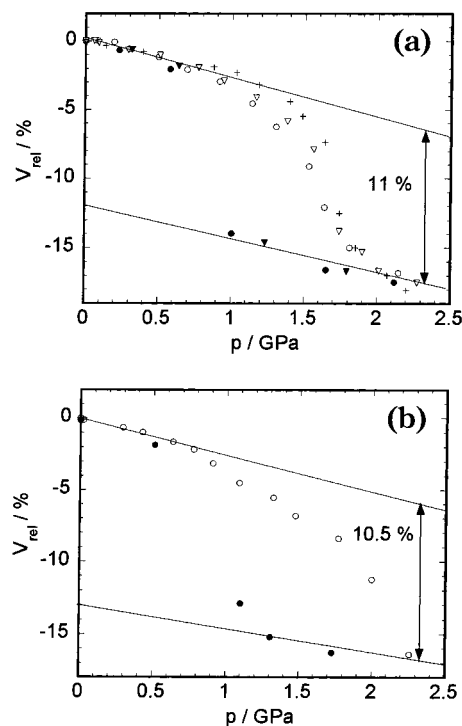
Experimental Section

High-pressure in situ X-ray diffraction experiments on cubic $ZrMo_2O_8$ and $HfMo_2O_8$ were carried out at the National Synchrotron Light Source, Brookhaven National Laboratory, using a multianvil press SAM85.[26] Two types of sample cells were used: (i) a "Teflon cell" in which the sample and fluorinert were contained inside a Teflon capsule imbedded in a boron-epoxy cube and (ii) a standard cell[26] in which the sample is enclosed in a corundum sample chamber that is contained inside a boron-epoxy cube with no pressure-transmitting fluid. The conditions in the standard cells were nonhydrostatic because of direct grain-to-grain contacts, whereas the Teflon cells provided a quasi-hydrostatic environment. This is supported by our observations of X-ray diffraction peak broadening and the recovered samples. The materials from the standard cells were compacted into a solid block, while those from the Teflon cells were loose powders.

Experiments were carried out with both energy-dispersive and monochromatic methods at pressures of up to ≈8.6 GPa. Monochromatic data were collected on imaging plates to obtain higher resolution than what was achievable by energy-dispersive diffraction, so that possible changes in lattice symmetry could be examined. In all cases the pressure was determined using NaCl and the Decker scale.[27] The standard and the sample were packed inside the cell as two successive layers, so that both powders experience the same pressure, while powder patterns of phase pure materials can be collected if the diffracting volume is chosen carefully. *d* spacings for all the strong, resolved peaks were extracted and lattice constants were calculated directly assuming cubic indexing and averaged over all usable peaks. All samples were recovered after the experiments and examined on a laboratory X-ray diffractometer using a silicon single-crystal sample support.

Results

Under quasi-hydrostatic conditions, the measured unit cell volume for cubic $ZrMo_2O_8$ showed a highly

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Figure 1. Relative change in unit cell volume upon compression of (a) three samples of cubic $ZrMo_2O_8$: Symbols represent (+) CLA9, (○) CLA46, and (▽) CLA67 and (b) cubic $HfMo_2O_8$. Open symbols are for values obtained upon compression; filled symbols denote changes during decompression.

nonlinear dependence on pressure (see Figure 1 a). The low-pressure values agreed within experimental error with those obtained from our previous neutron diffraction study.[3] A linear relationship could be fit to the points below 0.7 GPa, giving a relative volume compressibility of -2.3×10^{-2} GPa^{-1}. At higher pressures, an apparent increase in compressibility was observed, which we believe is indicative of the onset of a first-order phase transition. The monochromatic diffraction data showed no conclusive evidence for a change in lattice symmetry in the 0.7–1.5 GPa regime. Above 1.5 GPa, there was an abrupt decrease in the measured lattice constant, presumably associated with a first-order phase transition. The transition involves a volume reduction of ≈10.5–11%. Similar behavior was observed for $HfMo_2O_8$ (see Figure 1 b). The compressibility of the new high-pressure phase (subsequently called "hp", extrapolated V_0: 168 Å³/formula unit, 88.5% of cubic) is comparable to that of the ambient cubic $ZrMo_2O_8$. Both the monochromatic and EDXRD data showed a strong decrease in peak intensity and signs of peak splitting above 1.5 GPa (see Figure 2). Because of the background scattering from the sample cell and the limited range of usable data, the symmetry of the hp phase could not be determined. Lattice constants were extracted by indexing on a pseudo-cubic cell using the strongest peak in each group. The hp phase reconverted to the cubic structure upon decompression below ≈1.0 GPa.

Clearly, it would be desirable to establish the structural details of the hp phase. However, even data collected with monochromatic radiation and a diamond-anvil cell at 3 GPa in fluorinert did not allow an unambiguous determination of the metric symmetry
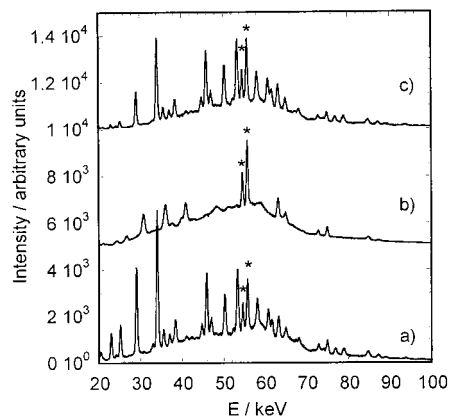
Figure 2. EDXRD patterns of cubic $HfMo_2O_8$: (a) Before compression, (b) at 2.25 GPa, and (c) after decompression. * indicates Hf fluorescence lines.
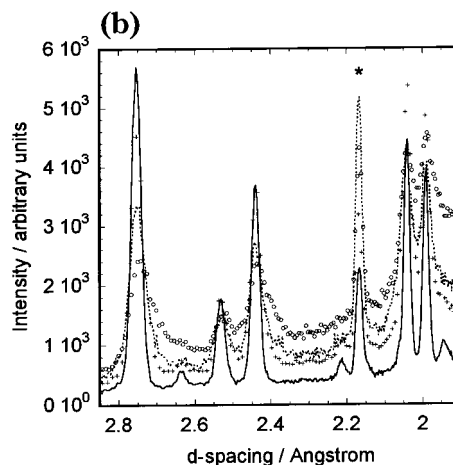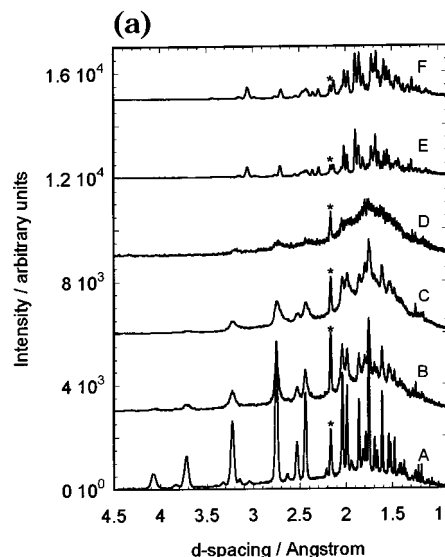
because of strong peak broadening and resulting overlaps.

Upon compression in a standard cell, cubic $ZrMo_2O_8$ started to amorphize at extremely low pressures (as low as 0.3 GPa), as evidenced by a pronounced increase in background scattering (see Figure 3 a). However, our previously collected neutron diffraction data showed no signs of amorphization up to 0.6 GPa, indicating that the stress state of the sample is important. Compression to 8.6 GPa in a standard cell led to complete amorphization. In another experiment, both hafnium and zirconium molybdate were packed into one cell with the NaCl standard separating them and compressed to 1.3 GPa. At this pressure, there were only weak Bragg peaks left. The amorphization onset for the molybdates is considerably lower than the 1.5 GPa reported for ZrW_2O_8.[12] Both values are low in comparison with other materials that undergo pressure-induced amorphization.[28]

Heating of the mostly amorphous molybdates under pressure resulted in the crystallization of monoclinic AMo_2O_8 (A = Zr, Hf) between 400 and 600 °C. While monoclinic $ZrMo_2O_8$ is known to be the thermodynamically stable form under ambient conditions,[29] no literature reports on monoclinic $HfMo_2O_8$ exist. The monoclinic phases could be quenched and were retained upon decompression.

Ex situ XRD patterns collected between 1 and 18 months after the experiments showed that the material amorphized in a standard cell and the monoclinic samples prepared by heating under pressure retained their structures. The patterns for all the samples recovered from Teflon cells were consistent with cubic $ZrMo_2O_8$ and $HfMo_2O_8$ and showed no signs of amorphization or second phases, demonstrating the complete reversibility of the transitions under pressure.

Discussion

Under hydrostatic conditions, cubic $ZrMo_2O_8$ and $HfMo_2O_8$ undergo a first-order phase transition between 0.7 and 2.0 GPa associated with an ≈10.5−11% volume decrease. The large pressure range over which the phase transition occurred could be due to sluggish conversion

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(a)

(b)

Figure 3. Peaks marked with * are not Bragg peaks. (a) EDXRD patterns of $ZrMo_2O_8$ during a standard cell experiment. Spectra at (A) ambient pressure (cubic), (B) 0.31 GPa, (C) 0.69 GPa, (D) 1.31 GPa, (E) 1.25 GPa and 600 °C (monoclinic), and (F) after quenching and decompression. (b) Changes in peak width with increasing pressure under nonhydrostatic conditions. Spectra at ambient pressure (−), 0.13 GPa (++++), 0.31 GPA (···), and 0.69 GPa (○○○).

kinetics. However, neutron diffraction data collected on cubic $ZrMo_2O_8$ after 1 month at 0.6 GPa in a helium gas cell provided no indication for any transformation. Additionally, a 75-min waiting period during the collection of monochromatic XRD data due to beam loss at ≈1.1 GPa did not lead to any discontinuities in the volume−pressure curve. Furthermore, the differences seen in Figure 1a for three $ZrMo_2O_8$ samples with distinct particle size and shape suggest that the broad transition range may be due to variation of stress inhomogeneities with morphology. The hp phase could not be recovered upon decompression. Although considerable hysteresis was observed, the material reconverted to the cubic form below 1.0 GPa. Patterns collected before and after compression were perfectly superimposable (see Figure 2).

The hp phase is of considerably lower density than the densest known polymorphs, ambient monoclinic[24] and Carlson's high-pressure triclinic $ZrMo_2O_8$.[25] Its density is comparable to that of the monoclinic high-pressure phase recently reported by Carlson (168 vs 164

$Å^3$/formula unit), but the XRD patterns are quite different. It should be noted that the hp phase is significantly denser than what would be expected for the orthorhombic structure formed upon compression of cubic ZrW_2O_8. The volume change associated with the phase transition in the molybdates is more than twice as large as that for the tungstate, suggesting a new structure for the hp phase. On the basis of simulations, Pryde et al. have proposed the existence of alternative high-pressure structures for ZrW_2O_8 with densities greater than that of the known orthorhombic form.[16] Remarkably, their calculated transition pressure (1.56 GPa) is close to that observed in our experiments.

The compression of cubic and trigonal $ZrMo_2O_8$ lead to different high-pressure phases, none of which are related to the ambient pressure monoclinic form, suggesting that no facile pathway exists for their interconversion. This is not surprising, as the connectivities of the three ambient pressure frameworks are very different and the coordination numbers of the metals are higher in monoclinic $ZrMo_2O_8$. Compression of the less dense cubic and trigonal polymorphs results in high-pressure phases that are presumably related to the original structures.

Under nonhydrostatic conditions, considerable differences were observed in the behavior of the $ZrMo_2O_8$ and $HfMo_2O_8$ samples, which were packed inside the same standard cell with an intermediate NaCl layer. A close examination of the diffraction data for cubic $ZrMo_2O_8$ compressed in a standard cell (Figure 3b) revealed that the intensity maxima of the cubic peaks stayed approximately in the same place, but tailing or shouldering to lower d spacings occurred with increasing pressure. This suggests that a significant fraction of the sample experienced little or no pressure. The tailing may arise from a distribution of lattice constants due to stress inhomogeneities within the sample. As the applied pressure was increased, the maximum in intensity of the cubic peaks decreased as more material was compressed. Additionally, the background scattering increased dramatically due to partial amorphization. The lattice constant of cubic $HfMo_2O_8$ in this experiment changed in the same way as that in a Teflon cell, although the peaks in the standard cell patterns were considerably broader than those in the Teflon cell patterns. This shows that there were also stress inhomogeneities and an associated distribution of lattice constants. However, the peak broadening was more symmetrical than that observed for $ZrMo_2O_8$ and the measured compressibility was identical to that under quasi-hydrostatic conditions, implying that the major part of the sample experienced all of the applied pressure.

The differences in the behavior of our $ZrMo_2O_8$ and $HfMo_2O_8$ samples in standard cells may be related to disparate sample morphologies. The $ZrMo_2O_8$ used in this experiment consisted of submicron rodlike particles that formed rice-grain-shaped agglomerates of $1-2$-μm diameter and several μm in length; the $HfMo_2O_8$ was composed of submicron isodimensional grains that tended to form dense agglomerates. Consequently, the grain-to-grain contacts and the resulting stress inhomogeneities in the two materials are likely to be different upon compression. As the morphology seems to influence the high-pressure behavior of these NTE materials and the processing and use of composites may involve highly nonhydrostatic conditions, control of particle shape could play a key role in producing high-quality materials.

Conclusions

Cubic $ZrMo_2O_8$ and $HfMo_2O_8$ undergo a fully reversible first-order phase transition involving a $10.5-11\%$ volume decrease between 0.7 and 2.0 GPa under quasi-hydrostatic conditions. The complete reversibility and high onset pressure of the phase transition in AMo_2O_8 could offer considerable advantages over ZrW_2O_8 in the processing and application of composites containing NTE materials. However, the onset of amorphization at pressures as low as 0.3 GPa under nonhydrostatic conditions may place severe limitations on the use of these materials. The different behaviors observed under hydrostatic and nonhydrostatic conditions suggest that the stress state of NTE fillers in composite materials needs to be carefully controlled.