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STRUCTURAL PROPERTIES OF CRYSTALLINE AND AMORPHOUS ZIRCONIUM TUNGSTATE FROM CLASSICAL MOLECULAR DYNAMICS SIMULATIONS

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We use molecular simulations to provide a conceptual understanding of a crystalline-amorphous interface for a candidate negative thermal expansion (NTE) material. Specifically, classical molecular dynamics (MD) simulations were used to investigate the temperature and pressure dependence on structural properties of ZrW_2O_8. Polarizability of oxygen atoms was included to better account for the electronic charge distribution within the lattice. Constant-pressure simulations of cubic crystalline ZrW_2O_8 at ambient pressure reveal a slight NTE behavior, characterized by a small structural rearrangement resulting in oxygen sharing between adjacent WO_4 tetrahedra. Periodic quantum calculations confirm that the MD-optimized structure is lower in energy than the idealized structure obtained from neutron diffraction experiments. Additionally, simulations of pressure-induced amorphization of ZrW_2O_8 at 300 K indicate that an amorphous phase forms at pressures greater than 10 GPa, and this phase persists when the pressure is decreased to 1 bar. Simulations were performed on a hybrid model consisting of amorphous ZrW_2O_8 in direct contact with the cubic crystalline phase. Upon equilibration at 300 K and 1 bar, the crystalline phase remains unchanged beyond a thin layer of disrupted structure at the amorphous interface. Detailed analysis reveals the transition in metal coordination at the interface.

I. INTRODUCTION

Materials that exhibit negative thermal expansion (NTE) offer the possibility of creating a zoned wasteform consisting of a core phase with radionuclide substitution contained within a pure shell phase. Upon heating, the radionuclide-rich core would contract, possibly forming an amorphous phase while still being contained by the shell phase. Further development of a zoned wasteform concept requires details regarding the structural stability of a crystalline-amorphous interface to determine the feasibility of NTE materials in such an application.

II. SIMULATION METHODS

MD simulations in the isothermal-isobaric ensemble were performed using the LAMMPS software[1] with interatomic potential parameters developed by Pryde *et al*.[2] Polarizability effects were included for O atoms, requiring a short timestep of 0.1 fs. Angle bending potentials for O-Zr-O and O-W-O interactions were omitted to allow for structural flexibility when simulating the amorphous phase. Initial atomic coordinates were taken from the published crystal structure.[3]

For simulations of the pure crystalline and amorphous phases, a 3 x 3 x 3 supercell was used with thermostat temperature (T) and barostat pressure (P) ranges of 1 – 500 K and 0 – 20 GPa, respectively. Each simulation was 1.2 ns long, and trajectory data from the final 1.0 ns was used for analysis.

The interface between crystalline and amorphous phases was simulated at 300 K and 1 bar by combining separately equilibrated 6 x 6 x 6 and 7 x 7 x 7 supercells of crystalline and amorphous (15 GPa) structures, respectively (Fig. 1). A stable interface was formed within 0.2 ns of simulation time, but the simulation was continued for an additional 6.0 ns with no significant changes in structural properties or potential energy.

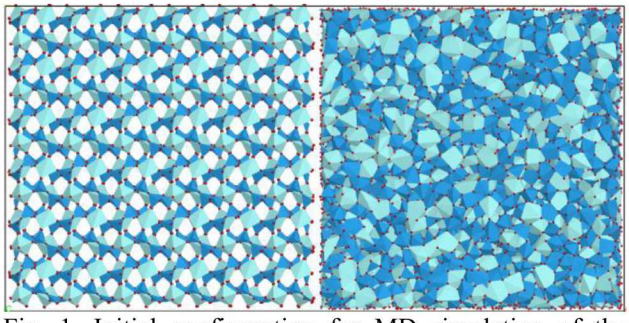

Fig. 1. Initial configuration for MD simulation of the interface between the crystalline (left) and amorphous (right) phases of ZrW_2O_8. Atom colors are Zr (light blue), W (dark blue), and O (red).

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III. RESULTS

III.A. PURE CRYSTALLINE AND AMORPHOUS PHASES

Fig. 2 shows the NTE behavior of the crystalline phase from MD simulations at 1 bar pressure. The average cell parameters are approximately 0.25 Å less than those obtained from diffraction experiments (9.18 Å at 0.3 K to 9.15 Å at 380 K).[3] Geometry optimization at constant pressure results in much better agreement in cell parameter (9.193 Å), but during MD simulation thermal effects induce a slight rearrangement of the WO_4 tetrahedra, causing a reduction in cell parameter. This structural rearrangement occurs with or without the angle bending interactions, with no change in cell parameters.

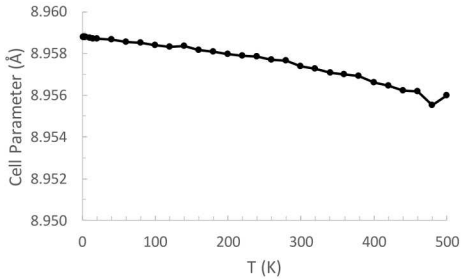

Fig. 2. Variation of ZrW_2O_8 lattice parameter with temperature from MD simulations of at 1 bar pressure.

Pressure-induced amorphization was simulated at 300 K. The amorphous phase formed at a barostat pressure of 5 GPa (Fig. 3). Increasing the barostat pressure from 10 GPa to 20 GPa caused only a slight decrease in cell parameter.

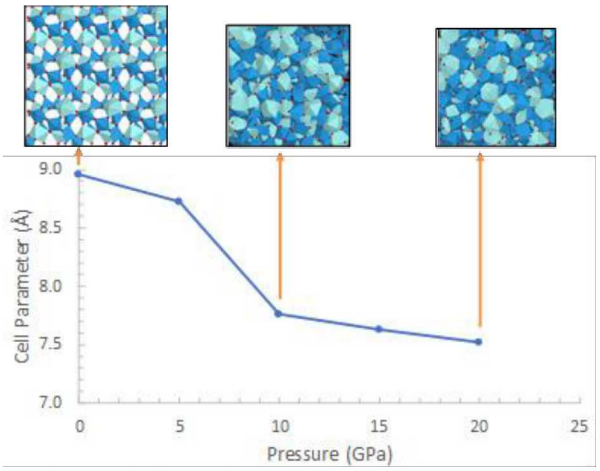

Fig. 3. Variation of ZrW_2O_8 lattice parameter with pressure from MD simulations at 300 K. Final snapshots are shown from simulations at 0 GPa, 10 GPa, and 20 GPa. Atom colors are Zr (light blue), W (dark blue), and O (red).

Subsequent simulations were started from the final configuration at each pressure, at a new barostat pressure of 1 bar. As seen in Fig. 4, the original crystal structure was recovered from the slightly distorted structure at 5 GPa, while a common amorphous phase with cell parameter 7.8 Å resulted at pressures greater than 10 GPa.

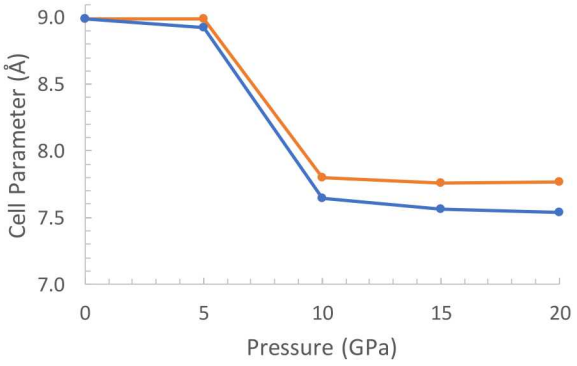

Fig. 4. Variation of ZrW_2O_8 lattice parameter with pressure from constant pressure MD simulations at a thermostat temperature of 300 K. Results are shown for simulations in which the high pressure was maintained (blue), and following relaxation to 1 bar (orange).

III.B. CRYSTALLINE-AMORPHOUS INTERFACE

A 6-ns MD simulation of the crystalline-amorphous interface indicates that the two phases are mutually stable. During the equilibration period there was a slight expansion (0.05 Å) in the supercell parameter perpendicular to the interface. This was likely due to the expansion of the amorphous phase when the effective pressure was reduced from 15 GPa to 1 bar. Similar behavior was seen when the pure amorphous phase was relaxed to 1 bar (Fig. 4).

After equilibrium was achieved, distinct crystalline, amorphous, and interface regions had formed, as seen by comparing the distribution of W-O and Zr-O coordination numbers (Fig. 5). In the crystalline phase, all W and Zr atoms had coordination numbers of 5 and 6, respectively. According to the experimental crystal structure of ZrW_2O_8, each W atom is coordinated by four O atoms between 1.7 – 1.8 Å with a fifth O atom at a distance of 2.4 Å.[3] In our simulated crystalline phase, the fifth O atom is located slightly closer (2.0 Å), resulting in a distorted bipyramidal structure.

In the interfacial region, the distributions of coordination numbers are broadened (5 – 7 and 6 – 10, for W-O and Zr-O, respectively), and the most probable Zr-O coordination number increases to 7.5. For the amorphous phase, the distributions shift to even greater values, as do the most probably coordination numbers for W-O (6.0) and Zr-O (9.0). Increases in metal coordination in the

amorphous phase is consistent with the increased density seen in the pure phase simulations (Fig. 3).

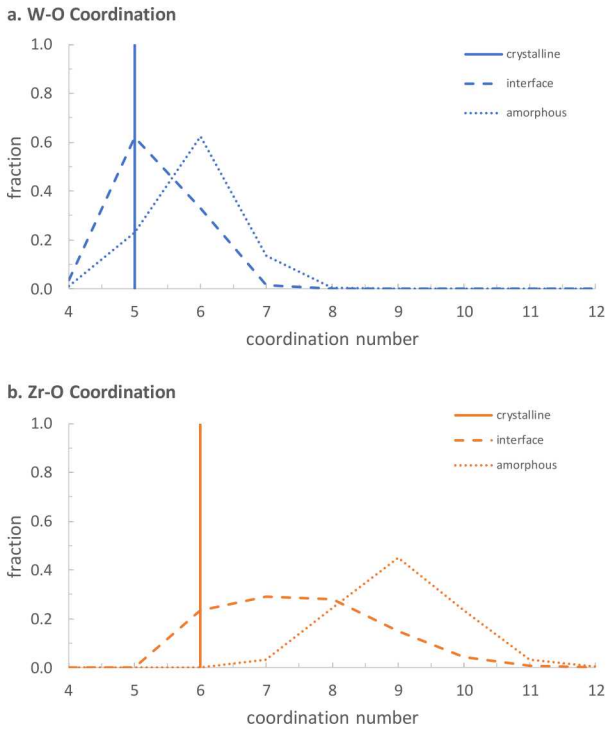

Fig. 5. Distribution of first-shell oxygen coordination numbers for a) W and b) Zr atoms from MD simulation (1 bar, 300 K) of the crystalline-amorphous interface of ZrW_2O_8. Solid, dashed, and dotted lines correspond to the crystalline, interface, and amorphous regions, respectively.

IV. CONCLUSIONS

The pressure and temperature dependence of structural properties of the NTE material ZrW_2O_8 were investigated using MD simulation. At a constant pressure of 1 bar, a slight NTE was seen over the temperature range 0 – 500 K. At a constant temperature of 300 K, pressure-induced amorphization occurred at a pressure of 10 GPa. Structural properties of the crystalline-amorphous interface were simulated at 300 K. The interface was stable throughout the 6-ns simulation, with distinct crystalline, amorphous, and interface regions identified by changes in metal coordination.

These MD simulation results provide atomic-level structural evidence indicating that the interface region in zoned ZrW_2O_8 wasteforms should remain stable upon amorphization of the core phase.

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