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In-situ investigation of $Hf_6Ta_2O_{17}$ anisotropic thermal expansion and topotactic, peritectic transformation

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ABSTRACT

The anisotropic coefficients of thermal expansion and the peritectic transformation of orthorhombic-$Hf_6Ta_2O_{17}$ to tetragonal-HfO_2 plus liquid at 2250 °C have been studied by *in-situ* X-ray powder diffraction from room temperature to complete melting (~2450 °C) in air, using a quadrupole lamp furnace (QLF) and a conical nozzle levitator (CNL) equipped with a CO_2 laser. The topotactic, peritectic transformation has been fully described by extracting the orientation relationship, lattice variant deformation and a motif (grouping) of cations that relates the two structures at the transformation temperature. The calculation of these two important parameters as well as identification of the motif is facilitated by a knowledge of the anisotropic coefficients of thermal expansion as a function of temperature. Symmetry decomposition has been performed to show that the orthorhombic-$Hf_6Ta_2O_{17}$ and tetragonal-HfO_2 structures are simply related by polyhedral rotations and loss of 1 mol of oxygen.

1. Introduction

The energy conscious world has spurred interest in energy generation and efficiency, leading to the desire for new and improved, high temperature materials [1]. Due to the harsh environments (high temperature and stresses) of energy generation, materials systems rather than individual materials are required for optimum operation. Thermal barrier coatings (TBCs) are a major component of these systems as they enable high temperature capabilities. The key material properties required for TBC's include: (i) tailorable thermal expansion coefficients, (ii) low thermal conductivity and (iii) high chemical stability at high temperature [2].

Li *et al.* [3] have measured the linear thermal expansion coefficient of $Hf_6Ta_2O_{17}$ from 25 to 1400 °C using a Netzch DIL402C dilatometer. They were able to determine that the linear thermal expansion coefficient of $9.59 \times 10^{-6}\ {}^\circ C^{-1}$ at 1200 °C was close to that of yttria stabilized zirconia YSZ (ZrO_2-6~8 wt% Y_2O_3). Li *et al.* [4] have measured the thermal conductivity of $Hf_6Ta_2O_{17}$ from 25 to 1600 °C using the laser flash method. They found that the thermal conductivity of ~3.75 W/mK ~at 1000 °C was slightly higher when compared to other TBC materials such as YSZ (~2.5 W/mK). Li *et al.* [5] also measured the chemical stability of $Hf_6Ta_2O_{17}$ in the presence of other TBC materials such as Al_2O_3, YSZ and Sm_2ZrO_7. $Hf_6Ta_2O_{17}$ did not react with Al_2O_3 and YSZ at 1600 °C, but reacted with Sm_2ZrO_7 at 1200 °C. The HfO_2-Ta_2O_5 phase diagram was also measured *in-situ* via X-ray powder diffraction up to 3000 C by McCormack *et al.* [51]. From the literature, it is clear that $Hf_6Ta_2O_{17}$ is a prime candidate for applications as a TBC.

The crystal structure of $Hf_6Ta_2O_{17}$ has only recently been elucidated by McCormack and Kriven [6]. They have shown that $Hf_6Ta_2O_{17}$ has a superstructure, with space group symmetry *Ima*2 (S.G. 46) and room temperature lattice parameters of $a = 8 \times 5.1038 = 40.837$ Å, b = 4.9434 Å, and c = 5.263 Å. The atomic structure is based on a series of asymmetric structural units of cation-centered oxygen units as follows: (i) one set of symmetry-equivalent, six-coordinated polyhedra, (ii) three sets of symmetry-equivalent, seven-coordinated polyhedra and (iii) one set of symmetry-equivalent, eight-coordinated anti-polyhedra [6,7]. Now that the crystal structural information is available for $Hf_6Ta_2O_{17}$, scientists can start to conduct more detailed analyses, based on atomic mechanisms regarding thermal expansion, thermal conductivity and chemical reactivity.

This study aims to extend and improve current knowledge by measuring the anisotropic coefficients of thermal expansions for $Hf_6Ta_2O_{17}$ from room temperature up to its complete melting point

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(~2450 °C). *In-situ*, high temperature, X-ray diffraction, in air was carried out by means of a quadrupole lamp furnace (QLF) [8] and a conical nozzle levitator system equipped with a CO_2 laser [9–16]. Both the QLF [17–21] and CNL [22,23] systems have been used in the past to determine coefficients of thermal expansion. These accurate and complete measurements will be extremely useful for $Hf_6Ta_2O_{17}$ in engineering applications.

This study will take a step further and show how *in-situ* diffraction can be used to determine the orientation relationship and lattice variant deformation for the topotactic, peritectic transformation. From these, a symmetry decomposition will be performed to show that the orthorhombic-$Hf_6Ta_2O_{17}$ and the tetragonal-HfO_2 phases are related to each other via simple polyhedral rotations.

These factors, viz., thermal expansion, orientation relationship and lattice variant strain will atomically fully describe $Hf_6Ta_2O_{17}$ from room temperature, through the topotactic peritectic transformation at ~2250 °C, up to complete melting at ~2450 °C.

2. Experimental procedure

2.1. Powder synthesis and preliminary characterization [24–26]

Hafnium tantalate ($Hf_6Ta_2O_{17}$) was synthesized as a powder by the organic steric entrapment of cations [24–26]. Hafnium (IV) chloride, 99.9 % (metal basis) (Alfa Aesar, Inc., Ward Hill, MA, USA) was dissolved in deionized water. Tantalum (V) chloride, 99.99 % (metal basis) (Alfa Aesar, Inc., Ward Hill, MA, USA) was dissolved in isopropanol. The mass of hafnium (IV) chloride and tantalum (V) chloride was determined based on cationic stoichiometry of $Hf_6Ta_2O_{17}$. The two solutions were mixed and stirred for 1 h. Ethylene glycol (Aldrich Chemical Company, Milwaukee, WI, USA) having a molecular weight of 67.07 amu, was added in the proportion to maintain a cation valence charge to ethylene glycol monomer ratio of 4:1. After the addition of the steric entrapping agent (ethylene glycol), the solution was stirred for 1 h at room temperature, followed by heating at 300 °C, until enough water and isopropanol were evaporated, forming a viscous gel. The gel was subsequently dried overnight at 100 °C to produce a dry, porous mass.

The porous mass was then ground with a zirconia mortar and pestle, calcined and crystallized, at 1050 °C for 3 h in a zirconia crucible, at a heating and cooling rate of 10 °C/min. The powders were then pressed into pellets in a Carver press at a load of ~60 MPa. These pellets were then annealed at 1300 °C in a platinum crucible for 10 h at a heating and cooling rate of 10 °C/min. The annealed powders were then ground and sieved to <45 μm.

Crystalline phase composition of the samples was examined by powder X-ray diffraction (XRD) with a Bruker D5000 diffractometer (Bruker AXS Inc., Madison, WI, USA), using CuK_α radiation ($\lambda = 1.5418$ Å, 40 kV, 30 mA). XRD patterns were acquired over a 2θ range from 10 ° to 65 ° at 1 °/min and step size of 0.02 °. The crystalline phase was identified with reference to the International Centre for Diffraction Data PDF-4+ database (ICDD v. 2015, International Centre for Diffraction Data, Newton Square, PA) accessed through Jade 9.4.1 (Materials Data Inc., Livermore, CA, USA).

Elemental composition was measured by X-ray fluorescence (XRF) spectroscopy in a Shimadzu EDX-7000 (Shimazdu America Inc., Chicago, IL, USA) by collecting characteristic X-rays for elemental hafnium and tantalum.

Bulk density was determined by pycnometry with an AccuPyc II 1340 gas pycnometer (Micromeritics Instrument Corp., Norcross, GA, USA) and compared with the theoretical X-ray density.

2.2. High temperature X-ray diffraction

2.2.1. Quadrupole lamp furnace (QLF) [8,17–21]

The annealed $Hf_6Ta_2O_{17}$ powder was mixed with 10 wt% Pt powder (99.99 %; Sigma-Aldrich, St Louis, MO, USA) in a mortar and pestle. The mixed powder was then sieved using a standard 325-mesh (45 μm), loosely packed into a sapphire capillary (SapphiT OD = 1.00mm, ID = 0.6 mm; Crytur, Turnov, Czech Republic) and mounted in a longer alumina tube (OD = 2 mm, ID = 1.2 mm; Alfa Aesar, Inc., Ward Hill, MA). The sample was heated in air in a quadrupole lamp furnace (QLF) [8] from room temperature to a maximum of 1600 °C, in approximately 50 °C steps with a 3 min soak time. The experiments were conducted at Beamline 33-BM-C at the Argonne National Laboratory Advanced Photon Source (APS) in Lemont, IL, USA. The X-ray powder diffraction (XRPD) patterns were collected at each temperature with the Pilatus 70 K detector. The sample to detector distance and wavelength were determined by means of a LaB_6 standard (SRM 660a; National Institute of Standards and Technology, Gaithersburg, MD) and were found to be 1040 mm and 0.589957 Å, respectively.

The resulting XRPD patterns were refined via the Rietveld method using the General Structure Analysis System Two (GSAS-II) program [27]. The background, lattice constants, scale factors, atomic positions and profile functions were refined for each temperature. The well-characterized thermal expansion of platinum [8] was used to accurately calculate the temperature of the powder diffraction patterns to an accuracy of ±4 °C [8,28]. This error had two sources: (i) the variance in thermal expansion of the standard and (ii) the d-spacing resolution of the X-ray set-up.

2.2.2. Conical nozzle levitator (CNL) equipped with a CO_2 laser [9–16,22,23]

The $Hf_6Ta_2O_{17}$ was processed into polycrystalline sintered spheroids, 2–3mm in diameter, by means of a vibrating table method [29]. Ceramic slurries were prepared from 87 vol% $Hf_6Ta_2O_{17}$ powder having a 200 μm particle size, 5 vol% methyl cellulose binder (Sigma-Aldrich, St Louis, MO, USA), 1 vol% Darvin® dispersant (Vanderbilt Company, Inc., Norwalk, CT, USA) and 7 vol% water. This slurry was vibrated at a frequency of 70 Hz in a cube-walled container having 30 mm dimensions for approximately 5 min, or until the beads had sufficient green strength. This method is described in more detail by Santos *et al.* [29]. The resulting highly spherical beads were heat treated at 1300 °C for 6 h at a heating rate of 2 °C/min and cooling rate of 8 °C/min.

In-situ, high-temperature, synchrotron XRPD experiments were performed on the $Hf_6Ta_2O_{17}$ beads at the Advanced Photon Source (APS), Argonne National Laboratory (ANL), Lemont, IL, USA, at Beamline 6-ID-D. Hafnium tantalum sintered oxide beads were levitated in an argon stream mixed with 21% oxygen (to imitate air) in a conical nozzle levitator (CNL) system [10–16,22,23]. The levitated sample was heated using the beam from a 400 W sealed tube CO_2 laser (10.6 μm, Synrad FSi401SB, Mukilteo, WA, USA) that was partially focused on to the top surface of the sample. This arrangement enabled the sample to be heated to a temperature of approximately 3000 °C, which was above the melting point of the sample. The sample temperature was controlled by adjusting the laser beam power. A CHINO pyrometer (900 nm, 10 m s response time, 700–3500 °C, IR-CAS8CS; Chibo, Tokyo, Japan) monitored the temperature of the bead surface incident with the laser and X-ray beam. The measured radiometric temperature was corrected using a spectral emissivity of 0.92 at the pyrometer wavelength. The CNL system setup has been described by Weber *et al.* [9]. The XRPD patterns were collected at ~100 °C temperature intervals. The sample was held at the desired temperature for approximately 3 min before a measurement was taken. The XRPD patterns were