

## Effect of annealing on the elastic moduli of amorphous zirconium tungstate

R.F.L. Lorenzi, J.E. Zorzi, C.A. Perottoni\*

Universidade de Caxias do Sul, Instituto de Materiais Cerâmicos, 95765-000 Bom Princípio, RS, Brazil



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### ABSTRACT

Amorphous zirconium tungstate ( $a\text{-ZrW}_2\text{O}_8$ ), prepared at 7.7 GPa, was subjected to successive heat treatments at increasingly higher temperatures, up to 640 °C. Evidence of recrystallization into  $\alpha\text{-ZrW}_2\text{O}_8$  was found in the room temperature X-ray powder diffraction pattern of samples previously heated above 600 °C. Changes in elastic moduli and linear thermal expansion coefficient upon annealing of  $a\text{-ZrW}_2\text{O}_8$  up to 600 °C cannot be accounted for by assuming a composite sample consisting of  $\alpha\text{-ZrW}_2\text{O}_8$  domains dispersed into an amorphous zirconium tungstate matrix. The irreversible relaxation of  $a\text{-ZrW}_2\text{O}_8$  and recrystallization into  $\alpha\text{-ZrW}_2\text{O}_8$  is accompanied by an increase of bulk modulus (from 61.8(8) GPa to 74.4(9) GPa) and Poisson's ratio (from 0.267(3) to 0.302(3)) and diminution of density (from 6.54(1) g/cm<sup>3</sup> for  $a\text{-ZrW}_2\text{O}_8$  to 5.18(1) g/cm<sup>3</sup> for  $\alpha\text{-ZrW}_2\text{O}_8$ ). Despite the greater density,  $a\text{-ZrW}_2\text{O}_8$  (as well as  $\gamma\text{-ZrW}_2\text{O}_8$ , a high pressure polymorph) is more compressible than  $\alpha\text{-ZrW}_2\text{O}_8$ , possibly owing to the new degrees of freedom provided by lowering symmetry, which allow external stresses to be accommodated by polyhedral tilting. Furthermore, the observed increase of Poisson's ratio upon thermal treatments at increasingly higher temperatures indicates that annealing of  $a\text{-ZrW}_2\text{O}_8$  is accompanied by the irreversible reduction in the average number of bridging oxygen atoms.

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### 1. Introduction

Zirconium tungstate ( $\text{ZrW}_2\text{O}_8$ ) is a ceramic material discovered by Graham et al. in 1959 in an attempt to stabilize the crystal structure of zirconia by the addition of tungsten trioxide [1]. Thermodynamically stable from 1380 K to 1530 K, the cubic phase of zirconium tungstate ( $\alpha\text{-ZrW}_2\text{O}_8$ ) can be retained metastably by rapid cooling. Once formed, a kinetic barrier precludes the decomposition of zirconium tungstate below 1050 K [2]. This compound is well known due to its unusual physical properties, particularly negative thermal expansion (NTE). First reported by Martinek and Hummel, NTE in  $\alpha\text{-ZrW}_2\text{O}_8$  is observed from 0.3 K to 1443 K [2,3].

The  $\alpha\text{-ZrW}_2\text{O}_8$  crystal structure can be described as a tridimensional arrangement of corner-sharing  $\text{ZrO}_6$  octahedra and  $\text{WO}_4$  tetrahedra [2]. In the latter, only three of the four oxygen atoms are shared with Zr. The fourth oxygen, bonded only to W, is referred to as terminal oxygen. Upon increasing pressure, at room temperature,  $\alpha\text{-ZrW}_2\text{O}_8$  first converts to an orthorhombic phase ( $\gamma\text{-ZrW}_2\text{O}_8$ , space group  $\text{P}2_12_12_1$ ) above 0.2 GPa, and then undergoes pressure induced amorphization (PIA) above about 1.5 GPa [4,5]. Both  $\gamma\text{-ZrW}_2\text{O}_8$  and amorphous zirconium tungstate ( $a\text{-ZrW}_2\text{O}_8$ ) are characterized by an increase of W coordination, owing to new W–O bonds formed between the terminal

oxygens and neighbor W [4,6]. Owing to these new W–O bonds,  $a\text{-ZrW}_2\text{O}_8$  can be retained back to ambient pressure [5].

Amorphous zirconium tungstate recrystallizes above 600 °C at ambient pressure, first into the high temperature polymorph ( $\beta\text{-ZrW}_2\text{O}_8$ ) and, upon cooling, to  $\alpha\text{-ZrW}_2\text{O}_8$  [5,7]. Prior to recrystallization,  $a\text{-ZrW}_2\text{O}_8$  undergoes exothermic relaxation, which manifest itself by irreversible changes in the X-ray diffraction pattern, thermal expansion coefficient, Raman spectrum, sample dimensions and color [8,9]. These changes can be understood as resulting from an irreversible rearrangement of the W–O units formed by bonding of terminal oxygens during pressure-induced amorphization [4,6]. Evidences that the annealing of  $a\text{-ZrW}_2\text{O}_8$  is accompanied by the reduction of the average W–O bond length (probably resulting from the reduction of W coordination number) include the shift toward higher frequencies of Raman peaks assigned to internal modes of tungsten first coordination polyhedra [9]. The recrystallization of  $a\text{-ZrW}_2\text{O}_8$  is endothermic, i.e., the last step of the transition amorphous  $\rightarrow$  crystalline, above 600 °C, is accompanied by the absorption of heat and entropy increase [10,7]. However, taking into account the heat released during the structural relaxation that precedes recrystallization, the overall room temperature enthalpy of transition from  $a\text{-ZrW}_2\text{O}_8$  to  $\alpha\text{-ZrW}_2\text{O}_8$  is negative [7,11].

In order to further explore the evolution of  $\alpha\text{-ZrW}_2\text{O}_8$  upon annealing, in this work the effect of thermal treatments at increasing temperatures on the room temperature elastic constants of  $a\text{-ZrW}_2\text{O}_8$  was explored by means of resonant ultrasound spectroscopy (RUS) [12–15]. This experimental technique allows the simultaneous determination of

\* Corresponding author.

E-mail address: [caperott@ucs.br](mailto:caperott@ucs.br) (C.A. Perottoni).

the symmetry-independent elastic constants ( $c_{11}$  and  $c_{12}$ , for isotropic materials) by measuring the sample's resonant frequencies, mass and physical dimensions. Resonant ultrasound spectroscopy is particularly well suited for the analysis of small samples prepared under high pressures, such as the samples of zirconium tungstate prepared for this work.

## 2. Material and methods

The sample of  $\alpha$ -ZrW<sub>2</sub>O<sub>8</sub> used in this work was prepared by pressing pellets of  $\alpha$ -ZrW<sub>2</sub>O<sub>8</sub> (Wah Chang Co., Albany, OR) to 7.7 GPa at room temperature, for 2 h, in a toroidal high-pressure chamber. Pressure calibration was checked using bismuth phase transition at 7.7 GPa. The amorphous state of the sample was checked by X-ray diffraction (XRD) at ambient conditions, using a Si single crystal sample holder, nearly background-free, in a Shimadzu XRD 6000 diffractometer operating in Bragg–Brentano geometry, with Cu K $\alpha$  radiation, equipped with Soller slits, a 1° divergence slit and a 1° scattering slit in the primary beam, and a 0.30 mm receiving slit and a graphite monochromator in the secondary beam. The scan was performed at 0.05° per step, from 15° to 100° 2 $\theta$ , and an acquisition time of 4 s per step.

Resonant ultrasound spectroscopy was carried out with an equipment consisting of a signal generator (DS345, Stanford Research, USA) and a lock-in amplifier (SR844, Stanford Research, USA), both computer-controlled [12,15]. RUS spectra were obtained from samples in the form of parallelepiped, with edges around 2 mm long, carefully polished to ensure parallelism of the opposite faces. Sample dimensions and mass were measured within  $\pm 5 \mu\text{m}$  and  $\pm 10 \mu\text{g}$ , respectively. After each successive thermal treatment, sample density at room temperature was calculated from mass and sample's dimensions.

For the RUS measurements, the sample of zirconium tungstate was supported by its opposite vertices by making a weak contact between two piezoelectric transducers. One of the piezoelectric transducers is connected to the signal generator. At every resonance of the sample, the second piezoelectric transducer generates a peak voltage, which is detected by the lock in amplifier. RUS spectra were taken in the frequency range from 0.4 to 1.2 MHz, yielding around a dozen resonant frequencies. From the set of resonant frequencies, the independent elastic constants  $c_{11}$  and  $c_{12}$  were estimated using a computer code developed for samples in the form of a parallelepiped (available at <http://www.magnet.fsu.edu/inhousersearch/rus/>).

Two different samples of amorphous zirconium tungstate were subjected to room temperature RUS analysis and annealed at increasingly higher temperatures, successively. Each sample was separately heated at 2 °C/min up to a maximum annealing temperature (ranging from 50 °C to 640 °C), kept at the maximum temperature for 5 min and then brought back to room temperature, when density measurement and RUS analysis were performed and a new cycle was initiated, increasing the maximum annealing temperature. Heat treatments up to 450 °C were performed on a Q2000 differential scanning calorimeter (TA Instruments, USA) and, from 450 °C to 640 °C, on a simultaneous thermal analyzer STA 449F3 (Netzsch, Germany). All thermal treatments were conducted under a flow of 50 ml/min of ultra-pure nitrogen (99.999%).

Density functional (DFT) calculations were performed to estimate the binding energy density for  $\alpha$ - and  $\gamma$ -ZrW<sub>2</sub>O<sub>8</sub>. Calculations were performed using Crystal06 [16]. The optimized crystal structures for  $\alpha$ - and  $\gamma$ -ZrW<sub>2</sub>O<sub>8</sub>, atom-centered gaussian basis sets, and further calculation details are given elsewhere [6,17]. Binding energy densities were estimated according to

$$\rho_{BE} = \frac{E - ZE_{ZrW_2O_8}}{V} \quad (1)$$

where  $E$  is the total DFT energy,  $V$  is the volume,  $Z$  is the number of ZrW<sub>2</sub>O<sub>8</sub> units – all these quantities are referred to the primitive unit cell – and  $E_{ZrW_2O_8}$  is the sum of the DFT energies of the isolated atoms.

## 3. Results and discussion

The analysis of the X-ray powder diffraction pattern shown in Fig. 1 indicates the complete amorphization of the sample processed at 7.7 GPa, in agreement with previous results [18]. Sample remains X-ray amorphous even after heated to 600 °C, at ambient pressure. However, evidences of the presence of  $\alpha$ -ZrW<sub>2</sub>O<sub>8</sub> are seen in the X-ray diffraction pattern taken from the sample previously heated to 610 °C, thus giving a clear indication that  $\alpha$ -ZrW<sub>2</sub>O<sub>8</sub> domains large enough to yield well defined Bragg peaks are formed only above 600 °C. The sample is essentially fully converted into  $\alpha$ -ZrW<sub>2</sub>O<sub>8</sub> upon annealing at 640 °C.

Fig. 2 shows the room temperature elastic moduli  $c_{11}$  and  $c_{12}$ , and density, for samples of amorphous zirconium tungstate previously heated to increasingly higher annealing temperatures. The equivalent bulk ( $B$ ) and shear ( $G$ ) moduli, as well as Poisson's ratio ( $\nu$ ) are compared to some results from literature in Table 1. For a homogeneous and isotropic sample,  $B = (c_{11} + 2c_{12})/3$ ,  $G = (c_{11} - c_{12})/2$ , and  $\nu = c_{12}/(c_{11} + c_{12})$  [19].

Both  $c_{11}$  and  $c_{12}$ , measured at room temperature, increase almost linearly upon increasing the maximum temperature of the previous annealing, up to 300 °C. Further increase of the annealing temperature from 300 °C to 600 °C is accompanied by only a modest increase of  $c_{11}$  and  $c_{12}$ . The onset of recrystallization (between 600 °C and 610 °C) has only a minor effect on both  $c_{11}$  and  $c_{12}$ . On the other hand, the onset of recrystallization has a marked effect on sample's density, as discussed below. More pronounced changes in both  $c_{11}$  and  $c_{12}$  are observed as recrystallization proceeds, for samples heated above 610 °C. The elastic constants at room temperature for the sample annealed at 640 °C are within  $\pm 10\%$  of previous results for monocrystalline  $\alpha$ -ZrW<sub>2</sub>O<sub>8</sub> at 300 K [20].

Fig. 2(c) shows the room temperature density of  $\alpha$ -ZrW<sub>2</sub>O<sub>8</sub> after annealing at different temperatures. After a steady reduction upon increasing annealing temperature, the onset of recrystallization into  $\alpha$ -ZrW<sub>2</sub>O<sub>8</sub> is accompanied by a sudden decrease of density (about 12%) for samples previously heated between 600 °C and 610 °C. The measured density for the sample recovered from annealing at 640 °C, 5.18(1) g/cm<sup>3</sup>, is within 2% of  $\alpha$ -ZrW<sub>2</sub>O<sub>8</sub> theoretical (crystallographic) density.

One may argue that the observed dependency of zirconium tungstate elastic moduli on the maximum annealing temperature could result from the nucleation and growth of small  $\alpha$ -ZrW<sub>2</sub>O<sub>8</sub> domains in the amorphous ZrW<sub>2</sub>O<sub>8</sub> matrix. For such an isotropic two-phase composite, the linear coefficient of thermal expansion,  $\alpha$ , is given by [21]

$$\alpha = \alpha_2 + \frac{\alpha_1 - \alpha_2}{1/B_1 - 1/B_2} \left[ \frac{1}{B} - \frac{1}{B_2} \right] \quad (2)$$

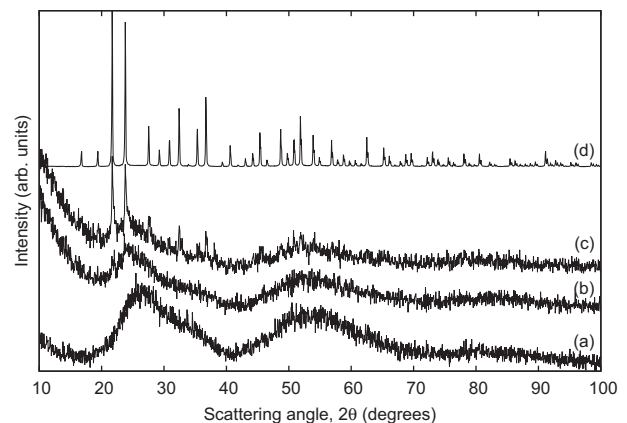


Fig. 1. Room temperature X-ray powder diffraction patterns of amorphous zirconium tungstate (a) as prepared and after heated to (b) 600 °C, (c) 610 °C, and (d) 640 °C.

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