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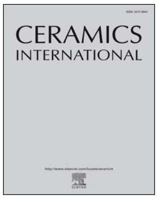

Sintering behaviour, microstructural characterisation and thermal expansion properties of Sn substituted $ZrMo_2O_8$

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ABSTRACT

The coefficient of thermal expansion (CTE) of $ZrMo_2O_8$ can be fine-tuned by controlling the amount of tin substitution in zirconium lattice sites. The sintering challenges associated with this material and the optimal sintering conditions were investigated in this study. Powders of tin substituted $ZrMo_2O_8$ were synthesised by co-precipitation technique. X-ray diffraction studies confirmed the formation of cubic $SnMo_2O_8$. Sintered pellets were produced from the powders and optimal sintering without decomposition of the phase was achieved at the expense of porosity. The material was found to be thermally stable up to 600 °C using thermogravimetric analysis. Dilatometric analysis of the sintered compacts shows that the CTE of the sample is in the order of 3.9×10^{-6}/K, between 25 °C and 600 °C.

1. Introduction

Materials that exhibit negative thermal expansion (NTE) employ supramolecular structural mechanisms such as displacive phase transitions from a distorted to a structurally stable phase, magnetostrictive transitions, librations and rigid unit modes (RUM) [1]. These mechanisms supersede the thermal expansion that occurs due to lengthening of interatomic bond lengths when heated. Materials belonging to zirconium tungstate (ZrW_2O_8) family, zirconium vanadate family (ZrV_2O_7), scandium tungstate family ($Sc_2(WO_4)_3$) and aluminium phosphates ($AlPO_4$) exhibit NTE based on RUM mechanism [2–4]. ZrW_2O_8 family has AM_2O_8 type cubic structure (where A = Zr, Hf and M = W, Mo) consisting of AO_6 octahedra and MO_4 tetrahedra connected by corner-sharing oxygen atoms [5]. The transverse vibrations of the corner-sharing atoms can lead to tilting of the polyhedra causing the exhibition of NTE by RUMs [6]. ZrW_2O_8 has been well studied in the past owing to the exhibition of negative thermal expansion behaviour over a wide range of temperature from 0.3 to 1050 K [7–10]. However, the phase transition that accompanies ZrW_2O_8 on application of pressures above 0.2 GPa impedes its use in composites and promoted the study of similar systems such as HfW_2O_8 and $ZrMo_2O_8$ [11,12].

The first reproducible production of cubic $ZrMo_2O_8$ was described by Cora Lind *et al.*, in 1998 by the dehydration of $ZrMo_2O_7(OH)_2{\cdot}2H_2O$ [13]. Among AM_2O_8 materials, tin molybdate ($SnMo_2O_8$) is unique because of its exhibition of positive thermal expansion (PTE). This anomalous behaviour was attributed to the relatively smaller cell volume and increased stiffness of the SnO_6 octahedra. The ordering of MoO_4 tetrahedra also significantly affects the thermal expansion properties of $SnMo_2O_8$ [14]. In 1988, Buiten described a way to produce stable cubic $SnMo_2O_8$ for the first time by leading $SnCl_4$ in oxygen atmosphere over a fluidised bed of MoO_3 [15]. Previous studies have shown that controlling the coefficient of thermal expansion (CTE) of ZrW_2O_8 and $ZrMo_2O_8$ by doping are not very effective [16–19]. Tallentire et al., reported a wide range of solubility of Sn in $ZrMo_2O_8$ at the A site using co-precipitation route, thus successfully controlling the CTE by chemical substitution. The CTE in each case was found by means of change in lattice parameter using powder X-ray diffraction (XRD). It was shown that the CTE could be controlled by zirconium substitution and at compositions close to equimolar ratios of Sn and Zr, the CTE was very close to zero [14].

The present work continues on the idea that isotropically expanding material with very low CTE can be achieved in a single phase by substituting A site in negatively expanding $ZrMo_2O_8$ with positively expanding species such as Sn in equimolar ratios with emphasis on the sintering aspects of this material. The usage of this material in near-net shaped component form requires bulk manufacturing and that requires a comprehensive understanding of sintering mechanisms followed by microstructural evolution which have not been addressed in the literature. The current work seeks to understand the challenges in the sintering of this material in bulk form and deduce optimal sintering conditions. A composition containing equal molar ratios of Sn and Zr was chosen and was used to prepare sintered compacts. Detailed

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microstructural characterisation was carried out and the sintering behaviour was analysed. The CTE of the sintered samples were determined by dilatometry to understand the influence of any additional phases and thus achieve a more realistic estimate.

2. Materials and methods

2.1. Synthesis of $Sn_xZr_{1-x}Mo_2O_8$ powders

Sn substituted $ZrMo_2O_8$ were prepared using wet chemical route employing coprecipitation process [14]. 5.261 g of $SnCl_4{\cdot}5H_2O$ and 4.830 g of $ZrOCl_2{\cdot}8H_2O$ (Sigma-Aldrich Chemicals, India) were dissolved in a beaker containing water. 10.687 g of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Johnson Matthey Chemicals, India) was dissolved separately in another beaker of water to form a clear solution. The two solutions were then mixed dropwise by adding through dropping funnel and stirred using a magnetic stirrer continuously for 12 h. The resulting solution was dried in an oven at 50 °C in ambient atmosphere for 12 h to evaporate the water content. The dried powders were pulverised in mortar and pestle and were heat-treated in a furnace at 400 °C, 500 °C, 590 °C and 700 °C and held for 30 min at each of these temperatures in ambient atmosphere. The expected stoichiometry of the heat-treated powder was $Sn_{0.5}Zr_{0.5}Mo_2O_8$.

2.2. Sintering

The heat-treated powders of the samples were compacted using a hydraulic press at a pressure of 350 MPa, using polyvinyl alcohol (PVA) as a binder, to form pellets. The pellets were then sintered at three different temperatures viz., 400 °C, 500 °C and 600 °C for three different soaking periods viz. 4, 8 and 12 h each in ambient atmosphere at a heating rate of 2 °C/minute.

2.3. Physical and spectrochemical characterisation

2.3.1. Density measurements

The densities of the pellets were measured using water displacement method employing Archimedes principle. The dry weight of the sample was measured using a digital balance. After taking the dry weight, the sample was submerged in water for two hours at 50 °C. The submerged weight of the sample was then taken while being suspended in water using a steel wire setup. Care was taken to ensure no bubbles were present on the sample or on the walls of the beaker. The sample was then taken out of the beaker and wiped clean using a tissue to remove the water adhering to the surface. The weight of the soaked sample was then taken. These weights were used to calculate the bulk density of the pellets.

2.3.2. Induction coupled plasma optical emission spectrometry (ICP-OES)

ICP-OES (Thermo Fischer iCAP6500 DUO view) was carried out for the powder samples heat-treated at 590 °C to obtain the chemical composition data. The experiment was restricted only to the 590 °C heat-treated powders as it displayed higher amount of the desired cubic phase (discussed later in results). A small amount of the sample was weighed to find the mass and was then dissolved in this digestion mixture. This solution was converted to an aerosol and was sprayed into argon plasma. The elements present in the solution was atomised or ionised at very high temperature of about 6500 K. This temperature results in the electronic excitation of atoms and ions leading to the emission of light. Echelle optics was used to split the spectrum of the emission lines. The intensity of the emitted radiation from the excited ions and atoms were used to determine the concentrations of the elements.

2.4. Structural characterisation

2.4.1. X-ray diffraction

The X-ray diffraction (XRD) of heat-treated powders and the sintered samples were carried out using Bruker Discover D8 diffractometer (USA). A collimated beam of Cu K_α radiation with a wavelength of 0.154 nm was used to irradiate the sample. The data was collected over a range of 10° to 60° (2θ) with a step size of 0.15° and scan rate of 2 s/step. The accelerating voltage used was 30 kV and the current was set at 25 mA. The sintered samples were well polished to achieve a flat surface prior so that any effects of surface irregularities can be prevented. Phase analysis was carried out with the diffraction data using X′pert high score plus software and International Center for Diffraction Data (ICDD) database. The diffractograms were subjected to background correction and removal of $K_{\alpha 2}$ peaks before analysis.

2.4.2. Scanning electron microscopy (SEM)

Microstructural analysis was carried out using Hitachi S4800 scanning electron microscope (Japan). The pellets were well polished prior to SEM, using SiC abrasive papers of fine grit sizes from 1500 to 5000. Gold sputter coating of approximately 5 nm thickness was carried out on the samples before imaging to prevent charging effects. All the images were taken in high vacuum at a voltage of 5 kV in secondary electron (SE) mode. Energy dispersive X-ray spectroscopic (EDS) data was also collected using Si(Li) – Liquid N_2 cooling type X-ray detector (Horiba, Japan) for sintered samples. The EDS data was collected for qualitative chemical analysis over an area to find out the elements present. Point EDS was also carried at to identify the secondary phases formed.

2.5. Thermal characterisation

2.5.1. Thermogravimetry

Thermogravimetry (TGA) and differential scanning calorimetry (DSC) was done using Netzsch STA 409 (Germany). The sintered samples showing the best results based on microstructure and density were alone investigated using TGA and DSC to observe their thermal stability. The tests were carried out in an inert atmosphere of argon with a flow rate of 50 ml/min. Approximately 5 mg of the sample was taken in a small cylindrical alumina crucible and was placed on the platinum holder. The temperature range that was chosen for investigation was 25 °C to 700 °C, and the heating was carried out at a rate of 5 °C/min.

2.5.2. Dilatometry

Dilatometry was executed using a vertical push-rod type dilatometer, SETSYS Evolution TMA (France). Thermal expansion studies of the sintered samples were carried out using fused alumina as the pushrod. Spacers made of 99% pure alumina were placed between the sample and the pushrod to prevent any undesirable interaction. Baselines were run before testing the sample to account for equipment contribution during measurements. These baseline values were subtracted from the measurement values of the sample. The dimensional changes of the samples were measured over the range 30 °C to 600 °C at a constant heating rate of 5 °C/min. The experiment was carried out in an inert atmosphere of argon. The samples were made into small bars of dimensions 4 × 4 × 8 mm. The tests were performed only for the samples showing the best results based on microstructure and density. $SnMo_2O_8$ samples without any Zr addition were prepared through the same route and were also subjected to dilatometry for the purpose of comparison.

3. Results

3.1. Density measurements

The density of the pellets sintered in various conditions was