Ultra-low thermal expansion behavior of spark plasma sintered Sn-doped ZrMo$_2$O$_8$

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1 | INTRODUCTION

Certain materials exhibit negative thermal expansion (NTE) by structural mechanisms that override the effect of bond lengthening in response to thermal stimuli. This behavior could occur because of several reasons such as displacive phase transitions of a distorted phase, librations, transverse vibrations, and coupled polyhedral rotation (otherwise known as rigid unit modes or quasi-rigid unit modes).$^{1-3}$ γ-ZrMo$_2$O$_8$ belongs to class of NTE materials called AM$_2$O$_8$ (A = Zr, Hf and M = W, Mo) which exhibits isotropic and reversible NTE by virtue of its unique structure.$^4$ The characteristic structure of AM$_2$O$_8$ materials is cubic and is analogous to NaCl structure wherein the AO$_6$ octahedra occupy the Na positions and MO$_4$ tetrahedra occupy the Cl positions. The polyhedra in AM$_2$O$_8$ materials can undergo coupled rotation to accommodate the vibrations associated with thermal energy and thus show macroscopic contraction.$^{3,5,6}$ Lind et al.$^4$ were the first to demonstrate a reproducible process to synthesize cubic ZrMo$_2$O$_8$ from ZrMo$_2$O$_7$(OH)$_2$.2H$_2$O by controlled heat treatment. The preparation of SnMo$_2$O$_8$ with cubic crystal structure was accomplished by reacting SnCl$_4$ in oxygen atmosphere with MoO$_3$ and was illustrated by Buiten in 1988.$^7$ However, its structure was explained much later in 2017 wherein it was found that SnMo$_2$O$_8$ exhibits two cubic polymorphs. The room temperature phase (α) is related to β-ZrW$_2$O$_8$, and the high-temperature form (β) was related to γ-ZrMo$_2$O$_8$.$^8$ Among AM$_2$O$_8$ phases, SnMo$_2$O$_8$ alone shows positive thermal expansion (PTE) at all temperatures till decomposition. Tallentire et al.$^9$ demonstrated that Sn can be doped in Zr lattice positions through wet chemical routes. The coefficient of thermal expansion (CTE) of the powder...
particles thus produced was found using X-ray diffraction, and it was found that the NTE behavior exhibited by γ-Zr-Mo₂O₈ can be tuned by adjusting the Sn concentration.

These materials which offer precise control over dimensional stability have potential uses as microelectronic substrates and thermomechanical actuators. However in order for this material to have usefulness in such engineering applications, it is essential to understand its sintering behavior. In another study by the same authors, it was found that conventional pressureless sintering of Sn-doped ZrMo₂O₈ is always accompanied by decomposition reactions. To minimize the formation of secondary phases such as trigonal α-ZrMo₂O₈ and MoO₃, it is required to have close control of the sintering conditions as explained by the same authors in another paper. CTE of the sintered samples calculated using dilatometric results was found to be higher than the values predicted using lattice parameter variations using X-ray diffraction results of powder samples. The increased values were attributed to the CTE contribution of the secondary phases of MoO₃ and trigonal ZrMo₂O₈ present in the sintered samples after heat treatment.

Spark plasma sintering (SPS) or field-assisted sintering technique (FAST) facilitates densification of powders by subjecting to them large electrical fields for a very short time period. The extreme high rates of heating observed during SPS in a vacuum environment enable green compacts to be sintered to their near-theoretical densities without allowing the formation of secondary phases and retards the decomposition reactions. Previous research on SPS of ZrW₂O₈ composites demonstrates the success of the method in achieving near-theoretical densities. Wei et al discussed how W can be partially substituted with Mo to overcome sinterability issues that arise due to the low-temperature phase transition in ZrW₂O₈. While these studies suggest solutions to address the discontinuity in the thermal expansion behavior of ZrW₂O₈, there are no prior reports on SPS of ZrMo₂O₈ to the best of our knowledge. Liu et al discuss how thin films of cubic ZrMo₂O₈ can be prepared using sol-gel approach. But the complexity of the process, presence of amorphous residues and limited forming ability limit the effectiveness of this method. In this work, Sn-doped ZrMo₂O₈ was sintered using SPS at various temperatures and the thermal expansion properties of each sample were studied using dilatometry. The CTE of the SPS-sintered samples was then compared with that of the conventional pressureless sintered samples.

2 EXPERIMENTAL PROCEDURES

2.1 Synthesis

The synthesis of SnₓZr₁₋ₓMo₂O₈ powder particles was carried out through co-precipitation route using SnCl₄·5H₂O, ZrOCl₂·8H₂O, and (NH₄)₆Mo₇O₂₄·4H₂O. The detailed powder synthesis procedure has been discussed in a previous work. Densification was achieved by SPS using Dr Sinter 625, Fuji Electronic Industrial Co. Ltd. The powder particles were taken in a graphite die of 10 mm in diameter and rammed well to remove any trapped air. The die and the punches were lined with a graphite foil to prevent sticking of particles to the walls of the die and faces of the punches after sintering. Sintering was carried out at three different temperatures of 400, 500 and 600°C with a holding time of 10 minutes in each case. The pressure and the heating rate were maintained constant at 30 MPa and 100°C/min, respectively, for all the samples.

2.2 Physical and spectrochemical characterization

2.2.1 Density measurements

Standard Archimedes’ water displacement method was used to calculate the densities of the sintered pellets. The pellets were weighed using a digital balance and were then submerged in a beaker containing water at 50°C for 2 hours. The submersion was carried out using a steel wire set-up, and the weight of the sample in the water was taken. The sample was then taken out if water and wiped to remove any water droplets adhering to the surface. The weight of the sample was then noted. The three weights were then used to calculate the bulk density of the sample.

2.3 Structural characterization

2.3.1 X-ray diffraction

Polished sintered samples with flat surface were subjected to X-ray diffraction (Bruker Discover D8 diffractometer) for the identification of the different phases present in the sample. Cu Kα (λ = 0.154 nm) was used for irradiation of the sample. The scan range (2θ) was from 10° to 60° at 0.15° steps carried out at a rate of 2 s/step. The accelerating voltage and current were set at 30 kV and 25 mA, respectively. Panalytical X’pert high score plus software and International Center for Diffraction Data (ICDD) database were used for analyzing the diffraction data.

2.3.2 Scanning electron microscopy (SEM)

The SPS pellets were well polished using fine grit SiC abrasive papers to achieve a smooth surface and were observed using Hitachi S4800 scanning electron microscope. The sample was subjected to a conductive gold sputter coating before exposure to the electron beam to prevent ionizing effects. The observations
were carried out at high-vacuum conditions in secondary electron (SE) mode with a potential of 5 kV. Qualitative elemental analysis was carried out using energy-dispersive X-ray spectroscopy which was collected using a lithium-doped silicon detector with liquid nitrogen coolant (Horiba).

2.4 | Thermal characterization

2.4.1 | Dilatometry

The coefficients of thermal expansion of the sintered samples were found using a vertical pushrod type dilatometer, SETSYS Evolution TMA. The pushrod was made of fused alumina, and baselines were run to find and negate the equipment contribution. The samples were polished to have a diameter of 8 mm and a height of 4 mm prior to experimentation. Care was taken to ensure that the top and bottom surfaces were parallel. The sample measurements were carried out over the temperature range 30-600°C at a heating rate of 5°C/min in inert argon atmosphere.

3 | RESULTS

3.1 | Density variation

The variation in density values of the sintered pellets is shown in Figure 1. It is seen that the density of the pellets increases with increase in sintering temperature. By increasing the sintering temperature from 400°C to 500°C, there was an improvement in the density of 8.3% from 2.40 to 2.64 g/cm³. Further increase in the sintering temperature to 600°C yielded a significantly higher density of 3.60 g/cm³. The deviation in measurements was found to be minimal and was <0.05 g/cm³ in all the cases.

3.2 | Phase analysis

The X-ray diffractograms of the samples sintered by SPS at three different temperatures are shown in Figure 2. Peaks of cubic ZrMo2O8 phase appear at 24°, 22° and 27.5° of 2θ and are marked by the ♦ symbol. Since there are no reference patterns available in the ICDD for cubic ZrMo2O8 phase, the obtained peak positions are compared with the data published by Lind et al. The diffractograms also show the presence of peaks of trigonal α-ZrMo2O8 at 23.46°, 30.89° and 50.42° of 2θ corresponding to ICDD: 98-007-1870. It is also noticed that the phase formation of MoO3 occurs at all the sintering temperatures and was referenced using ICDD: 98-007-1870. The peaks of trigonal α-ZrMo2O8 are marked by * and those of MoO3 by # symbols, respectively. However, the presence of monoclinic β-ZrMo2O8 phase was not seen in any of the samples. The relative intensity of the MoO3 peaks increases as the sintering temperature increases from 400 to 600°C. The highest phase fraction of cubic MoO3 was present in the sample sintered at 600°C for 10 minutes.

3.3 | Microstructural evolution

The microstructural changes occurring in the sample as function of sintering temperature are presented in Figure 3. Representative SE micrographs illustrated in Figure 3A-C correspond to the polished SPS samples prepared at 400, 500 and 600°C, respectively. It can be seen that at 400°C, the particles are irregular in size and morphology and distributed...
non-uniformly. For the samples sintered at 500 and 600°C, the average particle size based on image analysis of the micrographs was 400 nm. At 600°C, the uniform ball-like morphology of the sintered particles appears more evident. There is no visible evidence for the growth of needle-like MoO$_3$ crystals in the micrographs. The presence of voids is noticed in all the three micrographs and accounts for the density variation. Detailed analysis of the challenges involved in the densification of this material has been carried out by the same authors and has been published elsewhere.$^{14}$

3.4 | Thermal expansion behavior

Figure 4 illustrates the plots of dimensional changes in the samples sintered at different conditions with temperature. The ordinate axis presents the dimensional change as a ratio of the increase/decrease in dimension with change in temperature to the original dimension. It is noticed that the displacement curve shows minor fluctuations in the observed temperature range. After 500°C, the measured displacements show a negative slope for the samples sintered at 400 and 500°C, whereas a positive slope is recorded for the 600°C sintered sample. The CTE calculated for 400, 500 and 600°C is $-2.14 \times 10^{-6}/°C$, $0.57 \times 10^{-6}/°C$ and $1.43 \times 10^{-6}/°C$ in the temperature range 30-500°C.

4 | DISCUSSION

4.1 | Sintering behavior

The theoretical density of cubic ZrMo$_2$O$_8$ is 3.398 g/cc and increases to 3.612 g/cc when Sn is doped in half of zirconium lattice sites. Experimental density calculations yield relative densities of 66%, 73% and 99% when sintered at 400, 500 and 600°C, respectively. The accuracy of the relative density values also depends on the extent of doping and the concentration of secondary phases. Detailed chemical analysis is needed to estimate the exact phase composition and requires further study. The cubic phase of ZrMo$_2$O$_8$ is metastable and tends to transform to monoclinic or trigonal phase during heat treatment process. This coupled with the competing decomposition reaction of the phase makes the sintering of this material challenging. On observing the X-ray diffractograms, it is seen that the relative intensities of MoO$_3$ increase with increase in sintering temperature. However, it is speculated...
that due to the short sintering times, MoO$_3$ particles do not undergo any grain growth during the densification process. The microstructures do not reveal any large MoO$_3$ grains and thus support the speculation.

Previous efforts in sintering the material using conventional pressureless sintering presented significant challenges in the densification of the pellet. Decomposition of the phase leading to the formation of MoO$_3$ limited the sintering temperature and time thus compromising the final pellet density.\textsuperscript{14} SPS drastically reduces the problem of decomposition and MoO$_3$ formation while achieving a higher density than conventionally sintered samples. This is due to two reasons: (a) The heating is carried out over a very short duration of few minutes with a very high heating rate. This aids in faster densification and does not allow much time for decomposition. (b) The heating is carried out entirely in vacuum. The reduced partial pressure of O$_2$ does not facilitate the growth of MoO$_3$ in the material. This is evidenced by the lack of large crystals of MoO$_3$ in micrographs of SPS sintered samples in Figure 3.

4.2 | Thermal expansion characteristics

The displacement curves of the optimally sintered samples obtained from both SPS and conventional sintering are presented in Figure 5. Both samples show very low CTE in the temperature range of 25-500°C. The SPS samples of Sn-doped ZrMo$_2$O$_8$ sintered at 500°C demonstrate CTE in the order of $10^{-7}/\text{°C}$. The minor variations in the displacement curves till 100°C are attributed to temperature stabilization. The CTE of the samples was found to increase with increase in the sintering temperature from negative to near zero to slightly positive. The samples sintered at 500°C for 10 minutes exhibit very low CTE of $5.7 \times 10^{-7}/\text{°C}$ in the temperature range 30-550°C. On further increase in sintering temperature to 600°C, the CTE starts to increase. This could be attributed to the onset of decomposition reactions at 600°C. The increased phase fraction of MoO$_3$ contributes to the higher CTE.

The CTE of the spark plasma-sintered samples is compared with that of conventionally sintered samples of Sn-doped ZrMo$_2$O$_8$ along with pure ZrMo$_2$O$_8$ and SnMo$_2$O$_8$ (values available only till 250°C) taken from literature and is presented in Figure 6 to attain a consolidated view\textsuperscript{14,21}. Pure cubic ZrMo$_2$O$_8$ exhibits strong NTE characteristics with a CTE of $-5 \times 10^{-6}/\text{°C}$, whereas pure SnMo$_2$O$_8$ displays PTE coefficient in the whole temperature range from 25 to 600°C. The PTE occurs due to a number of factors including the high stiffness of SnO$_6$ octahedra, ordering of MoO$_4$ tetrahedra and small cell volume which overwhelms the negative Gruneisen parameter modes. Replacing 50% of Zr with Sn in ZrMo$_2$O$_8$ counters the NTE behavior of ZrMo$_2$O$_8$ and brings the CTE close to 0. Doping or creating solid solution to control thermal expansion offers a significant advantage over synthesizing composites by eliminating the issue of mechanical failure originating at the interfaces due to differential expansion. Further, the isotropic nature of this expansion prevents the occurrence of internal stresses within the phase.

4.3 | Comparison with other commercially available low thermal expansion materials

A comparison of the different classes of low CTE materials is presented in the form of a radar plot in Figure 7. Lithium
aluminosilicate (LAS)-based glass-ceramics are the most readily available commercial solutions for applications requiring materials with low thermal expansion.\textsuperscript{22–25} Glass-ceramics consists crystalline phase with low or negative CTE within an amorphous positively expanding matrix. The overall CTE is tuned by controlling the amount of crystallization thus leading to values of \(-2\) to \(0.5 \times 10^{-6}/K\). However, the synthesis process is often complicated requiring a staged process of glass melting at \(1650\)°C followed by annealing at \(500\)°C and crystallization at \(\sim 750\)°C.\textsuperscript{22} The actual heating profiles adopted for commercial manufacturing are often more complicated and are influenced by glass viscosity and impurities. Metal matrix composites (MMC) or ceramic matrix composites (CMC) with NTE fillers are often the considered as the usual alternative to glass-ceramics. Several reports on controlling thermal expansion of the matrix by blending with 20-70 vol\% of \(\text{ZrW}_2\text{O}_8\) particles are available in the literature with the resulting overall CTE varying from \(1.6 \times 10^{-6}/K\) to \(9 \times 10^{-6}/K\).\textsuperscript{26–28} The main limitation of such composites arises from the phase transition of \(\text{ZrW}_2\text{O}_8\) from \(\alpha\)-cubic to \(\gamma\)-orthorhombic phase at low pressures of 200 MPa. The \(\alpha\) phase also transforms to \(\beta\)-cubic phase at a temperature of 155°C through order-disorder transition accompanied by changes in CTE.\textsuperscript{29} Thus, the variation of CTE is not only dependent on the volume fraction of the NTE particles but also dependent on the corresponding phase transition that it may undergo during processing. Hot pressing or hot isostatic pressing is often the preferred technique for the processing and sintering of ceramics to attain high densities. The residual stresses generated by the CTE mismatch between the fillers and matrix often leads to processing difficulties in such composites. In comparison with glass-ceramics and MMCs, Sn-substituted \(\text{ZrMo}_2\text{O}_8\) offers a facile way of synthesizing a ULE material. The controllable CTE by doping at the Zr site and the relative ease of processing offers it a definite edge over the other two candidates.

5 | CONCLUSION

Sn-doped \(\text{ZrMo}_2\text{O}_8\) has been successfully synthesized using SPS at three different temperatures. Formation of the cubic \(\text{ZrMo}_2\text{O}_8\) phase confirmed using X-ray diffraction. The density variation with temperature was studied and correlated with the microstructures. The dependence of the thermal expansion coefficient on the density and the presence of secondary phases were discussed. The results were then compared with that of conventional pressureless sintered samples. It is evident that the spark plasma-sintered samples possess lower CTEs with the sample sintered at \(500\)°C exhibiting CTE in the order of \(10^{-7}/\text{°C}\) due to low secondary phase fractions and low porosity.

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