Synthesis and Characterization of SrHfO₃ Co-doped with Gd₂O₃ and Yb₂O₃ (SHGY)

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Abstract

A new material SHGY is obtained after synthesizing SrHfO_3 co-doped with rare earth oxides (5 mol% Gd_2O_3 and 5 mol% Yb_2O_3). This process is carried out by a mechanical solid-state synthesis method. The synthesized powder is annealed at 1450°C keeping rate of increase of $3^\circ\text{C}/\text{min}$ for 2 hours. The phase and structural information of synthesized powder is characterized by X-Ray Diffraction (XRD) technique. The powder sample is sintered by Spark Plasma Sintering (SPS) at 1700°C for 15 minutes to form into a pellet. The microstructure analysis is done by using Field Emission Scanning Electron Microscopy (FESEM) followed by composition analysis by Energy Dispersive Spectroscopy (EDS). The phase purity is examined by Thermal Gravimetric Analysis and Differential Thermal Analysis (TG-DTA) and studies conclude that weight loss is $< 3\%$ and there are no changes in phase transformation. Finally, Thermal Expansion Coefficient (CTE) is studied by a Dilatometer. Results stated there is an increase in the CTE in the range of $8.82\text{--}13.0 \times 10^{-6} \text{K}^{-1}$ calculated temperature range $100\text{--}1000^\circ\text{C}$. This result of CTE showed there is a 19.2% ($10.5 \times 10^{-6} \text{K}^{-1}$ ($200\text{--}1100^\circ\text{C}$)) increase compared to the YSZ. This aids in the reduction of thermal mismatches between the substrate and topcoat in Thermal barrier applications (TBC).

1 Introduction

Generally, Thermal insulation coatings are the most complex structures. To reduce these complexity Thermal Barrier Coatings (TBC) are used. These coatings also improve performance, efficiency and longer component life times of the metallic substrates. Nowadays, researchers aimed at developing the coatings for the application of a jet engine, aircrafts, gas turbine blades and vanes etc., [1–3]. In TBC's, ceramic materials are coated on the substrate and this coated is treated as a topcoat layer. Material should possess a good number of predominant properties for instance phase stability, high thermal expansion coefficient ($> 9 \times 10^{-6} \text{K}^{-1}$), low thermal conductivity ($< 2 \text{ W.m}^{-1}.\text{K}^{-1}$), high fracture toughness and low sintering rate to justify the properties of topcoat layer [4 & 13]. The standard ceramic materials like YSZ (7–8% Y_2O_3 stabilized ZrO_2) have low thermal conductivity, phase stability and chemically inert at a temperature below 1200°C . Beyond this temperature, YSZ there are phase transformations that occur from t-tetragonal and cubic (t + c) and finally changed to monoclinic (m) structure. Due to this phase transformation, deposited YSZ showed a significant change in its volume which is noticeable. This change causes crack formation in the coatings, degradation of strain tolerance and accelerated sintering for high temperatures [4–5]. To overcome this problem, researchers are executing new TBC materials or doping in the present material which can satisfy the TBC requirements which are mentioned above.

Recently, perovskites (ABO_3) materials have been considered as a substitute for YSZ top coat for TBC applications. The Sr series perovskites like SrZrO_3 [6–9], SrHfO_3 [10–11], SrTiO_3 [15], SrMoO_3 [15], SrRuO_3 [11], SrCeO_3 [12 & 15] are studied till now. Materials which sustain high melting points are suitable for these applications, among the above mentioned materials SrHfO_3 have high melting point (3200K)

[15]. Kennedy, examined the phase transformation of SrHfO_3 by high resolution neutron powder diffraction method and reported as follows [10–11]:

Orthorhombic (700°C) $\rightarrow$ pseudo-tetragonal (830°C) $\rightarrow$ tetragonal (1170°C) $\rightarrow$ Cubic

Previous studies on SrHfO_3 primarily emphasis [13–16] the thermal and mechanical properties. From these results they concluded thermal conductivity is 5.2W/m.K at room temperature which is compared with the theoretical studies [11]. This is too high compared to the TBC requirements, thus giving a negative influence for these applications. To overcome these problems further research has been done by adding dopants materials in SrHfO_3 . By this thermal conductivity is reduced leaving no change in the thermal expansion coefficient (CTE) between topcoat and substrate [17–19]. Lesser values of CTE lead to high thermal mismatches between the surfaces. To overcome this problem materials should be co-doped in SrHfO_3 . Selection of these dopant materials are most important. So, that this final material can increase the CTE for the TBC application.

Rare earth oxide materials viz., Gd_2O_3 and Yb_2O_3 and combinations of these materials in SrHfO_3 may have been suitable for TBC applications. Phonon mean free path is inversely proportional to the square of the atomic weight difference between the solute. By choosing low values of Phonon mean free path leads to the reduction of thermal conductivity. Gd (157.25u), Yb (173.04u) and Hf (178.49u) has low phonon mean free path when doped in SrHfO_3 . This satisfies the above statement when compared to the Y (88.9u) and Zr (99.224u) doping in YSZ [20]. Still a lot of research is necessary to study the influence of rare earth oxide materials doping with SrHfO_3 .

The main objective of this paper is to synthesize Rare earth oxide materials (Gd_2O_3 and Yb_2O_3) doped in SrHfO_3 to form a new material SHGY by using mechanical solid state method. SHGY is annealed at 1450°C keeping a rate of increase of 3°C/min for 2 hours and characterized by XRD to study the phase evaluation. The final powder is sintered by using spark plasma sintering (SPS). This helps in converting powder into a pellet. The phase stability and thermal properties such as thermal expansion coefficient and surface morphology are characterized by using TG-DTA, Dilatometer and FESEM respectively.

2 Experimental Procedure

2.1 Chemicals used for synthesis

SrCO_3 ($\geq 99.9\%$, Sigma-Aldrich, USA), HfO_2 (Sigma-Aldrich, USA), Yb_2O_3 (99.99% Ultra nanotech Pvt. Ltd) and Gd_2O_3 (99%, Ultra nanotech Pvt. Ltd).

2.2 Synthesis of SHGY powder

SHGY powder was prepared by choosing SrCO_3 , HfO_2 , 5 mol% Gd_2O_3 , 5 mol% Yb_2O_3 mixed in a ball mill zirconium jar in the presence of methanol by a mechanical solid-state method taking balls to powder ratio 1:10. The powders were milled for one hour maintaining speed with 500 rpm throughout the milling

to get a homogeneous mixing. Then the mixed powder was annealed in alumina crucible at 1450°C for 24 hours with a rate of increase 3°C in furnace to decompose the carbonates of SrCO₃ from these powders. In order to obtain the single phase material, the synthesis process was repeated for three times.

2.3 Sintering procedure for preparing pellet using Spark Plasma Sintering (SPS)

The obtained synthesized powder was sintered by using SPS technique by using graphite die and a punch. Figure 1 shows the schematic representation of the SPS procedure to convert the powder into a pellet. The synthesized SHGY powder is poured into the graphite die with dimensions of 20 mm inner diameter. In order to separate the powder from graphite punch surfaces, graphite foil was used. Sintering was carried out at the temperature of 1700°C in a vacuum atmosphere at applied pressure of 50 MPa with a heat rate 100°C min⁻¹ and maintained 15 min holding time and followed by the cooling rate at 150°C min⁻¹. SPS temperature was measured by using a thermocouple at a hole drilled in the die which was placed 4 mm away from the sample. Then the experiment was conducted by applying vacuum pressure, initially at 15 MPa onto the powder and then it was gradually increased to a maximum of 50 MPa. When the pressure has reached the sintering temperature then the maximum applied pressure is applied during sintering holding time. Finally, the outcome of the pellet was in 20 mm diameter with 3 mm thickness. During the SPS process, chamber vacuum pressure and temperature values were recorded and plotted against time as shown in Fig. 2.

3 Characterization Of Shgy

The X-ray diffraction (XRD) (Model XPERT-PRO) characterization technique is used for phase analysis of the synthesized powder at a wavelength of 1.5406 Å using Cu-Kα ray at 30 kV with the scan range 10–80° (2θ). The obtained graph was validated with X'pert High score plus software. The powder SHGY is sintered by Spark Plasma Sintering (SPS) for making pellet. Through Archimede's technique, the density of the pellet was measured by using a Densitometer. The phase stability of the material was recorded from 30°C (room temperature) to 1130°C in nitrogen gas atmosphere at 10°C/min rate of increase by using TG-DTA equipment. The Coefficient of thermal expansion (CTE) was characterized by a Dilatometer (VBCRC lab) from 30°C (room temperature) to 1000°C at an increase rate of 10°C. The microstructure and elemental analysis of the sintered pellet was investigated by Field Emission Scanning Electron Microscopy (FESEM) (JEOL) for this 10 kV accelerated voltage. Elemental analysis by Energy Dispersive X-ray Spectroscopy (EDS).

4 Results And Discussion

4.1 XRD characterization of synthesis powder (SHGY)

XRD characterization is done for the synthesized powder SHGY was annealed at 1450°C temperature and 3°C/ min rate of increase for 24 hours for 3 times to form a single phase. The obtained XRD pattern of

SHGY compared with the standard pattern of orthorhombic SrHfO₃ PDF code 00-045-0211 and the results is also validated with X'pert High score software and observed the same with the literature [19]. This result can be appreciated that no intermediate phase has been noticed, all the peaks in the XRD data reflects SrHfO₃ phase. XRD pattern of SHGY shown in Fig. 3 (a-b) from the result, maximum peak position at 31.086° with (h k l) values (1 0 1), and other peaks with (h k l) values of (1 2 1), (2 0 2), (1 0 3), (3 2 1) and (2 4 2) respectively. Because of that annealing temperature and the bigger ionic radius of Gd³⁺(0.94Å) and Yb³⁺(0.84Å) compared to the Hf⁴⁺(0.71Å) the doping of Gd₂O₃ and Yb₂O₃ were done properly with SrHfO₃ [19&20]. Figure 3 (b) shows that SHGY is formed fully without any other secondary phases.

The SHGY powder sample is sintered by the SPS method to make a pellet. Bulk density (ρ) of pellet is 7.5 g/cm³ with the relative density of 95.1% and the fractional porosity is 4.9% is measured by Archimede’s technique by a densitometer from Eq. (1). Table.1 shows the bulk density, relative density and fractional porosity results which are in good agreement with the XRD powder density (7.74 g/cm³) results.

Fractional porosity (%) = 1-Relative density (%)

Eq. (1)

Table 1
 Bulk density, Relative density and fractional porosity of the sintered pellet

Material	Bulk Density (ρ) (g/cm ³)	Relative Density (%)	Fractional Porosity (%)
SHGY	7.5	95.1	4.9

4.2 FESEM and EDS Characterization of SHGY

FESEM technique helps to view the surface morphology of SHGY pellet surface. As the material is ceramic, the FESEM is characterized for conductive materials. Firstly, the gold film was coated on the nonconductive material SHGY pellet surface which helps electrons pass into the SHGY by conductive surface. The grain boundaries are formed due to sintering which is absorbed from the micrograph clearly shown in Fig. 4 (a) Fig. 4 (b) at 10 kV and 15 kV respectively measured at 33000X and 30000X magnification respectively. The grain size measured is the range of 68–77 nm and observed the grains are bounded tightly without any voids. The elements which were presented in the pellets were Sr, Hf, Gd, Yb, and O confirmed by the EDS as shown in Fig. 4 (c).The peaks of Sr, Hf, Gd, Yb, and O shows perfect doping is done. It was clearly shown that there are no other element peaks present in the spectrum that conclude that there are no impurities present in the pellet and the whole pellet is SHGY in single phase.

4.3 TG-DTA characterization of SHGY

To further strengthen our earlier observations about phase stability, a systematic TG-DTA study of the prepared sintered SHGY was carried out from room temperature to 1130°C in a nitrogen gas atmosphere with 10°C/min rate of increase as shown in Fig. 5. The TG plot shows the weight loss is in three steps

attributable to (i) Dehydration, which can be caused by the absorbed moisture weight loss of 2% at about 100°C [21] (ii) Decomposition, low molecular weight compounds such as additives, crystallization water and first decomposition products such as intermediate carbonate and (iii) Finally weight loss of < 3% at 970°C in the plot. Thereafter from the DTA plot no abnormal changes occur during the process means that there is no entropy change, which implies that no organic matter is present in the sample and combustion is completed. There are no peaks observed for any considerable phase transition taking place in the sample up to this temperature.

4.4 Thermal expansion coefficient (CTE) of SHGY

The Coefficient of thermal expansion (CTE) of the SHGY is a significant property for influencing the durability of TBC when increasing temperature from lower to higher. The residual stresses developed between the substrate and the topcoat material due to the mismatch of the CTE. In this present work, the CTE was measured by the dilatometer in the presence of nitrogen gas with a 10°C rate of increase and measured from room temperature to 1000°C. The obtained graph was increased linearly and values range from $8.82\text{--}13.1 \times 10^{-6} \text{K}^{-1}$ (100–1000°C) as depicted in Fig. 6 which is high as compared with SrHfO₃ and also for YSZ [17& 22]. During measurement there are no abnormal changes, indicating that enhance the phase stability and increase the CTE because of co-doping rare earth oxides Gd₂O₃ and Yb₂O₃.

Conclusion

Rare earth oxides such as Gd₂O₃ and Yb₂O₃ co-doping with SrHfO₃ (SHGY) influence on the phase stability and thermal properties was investigated. The conclusions drawn from the work are as follows:

- SHGY was successfully synthesized by a mechanical solid-state method and it has a good phase stability which was characterized by XRD and validated with standard data.
- Powder sample was sintered at 1700°C temperature by using SPS, resulting with relative density is 95.1% of bulk density and fractional porosity is 4.9%.
- The microstructure of grain boundaries and the elemental compounds of SHGY pellet were observed by using FESEM and EDS. The grain size is in the range of 68-77nm.
- Phase purity was examined by TG-DTA from these results and concluded that the weight loss is less than 3%, and there is no phase transformation observed that means there is no phase transformation occurred.
- SHGY shows excellent phase stability up to 1700°C sintering temperature which is achieved by adding co-doping of Gd₂O₃ and Yb₂O₃ and this is superior to YSZ.
- The CTE is also increased 19.2% increased compare to the SrHfO₃e. ($8.82\text{--}13.0 \times 10^{-6} \text{K}^{-1}$ (100-1000°C). These causes reduce the thermal mismatches between the substrate and topcoat in the thermal barrier applications whereas in gas turbine blades, vanes etc.

Declarations

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Figures

(a) Working of SPS

(b) Powder

(c) Pellet

Figure 1

Schematic representation of the SPS procedure to covert powder to pellet of SHGY

(a) Working of SPS

(b) Powder

(c) Pellet

Figure 1

Schematic representation of the SPS procedure to covert powder to pellet of SHGY

Figure 2

Vacuum pressure and temperature of the SPS chamber were plotted against time

Figure 2

Vacuum pressure and temperature of the SPS chamber were plotted against time

Figure 3

Figure 4

(a-c). Morphology and Elemental analysis of SHGY (a).Morphology of SHGY(10kV) (b).Morphology of SHGY (15kV) (c).Elemental analysis of SHGY pellet

Figure 5

TG-DTA plot for sintered SHGY

Figure 5

TG-DTA plot for sintered SHGY

Figure 6

Thermal expansion plot of SHGY

Figure 6

Thermal expansion plot of SHGY