Very low thermal conductivity in lanthanum phosphate–zirconia ceramic nanocomposites processed using a precipitation–peptization synthetic approach†

Kottarathil Shijina, a Sasidharan Sankar, a Mohan Midhun, a Meerankhan Firozkhan, a Balagopal Narayanan Nair, b Krishna Gopakumar Warrier a and Unnikrishnan Nair Saraswathy Hareesh* a

A wet chemical synthetic approach involving precipitation–peptization mechanisms was successfully adopted for the development of LaPO4–ZrO2 nanocomposites with the ZrO2 content varying in the 5–20 wt% range. Stoichiometric lanthanum phosphate, formed as nanofibrils during the precipitation reaction with orthophosphoric acid, was subsequently transformed into nanorods of ~10 nm width and <100 nm length upon peptization at pH 2. Zirconia dispersions were homogeneously incorporated as ultrafine particulates through zirconium oxychloride hydrolysis using ammonia. The nanocomposite precursor thus obtained could be densified to >98% TD for the LaPO4–10 wt% ZrO2 composition upon sintering at 1600 °C. The addition of ZrO2 to LaPO4 impeded densification and grain growth inhibition of up to 50% was obtained for LaPO4–20 wt% ZrO2 nanocomposites. Furthermore, the nanocomposites indicated very low thermal conductivity values (1 W m⁻¹ K⁻¹) compared to single phase LaPO4. The non-reactivity of LaPO4 and ZrO2 at high temperatures and the low thermal conductivity values of LaPO4–ZrO2 render them effective for high temperature thermal insulation applications.

1. Introduction

Lanthanum phosphate (LaPO4), a major constituent of the family of rare earth phosphates, is considered to be a potential high temperature material because of its excellent thermal phase stability, high melting temperature (>1900 °C), 1 low thermal conductivity (3.61 W m⁻¹ K⁻¹ at room temperature and 1.30 W m⁻¹ K⁻¹ at 1000 °C), 2 chemical inertness, 3 reasonably low thermal expansion coefficient 4 and appreciable thermal shock resistance. 5

By virtue of the mentioned properties, LaPO4 is often recommended for thermal insulation applications and is a candidate material for thermal barrier coatings. The control and maintenance of LaPO4 stoichiometry during the synthesis of LaPO4 has been one of the pressing problems reported for its phase instability and limited utilization in high temperature applications. 6 The synthesis of LaPO4 using the modified sol gel process has been very effective in overcoming stoichiometry related issues and has thus been the preferred synthetic route for the synthesis and fabrication of LaPO4 based ceramics for a variety of applications. 7, 8 LaPO4 is also widely investigated as a suitable interphase as well as reinforcement material for ceramic matrix composites. 9, 10 LaPO4 being a soft ceramic with hardness values less than 5 GPa 11 finds application in the processing of machinable and high temperature stable ceramic composites 12–14.

Zirconia (ZrO2) is a widely used ceramic material for applications ranging from electrodes 15 to fuel cells 16 and catalysts 17, 18. Yttria stabilised ZrO2 (YSZ) has been reported to perform well as thermal barrier coatings (TBCs) and is used to protect as well as insulate hot-section metal components in advanced gas-turbine and diesel engines. 19 Conversely, this material has a limiting operation temperature due to sintering and phase transitions at elevated temperatures. It is an essential fact that next generation TBCs and insulation materials are designed to operate at higher temperatures for which newer materials with interesting and stable properties are required. Stabilization of ZrO2 using oxide materials like Y2O3 (yttria stabilized zirconia, YSZ) has been a fruitful development in the area of thermal insulation. However, YSZ when used at higher temperatures has the major disadvantage of phase partitioning into a metastable tetragonal (t') phase via diffusion into the equilibrium tetragonal (t) and cubic phases (c) at high temperatures. 6 In this case, the tetragonal...
phase will then transform into the monoclinic phase (m) during cooling, resulting in the disintegration and failure of the coatings.\(^5\) Fully dense YSZ has a thermal conductivity of around 2.3 W m\(^{-1}\) K\(^{-1}\) at 1000 °C and is higher than that of LaPO\(_4\) at similar temperature.\(^2,1,2\) On the other hand, LaPO\(_4\) with its excellent high temperature properties suffers from grain growth\(^5\) at above 1450 °C. Grain growth inhibition by second phase incorporation is therefore a viable strategy to obtain fine grained microstructures for application at higher temperatures. The present work is therefore an attempt to design and synthesize a composite of LaPO\(_4\) with ZrO\(_2\) to improve the microstructural features without deleteriously affecting the thermal properties. A sol–gel based technique is used for the synthesis of LaPO\(_4\)-ZrO\(_2\) composites and the results indicate the possibility of using LaPO\(_4\)-ZrO\(_2\) as an efficient thermal barrier ceramic. Thermal properties as well as morphological features of the composites are presented and discussed in this paper.

2. Experimental

LaPO\(_4\) sol is prepared using a modified sol–gel technique involving a precipitation–peptization approach. LaPO\(_4\) is precipitated from 0.5 M lanthanum nitrate hexahydrate (La(NO\(_3\))\(_3\)·6H\(_2\)O, 99.9%, M/s Indian Rare Earths Ltd, India) salt solution (18.51 g) using orthophosphoric acid (H\(_3\)PO\(_4\) (2.72 ml) (88% SD Fine Chemicals, India), and is then flocculated using ammonia solution (25%, Merck India), under stirring. The flocculation occurs at pH 7 and is confirmed by the addition of ammonia to the decanted solution when no precipitate formation is observed.\(^7\) After washing the precipitate in warm water to remove excess ions and phosphates, it is redispersed in demineralized water using nitric acid (H\(_2\)NO\(_3\), 20%) and further peptized under vigorous stirring to obtain LaPO\(_4\) sol at pH 2. For the composite precursor, zirconium oxy chloride (99.9%, M/s Indian Rare Earths Ltd, India) solution corresponding to 5–20 wt% is added to the LaPO\(_4\) sol stabilised at pH 2. Ammonia solution (25%) is added until the mixed sol reaches the pH value of 8. The precipitate thus formed is washed, dried and heated at 800 °C for 3 h in air. The powder thus obtained is then milled in an aerodynamic medium using alumina balls with 2 wt% poly vinyl alcohol (PVA, molecular weight: 13,000–23,000, Sigma Aldrich, USA) as a binder, dried and compacted to pellets of 12 mm in diameter and 3 mm in thickness for sintering studies. Sintering was performed using a high temperature furnace (Nabertherm, Germany) in the temperature range of 1400–1600 °C in an air atmosphere at a heating rate of 3 °C min\(^{-1}\) and a soaking time of 2 h. LaPO\(_4\) monoliths were sintered at 1300 °C/2 h.

X-ray diffraction measurements (Philips PW 1710, the Netherlands) were carried out, in the 2θ range of 20–60° using Cu Kα radiation, for confirming the phase formation of the precursor phases. TEM imaging, using a FEI Tecnai 30 G2 S-TWIN microscope operating at an accelerating voltage of 300 keV, was carried out to elucidate the morphological features of the precursors and calcined powders. The composite precursor obtained after calcination at 800 °C was compacted at a pressure of 200 MPa to pellets of 11 mm diameter. Densification was carried out in the temperature range of 1400–1600 °C. The sintered pellets were characterized using X-ray diffraction for phase identification. Density measurements of the composite samples were carried out using the Archimedes method. Microstructural evaluations including the grain growth pattern of the composites were evaluated using scanning electron microscopy (JEOL JSM-5600LV SEM microscope, Japan) on polished and thermally etched specimens. Laser flash technology (Flash Line TM2000, Anter Corporation, USA) was used to determine the thermal properties of the composite samples in the form of pellets having 11 mm diameter and 2 mm thickness.

3. Results and discussion

The stoichiometry of rare earth phosphates is one of the parameters essential for the use of such materials in high temperature operations. One strategic solution to overcome the stoichiometry related barrier is the use of wet chemical synthetic approaches where the molecular level control of stoichiometry is ensured through precipitation–peptization mechanisms. Since lanthanum nitrate is hygroscopic, the exact amount of La\(^{3+}\) ion reacting with phosphate ions is often difficult to realise. Therefore, the amount of lanthanum nitrate will be always less compared to the stoichiometric requirements of H\(_3\)PO\(_4\). After the precipitation reaction, the addition of ammonia (added for the flocculation of precipitate) converts the excess phosphate to soluble ammonium phosphate, which could be easily removed while washing the precipitate for the removal of nitrate ions. The incorporation of zirconium oxychloride after the peptization stage, during the preparation of composite samples, helps in obtaining uniform dispersion of the second phase in the ceramic matrix (LaPO\(_4\)) as well as in forming stoichiometric LaPO\(_4\)-ZrO\(_2\) in the preparation of LaPO\(_4\)-ZrO\(_2\) composite precursors.

3.1 Morphological studies

The TEM images obtained for the LaPO\(_4\)-10 wt% ZrO\(_2\) composite precursor (as precipitated) and powder (calcined at 800 °C) are presented in Fig. 1. The composite precursor is characterised by the nanorods of LaPO\(_4\) that are approximately 10 nm in length and more than 100 nm in length (Fig. 1a). The calcined precursor at 800 °C retained the nanorod morphology of the LaPO\(_4\) phase while ZrO\(_2\) was seen as spherical particles of less than 10 nm diameter (Fig. 1b).

The EDAX spectrum of the calcined precursor (Fig. 1c) provided a clear indication of the formation of the nanocomposite with peaks for La, P, O and Zr. The lattice spacing of the LaPO\(_4\) and ZrO\(_2\) phases in the composite was also measured and marked in the HRTEM image (Fig. 1d). The SAED pattern of the composite calcined at 800 °C (Fig. 1e) indicated d-spacing values for LaPO\(_4\) and ZrO\(_2\) phases confirming the EDAX results. The TEM images of the LaPO\(_4\) monolith are presented in Fig. S1 and S2 in the ESL.\(^†\)

3.2 Phase identification

X-Ray diffraction patterns presented in Fig. 2 provide the phase evolution with calcination and sintering. The pattern of
as-precipitated LaPO₄–10 wt% ZrO₂ indicated only hexagonal phases of LaPO₄ while ZrO₂, being present as amorphous zirconium hydroxide, is not identified. On calcination, the LaPO₄ transformed from the hexagonal to the monoclinic phase and zirconium hydroxide is converted to ZrO₂. The tetragonal ZrO₂ phases are thus seen at 800 °C. The diffraction peaks indexed to (200), (120) and (012) represent crystal planes of monoclinic LaPO₄ appearing at 2θ values of 26°, 28° and 30° (jcpds file no. 35-0731), while the peaks indexed to (112) and (211) correspond to tetragonal ZrO₂ (jcpds file no. 80-0965). The XRD profile of the composite at 1400 °C indicates a well crystallised pattern with the peaks for monoclinic LaPO₄ and tetragonal ZrO₂. The tetragonal phase in ZrO₂ is stabilized by La³⁺ ions. The La³⁺ ions replace Zr⁴⁺ ions and the subsequent strain in ZrO₂ impedes the transformation of tetragonal to monoclinic ZrO₂. The pattern evidences no reaction or formation of new phases, indicating the thermal stability of the composite for high temperature applications. The phase evolution with temperature is similar for all the compositions except for the increase in intensity of ZrO₂ peaks with increasing ZrO₂ content. The phase evolution in monolithic LaPO₄ is presented in Fig. S3 (ESI†) for comparison.

3.3 Densification studies

Plots of % theoretical density (TD) with the ZrO₂ content at the respective sintering temperatures of the composites are presented in Fig. 3. LaPO₄ monoliths could be sintered (>98% TD) at T ~ 1300 °C while the composite samples required a temperature of 1600 °C for all the four compositions to yield sintered density values greater than 95% of TD. The LaPO₄–10 wt% ZrO₂ composite samples yielded sintered density of >98% TD, whereas samples with 5 and 15 wt% ZrO₂ gave density values of >95% of TD. The decrease in density upon the addition of ZrO₂ could be attributed to the delay in sintering due to the distribution of fine ZrO₂ particles at the grain boundaries of LaPO₄ as observed in the SEM micrographs discussed below.

The composite pellets after mirror polishing and thermal etching are observed under a scanning electron microscope for microstructural evaluation. Fig. 4 shows the SEM micrographs obtained for the composite samples sintered at 1600 °C. The rod morphology of LaPO₄ observed in the composite precursor stages transforms into regular shaped grains characteristic of sintered ceramics. Fig. S4 (ESI†) provides the microstructure of LaPO₄ at 1600 °C where sintered grains as large as 4 μm are formed. In the case of composites (Fig. 4a–d), ultrafine zirconia particles are seen to be uniformly distributed along the grain boundaries.

As a result of such homogeneous distribution, the LaPO₄ grain size reduced considerably due to the addition of 5–20 wt% ZrO₂ compared to pure LaPO₄. At 20 wt% ZrO₂ content, the grain size of LaPO₄ was inhibited to ~50%, ending up with an average grain size of ~1–2 μm (Fig. 5). The distribution of ZrO₂ particles in the composite samples is evident from the micrographs obtained.
and the reduction in grain size of LaPO₄ with increasing ZrO₂ content is quantified in Fig. 5. ZrO₂ is well known to create Zener pinning and as a non-sintering inclusion cause grain growth inhibition of the matrix phase in ceramic composites. In the present study, the absence of any reaction between LaPO₄ and ZrO₂ phases and the homogeneous distribution of ultrafine ZrO₂ induced considerable grain growth inhibition, as has been observed earlier for ceramics like alumina. In this case, as the thermal expansion coefficient of ZrO₂ is higher than LaPO₄, the presence of uniformly distributed ZrO₂ grains at the LaPO₄ grain boundaries provided grain growth pinning and the sintered grain sizes reduced considerably with the addition of an increasing amount of ZrO₂. The two phases coexisted and caused a reduction in the grain growth. In addition to this we believe that the presence of La³⁺ could induce oxygen vacancies and strain in ZrO₂ crystals thus stabilizing the tetragonal phase. The reduction in sintered grain size for composites with >98% TD will certainly improve the mechanical properties of the composite at higher temperatures.

3.4 Thermal conductivity

Thermal behaviours of the composite samples are analysed using a laser flash technique, where an energy pulse heats one side of the sample pellet while the temperature increase on the rear as a result of the energy input with time is detected. The change in thermal conductivity of the composite sample (LaPO₄–10 wt% ZrO₂) with respect to temperature is compared with that of monolithic LaPO₄ having the same density (Fig. 6). A LaPO₄ monolith shows a thermal conductivity value of 3.2 W m⁻¹ K⁻¹ at 25 °C and shows a decreasing trend with the increase in temperature and is in accordance with the published literature. In the composite samples, LaPO₄–10 wt% ZrO₂ showed low conductivity values of 2.1 W m⁻¹ K⁻¹ and 1.4 W m⁻¹ K⁻¹ at room temperature and at 200 °C, respectively. The LaPO₄–20 wt% ZrO₂ nanocomposite displayed very low thermal conductivity value of 1 W m⁻¹ K⁻¹ at 400 °C. These values are significantly lower than the values reported for YSZ at higher temperatures. As indicated earlier (Fig. 5), the grain size of LaPO₄ decreases with the addition of ZrO₂. Generally, for polycrystalline materials, the thermal conductivity is related to the phonon scattering generated by the grain boundaries. With increase in the percentage of ZrO₂, the grain size of the LaPO₄–ZrO₂ nanocomposite decreased and consequently the grain boundary area increased. Therefore, the decrease in thermal conductivity of nanocomposites was caused by the increase in phonon scattering generated by the lowering of the grain size leading to an increase in the total grain boundary length.

4. Conclusions

LaPO₄ based ZrO₂ composites (LaPO₄–ZrO₂) have been successfully developed for the first time involving a unique wet chemical approach with precipitation–peptization mechanisms. Among the
nanocomposites thus developed with varying zirconia content (5–20 wt%), LaPO₄–10 wt% ZrO₂ achieved >98% TD on sintering at 1600 °C. The stability of the composite at higher temperatures is confirmed using phase identification and microstructural evaluation wherein no reaction between the constituent phases is observed. Microstructural evaluation confirmed the excellent grain growth inhibition of LaPO₄ due to the presence of ZrO₂. Composite samples showed very low thermal conductivity values; LaPO₄–10 wt% ZrO₂ with >98% TD gave conductivity values of 2.1 W m⁻¹ K⁻¹ and 1.4 W m⁻¹ K⁻¹ at room temperature and at 200 °C, respectively. This lower thermal conductivity, leading to excellent insulation properties, could help in the application of these materials in thermal insulation as well as in thermal barrier coatings.

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Notes and references

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