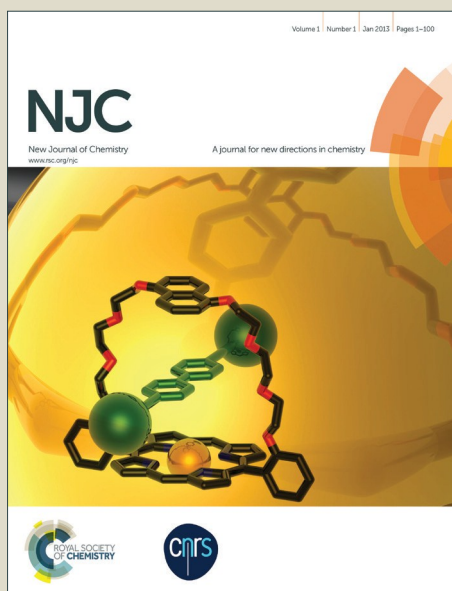


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Very Low Thermal Conductivity in Lanthanum Phosphate-Zirconia Ceramic Nanocomposites Processed by a Precipitation-Peptization Synthetic Approach

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A wet chemical synthetic approach involving precipitation-peptization mechanisms was successfully adopted for developing LaPO₄-ZrO₂ nanocomposites with ZrO₂ content varying in the 5-20 wt% range. Stoichiometric lanthanum phosphate, formed as nano fibrils during the precipitation reaction with orthophosphoric acid was subsequently transformed to nanorods of ~10 nm width and <100 nm length on 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% ZrO₂ composition on sintering at 1600 °C. The ZrO₂ addition to LaPO₄ impeded densification and grain growth inhibition up to 50% was obtained for LaPO₄-20 wt% ZrO₂ nanocomposites. Furthermore, the nanocomposites indicated very low thermal conductivity values (1 W/mK) 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 as a potential high temperature material because of its excellent thermal phase stability, high melting temperature >1900 °C,¹ low thermal conductivity (3.61 W/mK at room temperature and 1.30 W/mK at 1000 °C),² chemical inertness,³ reasonably low thermal expansion coefficient⁴ 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 La:PO₄ stoichiometry during synthesis of LaPO₄ has been one of the pressing problems reported for its phase instability and limited utilization in high temperature

applications.⁶ Synthesis of LaPO₄ by the modified sol gel process has been very effective to overcome stoichiometry related issues and has thus been the preferred synthetic route for the synthesis and fabrication of lanthanum phosphate based ceramics for a variety of applications^{7,8}. LaPO₄ is widely investigated also 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 GPa¹¹ finds applications 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 electrodes¹⁵ to fuel cells¹⁶ and catalysts.^{17,18} Yttria stabilised ZrO₂ (YSZ) is reported to perform well as thermal barrier coatings (TBC) 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

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with interesting and stable properties are required. Stabilization of ZrO_2 using oxide materials like Y_2O_3 , (Yttria stabilized Zirconia, YSZ) has been a fruitful development in the area of thermal insulation. However YSZ on being used at higher temperatures has got the major disadvantage of phase partitioning into metastable tetragonal (t') phase by diffusion into the equilibrium tetragonal (t) and cubic phases (c) at high temperatures.⁶ In this case, the tetragonal phase will then transform into monoclinic phase (m) during cooling, resulting in disintegration and failure of the coatings.²⁰ Fully dense YSZ has a thermal conductivity of around 2.3 W/mK at 1000 °C and is higher than that of $LaPO_4$ at similar temperature.^{21,22} On the other hand, $LaPO_4$ with its excellent high temperature properties suffer from grain growth⁵ above 1450 °C. Grain growth inhibition by second phase incorporation is therefore a viable strategy to obtain fine grained microstructure for applications 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. Sol-gel based technique is used for the synthesis of $LaPO_4$ - ZrO_2 composite 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 modified sol-gel technique involving a precipitation-peptization approach. $LaPO_4$ is precipitated from 0.5 M lanthanum nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$, 99.9%, M/s Indian Rare Earths Ltd. India) salt solution (18.51 g) using orthophosphoric acid (H_3PO_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 on decant solution when no precipitate formation is observed.⁷ After washing the precipitate in slightly warm water to remove excess ions and phosphates, it is redispersed in demineralized water using nitric acid (HNO_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 weight % is added to the $LaPO_4$ sol stabilised at pH 2. Ammonia solution (25%) is added until the mixed sol reached the pH value of 8. The precipitate thus formed is washed, dried and heated at 800 °C for 3h in air. The powder thus obtained is then milled in aqueous medium using alumina balls with 2 wt% Poly Vinyl Alcohol (PVA, Molecular weight: 13000-23000, Sigma Aldrich, USA)) as a binder, dried and compacted to pellets of 12 mm diameter and 3 mm thickness for sintering studies. Sintering was performed using a high temperature furnace (Nabertherm, Germany) in the temperature range of 1400-1600 °C in air atmosphere at a heating rate of 3 °C/min and soaking time of 2 h. $LaPO_4$ monoliths were sintered at 1300 °C/ 2h.

X-ray diffraction measurements (Philips PW 1710, The Netherlands) were carried out, in the 2θ range of 20–60° using Cu K α radiation, for confirming the phase formation of 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. Sintered pellets were characterized using X-ray diffraction for phase identification. Density measurements of the composite samples were carried out by using Archimedes method. Microstructural evaluations including the grain growth pattern of the composites were evaluated from 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 11mm diameter and 2 mm thickness.

3. Results and Discussion

The stoichiometry of rare earth phosphates is one of the parameters essential for the usage of such materials for high temperature operations. One strategic solution to overcome

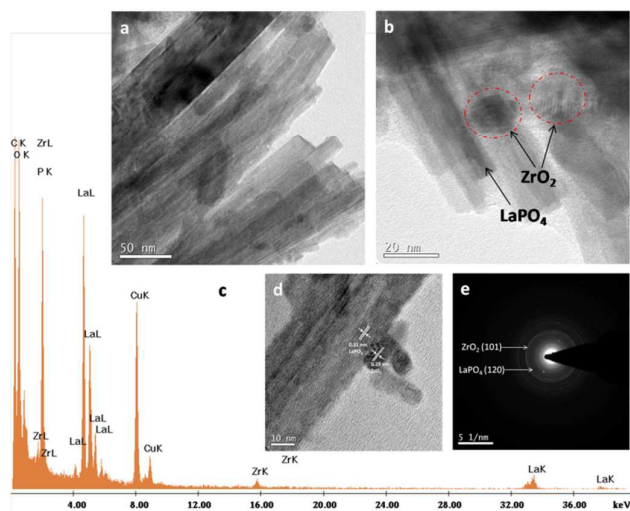


Fig. 1 TEM micrographs of (a) LaPO₄-10 wt% ZrO₂ composite precursor, (b) calcined at 800 °C, (c) EDAX pattern of composite calcined at 800 °C, (d) HR TEM image of composite calcined at 800 °C, (e) SAED pattern of composite calcined at 800 °C.

the stoichiometry related barrier is the use of wet chemical synthetic approaches where in molecular level control of stoichiometry is ensured through precipitation-peptization mechanisms. Since lanthanum nitrate is hygroscopic, the exact amount of La³⁺ ion to react with phosphate ions is often difficult to realise. Therefore, the amount of lanthanum nitrate will be always lesser compared to the stoichiometric requirements of H₃PO₄. 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 removal of nitrate ions. 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 (LaPO₄) as well as for forming stoichiometric LaPO₄ in the preparation of LaPO₄-ZrO₂ composite precursors.

3.1 Morphological studies

The TEM images obtained for the LaPO₄-10 wt% ZrO₂ composite precursor (as precipitated) and powder (calcined at 800 °C) are presented in Fig. 1. The composite precursor is characterised by nanorods of LaPO₄ that are approximately 10 nm in width and more than 100 nm in length (Fig 1a). The calcined precursor at 800 °C retained the nanorod morphology of LaPO₄ phase while ZrO₂ is seen as spherical particles of less than 10 nm diameter (Fig. 1b).

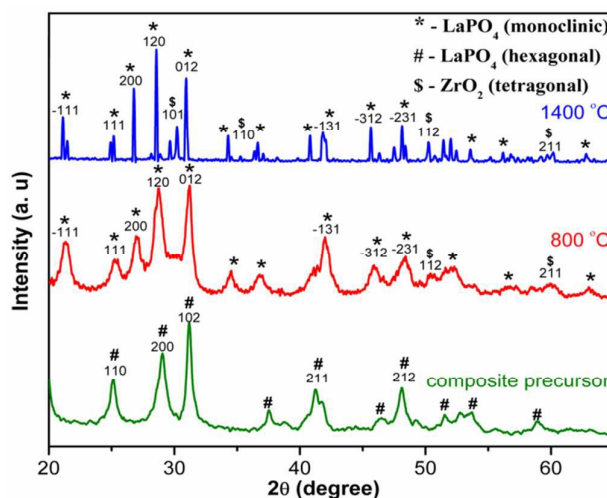


Fig. 2 X-ray diffraction pattern for LaPO₄-10 wt%ZrO₂ composite precursor, calcined at 800 and 1400 °C.

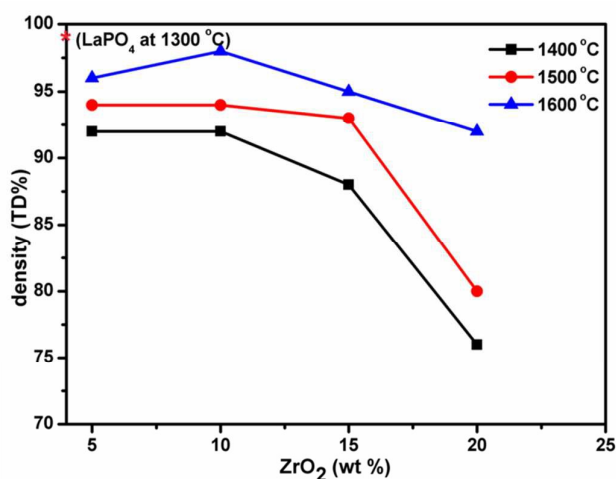


Fig. 3 Plot showing densities acquired for the composite samples with respect to sintering temperature and ZrO₂ addition.

The EDAX spectrum of the calcined precursor (Fig. 1c) provided clear indication of the formation of the nanocomposite with peaks for La, P, O and Zr. The lattice spacing of the LaPO₄ and ZrO₂ 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 LaPO₄ and ZrO₂ phases confirming the EDAX results. The TEM images of LaPO₄ monolith is presented in Fig. S1 and S2 for information.

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

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phases of LaPO_4 while ZrO_2 , being present as amorphous zirconium hydroxide, is not identified. On calcination, the LaPO_4 transformed from hexagonal to monoclinic phase and zirconium hydroxide is converted to ZrO_2 . The tetragonal ZrO_2 phases are thus seen at 800 °C. The diffraction peaks indexed to (200), (120) and (012) represent crystal planes of monoclinic LaPO_4 appearing at 2θ values of 26°, 28° and 30° (jcpds file no. 35-0731) while the peaks indexed as (112) and (211) correspond to tetragonal ZrO_2 (jcpds file no. 80-0965). The XRD profile of composite at 1400 °C indicate a well crystallised pattern with the peaks for monoclinic LaPO_4 and tetragonal ZrO_2 . The tetragonal phase in ZrO_2 is stabilized by La^{3+} ions. La^{3+} ions replace Zr^{4+} ions and the subsequent strain in ZrO_2 impedes transformation of tetragonal to monoclinic ZrO_2 .²⁵ The pattern evidence 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 ZrO_2 peaks with increasing ZrO_2 content. Phase evolution in monolithic LaPO_4 is presented in Fig. S3 for comparison.

3.3 Densification studies

Plot of % theoretical density (TD) with ZrO_2 content at the respective sintering temperatures of the composites are presented in Fig. 3. LaPO_4 monoliths could be sintered (>98% TD) at $T \sim 1300$ °C while the composite samples required 1600 °C for all the four compositions to yield sintered density values greater than 95 % of TD. The LaPO_4 -10% ZrO_2 composite samples yielded sintered density of >98% TD, whereas samples with 5 and 15% ZrO_2 gave density values >95% TD. The decrease in density on the addition of ZrO_2 could be attributed to the delay in sintering due to the distribution of fine ZrO_2 particles at the grain boundaries of LaPO_4 as observed in the SEM micrographs discussed below.

The composite pellets after mirror polishing and thermal etching are observed under scanning electron microscope for the microstructural evaluation. Fig. 4 shows the SEM micrographs obtained for composite samples sintered at 1600 °C. The rod morphology of LaPO_4 observed in the composite precursor stages transform to regular shaped grains characteristic of sintered ceramics. Fig. S4 provides the microstructure of LaPO_4 at 1600 °C where sintered grains as

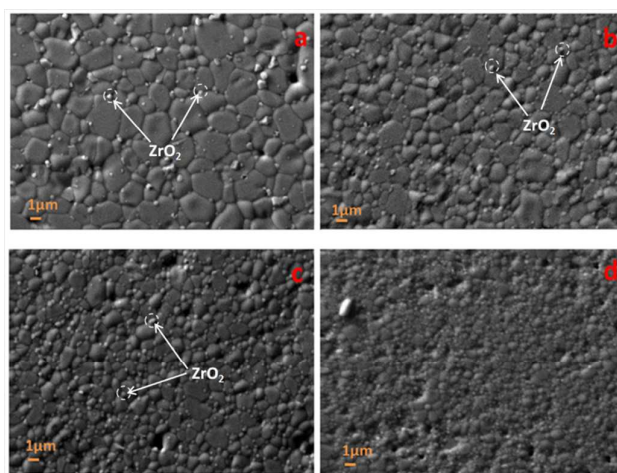


Fig. 4 SEM micrographs of LaPO_4 - ZrO_2 composites sintered at 1600 °C (a) LaPO_4 -5% ZrO_2 (b) LaPO_4 -10% ZrO_2 (c) LaPO_4 -15% ZrO_2 (d) LaPO_4 -20% ZrO_2 .

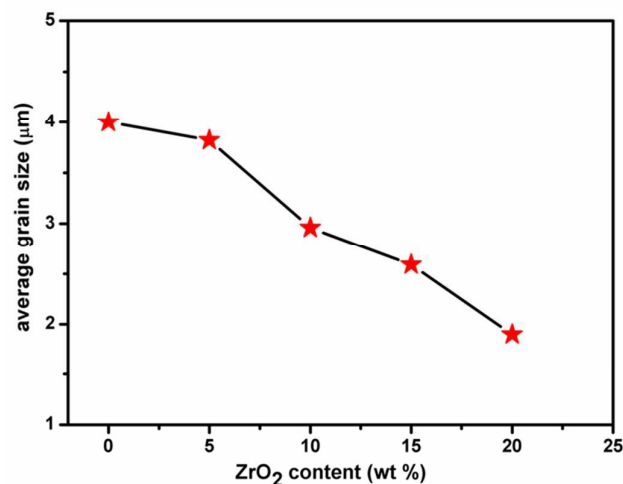


Fig. 5 Grain reduction pattern for 1600 °C calcined LaPO_4 and composites of varying ZrO_2 content.

large as 4 µm are formed. In the case of composites (Fig. 4 a-d) ultrafine zirconia particles are seen uniformly distributed along the grain boundaries.

As a result of such homogeneous distribution, the LaPO_4 grain size reduced considerably due to the addition of 5-20 wt% ZrO_2 , compared to pure LaPO_4 . With 20% ZrO_2 content, the grain size of LaPO_4 was inhibited to $\sim 50\%$, ending up with an average grain size of $\sim 1-2$ µm (Fig. 5). The distribution of ZrO_2 particles in the composite samples is evident from the micrographs obtained and the reduction in grain size of LaPO_4 with increasing ZrO_2 content is quantified in Fig. 5. ZrO_2 is well known to create Zener pinning²³ 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

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reaction between LaPO_4 and ZrO_2 phases and the homogeneous distribution of ultrafine ZrO_2 induced considerable grain growth inhibition²⁴ as has been observed earlier for ceramics like alumina. In this case, as the thermal expansion coefficient of ZrO_2 is higher than LaPO_4 , the presence of uniformly distributed ZrO_2 grains at the LaPO_4 grain boundaries provided grain growth pinning and the sintered grain sizes reduced considerably with increasing amount of ZrO_2 addition. The two phases coexisted and caused a reduction in the grain growth. In addition to this we believe the presence of La^{3+} could induce oxygen vacancies and strain in ZrO_2 crystals thus stabilizing tetragonal phase.²⁵ 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 behaviour 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 (LaPO_4 -10wt% ZrO_2) with respect to temperature is compared with that of monolithic LaPO_4 having same density (Fig 6). LaPO_4 monolith indicates a thermal conductivity value of 3.2 W/mK at 25 °C and show a decreasing trend with increase in temperature and is in accordance with published literature.¹⁸ In the composite samples, LaPO_4 -10wt% ZrO_2 showed low conductivity values of 2.1 W/mK and 1.4 W/mK at room temperature and at 200 °C respectively. LaPO_4 -20 wt% ZrO_2 nanocomposite displayed very low thermal conductivity value of 1 W/mK at 400 °C. These values are significantly lower than values reported for YSZ at higher temperatures. As indicated earlier (Fig 5) the grain size of LaPO_4 decrease with ZrO_2 addition.²⁶ Generally, for polycrystalline materials, the thermal conductivity is related to the phonon scattering generated by the grain boundaries. With increase in percentage of ZrO_2 , the grain size of the LaPO_4 - ZrO_2 nanocomposite decreased and consequently grain boundary area increased. Therefore, the decreasing thermal conductivity of nanocomposites was caused by increasing phonon scattering generated by lowering of grain size leading to an increase in the total grain boundary length²⁷.

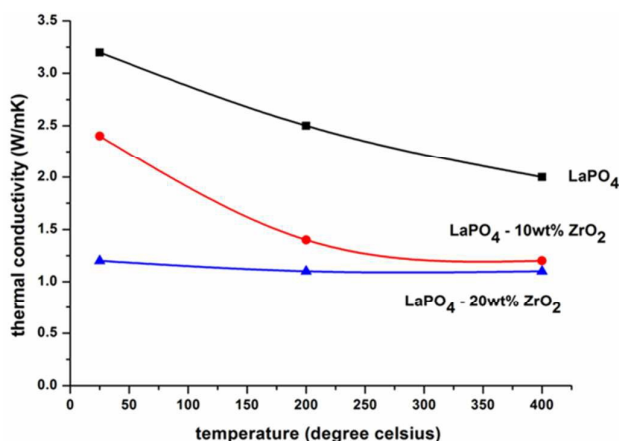


Fig. 6 Thermal conductivity values obtained for the samples with varying composition sintered at 1600 °C in the temperature range 25- 400 °C.

Conclusions

LaPO_4 based ZrO_2 composites (LaPO_4 - ZrO_2) are 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%), the LaPO_4 -10% ZrO_2 achieved >98% TD on sintering at 1600 °C. The stability of the composite at higher temperature is confirmed using phase identification and microstructural evaluation where in no reaction between the constituent phases is observed. Microstructural evaluation confirmed the excellent grain growth inhibition of LaPO_4 by the presence of ZrO_2 . Composite samples showed very low thermal conductivity values; LaPO_4 -10wt% ZrO_2 with >98% TD gave conductivity values of 2.1 W/mK and 1.4 W/mK at room temperature and at 200 °C respectively. This lower thermal conductivity, leading to excellent insulation property could help in the application of these materials in thermal insulation as well as in thermal barrier coatings.

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Space Centre, Thiruvananthapuram, India) are acknowledged for thermal conductivity measurements.

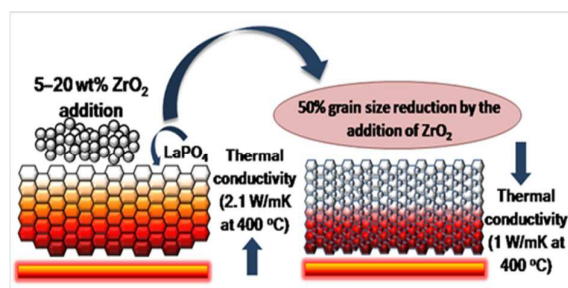
Notes and references

- 1 M. K. Cinibulk, G. E. Fair, and R. J. Kerans, *J. Am. Ceram. Soc.*, 2008, **91**, 2290; Y. Hikichi and T. Nomura, *J. Am. Ceram. Soc.*, 1987, **70**, 252.
- 2 A. Du, C. Wan, Z. Qu and W. Pan, *J. Am. Ceram. Soc.*, 2009, **92**, 2687.
- 3 H. Onoda, K. Tange, and I. Tanaka, *J. Mater. Sci.*, 2008, **43**, 5483.
- 4 Y. Hikichi, T. Ota and T. Hattori, *Miner. j.*, 1997, **19**, 3123.
- 5 S. S. Sujith, S. L. Arun Kumar, R. V. Mangalaraja, A. Peer Mohamed and S. Ananthakumar, *Ceram. Inter.*, 2014, **40**, 15121.
- 6 W. Pan, S. R. Phillpot, C. Wan, A. Chernatynskiy and Z. Qu, *Mater. Res. Bull.*, 2012, **37**, 917.
- 7 S. Sankar and K. G. Warriar, *J. Sol-Gel Sci. Technol.*, 2011, **58**, 195; S. Sankar, G. P. V. Prajeesh, V. N. Anupama, B. Krishnakumar, P. Hareesh, B. N. Nair, K. G. Warriar and U. S. Hareesh, *J. Hazard. Mater.*, 2014, **275**, 222
- 8 S. Sankar, B. N. Nair, T. Suzuki, G. M. Anilkumar, M. Padmanabhan, U. S. Hareesh and K. G. K. Warriar, *Sci. Rep.*, 2016, **6**, 22732.
- 9 D. B. Marshall, P. E. D. Morgan, R. M. Housley and J.T. Cheung, *J. Am. Ceram. Soc.*, 1998, **81**, 951.
- 10 E. E. Boakye, R. S. Hay, P. Mogilevsky and M. K. Cinibulk, *J. Am. Ceram. Soc.*, 2008, **91**, 17.
- 11 J. B. Davis, D. B. Marshall, P. E. D. Morgan, *J. Eur. Ceram. Soc.*, 2000, **20**, 583.
- 12 S. Sankar, A. N. Raj, C. K. Jyothi, K. G. K. Warriar and P. V. A. Padmanabhan, *Mater. Res. Bull.*, 2012, **47**, 1835.
- 13 K. Rajesh, K. V. Baiju, M. Jayasankar and K.G. Warriar, *J. Am. Ceram. Soc.*, 2008, **91**, 2415.
- 14 R. Wang, W. Pan, J. Chen, M. Jiang, Y. Luo and M. Fang, *Ceram. Inter.*, 2003, **29**, 19.
- 15 W. Qi, S. Chen, Y. Wu and K. Xie, *RSC Adv.*, 2015, **5**, 47599.
- 16 M. Liu, X. Qi, Z. Lv and Q. Meng, *Int. J. Hydrogen Energ.*, 2013, **38**, 1976; S. Park, J. M. Vohs and R. J. Gorte, *Nature*, 2000, **404**, 265.
- 17 V. Grover, R. Shukla and A. K. Tyagi, *Scr. Mater.*, 2007, **57**, 699.
- 18 W. Li, H. Huang, H. Li, W. Zhang and H. Liu, *Langmuir*, 2008, **24**, 835.
- 19 M. R. Winter and D. R. Clarke, *J. Am. Ceram. Soc.*, 2007, **90**, 533.
- 20 A. M. Limarga, S. Shian, M. Baram and D. R. Clarke, *Acta Mater.*, 2012, **60**, 5417.
- 21 X. Q. Cao, R. Vassen and D. Stoeber, *J. Eur. Ceram. Soc.*, 2004, **24**, 110.
- 22 N. P. Padture, M. Gell and E. H. Jordan, *Science*, 2002, **296**, 280.
- 23 D. Fan, L. Q. Chen and S. P. P. Chen, *J. Am. Ceram. Soc.*, 1998, **81**, 526.
- 24 K. Prasad, D. V. Pinjari, A. B. Pandit and S. T. Mhaske, *Ultrason. Sonochem.*, 2011, **18**, 1128.
- 25 X. Ren, S. Guo, M. Zhao and W. Pan, *J. Mater. Sci.*, 2014, **49**, 2243.
- 26 J. T. Lin and H. Y. Lu, *Ceram. Inter.*, 1988, **14**, 251-258.
- 27 S. H. Kima, Z. Y. Fub, K. Niiharac and S. W. Leea, *J. Ceram. Process. Res.*, 2011, **12**, 240.

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Ultrafine dispersions of ZrO₂ nano particles in LaPO₄ matrix create very low thermal conductive (1 W/mK) ceramics