Effects of Doping on Thermal Conductivity of Pyrochlore Oxides for Advanced Thermal Barrier Coatings

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Abstract
Pyrochlore oxides of general composition, \(\text{A}_2\text{B}_2\text{O}_7\), where \(\text{A}\) is a 3+ cation (La to Lu) and \(\text{B}\) is a 4+ cation (Zr, Hf, Ti, etc) have high melting point, relatively high coefficient of thermal expansion, and low thermal conductivity which make them suitable for applications as high-temperature thermal barrier coatings. The effect of doping at the A site on the thermal conductivity of a pyrochlore oxide \(\text{La}_2\text{Zr}_2\text{O}_7\), has been investigated. Oxide powders of various compositions \(\text{La}_2\text{Zr}_2\text{O}_7\), \(\text{La}_{1.7}\text{Gd}_{0.3}\text{Zr}_2\text{O}_7\), \(\text{La}_{1.7}\text{Yb}_{0.3}\text{Zr}_2\text{O}_7\) and \(\text{La}_{1.7}\text{Gd}_{0.15}\text{Yb}_{0.15}\text{Zr}_2\text{O}_7\) were synthesized by the citric acid sol-gel method. These powders were hot pressed into discs and used for thermal conductivity measurements using a steady-state laser heat flux test technique. The rare earth oxide doped pyrochlores \(\text{La}_{1.7}\text{Gd}_{0.3}\text{Zr}_2\text{O}_7\), \(\text{La}_{1.7}\text{Yb}_{0.3}\text{Zr}_2\text{O}_7\) and \(\text{La}_{1.7}\text{Gd}_{0.15}\text{Yb}_{0.15}\text{Zr}_2\text{O}_7\) had lower thermal conductivity than the un-doped \(\text{La}_2\text{Zr}_2\text{O}_7\). The \(\text{Gd}_2\text{O}_3\) and \(\text{Yb}_2\text{O}_3\) co-doped composition showed the lowest thermal conductivity.

Introduction
Higher operating temperatures of turbine engines result in lower fuel consumption, higher efficiency, and lower emissions. The base materials (super-alloys, Si-based ceramics, etc.) used for the hot-section components of turbine engines are limited in their upper use temperature by their physical, mechanical and corrosion characteristics. To further increase their operating temperature, thermal barrier coatings (TBCs) are applied as thin layers on their surfaces. The current state-of-the-art TBC material in commercial use is partially yttria-stabilized zirconia (YSZ) which is applied on engine components by plasma spraying or by electron-beam physical vapor deposition (EB-PVD). At temperatures higher than 1200 °C, the relatively porous YSZ layers are prone to sintering which increases thermal conductivity and makes them less effective. The sintered and densified coatings can also reduce thermal stress/strain tolerance, which can significantly reduce the coatings durability. To further increase the operating temperature of turbine engines, alternate TBC materials with lower thermal conductivity and better sintering resistance are needed (refs. 1 to 6).

Under NASA’s Ultra Efficient Engine Technology (UEET) program, advanced TBCs are being developed (refs. 7 to 9) to provide vital thermal protection for turbine engine hot-section components such as combustor liner, turbine blades, turbine vanes, etc. at gas temperatures exceeding 1650 °C (3000 °F) in harsh combustion environments. The new TBCs are required to have significantly increased phase stability, lower lattice and radiation thermal conductivity, and improved sintering and thermal stress resistance under the engine high-heat-flux and severe thermal cycling conditions. Pyrochlore oxides of general composition, \(\text{A}_2\text{B}_2\text{O}_7\), where \(\text{A}\) is a 3+ cation (La to Lu) and \(\text{B}\) is a 4+ cation (Zr, Hf, Ti, etc) are
one such class of ceramic materials. These oxides have high melting point, relatively high coefficient of thermal expansion, and low thermal conductivity which make them suitable for applications as high-temperature thermal barrier coatings. Samarium and europium zirconates are also being considered as candidate materials (ref. 1) for neutron absorption and control rod applications in nuclear reactors.

Recently, it has been reported (refs. 9 and 10) that co-doping of YSZ (4.6 mol% Y₂O₃) with one or more oxides (Yb₂O₃, Gd₂O₃, Nd₂O₃, Sm₂O₃, Er₂O₃, Sc₂O₃, NiO) results in lower thermal conductivity due to defect cluster formation. The primary objective of the present study was to devise approaches to further lower the thermal conductivity of pyrochlore oxide compounds. An oxide doping approach was used where part of cation A was substituted by other cations, e.g., A₁₋ₓMₓB₂O₇, (where x = 0 – 0.5 and M = rare earth or other cations) in the pyrochlore materials. The effects of co-doping at the pyrochlore A-site on thermal conductivity were also investigated.

Materials and Experimental Methods

Powder Synthesis

Sol-gel citric acid method was used for the powder synthesis of La₂Zr₂O₇ and its doped compounds. Details of powder processing are described elsewhere (ref. 11). Briefly speaking, stoichiometric amounts of La, Gd, and Yb nitrates, and zirconium oxide dinitrate (ZrO(NO₃))₂ were dissolved in water. Calculated amount of citric acid (HOC(CH₂COOH)₂COOH), about 1.2 to 3 mole per mole of metals in the nitrate solution, was separately dissolved in water. The metal nitrate solutions were gradually added to the boiling citric acid solution. A clear yellowish solution resulted depending on the composition of the metal nitrate mixtures. The resulting solutions were heated at ~110 °C for about 48 hr to evaporate water and resulting in the formation of clear orange gels. On further heat treatment, the gels turned into yellowish foams. The resulting foams were slowly heated (1 °C/min) to 350 °C and held for 5 to 8 hr to remove volatile organic compounds. The resulting brown porous materials were amorphous zirconates and some charred organic material. The foams were grinded into powder and further calcined at 800 °C for 5 to 8 hr to burn off residual carbon. The resulting powders were found to be partially crystalline zirconates from x-ray diffraction.

Hot Pressing

For thermal conductivity measurements, ~10 g of the above powder was unidirectionally hot-pressed using a 25.4 mm diameter graphite die at 1600 °C and 27.6 MPa (4 ksi) pressure for 4 hr in vacuum to produce 2- to 3-mm-thick disks. Spray dried La₂Zr₂O₇ powders from commercial source were also hot pressed into disks. The hot pressed discs were heat treated for 8 hr at 800 °C in air for oxidation of the surface carbon layer deposited on the samples during hot pressing.

X-ray Diffraction and Density

X-ray diffraction (XRD) analysis was carried out on hot pressed specimens for crystalline phase identification. XRD patterns were recorded at room temperature using a step scan procedure (0.02°/20 step, time per step 0.5 or 1 s) in the 2θ range 10 to 70° on a Philips ADP–3600 automated diffractometer equipped with a crystal monochromator employing Cu Kα radiation. Physical densities of hot pressed discs were determined from weight and volume of each specimen.

Thermal Conductivity Testing

One inch diameter (25.4 mm) hot pressed discs of sol-gel derived powders were used for thermal conductivity measurements. Thermal conductivity testing of the ceramic materials was carried out using a 3.5 kW CO₂ laser (wavelength 10.6 μm) high-heat flux rig. A schematic diagram of the test rig is shown in figure 1. Photos of the actual test facilities and the general test approach have been described elsewhere.
In this steady-state laser heat flux test method, the specimen surface was heated by a laser beam, and backside air-cooling was used to maintain the desired temperature. A uniform laser heat flux was obtained over the 23.9 mm diameter aperture region of the specimen surface by using an integrating ZnSe lens combined with the specimen rotation. Platinum wire flat coils (wire diameter 0.38 mm) were used to form thin air gaps between the top aluminum aperture plate and stainless-steel back plate to minimize the specimen heat losses through the fixture.

Thermal conductivity \( k_{\text{ceramic}} \) of ceramic materials can be determined from the pass-through heat flux \( q_{\text{thru}} \) and measured temperature difference \( \Delta T_{\text{ceramic}} \) across the ceramic specimen thickness \( l_{\text{ceramic}} \) under the steady-state laser heating conditions

\[
k_{\text{ceramic}} = \frac{q_{\text{thru}}}{\Delta T_{\text{ceramic}}} \cdot l_{\text{ceramic}}
\]  

(1)

The actual pass-through heat flux \( q_{\text{thru}} \) for a given ceramic specimen was obtained by subtracting the laser reflection loss (measured by a 10.6 \( \mu \)m reflectometer) and the calculated radiation heat loss (total emissivity was taken as 0.50 for the oxides) at the ceramic surface from the laser delivered heat flux (i.e., \( q_{\text{thru}} = q_{\text{delivered}} - q_{\text{reflected}} - q_{\text{radiated}} \)). Note that the non-reflected laser energy (approx. 97 percent of the total delivered laser energy) is absorbed at or near the specimen surfaces because of the quite high emissivity at the 10.6 \( \mu \)m laser wavelength region for the oxides. For the hot pressed bulk specimens, the temperature difference \( \Delta T_{\text{ceramic}} \) in the ceramic was directly measured by using two 8 \( \mu \)m pyrometers at both specimen front heating and back side air cooling surfaces.

**Results and Discussion**

Densities of hot pressed specimens of various compositions are given in table I. The hot pressed pyrochlore oxides had high density and low porosity due to the small particle size of the sol-gel derived...
powders used. X-ray diffraction patterns from the hot pressed specimens of pyrochlore oxides of various compositions are shown in figure 2. La₂Zr₂O₇ (pyrochlore A₂B₂O₇ structure) was the only phase present in each sample. Figure 3 shows thermal conductivity of La₂Zr₂O₇ (pyrochlore A₂B₂O₇ structure) hot-pressed specimens as a function of surface test temperature. The La₂Zr₂O₇ specimens had low porosity due to the small particle sizes of La₂Zr₂O₇ powder used. In particular, the specimens fabricated with the sol-gel derived powder achieved the theoretical density. These high density, low porosity La₂Zr₂O₇ specimens showed significant thermal conductivity increases starting at 900 °C because of the increased radiation contribution with increasing temperature. The small amount of micro-porosity in the spray-dried powder processed specimen did not affect the lattice thermal conductivity dramatically. However, the micro-porosity in the specimen significantly reduced the radiation conductivity as compared to the almost pore-free, sol-gel powder processed specimens. The conductivity increased by more than 100 percent for the very dense specimens because of the increased radiation heat-transfer under thermal gradient conditions. Figure 4 shows the thermal conductivity of hot-pressed specimens of La₂Zr₂O₇, La₁.₇Gd₀.₃Zr₂O₇, La₁.₇Yb₀.₃Zr₂O₇ and La₁.₇Gd₀.₁₅Yb₀.₁₅Zr₂O₇ as a function of surface test temperature. It may be seen that thermal conductivity decreases with increase in temperature up to ~950 °C and thereafter increases at higher temperatures. Similar behavior has been observed (ref. 1) for thermal conductivity of samarium and europium zirconates. The decrease in thermal conductivity up to ~950 °C may be assigned to lattice thermal conduction. Significant thermal conductivity increases starting at ~950 °C for these specimens may be attributed to the increased contribution of the radiative component of heat conduction, also known as photon thermal conductivity, with increasing temperature. The conductivity can increase by more than 100 percent for the very dense specimens because of the increased radiation heat-transfer under thermal gradient conditions. Figure 4 shows that the rare earth oxide doped pyrochlores La₁.₇Gd₀.₃Zr₂O₇, La₁.₇Yb₀.₃Zr₂O₇ and La₁.₇Gd₀.₁₅Yb₀.₁₅Zr₂O₇ had lower thermal conductivity than the un-doped La₂Zr₂O₇. The Gd₂O₃ and Yb₂O₃ co-doped materials showed the lowest thermal conductivity. Thermal conductivity of material co-doped with (Gd + Yb) is ~30 percent lower than that of undoped oxide. These results clearly demonstrate that thermal conductivity of pyrochlore oxides can be greatly reduced by doping and specially through co-doping with other cations. Doping (ref. 4) of lanthanum zirconate with trivalent rare-earth elements Nd, Eu, Dy, and Gd resulted in similar reduction in thermal conductivity.

<table>
<thead>
<tr>
<th>Pyrochlore, A₂B₂O₇</th>
<th>Density, g/cm³</th>
<th>Crystalline phase from XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>La₂Zr₂O₇</td>
<td>5.72</td>
<td>La₂Zr₂O₇</td>
</tr>
<tr>
<td>La₁.₇Gd₀.₃Zr₂O₇</td>
<td>5.71</td>
<td>La₂Zr₂O₇</td>
</tr>
<tr>
<td>La₁.₇Yb₀.₃Zr₂O₇</td>
<td>5.74</td>
<td>La₂Zr₂O₇</td>
</tr>
<tr>
<td>La₁.₇Gd₀.₁₅Yb₀.₁₅Zr₂O₇</td>
<td>5.72</td>
<td>La₂Zr₂O₇</td>
</tr>
</tbody>
</table>

Thus, doping or co-doping with one or more cations at the A sites in A₂B₂O₇ pyrochlores, such as La₂Zr₂O₇, results in lower thermal conductivity. These ceramic materials have great potential as thermal barrier coatings at much higher temperatures than the state-of-the-art partially yttria-stabilized zirconia. These TBCs would result in greater reduction in temperature across the coating which would translate to higher operating temperatures of turbine engines with lower fuel consumption, higher efficiency, and lower emissions. Thermal barrier coatings using doped pyrochlore oxides would be plasma sprayed and characterized. The results of these investigations would be reported in the future.
Figure 2.—X-ray diffraction patterns pyrochlore oxides specimens of various compositions La$_2$Zr$_2$O$_7$, La$_{1.7}$Gd$_{0.3}$Zr$_2$O$_7$, La$_{1.7}$Yb$_{0.3}$Zr$_2$O$_7$, and La$_{1.7}$Gd$_{0.15}$Yb$_{0.15}$Zr$_2$O$_7$, made by hot-pressing of sol-gel derived powders.

Figure 3.—Thermal conductivity of dense La$_2$Zr$_2$O$_7$ type hot-pressed specimens as a function of surface test temperature. The thermal conductivity can increase by more than 100 percent at high temperature for the very dense, sol-gel powder processed specimens because of the increased radiation heat-transfer under thermal gradient conditions.
Summary and Conclusions

Pyrochlore oxide powders of various compositions were synthesized by sol-gel process and hot pressed into 2.54 cm diameter discs. Thermal conductivity was measured up to ~1500 °C using a steady-state laser heat flux test method. Doping with rare earth cations at the A sites in La$_2$Zr$_2$O$_7$ (A$_2$B$_2$O$_7$) pyrochlore greatly reduced the thermal conductivity. The modified pyrochlores compositions would be useful as thermal barrier coating materials at much higher temperatures than state-of-the-art partially yttria-stabilized zirconia.

References


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Pyrochlore oxides of general composition, A₂B₂O₇, where A is a 3+ cation (La to Lu) and B is a 4+ cation (Zr, Hf, Ti, etc.) have high melting point, relatively high coefficient of thermal expansion, and low thermal conductivity which make them suitable for applications as high-temperature thermal barrier coatings. The effect of doping at the A site on the thermal conductivity of a pyrochlore oxide La₂Zr₂O₇, has been investigated. Oxide powders of various compositions La₂Zr₂O₇, La₁.₇Gd₀.₃Zr₂O₇, La₁.₇Yb₀.₃Zr₂O₇ and La₁.₇Gd₀.₁₅Yb₀.₁₅Zr₂O₇ were synthesized by the citric acid sol-gel method. These powders were hot pressed into discs and used for thermal conductivity measurements using a steady-state laser heat flux test technique. The rare earth oxide doped pyrochlores La₁.₇Gd₀.₃Zr₂O₇, La₁.₇Yb₀.₃Zr₂O₇ and La₁.₇Gd₀.₁₅Yb₀.₁₅Zr₂O₇, had lower thermal conductivity than the un-doped La₂Zr₂O₇. The Gd₂O₃ and Yb₂O₃ co-doped composition showed the lowest thermal conductivity.