Low-Thermal-Conductivity Pyrochlore Oxide Materials Developed for Advanced Thermal Barrier Coatings

When turbine engines operate at higher temperatures, they consume less fuel, have higher efficiencies, and have lower emissions. The upper-use temperatures of the base materials (superalloys, silicon-based ceramics, etc.) used for the hot-section components of turbine engines are limited by the physical, mechanical, and corrosion characteristics of these materials. Thermal barrier coatings (TBCs) are applied as thin layers on the surfaces of these materials to further increase the operating temperatures. 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. At temperatures higher than 1000 °C, 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 and strain tolerance, which can reduce the coating’s durability significantly. Alternate TBC materials with lower thermal conductivity and better sintering resistance are needed to further increase the operating temperature of turbine engines.

Under NASA’s Ultra Efficient Engine Technology (UEET) Project, advanced TBCs are being developed to provide vital thermal protection for turbine engine hot-section components, such as combustor liners, turbine blades, and turbine vanes at gas temperatures exceeding 1650 °C (3000 °F) in harsh combustion environments. The new TBCs must 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, \( A_2B_2O_7 \), where \( A \) is a 3+ cation (lanthanum to lutetium) and \( B \) is a 4+ cation (zirconium, hafnium, titanium, etc.), are one such class of ceramic materials. These oxides have a high melting point, a relatively high coefficient of thermal expansion, and low thermal conductivity, which make them suitable for applications as high-temperature thermal barrier coatings. The primary objective of this study at the NASA Glenn Research Center 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., \( A_{1-x}M_xB_2O_7 \), where \( x = 0 – 0.5 \) and \( M = \) rare earth or other cations) in the pyrochlore materials.

Powders of various compositions were synthesized by the sol-gel method and hot pressed into dense 1-in.-diameter disks. The thermal conductivity of these disks was measured at temperatures up to 1550 °C using a steady-state laser-heat-flux technique. As an example, results for \( La_{2-x}M_xZr_2O_7 \) systems (where \( M = \) gadolinium (Gd), ytterbium (Yb), or Gd + Yb) are shown in the graph. The rare-earth-oxide-doped pyrochlores \( (La,Gd)_2Zr_2O_7 \), \( (La,Yb)_2Zr_2O_7 \), and \( (La,Gd,Yb)_2Zr_2O_7 \) have lower thermal conductivity than the undoped \( La_2Zr_2O_7 \). The thermal conductivity of material codoped with Gd + Yb is ~30 percent lower.
lower than that of the undoped oxide. These results clearly demonstrate that the thermal conductivity of pyrochlore oxides can be reduced greatly by doping, especially through codoping with other cations.

Thermal conductivity as a function of surface test temperature of hot-pressed doped and undoped La$_2$Zr$_2$O$_7$. The rare-earth-doped and codoped pyrochlore oxides showed lower thermal conductivity than the undoped La$_2$Zr$_2$O$_7$.

Thus, doping or codoping with one or more cations at the A sites in A$_2$B$_2$O$_7$ pyrochlores, such as La$_2$Zr$_2$O$_7$, results in lower thermal conductivity. These ceramic materials have great potential as TBCs at much higher temperatures than with the state-of-the-art YSZ zirconia. These new TBCs would greatly reduce the temperature across the coating, which would translate to turbine engines with higher operating temperatures, lower fuel consumption, higher efficiency, and lower emissions.

**Bibliography**


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