NOTE

Effect of co-doping with calcium and transition metals on the infrared emissivity of $\text{La}_2(\text{Zr}_{0.7}\text{Ce}_{0.3})_2\text{O}_7$ ceramics for high-temperature thermal protection applications

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The $\text{La}_2(\text{Zr}_{0.7}\text{Ce}_{0.3})_2\text{O}_7$ (LZ7C3) ceramics co-doped with Ca^{2+} and different transition metal cations (Fe^{3+} , Cr^{3+}) were fabricated by the pressureless-sintering method. The influence of doping on the phase structure, microstructure and infrared emissivity (0.75–2.5, 3–5, 8–14 μm) was investigated. The infrared emissivity of LZ7C3 in the wavelength range 0.75–2.5 and 3–5 μm was significantly enhanced by co-doping, especially with Ca^{2+} and Cr^{3+} . The infrared emissivity in the wavelength range 0.75–2.5 μm could be improved from 0.069 (LZ7C3) to 0.876 at room temperature, and from 0.463 (LZ7C3) to 0.877 in 3–5 μm at 300 °C, by co-doping with Ca^{2+} and Cr^{3+} . On the other hand, doping had an insignificant effect on the infrared emissivity of LZ7C3 in the 8–14 μm range at 300 °C due to its high emissivity value (0.962) in the 8–14 μm range.

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Hypersonic vehicles have undergone rapid development in recent years. Metal materials such as superalloys have been widely used in the hypersonic vehicles due to their unique advantages such as inherent ductility, design flexibility and low maintenance cost.^{1,2)} However, hypersonic vehicles encounter severe aerodynamic heat during the course of service, where the service temperature can reach 1000 °C or above, thus, resulting in deterioration of the mechanical properties of the metal materials.³⁾ Therefore, it is important to reduce the surface temperature through appropriate methodologies, such as thermal barrier coatings (TBCs) and thermal radiation coatings.^{1)–5)}

TBCs with low thermal conductivity have been widely used for protecting the thermal section components of the advanced turbine engines and hypersonic flight vehicles to improve their thermal resistance and durability.^{3,4)} High infrared radiation coating can effectively dissipate the

surface heat of the aircrafts. Van Wei et al. found that the surfaces with an infrared emissivity of 0.5 and 1.0 at a speed of Mach 7 and a pressure of 0.24 atm have a temperature of 1500 and 1300 °C, respectively.⁵⁾ According to the Wien's displacement law and Blackbody radiation law, for the blackbody temperature of 1000 °C, 97% of the electromagnetic energy emitted by a blackbody in thermal equilibrium is below 14 μm , and 76% is below 5 μm .⁶⁾

In recent years, many research studies have been carried out for improving the infrared radiation performance of the ceramic materials with low thermal conductivity, such as $\text{LaMgAl}_{11}\text{O}_{19}$,⁷⁾ $\text{Ln}_2\text{Zr}_2\text{O}_7$,²⁾ $\text{Ln}_2\text{Hf}_2\text{O}_7$,³⁾ LaAlO_3 ⁸⁾ and HfO_2 .⁵⁾ $\text{La}_2(\text{Zr}_{0.7}\text{Ce}_{0.3})_2\text{O}_7$ (LZ7C3) with pyrochlore and fluorite structures has attracted significant attention of the researchers because of its excellent comprehensive performance.^{9)–15)} The plasma sprayed coating shows a better sintering-resistance compared to $\text{LaMgAl}_{11}\text{O}_{19}$ and 8YSZ at high temperature, with no shrinkage even after calcination at 1400 °C for 15 h.¹⁴⁾ The linear thermal expansion coefficient of LZ7C3 is about $10.66 \times 10^{-6} \text{ K}^{-1}$, similar to that of 8YSZ. The thermal conductivity of LZ7C3 is $0.87 \text{ W} \cdot \text{m}^{-1} \text{ K}^{-1}$, lower than that of 8YSZ and $\text{La}_2\text{Zr}_2\text{O}_7$.¹⁵⁾

The ceramics with pyrochlore structure, such as $\text{Sm}_2\text{Zr}_2\text{O}_7$, have been reported to have high infrared radiation performance by transition metal cation doping.²⁾ The

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ceramics with fluorite structure with same oxygen vacancy as pyrochlore structure, such as $\text{Sm}_2\text{Hf}_2\text{O}_7$,³⁾ have also been observed to exhibit high infrared radiation performance by transition metal cation doping. LZ7C3 with both pyrochlore and fluorite structures has the potential to demonstrate high radiation performance by appropriate ion doping.

In this study, LZ7C3 ceramics co-doped with Ca^{2+} and different transition metal cations (Fe^{3+} , Cr^{3+}) were fabricated by the pressureless sintering method, and the influence of different co-doping ions on their phase, microstructure and infrared radiation performance in near- and mid-infrared regions (0.75–2.5, 3–5, 8–14 μm) was studied.

In the present study, high purity ($\geq 99.99\%$) La_2O_3 , ZrO_2 , CeO_2 , CaO , Fe_2O_3 and Cr_2O_3 with particle size of 500 nm were used as raw materials. Firstly, the raw powders were heat-treated at 1000 °C for 2 h in a box furnace before weighing. Subsequently, for each composition, the weighed powders were mixed by using a planetary mill with zirconia balls in alcohol for 6 h, followed by rotary drying to obtain uniform powder samples. The dried powder mixtures were subsequently compacted into $\varnothing 40$ mm disks under uniaxial pressure of 30 MPa followed by the cold isostatic pressing at 250 MPa. Finally, the bulk materials were pressureless-sintered into samples about 5 mm thick at 1550 °C for 10 h in air.

The phase structure of the as-synthesized ceramics was characterized by X-ray diffraction (XRD) using a STOFDARMSTADT STOE/2 X-ray diffractometer operating at a current and voltage of 40 mA and 40 kV respectively. The microstructure of the samples was observed using a HitachRegulus8100 Scanning Electron Microscope (SEM) at an operating voltage of 20 kV. The near-infrared optical absorption spectra of the samples were obtained by the reflection method using a ultraviolet visible near infrared (UV–VIS–NIR) spectrometer (Lambda 950, PerkinElmer, America) equipped with an internal integrating sphere at room temperature. The infrared emissivity in the wavelength ranges 3–5 and 8–14 μm at 300 °C was directly determined using a reflection method by employing a dual-band IR emissivity meter (IR-2, Shanghai Institute of Technological Physics, China). Surfaces for all measurements were as-synthesized without artificial processing.

The XRD patterns of LZ7C3, $\text{La}_{1.9}\text{Ca}_{0.1}(\text{Zr}_{0.7}\text{Ce}_{0.3})_{1.9}\text{Fe}_{0.1}\text{O}_{6.9}$ (LZ7C3Fe) and $\text{La}_{1.9}\text{Ca}_{0.1}(\text{Zr}_{0.7}\text{Ce}_{0.3})_{1.9}\text{Cr}_{0.1}\text{O}_{6.9}$ (LZ7C3Cr) ceramics are shown in Fig. 1. As can be observed, LZ7C3 and LZ7C3Fe display a mixture of pyrochlore and fluorite structures. Compared with LZ7C3, LZ7C3Fe has a weaker fluorite peak which indicates a lower extent of the fluorite phase. Instead, LZ7C3Cr ceramic displays a single pyrochlore structure.

Figure 2 shows the SEM micrographs and images of the as-synthesized ceramics. As shown in Fig. 2(a), the microstructure of LZ7C3 shows numerous pores due to the low sintering temperature. However, the microstructures of LZ7C3Fe [Figs. 2(c) and 2(d)] and LZ7C3Cr [Figs. 2(e)

Fig. 1. XRD patterns of as-synthesized ceramics: (a) LZ7C3; (b) LZ7C3Fe; (c) LZ7C3Cr.

and 2(f)] display a dense structure. Obviously, the ion-doping ceramics are easier to sinter than LZ7C3 owing to the doping ions acting as sintering aid.¹⁶⁾

According to the Kirchhoff's law, the high emissivity corresponds to the high absorptivity.³⁾ Figure 3 shows the near-infrared absorptivity of the as-synthesized ceramics. The near-infrared absorptivity is noted to be significantly enhanced by co-doping with Ca^{2+} and transition metal cations (Fe^{3+} , Cr^{3+}) from 0.069 (LZ7C3) to 0.619 (LZ7C3Fe) and 0.876 (LZ7C3Cr). In addition, LZ7C3Cr has a higher absorptivity than LZ7C3Fe. The 3d orbit of Fe^{3+} , Cr^{3+} in the octahedral coordination generally split and produce d-d transitions, and the absorption generated by the d-d transitions of Fe^{3+} and Fe^{4+} as well as Cr^{3+} and Cr^{4+} generally corresponds to the visible range, verified by the evident increase in the spectral absorption in the 200–800 nm range, as shown in Fig. 4.⁸⁾

According to the UV–Vis absorption spectra, the band gap energy E_g of the samples can be empirically determined by the relation $(\alpha h\nu)^2 = A(h\nu - E_g)$,^{17),18)} where α is the absorbance of the sample, A is the constant related to the material, h is the Planck's constant, and ν is the photon frequency. Figure 5 shows the relationship of $h\nu$ and $(\alpha h\nu)^2$. In case Ca^{2+} and the transition metal cations (Fe^{3+} , Cr^{3+}) were co-doped in LZ7C3, the Ca^{2+} ions would occupy A site of La^{3+} , and the transition metal cations (Fe^{3+} , Cr^{3+}) at B site would transform to the tetravalent ions (Fe^{4+} , Cr^{4+}) by electron transition in this case (high oxygen pressure) for charge compensation.^{17),18)} Thus, the concentration of the tetravalent ions (Fe^{4+} , Cr^{4+}) in the samples was increased by co-doping with Ca^{2+} and the transition metal cations (Fe^{3+} , Cr^{3+}). It consequently resulted in the introduction of the impurity energy level and a decrease in the band gap energy E_g from 2.512 eV (LZ7C3) to 1.750 eV (LZ7C3Fe) and 1.651 eV (LZ7C3Cr), as seen in Fig. 5. The observed phenomenon could increase the concentration of the free carriers, thus, resulting in enhanced free carrier absorption.^{17),18)} Cr^{3+} was more effective than Fe^{3+} in decreasing the band gap energy E_g ,

Fig. 2. SEM images and photographs of the as-synthesized ceramics: (a, b) LZ7C3; (c, d) LZ7C3Fe; (e, f) LZ7C3Cr.

Fig. 3. Near-infrared emissivity of the as-synthesized ceramics.

Fig. 4. The UV-VIS absorptivity spectra of the as-synthesized ceramics.

resulting in more free carriers and superior near-infrared emissivity property.

The free carrier absorption as well as lattice absorption contribute mainly to the absorptivity of the material in the wavelength ranges 1–6 and 6–15 μm , respectively.³⁾ The near-infrared emissivity (0.75–2.5 μm) was significantly enhanced by co-doping with Ca^{2+} and the transition metal cations (Fe^{3+} , Cr^{3+}), as studied above. With same emis-

sivity mechanism as 0.75–2.5 μm , the emissivity for 3–5 μm range was also significantly enhanced from 0.463 (LZ7C3) to 0.660 (LZ7C3Fe) and 0.877 (LZ7C3Cr) at 300 $^{\circ}\text{C}$, as seen in **Table 1**. Instead, doping had an insignificant effect on the infrared emissivity of LZ7C3 in the wavelength range of 8–14 μm at 300 $^{\circ}\text{C}$, which might be attributed to the high emissivity value of LZ7C3 (0.962) in the 8–14 μm range.

Fig. 5. Plots of $(\alpha h\nu)^2$ versus photo energy ($h\nu$) for calculation of band gap of the as-synthesized ceramics.

Table 1. The infrared emissivity of LZ7C3, LZ7C3Fe and LZ7C3Cr in the wavelength range of 3–5 and 8–14 μm at 300 $^\circ\text{C}$

Samples	3–5 μm	8–14 μm
LZ7C3	0.463	0.962
LZ7C3Fe	0.660	0.950
LZ7C3Cr	0.877	0.971

In summary, LZ7C3 ceramics co-doped with Ca^{2+} and different transition metal cations (Fe^{3+} , Cr^{3+}) were fabricated by the pressureless-sintering method. LZ7C3 and LZ7C3Fe exhibited a mixture of pyrochlore and fluorite structures, whereas LZ7C3Cr ceramic displayed a single pyrochlore structure. The infrared emissivity of LZ7C3 in the wavelength range 0.75–2.5 and 3–5 μm was significantly enhanced by co-doping, especially with Ca^{2+} and Cr^{3+} . The infrared emissivity in the wavelength range 0.75–2.5 μm could be improved from 0.069 (LZ7C3) to 0.876 at room temperature, and from 0.463 (LZ7C3) to 0.877 in 3–5 μm at 300 $^\circ\text{C}$, by co-doping with Ca^{2+} and Cr^{3+} . On the other hand, doping had an insignificant effect

on the infrared emissivity of LZ7C3 in the wavelength range of 8–14 μm at 300 $^\circ\text{C}$ owing to its high emissivity value (0.962).

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