

# Influence of $Er^{3+}$ doping on the mechanical and thermophysical properties of $(Er_x Y_{1-x})_3 Al_5 O_{12}$ ceramics

Xuanli Wang<sup>1,2</sup>, Jinxin Xing<sup>1</sup>, Min Xie<sup>1</sup>, Rende Mu<sup>3</sup>, Xiwen Song<sup>1,\*</sup>

<sup>1</sup>Inner Mongolia Key Laboratory of Advanced Ceramics and Device, School of Materials and Metallurgy, Inner Mongolia University of Science and Technology, Baotou 014010, China

<sup>2</sup>Collaborative Innovation Center of Integrated Exploitation of Bayan Obo Multi-Metal Resources, Inner Mongolia University of Science and Technology, Baotou 014010, China

<sup>3</sup>Key Laboratory of Advanced Corrosion and Protection for Aviation Materials, Beijing Institute of Aeronautical Materials, Aero Engine Corporation of China, Beijing 100095, China

Received 14 August 2022; Received in revised form 16 October 2022; Accepted 20 December 2022

# Abstract

In this work,  $Er^{3+}$  was selected to replace  $Y^{3+}$  in the yttrium aluminium garnet (YAG) in order to improve its mechanical and thermophysical properties. A series of  $(Er_xY_{1-x})_3Al_5O_{12}$  (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0) ceramics were prepared by solid-state synthesis method at 1000 °C and finally sintered at 1600 °C for 5 h. The microstructure and morphology of the prepared ceramics were investigated. The results showed that all  $Er^{3+}$  doped  $Y_3Al_5O_{12}$  ceramics exhibited single garnet-type YAG phase and good compactness. With the increase of  $Er^{3+}$  doping concentration, the thermal conductivity of the  $(Er_xY_{1-x})_3Al_5O_{12}$  ceramics decreased slowly and then increased subsequently. Among the investigated specimens, the  $(Er_{0.7}Y_{0.3})_3Al_5O_{12}$  had the lowest thermal conductivity (1.51 W/m·K, at 1000 °C), which was about 28% lower than that of the pure YAG (2.1 W/m·K, at 1000 °C). As the  $Er^{3+}$  doping concentration increased, the thermal expansion coefficient of the  $(Er_xY_{1-x})_3Al_5O_{12}$  ceramics hardly changed, remaining around 9.08 × 10<sup>-6</sup> K<sup>-1</sup> at 1200 °C. Moreover, when the  $Er^{3+}$  doping concentration exceeded 0.5, the mechanical properties of the  $(Er_xY_{1-x})_3Al_5O_{12}$  ceramics increased suddenly. Specifically, the hardness increased from 14.28 to 16.53 GPa and the bending strength increased from 231.74 to 324.49 MPa.

*Keywords:* thermal barrier coating,  $Y_3Al_5O_{12}$ ,  $Er^{3+}$  doping, mechanical and thermophysical properties

# I. Introduction

Thermal barrier coatings (TBCs) are a high efficiency blade cooling technology which has been generally applied to the hot sections of turbine engines to segregate the underlying metallic substrate material from oxidation and corrosion at high temperatures [1–3]. Yttrium stabilized zirconia (6–8 wt.% YSZ), with low thermal conductivity and high thermal expansion coefficient, is the most widely used TBCs material [4,5]. However, YSZ cannot adapt to the demands of advanced turbine engines above 1200 °C because of the phase transformation, high-temperature sintering and thermal oxide growth [6–8]. Therefore, the development of new thermal barrier coatings with superior durability above 1200 °C is imperative for the application of turbine engines.

Yttrium aluminium garnet ( $Y_3Al_5O_{12}$ , YAG) has superior high temperature stability, excellent sintering resistance and extremely low oxygen ion transmittance, which is considered as a promising candidate for TBCs [9,10]. However, the relatively high thermal conductivity of YAG has become the basic bottleneck for its further application [11]. Currently, the most common method for reducing the thermal conductivity of YAG is the introduction of point defects by doping modification [12–15]. On the basis of YAG crystal structure,  $Al^{3+}$  lattice sites can hardly be replaced by rare earth ions (RE<sup>3+</sup>) due to the relatively large difference in ionic radius between  $Al^{3+}$  and RE<sup>3+</sup>. Nevertheless, the dodec-

<sup>\*</sup>Corresponding author: tel: +86 13947280993

e-mail: xiwensong@126.com

ahedral  $Y^{3+}$  lattice sites can be replaced by a certain number of trivalent rare earth ions to reduce the thermal conductivity since they have similar ionic radius. For example, Xue *et al.* [16,17] selected Gd<sup>3+</sup> with larger ionic radius to partially replace the Y<sup>3+</sup> in YAG. It was found that with the increase of Gd<sup>3+</sup> doping concentration, the thermal conductivity of  $(Y_{1-x}Gd_x)_3Al_5O_{12}$  first decreased and then increased. The  $(Y_{0.8}Gd_{0.2})_3Al_5O_{12}$  ceramics exhibited the lowest thermal conductivity, which was about 1.51 W/m·K at 1200 °C. At the same time, they also selected Yb<sup>3+</sup> with smaller ionic radius to dope YAG. It was found that when the Yb<sup>3+</sup> doping concentration equalled to 0.3, the  $(Y_{0.7}Yb_{0.3})_3Al_5O_{12}$  ceramics had the lowest thermal conductivity, which was about 1.62 W/m·K at 1000 °C.

In order to obtain lower high-temperature thermal conductivity, higher thermal expansion coefficient and excellent mechanical properties, in this work  $Er^{3+}$  with similar ionic radius was selected to replace  $Y^{3+}$  at dodecahedral lattice sites of YAG and prepare ( $Er_x Y_{1-x}$ )\_3Al\_5O\_{12} (Er-YAG) ceramics. A series of ( $Er_x Y_{1-x}$ )\_3Al\_5O\_{12} (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0) ceramics was prepared by solid-state synthesis method at 1000 °C and finally sintered at 1600 °C for 5 h. The effects of  $Er^{3+}$  doping concentration on the phase composition and microstructure of the prepared ceramics were investigated. In addition, the thermophysical properties at high temperature and the mechanical properties of ( $Er_x Y_{1-x}$ )\_3Al\_5O\_{12} ceramics were also discussed systematically.

# **II. Experimental**

#### 2.1. Preparation

 $(\text{Er}_{x}\text{Y}_{1-x})_{3}\text{Al}_{5}\text{O}_{12}$  (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0) powders were prepared through a solid-state synthesis method. Er<sub>2</sub>O<sub>3</sub> (HangZhou WanJing Co. Ltd, AR Grade, purity  $\geq 99.99\%$ ), Y<sub>2</sub>O<sub>3</sub> (ShangHai YueKai Co. Ltd., AR Grade, purity  $\geq$ 99.99%) and Al(OH)<sub>3</sub> (Feng-Fan Chemical Co. Ltd, AR Grade, purity ≥99.99%) powders were used as raw materials, which were calcined at 600 °C for 3 h to remove adsorbed water and carbon dioxide before weighing. The appropriate amounts of individual oxides were added in ethanol and mechanically milled for 24 h. After ball milling, the powders were further ground on the grinding machine. Then, the powders were calcined at 1000 °C for 3 h in air atmosphere. The calcined powders were put into the ball mill tank again for secondary ball milling. After ball milling, the powders were ground again on the grinding machine. The obtained powders were dry-pressed at 8 MPa and isostatically cold pressed at 200 MPa to form bulk samples which were then sintered at 1600 °C for 5 h in the air to produce ceramics.

#### 2.2. Characterization

The phase composition of the Er-YAG ceramics was identified by X-ray diffraction (XRD, PANalyti-

cal X'PertPRO). The current was 20 mA, the sweeping range was 20–80° and the sweeping speed was 0.03 °/s. The surface morphology and elemental analysis of the sintered ceramics were characterized by field emission scanning electron microscopy (FESEM, Zeiss, Sigma 500) equipped with energy dispersive spectrometer (EDS). The thermal diffusivity of the samples with a dimension of 12.2–12.7 mm in diameter and 2 mm in thickness was collected by laser flash device (Netzsch LFA427, Germany) from room temperature to 1000 °C.

The thermal conductivity k was calculated from volume density  $\rho$ , thermal diffusivity  $\alpha$  and specific heat capacity  $C_p$  of  $(\text{Er}_x \text{Y}_{1-x})_3 \text{Al}_5 \text{O}_{12}$  ceramics by Eq. 1 [18]. The volume density of ceramics was measured by the Archimedes drainage method and the specific heat capacity of samples was calculated through the Neumann-Kopp rule [19]. Since the sintered ceramic samples were not completely dense, the calculated value of thermal conductivity k needed to be corrected by the thermal conductivity  $k_0$  of fully dense ceramic materials. The revised formula was Eq. 2 [20], where  $\Phi$  was the fractional porosity. Meanwhile,  $\Phi$  was determined by Eq. 3, where  $\rho_t$  was the theoretical density.

$$k = \rho \cdot \alpha \cdot C_p \tag{1}$$

$$\frac{k}{k_0} = 1 - \frac{4\Phi}{3}$$
 (2)

$$\Phi = 1 - \frac{\rho}{\rho_t} \tag{3}$$

Thermal expansion coefficients of the Er-YAG ceramics were measured by high-temperature dilatometer (Netzsch DIL402C, Netzsch, Germany). The round rod-shaped  $Al_2O_3$  was used as the sample support. The size of the tested sample was  $3.0 \text{ mm} \times 4.0 \text{ mm} \times 25.0 \text{ mm}$ . The test temperature ranged from room temperature to 1200 °C, the heating rate was 5 °C/min, and tested in air atmosphere. In this experiment, the average linear expansion coefficient  $\lambda$  was used to represent the average change in length under the condition of increasing temperature, which was expressed as Eq. 4 [21]:

$$\lambda = \frac{\Delta L}{L_0 \cdot \Delta T} \tag{4}$$

Furthermore, in order to investigate the influence of  $Er^{3+}$  doping concentration on the bending strength of the  $(Er_x Y_{1-x})_3 Al_5 O_{12}$  ceramics, the three-point bending strength was measured by micro-controlled electronic universal testing machine (WDW3200, Chuangyuan Testing Equipment Co. Ltd). In addition, the Vickers hardness of the Er-YAG ceramics was measured by microhardness tester (EM-4500, Shanghai Hengyi Precision Instrument Co. Ltd), in which the loading capacity was 1000 GF (9.8 N) and the holding time was 15 s. Each sample was tested at five points and the average value of the measurement results was taken as the final data.



Figure 1. XRD pattern (a) and lattice parameter (b) of Er-YAG ceramics

### III. Results and discussion

#### 3.1. Phase composition of Er-YAG ceramics

XRD patterns and lattice parameters of the  $(\text{Er}_x \text{Y}_{1-x})_3 \text{Al}_5 \text{O}_{12}$  (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9and 1.0) ceramics are shown in Fig. 1. It can be seen from Fig. 1a that all the  $(\text{Er}_x \text{Y}_{1-x})_3 \text{Al}_5 \text{O}_{12}$  ceramics exhibit single  $\text{Y}_3 \text{Al}_5 \text{O}_{12}$  phase and no other diffraction peaks have been observed. It is worth noting that with the increase of  $\text{Er}^{3+}$  doping concentration, all diffraction peaks shift to a higher  $2\theta$  direction. According to the Bragg's formula  $2d \cdot \sin \theta = n \cdot \lambda$  [22], with the increase of diffraction angle  $\theta$ , the crystal plane spacing *d* becomes smaller, resulting in the contraction of lattice structure, which is consistent with the decreasing trend of lattice parameter as shown in Fig. 1b. Since the radius of  $\text{Er}^{3+}$  ion (1.08 Å) is slightly smaller than that of  $Y^{3+}$  ion (1.10 Å), but larger than that of  $Al^{3+}$  ion (0.54 Å), this indicates that the  $\text{Er}^{3+}$  ions occupy part of the lattice positions of  $Y^{3+}$  ions in  $Y_3Al_5O_{12}$  cells. However, the ( $\text{Er}_xY_{1-x}$ )<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> ceramics still retain the garnet crystal structure, which can be testified in Fig. 1a, manifesting that the substitution of  $\text{Er}^{3+}$  for  $Y^{3+}$  has no effect on the crystal structure of  $Y_3Al_5O_{12}$  ceramic.



Figure 2. FESEM images and EDS analysis of Er-YAG ceramics for x: a) 0, b) 0.1, c) 0.3, d) 0.5, e) 0.7, f) 0.9 and g) 1.0

#### 3.2. Microstructure of Er-YAG ceramics

Microstructures of the  $(Er_xY_{1-x})_3Al_5O_{12}$  ceramics sintered at 1600 °C for 5 h are shown in Fig. 2. It can be seen from the surface morphology that all the samples have granular structure with irregular polygon shape. There is no abnormal grain growth and the grain boundary is clear. Besides, with the increase of  $Er^{3+}$  doping concentration, the number of secondary phase grains in the  $(Er_{r}Y_{1-r})_{3}Al_{5}O_{12}$  ceramics increases. In order to explore the secondary phase, (Er<sub>0.7</sub>Y<sub>0.3</sub>)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> ceramics is analysed by EDS as a representative. As shown in Figs. 2e1 and 2e2, the ceramics is composed of elements O, Al, Fe, Y and Er. Among them, Fe mainly comes from the impurities in raw materials and its atomic proportion is only about 0.3%, which could be almost ignored. The remaining four elements are the main elements of the Er-YAG ceramics. By calculating the atomic percentage of the four elements in Fig. 2e1, the proportional relationship of Er and Y is approximately 7:3 and the ratio of Al and O is about 5:12, which is in good agreement with the proportion of each atom in the (Er<sub>0.7</sub>Y<sub>0.3</sub>)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> ceramics. Similarly, by calculating the atomic percentage of the four elements in Fig. 2e2, we could find that the amount of Al and Y is very small and the proportion of Er and O is close to 2:3, which is consistent with the atomic proportion of  $Er_2O_3$ . From the above calculation, it can be confirmed that the main component of white grains in Fig. 2e is  $(Er_{0.7}Y_{0.3})_3Al_5O_{12}$  and the major ingredient of black grains in Fig. 2e is Er<sub>2</sub>O<sub>3</sub>. In this experiment, ball milling method was used for the material mixing procedure. Although the materials have been ball milled for two times, it was still difficult to achieve an absolutely uniform mixture of substances. Therefore, in the process of ceramic sintering, it was inevitable that a small amount of  $Er_2O_3$  raw material could not be mixed into the YAG matrix and remained in the ceramics in the form of secondary phase impurities. As mentioned above, the number of secondary phase grains in the  $(Er_{r}Y_{1-r})_{3}Al_{5}O_{12}$  ceramics increases with the increase of Er<sup>3+</sup> doping concentration, indicating that the amount of  $Er_2O_2$  that cannot be dissolved into YAG gradually increases, but it still exists as a small amount of impurity. Since the content of Er<sub>2</sub>O<sub>3</sub> impurity is very small and the diffraction peak position of  $Er_2O_3$  and YAG is

close, therefore, they are difficult to distinguish in XRD patterns, resulting in the identification of the single YAG phase, as shown in Fig. 1a.

# 3.3. Thermal conductivity of Er-YAG ceramics

The specific heat capacity of the  $(\text{Er}_x Y_{1-x})_3 \text{Al}_5 \text{O}_{12}$  ceramics at different temperatures is shown in Table 1. It can be clearly seen that when the temperature rises to 1000 °C, the specific heat capacity of all the ceramics increases continuously, while the specific heat capacity of the Er-YAG ceramics decreases with the growth of  $\text{Er}^{3+}$  doping concentration.

The thermal diffusivity of the  $(\text{Er}_{x}\text{Y}_{1-x})_{3}\text{Al}_{5}\text{O}_{12}$  ceramics measured by laser flash method is shown in Fig. 3. It can be seen from Fig. 3a that the thermal diffusivity of the  $(\text{Er}_{x}\text{Y}_{1-x})_{3}\text{Al}_{5}\text{O}_{12}$  ceramics decreases gradually with the increase of temperature, and the minimum value appears at 1000 °C. As shown in Fig. 3b, the thermal diffusivity decreases at first and then increases with the growth of  $\text{Er}^{3+}$  doping concentration. The minimum value appears at x = 0.7. Therefore, when the temperature rises to 1000 °C and the  $\text{Er}^{3+}$  doping concentration equals to 0.7, the  $(\text{Er}_{0.7}\text{Y}_{0.3})_{3}\text{Al}_{5}\text{O}_{12}$  ceramics has the minimum thermal diffusivity, which is equal to 0.456 mm<sup>2</sup>/s.

Figure 4 shows the thermal conductivity of the  $(\text{Er}_{x}\text{Y}_{1-x})_{3}\text{Al}_{5}\text{O}_{12}$  ceramics from room temperature to 1000 °C, which is calculated through Eq. 1-3. It is obviously noted from Fig. 4a that the thermal conductivity of all the samples gradually decreases when the temperature rises to 1000 °C. As shown in Fig. 4b, the thermal conductivity of the Er-YAG ceramics decreases first and then increases with the growth of Er<sup>3+</sup> doping concentration, which is consistent with the variation of thermal diffusivity. Moreover, the thermal conductivity of the  $(\text{Er}_{x}\text{Y}_{1-x})_{3}\text{Al}_{5}\text{O}_{12}$  (x = 0.1, 0.3, 0.5, 0.7 and 0.9) ceramics is lower than that of pure  $Y_3Al_5O_{12}$  and  $Er_3Al_5O_{12}$ at the same temperature. The minimum thermal conductivity (1.5 W/m·K, 1000 °C) of the Er-YAG ceramics occurs at x = 0.7, which is about 28% lower than that of the pure YAG (2.1 W/m·K, 1000 °C). The reason for this phenomenon is the lattice distortion caused by different ion substitution, meanwhile, the difference of atomic masses between Er<sup>3+</sup> and Y<sup>3+</sup> ions will aggravate phonon scattering, leading to the reduction of ther-

| Table 1. Specific hear | t capacity of Er | -YAG ceramics at | different temperatures |
|------------------------|------------------|------------------|------------------------|
|------------------------|------------------|------------------|------------------------|

|     | Specific heat capacity, $C_p$ [J·K <sup>-1</sup> ·kg <sup>-1</sup> ] |        |        |        |        |         |  |  |
|-----|--|--------|--------|--------|--------|---------|--|--|
| x   | 25 °C  | 200 °C | 400 °C | 600 °C | 800 °C | 1000 °C |  |  |
| 0   | 0.59   | 0.74   | 0.80   | 0.83   | 0.86   | 0.87    |  |  |
| 0.1 | 0.57   | 0.72   | 0.77   | 0.80   | 0.82   | 0.84    |  |  |
| 0.3 | 0.53   | 0.67   | 0.72   | 0.75   | 0.77   | 0.78    |  |  |
| 0.5 | 0.50   | 0.62   | 0.67   | 0.70   | 0.72   | 0.73    |  |  |
| 0.7 | 0.47   | 0.59   | 0.63   | 0.66   | 0.68   | 0.69    |  |  |
| 0.9 | 0.45   | 0.55   | 0.60   | 0.62   | 0.64   | 0.65    |  |  |
| 1.0 | 0.42   | 0.53   | 0.58   | 0.60   | 0.61   | 0.63    |  |  |



Figure 3. Thermal diffusivity of Er-YAG ceramics as a function of temperature (a) and Er<sup>3+</sup> doping concentration (b)



Figure 4. Thermal conductivity of Er-YAG ceramics as a function of temperature (a) and Er<sup>3+</sup> doping concentration (b)

mal conductivity. In addition, on the basis of the SEM picture in Fig. 2, when the  $\text{Er}^{3+}$  doping concentration is 0.7, the grain size distribution of the  $(\text{Er}_{0.7}\text{Y}_{0.3})_3\text{Al}_5\text{O}_{12}$  ceramics is uniform and the grain size of the ceramics is the smallest, thus, the  $(\text{Er}_{0.7}\text{Y}_{0.3})_3\text{Al}_5\text{O}_{12}$  ceramics has the lowest thermal conductivity at 1000 °C.

According to the Clarke's minimum thermal conductivity shown in Eq. 5 [23], the influence of  $\text{Er}^{3+}$  doping concentration on the thermal conductivity of the  $(\text{Er}_x \text{Y}_{1-x})_3 \text{Al}_5 \text{O}_{12}$  ceramics can be analysed:

$$k_{min} \approx 0.87 k_B \cdot N_A^{2/3} \frac{N^{2/3} \cdot \rho_t^{1/6} \cdot E^{1/2}}{M^{2/3}}$$
(5)

where  $k_B$  is the Boltzmann constant,  $N_A$  is the Avogadro's constant,  $\rho_t$  is the theoretical density, E is the Young's modulus, M is the molar mass and N is the amount of substance. On the one hand, the thermal conductivity of sample will be reduced with the increase of molar mass, i.e. the thermal conductivity of the Er-YAG ceramics decreases with the growth of  $\text{Er}^{3+}$  doping concentration. On the other hand, the lattice parameter of the  $(\text{Er}_x Y_{1-x})_3 \text{Al}_5 \text{O}_{12}$  ceramics decreases with the increase of  $\text{Er}^{3+}$  doping concentration, implying that the theoretical density increases. On the basic of Eq. 5, the thermal conductivity of the Er-YAG ceramics will increase with the growth of  $\text{Er}^{3+}$  doping concentration due to the increase of their theoretical density. Therefore, both the molar mass and theoretical density have an effect on the thermal conductivity of the Er-YAG ceramics.

#### 3.4. Er-YAG thermal expansion coefficient

Figure 5 shows the thermal expansion properties of the  $(Er_x Y_{1-x})_3 Al_5 O_{12}$  ceramics from room temperature to 1200 °C. The curves of linear dimension change rate of ceramics with the temperature are shown in Fig. 5a. It can be seen that with the increase of temperature, the linear change rate of all the ceramics increases, indicating that the Er-YAG ceramics have good stability in the range of room temperature to 1200 °C. According to Eq. 4, the thermal expansion coefficient in the whole temperature range can be obtained by linear fitting of calculation of the measured linear change rate data. From Fig. 5b, it can be seen that the thermal expansion coefficient of the  $(\text{Er}_x Y_{1-x})_3 \text{Al}_5 \text{O}_{12}$  ceramics fluctuates between  $8.98 \times 10^{-6}$  and  $9.18 \times 10^{-6} \text{ K}^{-1}$  in the range of room temperature to 1200 °C, and is similar to that of the  $Y_3Al_5O_{12}$  ceramics. The reason for this is closely related to the doping position of Er<sup>3+</sup> in Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> structure. YAG belongs to the cubic crystal system and the general chemical formula is  $L_3B_2(AO_4)_3$  (L, A and B



Figure 5. Thermal expansion properties of Er-YAG ceramics: a) curve of linear change rate with different temperatures and b) coefficient of thermal expansion



Figure 6. Hardness (a) and bending strength (b) of Er-YAG ceramics with different Er<sup>3+</sup> doping concentrations

represent three kinds of lattice positions, respectively).  $Y^{3+}$  is located in the L position of dodecahedron coordinated by eight O<sup>2-</sup>; Al<sup>3+</sup> is located in the B octahedral position coordinated by six O<sup>2-</sup> and the A lattice of tetrahedron coordinated by four O<sup>2-</sup>. Therefore, YAG cell can be regarded as the connecting network of dodecahedron, octahedron and tetrahedron. Among them, octahedron and tetrahedron are the structural skeleton of YAG crystal structure. However, since the volume of dodecahedron is relatively large, the whole YAG crystal structure will not be greatly affected even if cations with larger ionic radius are introduced for doping replacement. According to the analysis of XRD results, Er<sup>3+</sup> just occupies the  $Y^{3+}$  lattice positions in dodecahedron. Thus, the structure of YAG is almost unaffected, and its thermal expansion coefficient is almost unchanged.

# 3.5. Mechanical properties of Er-YAG ceramics

The effects of  $\text{Er}^{3+}$  doping concentration on the hardness and bending strength of the  $(\text{Er}_x Y_{1-x})_3 \text{Al}_5 \text{O}_{12}$  ceramics are shown in Fig. 6. As it can be seen, the hardness and bending strength of the ceramics have similar change tendency. When the  $\text{Er}^{3+}$  doping concentration exceeds 0.5, the hardness and bending strength both increase suddenly and then after  $\text{Er}^{3+}$  completely replaced  $Y^{3+}$ , the hardness and bending strength both decrease instead. The reason for this phenomenon is that when the  $Er^{3+}$  doping concentration is more than half, most of the  $Y^{3+}$  dodecahedral lattice sites in YAG crystal structure are occupied by  $Er^{3+}$  with smaller ionic radius. Thus, the crystal plane spacing decreases and binding energy increases, resulting in the growth of hardness and bending strength. However, when the Er<sup>3+</sup> doping concentration equals to 1.0, it can be seen from the SEM picture in Fig. 2 that the grain size in Er<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> ceramics increases, thus the hardness and bending strength suddenly decrease after  $Er^{3+}$  completely replaced  $Y^{3+}$ in Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> ceramics. As shown in Fig. 6a, the maximum hardness of the Er-YAG ceramics is 16.53 GPa at x = 0.9, which is about 15.76% higher than that of the pure YAG ceramic (14.28 GPa). It can be seen from Fig. 6b that the bending strength of the Er-YAG ceramics exceeds 300 MPa when the  $Er^{3+}$  doping concentration is between 0.5 and 0.9. The average bending strength of the  $(\text{Er}_{x}\text{Y}_{1-x})_{3}\text{Al}_{5}\text{O}_{12}$  (x = 0.5, 0.7 and 0.9) ceramics equals to 316.7 MPa. It is worth mentioning that the  $(Er_{0.5}Y_{0.5})_{3}Al_{5}O_{12}$  ceramics exhibits maximum bending strength of 324.49 MPa, which is about 40% higher than that of the YAG sample without doping  $Er^{3+}$ . The improvement of hardness and bending strength can enhance the ability of the  $(Er_x Y_{1-x})_3 Al_5 O_{12}$  ceramics as TBCs to cope with complex working environment, such as the impact of dust particles in the air during highspeed operation.

# **IV.** Conclusions

 $(\text{Er}_{x}\text{Y}_{1-x})_{3}\text{Al}_{5}\text{O}_{12}$  (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0) ceramics comprised of single garnet-type  $Y_3Al_5O_{12}$ phase were successfully prepared by solid state synthesis at 1000 °C and finally sintering at 1600 °C for 5 h.  $Er^{3+}$  substituted dodecahedral  $Y^{3+}$  sites can effectively reduce the thermal conductivity of YAG ceramics at high temperature. When Er3+ doping concentration rose up to 0.7, the  $(Er_{0.7}Y_{0.3})_3Al_5O_{12}$  ceramics had the lowest thermal conductivity  $(1.51 \text{ W/m} \cdot \text{K})$ , 1000 °C), which was about 28% lower than that of the pure YAG (2.1 W/m·K, 1000 °C). As the  $Er^{3+}$  doping concentration increased, thermal expansion coefficient of the  $(\text{Er}_{x}\text{Y}_{1-x})_{3}\text{Al}_{5}\text{O}_{12}$  ceramics hardly changed, remaining around  $9.08 \times 10^{-6} \text{ K}^{-1}$  at 1200 °C. When the  $Er^{3+}$  doping concentration exceeded 0.5, the hardness and bending strength both suddenly increased. The (Er<sub>0.9</sub>Y<sub>0.1</sub>)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> ceramics had the highest hardness of 16.53 GPa, and the  $(\text{Er}_{x}\text{Y}_{1-x})_{3}\text{Al}_{5}\text{O}_{12}$  (x = 0.5, 0.7 and 0.9) ceramics exhibited an average bending strength of 316.7 MPa. The mechanical properties of the  $(\text{Er}_{x}\text{Y}_{1-x})_{3}\text{Al}_{5}\text{O}_{12}$  ceramics were much higher than that of the YAG ceramic without doping Er<sup>3+</sup>. In conclusion, comprehensive consideration of the above mechanical and thermophysical properties of the  $(Er_x Y_{1-x})_3 Al_5 O_{12}$  ceramics, the ceramics with  $Er^{3+}$  doping concentration between 0.7 and 0.9 could be selected as potential thermal barrier coating materials for their low thermal conductivity, stable thermal expansion coefficient, high hardness and bending strength.

Acknowledgment: This work was supported by the National Science and Technology Major Project (J2019-VI-0002), the Inner Mongolia Natural Science Foundation Project (2020LH05028), the Inner Mongolia University of Science and Technology Innovation Fund Project (2019QDL-B03) and the Fundamental Research Funds for Inner Mongolia University of Science & Technology.

# References

- J.J. Yan, G. Yan, H.Y. Chen, Z.Y. Liu, L. Yang, Y.C. Zhou, "Real-time detection of damage evolution and failure of EB-PVD thermal barrier coatings using an environmental simulator with high-temperature and high-speed rotation", *Surface Coat. Technol.*, 439 (2022) 128416.
- Z. Meng, Y. Liu, Y. Li, X. He, "The performance evaluation for thermal protection of turbine vane with film cooling and thermal barrier coating", *Appl. Therm. Eng.*, 210 (2022) 118405.
- Z. Shen, Z. Liu, G. Liu, L. He, R. Mu, Z. Xu, "The morphology, thermal property, and failure mechanism of GdNdZrO thermal barrier coatings by EB-PVD", *Int. J. Appl. Ceram. Tec.*, 18 (2021) 1623–1629.
- P. Zhao, H. Zheng, G. Li, Y. Geng, Y. Xiao, H. Guo, P. Peng, "Mechanical properties, thermophysical properties and electronic structure of Yb<sup>3+</sup> or Ce<sup>4+</sup>-doped La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> based TBCs", *J. Rare Earth.*, **41** (2023) 588–598.

- F. Zhou, Y. Wang, M. Liu, C. Deng, Y. Li, Y. Wang, X. Zhang, "Bonding strength and thermal conductivity of novel nanostructured La<sub>2</sub>(Zr<sub>0.75</sub>Ce<sub>0.25</sub>)<sub>2</sub>O<sub>7</sub>/8YSZ coatings", *Appl. Surf. Sci.*, **481** (2019) 460–465.
- T. Jiang, M. Xie, X. Wang, X. Song, "Effects of Nb<sup>5+</sup> doping on thermal properties of Gd<sub>2</sub>(Zr<sub>1-x</sub>Nb<sub>x</sub>)<sub>2</sub>O<sub>7+x</sub> ceramics", *Adv. Appl. Ceram.*, **119** (2020) 212–217.
- B. Zou, X. Cai, Y. Zhang, P. Huang, Y. Wang, X. Xue, X. Cao, "Superposed structure of double-ceramic layer based on YSZ/LaMgAl<sub>11</sub>O<sub>19</sub> thermal barrier coating", *Ceram. Int.*, 48 (2022) 12423–12429.
- K.M. Doleker, A.C. Karaoglanli, "Comparison of oxidation behavior of YSZ and Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> thermal barrier coatings (TBCs)", *Surface Coat. Technol.*, **318** (2016) 198– 207.
- R. Kumar, S. Rommel, C. Jiang, E.H. Jordan, "Effect of CMAS viscosity on the infiltration depth in thermal barrier coatings of different microstructures", *Surface Coat. Technol.*, 432 (2022) 128039.
- R.C. Pullar, M.D. Taylor, A.K. Bhattacharya, "The sintering behaviour, mechanical properties and creep resistance of aligned polycrystalline yttrium aluminium garnet (YAG) fibres, produced from an aqueous sol-gel precursor", *J. Eur. Ceram. Soc.*, **19** (1999) 1747–1758.
- P.H. Klein, W.J. Croft, "Thermal conductivity, diffusivity, and expansion of Y<sub>2</sub>O<sub>3</sub>, Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>, and LaF<sub>3</sub> in the range 77°-300°K", *J. Appl. Phys.*, **38** (1967) 1603–1607.
- J. Wang, F. Xu, R.J. Wheatley, N. Ne, "Yb<sup>3+</sup> doping effects on thermal conductivity and thermal expansion of yttrium aluminium garnet", *Ceram. Int.*, 42 (2016) 14228–14235.
- Y.G. Liu, P. Peng, M. Fang, Z. Huang, "Y<sub>3x</sub>Er<sub>x</sub>Al<sub>5</sub>O<sub>12</sub> aluminate ceramics: Preparation, thermal properties and theoretical model of thermal conductivity", *Adv. Eng. Mater.*, 14 (2012) 170–177.
- 14. N.P. Padture, P.G. Klemens, "Low thermal conductivity in garnets", *J. Am. Ceram. Soc.*, **80** (2010) 1018–1020.
- K. Rishi, J.W. Wang, J. Chen, C. Drew, F. Joseph, S. Sina, R. Jeffery, G. Maurice, E.H. Jordan, "Low thermal conductivity yttrium aluminum garnet thermal barrier coatings made by the solution precursor plasma spray: Part I — processing and properties", *J. Therm. Spray Techn.*, 27 (2018) 781–793.
- Z. Xue, Y. Ma, S. Gong, H. Guo, "Influence of Yb<sup>3+</sup> doping on phase stability and thermophysical properties of (Y<sub>1-x</sub>Yb<sub>x</sub>)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> under high temperature", *Ceram. Int.*, **43** (2017) 7153–7158.
- Z. Xue, Y. Ma, H. Guo, "The influence of Gd doping on thermophysical properties, elasticity modulus and phase stability of garnet-type (Y<sub>1-x</sub>Gd<sub>x</sub>)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> ceramics", *J. Eur. Ceram. Soc.*, **37** (2017) 4171–4177.
- L. Guo, H. Guo, H. Peng, S. Gong, "Thermophysical properties of Yb<sub>2</sub>O<sub>3</sub> doped Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and thermal cycling durability of (Gd<sub>0.9</sub>Yb<sub>0.1</sub>)<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>/YSZ thermal barrier coatings", *J. Eur. Ceram. Soc.*, **34** (2014) 1255–1263.
- V.J. Wood, "Materials thermochemistry", Surf. Eng., 9 (1993) 277–278.
- W. Jie, X. Wei, N.P. Padture, P.G. Klemens, M. Gell, E. Garcia, P. Miranzo, M.I. Osendi, "Low thermal conductivity rare earth zirconates for potential thermal barrier coating applications", *J. Am. Ceram. Soc.*, **85** (2002) 3031–3035.
- 21. S. Yoon, G. Lee, G. Go, "Linear thermal expansion behavior of compacted bentonite buffer materials", *Case Studies*

Thermal Eng., **32** (2022) 101889.

 S. Guo, Z. Jiang, J. Wu, X. Qie, T. Yu, K. Guo, D. Hou, J. Huang, "Research on a tunable monochromatic X-rays source in (5~40) keV", *Appl. Radiat. Isotopes*, **181** (2022) 110096.

23. D.R. Clarke, "Materials selection guidelines for low thermal conductivity thermal barrier coatings", *Surface Coat. Tech.*, **163** (2003) 67–74.