EFFECTS OF Dy3+-DOPING ON THE THERMOPHYSICAL PROPERTIES OF Ba2YbAlO5 CERAMICS

VPLIV DOPIRANJA Ba2YbAlO5 KERAMIKE Z Dy3+ NA NJENE TERMOFIZIKALNE LASTNOSTI

Ling Liu1,2, Wei Zheng1,2, Zhouwei Zhang1,2, Zhuang Ma1,2
1Beijing Institute of Technology, School of Materials Science and Engineering, no. 5 Zhongguancun South Street, Beijing 100081, China
2Beijing Institute and Technology, National Key Laboratory of Science and Technology on Materials under Shock and Impact, no. 5 Zhongguancun South Street, Beijing 100081, China

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Ba2(Dy,Yb1–x)AlO5 ceramics were prepared by solid-state sintering in air for 10 h at 1560 °C. The influence of Dy3+ doping on the thermal physical properties of Ba2YbAlO5 was studied. The phase structure of these ceramics were identified by X-ray diffraction, which indicates that all of these ceramics have a perovskite structure. The thermal physical properties of these ceramics measurement show that the thermal expansion coefficient of them by Dy3+ doped significantly increased, and the maximum value of about 12.2 × 10–6 K–1 was reached at x = 0.3. The thermal conductivity of Ba2(Dy,Yb1–x)AlO5 decreased firstly and then increased with the increasing of x. For samples with the same compound point x = 0.2, the minimum value (0.998 W·m–1·K–1) was realized. The excellent thermal physical properties mean that these solid solutions are potential materials for ceramic layers in thermal barrier coatings.

Keywords: perovskite-like ceramics, thermal expansion coefficient, thermal conductivity, thermal barrier coatings

1 INTRODUCTION

Thermal barrier coatings (TBCs) are widely used to protect the hot-section components of gas turbines from hot gases.1 With the development of aeroengines to high thrust-weight ratios and high inlet temperatures, the requirements for thermal insulation performance of TBCs will also be improved. The most advanced TBC material is yttria stabilized zirconia (YSZ), but YSZ still has some disadvantages when exposed to high temperatures (>1200 °C) for extended intervals, because the phase transition and shrinkage can damage the coatings.2 Therefore, it is very urgent to develop alternatives to YSZ for advanced TBC applications. The excellent ceramic candidates for TBCs must possess a few important performances, such as low thermal conductivity, appropriate thermal expansion, good phase stability at high temperature and so on.3 Among the thousands of possible candidates, anionic defect aluminates Ba2RAIO5 (R represents rare-earth element) such as Ba2YbAlO5 show a lower thermal conductivity and high thermal expansion coefficient (TEC), which gives them great potential for applications in the field of TBCs.4 The main purpose of the present study is to find ways to further improve its heat insulation ability. But there are few reports on the thermal physical performance data of Ba2RAIO5, which is doped with rare-earth oxides. In this paper, the Ba2YbAlO5 was doped in In sites by Dy3+, in order to improve the thermal physical properties of Ba2RAIO5. The influence of the Dy3+-doping concentration on the thermal conductivity and TECs of Ba2RAIO5 was also studied.

2 EXPERIMENTAL PART

Ba2(Dy,Yb1–x)AlO5 (x = 0–0.3) samples were synthesized by solid-state reaction using BaCO3, Al2O3 (purity ≥99.0 %, Beijing Chemical Co. Ltd.), Yb2O3 and Dy2O3 (purity ≥99.99 %, Rare-Chem Hi-Tech Co. Ltd.), the powders of Ba2(Dy,Yb1–x)AlO5 (x = 0–0.3) were sufficiently mixed with ethanol for 6 h and dried at 120 °C overnight and then calcined at 1200 °C for 8 h. The obtained powders were subjected to cold isostatic...
pressing at a pressure of 100 MPa and sintered in air at 1560 °C for 10 h.

The microstructures of the pellets were characterized by scanning electron microscopy (SEM, Philips S-4800, Hitachi Ltd., Yoshida-Cho, Totsuka-Ku, Yokohama, Japan). The phase compositions of the sintered ceramics was determined by X-ray diffraction (XRD, RIGAKU D/Max-rB, Rigaku International Corp., Sendagaya, Shibuya-Ku, Tokyo, Japan). The thermal conductivity of the samples with the size of φ12.7 mm × 2.0 mm were processed. The thermal diffusivity (a) of each sintered sample was measured using a laser-flash method (Model NETZSCH LFA 427, Netzsch Co., Ltd., Selb, Germany) and the densities (ρ) of the bulks were measured according to Archimedes’ principle. The thermal conductivity k is calculated in ref.5. The TECs between room temperature and 1300 °C of the sintered samples having a size of 25 mm × 4 mm × 3 mm were obtained using a high-temperature expansion meter (NETZSCH DIL 402C, Netzsch Co. Ltd., Selb, Germany).

3 RESULTS AND DISCUSSION

Figure 1 shows the phase compositions of the Ba2(Dy,xYb1–x)AlO5 (x = 0–0.3) bulks synthesized at 1560 °C for 10 h. It can be seen that the X-ray diffraction patterns of the samples agree with the standard spectrum (37-0292) of the perovskite structured Ba2YbAlO5, and there is no other phase in each sample. A pure Ba2(Dy,xYb1–x)AlO5 (x = 0–0.3) ceramic with the perovskite structure was synthesized.

Figure 2 shows the microstructures of partial Ba2(Dy,xYb1–x)AlO5 (x = 0, 0.3) ceramics. It can be seen that the surface morphology of the sample before the experiment is flat and dense (Figure 2a). Ba2(Dy,0.3Yb1–0.7)AlO5 (x = 0, 0.3) ceramics have a flat shape. From Figure 2a and 2b it can be seen that the microstructures of the synthesized products are dense, but there are some obvious pores. In Table 1 the volume density and relative density of Ba2(Dy,xYb1–x)AlO5 (x = 0, 0.3) with accurate measurements using Archimedes’ method are listed.

Table 1: Densities and relative densities of Ba2(Dy,xYb1–x)AlO5 (x = 0–0.3) ceramics

<table>
<thead>
<tr>
<th>Samples</th>
<th>Experimental density (g/cm³)</th>
<th>Relative density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba2YbAlO5</td>
<td>6.333</td>
<td>99.70</td>
</tr>
<tr>
<td>Ba2(Dy0.1Yb0.9)AlO5</td>
<td>6.321</td>
<td>99.86</td>
</tr>
<tr>
<td>Ba2(Dy0.2Yb0.8)AlO5</td>
<td>6.309</td>
<td>99.60</td>
</tr>
<tr>
<td>Ba2(Dy0.3Yb0.7)AlO5</td>
<td>6.297</td>
<td>98.80</td>
</tr>
</tbody>
</table>

Figure 3a shows the thermal diffusivities as function of temperature for different Ba2(Dy,xYb1–x)AlO5 ceramics. Obviously, the thermal diffusivities monotonically decrease with the increase of temperature, i.e., T−1 dependence of diffusivity for Ba2(Dy,xYb1–x)AlO5 ceramics exhibits a major phonon-conduction behavior, which is very common in polycrystalline materials.6

After the porosity correction the temperature dependence of the thermal conductivity of Ba2YbAlO5 with different Dy3+ contents is shown in Figure 3b. As can be seen from Figure 3b, as the doping content of Dy3+ increases to x = 0.2, the thermal conductivity decreases gradually and then increases at x = 0.3. Obvi-
ously, the thermal conductivity of $\text{Ba}_2(\text{Dy}_{y}\text{Yb}_{1-y})\text{AlO}_5$ bulk ceramics at 1200 °C is the lowest at ~0.998 W·m⁻¹·K⁻¹. In insulating materials, thermal conductivity is caused by changes in lattice vibrations, which are often described by phonon scattering theory. The deformation of the crystal structure and different ion radius will affect the phonon scattering. The composition of the atomic weight may lead to varying degrees of phonon scattering. Usually, the coefficient of thermal conductivity increases with the decrease of atomic mass. The low thermal conductivity of $\text{Ba}_2(\text{Dy}_{y}\text{Yb}_{1-y})\text{AlO}_5$ ($y = 0.1, 0.2$) is attributed to the increase of additional phonon scattering by substitutional solute cation Dy³⁺ replacing the host cation Yb³⁺ and RO₆ octahedron tilting.

The ion radius of Dy³⁺ ions and Yb³⁺ ions is 0.091 nm and 0.086 nm, respectively, according to the following Equation (1):

$$ l_p = \frac{2c\alpha^4\omega^4}{\pi\nu^3}J^2\gamma^2 \left( \frac{\Delta R^2}{R} \right) $$

where, $\alpha^2$ is the volume per atom, $\nu$ the transverse wave speed, $\omega$ the phonon frequency, $c$ the concentration per atom, $J$ the constant, $\gamma$ the Grüneisen parameter, $R$ the average ionic radius of the host atom, $\Delta R$ the differences of ionic radius between the substituted and the substituting atoms. It can be seen that for the normal polycrystalline ceramic oxide, the mean free path of the phonon is proportional to the square of the ion radius difference between the solute and the host cation. The radius difference between Dy³⁺ and Yb³⁺ results in an effective phonon scattering. This contributes to the lower thermal conductivity of Dy³⁺ doped $\text{Ba}_2\text{YbAlO}_5$. At the same time, since the $\text{Ba}_2\text{RAIO}_5$ compound is a perovskite variant, their structural stability can be described by a tolerance factor as Equation (2):

$$ t = \frac{r_{\text{Ba}} + r_0}{\sqrt{2(r_{\text{R,Al}} + r_0)}} $$

where, $r_{\text{Ba}}$ is the radius of Ba²⁺, $r_0$ the radius of O²⁻, and $r_{\text{R,Al}}$ the average radius of R³⁺ and Al³⁺. For the monoclinic perovskite belonging to the $\text{Ba}_2\text{RAIO}_5$ compound, a decrease in tolerance means that the BO₆ octahedral must be tilted to match the AO₁₂ polyhedron, which results in additional phonon scattering. Since Dy³⁺ has a larger radius than Yb³⁺, the tolerance factor decreases as the Dy³⁺ doping content increases. Thus additional phonon scattering increases due to the increase in the BO₆ octahedral tilt. Therefore, the thermal conductivity of $\text{Ba}_2(Dy_x\text{Yb}_{1-x})\text{AlO}_5$ decreases with an increase of the Dy³⁺ content.

It is well known that Dy (162.5) has a smaller atomic weight than Yb (173). The thermal conductivity of $\text{Ba}_2(Dy_x\text{Yb}_{1-x})\text{AlO}_5$ samples increased significantly at $x = 0.3$ due to the decrease in atomic mass. With an increase of the Dy³⁺ content, the decrease of atomic mass will weaken the phonon scattering, resulting in an increase in the thermal conductivity.

**Figure 3:** a) Thermal diffusivity and b) thermal conductivity versus temperature for $\text{Ba}_2(Dy_x\text{Yb}_{1-x})\text{AlO}_5$ ($x = 0$–0.3) ceramics

**Figure 4:** TECs of $\text{Ba}_2(Dy_x\text{Yb}_{1-x})\text{AlO}_5$ ($x = 0$–0.3) ceramics

The TECs of $\text{Ba}_2(Dy_x\text{Yb}_{1-x})\text{AlO}_5$ ($x = 0$–0.3) ceramics. It can be seen that with the increase of Dy³⁺-doping content, the TEC of $\text{Ba}_2(Dy_x\text{Yb}_{1-x})\text{AlO}_5$ ($x = 0$–0.3) decreases from 11.75×10⁻⁶/K to 12.2×10⁻⁶/K. The TEC ($a$) is closely related to the lattice energy ($E$), which can be given by the following Equation (3):

$$ a = \frac{a}{E + b} $$

**Figure 4:** TECs of $\text{Ba}_2(Dy_x\text{Yb}_{1-x})\text{AlO}_5$ ($x = 0$–0.3) ceramics
where \(a\) and \(b\) are both constants, and the lattice energy is given as Equation (4):

\[
E = N \frac{z_+ z_-}{R} A e \left(1 - \frac{1}{n}\right) \tag{4}
\]

where, \(N\) is the Avogadro constant, \(z_+\) and \(z_-\) the charge of positive and negative ions, respectively, \(R\) the distance between positive and negative ions, \(A\) the Madelung constant, \(e\) an electronic power, and \(n\) the constant. When the oxide ceramics have the same crystal structure, the larger radii of the positive ions in the lattice leads to a large distance between the positive ions and the negative ions, which will lead to higher TEC. Therefore, the thermal expansion coefficient is improved due to the relatively large radius of the Dy\(^{3+}\).

### 4 CONCLUSIONS

Ba\(_2\)(Dy\(_x\)Yb\(_{1-x}\))AlO\(_5\) (\(x = 0\)–0.3) compounds with perovskite-like structure were synthesized by solid-state sintering. The effect of Dy\(^{3+}\) Doping on the thermal conductivity and the TECs were investigated. The results show that the thermal properties are improved due to Dy\(^{3+}\) doping in the range of \(x < 0.3\). The lower thermal conductivity of Ba\(_2\)(Dy\(_x\)Yb\(_{1-x}\))AlO\(_5\) \((x = 0.1, 0.2)\) can be mainly attributed to the larger ionic radius of the substitutional cation in the materials. Compared with the thermal conductivity \((1.14 \text{ W m}^{-1}\text{K}^{-1})\) and TEC \((11.75 \times 10^{-6} \text{ K}^{-1})\), the aluminates Ba\(_2\)(Dy\(_x\)Yb\(_{1-x}\))AlO\(_5\) \((x = 0.1, 0.2)\) ceramics are better than that of Ba\(_2\)YbAlO\(_5\). At \(x = 0.2\), the thermal conductivity reached a minimum value of about 0.998 W m\(^{-1}\)K\(^{-1}\), the TEC reached a maximum value of about 12.2 \times 10^{-6} \text{ K}^{-1} at \(x = 0.3\). The modified aluminates should be explored as candidate materials for the ceramic layer in a TBCs system.

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### 5 REFERENCES

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