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EFFECTS OF Dy^{3+}-DOPING ON THE THERMOPHYSICAL PROPERTIES OF Ba_2YbAlO_5 CERAMICS

VPLIV DOPIRANJA Ba_2YbAlO_5 KERAMIKE Z Dy^{3+} NA NJENE TERMOFIZIKALNE LASTNOSTI

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$Ba_2(Dy_xYb_{1-x})AlO_5$ ceramics were prepared by solid-state sintering in air for 10 h at 1560 °C.The influence of Dy^{3+} doping on the thermal physical properties of Ba_2YbAlO_5 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 Dy^{3+} doped significantly increased, and the maximum value of about $12.2 \times 10^{-6}K^{-1}$ was reached at $x = 0.3$. The thermal conductivity of $Ba_2(Dy_xYb_{1-x})AlO_5$ 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 $W \cdot m^{-1} \cdot K^{-1}$) 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

Avtorji prispevka so pripravili $Ba_2(Dy_xYb_{1-x})AlO_5$ keramiko s postopkom sintranja v trdnem stanju in raziskovali vpliv različne količine dodatka Dy^{3+} na njene termofizikalne lastnosti. Sintranje je potekalo na zraku 10 ur pri 1560 °C. Fazno strukturo te keramike so identificirali z rentgensko difrakcijo. Ta je pokazala, da ima keramika perovskitno strukturo. Meritve termofizikalnih lastnosti te keramike so pokazale, da toplotni razteznostni koeficient z dodatkom Dy^{3+} znatno naraste in doseže maksimalno vrednost okoli $12{,}2 \times 10^{-6}$ K^{-1} pri $x = 0{,}3$. Toplotna prevodnost $Ba_2(Dy_xYb_{1-x})AlO_5$ najprej pada in nato narašča z dodatkom Dy^{3+}. Tako je naprimer pri vzorcih z enako sestavo in $x = 0{,}2$ dosežena minimalna vrednost 0,998 $W \cdot m^{-1} \cdot K^{-1}$. Odlične termofizikalne lastnosti pomenijo, da so te trdne raztopine materiali, potencialno uporabni kot termične pregrade v keramičnih prevlekah.

Keywords: perovskitna keramika, toplotni razteznostni koeficient, toplotna prevodnost, prevleke, uporabne kot termične pregrade

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 Ba_2RAlO_5 (R represents rare-earth element) such as Ba_2RAlO_5 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 Ba_2RAlO_5, which is doped with rare-earth oxides. In this paper, the Ba_2YbAlO_5 was doped in In sites by Dy, in order to improve the thermal physical properties of Ba_2RAlO_5. The influence of the Dy^{3+}-doping concentration on the thermal conductivity and TECs of Ba_2RAlO_5 was also studied.

2 EXPERIMENTAL PART

$Ba_2(Dy_xYb_{1-x})AlO_5$ (x = 0~0.3) samples were synthesized by solid-state reaction using $BaCO_3$, Al_2O_3 (purity ≥99.0 %, Beijing Chemical Co. Ltd.), Yb_2O_3 and Dy_2O_3 (purity ≥99.99 %, Rare-Chem Hi-Tech Co. Ltd.), the powders of $Ba_2(Dy_xYb_{1-x})AlO_5$ (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 (λ) 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 $Ba_2(Dy_xYb_{1-x})AlO_5$ (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 Ba_2YAlO_5, and there is no other phase in each sample. A pure $Ba_2(Dy_xYb_{1-x})AlO_5$ (x = 0~0.3) ceramic with the perovskite structure was synthesized.

Figure 2 shows the microstructures of partial $Ba_2(Dy_xYb_{1-x})AlO_5$ (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**). $Ba_2(Dy_xYb_{1-x})AlO_5$ (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 $Ba_2(Dy_xYb_{1-x})AlO_5$ (x = 0,0.3) with accurate measurements using Archimedes' method are listed.

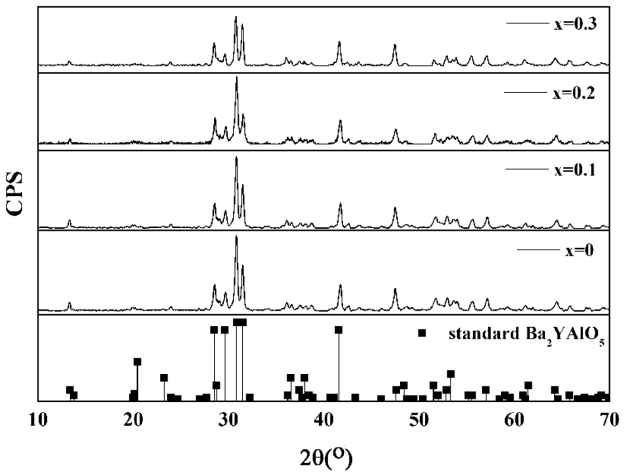

Figure 1: X-ray diffractograms of $Ba_2(Dy_xYb_{1-x})AlO_5$ (x = 0~0.3) bulks

Table 1: Densities and relative densities of $Ba_2(Dy_xYb_{1-x})AlO_5$ (x = 0~0.3) ceramics

Samples	Experimental density (g/cm^3)	Relative density (%)
Ba_2YbAlO_5	6.333	99.70
$Ba_2(Dy_{0.1}Yb_{0.9})AlO_5$	6.321	99.86
$Ba_2(Dy_{0.2}Yb_{0.8})AlO_5$	6.309	99.60
$Ba_2(Dy_{0.3}Yb_{0.7})AlO_5$	6.297	98.80

Figure 3a shows the thermal diffusivities as function of temperature for different $Ba_2(Dy_xYb_{1-x})AlO_5$ ceramics. Obviously, the thermal diffusivities monotonically decrease with the increase of temperature, i.e., λT^{-1}, between room temperature and 1200 °C. The T^{-1} dependence of diffusivity for $Ba_2(Dy_xYb_{1-x})AlO_5$ 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 Ba_2YbAlO_5 with different Dy^{3+} contents is shown in **Figure 3b**. As can be seen from **Figure 3b**, as the doping content of Dy^{3+} increases to x = 0.2, the thermal conductivity decreases gradually and then increases at x = 0.3. Obvi-

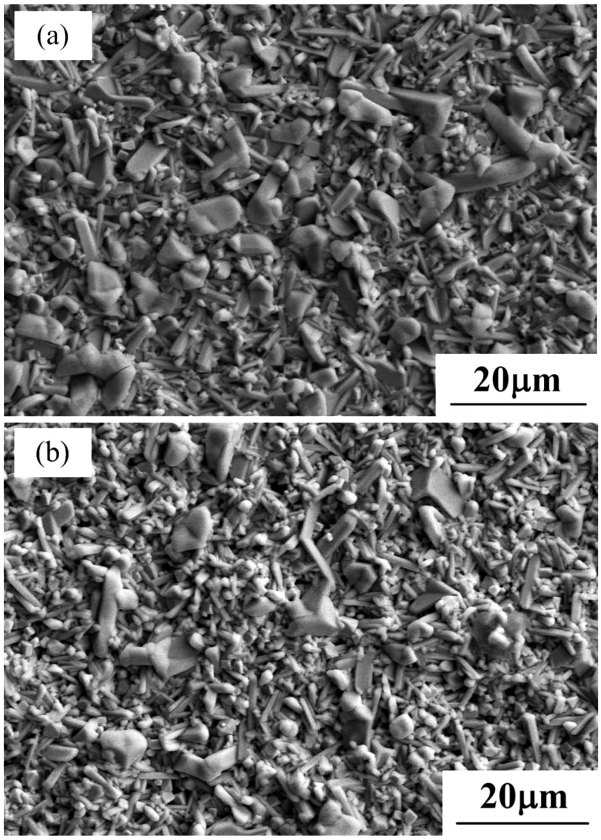

Figure 2: SEM of $Ba_2(Yb_xDy_{1-x})AlO_5$ (x = 0, 0.3) ceramics: a) x = 0, b) x = 0.3

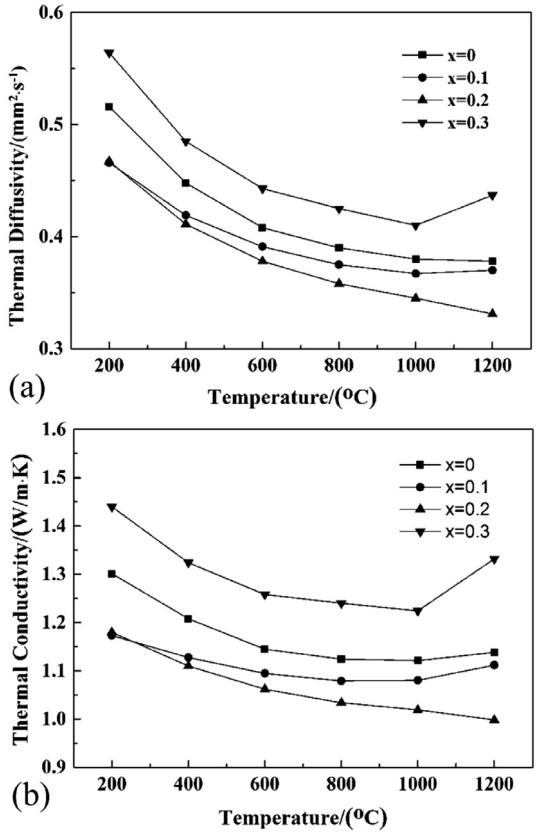

Figure 3: a) Thermal diffusivity and b) thermal conductivity versus temperature for $Ba_2(Dy_xYb_{1-x})AlO_5$ (x = 0~0.3) ceramics

ously, the thermal conductivity of $Ba_2(Dy_{0.2}Yb_{0.8})AlO_5$ bulk ceramics at 1200 °C is the lowest at ~0.998 $W{\cdot}m^{-1}{\cdot}K^{-1}$. 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 $Ba_2(Dy_xYb_{1-x})AlO_5$ (x = 0.1, 0.2) is attributed to the increase of additional phonon scattering by substitutional solute cation Dy^{3+} replacing the host cation Yb^{3+} and RO_6 octahedron tilting.

The ion radius of Dy^{3+} ions and Yb^{3+} ions is 0.091 nm and 0.086 nm, respectively, according to the following Equation (1):[7]

$$\frac{1}{l_p}=\frac{2ca^3\omega^4}{\pi v^3}J^2\gamma^2\left(\frac{\Delta R}{R}\right)^2 \quad (1)$$

where, a^3 is the volume per atom, v the transverse wave speed, ω the phonon frequency, c the concentration per atom, J the constant, γ the Grüneisen parameter, R the average ionic radius of the host atom, ΔR 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 Dy^{3+} and Yb^{3+} results in an effective phonon scattering, This contributes to the lower thermal conductivity of Dy^{3+} doped Ba_2YbAlO_5. At the same time, since the Ba_2RAlO_5 compound is a perovskite variant, their structural stability can be described by a tolerance factor as Equation (2):[8]

$$t=\frac{r_{Ba}+r_0}{\sqrt{2}(\bar{r}_{R,Al}+r_0)} \quad (2)$$

where, r_{Ba} is the radius of Ba^{2+}, r_O the radius of O^{2-}, and $\bar{r}_{(R,Al)}$ the average radius of R^{3+} and Al^{3+}. For the monoclinic perovskite belonging to the Ba_2RAlO_5 compound, a decrease in tolerance means that the BO_6 octahedral must be tilted to match the AO_{12} polyhedron, which results in additional phonon scattering. Since Dy^{3+} has a larger radius than Yb^{3+}, the tolerance factor decreases as the Dy^{3+} doping content increases. Thus additional phonon scattering increases due to the increase in the BO_6 octahedral tilt. Therefore, the thermal conductivity of $Ba_2(Dy_xYb_{1-x})AlO_5$ (x = 0, 0.1, 0.2) decreases with an increase of the Dy^{3+} content.

It is well known that Dy (162.5) has a smaller atomic weight than Yb (173). The thermal conductivity of $Ba_2(Dy_xYb_{1-x})AlO_5$ samples increased significantly at x = 0.3 due to the decrease in atomic mass. With an increase of the Dy^{3+} content, the decrease of atomic mass will weaken the phonon scattering, resulting in an increase in the thermal conductivity.

Figure 4 shows the TECs of the dense $Ba_2(Dy_xYb_{1-x})AlO_5$ (x = 0~0.3) ceramics. It can be seen that with the increase of Dy^{3+}-doping content, the TEC of $Ba_2(Dy_xYb_{1-x})AlO_5$ (x = 0~0.3) increases from 11.75×10^{-6}/K to 12.2×10^{-6}/K. The TEC (α) is closely related to the lattice energy (E), which can be given by the following Equation (3):

$$\alpha=\frac{a}{E+b} \quad (3)$$

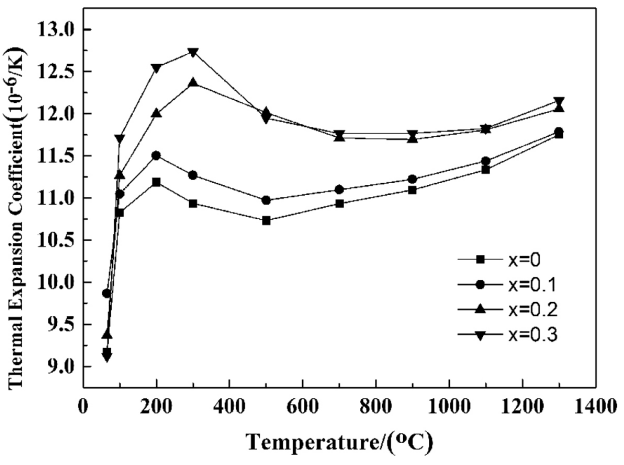

Figure 4: TECs of $Ba_2(Dy_xYb_{1-x})AlO_5$ (x = 0~0.3) ceramics

where *a* and *b* are both constants, and the lattice energy is given as Equation (4):

$$E = N\frac{z_+ z_-}{R}Ae^2\left(1-\frac{1}{n}\right) \quad (4)$$

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

$Ba_2(Dy_xYb_{1-x})AlO_5$ (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 $Ba_2(Dy_xYb_{1-x})AlO_5$ (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 $W\,m^{-1}K^{-1}$) and TEC (11.75×10^{-6} K^{-1}), the aluminates $Ba_2(Dy_xYb_{1-x})AlO_5$ (x = 0.1, 0.2) ceramics are better than that of Ba_2YbAlO_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 12.2×10^{-6} 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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