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# Thermal and mechanical properties of Yb&Mg co-doped $InFeZnO_4$

Bolun Zhao, Yanling Pei*, Lihua Zhang, Shengkai Gong, Li-Dong Zhao

*School of Materials Science and Engineering, Beihang University, Beijing 100191, China*

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ABSTRACT

$In_{0.4}Yb_{0.6}FeZnO_4$ was confirmed to possess the lowest thermal conductivity in Yb-doped $InFeZnO_4$. To further reduce the thermal conductivity, $In_{0.4}Yb_{0.6}FeZn_{1-x}Mg_xO_4$ (x = 0, 0.1, 0.2,…, 0.8, 0.9, 1.0) ceramics were synthesized by solid state reaction at 1300 °C for 30 h. XRD results indicated that single phase $In_{0.4}Yb_{0.6}FeZn_{1-x}Mg_xO_4$ ceramics were successfully synthesized with layered $YbFe_2O_4$-type crystal structure in the hexagonal $R\bar{3}m$ space group. It was found that the thermal conductivity of $In_{0.4}Yb_{0.6}FeZn_{0.5}Mg_{0.5}O_4$ (x = 0.5) reached a minimum value of 1.13 W $m^{-1}$ $K^{-1}$ at 1000 °C. The investigations on the thermal stability, thermal expansion coefficient, abradable property and erosion wear resistance indicate that $In_{0.4}Yb_{0.6}FeZn_{0.5}Mg_{0.5}O_4$ ceramics are promising thermal barrier coatings.



## 1. Introduction

Thermal barrier coatings (TBCs) are widely used to protect hot sections of metallic components in advanced turbine engines, which can increase the inlet temperature with a consequent improvement of the efficiency, or reduce the requirements for cooling systems [1]. One of the most common TBC material is 8 wt% yttria stabilized zirconia (8YSZ), as it has low thermal conductivity (2.1 W $m^{-1}$ $K^{-1}$), relatively high thermal expansion coefficient (11 × $10^{-6}$ $K^{-1}$) and chemical inertness in combustion atmospheres. However the phase transition of YSZ leads to instability in long-term service over 1200 °C [2]. Therefore, an urgent demand for alternative TBC materials is raised. Researches on the rare-earth zirconates, $Ln_2Zr_2O_7$ (Ln = rare-earth elements) have revealed the promising thermo-physical properties, such as thermal conductivity values range from 1.1 to 1.2 W $m^{-1}$ $K^{-1}$, which is much lower than that of YSZ [3]. However, thermal expansion coefficients of $Ln_2Zr_2O_7$ ceramics are lower than those of metallic substrates, resulting in high thermal stress in TBCs applications [4].

Generally, the selection of TBC material is restricted by several requirements: low thermal conductivity, high melting temperature, high thermal expansion coefficient and phase stability at elevated temperature [5,6]. Recently, a new compound, $InFeZnO_4$, was discovered as a promising TBC. $InFeZnO_4$ possesses low thermal conductivity (1.36 W $m^{-1}$ $K^{-1}$ at 1200 °C), high thermal expansion coefficient (11.7 × $10^{-6}$ $K^{-1}$ at 1200 °C) and no phase transition until 1400 °C [7,8], these outstanding properties meet the requirement of TBCs. Investigations of $In_{1-x}Yb_xFeZnO_4$ (x = 0, 0.1, 0.2,…, 0.8, 0.9, 1.0) show that the thermal conductivity of $In_{0.4}Yb_{0.6}FeZnO_4$ (x = 0.6) could achieve a minimum of 1.19 W $m^{-1}$ $K^{-1}$ at 1000 °C [9], indicating that the thermal conductivity could be reduced by introducing point defects through Yb doping. In this paper, we selected $In_{0.4}Yb_{0.6}FeZnO_4$ as matrix and doped Zn sites with different Mg fractions, $In_{0.4}Yb_{0.6}FeZn_{1-x}Mg_xO_4$ (x = 0, 0.1, 0.2,…, 0.8, 0.9, 1.0) ceramics were synthesized and the thermal transport properties were investigated. It was found that the thermal conductivity of $In_{0.4}Yb_{0.6}FeZn_{0.5}Mg_{0.5}O_4$ (x = 0.5) reached the minimum value of 1.13 W $m^{-1}$ $K^{-1}$ at 1000 °C, which is ~5% lower than that of $In_{0.4}Yb_{0.6}FeZnO_4$ and ~22% lower than that of $InFeZnO_4$. We found that there is no transformation of structure and composition occurred up to 1350 °C and the crystal structure ($YbFe_2O_4$ type) maintained after annealing treatment at 1350 °C for 100 h. The thermal expansion coefficient increased along with the elevating temperature and reached the value of 11.63 × $10^{-6}$ $K^{-1}$ at 1350 °C, which is higher than that of $Sm_2Zr_2O_7$, a promising coating material. The friction coefficients of $In_{0.4}Yb_{0.6}FeZn_{0.5}Mg_{0.5}O_4$ at room temperature, 400 °C and 800 °C are lower than those of 8YSZ. Rockwell hardness of $In_{0.4}Yb_{0.6}FeZn_{0.5}Mg_{0.5}O_4$ ($73HR_{45Y}$) was lower than that of 8YSZ ($87HR_{45Y}$). Erosion rate of $In_{0.4}Yb_{0.6}FeZn_{0.5}Mg_{0.5}O_4$ decreased with increasing impact angle and temperature. Under the experimental condition of (30°,60°,90°) × 20 °C and 60° × (20 °C, 400 °C, 800 °C), the erosion rates varied between 2.339 × $10^{-4}$ $cm^{-3}$ $g^{-1}$ and 36.486 × $10^{-4}$ $cm^{-3}$ $g^{-1}$.

* Corresponding author.
*E-mail address:* peiyanling@buaa.edu.cn (Y. Pei).

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## 2. Experimental

### 2.1. Synthesis

$In_{0.4}Yb_{0.6}FeZn_{0.5}Mg_{0.5}O_4$ samples (x = 0, 0.1, 0.2,…, 0.8, 0.9, 1.0) were prepared by means of solid-state synthesis using $In_2O_3$ (99.99%), $Yb_2O_3$ (99.99%), $Fe_2O_3$ (99.9%), ZnO (99.99%) and MgO (99.99%) as starting powders. All powders were calcined at 600 °C for 6 h in air to remove the possibly absorbed water. Then the starting powders were weighed in mole ratio of $In_2O_3$:$Yb_2O_3$:$Fe_2O_3$:ZnO:MgO = 0.4:0.6:1:2(1-x):2x, dissolved in absolute ethyl alcohol and fully mixed by planetary ball mill (QM-3SP4) at 400 r/min for 10 h. The mixtures were dried in oven at 110 °C for 2 h. The obtained powders were cold pressed in a Φ15 mm steel die under uniaxial pressure of 250 MPa, and then sintered in BeO crucibles at 1300 °C under air for 30 h.

### 2.2. X-ray diffraction and scanning electron microscopy

The phase structure of synthesized samples was measured by X-ray diffraction (XRD, Rigaku D/Max 2200 PC, Cu α). The fracture morphology and composition of $In_{0.4}Yb_{0.6}FeZn_{0.5}Mg_{0.5}O_4$ samples (x = 0, 0.1, 0.2,…, 0.8, 0.9, 1.0) were analyzed by scanning electron microscope (SEM, CamScan 3400) and electron probe micro-analyzer (EPMA) with energy dispersive spectroscopy (EDS), respectively.

### 2.3. Thermal conductivity

Thermal conductivity (λ) was calculated by Eq. (1) with thermal diffusivity (α), specific heat capacity ($C_p$) and density (ρ).

$$\lambda = C_P \cdot \alpha \cdot \rho \tag{1}$$

Thermal diffusivity (α) was measured using a laser-flash apparatus (Netzsch LFA 427) in atmosphere of argon at 25°C-1000 °C. Dimensions of the samples were about 12.7 mm in diameter and about 1.5 mm in thickness. The specific heat capacities ($C_p$) were calculated by the Neumann-Kopp rule [10] using heat capacities of $In_2O_3$, $Yb_2O_3$, $Fe_2O_3$, ZnO and MgO obtained from the thermodynamic database [11]. The uncertainty of the thermal conductivity is estimated to be within 10%, comprising uncertainties of 3% for the thermal diffusivity, 5% for the specific heat, and 3% for the sample density. As the sintered samples were not fully dense, the porosities (Φ) were calculated by experimental densities (ρ) and theoretical densities ($\rho_0$) using Eq. (2). Experimental densities were determined by Archimedes' method and theoretical densities were calculated with lattice parameters obtained from XRD patterns and relative molecular mass of compounds. The measured thermal conductivities were extrapolated to the fully dense case by Eq. (3), where $\lambda_0$ is thermal conductivity of fully-dense sample and λ is measured thermal conductivity.

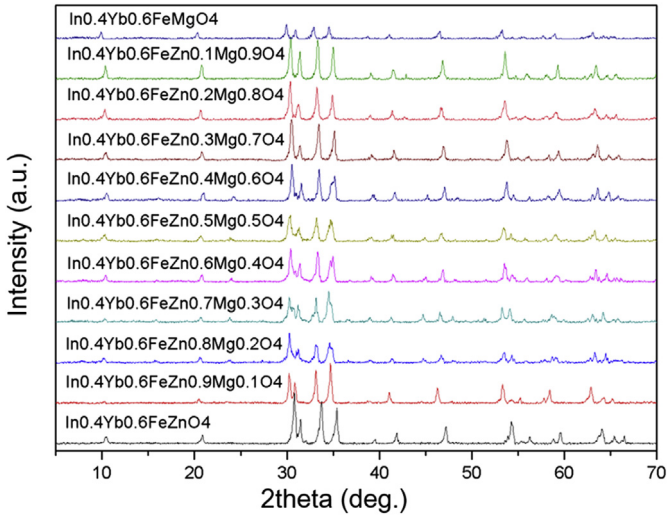


**Fig. 1.** Powder XRD patterns of $In_{0.4}Yb_{0.6}FeZn_{1-x}Mg_xO_4$.

$$\Phi = 1 - \frac{\rho}{\rho_0} \tag{2}$$

$$\frac{\lambda}{\lambda_0} = 1 - \frac{4}{3}\Phi \tag{3}$$

### 2.4. Thermo-physical properties

Thermal stability of $In_{0.4}Yb_{0.6}FeZn_{0.5}Mg_{0.5}O_4$ was investigated by differential scanning calorimetry (DSC) up to 1400 °C with heating rate of 15 °C/min in argon atmosphere. The high temperature annealing treatment was carried out under the condition of 1350 °C × 100 h. Thermal expansion coefficients (TECs) of the bulk material was measured using putter method and was calculated by Eq. (4) with the original length of the cylinder bulk material ($l_0$), temperature increment (dT) and length increment (dl). The sample size is 4 mm × 4 mm × 25 mm.

$$\mathrm{TECs} = \frac{1}{l_0}\frac{\mathrm{d}l}{\mathrm{d}T} \tag{4}$$

### 2.5. Mechanical properties

#### 2.5.1. Abradable property

Abradable property of $In_{0.4}Yb_{0.6}FeZn_{0.5}Mg_{0.5}O_4$ was characterized by friction coefficient and Rockwell hardness. The friction coefficients were measured by SRV-4 high-temperature friction and wear test machine for 20 min at room temperature, 400 °C and 800 °C, respectively, using Φ24 mm × 7.88 mm sample. The Rockwell hardness of $In_{0.4}Yb_{0.6}FeZn_{0.5}Mg_{0.5}O_4$ was measured using HSRD-45 electric surface Rockwell hardness test machine under 45 kg pressure and $HR_{45Y}$ staff gauge. 8YSZ was selected as a reference material in these two experiments.

#### 2.5.2. Erosion wear resistance

Erosion wear resistance of $In_{0.4}Yb_{0.6}FeZn_{0.5}Mg_{0.5}O_4$ material is

**Table 1**
Experimental densities (ρ), theoretical densities ($\rho_0$) and porosities (Φ) of $In_{0.4}Yb_{0.6}FeZn_{1-x}Mg_xO_4$ samples.

| Sample | ρ | $\rho_0$ | Φ |
|---|---|---|---|
| $In_{0.4}Yb_{0.6}FeZnO_4$ | 5.574 | 6.610 | 15.64% |
| $In_{0.4}Yb_{0.6}FeZn_{0.9}Mg_{0.1}O_4$ | 5.729 | 6.508 | 11.97% |
| $In_{0.4}Yb_{0.6}FeZn_{0.8}Mg_{0.2}O_4$ | 5.339 | 6.417 | 16.79% |
| $In_{0.4}Yb_{0.6}FeZn_{0.7}Mg_{0.3}O_4$ | 5.092 | 6.336 | 19.63% |
| $In_{0.4}Yb_{0.6}FeZn_{0.6}Mg_{0.4}O_4$ | 5.599 | 6.245 | 10.35% |
| $In_{0.4}Yb_{0.6}FeZn_{0.5}Mg_{0.5}O_4$ | 5.488 | 6.153 | 10.81% |
| $In_{0.4}Yb_{0.6}FeZn_{0.4}Mg_{0.6}O_4$ | 5.189 | 6.091 | 14.82% |
| $In_{0.4}Yb_{0.6}FeZn_{0.3}Mg_{0.7}O_4$ | 5.083 | 6.020 | 15.57% |
| $In_{0.4}Yb_{0.6}FeZn_{0.2}Mg_{0.8}O_4$ | 4.856 | 5.942 | 18.27% |
| $In_{0.4}Yb_{0.6}FeZn_{0.1}Mg_{0.9}O_4$ | 4.828 | 5.861 | 17.62% |
| $In_{0.4}Yb_{0.6}FeMgO_4$ | 4.898 | 5.783 | 15.30% |