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Incorporation of Zn^{2+} ions into Al_2O_3:Er^{3+}/Yb^{3+} transparent ceramics: An effective way to enhance upconversion and near infrared emission

Qinghua Yang[a,b,c], Benxue Jiang[a,*], Shuilin Chen[a,b], Yiguang Jiang[a,b], Pande Zhang[a,b], Jun Wang[a,*], Shiqing Xu[c], Long Zhang[a]

[a] Key Laboratory of Materials for High Power Laser, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Science, Shanghai 201800, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] College of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, China

A R T I C L E I N F O

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A B S T R A C T

Al_2O_3: Er^{3+}/Yb^{3+} transparent ceramics codoped with Zn^{2+} ions with intense upconversion and near infrared emission were prepared by conventional solid-state reaction and vacuum and hot isostatic pressing sintering. The effects of Zn^{2+} incorporation to the structure, transparent, upconversion and NIR luminescence were discussed in detail. The as prepared Al_2O_3 ceramics exhibited a total transmittance of ~ 75% in infrared regions (800–3300 nm) and ~ 50% in visible regions (500–800 nm). Under the excitation of a 980 nm laser diode, the as prepared Al_2O_3 ceramics displayed two tense upconversion emission peaks of a green one centered at 550 nm and a red one centered at 660 nm and a tense near infrared emission peak centered at 1.532 µm, characteristic of Er^{3+} emission. Compared with Er^{3+}/Yb^{3+} doped only, Zn^{2+} codoped Al_2O_3:Er^{3+}/Yb^{3+} transparent ceramics showed higher upconversion and near infrared emission of ~ 11 times and ~ 4 times, respectively. The enhancement mechanism due to incorporation of Zn^{2+} ions was also discussed in detail.

1. Introduction

Due to their intense radiation in the visible, near infrared (NIR) and middle infrared (MIR) regions under the excitation of a 980 nm laser diode, Er^{3+}/Yb^{3+} co-doped Al_2O_3 materials are widely applied in color displays, upconvertors, telecommunications, eye-safe telecommunication window, optical sensors, optical temperature sensing, and so on [1–3]. Recently, more and more attentions have been devoted to these new function materials [4–12]. Such as, Dong et al. [4] prepared 0.1at%Er^{3+}/0–2at%Yb^{3+} co-doped Al_2O_3 powders with visible and NIR emissions by Sol-gel method. Gonçalves et al. [9] also prepared polycrystalline powders of α-Al_2O_3: 1–2molEr^{3+}, 2–5 mol%Yb^{3+} by Sol-gel process. And Zhu et al. [10] prepared 1 mol%Er^{3+} – 10 mol%Yb^{3+} co-doped Al_2O_3 thin films with strong photoluminescence spectrum of 1.4–1.7 µm. Li et al. [12] prepared 0.3 mol%Er^{3+} – 3.6 mol%Yb^{3+} co-doped Al_2O_3 films with upconversion luminescence of 529–549 nm on SiO_2/Si substrate using a medium frequency magnetron sputtering system. However, much of the studies about Er^{3+}/Yb^{3+} co-doped Al_2O_3 materials are either powders or films.

Compared with Al_2O_3 powders and films, Al_2O_3 transparent ceramics are suitable for dosimeters, laser host materials, high-brightness LED, and so on [13,14]. However, due to second phase and great grans caused by high dopant, it is well known that adding the required amount of dopant, usually higher than 0.1 mol%, inevitably results in inclusions, which will strongly deteriorate the transparency. Therefore, it is a challenging topic to prepare transparent alumina with luminescence properties [15,16].

To best of our knowledge, in the past years, there are only a few works dealing with transparent Al_2O_3 ceramics doped with optically (photoluminescence) active rare earth (RE) and transition metal (TM) ions. Such as, Cr^{3+} doped transparent alumina prepared by conventional sintering process under vacuum condition exhibiting thermo luminescence (TL) and optically stimulated luminescence was designed as potential TL dosimetry materials [17]. So were the Ti^{4+} and Mg^{2+} doped materials [18]. While, Er^{3+}, Eu^{3+} or Nd^{3+} doped transparent Al_2O_3 ceramics prepared by a combination of wet shaping technique (slipe casting), pressure less pre-sintering, and hot isostatic pressing (HIP) method was designed as a promising material for LED applications [19]. Tb^{3+} doped ones prepared by spark plasma sintering (SPS) had exciting prospects for high energy laser technology [20]. Nd_2O_3 doped Al_2O_3 translucent ceramics with tense NIR emission were fabricated using the conventional solid-state reaction and vacuum sintering [21]. It can be concluded that no work is investigating on transparent Er^{3+}/Yb^{3+} co-doped Al_2O_3 ceramics with effective upconversion and

* Corresponding authors.
E-mail addresses: jiangsic@foxmail.com (B. Jiang), jwang@siom.ac.cn (J. Wang).

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Table 1
Compositions of raw materials.

No.	Al_2O_3/mol%	Er_2O_3/mol%	Yb_2O_3/mol%	ZnO/mol%
a	100	–	–	–
b	99.90	0.05	0.05	–
c	99.85	0.05	0.05	0.05

NIR luminescence properties.

Therefore, in the present paper, it is aimed at preparation of transparent Er^{3+}/Yb^{3+} codoped Al_2O_3 ceramics with effective upconversion and NIR luminescence properties. In addition, as singh et al. [1] have observed the enhancement of upconversion and near infrared emissions due to the presence of Zn^{2+} in Er^{3+}/Yb^{3+} co-doped Al_2O_3 powders. In the present work, the effects of Zn^{2+} incorporation to the structure, transparent, upconversion, and NIR luminescence were also discussed in detail.

2. Experimental procedure

2.1. Sample preparation

High-purity powders of Al_2O_3 (99.95%, 0.25–0.45 µm, Alfa Aesar), Er_2O_3 (99.99%, 40 nm, Aladdin), Yb_2O_3 (99.99%, 40 nm, Aladdin) and ZnO (99.99%, 40 nm, Aladdin) were used as starting materials. The dopant of Er_2O_3, Yb_2O_3 and ZnO are 0.05 mol%, 0.05 mol% and 0.05 mol%, respectively, and samples of none dopant and only 0.05 mol % Er_2O_3/0.05 mol% Yb_2O_3 doped sample were used as the comparison, the detail compositions were given in Table 1. 40 g Al_2O_3 and corresponding contents of Er_2O_3, Yb_2O_3 and ZnO were weighed and mixed by ball-milling in anhydrous alcohol for 12 h. The mixtures were dried in an oven at 70 °C for 4 h, sieved under 200 meshes sieve, dry-pressed under 100 MPa into Ø 20 mm discs and finally cold-isostatically pressed under 250 MPa.

The obtained green bodies were sintered at 1650 °C for 5 h under vacuum atmosphere. To remove the residual closed porosity, the obtained ceramic underwent HIP processing with an argon gas pressure of 200 MPa at 1700 °C for 2 h. To remove oxygen vacancies or other electronic defects bring in the reducing atmosphere during the HIP process, the specimens were annealed at 1450 °C for 10 h in an air atmosphere. Finally, $Er^{3+}/Yb^{3+}/Zn^{2+}$ codoped alumina transparent ceramics were prepared.

The ceramic samples were machined into sizes with Ø = 13 mm × 1 mm and two mirror-polished faces. And in order to measure the grain size of the as prepared ceramics, the mirror-polished samples were thermal etched at 1350 °C for 1 h.

2.2. Characterization

The structure were analyzed and characterized by X-ray diffraction (XRD, D8 ADVANCE, Bruker, Germany) with graphite monochromatized CuKα radiation (λ = 0.15418 nm) in the 2θ range of 10–80°, Raman spectra (inVia, Renishaw, UK) under 785 nm excitation, electron paramagnetic resonance spectra (EPR, JES-FA200, Japan) in X-band mode, equipped with a dual cavity operating at 100 kHz field modulation at room temperature, scanning electron microscope (SEM, HITACHI SU-8010, Japan) and energy dispersive X-ray spectroscope (EDS, TEAM Apollo XL, EDAX) using the unit attached to the SEM.

The optical properties were recorded by absorption spectrophotometer (UV 3600, SHIMADZU, Japan) between 300–3300 nm and fluorescence spectrophotometer (FL3–211, HORIBA Jobin Yvon, France) with the excitation of a 980 nm laser diode (LD). The fluorescence decay curve was measured with a light pulse of 980 nm LD and a HP546800B 100-MHz oscilloscope.

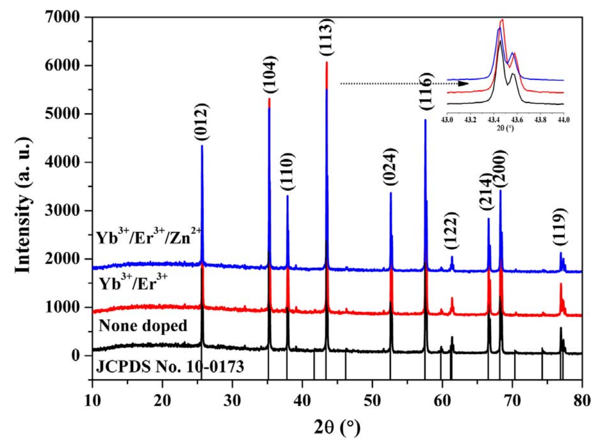

Fig. 1. XRD patterns of none doped, Er^{3+}/Yb^{3+} and $Er^{3+}/Yb^{3+}/Zn^{2+}$ doped Al_2O_3 transparent ceramics (in set is enlarged XRD patterns of (113)).

3. Results and discussions

3.1. Structural properties

Fig. 1 shows the XRD patterns of none doped, Er^{3+}/Yb^{3+} and $Er^{3+}/Yb^{3+}/Zn^{2+}$ doped Al_2O_3 transparent ceramics. The results reveal that all the diffraction patterns of the samples match well to trigonal α-Al_2O_3 phase (JCPDS No. 10-0173), and no other impurity peaks are detected, independent of different dopant. α-Al_2O_3 has a typical corundum structure with hexagonal close packed (hcp) of O^{2-} ions and Al^{3+} ions filling the 2/3 octahedral holes of the crystal. As shown in Fig. 2, in the direction of C-axis, in every two [AlO_6] octahedron filling with Al^{3+} ions, there is a hollow octahedron coplanar with it. On the basis of the tolerance factor and thermodynamic considerations, the site occupancy of RE ions in the corundum material is well explained by Wang et al. [22] using both high-resolution scanning transmission electron microscopy and secondary ion mass spectroscopy. According to Wang et al., Er^{3+} and Yb^{3+} ions will strongly segregate to the Al_2O_3 grain boundaries. While, as the ionic radius of Zn^{2+} (~ 0.75 Å) is near to that of Al^{3+} (~ 0.53 Å), and Houng et al. [23] have proved that Zn^{2+} can be substituted by Al^{3+}. Therefore, Al-sites will be occupied by Zn, and the overall stoichiometry can be presented through the following stoichiometry relationship:

$$(Al_2Zn_x)O_{3+x} \rightarrow (Al_{2-x}Zn_x')(O_{3-x}\frac{x}{2}V_O^{\bullet\bullet}) + \frac{x}{2}Al_2O_3 \quad (1)$$

Where, oxygen vacancies are generated to balance the charge. As a support for this relationship, as shown in inset of Fig. 1, the position of the diffraction peaks moves towards smaller angles with the Zn^{2+} doping. Shifting of peak positions toward a smaller angle reflects a slight expansion of the unit cell volume due to the difference in the size of Al^{3+} ions and Zn^{2+} ions, and leads to lattice mismatch.

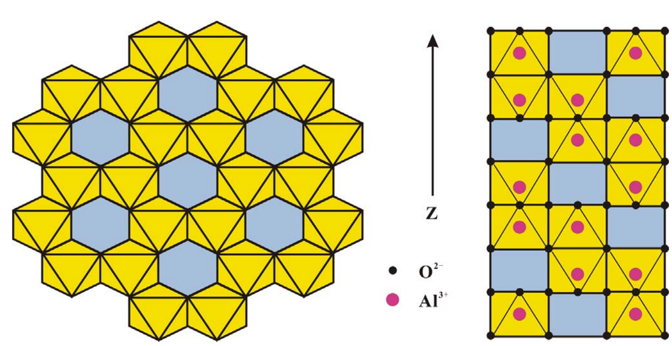

Fig. 2. α-Al_2O_3 super cell model. Polyhedra have been drawn to show the coordination of each cation.