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Fabrication and properties of Er/Tm/Pr tri-doped yttrium lanthanum oxide transparent ceramics

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ABSTRACT

Er/Tm/Pr tri-doped yttrium lanthanum oxide transparent ceramics were fabricated by conventional ceramics processing. Their microstructures and spectroscopic properties were investigated. The energy transfer mechanism between Tm^{3+}, Pr^{3+} and Er^{3+} was also discussed. The Er/Tm/Pr:$(Y_{0.9}La_{0.1})_2O_3$ ceramics display a dense structure with no pores and uniform grains of about 40 μm. The results shows that population inversion between the $^4I_{11/2}$ and $^4I_{13/2}$ level of Er:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics is enhanced by co-doping Tm^{3+} and low amount of Pr^{3+} (0.5 at.%). When concentration of Pr^{3+} ions is high (2 at.%), 2.7 μm emission is restrained significantly due to the concentration quenching of Pr^{3+} ions. This Er/Tm/Pr tri-doped yttrium lanthanum oxide transparent ceramics can be considered as a promising material for mid-infrared lasers.

1. Introduction

Er^{3+}-doped lasers provide an important infrared fluorescent emission around 2.7 μm which draws attention from various useful applications including medical care, optical communication techniques and environment monitoring [1–4]. Despite the considerable amount of investigations on 1.5 μm laser emission from Er^{3+} single-doped materials, the laser characteristics of the 2.7 μm emission ($^4I_{11/2} \rightarrow {}^4I_{13/2}$) obtained by using 980 nm laser diode (LD) are not satisfactory due to the 1.5 μm emission ($^4I_{13/2} \rightarrow {}^4I_{15/2}$). It is well-known that the lifetime of lower level ($^4I_{13/2}$) is considerably longer than the upper level ($^4I_{11/2}$) lifetime, leading to a population bottleneck which is not beneficial between the $^4I_{11/2}$ and $^4I_{13/2}$ levels [5–9].

Co-doping of Tm^{3+} or Pr^{3+} with Er^{3+} could be a resultful solution to overcome the population inversion problem [10–12]. Pr^{3+}:$^3F_{3,4}$ level and Tm^{3+}:$^3F_4$ level are so closely spaced to Er^{3+}:$^4I_{13/2}$ level that the energy can be easily transferred. Er^{3+}:$^4I_{13/2}$ level is deactivated due to the energy transfer mechanism between Tm^{3+}, Pr^{3+} and Er^{3+}. Additionally, many cases have demonstrated that laser materials with certain rare earth ions are able to increase the intensity of the 2.7 μm laser emission [13–16]. Few articles, however, have been reported on the 2.7 μm laser emission in Er/Tm/Pr tri-doped transparent ceramics.

As a favorable kind of laser host materials, Y_2O_3 has been investigated for many years due to its excellent high thermal conductivity (13.6 W/mK), high refractive index, good chemical and mechanical properties [17]. Unfortunately, it is difficult to grow high optical quality Y_2O_3 crystals using the conventional growth methods because of its high melting point (~2430 °C) and structural phase transition from hexagonal system to cubic system at ~2280 °C. Recently, we have investigated Y_2O_3-based transparent ceramic and found that the sintering temperature could be decreased remarkably without influence on optical quality by doping La_2O_3 as an additive [18].

In this paper, Er/Tm/Pr:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics with high optical parameters were fabricated by solid state sintering method. Microstructure, transmittance and sensitization of Tm^{3+} and Pr^{3+} ion toward the 2.7 μm emitted light of Er^{3+} ion were investigated.

2. Experimental procedure

The starting commercial nanopowders of Er_2O_3, Pr_6O_{11}, Tm_2O_3, La_2O_3 and Y_2O_3 with purity of 99.99% were weighed according to the composition ($Pr_xEr_{0.02}Tm_{0.02}Y_{0.86-x}La_{0.1})_2O_3$ (x = 0, 0.005, 0.01, 0.02). Er/Pr co-doped yttrium lanthanum oxide transparent ceramics were also fabricated and investigated as comparisons, the concentration of Er and Pr ions is 2 at.%. The powders were mixed by ball-milling treatment for 6 h and calcined at 1100 °C for 5 h in air. Samples were isostatically pressed to the disks with 15 mm in diameter and 5 mm in thickness at 200 MPa and sintered at 1600–1800 °C in H_2 atmosphere. All samples were double-sided polished for spectral spectra analysis.

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Microstructures were observed with optical microscopy (Model BX60, OLYPMUS, Japan). Both linear transmittance and absorption spectra were measured with a spectrophotometer (Model V-570, JASCO) pumped by Xe light. The emission spectra were measured in the range of 1400–2000 nm and 2500–2800 nm with a fluorescence spectrophotometer (FLSP920, Edinburgh Analytical Instruments Ltd., Edinburgh, U.K.) excited by 980 nm laser diode (LD), of which the resolution is 1 nm. All spectroscopic analysis were tested at room temperature.

3. Results and discussion

Fig. 1 is the photograph of $(Pr_xEr_{0.02}Tm_{0.02}Y_{0.86-x}La_{0.1})_2O_3$ (x = 0–0.02) transparent ceramics. Obviously, all five samples have high transparency and letters under the samples can be seen clearly.

Fig. 2 shows the in-line optical transmittance spectra of Er/Tm/Pr tri-doped transparent ceramic with 2.5 mm in thickness. The maximum transmittance reaches up to 70% in the range of 2000–2500 nm wavelength.

Fig. 3 displays the XRD patterns of Er/Tm/Pr tri-doped transparent ceramics. The diffraction peaks of the ceramic can be indexed as a cubic Y_2O_3 phase (JCPDS card, No. 41-1105) and no other phases were detected. This indicates that all composition have formed solid solution completely.

Fig. 4 shows the microstructure of tri-doped transparent ceramics with different Pr^{3+} concentration. All the tri-doped samples have a dense structure. The average grain size of the tri-doped ceramics is 40 μm around, and the grain boundaries are clear without any pores or impurities.

The absorption spectrum of Er/Tm/Pr:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramic is presented in Fig. 5. The absorption spectra of Er^{3+}, Tm^{3+} and Pr^{3+} single-doped $(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics are also shown below allowing for comparisons. The absorption spectrum of tri-doped sample is the superposition of those of the three single-doped transparent ceramics spectra. It is evident that Pr^{3+} contributes a large proportion to the absorption peaks of tri-doped spectrum with high intensity, which indicates that Pr^{3+} may have a greater impact on the spectral properties than Er^{3+} and Tm^{3+}. However, taking the fluorescence quenching of Pr^{3+} ions into consideration, high doping amount of Pr^{3+} would be inadvisable.

Fig. 6 is the 1.5 μm emission spectra of Er, Er/Pr, Er/Tm and Er/Tm/Pr $(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics excited by 980 nm laser diode at room temperature. The concentration of Er and Tm ions in all the samples is 2 at.% and Pr ions is 0.5 at.%. The 1.5 μm emitted light of Er^{3+} ions is clearly suppressed under the situation that Tm^{3+} and Pr^{3+} ions are co-doped with Er^{3+} ions separately or together. It is also worth mentioning that there is an emission at 1900 nm corresponding to the Tm^{3+}:$^3F_4 \rightarrow {}^3H_6$ (see Fig. 9, ET1). Since Tm^{3+} has no absorption band matching to the 980 nm excitation used for the experiment, it appears to be an energy transfer from Er^{3+} to Tm^{3+}. This phenomenon indicates that Tm^{3+} suppresses the 1.5 μm emission of Er^{3+} ions, but also grabs the energy from Er^{3+} ion leading to a high 1.9 μm emission which is not beneficial to the 2.7 μm emission enhancement. On the other hand, the emission spectra of Er/Pr and Er/Tm/Pr:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics presents are almost two straight lines in the wavelength

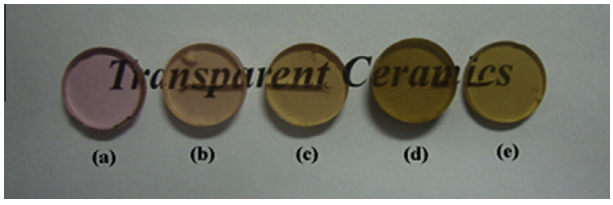

Fig. 1. Photograph of $(Pr_xEr_{0.02}Tm_{0.02}Y_{0.86-x}La_{0.1})_2O_3$ transparent ceramics (a) x = 0, (b) x = 0.005, (c) x = 0.01, (d) x = 0.02, and (e) Pr^{3+}/Er^{3+} co-doped sample.

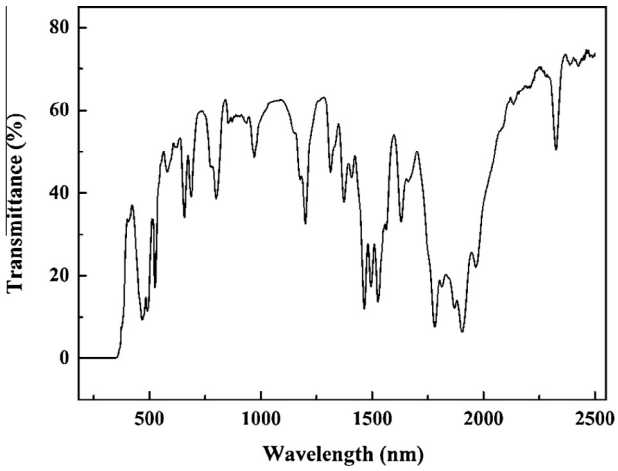

Fig. 2. In-line optical transmittance spectra of Er/Tm/Pr:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramic.

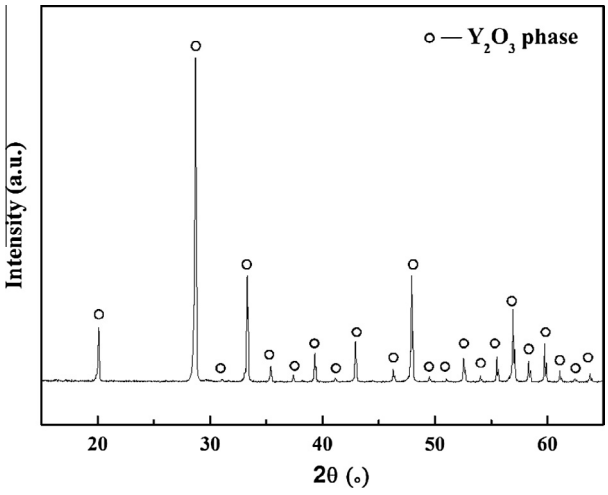

Fig. 3. XRD pattern of Er/Tm/Pr:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramic.

of 1400–2000 nm. Therefore, Pr^{3+} has more inhibition effect on the 1.5 μm light emission compared to Tm^{3+}.

In order to obtain 2.7 μm emission enhancement, Er/Tm/Pr:$(Y_{0.9}La_{0.1})_2O_3$ with different Pr^{3+} concentration were fabricated. Fig. 7 compares the mid-infrared emission spectra of Er/Tm/Pr tri-doped sample under 980 nm excitation with different Pr^{3+} concentrations. The 2.7 μm emission intensity of Er/Tm/Pr:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics exceeds that of Er/Tm co-doped samples when the Pr^{3+} concentration is 0.5 at.%. As the concentration of Pr^{3+} increases to 2 at.%, the emission peaks of 2.7 μm fluorescence is weakened significantly. These experimental results reveals that combining lower Pr^{3+} and Tm^{3+} simultaneously can help achieve the 2.7 μm emission enhancement in Er/Tm/Pr:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics.

Fig. 8 is the 2.7 μm emission spectra of Er, Er/Pr, Er/Tm and Er/Tm/Pr doped transparent ceramics excited by 980 nm laser diode. The concentration of Er, Tm and Pr ions in all the samples is 2 at.%. Emission at 2.7 μm is observed due to the Er^{3+}:$^4I_{11/2} \rightarrow {}^4I_{13/2}$. The 2.7 μm emission intensity of Er/Tm/Pr tri-doped becomes weaker than Er/Tm co-doped sample while that of Er/Pr co-doped samples is the weakest. The experimental result indicates that 2.7 μm emitted light of Er^{3+} ion can be suppressed by high concentration of Pr^{3+}. As shown in Fig. 9, since the energy-level gap between Pr^{3+}:$^1G_4$ and Er^{3+}:$^4I_{11/2}$ levels is as small as that