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Optical properties of Er^{3+}/Yb^{3+}-codoped transparent PLZT ceramic

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Abstract

Optical absorption and emission spectra of Er^{3+}/Yb^{3+} ions in PLZT ($Pb_{1-x}La_xZr_yTi_{1-y}O_3$) ceramic have been studied. Based on the Judd—Ofelt (J–O) theory, the J–O intensity parameters were calculated to be $\Omega_2 = 2.021 \times 10^{-20}\,cm^2$, $\Omega_4 = 0.423 \times 10^{-20}\,cm^2$, $\Omega_6 = 0.051 \times 10^{-20}\,cm^2$ from the absorption spectrum of Er^{3+}/Yb^{3+}-codoped PLZT. The J–O intensity parameters have been used to calculate the radiative lifetimes and the branching ratios for some excited $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$ $^4F_{9/2}$, and $^4S_{3/2}$ levels of Er^{3+} ion. The stimulated emission cross-section ($8.24 \times 10^{-21}\,cm^2$) was evaluated for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}. The upconversion emissions at 538, 564, and 666 nm have been observed in Er^{3+}/Yb^{3+}-codoped PLZT by exciting at 980 nm, and their origins were identified and analyzed.

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Keywords: Er^{3+}/Yb^{3+} ions; Optical properties; PLZT ceramics; Judd–Ofelt analysis; Upconversion

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1. Introduction

The transparent lanthanum-modified lead zirconate titanate (PLZT) ceramics that have the perovskite structure and strong electro-optic effect have been widely used in active electro-optical devices such as optical modulator, optical switches, and optical filters [1,2]. Its interrelated properties and applications have been studied for over 30 years. However, in recent years, there has been an increasing interest in rare-earth-doped PLZT ceramics because rare-earth-doped PLZT ceramics with electro-optic effect are promising for use as optical sources, optical amplifiers, zero-loss electro-optical elements, and monolithic multifunction compact devices [3]. Nd^{3+}, Eu^{3+}, Er^{3+}, and Yb^{3+} ions were doped into PLZT ceramics, and the spectroscopic characteristics of this new transparent ceramics were studied [3–6]. PLZT may be easily substituted with rare earth ions for La without any restrictions up to relatively high concentrations (28 at%) and its electro-optic effects are up to 20 times larger than that of $LiNbO_3$ crystals [3]. Another great advantage lies in the fabrication method since the ceramic processes are usually faster and less costly than the sophisticated crystal growth processes. The rare-earth-doped PLZT also presents lower phonon energy and higher refraction index, which result in higher transition probabilities than in rare-earth-doped $LiNbO_3$, and ceramics usually have better mechanical, thermal, and chemical resistances [6]. In this paper, we analyze the optical absorption, the infrared luminescence, and the upconversion fluorescence properties of Er^{3+}/Yb^{3+}-codoped PLZT ceramic. The Judd–Ofelt (J–O) intensity parameters of Er^{3+} in Er^{3+}/Yb^{3+}-codoped PLZT ceramic were calculated using the J–O theory [7,8]. The calculated values of the J–O intensity parameters were utilized in evaluating the various radiative parameters such as the radiative lifetimes, the fluorescence branch ratios of

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some excited levels of Er^{3+} ion, and the stimulated emission cross-section for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ion. To our knowledge, the spectroscopic characterization of transparent PLZT doped with Er^{3+}/Yb^{3+} ions was studied for the first time.

2. Experiments

The sample of Er^{3+}/Yb^{3+}-codoped PLZT was prepared using the mixed-oxide method at the Boston Applied Technologies Inc., USA [2]. This sample with dimensions 3.04 mm × 3.04 mm × 2 mm consists of 65 mol% lead zirconate plus 35 mol% lead titanate and 8 mol% lanthanum in the form of La_2O_3, i.e., 8/65/35, to which 0.5 mol% Er^{3+} ions in the form of Er_2O_3 and 2.5 mol% Yb^{3+} ions in the form of Yb_2O_3 had been added. The origins of components were PbO, La_2O_3, ZrO_2, TiO_2, Er_2O_3, and Yb_2O_3, respectively. The quantities of Er^{3+} and Yb^{3+} ions in the sample are 1.39×10^{20} and $6.70 \times 10^{20}\,cm^{-3}$, respectively. The absorption spectrum of Er^{3+}/Yb^{3+}-codoped PLZT was recorded in the spectral region 400–1800 nm, which was measured with an UV–VIS–NIR spectrophotometer (Perkin-Elmer Lambda 900). The fluorescence spectrum (in the spectral region of 1300–1800 nm), the upconversion fluorescence spectrum, and the lifetime measurement were recorded using a steady-state/lifetime spectrofluorometer (Edinburgh FLS 920). All measurements were performed at room temperature.

3. Results and discussion

3.1. J–O analysis

The absorption spectrum of Er^{3+}/Yb^{3+}-codoped PLZT ceramic is shown in Fig. 1. All the absorption bands originate from the ground $^4I_{15/2}$ state (Er^{3+}) except for the 872–1053 nm region. The 872–1053 nm band is attributed to the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition of Er^{3+}, and the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+}. In Er^{3+}-doped PLZT ceramic the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ absorption band is weaker than the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ Er^{3+} band, which appears at about 1440–1590 nm (see inset in Fig. 1). In Er^{3+}/Yb^{3+}-codoped PLZT ceramic the 872–1053 nm band is more intense than the 1480–1580 nm band and moreover it is the most intense of the observed absorption Er^{3+} bands. Yb^{3+} gives rise to such an intense absorption band because the absorption band due to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ Yb^{3+} transition appears at about 872–1053 nm. Co-doping Yb^{3+} is for the purpose of increasing strength of the absorption of the pump light (about 980 nm) and Yb^{3+} is a useful sensitizer.

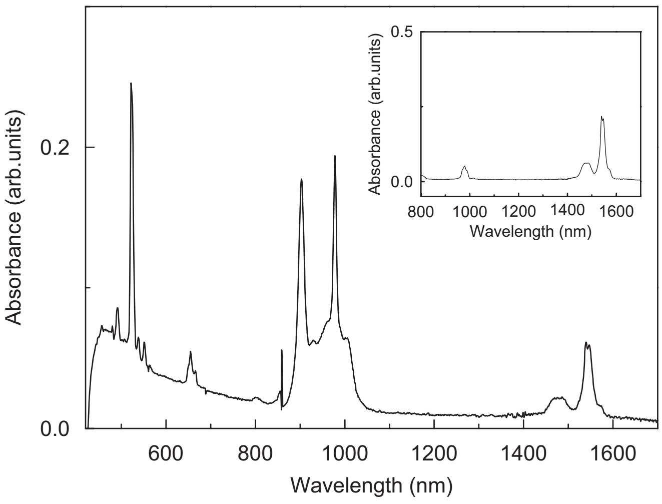

Fig. 1. Absorption spectrum of Er^{3+}/Yb^{3+}-codoped PLZT ceramic with 0.5 mol% Er^{3+} and 2.5 mol% Yb^{3+}. The inset shows the absorption spectrum of Er^{3+} doped PLZT ceramic with 2.0 mol% Er^{3+} ions.

The band positions along with assignment in the absorption spectrum are shown in Table 1. The radiative transitions within the $4f^n$ configuration of a rare earth ion can be analyzed by the J–O approach. According to the J–O theory, the oscillator strength of an electric-dipole absorption transition from the initial state to the final state may be written in the form of

$$f_{\text{calc}} = \frac{8\pi^2 mc}{3h\lambda(2J+1)} \frac{(n^2+2)^2}{9n} \times \sum_{t=2,4,6} \Omega_t |\langle f^N \Psi_J || U^{(t)} || f^N \Psi'_{J'} \rangle|^2, \tag{1}$$

where λ is the mean wavelength of the absorption band; m, e, h, and c are the mass of the electron, the electron charge, the Planck constant, and the velocity of light, respectively; J is the total angular momentum of the initial level ($J = 15/2$ in Er^{3+}), and n is the refractive index, which is 2.401 for Er^{3+}/Yb^{3+}-codoped PLZT. The elements $U^{(t)}$ are the doubly reduced unit tensor operators, which are given in Ref. [9] for the Er^{3+} ion. Ω_t are the J–O intensity parameters, $f^N\Psi_J$ are the wave function of the states with N electrons in 4f shell having total angular momentum J. The parameters Ω_2, Ω_4, and Ω_6 are independent of the electronic quantum numbers with the ground configuration of the Er^{3+} ion. They may be regarded as phenomenological parameters that characterize the radiative transition probabilities within the ground configuration.

The experimental oscillator strengths of the transitions can be obtained by integrating absorbance for each band.

Table 1
Measured and calculated oscillator strengths of Er^{3+} in Er^{3+}/Yb^{3+}-codoped PLZT ceramic (all the transitions are from $^4I_{15/2}$)

Level	λ (nm)	f_{expt} ($\times 10^{-6}$)	f_{calc} ($\times 10^{-6}$)
$^4F_{7/2}$	492	0.477	0.360
$^2H_{11/2}$	522	5.824	5.822
$^4S_{3/2}$	551	0.244	0.038
$^4F_{9/2}$	655	0.732	0.721
$^4I_{9/2}$	806	0.120	0.172
$^4I_{13/2}$	1535	0.909	0.201 (f_{ed}), 0.741 (f_{md})

rms $\Delta f = 0.14 \times 10^{-6}$.