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Radiative Properties of Tm^{3+} Doped in Transparent PLZT for Active Electro-optical Applications

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The optical transition probability of Tm^{3+} (7.0 mol%) doped PLZT was investigated because of its great interest in many fields such as optical communications in the mid-infrared waveband and medical instrumentation. The absolute intensities of its forced electric dipole transitions between 420 and 2000 nm were measured. According to Judd-Ofelt (J-O) theory, three phenomenological parameters, Ω_2=9.133×10^{-21} cm^2, Ω_4=1.529×10^{-21} cm^2 and Ω_6=1.712×10^{-21} cm^2, were obtained. The J-O intensity parameters were used to calculate the radiative lifetime (7.493 ms) of the excited $^3F_4$ level. The stimulated emission cross-section for the $^3F_4 \rightarrow {}^3H_6$ transition was also evaluated. Analysis reveals that Tm^{3+}-doped PLZT is promising for use as efficient optical amplification devices or zero-loss electro-optical devices.

Key words: Tm^{3+}, PLZT, Judd-Ofelt analysis, Radiative lifetime

I. INTRODUCTION

The search for rare-earth doped laser materials remains an open subject. In the past few years, ceramic laser materials have been shown to have many advantages compared to crystals and glasses, such as lower cost fabrication, high melting temperature and large size samples which are more easily manufactured [1-3]. Mass production of ceramic laser materials is possible because no sophisticated techniques or expensive equipment are needed, compared with what is involved in single-crystal growth and subsequent fabrication.

There has been remarkable interest in rare-earth-doped ferroelectric ceramics, which are a suitable material for novel integrated-optic devices formed by a combination of lasers/amplifiers with electro-optic (EO) and nonlinear-optic waveguide components [4]. Recently, we have made a new highly transparent, electro-optic ceramic material, Tm^{3+} doped $Pb_{1-x}La_xZr_yTi_{1-y}O_3$ (PLZT) (Tm^{3+}:PLZT), which has exceptionally high EO effect. The EO-based laser materials have unique features in phase and mode self-modulation that will lead to a revolutionary laser system of higher efficiency, more compactness, and integrated multi-functions [5-7]. Besides these advantages, the $Pb_{1-x}La_xZr_yTi_{1-y}O_3$ ceramic can be easily made with rare earth ions substituted for La without any restrictions up to a relatively high concentration (28%) and its EO effects are up 20 times larger than $LiNbO_3$ (i.e., r_{33}(PLZT)≈600 pm/V, r_{33}($LiNbO_3$)≈31 pm/V), which is an industrial workhorse for EO applications [8]. The photoluminescence (PL) spectra of Tm^{3+} (7.0 mol%) doped PLZT is in the 1865 nm region under a diode laser pump at a wavelength of 790 nm. The 1.8 μm laser emissions are of great interest in many fields and applications, such as optical communications in the mid-infrared waveband, coherent laser radar, and medical instrumentation [9-12], so the radiative properties of Tm^{3+}:PLZT were investigated [13].

In this work, we applied Judd-Ofelt theory [14,15], a standard tool for calculating the parity of forbidden electric diode radiative transition rates among the various levels of rare earth ions in all kinds of hosts [16-20], to investigate the radiative transition probabilities of Tm^{3+}:PLZT. We analyzed the absorption and fluorescence spectra of Tm^{3+}:PLZT. A set of three optical intensity parameters specifying the electric-dipole moment between any two levels can be determined by a least squares fitting of the measured spectral absorption. The calculated values of the optical intensity parameters were utilized in evaluating the various radiative parameters, such as the radiative lifetime of the $^3F_4$ level, and the stimulated emission cross section for the $^3F_4 \rightarrow {}^3H_6$ transition.

II. EXPERIMENTS

The sample of Tm^{3+}:PLZT with dimensions of 3.04 mm×3.04 mm×2 mm consisted of 65 mol% lead zirconate plus 35 mol% lead titanate and 10 mol% lanthanum in the form of La_2O_3, to which had been added 7 mol% Tm^{3+} in the form of Tm_2O_3. The origins of the sample's components were PbO, La_2O_3, ZrO_2, TiO_2 and Tm_2O_3. Wafer samples were prepared by lapping

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and polishing techniques. The density of PLZT was determined to be 7.774 g/cm^3 by the standard Archimedes immersion method using trichloroethylene as the liquid medium. The absorption spectrum of Tm^{3+} doped PLZT in the spectral region of 490-2000 nm was measured with a Perkin Elmer spectrophotometer and Ocean Optics fiber optic spectrometer. For PL measurement, the sample was excited by a diode laser at wavelength 790 nm. The luminescence emitted by the sample was observed at 90° with respect to the axis of the excitation laser light and analyzed by a 1-m McPherson Model 2051 monochromator with a grating of 600/mm.

III. RESULTS AND DISCUSSION

The absorption spectrum of Tm^{3+}:PLZT is shown in Fig.1. A number of spectral lines are observed and assigned as transitions to the different excited states $^3F_4$, $^3H_5$, $^3H_4$, $^3F_3$, $^3F_2$ and $^1G_4$ from the ground $^3H_6$ state. The observed energy and the assignments of all these lines are given in Table I. Figure 2 shows the fluorescence spectrum of the sample in the 1865 nm region under a diode laser pump at wavelength 790 nm.

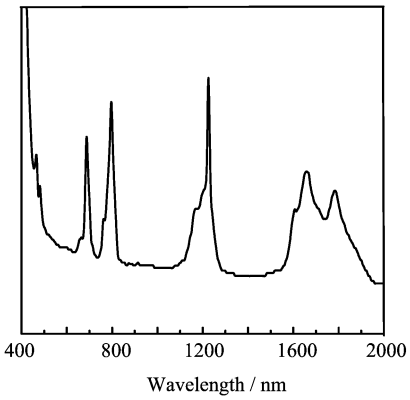

FIG. 1 Absorption spectrum of Tm^{3+} doped PLZT.

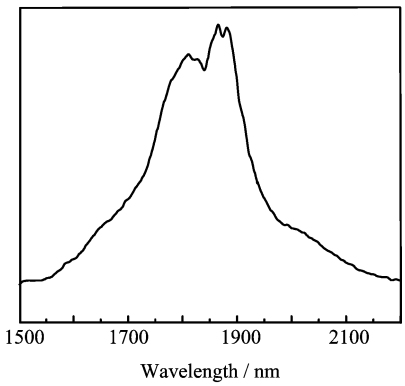

FIG. 2 Emission spectrum of Tm^{3+} doped PLZT.

TABLE I Absorption peaks, experimental and calculated line strengths for Tm^{3+} doped PLZT

Level	λ/nm	$S_{\rm expt}/10^{-21}$cm^2	$S_c/10^{-21}$cm^2
$^1G_4$	467	0.4565	0.5769
$^3F_2$, $^3F_3$	689	2.2182	2.3658
$^3H_4$	795	3.2664	3.3522
$^3H_5$	1227	2.7716	2.4276
$^3F_4$	1658	6.4074	6.4274

$rms(\Delta S)$=0.2849×10^{-21}cm^2.

The experimental line strength of an electric-dipole transition $S_{\rm expt}$ can be calculated from the following formula [21]:

$$\int k(\lambda){\rm d}\lambda = \rho\frac{8\pi^3e^2\overline{\lambda}}{3ch(2J+1)}\frac{1}{n}\frac{(n^2+2)^2}{9}S_{\rm expt} \qquad (1)$$

where $k(\lambda)$ is the absorption coefficient at wavelength λ; ρ is the Tm^{3+} ion concentration, which is 1.009×10^{21}/cm^3 for Tm^{3+}:PLZT; e, h and c are the electron charge, the Planck constant and velocity of light, respectively; $\overline{\lambda}$ is the mean wavelength of the absorption band; J is the total angular momentum of the initial level (J=6 in Tm^{3+}); and n is refractive index, which is 2.402 for Tm^{3+}:PLZT.

According to Judd-Ofelt theory, the line strength of an electric-dipole transition between the initial J manifold and the terminal J' manifold can be expressed as [22]

$$S = \sum_{t=2,4,6}\Omega_t|\langle(S,L)J\|U^{(\lambda)}\|(S',L')J'\rangle|^2 \qquad (2)$$

where the elements $\langle\|U^{(\lambda)}\|\rangle$ are the doubly reduced unit tensor operators, which have been found to be essentially independent of the ion environment [22] and are given in [23] for the Tm^{3+}.

The three coefficients Ω_2, Ω_4, Ω_6 contain implicitly the odd-symmetry crystal-field terms, radial integrals, and perturbation denominators. These coefficients, which are independent of electronic quantum numbers with the ground configuration of the Tm^{3+}, may be regarded as phenomenological parameters characterizing the radiative transition probabilities within the ground configuration. Using Eq.(1) and the values of the absorption spectrum of Tm^{3+}:PLZT, the experimental line strength $S_{\rm expt}$ for the electric dipole transition can be obtained. After $S_{\rm expt}$ is evaluated, the optical intensity parameter Ω_t can be derived by least-squares fitting of Eq.(2): Ω_2=9.133×10^{-21} cm^2, Ω_4=1.529×10^{-21} cm^2 and Ω_6=1.712×10^{-21} cm^2.

The calculated and measured values of the line strengths for each of the observed transitions are given in Table I. An immediate measure of the quality of the fit is given by root-mean-square (rms) deviation between the measured and calculated line strengths, which

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was defined as

$$rms(\Delta S) = \left[\frac{\sum(S_{expt} - S_c)^2}{N - M}\right]^{1/2} \quad (3)$$

where N is the number of transitions and M is the number of parameters determined.

The spontaneous emission probability A for an electric dipole transition between initial J manifold $|(S, L)J\rangle$ and terminal manifold $|(S', L')J'\rangle$ is given by

$$A[(S, L)J; (S', L')J'] = \frac{64\pi^4 e^2 \upsilon^3}{3h(2J+1)} \frac{n(n^2+2)^2}{9} \cdot \sum_{\lambda=2,4,6} \Omega_\lambda |\langle (S, L)J \| U^{(\lambda)} \| (S', L')J' \rangle|^2 \quad (4)$$

where υ is the frequency in inverse centimeters. The radiation lifetime τ_R for the transition involved can be written as

$$\frac{1}{\tau_R[(S, L)J]} = \sum\nolimits_{S,L,J} A[(S, L)J; (S', L')J'] \quad (5)$$

and the fluorescence branching ratio is obtained from

$$\beta[(S, L)J; (S', L')J'] = \frac{A[(S, L)J; (S', L')J']}{\sum_{S,L,J} A[(S, L)J; (S', L')J']} \quad (6)$$

The calculated transition probability, fluorescence branching ratio and radiative lifetime for the emission transitions of Tm^{3+}:PLZT are listed in Table II. In Table II, the calculated radiative lifetime of $^3F_4 \rightarrow {}^3H_6$ is about 7.493 ms. It is of the same order of magnitude as that for Tm^{3+} doped silica-glass systems for which laser phenomena have been reported [24,25].

Using the values for the radiative transitions probabilities calculated above, along with corresponding fluorescence spectra, the stimulated emission cross section of the $^3F_4 \rightarrow {}^3H_6$ transition can be determined by

$$\sigma = \frac{A \langle\lambda\rangle^4}{4\pi^2 n^2 c \Delta\lambda_{eff}} \quad (7)$$

where $\langle\lambda\rangle^4$ is the mean wavelength of the emission transition and $\Delta\lambda_{eff}$ are the effective bandwidth, defined as

$$\Delta\lambda_{eff} = \int \frac{I(\lambda)d\lambda}{I_{max}} \quad (8)$$

here I is the fluorescence intensity and I_{max} is the intensity at the band maximum. Through the above formula, we obtain that the stimulated emission cross-section of $^3F_4 \rightarrow {}^3H_6$ is 1.044×10^{-20} cm^2 and the effective bandwidth is 226.9 nm.

The radiative lifetime and stimulated emission cross section of $^3F_4$ is comparable with that of Tm^{3+}-doped glass systems of technological importance [25,26]. The effective band width 226.9 nm is also the same magnitude with those of Tm^{3+} in various glass matrices exhibiting optical amplification [27,28]. This large bandwidth is an advantage for broadband optical amplification. From these values, it is therefore concluded that the Tm^{3+}:PLZT could be used to develop a multifunction tunable laser and a multi-function broadband amplifier in the 1860 nm wavelength region.

TABLE II Transition probability (A), branching ratio (β) and radiative lifetime (τ_R) for the transitions of Tm^{3+} doped PLZT

Transitions	Energy/cm^{-1}	A/s^{-1}	β/%	τ_R/ms
$^4F_4 \rightarrow {}^3H_6$	5362	133.45	100	7.493
$^3H_4 \rightarrow {}^3H_6$	12495	728.95	90.25	1.238
$^3F_4$	6819	69.27	8.58	
$^3H_5$	4415	9.52	1.18	
$^3F_3 \rightarrow {}^3H_6$	14294	896.14	75.11	0.838
$^3F_4$	8618	34.68	2.91	
$^3H_5$	6214	261.28	21.90	
$^3H_4$	1799	1.05	0.08	
$^3F_2 \rightarrow {}^3H_6$	15022	326.03	33.75	1.035
$^3F_4$	9346	518.16	53.64	
$^3H_5$	6942	109.93	11.38	
$^3H_4$	2527	11.85	1.23	
$^3F_3$	728	0.01	≈0	
$^1G_4 \rightarrow {}^3H_6$	21130	613.11	46.08	0.751
$^3F_4$	15454	81.32	6.11	
$^3H_5$	13050	445.99	33.52	
$^3H_4$	8635	159.01	11.95	
$^3F_3$	6836	25.14	1.89	
$^3F_2$	6108	6.10	0.46	

IV. CONCLUSION

A new, highly transparent electro-optic ceramic material, Tm^{3+}:PLZT was fabricated. The EO effects of PLZT are up to 20 times larger than $LiNbO_3$, which is the industrial workhorse for EO applications. This EO-based laser material has unique features in phase and mode self-modulation that may lead to a new compact laser system with higher efficiency and integrated multifunctions. The PL spectra of Tm^{3+} (7.0 mol%) doped PLZT is in the 1865 nm region under a diode laser pump at wavelength 790 nm, and the radiative properties of Tm^{3+}:PLZT were investigated. Laser emitters in the 1.8 μm range are generating great interest in many fields and applications, such as optical communications in the mid-infrared waveband, coherent laser radar, and medical instrumentation. In this article, the absolute intensities of the forced electric dipole transitions of the Tm^{3+}:PLZT between 420 and 2000 nm were measured and theoretically accounted for in terms

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of the three phenomenological parameters defined in Judd-Ofelt theory for rare-earth intensities. The radiative lifetime of the metastable $^3F_4$ level, the radiative transition rate and the stimulated emission cross-section for the $^3F_4 \rightarrow {}^3H_6$ are also evaluated. The radiative property of the Tm^{3+}:PLZT ceramic shows that Tm^{3+} doped PLZT ceramic is promising for making active electro-optical devices.

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