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Judd ofelt analysis of the Er^{3+} ($4f^{11}$) absorption intensities in Er^{3+}-doped Sc_2O_3

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A spectroscopic study on Er^{3+} ($4f^{11}$) ions doped in Sc_2O_3 transparent ceramics was performed in order to assess its potential as a laser material for different emission wavelengths. The absolute intensities of the absorption bands in the 370 to 1600 nm range were measured at 300 K. The $\Omega_2, \Omega_4, \Omega_6$, Judd-Ofelt intensity parameters for Er^{3+} *f-f* transitions were determined and are comparable with the experimental parameters reported for Er^{3+} in other sesquioxides single crystals.

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1. Introduction

Er^{3+} doped laser materials are interesting for the development of lasers at different wavelengths from visible to near infrared (especially ~1.5 μm [1,2] and ~3 μm [3]) necessary for a series of applications. The laser emission at ~ 1.5 μm is used in fiber optics and optical amplifiers, for telecommunication or medicine. The visible emissions in green or red are attractive for upconversion laser devices pumped with infrared laser diodes [4-7]. The cubic sesquioxides, especially scandium oxide (Sc_2O_3) crystals with their very high thermal conductivity, chemical stability, optical properties (low phonons) and the possibility of doping with RE^{3+} are interesting as laser materials. However, due to their very high melting point ~ 2430°C [8], it is very difficult to grow such crystals with high optical quality and large sizes. In the recent years the transparent ceramics techniques have been developed to overcome this difficulty. Our investigation deals with the spectral properties of Er^{3+} doped Sc_2O_3 transparent ceramics.

The Sc_2O_3 – scandium sesquioxide forms at room temperature a cubic C-type structure, belonging to the $IA\bar{3}$ space group. The unit cell contains 16 formula units with 32 cations that form 24 sites of C_2 symmetry and 8 sites of C_{3i} symmetry. The C_2 site is an eightfold cubic structure with two oxygen vacancies on a face diagonal, while C_{3i} correspond to a cube with two vacancies on a body diagonal. The lattice constant is ~ 10Å and the cationic density ($3.334\times10^{22}/cm^3$) is rather high compared to other laser crystals. The RE^{3+} dopants are assumed to occupy randomly both sites, but the induced electric dipole transitions are symmetry allowed only for C_2 centers.

Some of the spectroscopic properties of Er^{3+} doped Sc_2O_3 transparent ceramics have been recently investigated in our group [9, 10]. In the present study, additional spectral parameters are determined in order to assess the perspectives of Er^{3+} doped Sc_2O_3 transparent ceramics as laser material, the Judd-Ofelt [11, 12] (JO) parameters. The Judd-Ofelt parameters are important for the understanding of the relationships between host and Er^{3+} emission properties. No JO analysis has been published for Er: Sc_2O_3 transparent ceramics, or even for single crystals.

2. Experimental methods

The Er-doped Sc_2O_3 transparent ceramics were prepared at Japan Fine Ceramics Center, Nagoya, Japan by solid-state synthesis followed by isostatic compression (~2 MPa) and vacuum sintering at 1750°C. The average size of grains is in the 30 μm range. The optical spectroscopic measurements of 0.3 at% Er: Sc_2O_3 were performed on an extended spectral range $6000cm^{-1}$ – $28000\ cm^{-1}$. The room temperature absorption spectra were measured with a set-up consisting of a Jarell Ash monochromator, S20 and S1 photomultipliers, Si and Ge photodiodes and a Lock in amplifier SR830 on line with a computer.

3. Results and discussion

A series of spectral parameters of Er^{3+} ions in the Sc_2O_3 transparent ceramics could be estimated on the basis of the Judd–Ofelt (JO) theory, which is used largely in evaluating the probability of the forced electric-dipole

transitions of rare-earth ions in various environments, and is often used to calculate the spectroscopic parameters, among them JO parameters. These parameters can be regarded as the phenomenological intensity parameters that characterize the radiative transition probability. The line strengths of the transitions between the ground $^4I_{15/2}$ Er^{3+} manifold and the excited J' manifolds can be calculated. According to the Judd-Ofelt theory, the line strength for forced electric dipole (e.d.) transitions between two manifolds characterized by their total angular momentum quantum numbers, J $\left|4f^n[S,L]J\right\rangle$ and J' $\left|4f^n[S',L']J'\right\rangle$ can be expressed in the following form:

$$S_{calc}^{ed} = \sum_{t=2,4,6} \Omega_t \left|\left\langle 4f^n[S,L]J\right\|U^{(t)}\left\|4f^n[S',L']J'\right\rangle\right|^2, \quad (1)$$

where $\Omega_{(t)}$ are JO parameters, $\left\langle\left\|U^{(t)}\right\|\right\rangle$ are the doubly reduced matrix elements of unit tensor operator calculated in the intermediate-coupling approximation. The values of the squared reduced elements for the chosen Er^{3+} transitions were taken from Carnall *et al.* [13]. The squared matrix elements are independent of the crystal host. The measured line strength, S_{meas} (J→J') of the chosen bands are determined using the following expression:

$$S_{meas}(J \to J') = \frac{3ch(2J+1)n}{N_0 3\pi^3 \overline{\lambda}_0}\left[\frac{9}{(n^2+2)^2}\right]\Gamma, \quad (2)$$

where c is the speed of light, h is the Planck constant, N_0 is the Er^{3+} ion concentration, n is the bulk index of refraction, $\overline{\lambda}$ is the mean wavelength of the absorption band that corresponds to the J→J' transition, $\Gamma = \int k(\lambda)d(\lambda)$ is the integrated absorption coefficient, k(λ) is the absorption coefficient function on λ. The factor $[9/(n^2+2)^2]$ represents the local field correction for the ion in a dielectric medium. From several experimental refractive indices of the bulk Sc_2O_3 given in [14, 15], the wavelengths dependence of the refractive indices was obtained by using a least-squared fitting program to the Sellmeier dispersion equation:

$$n^2(\lambda) = 1 + \frac{S\lambda^2}{\lambda^2 - \lambda_0^2}, \quad (3)$$

That provides the S= 2.856 and λ_0=76.896 nm constants, used to recalculate the values of the indices of refraction at the appropriate mean wavelengths of the Er^{3+} ion absorption.

To determine the Judd Ofelt (JO) parameters for Er^{3+} ($4f^{11}$) transitions in Sc_2O_3 transparent ceramic eleven absorption bands of the room temperature spectra were used. In Fig. 1-4 the room temperature absorption for C_2 centers in Er: Sc_2O_3 transparent ceramic ranging from 450 to 1600nm are presented. Only C_2 centers (3/4 from the actual Er^{3+} concentration) contribute to e.d. transitions. For $^4I_{15/2}\rightarrow{}^4I_{13/2}$ transition contain the magnetic dipole contribution too.

In order to estimate the JO parameters the experimental line strengths were measured using eq. (2). The values of the integrated absorbance and the mean wavelength were calculated after subtracting the base line of the spectrum. This base line subtraction affects the accuracy of the band integration and thus the accuracy of Ω_t parameters determination.

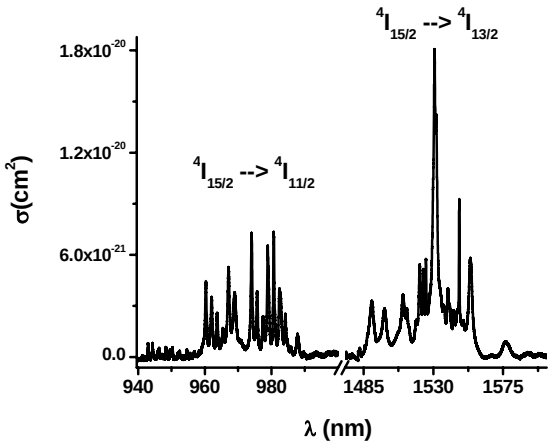

Fig.1 $^4I_{15/2}\rightarrow{}^4I_{13/2}$, $^4I_{15/2}\rightarrow{}^4I_{11/2}$ absorption cross-sections spectrum of 0.3at. % Er: Sc_2O_3 at 300K.

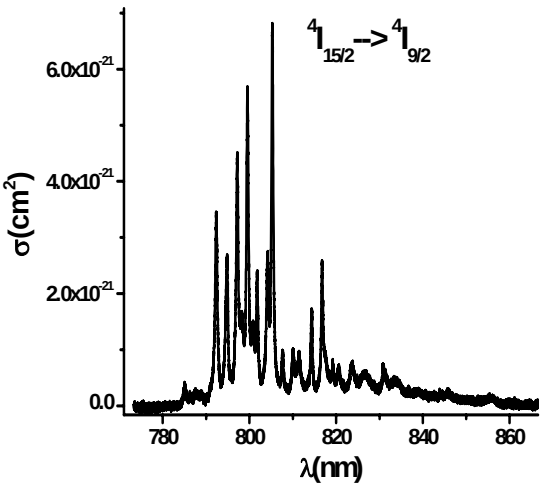

Fig.2 $^4I_{15/2}\rightarrow{}^4I_{9/2}$ absorption spectrum of 0.3at. % Er: Sc_2O_3 at 300K

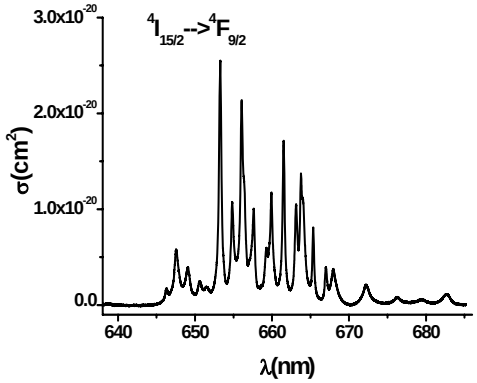

Fig.3 $^4I_{15/2}\rightarrow{}^4F_{9/2}$ absorption spectrum of 0.3at. % Er: Sc_2O_3 at 300K

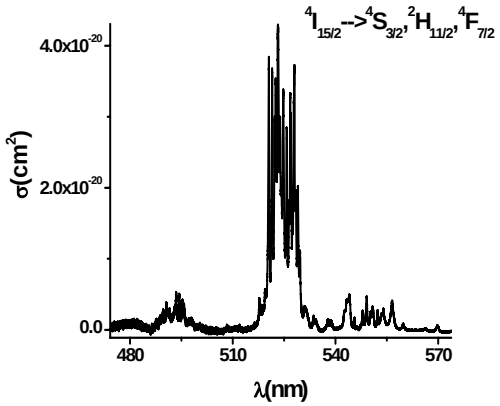

Fig.4 $^4I_{15/2}\rightarrow{}^4S_{3/2},{}^2H_{11/2},{}^4F_{972}$ absorption spectrum of 0.3at. % Er: Sc_2O_3 at 300K

Table 1. Measured and calculated absorption line strength of Er^{3+} in Sc_2O_3 transparent ceramic at 300K.

Transition from $^4I_{15/2}$ to excited states	$\bar{\lambda}$ (nm)	n	Γ (nm cm^{-1})	S_{meas} (10^{-20}cm^2)	S_{calc} (10^{-20}cm^2)
$^4I_{13/2}$	1512.5	1.965	28.53	1.553	1.398
$^4I_{11/2}$	976.86	1.968	5.105	0.445	0.421
$^4I_{9/2}$	802.9	1.97	3.11	0.326	0.300
$^4F_{9/2}$	658.99	1.973	9.8	1.264	1.216
$^4S_{3/2}$,	552.63	1.978	1.54	0.235	0.200
$^2H_{11/2}$	525.84	1.979	20.1	3.236	3.272
$^4F_{7/2}$	496.35	1.981	1.937	0.329	0.742
$^4F_{5/2}$, $^4F_{3/2}$	457.76	1.984	1.02	0.188	0.282
$^2G_{9/2}$, $^4F_{9/2}$	409.35	1.99	1.34	0.274	0.215
$^4G_{11/2}$	382.97	1.994	19.5	4.26	4.236
$^4G_{9/2}$	369.13	1.996	2.39	0.541	0.487

In Table I the mean wavelength, refractive indices, integrated absorption coefficients and measured and calculated line strength for several Er^{3+} transitions in Sc_2O_3 ceramic are given.

The intensity JO parameters $\Omega_2, \Omega_4, \Omega_6$ for Er^{3+} in Sc_2O_3 were determined by the procedure given in [16] and are given in Table II. As observed, the JO parameters obtained for Er^{3+} in Sc_2O_3 transparent ceramics are comparable with those obtained for Er^{3+}: Y_2O_3 single crystals [16].

Table 2. The JO parameters of Er^{3+}: Sc_2O_3 transparent ceramics (this work) and Er^{3+}: Y_2O_3 [16].

Host	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	Ω_6 (10^{-20} cm^2)	X= Ω_4/ Ω_6
Er^{3+}: Sc_2O_3	3.57	1.61	0.79	2.03
Er^{3+}: Y_2O_3	4.59	1.21	0.48	2.52

The values of the intensity parameters can then be used to recalculate the transition line strengths of the absorption bands using the Eq. (1). The calculated absorption line strength S_{calc} is given in Table I. A measure of the accuracy of the fit is given by rms deviation:

$$\Delta S_{rms} = \left[(q-p)^{-1}\sum(\Delta S)^2\right]^{1/2}, \qquad (4)$$

where $\Delta S = S_{calc} - S_{meas}$ is the deviation, q is the number of the transition analyzed and p is the number of the parameteres, that in this case are 11 and respectively 3. The values in Table I provide an rms deviation of 0.164×10^{-20}cm^2.

A spectroscopic quality factor X= Ω_4/ Ω_6 has been introduced by Kaminskii for Nd^{3+} $^4F_{3/2}$ -^4I_J transitions [17] as an important characteristic in predicting the stimulated emission for the laser active media. Similarly, one could use the same parameter to evaluate the upconversion emission for Er $^4S_{3/2}$ -$^4I_{15/2}$ transition in different hosts. According to [18] for Er^{3+} X varies from 0.126 to 3.372. In our case, Er^{3+}: Sc_2O_3 transparent ceramic, this factor is 2.2 (Table II), within this range.

4. Conclusions

Judd-Ofelt analysis of Er^{3+} ion optical intensities in Sc_2O_3 transparent ceramic was performed, and based on the absolute absorption data the three phenomenological parameters $\Omega_2, \Omega_4, \Omega_6$ were determined with. The estimated parameters are similar to those of Er^{3+} in Y_2O_3 single crystals. Similarly to Nd^{3+}, a spectroscopic quality factor $X= \Omega_4/ \Omega_6$ for the Er^{3+} green upconversion emission was determined to be 2.2, within the range for other hosts. These parameters can be used to estimate the radiative probabilities, radiative lifetimes, branching ratios for different transitions; that along with experimental lifetimes allow the determination of the quantum efficiencies. Such investigations are in progress.

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