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Judd-Ofelt Analysis of Er, Yb Co-doped Y_2O_3 Transparent Ceramics

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Abstract: This paper presents a spectroscopic study of Er, Yb co-doped Y_2O_3 transparent ceramics with 20 at% Yb^{3+} and varied Er^{3+} concentration (0.5 at% to 5 at%). Room-temperature absorption spectra and refractive indices were measured. Standard Judd-Ofelt analysis was applied and the intensity parameters were calculated. With Er^{3+} concentration increasing, Ω_2 decreases from 5.41 to 3.36, Ω_4 ranges from 0.96 to 1.29 and Ω_6 ranges from 0.64 to 0.72. The spectroscopic quality factor $X_{4/6}$ ranges from 1.46 to 1.88. The radiative lifetime of $^4I_{13/2}$ manifold is longest in the Er, Yb co-doped Y_2O_3 transparent ceramic with 0.5 at% Er^{3+} content. All suggest that the Er, Yb co-doped Y_2O_3 transparent ceramic could be a potential material for near-infrared laser application.

Key words: Judd-Ofelt; Y_2O_3; transparent ceramic

Among all the rare-earth (RE) ions, Er^{3+}-Yb^{3+} system has been proved to be one of the most attractive systems for laser oscillation, especially for the eye-safe region at around 1.5 μm and the water-absorption region at around 3 μm[1-3]. The broad absorption band of Yb^{3+} around 980 nm allows the system to be pumped efficiently by diode lasers. However, due to the low laser-induced damage threshold and the poor chemical/thermal stability of host materials, the development of this system is hampered.

Y_2O_3 transparent laser ceramic has earned a lot of attention as an alternative to single crystals to fabricate large scale laser material with engineered thermo-optic properties. This material shows high chemical/thermal stability, high thermal conductivity, high dopant capacity, high damage threshold and large transmittance range. Many works have been done to study RE doped Y_2O_3 transparent ceramics, such as Yb: Y_2O_3[4,5], Nd: Y_2O_3[6], Nd, Yb: Y_2O_3[7] and Er, Yb: Y_2O_3[8,9]. However, there are still some spectroscopic parameters that need to be determined in the Er, Yb: Y_2O_3 transparent ceramic for future application.

In this work, we used the Judd-Ofelt (J-O) theory to study the electric dipole transitions in the vacuum-sintered Er, Yb: Y_2O_3 transparent ceramics. The wavelength-dependent refractive indices were measured with ellipsometer. The optical intensity parameters, radiative transition probabilities and radiative lifetimes of Er^{3+} emission in the Er, Yb co-doped Y_2O_3 transparent ceramics were determined.

1 Experiment

Raw materials were 99.99% purity powders of Y_2O_3, Er_2O_3 and Yb_2O_3. La_2O_3 and ZrO_2 were used as sintering aids. The powders were mixed according to the formula $Y_{0.68-x}Yb_{0.2}La_{0.09}Zr_{0.03}Er_xO_{1.515}$ (x=0~0.05) and ball-milled in ethanol for over 10 h. The slurry was dried and sieved through a 200-mesh (74 μm) screen, and then pressed into pellets and cold isostatic pressed at 200 MPa for 2 min. The pressed pellets were sintered at 1800 ℃ for 20 h under 1.0×10^{-3} Pa. After sintering, the ceramics were annealed at 1450 ℃ for 10 h in air and polished on both sides.

The absorption spectra were measured with the UV-VIS-NIR spectrophotometer (UV-3600, Shimadzu, Tokyo, Japan), with a deuterium lamp as light source for the ultraviolet range and a halogen lamp for the visible and near-infrared range. The refractive indices were acquired with the ellipsometer (V-VASE, J.A. Woollam, Nebraska, USA).

2 Results and Discussion

2.1 Absorption spectra and refractive indices

Fig.1 shows the absorption coefficient obtained from the transmittance spectrum using the followed equation:

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$$\alpha(\lambda) = \frac{1}{d} \ln \frac{I}{I_0} = \frac{1}{0.43d} \log T \quad (1)$$

where α is the absorption coefficient; d is the thickness of the specimen; T is the in-line transmittance measured by the spectrophotometer; I_0 and I are the light intensity before and after transmitting through the specimen, respectively. After subtracting the baseline, the influence caused by surface reflection and scattering was ruled out and the absorption spectra of the Er, Yb: Y_2O_3 transparent ceramics were determined.

Fig.1 shows that there are 11 absorption bands in the Er^{3+} single-doped Y_2O_3 transparent ceramic, centered at 366, 379, 407, 453, 490, 522, 546, 654, 800, 980 and 1536 nm, which correspond to the Er^{3+} transition from $^4I_{15/2}$ to $^4G_{7/2}$+$^4G_{9/2}$+$^2K_{15/2}$, $^4G_{11/2}$, (^2G, ^4F, $^2H)_{9/2}$, $^4F_{3/2}$+$^4F_{5/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$, respectively. The absorption of Er^{3+} at around 980 nm ($^4I_{15/2}\rightarrow{}^4I_{11/2}$) is weak and narrow, while the absorption of Yb^{3+} ($^2F_{7/2}\rightarrow{}^2F_{5/2}$) is strong and broad. In the Er, Yb co-doped Y_2O_3, Er: $^4I_{15/2}\rightarrow{}^4I_{11/2}$ absorption band overlaps with Yb: $^2F_{7/2}\rightarrow{}^2F_{5/2}$ absorption bands, suggesting a possible energy transfer from Yb^{3+} to Er^{3+}. This demonstrates the possibility of efficient InGaAs diode pumping for the Er-Yb laser system.

To adopt the Judd-Ofelt analysis, the refractive index n of the bulk material is necessary. Fig.2 shows the wavelength-dependent refractive indices of Er, Yb co-doped Y_2O_3 transparent ceramics measured by the ellipsometer. The refractive indices decrease with the wavelength increasing and can be fitted with the Sellmeier equation:

$$n^2(\lambda) = 1 + \frac{B\lambda^2}{\lambda^2 - C} \quad (2)$$

where n is the refractive index and λ is the wavelength in vacuum. In this work, we assume that λ approximately equals to the wavelength in air. B and C are Sellmeier coefficients that can be determined from the experimental results. The Sellmeier coefficients calculated from Fig.2 are listed in Table 1.

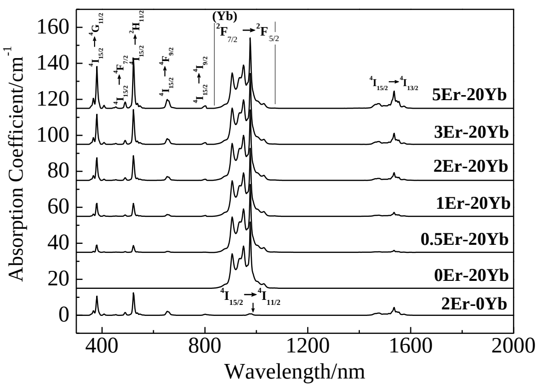

Fig.1 Absorption spectra of Er/Yb single-doped and co-doped Y_2O_3 transparent ceramics

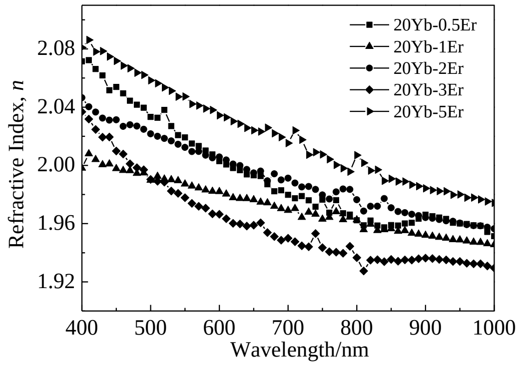

Fig.2 Refractive indices of the Er, Yb co-doped Y_2O_3 transparent ceramics

Table 1 Sellmeier coefficients of the refractive indices for the Er and Yb co-doped Y_2O_3 transparent ceramics

Specimen	Er content/at%	Yb content/at%	B	$C/\times10^4$
Specimen-1	0.5	20	2.74	2.99
Specimen-2	1	20	2.77	1.57
Specimen-3	2	20	2.80	2.17
Specimen-4	3	20	2.65	2.60
Specimen-5	5	20	2.87	2.71

2.2 Judd-Ofelt analysis

Absorption coefficients in Fig.1 were used to determine the phenomenological Judd-Ofelt parameters in Er, Yb co-doped Y_2O_3 transparent ceramics. The Er^{3+} absorption peaks used in Judd-Ofelt analysis are listed in Table 2. The Er^{3+}: $^4I_{15/2}\rightarrow{}^4I_{11/2}$ absorption overlapped with the Yb^{3+}: $^2F_{7/2}\rightarrow{}^2F_{5/2}$ absorption, so we didn't use it in the analysis. Some Er^{3+} absorption peaks overlapped with each other, so they were treated together. Details about the Judd-Ofelt analysis can be found in many works [10,11]. This method has been extensively used to understand the nature of lanthanide luminescence[12,13].

With the absorption coefficients in Fig.1, measured line strength $S_{meas}(J\rightarrow J')$ of the absorption bands can be determined using the following equation:

$$S_{meas}(J \rightarrow J') = \frac{3ch(2J+1)n}{8\pi^3\bar{\lambda}e^2N_0}\left[\frac{9}{(n^2+2)^2}\right]\int\alpha(\lambda)d\lambda \quad (3)$$

where α is the absorption coefficient; J and J' are the total angular momentum quantum numbers of the initial and final states, respectively; n is the refractive index; N_0 is the concentration of Er^{3+}; c is the speed of light in vacuum, h is the Plank constant and λ is the average wavelength obtained by the following equation:

$$\bar{\lambda} = \frac{\int\lambda\alpha(\lambda)d\lambda}{\int\alpha(\lambda)d\lambda} \quad (4)$$

The theoretical line strength can be expressed in the following form:

$$S_{cal}(J \to J') = \sum_{t=2,4,6} \Omega_t \left| \langle (S,L)J \| U^{(t)} \| (S',L')J' \rangle \right|^2 \quad (5)$$

where Ω_2, Ω_4 and Ω_6 are the Judd-Ofelt intensity parameters and $<\|U^{(t)}\|>$ are the doubly reduced matrix elements between states (S, L, J) and (S', L', J'). The matrix elements depend only on the angular momentum of the Er^{3+} states and are independent of the host material, which can be obtained from the tables of Nielson and Koster[14]. In this work, we used the matrix element value listed in the paper of Sardar et al (Table 2) [15]. Assuming $S_{meas}= S_{cal}$, the Judd-Ofelt intensity parameters Ω_2, Ω_4 and Ω_6 can be determined by least-square-error fitting. The results are listed in Table 3. From Table 3 we can see that Ω_2 decreases with increasing Er^{3+} concentration, which means that the crystal environment around the Er^{3+} ions becomes more and more disordered.

$X_{4/6}=\Omega_4/\Omega_6$ is defined as the spectroscopic quality factor. In our work, the $X_{4/6}$ factor of Er, Yb co-doped Y_2O_3 with different Er^{3+} concentration ranges from 1.46 to 1.88 (Table 3), which lays in the range of 0.126~3.372 for Er^{3+} according to Kaminskii's work[16]. The $X_{4/6}$ values in Er, Yb co-doped Y_2O_3 transparent ceramics are smaller than the values reported in Er single-doped Y_2O_3 single crystals and ceramics[17-19]. This suggests that the Er, Yb co-doped Y_2O_3 transparent ceramics may lead to better laser output.

With the intensity parameters Ω_2, Ω_4 and Ω_6, the radiative decay rates $A(J\to J')$ from the excited states (J) to the lower states (J') and the radiative lifetime τ of Er^{3+} were calculated according to the following equation:

$$A(J \to J') = \frac{64\pi^4 e^2}{3h\bar{\lambda}^3 (2J+1)} \frac{(n^2+2)^2}{9n} \sum_{t=2,4,6} \Omega_t \left| \langle (S,L)J \| U^{(t)} \| (S',L')J' \rangle \right|^2 \quad (6)$$

$$\tau(J) = \frac{1}{\sum_{J'} A(J \to J')} \quad (7)$$

Table 2 Parameters used in Judd-Ofelt analysis[15]

$^4I_{15/2}\to$	$[U^{(2)}]^2$	$[U^{(4)}]^2$	$[U^{(6)}]^2$	S_{meas} ($\times10^{-20}$ cm^2) 0.5at% Er	2at% Er	5at% Er
$^4G_{9/2}$+$^4G_{11/2}$	0.9183	0.7678	0.2407	5.867	5.459	3.891
$^2G_{9/2}$	0.0000	0.0189	0.2256	0.217	0.182	0.194
$^4F_{3/2}$+$^4F_{5/2}$	0.0000	0.0000	0.3504	0.244	0.134	0.131
$^4F_{7/2}$+$^2H_{11/2}$+$^4S_{3/2}$	0.7125	0.5594	0.9402	4.973	4.820	3.811
$^4F_{9/2}$	0.0000	0.5354	0.4618	0.839	0.994	0.910
$^4I_{9/2}$	0.0000	0.1733	0.0099	0.071	0.156	0.147
$^4I_{13/2}$*	0.0195	0.1173	1.4316	1.112	1.140	1.090

*Magnetic dipole transition has been substracted

Table 3 Calculated Judd-Ofelt intensity parameters Ω_2, Ω_4, Ω_6 ($\times10^{-20}$ cm^2) and the X factors

Sample	Ω_2	Ω_4	Ω_6	$X_{4/6}$	Ref.
0.5%Er-20%Yb-Y_2O_3 ceramic	5.41	0.96	0.64	1.50	This work
1%Er-20%Yb-Y_2O_3 ceramic	5.55	1.06	0.72	1.46	This work
2%Er-20%Yb-Y_2O_3 ceramic	4.81	1.23	0.65	1.88	This work
3%Er-20%Yb-Y_2O_3 ceramic	4.30	1.29	0.69	1.88	This work
5%Er-20%Yb-Y_2O_3 ceramic	3.36	1.02	0.69	1.47	This work
Er:Y_2O_3 single crystal	4.59	1.21	0.48	2.52	Ref [17]
0.5% Er:Y_2O_3 ceramic	5.34	1.63	0.59	2.76	Ref [18]
1% Er:Y_2O_3 nanocrystals	3.58	2.09	0.41	5.10	Ref [19]
Er:Y_2O_3 nanocrystals	5.4	1.22	0.92	1.33	Ref [20]

Table 4 Calculated radiative lifetime of Er^{3+} in Er, Yb co-doped x%Er-20%Yb-Y_2O_3 transparent ceramics (μs)

Manifolds	0.5	1	2	3	5
$^4I_{13/2}$	8701.83	7698.99	8162.02	8427.50	7833.76
$^4I_{11/2}$	4871.27	4458.38	4865.17	5203.05	4972.97
$^4I_{9/2}$	4579.97	4160.66	3681.09	3747.51	4022.98
$^4F_{9/2}$	572.51	528.74	483.03	490.80	509.18
$^4S_{3/2}$	531.06	487.00	516.68	520.19	461.66
$^2G_{9/2}$	203.42	200.47	205.12	216.36	214.48

where J and J' are the total angular momentum quantum numbers of the initial and final states, respectively; n is the refractive index, h is the Plank constant and λ is the average wavelength. We didn't list the calculated result of radiative decay rates $A(J\to J')$ in this paper to save space. The calculated radiative lifetime τ of several main manifolds are listed in Table 4. It can be seen that the calculated radiative lifetime of $^4I_{13/2}$ manifolds decreases with increasing Er^{3+} concentration. This suggests that low Er^{3+} concentration might be better for 1.5 μm laser application with Er, Yb co-doped Y_2O_3 transparent ceramics.

3 Conclusions

1) The Judd-Ofelt parameter Ω_2 decreases from 5.41 to 3.36 with Er^{3+} concentration increasing from 0.5 at% to 5 at%. The Ω_4 parameter ranges from 0.96 to 1.29 and the Ω_6 parameter ranges from 0.64 to 0.72.

2) The spectroscopic quality factor $X_{4/6}$ ranges from 1.46 to 1.88, which is smaller than that in the Er single-doped Y_2O_3 single crystals or ceramics, suggesting that Er, Yb co-doped Y_2O_3 transparent ceramics may have better laser performance.

3) With Er^{3+} concentration increasing from 0.5 at% to 5 at%, the theoretical radiative lifetime τ of $^4I_{13/2}$ manifold decreases from 8.70 ms to 7.83 ms, suggesting that Er, Yb co-doped Y_2O_3 transparent ceramics with low Er^{3+} concentration may be

better for 1.5 μm laser application.

References

1 Stange H, Petermann K, Huber G *et al. Applied Physics B Photophysics and Laser Chemistry*[J], 1989, 49(3): 269
2 Dinerman B J, Moulton P F. *Optics Letters*[J], 1994, 19(15): 1143
3 Aubourg A, Didierjean J, Aubry N *et al. Optics Letters*[J], 2013, 38(6): 938
4 Petrov V V, Pestryakov E V, Petrov V A *et al. Laser Physics*[J], 2014, 24(7): 074 014
5 Tokurakawa M, Takaichi K, Shirakawa A *et al. Applied Physics Letters*[J], 2007, 90(7): 071 101
6 Ikesue A, Kamata K, Yoshida K. *Journal of the American Ceramic Society*[J], 1996, 79(2): 359
7 Lupei V, Lupei A, Gheorghe C *et al. Optics Letters*[J], 2009, 34(14): 2141
8 Hou X R, Zhou S M, Jia T T *et al. Physica B Condensed Matter*[J], 2011, 406(20): 3931
9 Lu S Z, Yang Q H, Zhang B *et al. Optical Materials*[J], 2011, 33(5): 746
10 Judd B R. *Physical Review*[J], 1962, 127(3): 750
11 Ofelt G S. *Journal of Chemical Physics*[J], 1962, 37(3): 511
12 Ye Y X, Wei L H, Sheng W C *et al. Rare Metal Materials and Engineering*[J], 2014, 43(10): 2359
13 Yin B, Yang Z M, Yang G F *et al. Rare Metal Materials and Engineering*[J], 2008, 37(6): 1016 (in Chinese)
14 Nielson C W, Koster G F. *Spectroscopic Coefficients for the pn, dn, and fn Configurations*[M]. Cambridge, MA: MIT Press, 1964: 53
15 Sardar D K, Gruber J B, Zandi B *et al. Journal of Applied Physics*[J], 2003, 93(4): 2041
16 Kaminskii A A. *Crystalline Lasers: Physical Processes and Operating Schemes*[M]. New York: CRC Press, 1996: 101
17 Weber M J. *Physical Review*[J], 1968, 171(2): 283
18 Brown E E, Hommerich U, Bluiett A *et al. Journal of the American Ceramic Society*[J], 2014, 97(7): 2105
19 Luo W Q, Liao J S, Li R F *et al. Physical Chemistry Chemical Physics*[J], 2010, 12(13): 3276
20 Sardar D K, Nash K L, Yow R M *et al. Journal of Applied Physics*[J], 2007, 101(11): 113 115

Er, Yb 共掺氧化钇透明陶瓷的 Judd-Ofelt 参数计算

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摘　要：应用 Judd-Ofelt 方法对真空烧结的 Er，Yb 共掺氧化钇透明陶瓷的光谱学参数进行了研究。通过实验方法测得了不同 Er^{3+}掺杂量的 Er，Yb 共掺氧化钇透明陶瓷的室温吸收光谱和折射率，并结合 Judd-Ofelt 方法计算了不同 Er^{3+}掺杂浓度时的光谱学参数。随着 Er^{3+}掺杂量的增加，Ω_2 从 5.41 减小至 3.36。Ω_4 和 Ω_6 的范围分别为 0.96~1.29 和 0.64~0.72。 品质因子 $X_{4/6}$ 的范围为 1.46~1.88，显著优于 Er 掺杂氧化钇单晶中的品质因子。随着 Er^{3+}掺杂量从 0.5 at%增加至 5 at%，$^4I_{13/2}$ 能级的寿命从 8.7 ms 下降至 7.8 ms。计算结果表明，低掺杂浓度的 Er，Yb 共掺氧化钇透明陶瓷是一种有潜力的近红外激光材料。

关键词：Judd-Ofelt方法；Y_2O_3；透明陶瓷

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