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Analysis of optical transitions of Nd^{3+} in YAG nanocrystallites

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A novel approach to the analysis of optical transitions in Nd^{3+}-doped nanocrystallites is put forward, based on the Judd–Ofelt analysis of luminescence transitions associated with the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ bands. The procedure, requiring neither information on Nd^{3+} concentration nor transparent samples, greatly simplifies calculation of branching ratios of neodymium $^4F_{3/2} \rightarrow {}^4I_J$. The technique seems to be very useful in the spectroscopic assessment of Nd^{3+}-doped materials for laser and optoelectronic purposes. The effect of grain size in nanometric ceramics on the branching ratio is considered.

Key words: *nanometric ceramics*, *neodymium*, *spectroscopic parameter*, *Judd–Ofelt theory*

1. Introduction

Recently there has been a great interest in studying optical properties of rare-earth (RE) doped nanocrystals. These materials exhibit a number of novel interesting properties useful in designing new optoelectronic devices. Optical properties of RE doped nanocrystals depend on preparation conditions as well as on structural and morphological properties of individual particles. In particular, the processes of electronic relaxations are closely related to the size effect for very small nanoparticles (in the 1–30 nm range). This effect is associated with the electron-phonon confinement effect [1, 2] and may lead to inhomogeneous broadening of electronic transition linewidths, increased lifetimes and reduction of multiphonon relaxation and phonon-assisted energy transfer processes.

In the present paper, an analysis is performed of f-f transitions for Nd^{3+} doped YAG nanocrystals deduced from the luminescence spectra. The effect of nanocrystal grain sizes on optical properties of Nd:YAG was investigated.

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The Judd–Ofelt model [3,4] allows quantitative analysis of the intensities of f-f radiative transition in RE doped crystals. The Judd–Ofelt theory was first developed for liquids and gases and then successfully used for glasses and crystals with numerous local site symmetries of active ions. Based on absorption spectra measurements, this method allows determining empirical parameters Ω_λ which in turn allow predicting the radiative rate constants for any f-f transitions. A direct application of Judd –Ofelt method in the analysis of the spectra of RE doped nanocrystalline powders is difficult because of lack of high quality absorption spectra due to scattering effects. There are, however, several approaches using luminescence spectra to enhance the accuracy of Ω_λ parameters determination for Pr^{3+} [5] or calculate spectroscopic quality parameters for Nd^{3+} or Er^{3+}.

In the case of Nd^{3+} ion, one of the most important for laser applications, two techniques have been described in the literature [7, 8]. Both are based on the assumption that the probability of spontaneous emission for various transitions $^4F_{3/2} \rightarrow {}^4I_J$ (J = 15/2, 13/2, 11/2 and 9/2) is determined by the intensity parameters Ω_4 and Ω_6 only, whereas the Ω_2 parameter for which the matrix element $\langle|U^{(2)}|\rangle^2$ is close to 0, can be neglected. This allows to calculate the branching ratios $\beta_{JJ'}$ between $^4F_{3/2}$ and respective ^4I_J (J = 9/2, ..., 15/2) states of Nd^{3+} ion from the analytical expression

$$\beta_{JJ'}\left(X_{\mathrm{Nd}}\right) = \frac{\left(a_{J'}X_{\mathrm{Nd}} + b_{J'}\right)\lambda_{JJ'}^{-3}}{\sum_{J'}\left(a_{J'}X_{\mathrm{Nd}} + b_{J'}\right)\lambda_{JJ'}^{-3}} \tag{1}$$

where $a_{J'} = \left\langle {}^4F_{3/2}\left\|U^{(4)}\right\|{}^4I_{J'}\right\rangle^2$ and $b_{J'} = \left\langle {}^4F_{3/2}\left\|U^{(6)}\right\|{}^4I_{J'}\right\rangle^2$ are matrix elements of the irreducible tensor operators of ranks 4 and 6, respectively. The spectroscopic quality parameter X_{Nd} is defined as

$$X_{\mathrm{Nd}} = \frac{\Omega_4}{\Omega_6} \tag{2}$$

These dependencies are universal in their character and can be used to analyze Nd^{3+} doped glasses or other amorphous materials like ceramics, or even nontransparent media during the optimization process of its performance. Since only the Ω_4/Ω_6 ratio is necessary for calculations, relative band intensities are sufficient for determination of X_{Nd}**.** Moreover, there is no need to measure the concentrations of Nd^{3+} ions, which greatly simplifies the calculation procedure. The first method is applied for absorption bands, namely the relations between the $^4I_{9/2} \rightarrow {}^2P_{1/2}$ and $^4I_{9/2} \rightarrow {}^4I_{15/2}$ or $^4I_{9/2} \rightarrow {}^4I_{9/2}$ transitions are required [7]. This procedure may be used only for transparent or at least semitransparent media. For nontransparent media or for the samples not suitable for absorption measurements, scattering or fluorescence spectra may be used. The relation between the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ luminescence bands is also used

to estimate X_{Nd} value [9]. Due to the fact that the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition is located around 1.06 μm and the $^4F_{3/2} \rightarrow {}^4I_{13/2}$ is located around 1.35 μm, obtaining real values of the relative band intensities may prove difficult as most photodetectors does not cover both regions simultaneously. The method put forward in the present paper allows calculating spectroscopic parameters of Nd^{3+} ion by comparing luminescence intensities of two other bands.

2. Experimental

In the course of the experiments one single crystal and a series of nanometric $Y_3Al_5O_{12}$ (YAG) powders were measured. They were 1 at. % Nd:$Y_3Al_5O_{12}$ single crystal and 5.4 at. % Nd:YAG nanocrystals heated at 800, 100 and 1200 °C (the same material as in [6]), respectively.

All the spectra were recorded in the same conditions with a JobinYvon THR1000 1 meter spectrophotometer. A Hamamatsu photomultiplier with R406 characteristics was used together with a 1200 holographic grating. All spectra were corrected for spectral responsivity of the system, by dividing acquired data by a calibrating curve. The calibrating curve was obtained from black-body emissivity taking into account Planck law for a specific black-body temperature and acquisition equipment parameters.

3. Results and discussion

Due to a relatively high intensity and ease of measurement in near the IR range, it is proposed that the relation between two bands: $^4F_{3/2} \rightarrow {}^4I_{11/2}$ at 9447 cm^{-1} (hereafter referred to as γ_1) and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ around 11500cm^{-1} (γ_2) may be used to calculate the spectroscopic parameter of neodymium ion. As a matter of fact, $U^{(2)}$ matrix element may be taken equal to zero for all transitions under consideration.

The intensity of luminescence may be expressed as $I = AN_2 hc\tilde{\nu}$ where A is a spontaneous emission coefficient, N_2 is a population of emitting level and $hc\tilde{\nu}$ is the energy of a transition. Dividing $I_{\gamma 1}$ by $I_{\gamma 2}$ allows employing the above relation and relation (2) to construct an analytical expression

$$\frac{I_{\gamma 1}}{I_{\gamma 2}} = \frac{\bar{\nu}_{\gamma 1}}{\bar{\nu}_{\gamma 2}} \cdot \frac{A_{\gamma 1}}{A_{\gamma 2}} = \frac{\bar{\nu}_{\gamma 1}}{\bar{\nu}_{\gamma 2}} \cdot \left(\frac{\bar{\nu}_{\gamma 1}}{\bar{\nu}_{\gamma 2}} \right)^3 \cdot \frac{\chi_{\gamma 1}}{\chi_{\gamma 2}} \cdot \frac{\left\langle \left\| U_{\gamma 1}^{(4)} \right\| \right\rangle^2 X_{Nd} + \left\langle \left\| U_{\gamma 1}^{(6)} \right\| \right\rangle^2}{\left\langle \left\| U_{\gamma 2}^{(4)} \right\| \right\rangle^2 X_{Nd} + \left\langle \left\| U_{\gamma 2}^{(6)} \right\| \right\rangle^2} \tag{3}$$

Here $I_{\gamma 1}$ and $I_{\gamma 2}$ are intensities of the γ_1 and γ_2 bands respectively, $\bar{\nu}_{\gamma 1}$ and $\bar{\nu}_{\gamma 2}$ are wave numbers of the γ_1 and γ_2 transitions, respectively, $\chi_{\gamma 1}$ and $\chi_{\gamma 2}$ are local field cor-

rection factors for electric-dipole transitions of luminescence spectra where χ_i is defined as

$$\chi_i = \frac{n_i \left(n_i^2 + 2\right)^2}{9} \tag{4}$$

n_i describing the index of refraction for a given transition.

Table 1. Matrix elements for $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transitions [10]

γ	Transition	$\Delta\bar{\nu}$ [cm^{-1}]	$\langle\|U^{(2)}\|\rangle^2$	$\langle\|U^{(4)}\|\rangle^2$	$\langle\|U^{(6)}\|\rangle^2$
γ_1	$^4F_{3/2} \rightarrow {}^4I_{11/2}$ [1]	9500	0.0000	0.1136	0.4104
γ_2	$^4F_{3/2} \rightarrow {}^4I_{9/2}$ [2]	11350	0.0000	0.2293	0.0548

[1]Despite $^4F_{3/2} \rightarrow {}^4I_{11/2}$ also $^2K_{15/2} \rightarrow {}^4F_{3/2}$ could influence the transition around 9550 nm but the 514.5 nm excitation line does not excite the $^2K_{15/2}$ level.

[2]$U^{(2)}$ parameter was rejected. Transitions not excited by 514.5 nm line where not considered.

Denoting

$$I_r = \frac{I_{\gamma 1}}{I_{\gamma 2}} \left(\frac{\bar{\nu}_{\gamma 2}}{\bar{\nu}_{\gamma 1}} \right)^4 \frac{\chi_{\gamma 2}}{\chi_{\gamma 1}} \tag{5}$$

and recasting Eq. (3), one gets

$$X_{\mathrm{Nd}} = \frac{\left\langle \left\| U_{\gamma 1}^{(6)} \right\| \right\rangle^2 - I_r \left\langle \left\| U_{\gamma 2}^{(6)} \right\| \right\rangle^2}{I_r \left\langle \left\| U_{\gamma 2}^{(4)} \right\| \right\rangle^2 - \left\langle \left\| U_{\gamma 1}^{(4)} \right\| \right\rangle^2} \tag{6}$$

According to Table 1, $\langle\|U_{\gamma 1}^{(4)}\|\rangle^2 = 0.1136$, $\langle\|U_{\gamma 1}^{(6)}\|\rangle^2 = 0.4104$. For the γ_2 transition $\langle\|U_{\gamma 2}^{(4)}\|\rangle^2 = 0.2293$ and $\langle\|U_{\gamma 2}^{(6)}\|\rangle^2 = 0.0548$.

Preliminary calculations have shown that the value of the X_{Nd} parameter obtained with Eq. (6) is larger than that obtained from the Ω_λ parameters calculated from absorption spectra, e.g. $X_{\mathrm{Nd}} = 2.00$ versus 0.54 for Nd:YAG single crystal. It is expected that a quantitative X_{Nd} calculation would need a correction factor, specific for a given experimental setup. Once defined, it could be used to correct X_{Nd} for any other material. The correction factor was derived as a ratio of absorption-based to emission -based values of the spectroscopic parameters, e.g. 0.54/2.004 = 0.2695 hence $X'_{\mathrm{Nd}} = 0.2695 X_{\mathrm{Nd}}$. It is obvious that the correction factor is sensitive to any kind of changes done to the setup. Nevertheless, qualitative conclusions about X_{Nd} obtained from luminescence spectra can be drawn.

Assuming $\bar{\nu}_{\gamma 1}$ = 9450 cm^{-1} and $\bar{\nu}_{\gamma 2}$ =11500cm^{-1} from the dispersion characteristics of YAG one obtains $n_{\gamma 1}$=1.818 and $n_{\gamma 2}$=1.822. In fact, the barycenter of the band in calculations (Eq. (5)) was evaluated by means of the expression

$$\bar{\lambda} = \frac{\int \lambda \varepsilon(\lambda)}{\int \varepsilon(\lambda)} \tag{7}$$

and then recalculated to wavenumbers. $\varepsilon(\lambda)$ represents the emission spectrum.

According to Eq. (3), a spontaneous emission is required, what implies the use of low pumping power, far from stimulated emission condition or any thermalization effects. These effects, which may change proportions between respective emission bands, are undesired.

Table 2. Calculated Nd^{3+} spectroscopic parameters and branching ratios β_J of respective $^4F_{3/2} \rightarrow {}^4I_J$ transitions for different materials[1]

Material	Ω_2	Ω_4	Ω_6	X_{Nd}	X'_{Nd}	$\beta_{15/2}$	$\beta_{13/2}$	$\beta_{11/2}$	$\beta_{9/2}$	Ref.
	[10^{-20}cm^2]									
YAG single crystal	0.20	2.70	5.00	0.540		0.6	11.6	53.4	34.4	[11]
	0.37	2.29	5.97	0.384		0.7	12.7	56.4	30.2	[12]
	1.00	2.90	9.30	0.312		0.7	13.3	58.0	28.0	[13]
	0.00	3.20	4.60	0.696		0.5	10.7	50.8	38.0	[14]
	0.34	2.11	5.48	0.385		0.7	12.7	56.3	30.3	[15]
	0.35	2.36	13.02	0.181		0.8	14.6	61.3	23.4	[16]
	–	–	–	2.004	0.461	0.6	12.1	54.8	32.4	[2]
(nc)YAG 800 °C	–	–	–	2.352	0.541	0.6	11.6	53.3	34.5	[6][2]
(nc)YAG 1000 °C	–	–	–	2.081	0.479	0.6	12.0	54.5	32.9	
(nc)YAG 1400 °C	–	–	–	1.649	0.379	0.7	12.8	56.5	30.1	

[1](X_{Nd} from Ω parameters if given in the Table or from luminescence spectra, X'_{Nd} with correction factor from luminescence spectra).
[2]X_{Nd} calculated from luminescence spectra in present work, other X_{Nd} parameters were obtained from Eq. (2) basing on literature data.

It is interesting to note that literature data of X_{Nd} are very divergent varying from 0.2 up to 0.7. It comes from Eq. (1) that for $X_{Nd} > 2$ even large changes in X_{Nd} result in small changes in branching ratios. The error can be here estimated by the total differential equation for every parameter of Eqs. (4)–(6). The equation

$$\Delta X_{Nd} = \sum_{P=I_{\gamma 1}, I_{\gamma 2}, \nu_{\gamma 1}, \nu_{\gamma 2}, n_{\gamma 1}, n_{\gamma 2}} \frac{\delta X_{Nd}}{\delta P} \Delta P \tag{8}$$

was used to calculate absolute error with I, ν and n of both γ_1 and γ_2 bands as parameters. Here ΔP is the measurement error of, e.g., $\Delta I_{\gamma i}$, $\Delta \nu_{\gamma i}$ and $\Delta n_{\gamma i}$ equal to 5, 10 and 0.01, respectively. The total relative error $(\Delta X_{Nd}/X_{Nd})\times 100\%$ was calculated to be

20.2, 29.3 and 35.3% for samples heated at 800, 1000 and 1400 °C, and for X_{Nd} given in Table 2. The increase in the total relative error may be due to the decrease of X_{Nd} value. It is important to notice, however, that for $X_{Nd} > 2$, even large X_{Nd} changes do not introduce large changes of β_J values. For the samples examined in this work, for higher annealing temperatures, the spectroscopic parameter X_{Nd} systematically decreases due to increasing sizes of YAG grains [6]. The average grain sizes for YAG nanocrystals were 25, 100 and 2000 nm for the samples heated at 800, 100 and 1200 °C, respectively.

4. Conclusions

It was found that the observed trend of increasing X_{Nd} with increasing temperature of annealing of nanocrystallite ceramics is due to the increase of the grain size of nanocrystallites. The reason why the grain size affects the spectroscopic parameter is not clear at the moment. It is obvious that the grain size affects the luminescence spectrum due to thermalisation of the $^4F_{5/2}$ state from $^4F_{3/2}$. The thermalisation should affect the $^4F_{3/2}$ level emission in the same way, thus it should not change the relation between the bands resulting from emission from that level to different ^4I_J levels. Most probably, the thermalisation of the ground state states ^4I_J and the Stark levels within that states change the statistical distribution of electrons.

The method presented in this paper does not include cross relaxation processes responsible for concentration quenching in Nd^{3+} doped samples. The cross-relaxation reduces the total population of $^4F_{3/2}$ state but does not change the branching ratio distribution. Use of a low pumping power may eliminate the parasitical process considered.

The advantage of the presented method is a possibility of using fluorescence instead of absorption spectra. This simplifies the calculation method of the branching ratio eliminating necessity of the preparation of proper sample surfaces and making unnecessary knowledge of active ions concentration. Moreover, spectroscopic properties of non- or semi-transparent materials may now be easily assessed.

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