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Judd-Ofelt analysis of Nd^{3+} in CLNGG single crystals

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The analysis of the intensities of the f-f transitions of Nd^{3+} doped calcium lithium niobium gallium garnets (CLNGG) single crystals is presented. The JO parameters Ω_t (t=2,4,6) of Nd^{3+} in CLNGG are determined as $\Omega_2=2.18\times10^{-20}$ cm^2, $\Omega_4=2.96\times10^{-20}$ cm^2, $\Omega_6=4.19\times10^{-20}$ cm^2. These parameters are comparable to those reported for Nd^{3+} in CNGG single crystals. A series of other spectroscopic parameters based on Judd Ofelt theory, such as oscillator strengths, radiative transitions probabilities, and radiative lifetimes, branching ratios of the different Nd^{3+} transitions were determined.

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1. Introduction

The crystals with disordered structure determined by the multiple occupancy of specific crystallographic cationic site with ions of different species or with different valence states having broad absorption and emission bands could be a solution for the development of diode pumped ultra short pulsed lasers materials. Among these materials, the rare earths (RE^{3+}) doped calcium niobium gallium garnets (CNGG) or calcium lithium niobium gallium garnets (CLNGG) gained interest in the last years. These crystals have the advantage of iridium free technologies. X ray or Raman data show that the congruent composition of CNGG is different from the stoichiometric one, with excess of Nb^{5+} and with Ga^{3+} cationic vacancies that could be deleterious for high power regime of the lasers [1, 2]. It was also found that by Li^+ addition these vacancies could be eliminated and a new crystal is formed CNLGG - $Ca_3Li_{0.275}Nb_{1.775}Ga_{2.95}O_{12}$. RE^{3+} ions substitute the Ca^{2+} ions in dodecahedral sites and the charge compensation is accomplished by an excess of Nb^{5+} ions in octahedral sites in CNGG and by a proper proportion of Nb^{5+} and Li^+ ions in the octahedral sites in CLNGG; Ga^{3+} vacancies could also contribute. The low temperature spectra of Nd^{3+} revealed at least five nonequivalent centers [2, 3] slightly different in CNGG and CLNGG crystals. Spectroscopic characteristics of other RE^{3+} ions in these crystals have been reported [4].

The aim of this paper to present an analysis of the intensities of the f-f transitions of Nd^{3+} in CLNGG single crystals. Based on the room temperature spectra, the Judd - Ofelt intensity parameters Ω_t (t=2, 4, 6) are determined by considering a "quasi-center model" [5]. A series of other spectroscopic parameters based on Judd Ofelt theory, such as oscillator strengths, radiative transitions probabilities, and radiative lifetimes, branching ratios of the different Nd^{3+} transitions are determined.

2. Experimental

The Nd^{3+} in CLNGG single crystals were grown by Czochralski method in platinum crucibles. The optical spectroscopic measurements of 1.2 at% Nd^{3+}: CLNGG single crystals were performed on an extended spectral range 350 to 1600 nm. The absorption spectra were recorded with a setup consisting of a Jarell Ash monochromator, S20 and S1 photomultipliers, Si and Ge photodiodes and a Lock-in amplifier on line with a computer. The emission spectra were obtained by excitation with Xe lamp. A closed cycle He refrigerator was used for low temperature measurements.

3. Results and discussion

The room and low temperature Nd^{3+} high resolution absorption spectra corresponding to $^4I_{9/2} \rightarrow {}^4F_{3/2}$ of Nd: CLNGG single crystal present a complex structure induced by the disordered CLNGG crystal, meaning different environments around Nd^{3+} ions beyond the first O^{2-} dodecahedron (Fig.1). The low temperature spectra absorption revealed at least five nonequivalent centers [3] of Nd^{3+} in CLNGG single crystal. The multisite structure has been observed in emission spectra. The emission corresponding to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$, $^4F_{3/2} \rightarrow {}^4I_{13/2}$ transitions at 10K of Nd^{3+} in CLNGG single crystal are illustrated in Fig. 2.

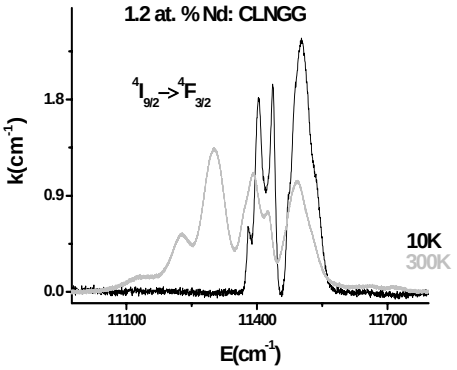

Fig. 1. 300K and 10K absorption spectra of $^4I_{9/2} \rightarrow {}^4F_{3/2}$ of Nd: CLNGG single crystal.

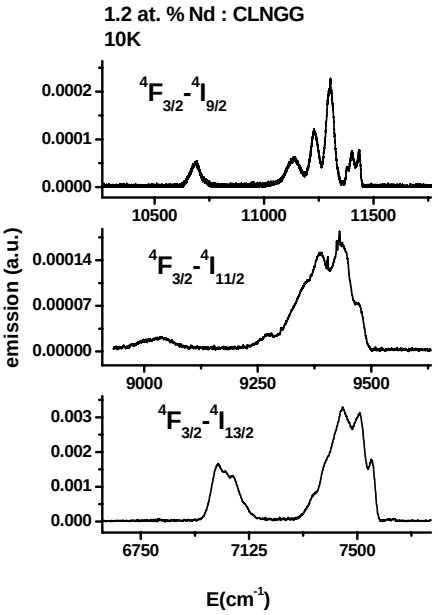

Fig. 2. The emission of $^4F_{3/2}$ Nd^{3+}: CLNGG single crystal at 10K to the $^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$ lower-lying level.

To determine the Judd-Ofelt (JO) intensity parameters for the corresponding Nd^{3+} ($4f^3$) transitions in Nd^{3+}: CLNGG single crystals nine absorption bands of the room temperature spectra were used. Since the J-O model applied to the spectroscopic analysis of rare earth ions can be found in literature [6-10] we only provide results of Nd^{3+} transitions in Nd^{3+}: CLNGG single crystal following the J-O analysis. The experimental value of the refractive indices for CLNGG were provided by Voronko et al.[4] and by using a least-square fitting program applied to the Sellmeier dispersion equation the refractive indices were obtained. The mean wavelength, refractive indices, integrated absorption coefficients and the measured and calculated line strengths for several Nd^{3+} manifolds listed in Table 1.

Table 1. Measured and calculated absorption line strength of Nd^{3+} in CLNGG single crystals at 300K.

Transition from $^4I_{9/2}$	$\bar{\lambda}$ (nm)	n	S_{meas} (10^{-20}cm^2)	S_{calc} (10^{-20}cm^2)
$^4F_{3/2}$	879.95	1.92	0.878	0.879
$^4F_{5/2}$, $^2H_{9/2}$	805	1.932	3.268	2.899
$^4F_{7/2}$, $^4S_{3/2}$	746.57	1.941	2.665	2.9048
$^4F_{9/2}$	681.77	1.954	0.301	0.204
$^2H_{11/2}$	637.66	1.965	0.0452	0.0518
$^4G_{5/2}$, $^2G_{7/2}$	586.36	1.982	4.195	4.1648
$^2K_{15/2}$, $^4G_{7/2}$, $^4G_{9/2}$	533.56	2.007	0.246	0.8168
$^2K_{15/2}$, $^2G_{9/2}$, $^2D_{3/2}$, $^4G_{11/2}$	517.87	2.016	0.0478	0.146
$^2P_{1/2}$	432.23	2.09	0.0849	0.1086

A measure of the accuracy of the fit is given by the rms deviation: $\Delta S_{rms} = \left[(q-p)^{-1}\sum(\Delta S)^2\right]^{1/2}$ where $\Delta S = S_{calc} - S_{meas}$ is the deviation, q is the number of the transitions analyzed and p is the number of the parameters (in our case these are 9 and respectively 3). The data from Table II provide an rms deviation of 0.299×10^{-20}cm^2.
The phenomenological intensity parameters for Nd^{3+} in CLNGG single crystals were determined and compared to those reported by A. A. Kaminskii et al. [1] for the Nd^{3+} in CNGG single crystals as it show in Table 2:

Table 2. The J-O intensity parameters for Nd^{3+} in CLNGG single crystals.

Materials	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	Ω_6 (10^{-20} cm^2)	Ref.
CLNGG	2.18	2.96	4.19	This work
CNGG	1.91	2.59	3.74	[1]

The spectroscopic quality factor, $X = \Omega_4/\Omega_6$ used to evaluate the stimulated emission for Nd $^4F_{3/2} \rightarrow {}^4I_J$ transitions, was estimated to be X = 0.7 from our JO parameters in CLNGG single crystals and is very close to that for Nd: CNGG, X ~ 0.69 [1].

The J-O parameters can be applied to calculate the emission line strengths corresponding to the transitions from the upper multiplet manifolds $^{2S+1}L_J$ to the corresponding lower-lying multiplet manifolds $^{2S'+1}L_{J'}$ of Nd^{3+}. Using these line strengths, the total spontaneous electric dipole emission transition probabilities from the excited state J to the terminating state J' is given by the expression:

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

The radiative lifetime τ_r for an excited state J and the fluorescence branching ratios β ($J \rightarrow J'$) for the various emission transitions from this state can be then calculated by:

$$\tau_r = \frac{1}{\sum A(J \rightarrow J')},$$

$$\beta(J \rightarrow J') = \frac{A(J \rightarrow J')}{\sum_{J'} A(J \rightarrow J')}$$

where $A(J \rightarrow J') = A^{ed}(J \rightarrow J') + A^{md}(J \rightarrow J')$.

The calculated values of the total spontaneous electric dipole emission transition probabilities ($A_{JJ'}$), branching ratios ($\beta_{JJ'}$) and radiative lifetime for the main emission transitions of Nd^{3+} in CLNGG are presented in Table 3. The values of branching ratios ($\beta_{JJ'}$) corresponding to the transitions from $^4F_{3/2}$ towards the $^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, $^4I_{15/2}$, respectively are in good agreement with the values of branching ratios obtained for Nd^{3+}: CNGG [1, 11].

Table 3. The calculated values of the total spontaneous emission transition probabilities ($A_{JJ'}$), branching ratios ($\beta_{JJ'}$) and radiative lifetime for the main emission transitions of Nd^{3+} in CLNGG.

Transition	$\left\|\langle U^{(2)}\rangle\right\|^2$	$\left\|\langle U^{(4)}\rangle\right\|^2$	$\left\|\langle U^{(6)}\rangle\right\|^2$	$\bar{\lambda}$ (nm)	n	S_{calc} (10^{-20}cm^2)	$A^{ed}_{JJ'}$ (s^{-1})	$\beta_{JJ'}$	τ_r (μs)
$^4F_{3/2}\rightarrow{}^4I_{9/2}$	0.0000	0.2296	0.0563	879.58	1.92	0.9163	1676.5	0.40	239
$^4I_{11/2}$	0.0000	0.1423	0.407	1073	1.90	2.13	2068.16	0.494	
$^4I_{13/2}$	0.0000	0.0000	0.2117	1360	1.89	0.888	415.83	0.099	
$^4I_{15/2}$	0.0000	0.0000	0.0275	1850	1.89	0.1154	21.4	0.005	

The kinetics emission of $^4F_{3/2}$ level of 0.6 at % Nd in CLNGG measured by A. Lupei et al. [3] by selective excitation show an average value of lifetime for the two intense Nd centers about ~ 224 μs.

4. Conclusions

High resolution optical investigations on Nd^{3+} doped calcium lithium niobium gallium garnets (CLNGG) single crystals with disordered structure were performed. The intensities parameters of the f-f transitions of Nd^{3+}: CLNGG were determined to be $\Omega_2=2.18\times10^{-20}$ cm^2, $\Omega_4=2.96\times10^{-20}$ cm^2, $\Omega_6=4.19\times10^{-20}$ cm^2. Other spectroscopic parameters based on Judd Ofelt theory were determined including the branching ratios of the four fluorescence originating from the $^4F_{3/2}$ Nd^{3+} level. These JO intensity parameters are comparable to those reported for Nd^{3+} in CNGG single crystals. The spectroscopic quality factor $X = \Omega_4/\Omega_6$ used to evaluate the stimulated emission for Nd $^4F_{3/2} \rightarrow {}^4I_J$ transitions, was estimated to be X = 0.7 from our JO parameters in CLNGG single crystals and is very close to that for Nd: CNGG, X ~ 0.69. Thus, the CLNGG: Nd grown crystals have similar spectroscopic quality factor as the congruent CNGG: Nd crystal.

Acknowledgements

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