Predict optical properties of Dy^{3+} ions doped double potassium gadolinium fluoride crystal from absorption spectra

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Abstract. Double potassium gadolinium fluoride crystal doped with 5.0 mol % of Dy^{3+} ions ($K_2GdF_5:Dy^{3+}$) was synthesized under hydrothermal condition. The absorption, luminescence spectra and lifetime of $K_2GdF_5:Dy^{3+}$ sample were measured at room temperature. Judd – Ofelt (JO) theory is used to study the spectral properties and to calculate the radiative transition probabilities. The prediced branching ratios (β_R), radiative lifetime (ι_R), integrated emission cross – section (Σ_{if}) and stimulated emission cross – sections ($\sigma(\lambda_p)$) of the $^4F_{9/2}$ excited level are reported.

Keywords: K_2GdF_5 single crystal, J-O theory.

1. Introduction

Spectroscopic investigations of rare earth (RE) doped glasses and crystals provide valuable information that includes energy level structure, radiative properties, stimulated emission cross-sections, etc. These insights play a key role to improve the existing or to develop new optical devices like lasers, sensors, hole burning high-density memories, optical fibers and amplifiers [1-5].

Nowadays, one of the most interesting fields of research is focused on the development of optical devices based on RE ions doped $AF-A'F-LnF_3$ systems (A, A' - alkali element, Ln - rare earth (RE) element). This is an important material for applications in optical area such as optical amplifiers, solid – state lasers. There have been many reports on spectral properties of these materials such as the $K_2YF_5:Tm^{3+}$, $K_2YF_5:Sm^{3+}$, $K_2YF_5:Nd^{3+}$, $K_2YF_5:Eu^{3+}$ crystals [6-9]. The authors showed the detailed researches on the spectral characteristics of RE^{3+} ions in K_2LnF_5 crystal. Dysprosium is one of the most popular rare earth elements, which is used extensively in optical devices. Several authors have studied its spectra in various matrices [1-5]. However, dysprosium doped in K_2GdF_5 crystal has received relatively less attention than other lanthanide ions despite many features of interest.

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In this works, we studied spectroscopic properties of Dy^{3+} ions in K_2GdF_5 crystal. Using the Judd – Ofelt theory to determine intensity parameters Ω_λ (λ = 2, 4, 6) by analyzing the absorption spectrum of $K_2GdF_5:Dy^{3+}$ crystal. In addition, we calculated the radiative transition probabilities, branching ratios, radiative lifetimes of $^4F_{9/2}$ excited state, stimulated emission cross – section for selected and briefly discussed the potential application of $K_2GdF_5:Dy^{3+}$ as efficient laser.

2. Experiment

The K_2GdF_5 crystals doped with 5.0 mol % of Dy^{3+} ions were obtained by hydrothermal synthesis at the Kurnakov Institute of General and Inorganic Chemistry, Moscow, Russia [7]. The XRD pattern of $K_2GdF_5:Dy^{3+}$ has shown that the fluoride K_2GdF_5 crystallizes in orthorhombic system, space group P_{nma}, a = 10,814 Å b = 6,623 Å c = 7.389 Å . The optical absorption spectra were performed using Jascco V670 spectrometer by wavelength scanning from 300 nm to 2000 nm. The photoluminescence (PL) spectra were recorded by Fluorolog - 3 spectrophotometer, model FL3 - 22, Horiba Jobin Yvon. All the measurements were performed at room temperature..

3. Theoretical introduction

The Judd-Ofelt (JO) theory was shown to be useful to characterize radiative transitions for RE-doped solids, as well as aqueous solutions, and to estimate the intensities of the transitions for rare-earth ions [1-7,9]. This theory defines a set of three intensity parameters, Ω_λ (λ = 2, 4, 6), that are sensitive to the environment of the rare-earth ions.

According to the JO theory [10], the electric dipole oscillator strength of a transition from the ground state to an excited state is given by

$$f_{cal} = \frac{8\pi^2 mc\nu}{3h(2J+1)} \frac{(n^2+2)^2}{9n} \sum_{\lambda=2,4,6} \Omega_\lambda \left\langle \psi J \left\| U^{(\lambda)} \right\| \psi' J' \right\rangle^2 \tag{1}$$

where n is the refractive index of the material, J is the total angular momentum of the ground state, Ω_λ are the JO intensity parameters and $\left\| U^{(\lambda)} \right\|^2$ are the squared doubly reduced matrix of the unit tensor operator of the rank λ = 2, 4, 6 are calculated from intermediate coupling approximation for a transition $\left| \psi J \right\rangle \to \left| \psi' J' \right\rangle$. These reduced matrix elements did not nearly depend on host matrix as noticed from earlier studies [11].

The oscillator strengths, f_{exp}, of the absorption bands were determined experimentally using the following formula [10]

$$f_{exp} = 4.318 \times 10^{-9} \int \alpha(\nu) d\nu \tag{2}$$

where $\alpha(\nu)$ is molar extinction coefficient at energy ν (cm^{-1}). The $\alpha(\nu)$ values can be calculated

from absorbance *A* by using Lambert – Beer's law, $A = \alpha(\nu)cd$, where *c* is concentration [dim: L^{-3}; units: $moll^{-1}$], *d* is the optical path length [dim: L; units: cm].

The oscillator strengths of the various observed transitions are evaluated through Eq. (1) and Eq. (2). A least squares fitting approach is then used for Eq. (2) to determine Ω_λ parameters which give the best fit between experimental and calculate oscillator strength.
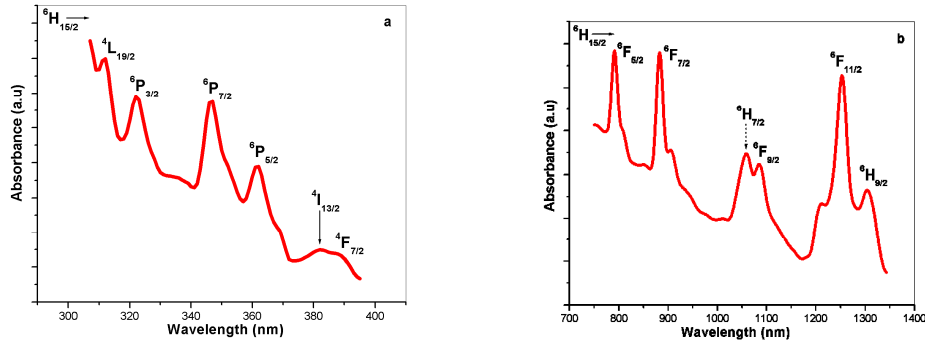

Fig. 1. The absorption spectra of $K_2GdF_5:Dy^{3+}$ crystal: (a) in the region 300 – 400 nm and (b) in the region 700 – 1400 nm.

The oscillator strengths of the various observed transitions are evaluated through Eq. (1) and Eq. (2). A least squares fitting approach is then used for Eq. (2) to determine Ω_λ parameters which give the best fit between experimental and calculate oscillator strength.

The JO parameters are used to predict the radiative properties of excited states of Ln^{3+} ion such as transition probabilities (A_R), radiative lifetime (ι_R), branching ratios (β_R), and stimulated emission cross – sections ($\sigma(\lambda_p)$). The details of this theory were shown in previous reports [7].
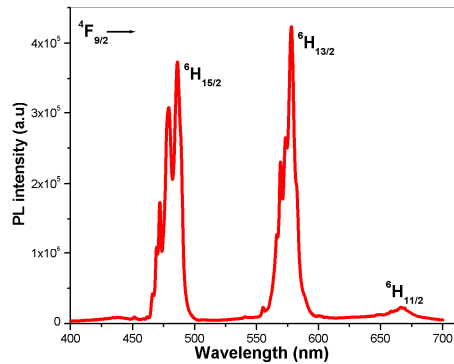

Fig. 2. The emission spectrum of $K_2GdF_5:Dy^{3+}$ crystal

4. Results and discussion

4.1. Absorption and emission spectra

The absorption spectra of K_2GdF_5 crystal doped with 5.0 mol % of Dy^{3+} ions are shown in Fig. 1a for the regions 300 – 400 nm and Fig. 1b for the regions 700 – 1400 nm. All the absorption bands originate from the ground state, $^6H_{15/2}$. The band positions along with assignments for K_2GdF_5:Dy^{3+} crystal are shown in Table 1, which are also compared with Dy^{3+} -diluted acid solution (aqua - ion) system [11].

As shown in Fig. 2, which illustrates the emission spectrum using the 365 nm excitation wavelength of xenon lamp source, three emission bands at 485, 577 and 667 nm are attributed to transitions from $^4F_{9/2}$ to $^6H_{15/2}$, $^6H_{13/2}$ and $^6H_{11/2}$, states, respectively, of Dy^{3+}ions.

Table 1. Energy transitions (v), the experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths for K_2GdF_5:Dy^{3+} crystal.

$^4H_{15/2}$ $\rightarrow$	v_c (cm^{-1})	v_a (cm^{-1})	f_{exp} ($\times 10^{-6}$)	f_{cal} ($\times 10^{-6}$)
$^6H_{9/2}$	7,662	7,700	0.86	0.56
$^6F_{11/2}$	7,984	7,700	2.67	4.53
$^6F_{9/2}$	9,199	9,100	1.44	3.16
$^6H_{7/2}$	9,474	9,100	0.98	0.21
$^6F_{7/2}$	11,325	11,000	1.83	2.97
$^6F_{5/2}$	12,642	12,400	1.15	1.54
$^4F_{7/2}$	25,773	25,754	0.54	0.56
$^4I_{13/2}$	25,974	25800	0.72	0.28
$^4P_{5/2}$	27,629	27,400	1.81	0.95
$^6P_{7/2}$	28,802	28,550	2.77	2.46
$^6P_{3/2}$	31,025	30,892	1.54	1.25
$^4L_{19/2}$	32,358	32,187	0.93	0.21
$\overline{\beta} = 1.017; \delta = -1.31$			rms = 0.96×10^{-6}	

4.2. Nephelauxetic effect- Bonding parameter

The bonding parameter (δ) is defined as $\delta = \left[(1-\overline{\beta})/\overline{\beta} \right] \times 100$, where $\overline{\beta} = (\sum \beta)/n$ and β (nephelauxetic ratio) = v_c/v_a, v_c and v_a are energies of the corresponding transitions in the complex and aqua – ion [10], respectively, and n is refers to the number of levels that are used to compute $\overline{\beta}$ values. The bonding parameter depends on the environmental field; δ can be received the positive or negative value indicating covalent or ionic bonding. In our sample, the values of $\overline{\beta}$ and δ bonding parameter are 1.017, - 1.31, respectively. Thus, in this case the bonding of Dy^{3+} ions with the local host is ionic bonding.

4.3. Oscillator strengths, J – O parameters

From the absorption spectra of the $K_2GdF_5:Dy^{3+}$ crystal, the experimental (f_{exp}) oscillator strengths of twelve absorption bands were determined using Eq. (1) and shown in table 1. All these absorption bands have been analyzed by using JO theory and were least squared fitted to yield the best fit values for the JO parameters Ω_2, Ω_4 and Ω_6. The accuracy of the fit is given by the rms deviation between the experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths [1-5,10]. In our case, the best – fitted JO parameters are $\Omega_2 = 2.42 \times 10^{-20}$ cm^2, $\Omega_4 = 0.96 \times 10^{-20}$ cm^2 and $\Omega_6 = 2.19 \times 10^{-20}$ cm^2 with the rms deviation of 0.96×10^{-6}. Table 3 shows the obtained JO parameters for various Dy^{3+} systems. The Ω_2 value of our crystal is smaller than that of the different hosts.

The characteristic feature of the Ω_2 is that it is sensitive to the local environment of the RE ions and is often related with the asymmetry of the coordination structure, polarizability of ligand ions or molecules and bonding nature [1-5]. The smallness of Ω_2 parameter in $K_2GdF_5:Dy^{3+}$ crystal compared with other hosts can be attributed to higher symmetry of the coordination structure surrounding the RE ion. In our case, the F^{-1} ions have high electronegative (≈ 4, in Pauling scale), therefore the Dy^{3+} - F^{-1} bond has the small covalency ($\delta < 0$). This also is a main reason to explain for the reduction of the Ω_2 values in the fluoride compounds.

Table 2. The JO parameters for Dy^{3+} doped various hosts

Host matrix	Ω_2 ($\times 10^{-20}$ cm^2)	Ω_4 ($\times 10^{-20}$ cm^2)	Ω_6 ($\times 10^{-20}$ cm^2)	Ref.
$K_2GdF_5:Dy^{3+}$	2.42	0.96	2.19	Present
$K_2SO_4 – ZnSO_4 – B_2O_3$	52.44	5.80	6.81	[5]
$ZnSO_4 – B_2O_3$	34.48	3.06	9.12	[5]
$Li_2SO_4 – ZnSO_4 – B_2O_3$	21.01	8.13	7.54	[5]
$Na_2SO_4 – ZnSO_4 – B_2O_3$	16.82	9.45	6.50	[5]
$GeO_2-B_2O_3-ZnO-LaF_3$	15.73	2.46	5.49	[3]
$PbO_5-K_2O-BaO-AlO_3-AlF_3$	12.3	2.67	2.30	[1]
$SiO_2-Al_2O_3-LiF-GdF_3$	4.53	0.66	2.40	[3]
$PbO-PbF_2$	2.13	2.10	1.0	[2]

4.4. Fluorescence properties

From the JO parameters and emission spectrum of $K_2GdF_5:Dy^{3+}$ crystal, the radiative properties such as the radiative transition rates (A_R), radiative lifetime (τ_R), stimulated emission cross section $\sigma(\lambda_p)$, integrated emission cross – section (Σ_{if}), branching ratios (β_R) and measured branching ratios (β_{mes}) were determined for the transitions from the $^4F_{9/2}$ excited level to lower levels, and displayed in Table 3.

In general, the luminescence branching ratio is a critical parameter to the laser designer, because it characterizes the possibility of attaining stimulated emission from any specific transition. In this work, the predicted branching ratio of $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition gets a maximum value and is 59.2 % where as the measured ratio is 52.5 %.

The measured and calculated lifetime of $^4F_{9/2}$ level is 1.14 ms and 1.72 ms, respectively. The discrepancy between the measured and calculated lifetime may be due to the additional non – radiative and energy transfer through cross – relaxation. The luminescence quantum efficiency of the fluorescent level is defined as the ratio of the measured lifetime to the calculated lifetime by JO theory, $\eta = \tau_{mes}/\tau_R$ [1,7].

The integrated emission cross – section, Σ_{if}, and stimulated emission cross – section, $\sigma(\lambda_p)$, are important parameters when considering the laser emission of the material [1-7]. When the integrated emission cross – section is greater than 10^{-18} cm, laser emission is probable if the upper state displays a proper lifetime, that is, if it has high quantum efficiency [6]. In our case, with the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition, the integrated emission cross – section is 1.13×10^{-18} cm and the luminescence quantum efficiency is 66.3 %. The large values of branching ratio, integrated emission cross – section, stimulated emission cross section and quantum efficiency suggest that the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition can give rise to lasing action.

Table 3. Predict the radiative transition rate, branching ratio and radiative lifetime, integrated emission cross – section , stimulated emission cross – section of $^4F_{9/2}$ level

$^4F_{9/2} \rightarrow$	v (cm^{-1})	A_R	β_R (%)	β_{mes} (%)	$\sigma(\lambda_p)(10^{-22}$ cm$^2)$	Σ_{if} (10^{-18} cm)	τ_R(ms)
$^6F_{1/2}$	7,283	0.04	0	-	-	-	1.72
$^6F_{3/2}$	7,845	0.08	0	-	-	-	
$^6F_{5/2}$	8,650	2.78	0.03	-	-	-	
$^6F_{7/2}$	10,082	2.97	0.04	-	-	-	
$^6H_{5/2}$	10,892	1.98	0.27	-	-	-	
$^6H_{7/2}$	11,955	10.91	1.38	-	-	-	
$^6F_{9/2}$	12,039	3.67	0.53	-	-	-	
$^6F_{11/2}$	13,361	10.42	1.30	-	-	-	
$^6H_{9/2}$	13,390	9.12	1.11	-	-	-	
$^6H_{11/2}$	15,269	29.11	3.36	3.94	1.16	0.03	
$^6H_{13/2}$	17,620	344.00	59.2	52.52	14.9	1.13	
$^6H_{15/2}$	21,140	166.00	19.20	43.54	3.08	0.15	

5. Conclusion

The present study yields a detailed picture of the spectral characteristics of Dy^{3+} ions in K_2GdF_5 crystal. The experimental and calculated oscillator strengths of absorption transitions of $K_2GdF_5:Dy^{3+}$ were determined. By using JO theory, we determined the intensity parameters (Ω_λ) and predicted radiative lifetime (t_R), branching ratios (β_R). These predicted values are good agreement with experimental values. The negative value of bonding parameter δ and the small value of intensity parameter Ω_2 show that the bonding of Dy^{3+} ions with the local host is ionic bonding and the coordination structure surrounding the RE ion has high symmetry. The large values of branching ratio,

integrated emission cross – section and stimulated emission cross section suggest that the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition can give rise to lasing action.

Acknowledgment

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