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Energy transfer studies of Dy^{3+} ions doped K_2GdF_5 crystal

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Abstract. Dy^{3+} -doped K_2GdF_5 single crystals were synthesized under hydrothermal condition. The UV excitation spectra and lifetimes of K_2GdF_5:Dy^{3+} were measured at room temperature. The excitation spectra have shown charge transfer state (CTS) of Dy^{3+} and energy transfer from Gd^{3+} to Dy^{3+} ions in K_2GdF_5:Dy^{3+} crystal. The decay curve of the K_2GdF_5 sample doped with 5.0 mol % Dy^{3+} ions is a non – exponential curve and is well fitted to the Inokuti – Hirayama model for $S = 6$. The energy transfer parameters (Q, C_{DA}) and the critical distance (R_0) are calculated.

Keywords: K_2GdF_5 single crystal, Inokuti – Hirayama model.

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1. Introduction

There is a continual interest in the development of new luminescent materials that can be utilized for the solid-state dosimeters and optoelectronic devices in industrial, scientific and medical applications. Crystal chemical features of stoichiometric fluoride compounds crystallizing in the ALnF systems (A - alkali element, Ln - rare earth (RE) element), such as $BaYF_4$, KYF_4, K_2YF_5 and K_2GdF_5 establish prerequisites for developing novel optical RE doped materials. Dysprosium is one of the most popular rare earth elements; its $4f^9$ electron configuration usually exists in triply ionized (Dy^{3+}). Spectroscopy of Dy^{3+} ions doped glasses has studied and used extensively in optical devices such as lasers, sensors, optical fibers and amplifiers [1,2,3]. Recently, there are some reports on optical properties of Dy^{3+} doped ALnF crystal. The authors have investigated the optical properties of these materials by using thermoluminescence [4,5], absorption, photoluminescence spectra and Judd – Ofelt theory [6,7,8].

In order completely contribute the spectroscopic picture of Dy^{3+} ions doped ALnF crystal, in this paper, we have investigated energy transfers of Dy^{3+} ions doped K_2GdF_5 single crystal by using the

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UV excitation spectra and decay curves. By fitting the non – exponential curve of the K_2GdF_5 to Inokuti – Hirayama model, we have determined energy transfer parameters such as rate of energy transfer through cross – relaxation (W_{ET}), energy transfer parameters (Q, C_{DA}) and critical distance (R_0).

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 [9]. The XRD patterns of K_2GdF_5:Dy^{3+} have 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 UV excitation spectra were recorded by Fluorolog – 3 spectrophotometer, model FL3 - 22, Horiba Jobin Yvon. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Excitation spectra and the energy transfer between Gd^{3+} and Dy^{3+} ions

The UV excitation spectra of the Dy^{3+} emission with monitoring at wavelengths 577 nm and 485 nm of the K_2GdF_5:Dy^{3+} single crystals are shown in Fig.1. The peaks at ~ 310, 320, 345, 360, 385, 425 and 450 nm are due to the 4*f* – 4*f* inner shell transition of Dy^{3+}. The broadband at ~ 300 nm is due to charge transfer state of Dy^{3+}. Two narrow lines peaking at 254 nm and 273 nm are observed in the UV - side, which c correspond to the transitions from the ground state $^8S_{7/2}$ of Gd^{3+} ion to its excited state ^6D_J (J = 7/2, 9/2) and ^6I_J (J = 11/2, 13/2) respectively [10]. These lines are not observed in the excitation and absorption spectra of the Dy^{3+} doped samples without Gd^{3+} component [11,12]. This implies that energy transfer from Gd^{3+} to Dy^{3+} ions occurred in this crystal. Consequently, the luminescence of Dy^{3+} ions in K_2GdF_5 could be strongly excited by the additional light with wavelengths 254 nm and 273 nm.

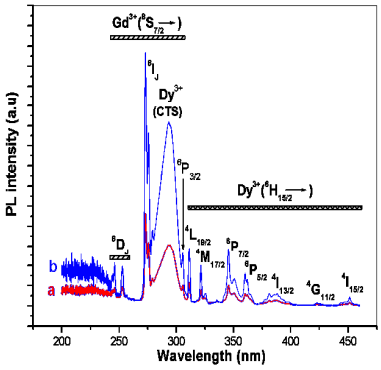

Fig.1. The UV excitation spectra of the K_2GdF_5: Dy^{3+} crystal at the emission wavelengths 577 nm (a) and 485 nm (b).

3.2. Quenching of lifetime with concentration

Fig. 2 presents the experimental decay curves of the K_2GdF_5 samples doped with 0.5 and 5.0 mol% of Dy^{3+} ions. The lifetimes of the $^4F_{9/2}$ level in Dy^{3+} ions have been determined and are 1.68 ms and 1.14 ms for 0.5 mol% and 5.0 mol%, respectively. The lifetimes were calculated by using the Judd – Ofelt theory for these samples are 1.73 ms and 1.72 ms, respectively. Thus, there is a good agreement between experimental and calculated lifetime at low concentration. However, as the concentration increases, the lifetime decreases which indicates the presence of non – radiative energy transfer processes from excited to neighboring unexcited Dy^{3+} ions. These processes can be expressed as [13]

$$\frac{1}{\tau_{mes}} = \frac{1}{\tau_R} + W_{MP} + W_{ET} \quad (1)$$

where τ_{mes} and τ_R are measured and calculated lifetimes, respectively. W_{MP} is the multiphonon relaxation rate and W_{ET} is rate of energy transfer through cross – relaxation. But in the case of Dy^{3+}, W_{MP} is negligible as there is a large energy gap of ~ 7400 cm^{-1} between the $^4F_{9/2}$ state and next lower level $^6F_{1/2}$. Hence, quenching of lifetime with concentration can be mainly due to energy transfer through cross – relaxation. Therefore

$$W_{ET} = \frac{1}{\tau_{mes}} - \frac{1}{\tau_R} \quad (2)$$

In our case, the values of the rate of energy transfer through cross – relaxation are 17.2 s^{-1} and 295.8 s^{-1} for the dopant concentration of 0.5 mol% and 5.0 mol%, respectively.

3.3. Decay curve analysis - Inokuti – Hirayama (IH) model

Inokuti – Hirayama developed a theory to account for energy transfer between $4f^n$ energy levels of RE^{3+} ions [14]. According to this model, at the concentrations of dopant ions lower 1,0 mol%), the interaction between the optically active RE ions is negligible, the fluorescence decay curves is nearly single exponential. However, when the concentration is large enough (larger 1,0 mol%), the interaction between these ions becomes so prominent that energy transfer takes place from an excited RE ion (donor) to a non – excited RE ion (acceptor), leading to a non – exponential shape of the decay curve [1,13,14]. This curve is given by

$$I = I_0 \exp\left\{-\frac{t}{\tau_0} - Q\left(\frac{t}{\tau_0}\right)^{3/S}\right\} \quad (3)$$

where t is the time after excitation, τ_0 is the intrinsic decay time of donor in absence of acceptor. The value of S (= 6, 8, 10) depends on whether the dominant mechanism of interaction is dipole –

dipole, dipole – quadrupole or quadrupole – quadrupole, respectively. By fitting the decay curve in framework of IH model, the dominant mechanisms of interaction are determined. The energy transfer parameter (Q) is defined as

$$Q = \frac{4\pi}{3}\Gamma\left(1-\frac{3}{S}\right)N_0 R_0^3 \tag{4}$$

where Γ(x) is the gamma function, its value is equal to 1.77 for dipole – dipole, 1.43 for dipole – quadrupole and 1.33 for quadrupole – quadrupole, respectively [1,8,10]; N_0 is the concentration of acceptors, which is almost equal to total concentration of RE ions; R_0 is the critical distance defined as donor – acceptor separation for which the rate of energy transfer to the acceptors is equal to the rate of intrinsic decay of the donor. The parameter Q is derived in the fitting process, where we used τ_0 value obtained for 0.5 mol %. The donor – acceptor energy transfer parameter C_{DA} is related to the R_0 by the relation.

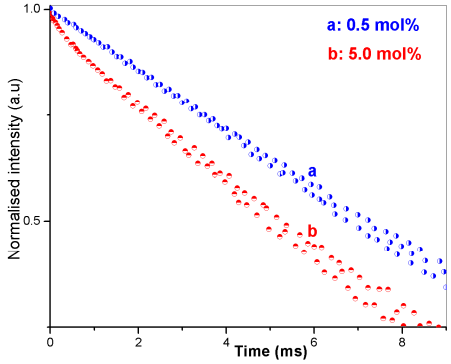

Fig.2. Decay profile for $^4F_{9/2}$ excited level of Dy^{3+} ions in K_2GdF_5 single crystal.

$$C_{DA} = R_0^s \tau_0^{-1} \tag{5}$$

By using the IH model, the fluorescence decay of the K_2GdF_5 sample doped with 5.0 mol% of Dy^{3+} ions to have a best fitting with S = 6, where we used τ_0 value (~ 1.68 ms) obtained for the K_2GdF_5 sample doped with 0.5 mol% of Dy^{3+} ions. The parameter (S) is good as agreement with other reports [1,8]. Energy transfer parameters Q, C_{DA} and critical distance (R_0) are calculated following (4) and (5): Q = 0.62; C_{DA} = 14.8×10^{-44} (cm^6s^{-1}) and R_0 = 6.67 (Å). The value of S = 6 to noted that the dominant interaction for energy transfer through cross – relaxation is of dipole – dipole type.

4. Conclusion

The present study yields a detailed picture of energy transfers of Dy^{3+} ions in K_2GdF_5 crystal. The UV excitation spectra have shown charge transfer state at ~ 300 nm of Dy^{3+} ions and energy transfer

from Gd^{3+} to Dy^{3+} ions at ~ 254 nm and 273 nm. By using the IH model, the non – exponential decay curve of the K_2GdF_5 sample doped with 5.0 mol% of Dy^{3+} ions is the best fitted with $S = 6$. This value has shown that the dominant interaction for energy transfer through cross – relaxation is of dipole – dipole type. The energy transfer parameters Q, C_{DA} and critical distance (R_0) are calculated: $Q = 0.62$, $C_{DA} = 14.8\times10^{-44}$ (cm^6s^{-1}) and $R_0 = 6.67$ (Å).

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