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The lifetime of Eu^{2+} fluorescence in $\text{CaF}_2:\text{Eu}^{2+}$ crystals

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Abstract. The lifetime of luminescence in $\text{CaF}_2:\text{Eu}^{2+}$ crystals has been investigated in a temperature range 15–320 K using a streak camera. Unlike the cases of other Eu^{2+} -doped crystals, an emission band with a peak at 425 nm was observed to have a lifetime which decreases with decreasing temperature. Such an unusual temperature dependence of the luminescence lifetime is suggested to be explained by taking into account the non-radiative process between the lowest $4f^65d$ level and the upper excited levels of the Eu^{2+} ion.

1. Introduction

A considerable amount of investigation has been carried out on the optical properties of Eu^{2+} -doped alkaline-earth halide or alkali halide crystals (see, e.g. a recent review article by Rubio (1991)). One of the important characters of these crystals is luminescence which is strong even at room temperature (RT). Therefore $\text{CaF}_2:\text{Eu}^{2+}$ and $\text{LiF}:\text{Eu}^{2+}$ crystals are widely used as scintillation phosphor materials.

The excitation of a $\text{CaF}_2:\text{Eu}^{2+}$ crystal with light lying in one of two UV absorption bands produces only one broad emission band with a peak at 424 nm at RT (Kobayashi *et al* 1980). The lifetime measurement of the blue emission has been carried out by Tolstoy (1955), Kisliuk *et al* (1968) and Kobayashi *et al* (1980). Kisliuk *et al* obtained lifetimes of 0.635 μs and 0.60 μs at 77 K and 4 K, respectively, while Kobayashi *et al* obtained the same value at 78 K as obtained at RT, which agrees with the cases of Eu^{2+} -doped alkali halides (Munoz *et al* 1988); unlike the measurements of Kisliuk *et al*, a temperature-dependent lifetime was not obtained by Kobayashi *et al*. It is well known in not only Eu^{2+} -doped crystals but also various phosphors that the luminescence lifetime is shortened with increasing temperature whenever a temperature dependence is observed. The experimental results of Kisliuk *et al* are quite different from the usual behaviour.

The present work was undertaken to clarify whether the reduction in lifetime with decreasing temperature is true in $\text{CaF}_2:\text{Eu}^{2+}$ crystals or not. For such a purpose we measure the luminescence lifetime at various temperatures. The luminescence of $\text{KCl}:\text{Eu}^{2+}$ crystals was also studied for comparison with the lifetime of $\text{CaF}_2:\text{Eu}^{2+}$.

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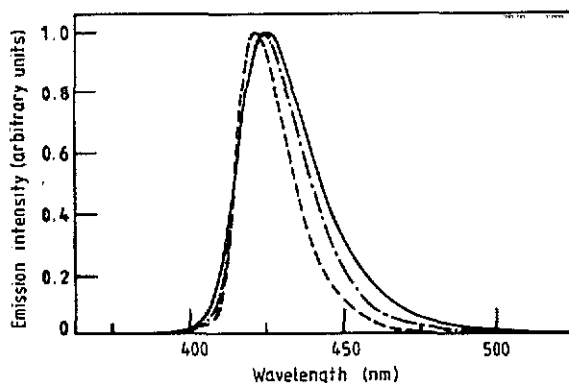


Figure 1. Time-resolved luminescence spectra (normalized) of $\text{CaF}_2:\text{Eu}^{2+}$, at 30 K (---), 170 K (- · -) and 290 K (—), measured with a streak time of $3 \mu\text{s}$ immediately after N_2 laser pulse excitation.

2. Experimental procedure and experimental results

Single crystals of $\text{CaF}_2:\text{Eu}^{2+}$ (0.1 mol% in the melt) and $\text{KCl}:\text{Eu}^{2+}$ (0.01 mol% in the melt) were excited by a Moletron UV14 N_2 laser. The pulse width of the laser is 4 ns, and its peak power is 425 kW. The crystal luminescence was collimated, from the direction perpendicular to the exciting light, to the entrance slit of a Jobin-Yvon HR 320 polychromator. The exit slit width was fixed at 15 mm. The luminescence intensity was detected with a Hamamatsu Photonics C2830 streak camera attached with a Hamamatsu Photonics Peltier-element-cooled charge-coupled device (CCD) photodetector. The luminescence decay and time-resolved spectrum were obtained using a Hamamatsu Photonics Temporal Analysis computer system.

$\text{CaF}_2:\text{Eu}^{2+}$ has two broad absorption bands in the UV region at RT: one (called the A band) is located at 420–330 nm, and the other (called the B band) at 260–200 nm. They are due to the electronic transitions $4f^7 \rightarrow 4f^65d$ in the Eu^{2+} ion. Therefore the N_2 laser emitting a 337.1 nm line excites the high-energy side of the A band. Such an excitation produces only one broad emission band with a peak at 425 nm at RT, in agreement with the previous results (Kobayashi *et al* 1980, Rubio 1991). The luminescence band shows a red shift with increasing temperature as seen in figure 1, where the luminescence intensity was accumulated for $3 \mu\text{s}$ after the laser pulse excitation. The blue emission band has an asymmetric lineshape with a long tail at low energies.

A single luminescence decay curve was observed in the semilogarithmic plot for the blue emission band at various temperatures between 15 and 300 K. No difference was observed between the lifetimes of the high-energy and low-energy sides of the blue emission band. At 15 K the lifetime was $0.620 \mu\text{s}$, while at 290 K it was $0.655 \mu\text{s}$. Our value at RT is close to the value of $0.63 \mu\text{s}$ obtained by Tolstoy (1955). In figure 2, the lifetime of the emission is plotted against temperature. The lifetime is found to become longer with increasing temperature.

Quite similar absorption and emission spectra are obtained for $\text{KCl}:\text{Eu}^{2+}$ regarding the position of the absorption and emission bands. For example, $\text{KCl}:\text{Eu}^{2+}$ has a broad emission band with a peak at 427 nm at RT, which is close to the 425 nm emission observed in $\text{CaF}_2:\text{Eu}^{2+}$. The luminescence lifetime $\text{KCl}:\text{Eu}^{2+}$, however, is different from that of

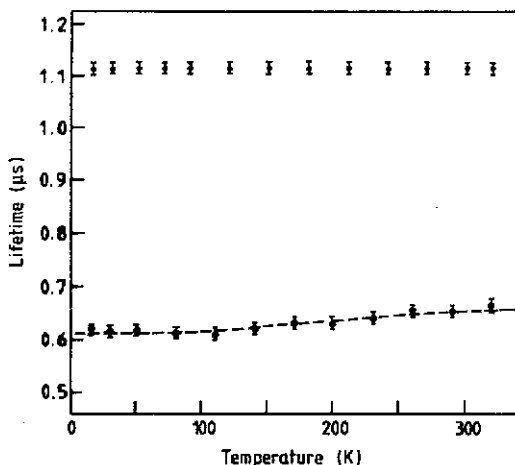


Figure 2. Temperature dependence of the lifetime of the emission in $\text{CaF}_2:\text{Eu}^{2+}$ (●) and of the emission in $\text{KCl}:\text{Eu}^{2+}$ (○): ---, curve obtained with equation (3) from the best fit to the experimental data of the Eu^{2+} emission.

$\text{CaF}_2:\text{Eu}^{2+}$ as shown in figure 2: the former is longer than the latter, e.g. $1.11 \mu\text{s}$ at 300 K, which is exactly the same as a recent measurement (Munoz *et al* 1988). Moreover, unlike the case of $\text{CaF}_2:\text{Eu}^{2+}$, the lifetime of $\text{KCl}:\text{Eu}^{2+}$ does not change with variation in temperature in the 15–320 K range in which our measurements were made. This is also in agreement with the observations of Munoz *et al* (1988).

3. Discussion

The Eu^{2+} luminescence lifetime of $\text{KCl}:\text{Eu}^{2+}$ was observed to be constant between 15 and 320 K in the present investigation. Munoz *et al* (1988) have observed that the lifetime of $\text{KCl}:\text{Eu}^{2+}$ is constant up to 600 K but that it decreases exponentially above about 600 K with increasing temperature. For $\text{CaF}_2:\text{Eu}^{2+}$, however, we observed that the value of the lifetime increases with increasing temperature. This is consistent with the observations of Kisliuk *et al*. Therefore we have given support to their observations.

Kisliuk *et al* (1968) have suggested that the increase in lifetime with increasing temperature is probably due to the existence of states of lower oscillator strength lying above the lowest excited level. According to the energy level diagram of the Eu^{2+} ion in the crystal (Downer *et al* 1983, Rubio 1991), the excited state ${}^6\text{P}_j$ produced by the f^7 electron configuration of the Eu^{2+} ion is located above the lowest excited state produced by the f^6d configuration.

Following the suggestion by Kisliuk *et al* (1968), we consider tentatively that two relaxed excited states (RESS) are responsible for the luminescence process of the blue emission in $\text{CaF}_2:\text{Eu}^{2+}$. The low-energy-lying RES I is related to the lowest excited state of the f^6d configuration, while the upper RES II is produced by the excited state of the f^7 configuration. The radiative transition from the RES I to the ground state (f^7) gives rise

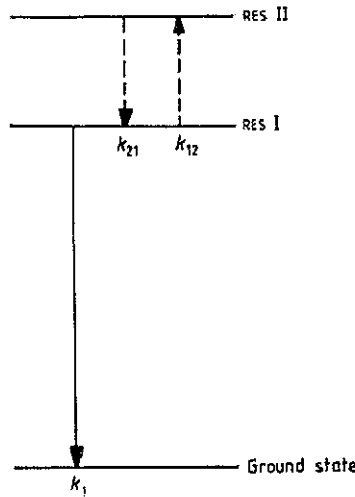


Figure 3. Energy level diagram (schematic) for the emission in $\text{CaF}_2:\text{Eu}^{2+}$: \downarrow , radiative transitions; \downarrow , \uparrow , non-radiative transitions.

to the blue emission, whose probability is defined by k_1 , as shown in figure 3. We assume that the transition from the RES II is forbidden, but that the non-radiative transition is allowed between the two RESs. The non-radiative transition between two RESs is characterized by the probability k_{12} for RES I \rightarrow II and k_{21} for RES II \rightarrow I. The two non-radiative probabilities are connected by

$$k_{12} = k_{21} \exp(-D/kT)$$

where D is the energy separation between RES I and RES II.

The rate equations for the populations N_1 and N_2 in the levels RES I and RES II, respectively, are given by

$$dN_1/dt = -(k_{12} + k_1)N_1 + k_{21}N_2 \quad (1)$$

$$dN_2/dt = k_{12}N_1 - k_{21}N_2. \quad (2)$$

We assume that the non-radiative relaxation process is a one-phonon process (Le Si Dang *et al* 1978), i.e.

$$k_{12} = Kn \quad k_{21} = K(n+1)$$

where n is the Bose-Einstein distribution function

$$n = [\exp(D/kT) - 1]^{-1}.$$

Equations (1) and (2) lead to a quadratic equation for decay time t :

$$k_{21}k_1t^2 - (k_{21} + k_{12} + k_1)t + 1 = 0. \quad (3)$$

Equation (3) gives two decay-time constants: the fast constant t_f and the slow constant t_s . When we choose appropriate values for D , K and k_1 , we can obtain a temperature dependence where t_f decreases as the temperature is increased, while t_s increases as observed for our blue emission of $\text{CaF}_2:\text{Eu}^{2+}$. Therefore we tried to determine the values of three parameters D , k_1 and K so as to obtain the best fit to the experimental data. The broken lines in figure 2 were obtained using values of $D = 269.8 \text{ cm}^{-1}$, $k_1 = 2.837 \times 10^6 \text{ s}^{-1}$ and $K = 1.631 \times 10^6 \text{ s}^{-1}$.

Downer *et al* (1983) estimated the energies of $4f^7$ levels using two-photon absorption spectroscopy; the lowest ${}^6\text{P}_{7/2}$ state has three components whose energies are 27 558, 27 564 and 27 588 cm^{-1} in $\text{CaF}_2:\text{Eu}^{2+}$. Taking into account the fact that the $4f^65d$ configuration has a zero-phonon line at around 24 213 cm^{-1} (Downer *et al* 1983, Rubio 1991), the separation D is estimated to be about 3300 cm^{-1} . Our value of $D = 269.8 \text{ cm}^{-1}$ deviates from this value. Thus the model of two excited states seems to be incorrect. But, if we take into account that the separation between $4f^6d$ and $4f^7$ levels is different between the absorption levels and the relaxed levels, our model is not unreasonable.

Another explanation for the shortening of the lifetime at low temperatures will be made by the electron trap at lattice defects at low temperatures as in the case of II-VI phosphors. In the near future we shall determine by quantitative analysis which mechanism is more probable.

Acknowledgments

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