

Investigation on charging processes and phosphorescent efficiency of $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$

Zhiyi He^a, Xiao-jun Wang^{b,c,*}, W.M. Yen^a

^a*Department of Physics, University of Georgia, Athens, GA 30460, USA*

^b*Department of Physics, Georgia Southern University, Statesboro, GA 30460, USA*

^c*Key Laboratory of Excited State Processes, CIOMP, CAS, Changchun 130033, China*

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Abstract

An optical charging process of $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$ has been investigated to examine its efficiency. In the charging process, the luminescence grows gradually before reaching the equilibrium intensity. The unreleased area above the charging curve represents the energy stored in the traps. It is found that the integrated intensity of the released phosphorescence after excitation is larger than that of the unreleased luminescence in the charging process. Under an intensive excitation, a decrease course of the luminescence in the charging process is observed. A quenching mechanism via cross relaxation among Eu^{2+} ions is proposed. The quantum efficiency is measured by comparing the integrated intensities of the phosphorescence and the pump light.

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1. Introduction

Persistent phosphors have been studied for several decades since the work was reported on the ZnS:Cu system [1,2]. More efficient systems, including $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$ and $\text{CaAl}_2\text{O}_4\text{:Eu,Nd}$ [3,4], have been widely used to replace the old system in the recent years due to the longer

duration of their phosphorescence. The phosphorescence duration and light output are very important features for the persistent phosphors. These features have intensively studied by many investigators using detrapping experiments such as phosphorescent decay and thermal luminescence that are related with the release process for the photons stored in the traps. However, the details of trapping in the charging process still need better understanding. The release process is influenced by the charging process. The persistent phosphors cannot be well characterized without consideration for their charging processes and efficiency, which

*Corresponding author. Department of Physics, Georgia Southern University, Statesboro, GA 30460, USA.

Tel.: +912 681 5503; fax: +912 681 0471.

E-mail address: xwang@GeorgiaSouthern.edu (X.-j. Wang).

can be studied by the comparison between the output of phosphorescence and the input of pump light. A study on the time dependence of luminescence in charging process of $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$ has been reported [5]. In the present work, the further investigation in details of the charging process reveals the interaction among the Eu^{2+} ions in trapping states and its influence on the luminescent efficiency, which allows us to have a better explanation to our previous results of fluorescent lifetime of Eu^{2+} in SrAl_2O_4 [6].

2. Experiments

The samples $\text{SrAl}_2\text{O}_4\text{:Eu}$ and $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$ have been prepared by mixing the powder materials SrCO_3 , Al_2O_3 , Dy_2O_3 , Eu_2O_3 according to the mole ratio of the products and adding 2% (in weight) of boric acid as flux. The mixtures are pressed into pellets and then sintered into ceramic samples at 1350°C for 2 h in a $\text{N}_2 + 5\% \text{H}_2$ reducing atmosphere. The concentrations of doped Dy and Eu are 1 mol% except for those particularly noted. The purity of all materials is 99.99%. All measurements are conducted at room temperature on a FluoroMax II spectrometer with a 500 W xenon lamp, providing a strong excitation by focusing the light on the samples. The samples are placed in water to avoid being heated by the

excitation light. A 4 W mercury lamp (365 nm) is used in a distance of 1 m from the measured samples as the weak excitation source. The shutter of excitation light is opened rapidly when the charging process measurement begins. The samples are heated at $100\text{--}150^\circ\text{C}$ in dark for 5 h to empty the traps before the charging process starts. Absorption rate is measured using the FluoroMax comparing the diffused light from the samples with that from a BaSO_4 sample that serves as a standard (100% reflection).

3. Results and discussion

Persistent phosphors exhibit an exponentially increasing luminescence under excitation by a light source with constant intensity, as shown in Fig. 1. The luminescence saturates after a sufficiently long exposure. Photon energy is deposited into the phosphors as trapped electrons or holes during excitation and subsequently released as phosphorescence. The energies stored during excitation and released after excitation are proportional to the areas S_1 and S_2 , respectively. A material showing larger charged area, S_1 , has a greater storability.

If the radiative efficiency is η_1 (defined as $\eta = N_e/(N_a - N_s)$, where N_e , N_a , and N_s are the photon numbers in emission, absorption, and in traps, respectively.), the number of traps that are

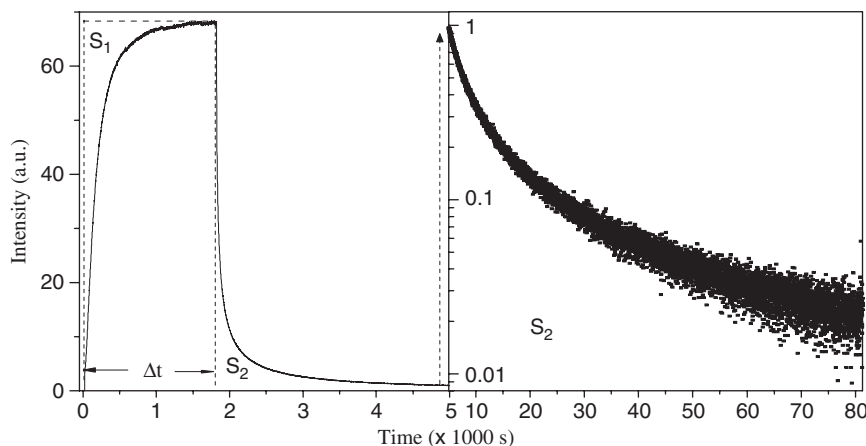


Fig. 1. The charging and release processes of $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$ (the intensity for phosphorescence is enlarged after 5000 s).

occupied can expressed as

$$N_1 = bS_1/\eta_1, \quad (1)$$

where b is a coefficient related to instrument response. Similarly, the number of traps that release electrons can be expressed as

$$N_2 = bS_2/\eta_2, \quad (2)$$

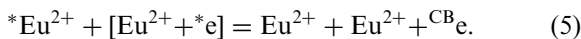
where η_2 is the radiative efficiency of the phosphorescence. The constant b will be the same if the measurement conditions remain unchanged. After the sample has been totally discharged, we have

$$N_1 = N_2. \quad (3)$$

Therefore

$$\eta_2/\eta_1 = S_2/S_1, \quad (4)$$

which provides a measure of the efficiency of the phosphorescence. $S_2 > S_1$ indicates that the radiative efficiency in the release process is higher than that in the charging process. Such an effect has also been observed by Shionoya [2] in similar studies conducted in zinc sulfide doped with Cu^+ ions in an electron trap model. The holes are left at the luminescent centers after the excited electrons are trapped by the trapping centers, and the transition for the holes released to the valence band is responsible for the quenching effect. In other words, the hole-trapped luminescent centers play a role as quenching centers. In the case of $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$, the hole trap model [3,4], in which Dy^{3+} ions serve as hole traps and the excited electrons are left at the Eu^{2+} sites, is accepted by most researchers. Accordingly, in $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$, the electron-trapped Eu^{2+} ions denoted as $[\text{Eu}^{2+}+^*e]$ act as the quenching centers. The excited Eu^{2+} ions ($^*\text{Eu}^{2+}$) return to their ground state via either a radiative transition or a non-radiative energy transfer to the $[\text{Eu}^{2+}+^*e]$ centers resulting in the release of the trapped electrons to the conduction band ($^{\text{CB}}e$). The energy transfer can be expressed as



The electrons in the conduction band ($^{\text{CB}}e$) can be re-trapped by other Eu^{2+} ions or recombine with the holes trapped at the Dy^{3+} sites. On average, the population of trapped carriers during the charging process is larger than that in the release

process. This leads to a lower luminescent efficiency in the charging process. The quenching mechanism by energy transfer in Eq. (5) is actually a cross relaxation between the $^*\text{Eu}^{2+}$ and $[\text{Eu}^{2+}+^*e]$ centers. Cross relaxation takes place via the pairs of the energy donors and acceptors existing in the crystal lattices [7] or the energy migration among the donors [8,9]. The latter is believed to be the case because of the overlap between the excitation and emission spectra of Eu^{2+} in SrAl_2O_4 , as shown in Fig. 2.

In several experiments under the same conditions of synthesis and measurement, the saturated intensity of the photoluminescence for Eu singly doped (1 mol%) samples is about 135% of the Eu and Dy doubly doped (both 1 mol%) samples. In comparison with the ratio of the released area S_2 to the charged area S_1 in Fig. 1 (~140%), this is in a good agreement with the quenching effect by the trapping centers induced by the co-doped Dy^{3+} ions. In our previous experimental results, the fluorescent lifetime of the Eu and Dy doubly doped sample is significantly shorter than that of the Eu singly doped sample [6]. For the doubly doped sample the transient fluorescence, under the pulse excitation above a continuous pump of a UV lamp to keep trapping states saturated, is also less intensive than that without being pumped by the UV lamp [10]. These facts strongly suggest that a quenching process occurs in the trapping states of $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$. In addition, beginning with a

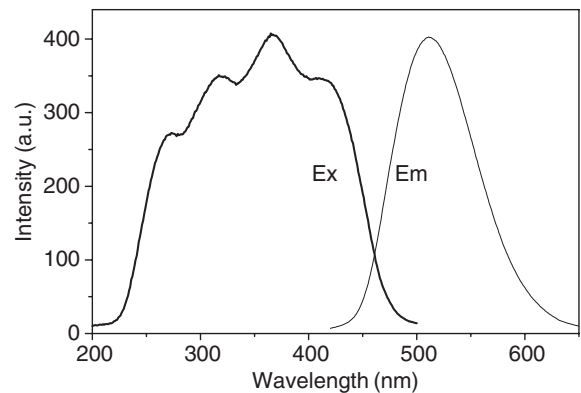


Fig. 2. Overlap between excitation (ex) and emission (em) spectra of $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$.

phosphor $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$ depleted of afterglow, unusual dynamics is observed when the sample is pumped with an intensive excitation light. Under the excitation at constant intensity, the fluorescence intensity grows rapidly and reaches saturation in 10 s, and then presents a decrease course as shown in Fig. 3(a). Fig. 3(b) shows the phosphorescence decays subsequent to the excitations on the same depleted phosphor for 10 and 4000 s, respectively. It is clear that the phosphorescence is more intense after the 4000 s duration pump than after the 10 s pump when the fluorescence is saturated. The traps continue to be fed by the excitation during the decreasing course (see Fig. 2). Shionoya [2] has assumed that the charging process of the persistent phosphor is accompanied by a luminescent efficiency decrease owing to the quenching effect of the trapping centers. He described a quenching curve which is submerged in the growth of the charging process. This is indeed observed in our experiment as shown in Fig. 3(a), the decreasing course in the charging

process of $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$. For simplification we assume that the traps have a single depth. Hence we should have a singly exponential growth of trapped population in the charging process [5]:

$$N = \alpha N_0(1 - \exp(-\beta t)), \quad (6)$$

where N_0 is the total number of the traps, αN_0 indicates the trapped population in equilibrium after sufficiently long excitation, proportional to the intensity of pumping light, and β the detrapping rate. At the beginning of the charging process shown in Fig. 1, the luminescent intensity starts almost from zero. This suggests that most electrons pumped by the photons are kept by traps and then the detrapped holes and electrons recombine at the Eu^{2+} sites. The population of the resulted excited Eu^{2+} ions and their luminescence should be proportional to the trapped population N . The quenching rate by cross relaxation is proportional to the product of populations of the energy donor and acceptor involved. In our case the excited Eu^{2+} ions is quenched by the Eu^{2+} ions in trapping states, the quenching rate is proportional to square of the trapped population. So that in the charging process the luminescent intensity, I , as a function of N can be expressed with two constants, p and q , as

$$I = pN - qN^2. \quad (7)$$

Under weak excitation N is small and the second term (qN^2 , $q \ll p$) has little influence. But if the excitation is strong enough, the luminescent intensity may decay with the increase of N in the manner described in Eq. (6). With suitable coefficients in Eqs. (6) and (7), one can find a decrease course at higher relative excitation intensity, i.e., the larger value of α in Eq. (6). The difference between the experimental result in Fig. 3(a) and the simulated decrease course in Fig. 4 is due to the simplification in Eq. (6). In fact there are several trap depths [11] and the charging process presents a multiple-exponential curve. Detailed investigations need to be performed in the future. In addition, an external quantum efficiency has been measured by comparing the phosphorescence output and the pump light input. The relative number of photons can

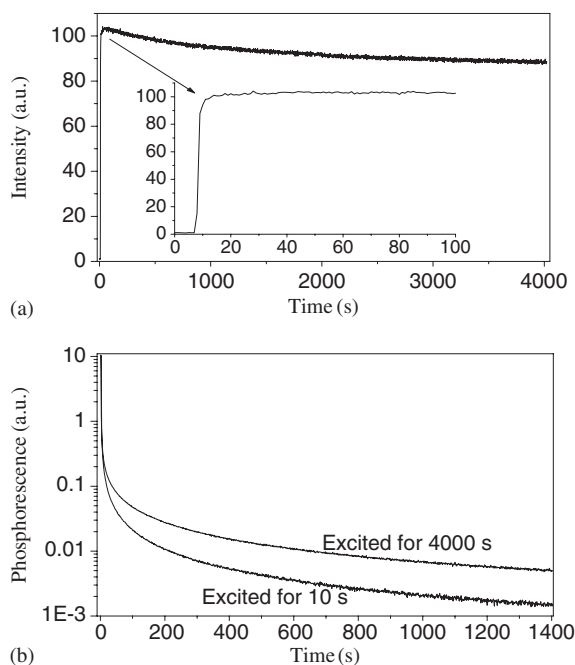


Fig. 3. (a) A decrease course in the process of $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$ under intensive excitation, (b) comparison of $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$ phosphorescence after 10 and 4000 s of excitation, respectively.

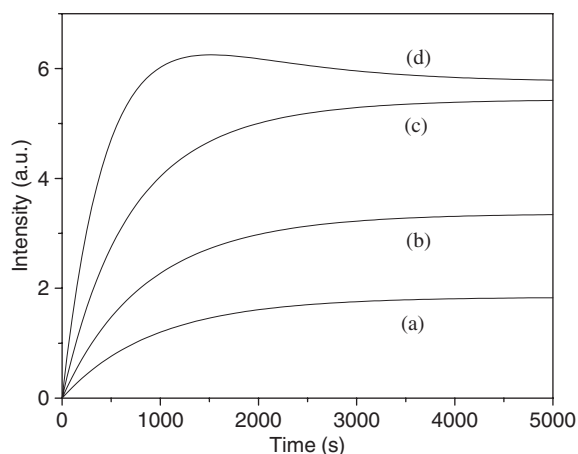


Fig. 4. Schematic charging processes under excitation with different intensities simulated by Eqs. (6) and (7) with the relative values: $\alpha = 1, 4, 8, 16$ for curves a, b, c, and d, respectively. Also, $N_0 = 1$, $\beta = 0.001$, $p = 1$, and $q = 0.04$.

be calculated by integrating both the wavenumber, $\tilde{\lambda}$, and time, t :

$$\eta = \int \int I_{\text{em}}(\tilde{\lambda}, t) d\tilde{\lambda} dt \Big/ \left[A(\tilde{\lambda}) \Delta t \int I_{\text{pump}}(\tilde{\lambda}) d\tilde{\lambda} \right], \quad (8)$$

where $I_{\text{em}}(\tilde{\lambda}, t)$ is the emission spectrum at release time t , $A(\tilde{\lambda})$ the absorption coefficient of the phosphor, Δt the pump time and $I_{\text{pump}}(\tilde{\lambda})$ the spectrum of the pump light source (a 365 nm lamp). Actually the line shape of the emission spectra of $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$ almost remains unchanged in both charging and release processes. Thus the ratio of the intensity at a specific wavenumber (or wavelength) to the integrated spectral area is independent on the time in measurement. This allows us to obtain the integrated intensity by monitoring at a single wavenumber (19305 cm^{-1} , 518 nm). In Fig. 1 the quantum efficiency of the phosphorescence, as a ratio for the photon number in phosphorescent emission to that in absorption of the pump light, is 2.17%. The overall luminescent efficiency including the emissions in charging and release processes is 22.7%.

4. Conclusions

In conclusion, it can be explained by the lower radiative efficiency in the charging process that the released area of the phosphorescence of $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$ is larger than the charged area. The luminescence is quenched by the Eu ions in trapping states via cross relaxation with the trapped electrons released into the conduction band. The quenching effect is confirmed by the decrease course of luminescence in the charging process under the intensive excitation. A simulation of the charging process under different excitation intensity has been demonstrated. The phosphorescent quantum yield is 2.17% of the absorption to the pump light.

Acknowledgments

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