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Nonexponential hole burning in Sm^{2+} doped mixed crystals

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Abstract

Kinetics of nonexponential hole burning in Sm^{2+} doped $\text{BaFCl}_{0.5}\text{Br}_{0.5}$ is investigated at 77 K. Recombination in two-photon hole burning and tunnelling in single-photon hole burning are considered to result in the decrease of the hole-burning rate with the increase of hole depth.

1. Introduction

The nonexponential dependence of hole depth on burning time in glasses has been reported [1–3]. The nonexponential feature exhibits the decrease of the burning rate with burning time. This effect is generally attributed to a dispersive distribution of the burning rate due to random fluctuation of the environments around hole-burning (HB) centers in glass [1, 2]. We also observed the nonexponential HB in Sm^{2+} doped alkaline earth metal fluoride halides. The HB mechanism in this system is electron transfer from Sm^{2+} ions to electron traps [4–6]. Therefore, Sm^{3+} ions are generated in the HB process. The generated Sm^{3+} ions are able to act as effective traps to recombine with electrons. The evidence for this behavior is that a burnt hole at a site in the inhomogeneous line becomes shallower and shallower with the process of burning another hole at another site. The recombination

rate should be proportional to the concentration of generated Sm^{3+} ions. Then, the recombination rate increases with the increase of hole depth. Meanwhile, the increase of hole depth leads to the decrease of the concentration of traps because some traps capture electrons in HB. The trapping rate will decrease in the HB process because the trapping rate is proportional to the concentration of traps. We consider that the increase of generated Sm^{3+} ions and reduction of traps can both reduce the burning rate with the increase of hole depth and lead to nonexponential HB.

We suggest in this work that the electron transfer from Sm^{2+} ions to traps may perform through two roads. The first road is two-step photoionization of Sm^{2+} , followed by trapping of the released electrons in the conduction band by traps. The second road is that electrons are excited in a single step from the ground state to the excited states $^5\text{D}_J (J = 0, 1, 2)$ of Sm^{2+} ions where the electrons transfer to adjacent traps by the tunnelling process. In this paper we report HB kinetics in Sm^{2+} doped $\text{BaFCl}_{0.5}\text{Br}_{0.5}$ at 77 K.

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2. Experimental

The sample of $\text{BaFCl}_{0.5}\text{Br}_{0.5}: 1\% \text{Sm}^{2+}$ was prepared as described previously [5, 6]. The spectral hole is burnt in the ${}^7\text{F}_0$ – ${}^5\text{D}_2$ transition of Sm^{2+} . A tunable dye laser, with a laser line width of 0.2 cm^{-1} , pumped by a pulsed Quanta-Ray DCR-2A Nd:YAG with a repetition frequency of 10 Hz and duration time of 10 ns, was used for both burning and gating laser beams, so the two-step hole burning in this research is a one-color two-photon process. In the HB process the intensity of fluorescence from the ${}^5\text{D}_1$ – ${}^7\text{F}_0$ transition is detected by a Spex-1403 monochromator in order to directly monitor the change of the hole depth with the excitation pulse number. The HB is performed at 77 K.

3. Theory

Fig. 1 shows the diagram of single-photon and two-photon HB process in Sm^{2+} doped alkaline earth metal fluoride halides. R_1 and R_2 are the excitation rates of the first step and the second step,

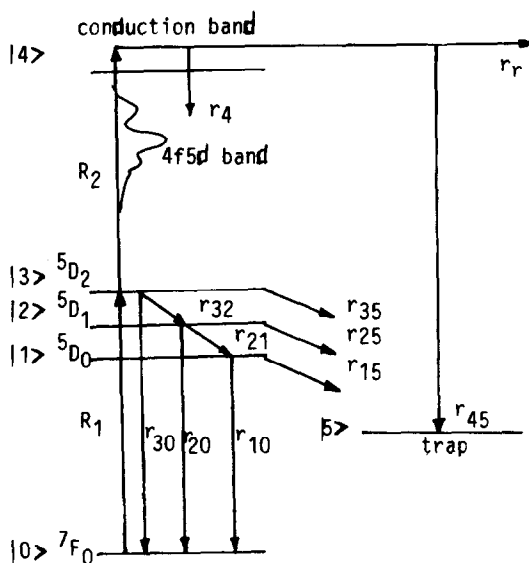


Fig. 1. Diagram of two-photon and single-photon hole burning in Sm^{2+} doped alkaline earth metal fluoride halides.

respectively. γ_4 is the electron transfer rate from the conduction band to the lower levels. γ_r is the recombination rate in the conduction band with the generated Sm^{3+} ions by HB and γ_{ij} ($i, j = 0, 1, 2, 3, 4, 5$) is the electron transfer rate from state $|i\rangle$ to state $|j\rangle$. We suppose that during excitation by each laser pulse the electrons excited from the ground state stay in the $|3\rangle$ and $|4\rangle$ states stably and do not transfer until the excitation is terminated.

During the excitation by the m th pulse, we have

$$\frac{dn_0(m, t)}{dt} = -R_1 n_0(m, t), \quad (1)$$

$$\frac{dn_3(m, t)}{dt} = R_1 n_0(m, t) - R_2 n_3(m, t), \quad (2)$$

$$\frac{dn_4(m, t)}{dt} = R_2 n_3(m, t), \quad (3)$$

with the initial conditions of

$$n_0(m, 0) = n_0(m-1), \quad (4)$$

$$n_3(m, 0) = 0, \quad (5)$$

$$n_4(m, 0) = 0, \quad (6)$$

$$0 \leq t \leq \Delta t, \quad (7)$$

where m is the pulse number ($m = 1, 2, 3, \dots$). $n_0(m, t)$, $n_3(m, t)$ and $n_4(m, t)$ are the concentrations of $|0\rangle$, $|3\rangle$ and $|4\rangle$ states corresponding to the hole site at time t during the m th pulse excitation, respectively. $n_0(m-1)$ is the concentration of $|0\rangle$ state corresponding to hole site before the m th pulse excitation. Δt is the pulse duration time which is 10 ns in this work. If $R_1 \Delta t \ll 1$ and $R_2 \Delta t \ll 1$, we obtain from Eqs. (1) to (7) that

$$n_3(m, \Delta t) = R_1 \Delta t n_0(m-1), \quad (8)$$

$$n_4(m, \Delta t) = R_1 R_2 \Delta t^2 n_0(m-1)/2. \quad (9)$$

At the end of the m th pulse, the electrons in the $|4\rangle$ and $|3\rangle$ states start to transfer and some of them are captured by traps. In the process of electron transfer from the conduction band, γ_{45} and γ_r are written as

$$\gamma_{45} = \sigma_t v [N_t(0) - (n_0(0) - n_0(m-1))], \quad (10)$$

$$\gamma_r = \sigma_r v (n_0(0) - n_0(m-1)), \quad (11)$$

where σ_t and σ_r are the trapping cross section and recombination cross section, respectively, v is the velocity of electrons in the conduction band. $N_t(0)$ and $n_0(0)$ are the concentrations of traps and HB

centres, i.e., the $|0\rangle$ state, corresponding to the hole site before burning, respectively. $[N_t(0) - (n_0(0) - n_0(m-1))]$ is the concentration of residual traps after irradiation by $m-1$ pulses. $(n_0(0) - n_0(m-1))$ is the concentration of generated Sm^{3+} ions after irradiation by $m-1$ pulses. In the process of electron transfer after the m th pulse and before the $(m+1)$ th pulse, we consider that γ_{45} and γ_r are unchanged as written in Eqs. (10) and (11), respectively. Hence, the number (Am) of electrons captured by traps from the conduction band in the time separation between the m th pulse and the $(m+1)$ th pulse is

$$Am = \gamma_{45}n_4(m, \Delta t)/(\gamma_4 + \gamma_r + \gamma_{45}), \quad (12)$$

where γ_4 is considered to be a constant in whole HB processes.

In the process of electron transfer from the $|3\rangle$ state, we neglect the number of electrons relaxed from the conduction band due to $n_3(m, \Delta t) \gg n_4(m, \Delta t)$ according to Eqs. (8) and (9). Then we have

$$dn_3(m, t)/dt = -(\gamma_{30} + \gamma_{32} + \gamma_{35})n_3(m, t), \quad (13)$$

$$dn_2(m, t)/dt = -(\gamma_{20} + \gamma_{21} + \gamma_{25})n_2(m, t) + \gamma_{32}n_3(m, t), \quad (14)$$

$$dn_1(m, t)/dt = -(\gamma_{10} + \gamma_{15})n_1(m, t) + \gamma_{21}n_2(m, t), \quad (15)$$

with the initial conditions of

$$n_2(m, \Delta t) = 0, \quad (16)$$

$$n_1(m, \Delta t) = 0, \quad (17)$$

$$t \geq \Delta t. \quad (18)$$

The number (Bm) of electrons completed tunnelling from $|3\rangle$, $|2\rangle$ and $|1\rangle$ states to traps after the m th pulse and before the $(m+1)$ th pulse is expressed as

$$Bm = \int_{\Delta t}^{\infty} \Delta t (\gamma_{35}n_3(m, t) + \gamma_{25}n_2(m, t) + \gamma_{15}n_1(m, t)) dt, \quad (19)$$

where γ_{35} , γ_{25} and γ_{15} should be close to each other because the energy separations of $|3\rangle$, $|2\rangle$ and $|1\rangle$

states are much smaller than the photoionization energy of Sm^{2+} in this system. Now we denote the tunnelling rate by γ_t . In the case of $\gamma_t \ll \gamma_{10}$, γ_{20} , γ_{21} , γ_{30} and γ_{32} and from Eqs. (13) to (17), Eq. (19) is approximately equal to

$$Bm = (\gamma_{10}\gamma_{20} + \gamma_{10}\gamma_{21} + \gamma_{10}\gamma_{32} + \gamma_{21}\gamma_{32}) \gamma_t n_3(m, \Delta t) / \gamma_{10}(\gamma_{20} + \gamma_{21})(\gamma_{30} + \gamma_{32}), \quad (20)$$

where γ_t is proportional to the concentration of traps adjacent to the HB centers and is written as

$$\gamma_t = C_t [N_t(0) - l(n_0(0) - n_0(m-1))u(m-1)], \quad (21)$$

where C_t is a constant, l is the ratio of the volume taken by whole HB centers to the effective tunnelling volume around the HB centers at hole site. $u(m-1)$ is the ratio of trapped electron number through tunnelling to the total trapped electron number before the m th excitation pulse. The concentration of HB centers corresponding to the hole site after the m th excitation pulse and before the next pulse's coming is written as

$$n_0(m) = n_0(m-1) - Am - Bm. \quad (22)$$

We write R_1 , R_2 and $n_0(0)$ as

$$R_1 = R'_1 I, \quad (23)$$

$$R_2 = R'_2 I, \quad (24)$$

$$n_0(0) = kN_0(0), \quad (25)$$

where R'_1 and R'_2 are constants, k is the ratio of HB center numbers at the hole site to that under the whole inhomogeneous line. $N_0(0)$ is the concentration of total HB centers under the inhomogeneous line before burning. I is the excitation density. According to Eqs. (8)–(12) and (20)–(25), and using $N_0(0)$, $n_0(0)$, $\sigma_t v N_0(0)$ and σ_t as the unit of $N_t(0)$, $n_0(m)$, γ_4 and σ_r , respectively, we obtain

$$n_0(m) = n_0(m-1) \{ 1 - \alpha I^2 [N_t(0) - k(1 - n_0(m-1))]/[\gamma_4 + \sigma_r k(1 - n_0(m-1))] + N_t(0) - k(1 - n_0(m-1))] - \beta I [N_t(0) - lk(1 - n_0(m-1))u(m-1)] \}, \quad (26)$$

with

$$\alpha = R'_1 R'_2 \Delta t^2 / 2, \quad (27)$$

$$\beta = R'_1 \Delta t C_t N_0(0) (\gamma_{10} \gamma_{20} + \gamma_{10} \gamma_{21} + \gamma_{10} \gamma_{32} + \gamma_{21} \gamma_{32}) / \gamma_{10} (\gamma_{20} + \gamma_{21}) (\gamma_{30} + \gamma_{32}), \quad (28)$$

$$n_0(0) = 1. \quad (29)$$

According to the definition of $u(m)$, we have

$$u(m) = \{ (1 - n_0(m-1))u(m-1) + \beta n_0(m-1)I[N_t(0) - lk(n_0(m-1))u(m-1)] \} / (1 - n_0(m)). \quad (30)$$

Using Eqs. (26) to (30), we can calculate the dependence of the HB center numbers at the hole site on the excitation pulse numbers. This dependence is measured in the experiment by detecting the change of fluorescence intensity from the 5D_1 – 7F_0 transition of Sm^{2+} ions with excitation pulse number at 77 K.

4. Results and discussion

Fig. 2 shows the calculated and measured burn patterns as a function of the excitation pulse number at variable excitation density, $I_0 = 1 \text{ MW/cm}^2$. It shows that the calculated data fit the experimental data well. In the simulation, we select

$$\alpha I_0^2 N_t(0) / (\gamma_4 + N_t(0)) = 0.0004, \quad (31)$$

$$\beta I_0 N_t(0) = 0.0002, \quad (32)$$

$$\sigma_r / (\gamma_4 + N_t(0)) = 600, \quad (33)$$

$$l / N_t(0) = 160, \quad (34)$$

$k = 0.025$, which value is obtained in experiment. The values of 0.0004 and 0.0002 indicate the two-photon HB rate and single-photon HB rate per pulse in the beginning of burning under the excitation density of I_0 , respectively. So single HB plays an important role in the beginning of HB. In Eq. (34), if $N_t(0) = 1$ then $l = 160$, it is indicated that the tunnelling volume around a HB center is very small. In this calculation, we define $l = 1$ for electron trapping in the conduction band. In Eqs. (10)

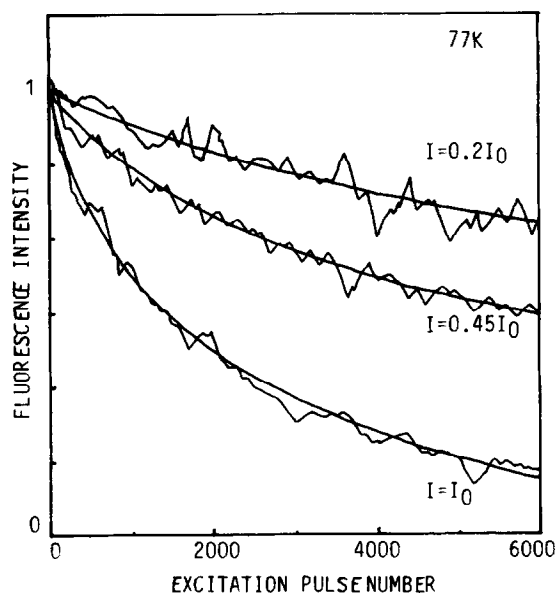


Fig. 2. Calculated and measured dependence of fluorescence intensity on the excitation pulse number for different excitation densities in $\text{BaFCl}_{0.5}\text{Br}_{0.5}:\text{Sm}^{2+}$ at 77 K.

and (21), the tunneling rate will reduce much faster than the trapping rate in the conduction band with increasing hole depth if $l = 160$. So two-photon HB becomes the main process with increasing hole depth and the tunnelling process makes an important contribution to nonexponential HB in the beginning of HB. From Eqs. (31) and (32), the two-photon HB becomes dominant with increasing excitation density. Eq. (33) gives $\sigma_r = 300$ if $\gamma_4 = 1$ and $N_t(0) = 1$. It shows that the electron recombination cross section with the ionized HB centres is about two orders greater than the capture cross section of traps. That is why the recombination process plays an important role on nonexponential HB even if the concentration of ionized HB centres is smaller than that of traps.

5. Conclusion

Two-photon HB and single-photon HB both occur in persistent spectral HB in $\text{BaFCl}_{0.5}\text{Br}_{0.5}:\text{Sm}^{2+}$ at 77 K. The recombination and tunnelling processes mainly lead to nonexponential HB.

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