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Laser-induced filling and thermal filling of spectral holes in $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$

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Laser-induced filling and temperature cycling experiments were conducted in the sample $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$. Under laser irradiation, the decay curve of the hole area is composed of a fast component and a slow component. In the temperature cycling curve, there are a slow decrease of the hole area from 77 to 200 K and a rapid drop above 300 K. The decay of the hole area with time at 77 k and 313 K follow a logarithmic law. Analysis of these results shows that there are two kinds of traps which govern hole burning and filling processes in the sample. One is related to some impurities or defects. Another is related to Sm^{3+} ions. The distribution of the potential well of the latter, produced by substitutional disorder, can be described by a two-level-system model.

1. Introduction

Spectral hole burning attracts much interest for its potential as high density optical storage technique. Following the first report on photon gated hole-burning material $BaFCl:Sm^{2+}$ by Macfarlane et al., we modified the material by using substitutionally disordered microcrystals $BaFCl_xBr_{1-x}:Sm^{2+}$ instead of $BaFCl:Sm^{2+}$, raised the ratio of the inhomogeneous width to the homogeneous width and succeeded in burning holes at 77 K [1,2]. The anomalous large inhomogeneous width was proven to be produced by substitutional disorder of Cl^- and Br^- neighbors around Sm^{2+} ions [3]. Recently we succeeded in hole burning in $Sr_{0.5}Ba_{0.5}FCl_{0.5}:Sm^{2+}$ at room temperature [4]. A 561.7 nm laser was used to pump transition from $^7F_0$ to $^5D_2$ of Sm^{2+}. A hole with width of 7 cm^{-1} and depth of 15% was obtained in the inhomogeneous width of 40 cm^{-1}.

In this paper, we report the results about laser induced filling and thermal filling. Two kinds of traps are found to govern hole burning and filling processes.

2. Experimental results and discussion

Laser-induced filling was studied using laser beam with different energy. It was found that laser beams with energy lower or higher than the transition energy from $^7F_0$ to $^5D_2$ had different effect. When a sample of $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ was irradiated by a 566 nm beam of a dye laser, pumped by a YAG laser, The area of a hole burned by the 560 nm laser decreased rapidly first with irradiation time, then approached a constant value (35% of the initial area), as shown in fig. 1. The energy of 566 nm is lower than the energy from $^7F_0$ to $^5D_2$, which is about 560 nm. When the sample was irradiated by laser beam with energy higher than the transition from $^7F_0$ to $^5D_2$, the area of the hole decreased rapidly first, then decayed slowly until the hole was erased. The laser-induced hole filling by 337.1 nm radiation from an N_2 laser is shown in fig. 2. The 532

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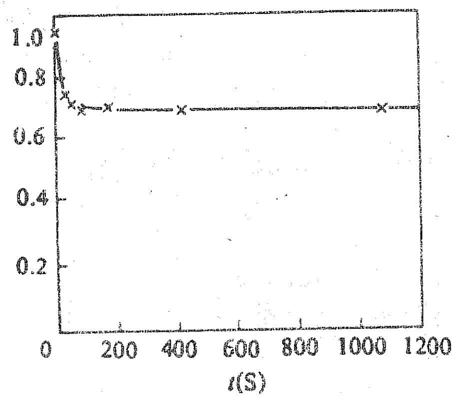

Fig. 1. 566 nm laser-induced hole filling. *A* is the area of a hole.

nm beam from the YAG laser has a similar filling curve as 337.1 nm. A 514.5 nm Ar laser irradiation can also erase holes.

Temperature cycling experiments were conducted. A hole was burned at 77 K using 560 nm laser beam. The sample was then heated to a higher temperature *T* and kept for 10 min, the area of the hole was measured at 77 K again. The above-mentioned procedure was repeated. The results were shown in fig. 3. The area of the hole decreases slowly in low temperature range from 77 to 200 K then does not vary much until 300 K, when it drops rapidly. The hole is erased above 340 K.

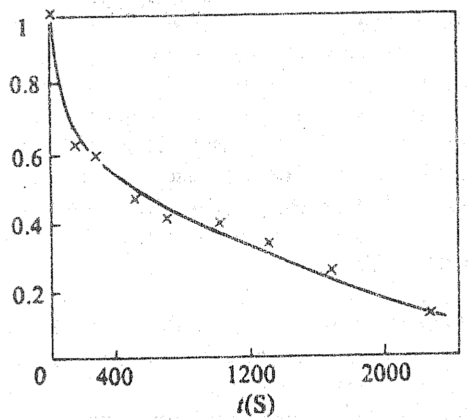

Fig. 2. 337.1 nm laser-induced hole filling. *A* is the area of a hole.

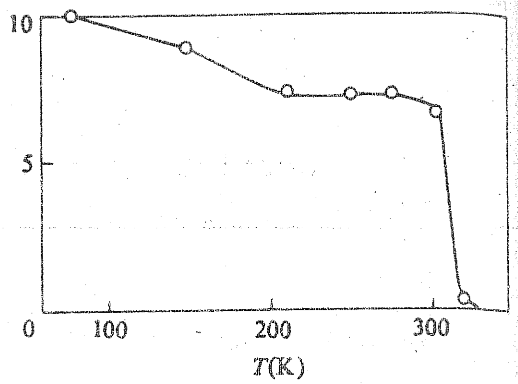

Fig. 3. Temperature cycling experiment. *A* is the area of a hole.

It is noted that the hole area decreases about 35% after the irradiation by the 566 nm beam, the initial fast decay under 532 or 337.1 nm irradiation and the slow decrease of the hole area from 77 to 200 K in the temperature cycling experiment. The slow decay under 532 or 337.1 nm irradiation and temperature cycling above 300 K make the hole area to decrease 65%. So we expect there are two kinds of traps, one of them captures 35% of the electrons ionized during hole burning, another captures 65% of the electrons.

Since the laser beams, which can produce slow decay of hole area and erase the hole, have energy corresponding to the transition $^7F_0$ to $4f^55d$ band, the traps responding to the slow decay in laser filling are Sm^{3+}. Another kind of trap may be due to impurities or defects, denoted as trap C.

The 566 nm laser is not resonant with any transition of Sm^{2+}. The only effect is to photoionize electrons from trap C into the conduction band. These electrons will be captured by Sm^{3+}. The hole area will decrease when Sm^{3+} ions capture electrons and change to Sm^{2+}. After long time irradiation, the electrons in trap C are depleted, so the hole area will remain constant.

When the sample is irradiated by either a 337.1 or 532 nm laser beam, the electrons of the trap C can be ionized into the conduction band. This effect explains the initial rapid decrease of the hole area shown in fig. 2. However, both the 337.1 and 532 nm laser beam can have another

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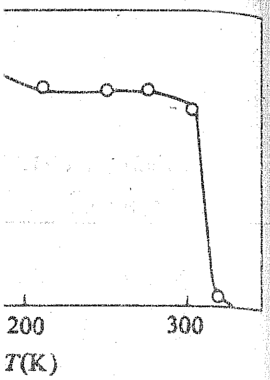

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effect. They can excite electrons of Sm^{2+} from $^7F_0$ to the $4f^55d$ band. Electrons relax from the $4f^55d$ band to ^5D_J levels, then they relax to the ground state to give luminescence or they are ionized into the conduction band after absorbing another photon of 337.1 or 532 nm. This effect can explain the slow decrease of the hole area shown in fig. 2.

This analysis is in agreement with the result of a temperature cycling experiment. During the cycling from 77 to 200 K, the electrons from trap C are thermalized into the conduction band, where they will be captured by Sm^{3+}. When Sm^{3+} ions capture electrons and change to Sm^{2+}, the hole will be filled partly. Since trap C captures 35% of the electrons ionized from Sm^{2+} during hole burning, the hole area will decrease about 35% after cycling from 77 to 200 K. This explanation is supported by the following experiment. After burning a hole at 77 K using 560 nm radiation, we irradiated the sample with the 566 nm laser beam for 2 min, then did a temperature cycling experiment. It was found that the hole area did not vary much from 77 to 300 K. The slow decrease from 77 to 200 K shown in fig. 3 did not appear. The behavior above 300 K was the same as in fig. 3. This indicates that trap C play main role in both processes of slow decrease under laser irradiation and temperature cycling from 77 to 200 K.

When the temperature rises above 300 K, the electrons of the ground state of Sm_B^{2+} are thermally activated and overcome the barrier between $Sm_A^{3+}Sm_B^{2+}$ and $Sm_A^{2+}Sm_B^{3+}$ configurations. Sm_A^{3+} ions get electrons and change to Sm_A^{2+} ions, the hole filling takes place. Sm_B^{2+} ions lose electrons and return to trap state Sm_B^{3+}. A and B denote hole burning sites and electron trapping sites.

In summary, the hole burning can be expressed as the following reaction equations:

$$Sm_A^{2+} + \hbar\omega_1 \rightarrow Sm_A^{2+}*,$$

$$Sm_A^{2+}* + \hbar\omega_2 \rightarrow Sm_A^{3+} + e,$$

then $e + \text{trap} \rightarrow \text{trap}^-$ or $e + Sm_B^{3+} \rightarrow Sm_B^{2+}$.

The thermal filling:

$$Sm_A^{3+}Sm_B^{2+} \xrightarrow{KT} Sm_A^{2+}Sm_B^{3+} \quad \text{or}$$

$$\text{trap}^- \xrightarrow{KT} \text{trap} + e,$$

then $e + Sm_A^{3+} \rightarrow Sm_A^{2+}$.

The laser-induced filling:

$$Sm_B^{2+} + \hbar\omega \rightarrow Sm_B^{2+}*,$$

$$Sm_B^{2+}* + \hbar\omega \rightarrow Sm_B^{3+} + e, \text{ or}$$

$$\text{trap}^- + \hbar\omega \rightarrow \text{trap} + e,$$

then $e + Sm_A^{3+} \rightarrow Sm_A^{2+}$, where the asterisk denotes the excited state.

The decay curves of the hole area with time were measured at 77 and 313 K. The decay process of the hole area at 77 K should be governed by trap C, while the decay at 313 K should be governed by trap Sm_B^{3+}. It was found that these two processes obey the following equation:

$$A(t)/A_1 = 1 - s\ \ln(R_1 t),$$

where A_1 is the hole area at t_1, R_1 is a parameter to the measuring experiments, $R_1 = 0.2\ \text{min}^{-1}$ for the decay at 313 K, $R_1 = 1/360\ \text{min}^{-1}$ for the decay at 77 K.

$$S = \left[\ln\left(\frac{R_1}{R_{\min}}\right)\right]^{-1}.$$

By fitting, we obtain $R_{\min} \approx 2 \times 10^{-3}\ \text{min}^{-1}$ for $T = 313$ K and $R_{\min} \approx 2 \times 10^{-7}\ \text{min}^{-1}$ for $T = 77$ K.

We tried to fit the decay curve at 313 K using an exponential law, but we failed. It indicates that the distribution of the barrier heights between $Sm_A^{3+}Sm_B^{2+}$ and $Sm_A^{2+}Sm_B^{3+}$ configurations cannot be neglected although the rapid drop in quite narrow temperature range implies a narrow distribution of the barrier heights. We measured the decay curve from 300 to 340 K in detail. By fitting this curve, the distribution of the barrier heights is studied.

According to the two-level-system model (TLS), the distribution function $P(V) \sim (1/V)^{1/2}$, where V is the barrier height or the depth of the potential well. In our case, release of electrons from Sm_B^{2+} begins at about 300 K; we modify the above equation to $P(V) \sim (1/(V-V_0)^{1/2}, V > V_0$. In the cycling from 77 K to T, electrons of the well with $V < V_T$ will be released, the electrons of the well with $V_T < V < V_{max}$ will remain, which corresponds to the hole area.

$$A(T)/A_0 = \int_{V_T}^{V_{max}} \left(\frac{1}{V-V_0} \right)^{1/2} dV \bigg/ \int_{V_0}^{V_{max}} \left(\frac{1}{V-V_0} \right)^{1/2} dV = 1 - \left(\frac{V_T - V_0}{V_{max} - V_0} \right)^{1/2} .$$

In our temperature cycling experiments, the sample kept at each temperature for $\tau = 10$ min. The electrons of wells with the depth V satisfying following equation will release:

$$\frac{1}{\tau} \leqslant R = R_0 \exp\left(-\frac{V}{KT} \right).$$

So $V_T = KT \ln(R_0 \tau)$, and

$$A(T)/A_0 = 1 - \left(\frac{T - T_0}{T_{max} - T_0} \right)^{1/2}$$

The measured data fit this equation quite well. In fitting, T_0 takes 313 K, R_0 takes 10^{12} S^{-1}, T_{max} was deduced to be 345 K, so $V_{max} = 1$ eV, $V_0 = 0.9$ eV, the distribution width of the well depth is about 0.1 eV. V_{max} is not sensitive to R_0. If we take $R_0 \approx 10^{11}$ s^{-1} or 10^{13} s^{-1}, V_{max} does not vary much.

The distribution of the potential wells is produced by substitutional disorder of Cl^- or Br^- neighbors around Sm^{2+} in $BaFCl_{0.5}Br_{0.5}$. The above results give an example which shows that the distribution of the potential wells produced by substitutional disorder can be described by a two-level-system model.

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