High-temperature stability of a spectral hole burnt in Sm-doped SrFCl crystals

Jiahua Zhang, Shihua Huang, and Jiaqi Yu

Changchun Institute of Physics, Academia Sinica, Changchun 130021, China

A long-lived spectral hole at high temperature is observed in SrFCl:Sm. The measured hole lifetimes at 292 and 315 K are approximately 14 days and 16 h, respectively. Thermally induced hole filling is studied by using the time-decay experimental data of the hole area at different temperatures and by assuming a thermally activated process. An average thermal activation energy of 1.2 eV needed for hole filling is deduced.

Persistent spectral hole burning (PSHB) has a potential application in frequency-domain optical storage. In practice, high-temperature PSHB and a stable hole are expected. Recently, attractive results for room-temperature PSHB have been reported in organic solutions,[1] microparticles,[2] and Sm-doped mixed crystals.[3,4] Hence an investigation of the stability of spectral holes at high temperature is necessary. In fact, the stability of the hole is affected directly by the spontaneous hole-filling process, which is usually assumed to manifest a tunneling process or a thermally activated process from the burnt to the unburnt configurations, which are decoupled by a barrier V.[5,6] It is usually believed that the barrier heights follow a Gaussian or a $V^{-1/2}$ distribution function.[7-9]

Since the first discovery of PSHB,[10] a persistent spectral hole has been observed in many materials. However, most of them exhibit the characteristic of a short-lived hole at high temperature. It is reported by Winnacker *et al.*[11] that burnt holes in BaFCl:Sm can still be probed after the sample is raised to room temperature for several days, but they did not investigate this in detail. In this Letter we report what is to our knowledge the first observation of a spectral hole with a lifetime of 14 days in Sm-doped SrFCl crystals at 292 K. Based on a thermally activated process, thermally induced hole filling is studied with the time-decay experimental data of the hole area.

SrFCl:Sm powder sample is prepared as described previously.[12] The nominal molar concentration of Sm in the sample is 0.02. A tunable dye laser, with a laser linewidth of 0.2 cm^{-1} and pumped by a pulsed Quanta-Ray DCR-2A Nd:YAG laser with a repetition frequency of 10 Hz, is used for both burning and gating laser beams, so hole burning in this research is a one-color two-photon process. The burning and monitoring beam power densities are 250 and 10 mW/cm^2, respectively. The spectral hole is burnt in the $^7F_0-^5D_2$ transition line of Sm^{2+} ions and probed in an excitation spectrum by monitoring $^5D_1-^7F_0$ emission with a D330 spectrometer, while the $^7F_0-^5D_2$ transition is scanned.

Time-decay experiments are performed in the following way: First, burn a hole at 77 K, immediately measure the hole area, raise the sample to a certain temperature T for a period of time t, and subsequently recool the sample down to 77 K, where the hole area is measured again.

The hole-burning mechanism in SrFCl:Sm has been studied recently.[13] The processes are described as follows: A narrow burning laser line selectively ionizes the Sm$^{2+}(A)$ ions in resonance with the laser to Sm$^{3+}(A)$ ions, then the released electrons are probably captured by the Sm$^{3+}(B)$ ions at any sites to form Sm$^{2+}(B)$ ions. That is, Sm^{3+} ions act as electron traps. This is supported by the fact that the spectral area of Sm^{2+} ions before and after burning of a hole is unchanged at 77 K or at room temperature, as shown in Figs. 1 and 2. Obviously the hole-burning process causes unchanged Sm^{2+} numbers and a changed distribution of Sm^{2+} sites, which leads to the constant spectral area and spectral redistribution of Sm^{2+} ions in hole burning. In Fig. 2 the absence of a hole after burning in the strong line is because that hole width for the $^7F_0-^5D_2$ transition at room temperature[3] approaches the strong line width of 7 cm^{-1}. The observed decrease of the strong line and the growth of the weak line after hole burning is interpreted as photoionization of Sm^{2+} ions, which corresponds to the strong line, and the increase of Sm^{2+} ions, which corresponds to the weak line produced by Sm^{3+} ions' trapping electrons.

Contrary to hole burning, in hole filling the trapped electrons are released from Sm$^{2+}(B)$ ions and then are recaptured by Sm$^{3+}(A)$ ions, leading to the recovery from the burnt configuration Sm$^{3+}(A)$Sm$^{2+}(B)$ to the unburnt configuration Sm$^{2+}(A)$Sm$^{3+}(B)$. From the experimentally observed temperature-dependent and time-dependent hole filling, we assume that hole filling is a thermally activated process with a filling rate of[9]

$$R = R_0 \exp(-V/kT), \qquad (1)$$

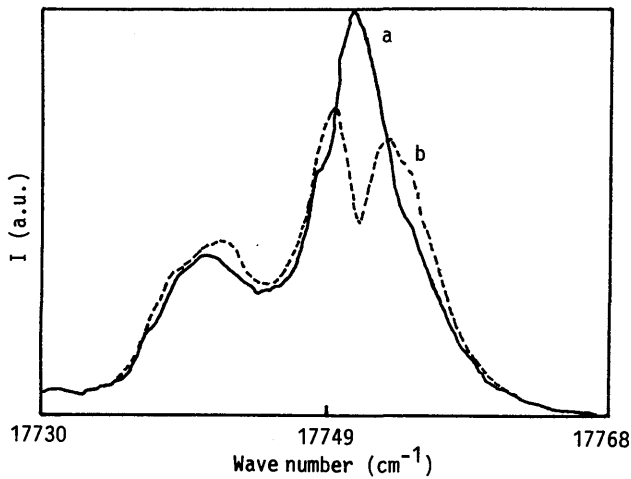where R_0 is the attempt frequency and V is the acti-

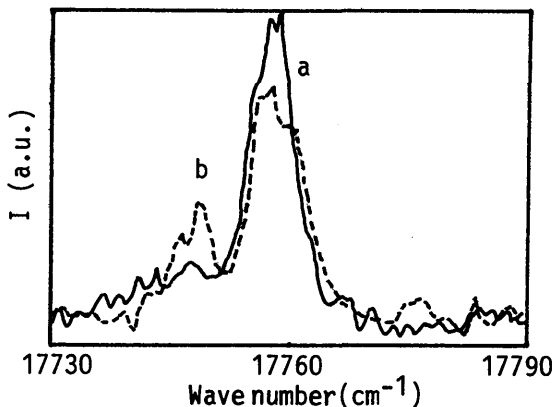Fig. 1. $^7F_0$–$^5D_2$ transition profiles of Sm^{2+} in SrFCl before (curve a) and after (curve b) burning a hole at 77 K.

Fig. 2. $^7F_0$–$^5D_2$ transition profiles of Sm^{2+} in SrFCl before (curve a) and after (curve b) burning a hole at room temperature.

vation barrier from the burnt to the unburnt configurations. The barriers generally follow a Gaussian or a $V^{-1/2}$ distribution. In this research we base our analysis on both of them, which are written as

$$g(V) = (2\pi\sigma^2)^{-1/2} \exp[-(V - V_0)^2/2\sigma^2], \quad (2)$$

with a central barrier height V_0 and width σ, and

$$g(V) = g_0/V^{1/2}, \quad (3)$$

with cutoff barrier heights of the minimum V_{min} and the maximum V_{max} for normalization. Here g_0 is a constant.

To describe time-decay experimental data of the hole area, which is proportional to the number of electrons that remain trapped, we normalize the hole area before temperature annealing to be 1 and denote the annealing time by t. The dependence of normalized hole area A on time t is given by

$$A = \int_{-\infty}^{+\infty} [\exp(-Rt)]g(V)dV. \quad (4)$$

For the respective distributions of barriers, the integral in Eq. (4) is evaluated numerically by using Eqs. (1)–(3).

Figure 3 shows the time-decay experimental data, which indicate that hole lifetimes at 292 and 315 K are approximately e^{14} s (14 days) and e^{11} s (16 h), respectively. The solid and dashed curves represent the calculated decay features according to Gaussian and $V^{-1/2}$ distributions, respectively. Figure 3 illustrates that the evaluations of Eq. (4) for both distributions can fit the data well by selecting the fitting parameters (with $R_0 = 5 \times 10^{14}$ s^{-1}) for the Gaussian distribution to be $V_0 = 1.20$ eV and $\sigma = 0.07$ eV and for the $V^{-1/2}$ distribution to be $V_{min} = 1.10$ eV and $V_{max} = 1.32$ eV. To prove that the choice of R_0 is the best we present in Fig. 4 fitted curves to the time-decay experimental data at 292 K calculated for R_0 values between 10^{14} and 10^{15} s^{-1} using the two distributions. It indicates that the
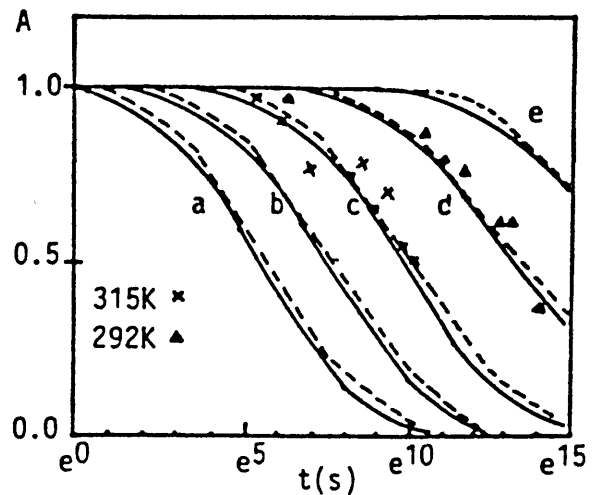

Fig. 3. Calculated time-decay curves of the normalized area of a hole burnt at 77 K as a function of annealing temperature at 350 K (curve a), 333 K (curve b), 315 K (curve c), 292 K (curve d), and 273 K (curve e). The solid and dashed curves correspond to a Gaussian and a $V^{-1/2}$ distribution of barrier heights, respectively. For comparison two sets of time-decay experimental data points have been included.
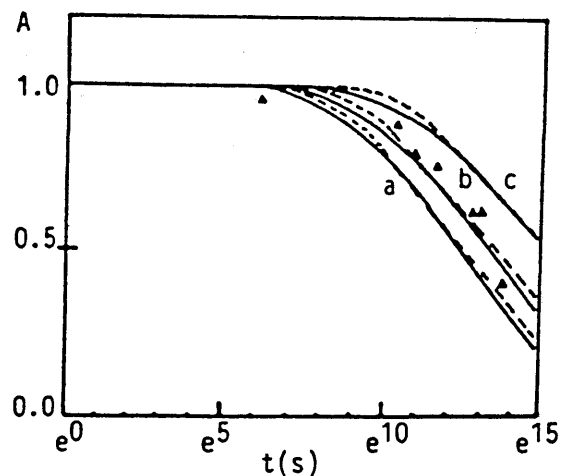

Fig. 4. Comparison of 292-K data from Fig. 3 with calculated curves for $R_0 = 10^{15}$ s^{-1} (curve a), 5×10^{14} s^{-1} (curve b), and 10^{14} s^{-1} (curve c). The solid and dashed curves are given by a Gaussian and a $V^{-1/2}$ distribution function, respectively.

best value of R_0 is indeed to 5×10^{14} s^{-1}. From the fitting parameters, we find that the two different distributions yield the same average barrier height of 1.20 eV, which is calculated by the formula

$$\int_{-\infty}^{+\infty} Vg(V)dV. \tag{5}$$

In the hole filling determined by the thermally activated process, the recovery from the burnt to the unburnt configurations should need a thermal activation energy, which is equal to the value of the barrier height from the burnt to the unburnt configurations, for a barrier crossing. The value of 1.20 eV, which is much larger than that obtained in other hole-burning materials,[1,4,5] may reasonably be considered to be the average thermal activation energy needed for hole recovery [i.e., electron release from $Sm^{2+}(B)$ ions produced by hole burning in SrFCl:Sm]; then a highly stable hole in this sample is expected. Obviously Sm^{3+} ions in SrFCl:Sm act as thermally stable traps of 1.2 eV, which is close to that for the CaS:Eu,Sm system.[14] The parameter R_0 is principally used for fitting the experimental data and can be physically assumed to be the electron transfer rate from $Sm^{2+}(B)$ ions to $Sm^{3+}(A)$ ions in the case of an absence of barriers from the burnt to the unburnt configurations in thermally induced hole filling.

It is worth stressing that the time-decay features shown in Fig. 3 are insensitive to the distribution functions of barrier heights. This phenomenon is probably caused by two reasons: (i) our data are not precise enough for the two distributions to be significantly distinguished, and (ii) the two series of calculated curves corresponding to the two distributions are indeed quite close. Despite these facts, we think that the dispersive distribution, i.e., Gaussian distribution, is physically the most reasonable. One of the reasons is that the $V^{-1/2}$ distribution function requires the cutoff barriers V_{min} and V_{max} for normalization, which seems to be rather artificial. To justify one of the two distributions, additional experiments must be done in detail. Finally, we note that powder samples probably make the burning power higher than with single-crystal samples owing to the strong scattering light for powder samples. Despite this, the results in this Letter should also fit crystal samples. The results reported here and the observation of room-temperature PSHB in $Sr_{0.5}Ba_{0.5}FCl_{0.5}Br_{0.5}$:Sm (Ref. 3) and $SrFCl_{0.5}Br_{0.5}$:Sm (Ref. 4) point out that Sm-doped alkaline earth metal fluoride halides can possibly play an important role in the application of PSHB at high temperature.

References

1. R. Menzel and P. Witte, J. Chem. Phys. **87**, 6769 (1987).
2. S. Arnold and C. T. Liu, Opt. Lett. **16**, 420 (1991).
3. J. Zhang, S. Huang, and J. Yu, Chin. J. Lumin. **12**, 181 (1991) (in Chinese).
4. R. Jaaniso and H. Bill, Europhys. Lett. **16**, 569 (1991).
5. W. Kohler, J. Meiler, and J. Friedrich, Phys. Rev. B **35**, 4031 (1987).
6. R. Jankowiak, R. Richert, and H. Bassler, J. Phys. Chem. **89**, 4569 (1985).
7. W. Kohler and J. Friedrich, Phys. Rev. Lett. **59**, 2199 (1987).
8. W. Kohler and J. Friedrich, Phys. Rev. **37**, 660 (1988).
9. A. Elschner and H. Bassler, J. Lumin. **43**, 33 (1989).
10. B. M. Kharlamov, R. I. Personov, and L. A. Bykovskaya, Opt. Commun. **12**, 191 (1974).
11. A. Winnacker, R. M. Shelby, and R. M. Macfarlane, Opt. Lett. **10**, 350 (1985).
12. J. Zhang, S. Huang, W. Qin, D. Gao, and J. Yu, Chin. J. Infrared Millimeter Waves **10**, 1 (1991) (in Chinese).
13. J. Zhang, S. Huang, W. Qin, D. Gao, and J. Yu, "Process of persistent spectral hole burning in SrFCl:Sm^{2+}," J. Lumin. (to be published).
14. S. Jutamulia, G. M. Storti, W. Seiderman, and J. Lindmayer, Proc. Soc. Photo-Opt. Instrum. Eng. **1401**, 113 (1990).