

Room-temperature persistent spectral hole burning in Sm^{2+} -doped fluoride glasses

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Persistent spectral hole burning is observed in Sm^{2+} -doped glasses at room temperature. The holes are burned in the ${}^7F_0 \rightarrow {}^5D_0, {}^5D_1$ lines of the Sm^{2+} ions in three kinds of fluoride glass. The dependence of the burning efficiency on the sample and on the burning intensity is measured. The intensity dependence is approximately linear, and no antihole is observed around the burned hole. The hole-burning mechanism is discussed. The temperature dependence of the homogeneous width is also measured.

Materials for high-temperature persistent spectral hole-burning have been investigated in recent years because of their potential application in frequency-domain optical storage. Recently room-temperature hole burning was realized in polystyrene microparticles¹ and in Sm^{2+} -doped mixed crystals.² In Sm^{2+} -doped crystals, substitutional disorder was introduced to increase the ratio of the inhomogeneous to the homogeneous width. It is of interest to explore the possibility of hole burning and the characteristics of Sm^{2+} in glass; Sm^{2+} -doped glass has larger structural disorder and many other differences in host characteristics compared with crystals. There were some difficulties in preparing Sm^{2+} -doped glasses, but Izumitani and Payne have succeeded in introducing divalent Sm ions into fluoride glasses.³ In these Sm^{2+} -doped fluoride glasses we observed room-temperature persistent spectral hole burning for the first time to our knowledge, and the results have been given in a brief paper.⁴ Recently room-temperature hole burning in Sm^{2+} -doped borate glass and fluorohafnate glass was also reported.^{5,6} In this Letter we report several experimental results concerning the hole-burning characteristics of Sm^{2+} -doped fluoride glasses, which show considerable difference from those of Sm^{2+} -doped crystals.

We have investigated three kinds of Sm^{2+} -doped glass: APO, AH4, and HBLAN. APO is an AlF_3 -based glass; AH4 is an AlF_3 and HfF_4 -based glass; and HBLAN has a composition in which ZrF_4 in the well-known ZBLAN glass is replaced by HfF_4 . The glass compositions and the sample preparation method were described previously.³ The concentrations of SmF_3 in the starting materials were 1–3 wt.%. The mixture was melted in a highly reducing atmosphere. The glasses obtained were transparent and brown or yellow colored owing to strong $4f \rightarrow 5d$ transitions in Sm^{2+} .

In the absorption spectra, broad bands that are due to the $4f^6 \rightarrow 4f^5 5d$ transitions of Sm^{2+} and several peaks that are due to the $4f^5 \rightarrow 4f^5$ transitions

of Sm^{3+} were observed.³ The intensity of one of the ${}^6H(4f^5) \rightarrow {}^6P(4f^5)$ absorption lines near $25\,100\text{ cm}^{-1}$ was compared with that of a glass melted without reducing gas and consequently containing only Sm^{3+} . There was no observable change in the absorption strength. If we assume that the probability of the ${}^6H(4f^5) \rightarrow {}^6P(4f^5)$ transition remains the same after the reduction process, it is suggested that most of the Sm ions in the starting materials remained trivalent and that in the product there are many fewer Sm^{2+} ions than Sm^{3+} ions. The ${}^7F_0 \rightarrow {}^5D_j$ lines were not observed in the absorption spectra because the absorption coefficients of these lines are extremely small (less than 0.001 cm^{-1}) in our samples.

We measured many and that in the product there are many fewer dependence of the homogeneous width between 30 and 300 K, using the fluorescence line narrowing (FLN) method. Resonant emission of the ${}^5D_0 \rightarrow {}^7F_0$ transition of Sm^{2+} in AH4 glass was observed with a chopper that alternately opens

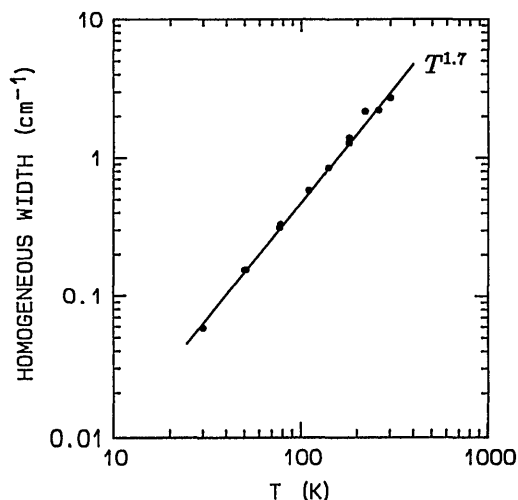


Fig. 1. Temperature dependence of the homogeneous width of the ${}^7F_0 \rightarrow {}^5D_0$ transition of Sm^{2+} in AH4 glass.

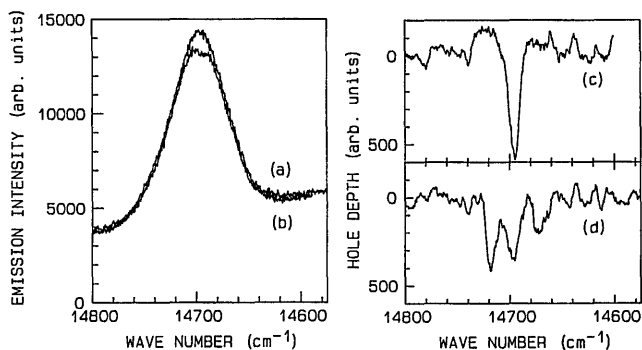


Fig. 2. Hole burning at 300 K in the ${}^7F_0 \rightarrow {}^5D_0$ transition of AH4:Sm. (a) Spectrum before hole burning, (b) spectrum after hole burning, (c) hole spectrum [difference signal of spectra (a) and (b)], (d) spectrum with three holes.

the optical paths from the laser to the sample and from the sample to the monochromator. The chopping frequency was 150 Hz, and the instrument linewidth was 0.15 cm^{-1} . The homogeneous width Γ_h (FWHM) was estimated from the FLN width (Γ_{FLN}) and the instrument linewidth (Γ_i) according to $\Gamma_h = (\Gamma_{\text{FLN}} - \Gamma_i)/2$. As is shown in Fig. 1, Γ_h is proportional to $T^{1.7}$. This weak temperature dependence is typical of rare-earth-doped glasses.⁷

Holes were burned in the ${}^7F_0 \rightarrow {}^5D_0$ and ${}^7F_0 \rightarrow {}^5D_1$ lines of Sm^{2+} near 14690 and 16050 cm^{-1} , respectively, by a tunable cw dye laser with a linewidth of 0.25 cm^{-1} . We obtained the hole spectra by scanning the attenuated laser over the lines while detecting the ${}^5D_0 \rightarrow {}^7F_2$ fluorescence near 13830 cm^{-1} through a low-resolution monochromator. The laser power for reading was less than 0.3% of that for burning.

Figures 2(a) and 2(b) are the excitation spectra of AH4:Sm at 300 K before and after hole burning, respectively, in the ${}^7F_0 \rightarrow {}^5D_0$ transition. The burning time and burning power were 600 s and $\sim 15 \text{ W/mm}^2$, respectively. The excitation profile before burning represents the inhomogeneous line shape. It is nearly Gaussian, with a FWHM of 58 cm^{-1} . The inhomogeneous widths for HBLAN and APO are 47 and 62 cm^{-1} , respectively. The inhomogeneous profiles observed in glasses are much broader than the widest inhomogeneous line of 39 cm^{-1} observed in Sm^{2+} -doped crystals.⁸ The ratio of inhomogeneous to homogeneous width is estimated from the FLN data to be ~ 20 at 300 K and ~ 400 at 77 K. The Gaussian line shape is different from the non-Gaussian line shapes in Sm^{2+} -doped mixed crystals, which have been attributed to different combinations of the nearest-neighbor species.⁹

As is shown in Fig. 2(c), a hole is clearly observed at 14696 cm^{-1} in the difference signal between spectra of Figs. 2(a) and 2(b). The hole width of 13 cm^{-1} is larger than twice the homogeneous width at 300 K ($\sim 6 \text{ cm}^{-1}$). The broadening of the hole is ascribable to spectral diffusion and/or saturation effects. The latter effect surely exists, because narrower hole widths (down to 9 cm^{-1}) were observed when sufficiently shallow holes were burned. However, at the present stage the quality of our spectra is not good enough for accurate extrapolation to zero burn power.

Hence the true hole width and the degree of contribution from spectral diffusion have not been estimated. Hole widths for the three glass compositions were nearly the same. The starting materials for our HBLAN glass are the same as the ones for fluorohafnate glass used by Hirao *et al.*,⁶ which showed a much broader hole width. This discrepancy can possibly be ascribed to the difference in the ratio of the starting materials, although no information about the ratio was given in Ref. 6.

The hole depth decreased spontaneously after burning, but as much as half of the initial hole was found to remain 11 h after burning. High-temperature stability of the hole was measured by a temperature cycling experiment. The hole was observed for the cycling temperatures as high as 110°C . The hole area after cycling through 110°C was $\sim 30\%$ of that of the initial hole. We tried to burn multiple holes in the inhomogeneous profile at 300 K. The first hole, shown in Fig. 2(c), was partially filled when the second and the third holes were burned at 14673 and at 14718 cm^{-1} , respectively. However, holes with a certain depth remained, and three holes were discernible, as shown in Fig. 2(d).

We determined the dependence of the burning rate on Sm concentration and glass composition at room temperature by comparing the time evolution of the hole in several samples. The increase of the hole depth was detected through the decrease of fluorescence intensity induced by the burning laser. In Fig. 3 the hole depth is normalized to the peak height of the ${}^7F_0 \rightarrow {}^5D_0$ band and is plotted as a function of the logarithm of the burning time. The curves are nearly straight, which means a broad dispersion of the burning efficiency.¹⁰ The burning rate depends on both Sm concentration and glass composition: It is higher for higher Sm concentration and increases in going from APO to AH4 to HBLAN. This dependence conforms to the sample dependence of the quantum yield and decay time of the emission from the 5D_0 state: The quan-

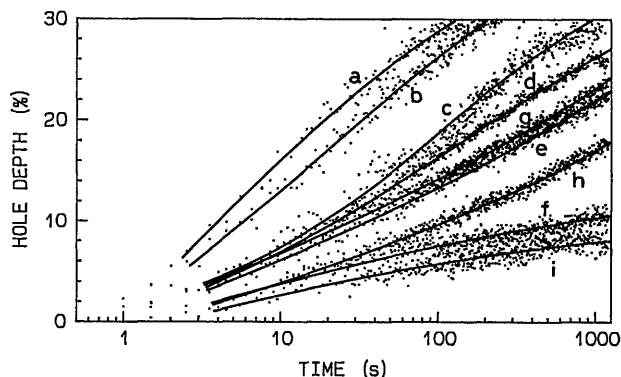


Fig. 3. Dependence of the time evolution on glass composition and Sm concentration at room temperature. The burning intensity was $\sim 40 \text{ W/mm}^2$. a, HBLAN:Sm, $4.9 \times 10^{20} \text{ cm}^{-3}$. b, HBLAN:Sm, $3.2 \times 10^{20} \text{ cm}^{-3}$. c, HBLAN:Sm, $1.6 \times 10^{20} \text{ cm}^{-3}$. d, AH4:Sm, $3.6 \times 10^{20} \text{ cm}^{-3}$. e, AH4:Sm, $2.4 \times 10^{20} \text{ cm}^{-3}$. f, AH4:Sm, $1.2 \times 10^{20} \text{ cm}^{-3}$. g, APO:Sm, $3.3 \times 10^{20} \text{ cm}^{-3}$. h, APO:Sm, $2.0 \times 10^{20} \text{ cm}^{-3}$. i, APO:Sm, $9.8 \times 10^{19} \text{ cm}^{-3}$. The solid curves are guides only.

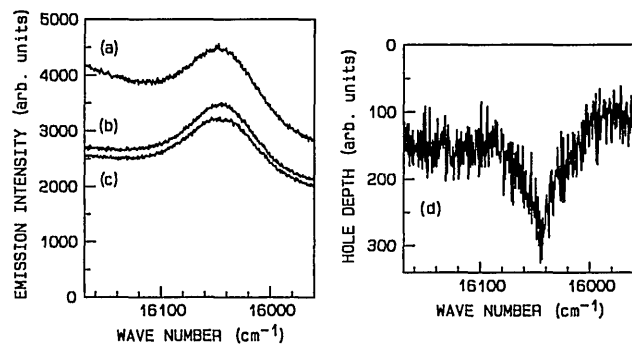


Fig. 4. Hole burning at 300 K in the ${}^7F_0 \rightarrow {}^5D_1$ transition of AH4:Sm. (a) Spectrum before hole burning, (b) spectrum after irradiation at 16150 cm^{-1} , (c) spectrum after hole burning at 16052 cm^{-1} , (d) hole spectrum [difference signal of spectra (b) and (c)].

tum yields of APO, AH4, and HBLAN with typical Sm concentrations are 33%, 9%, and 1%, respectively, and the emission decay times are 5, 3.5, and 2 ms, respectively.³ Thus one finds that a glass with a high quantum yield or a long decay time has a low hole-burning efficiency.

The intensity dependence of the burning rate has been determined from the time evolution of the hole detected through the fluorescence intensity. When the hole depth at 300 K was plotted as a function of the logarithm of the burning time, the curves for burning intensities ranging from 2 to 20 W/mm^2 were nearly parallel to one another. The amount of the shift of the curve was linear with the burning intensity. Because the intensity of the ${}^5D_0 \rightarrow {}^7F_2$ fluorescence was linear to the burning-laser intensity, the rate of the burning reaction from the excited 5D_0 state is considered to be independent of the burning intensity. No gating effect was observed when a hole was burned in the presence of an additional Ar-laser light. Instead, the ${}^7F_0 \rightarrow {}^5D_0$ line in the excitation spectrum decreased as a whole when the glass was irradiated with Ar-laser light alone.

Hole burning in the ${}^7F_0 \rightarrow {}^5D_1$ transition is shown in Fig. 4. Figure 4(a) is the excitation spectrum before burning. The ${}^7F_0 \rightarrow {}^5D_1$ line appears on an intense background because of the tail of the $4f^6 \rightarrow 4f^55d$ band. When the center of the ${}^7F_0 \rightarrow {}^5D_1$ line was irradiated with the burning laser, the intensities of both the line and the background decreased, and the hole was not clear in the difference spectrum. Hence we first bleached the background by irradiation at 16150 cm^{-1} [Fig. 4(b)] and then burned a hole at the center of the ${}^7F_0 \rightarrow {}^5D_1$ line [Fig. 4(c)]. As shown in Fig. 4(d), a hole is apparent in the difference spectrum between Figs. 4(b) and 4(c).

Although the mechanism of hole burning in this system is not clear at the present stage of the study,

the following discussion can be given. The linear behavior of the intensity dependence and the absence of the gating effect suggest that the hole burning in this system is not a two-photon process, as in Sm²⁺-doped crystals,¹¹ but a single-photon process. No antihole is observed around the burned hole in Fig. 2. Furthermore, a decrease of the whole line by the Ar-laser light irradiation and a decrease of the $4f^6 \rightarrow 4f^55d$ tail by the irradiation at the side of the ${}^7F_0 \rightarrow {}^5D_1$ line were observed as described above. These results mean that the total intensity of the emission from the 5D_0 level of Sm²⁺ decreases either by the direct excitation into the 5D_J state or by the excitation of the $4f^6 \rightarrow 4f^55d$ transition. Therefore nonphotochemical hole burning is probably not so important as the burning mechanism in the present case. Likewise, although photoinduced oxidation of Sm²⁺ is a possible burning mechanism, Sm³⁺ is not considered to be the main trap for the released electron. Taking account of the correlation between the hole-burning efficiency and the emission yield, we infer that the nonradiative decay pathway from the 5D_0 level that competes with the emission process is closely related to the hole-burning process. In Ref. 3 the initial process in the nonradiative decay was ascribed to the electron transition from the 5D_J states or the $5d$ states to the conduction-bandlike states. The hole-burning reaction is probably initiated by the same transition.

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