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Persistent spectral hole burning of sol-gel-derived Eu$^{3+}$-doped SiO$_2$ glass

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Persistent spectral hole burning (PSHB) was observed at temperatures higher than 77 K in the sol-gel-derived Eu$^{3+}$-doped SiO$_2$ glasses. Eu$_2$O$_3$-99SiO$_2$ (mole ratio) glass was prepared by heating gel synthesized from metal alkoxides at 400 to 1000 °C. The hole was burned in the $^7F_0\rightarrow^5D_0$ line of Eu$^{3+}$ ions by means of a Rhodamine 6G dye laser at 77 K and the burnt hole depth was measured as a function of temperature. The hole depth increased with increasing OH content in the glass. It was found that the hole burnt at 77 K was thermally filled and an average thermal barrier height for the hole filling was $\sim 0.3$ eV, which was higher for the glass heated at high temperature, indicating that the stable hole is burned with the increased heat-treatment temperature. It was concluded that the PSHB was formed by the optically activated rearrangement of proton in the first coordinating sphere of the Eu$^{3+}$ ions.

A detailed explanation of gel preparation is given elsewhere. The gel was heated in air at 50 °C/h to a given temperature of 400–1000 °C, where it was held for 2 h. The synthesized gel is porous, containing a large amount of water incorporated during synthesis. When heated, the gel transforms into glass according to a dehydration and polycondensation reaction. In the fluorescence spectra of glasses using a 463-nm excitation wavelength of a Xe lamp, four lines are observed at 580, 590, 615, and 650 nm in the visible wavelength region, all of which are attributed to the $^5D_0\rightarrow^7F_{j}$ transitions, respectively, of the Eu$^{3+}$ ions. The fluorescence spectrum of glass heated at 500 °C had weak intensity, which increased with the increased temperature and at 1000 °C reached an intensity higher than four times that at 500 °C (as will be shown in Fig. 2). This weakened fluorescence at low temperatures is due to the OH concentration quenching. The presence of OH groups in the first coordination sphere of Eu$^{3+}$ ions provides an effective pathway for the radiationless deexcitation via energy transfer to OH vibration, which results in quenching the fluorescence.

Hole-burning experiments were done on the excitation spectrum of the $^7F_0\rightarrow^5D_0$ transition of the Eu$^{3+}$ ions. Holes were burned by irradiating a tunable cw Ar$^+$-ion-laser-pumped Rhodamine 6G dye laser with a linewidth of $\sim 1.0$ cm$^{-1}$ full width at half maximum (FWHM) and a power of 20–300 mW/mm² for 30 min. Hole spectra were recorded by scanning the dye laser from 17 150 to 17 550 cm$^{-1}$ while monitoring the fluorescence of the $^5D_0\rightarrow^7F_2$ transition at 16 230 cm$^{-1}$. The laser power for scanning was already attenuated by neutral-density filters to less than 0.2% of that for burning. Figure 1 shows a typical hole spectrum of glass heated at 800 °C. A hole is clearly seen at the wave number of 17 287 cm$^{-1}$. The hole width and depth are $\sim 2$ cm$^{-1}$ and $\sim 10\%$, respectively. The hole depth, which is defined as the intensity ratio to the total fluorescence intensity and is normalized to the intensity before burning at the burning wave number, increases with burning time up to about 10% within...
a few hundred seconds (inset of Fig. 1). The hole depth linearly increased with the power of the laser and reached ~10% at 150 mW/mm². Antiholes were not observed near the holes. The hole burning experiments were done for glasses heated at 400–1000 °C with a power of 100 mW/mm² at 77 K, the depths of which are plotted in Fig. 2 as a function of heat-treatment temperature. It is evident that the hole depth decreased with increasing temperature and was not burned for the glass heated above 1000 °C. In Fig. 2, the fluorescence intensities of the \(^{5}D_0 \rightarrow ^{7}F_2\) transition are also plotted as a function of heat-treatment temperature: the dependence of the fluorescence intensity on temperature is in contrast to that of the hole depth. The increase in the fluorescence intensity with the increased temperature is due to the reduction of the OH groups around the Eu\(^{3+}\) ions. Thus, these experimental results indicate that the hole burning is related with the residual OH groups in the glass.

To study the effect of OH groups on the hole burning, the glasses were heated at 800 °C in air and vacuum, the PSHB and infrared (IR) absorption spectra of which are shown in Fig. 3. It is apparent that the hole burnt in glass heated for a long time decreases in depth and no hole is burned after 10 h. The IR spectrum of glass heated at 800 °C in air has two absorption bands at 3650 and 3400 cm\(^{-1}\), which are both assigned to the fundamental OH stretching. The position of the OH-absorption bands depends on the degree of association to neighboring oxygen through hydrogen bonding. The bands shift to low wave numbers with increasing strength of hydrogen bonding.\(^{20}\) The IR spectrum for SiO\(_2\) glass containing no Eu\(_2\)O\(_3\), measured for comparison, had a sharp absorption band at 3650 cm\(^{-1}\), which is both assigned to the fundamental OH stretching. The position of the OH-absorption bands depends on the degree of association to neighboring oxygen through hydrogen bonding. The bands shift to low wave numbers with increasing strength of hydrogen bonding.\(^{20}\)
the Eu$^{3+}$-doped glass, therefore, can be attributed to the OH
groups bound with the Eu$^{3+}$ ions through hydrogen bonding.
As shown in Fig. 3, the IR spectra preferentially decreased in
the intensity of the 3400 cm$^{-1}$ band during heating in
vacuum, which were deconvoluted into two bands at 3650
and 3400 cm$^{-1}$ using a Gaussian function and the result for
glass heated in air was shown in the inset of Fig. 3. Among
the deconvoluted bands, the absorption coefficient of the
3400 cm$^{-1}$ band decreases with increasing the heat-treatment
time, that is, 41, 11, and 2 cm$^{-1}$ for 0, 5, and 10 h, respectively.
On the other hand, the absorption coefficient of the
3650 cm$^{-1}$ band is insensitive to the time and constant at
20~28 cm$^{-1}$. These experimental results indicate that the OH
groups bound with Eu$^{3+}$ ions are preferentially liberated during
heating. The absorption coefficient of these bands is a
measure of the concentration of OH groups, although the extinction coefficient of these OH bonds is not determined in
this study. Figure 4 shows the relation between the hole
deepth and the absorption coefficient of the 3400 cm$^{-1}$ band,
satisfying the linear relation between two values. This indicates
that the presence of OH groups bound with the Eu$^{3+}$
ions is essential for the hole burning of the sol-gel-derived
Eu$^{3+}$-doped glasses. We propose that the hole is formed by
the concerted action of OH bonds in the first coordination
sphere surrounding the Eu$^{3+}$ ion. When the sample is irradiated
with the high power laser, a proton in the EuOH bonds
changes its position to form a different bonding feature. The
rearrangement of proton in the EuOH bonds results in the
hole burning. This burning mechanism is considered to be
different from that of the Sm$^{2+}$, where the photoionization of Sm$^{2+}$
into Sm$^{3+}$ by laser irradiation is the main
reaction.\textsuperscript{2,3}

The stability of the holes depends on the recovery of the
proton configuration from the burnt state to the unburnt state.
Assuming a thermally activated recovery process, the
optically activated state relaxes across the activation barrier to
the unburnt configuration state. To investigate the thermal
stability of the hole, the thermal hole-erase measurements
were performed for the glasses obtained by heating at 500
and 800 $^\circ$C. A hole was formed at 77 K, at which the hole
area was measured. After cycling through a certain temperature
higher than 77 K, the area was again measured at 77 K.
During this process, all the products with barriers lower than
the activation barrier corresponding to that temperature re-
cover to the unburnt state. The PSHB spectra, recorded after
cycling up to 160 K, of glass heated at 800 $^\circ$C are shown in
the inset of Fig. 1. The hole area that remains after this
thermal cycle is normalized to unity at 77 K and plotted in
Fig. 5 as a function of temperature. It is obvious that the hole
area decreases as the temperature increases. The fraction of the
remaining hole, $F$, is a measure of the fraction of the
photoproducts whose activation barriers are greater than a
critical barrier height, $V$, and given by\textsuperscript{24-26}

\begin{equation}
FF = 1 - \int_0^{tmax} [f(V)] g(V) dV,
\end{equation}

where $R_0$ is the attempt frequency of protons and $t$ is the
holding time at a certain cycling temperature $T_{\text{max}}$. Assuming
that the barrier height follows a Gaussian distribution, $g(V)$
is written as

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

with a central barrier height $V_0$ and the width $\sigma$. A fit of
the data using Eq. (1) for both glasses is shown by solid curves
in Fig. 5, where the fitting parameters are $V_0=0.27$ eV,
$\sigma=0.051$ eV and $V_0=0.33$ eV, $\sigma=0.098$ eV for glasses
heated at 500 and 800 $^\circ$C, respectively. The obtained $V_0$ values
are smaller than that required for the dissociation of proton
from the EuOH bond which is estimated as $\sim 1$ eV or
larger from the measurement of proton conductivity of
glasses.\textsuperscript{21} Therefore it is considered that the hole burning is
caused not by the dissociation of proton but by the optically
activated rearrangement of position of protons in the Eu-O
polyhedral. It is worth stressing that the $V_0$ value for glass
heated at high temperature is larger than that heated at low
temperature. This finding is good guidance for the develop-
ment of the glasses exhibiting PSHB at high temperature. However, it should be noted that the hole depth declines with this increased heat-treatment temperature.

We conclude that the hole burning in the Eu$^{3+}$-doped glass is caused by the photoactivated rearrangement of protons in the first coordinating sphere of Eu$^{3+}$ ions. The burnt state has an activation barrier height of ~0.3 eV higher than that of the unburnt state. The hole depth proportionally increases with the increase of OH content. The sol-gel method is appropriate to prepare the PSHB glasses because of its possibility to contain a large amount of OH bonds.

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