Journal of Luminescence 56 (1993) 51–55
North-Holland

JOURNAL OF
LUMINESCENCE

Inhomogeneous broadening and trap effect in hole burning of Sm^{2+}-doped mixed crystals

Jiahua Zhang, Shihua Huang and Jiaqi Yu

Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021, China

We report the results of the inhomogeneous broadening and high temperature hole burning in $M_yM'_{1-y}FCl_{0.5}Br_{0.5}:Sm^{2+}$ system (M, M′ = Ca, Sr, Ba; $y = 0$–1). The influence of Sm^{3+} as electron trap on hole burning is discussed and new trap is introduced in Yb-doped $SrFCl:Sm^{2+}$ crystals.

1. Introduction

In recent years, much research work has been performed on spectral hole burning. One of the important reasons is that hole burning has a potential use in frequency domain optical storage. In practice, high temperature photon gated persistent hole burning is required. One of the factors limiting the hole burning temperature is the ratio of the inhomogeneous line width to the hole width. The ratio decreases rapidly with increasing temperature because of the unchanged inhomogeneous line width and the exponentially increased hole width with increasing temperature, so hole burning is impossible as the hole width is equivalent to the inhomogeneous line width at a temperature. Obviously, to broaden the inhomogeneous line is necessary to raising hole burning temperature. In 1985, Winnacker et al. [1] first reported photon gated persistent hole burning in $BaFCl:Sm^{2+}$ at 2 K. However, high temperature hole burning cannot be performed in this material because of the narrow inhomogeneous line of Sm^{2+}. In this case, we started to experiment on inhomogeneous broadening and successfully prepared a high temperature hole burning system $BaFCl_xBr_{1-x}:Sm^{2+}$ [2,3], in which the inhomogeneous line is broadened greatly and the line width approaches a maximum with $x = 0.5$. Liquid nitrogen temperature hole burning was observed for the first time in $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ in our laboratory [2]. Since then, the investigations on high temperature hole burning in $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ have been undertaken [4,5] and room temperature hole burning was realized in $SrFCl_{0.5}Br_{0.5}:Sm^{2+}$ crystals by Jaaniso et al. [6]. Considering the useful properties of $MFCl_{0.5}Br_{0.5}:Sm^{2+}$ systems (M = group II ion), our interest is to understand if the inhomogeneous line can be broadened further when Br and the other alkaline earth metals are simultaneously doped to $BaFCl:Sm^{2+}$ matrix. Therefore we prepared the $M_yM'_{1-y}FCl_{0.5}Br_{0.5}:Sm^{2+}$ series ($M_yM'_{1-y}$ series) (M, M′ = Mg, Ca, Sr,, Ba; $y = 0$–1). Fortunately the inhomogeneous line in the series is indeed broadened further and room temperature hole burning was observed by Holliday et al. in $Sr_{0.5}Mg_{0.5}FCl_{0.5}Br_{0.5}:Sm^{2+}$ prepared in our laboratory [7]. In the paper we mainly report the results of inhomogeneous broadening and high temperature hole burning in the Ca_ySr_{1-y} and Sr_yBa_{1-y} series.

Although the Sm^{2+}-doped mixed crystals have some useful properties of high temperature photon gated hole burning [2–7] and high temperature stable hole [1,8], there is a problem to be solved. That is hole refilling in the hole burning process. The hole burning mechanism in this system is considered to be photoionization of Sm^{2+} following electron trapping, and Sm^{3+} ions usually act as

Correspondence to: Dr. J. Zhang, Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021, China.

0022-2313/93/$06.00
SSDI 0022-2313(93)E0056-4

3,896,420 (1975). G. Castro,
and H.P. Trommsdorf, U.S.
(1982) 77. U.S. Patent No.
A. Friedlander and S. Meth,
84).
132071 (1984).
P. Wild, J. Chem. Phys. 92
U.P. Wild, J. Chem. Phys.
d A. Renn, J. Mol. Elect. 7
ent Spectral Hole-Burning:
ringer, Berlin, 1988).
S.R. Hartmann, Phys. Rev.
and I.D. Abella, Phys. Lett.
C. Rand and R.G. Brewer,
er, Phys. Rev. A 32 (1985)
R. Kaarli, Phys. Rev. B 42
imagnetic Resonance, ed.
York, 1972) p. 263.
Rev. A 29 (1984) 3452.
. DeVoe and R.G. Brewer,
8.
elby, Opt. Lett. 6 (1981) 96.
e, R.S. Meltzer, W.M. Yen,
Macfarlane, Phys. Rev. Lett.
486.
Phys. Rev. B 44 (1991)
3 (1986) 514.
, Phys. Rev. A 39 (1989)
, Phys. Rev. A 37 (1988)
. 36 (1991) 1943.
ends not only on assumed
pulse width and the Rabi
e calculated probe width
idth) is actually narrower
ogeneous line width of
ing effect for certain ranges
encies was earlier noted in
d J. Yu, J. Lumin. 53 (1992)

traps. In this case, hole refilling occurs in the hole burning process [9]. That means, writing can erase the stored information. To avoid this effect, introducing another effective trap instead of Sm^{3+} is necessary. The introducing of new trap will be reported finally.

2. Experimental

The samples were prepared with high temperature solid state reaction/ Growth conditions are similar to that described previously [2]. In measuring fluorescence spectra, 337.1 nm line of a nitrogen laser was used as an excitation source. A Spex-1403 monochromator was used to detect the fluorescence. The data were processed by a microcomputer. A tunable dye laser, with 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, was used for both burning and gating laser beams, so hole burning in this research is a one-color two-photon process. 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.

3. Results and discussion

3.1. Inhomogeneous broadening and high temperature hole burning

Persistent spectral hole can be burnt and probed in the three metastable ^5D_J $(J = 0, 1, 2)$ excited states of $4f^6$ configuration of Sm^{2+}. The inhomogeneous width of these energy levels increases from several wave numbers to more than 20 cm^{-1} in $BaFCl_xBr_{1-x}$:Sm^{2+}, with x approaching 0.5. To further broaden the inhomogeneous width, we add Ca, Sr ions to the system with $x = 0.5$ to form the Ca_ySr_{1-y} series and the Sr_yBa_{1-y} series. Their fluorescence spectra were measured at 77 K. The inhomogeneous line width (Γ_i) and the energy (E_{J0}) of ^5D_J–$^7F_0$ emissions in the two series are shown in Tables 1 and 2, respectively. In the tables, we find that the inhomogeneous line widths are beyond 30 cm^{-1} with $y = 0.2$–0.8, but the rate of the variation of Γ_i with y is smaller than that with x observed in $BaFCl_xBr_{1-x}$:Sm^{2+} system, while the energy E_{J0} increases as y decreases. The results are discussed as follows.

In BaFCl:Sm^{2+}, the Sm^{2+} ion substitutes the Ba site and has C_{4v} symmetry. $BaFCl_xBr_{1-x}$:Sm^{2+} has the same structure and the ligands Cl^- and Br^- around Sm^{2+} have different configurations with different probabilities. The spread of energy levels is mainly dependent on the randomness of the nearest anions of Cl^- and Br^-, and the greatest substitutional disorder occurs at $x = 0.5$ [3]. In the $M_yM'_{1-y}$ series, the substitutional disorder is reasonably even greater but the composition of anions of 0.5 is constant and the cations are located at

Table 1
The values of inhomogeneous line width Γ_i (cm^{-1}) and energy E_{00} (cm^{-1}) in Ca_ySr_{1-y} series with different y

y:	0.2	0.4	0.5	0.55	0.7	0.8
Γ_i:	33	32	35	38	38.5	39
E_{00}:	14 483	14 480	14 474	14 466	14 458	14 450

Table 2
The values of Γ_i (cm^{-1}) and energy E_{J0} $(J = 0, 1, 2)$ (cm^{-1}) in Sr_yBa_{1-y} series with different y

y	0	0.25	0.4	0.5	0.65	0.75	1
Γ_i	26	27	28	31	28	29	24
E_{00}	14 534	14 528	14 527	14 512	14 510	14 502	14 483
Γ_i	26	34	30	38	32	33	31
E_{10}	15 879	15 871	15 871	15 856	15 852	15 842	15 819
Γ_i	26	26	26	34	35	27	20
E_{20}	17 820	17 809	17 807	17 791	17 789	17 781	17 760

f Sm^{2+}. The in-
rgy levels increases
more than 20 cm^{-1}
pproaching 0.5. To
eous width, we add
$x = 0.5$ to form the
$_{-y}$ series. Their flu-
ed at 77 K. The in-
d the energy (E_{J0})
series are shown in
the tables, we find
widths are beyond
the rate of the vari-
an that with x ob-
system, while the
ses. The results are

n substitutes the Ba
aFCl$_x$Br$_{1-x}$:Sm^{2+}
igands Cl$^-$ and Br$^-$
onfigurations with
d of energy levels is
mness of the nearest
e greatest substitu-
= 0.5 [3]. In the
al disorder is reas-
nposition of anions
ions are located at

th Γ_i (cm^{-1}) and energy
ferent y

55	0.7	0.8
:	38.5	39
466	14458	14450
	1	
	24	
	14483	
	31	
	15819	
	20	
	17760	

---

farther sites than anions to Sm^{2+} ions, so that the influence of combinations of different cations on the inhomogeneous line width is smaller than that of anions. The change of energy with y should be attributed to the variation of cation radius, which perturbs the crystal field. The change of energy with x in BaFCl$_x$Br$_{1-x}$:Sm^{2+} is also found. We have observed that the energy changes linearly with x or y and follows the experimental relationships below:

$$E_{00} = 14\,550 - 24.7x \text{ (BaFCl}_x\text{Br}_{1-x}\text{)}, \quad (1)$$

$$E_{00} = 14\,498 - 58.1y \text{ (Ca}_y\text{Sr}_{1-y}\text{ series)}, \quad (2)$$

$$E_{00} = 14\,546 - 61.0y \text{ (Sr}_y\text{Ba}_{1-y}\text{ series)}, \quad (3)$$

$$E_{10} = 15\,885 - 61.0y \text{ (Sr}_y\text{Ba}_{1-y}\text{ series)}, \quad (4)$$

$$E_{20} = 17\,828 - 61.0y \text{ (Sr}_y\text{Ba}_{1-y}\text{ series)}. \quad (5)$$

According to the above results, it is possible to mix the powder samples with different x or y together in proper proportion to form a mixture with a large inhomogeneous line width. In Eqs. (1)–(5), the energy changes faster with y than x and E_{J0} changes with the same slope in Sr$_y$Ba$_{1-y}$ series. In view of this, three samples in the Sr$_y$Ba$_{1-y}$ series with $y = 0$, 0.25 and 0.65 are selected to mix together in a reasonable proportion. The inhomogeneous line shape in the mixture should be determined by the overlapping of the inhomogeneous lines of the three samples. To ^{7}F$_0$–^{5}D$_2$ transition, a inhomogeneous line width of 62.5 cm^{-1} in the mixture is estimated by using the data of E_{20} and Γ_i in Table 2. Figs. 1(a) and (b) show the excitation spectrum before and after burning three holes in the mixture at 77 K, respectively. The width of the spectral distribution is 65 cm^{-1}, which is in agreement with the estimation (62.5 cm^{-1}). In this way, a large inhomogeneous broadening can be realized while the homogeneous width is unchanged. In theory, room temperature hole burning in the mixture is possible. The experiment has not been done in the mixture; instead room temperature hole burning has been performed in the Sr$_y$Ba$_{1-y}$ series with $y = 0.5$.

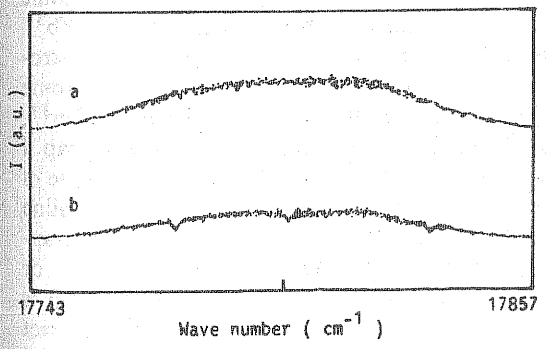


Fig. 1. The excitation spectra before (a) and after (b) burning three holes in the mixture of Sr$_y$Ba$_{1-y}$ series with different y of 0, 0.25 and 0.65 at 77 K.

Fig. 2 shows the normalized hole shape burn in the Sr$_y$Ba$_{1-y}$ series ($y = 0.5$) at room temperature. The burning time is 10 min. A hole with width of 7 cm^{-1} and depth of 15% is probed. At room temperature, ^{5}D$_2$–^{7}F$_0$ emission has quenched and the non-radiative emission rate rises rapidly compared to that at 77 K; then the homogeneous line width of ^{5}D$_2$–^{7}F$_0$ emission increases faster than that of ^{5}D$_1$–^{7}F$_0$, ^{5}D$_0$–^{7}F$_0$ emissions with increasing temperature. It is reasonable to suppose that the hole burnt in ^{7}F$_0$–^{5}D$_1$ or ^{7}F$_0$–^{5}D$_0$ transition at room temperature is narrower than 7 cm^{-1}. The evidence for this is that the hole widths for ^{7}F$_0$–^{5}D$_0$ and ^{7}F$_0$–^{5}D$_1$ transitions in SrFCl$_{0.5}$Br$_{0.5}$:Sm^{2+} at room temperature are both less than 5 cm^{-1} [6], and the hole width for ^{7}F$_0$–^{5}D$_1$ transition in Sr$_{0.5}$Mg$_{0.5}$ FCl$_{0.5}$Br$_{0.5}$: Sm^{2+} is less than 7 cm^{-1} [7]. In view of these results, the M$_y$M$'_{1-y}$ series and their mixture are promising materials for room temperature hole burning, and the latter may have the advantage of multi-hole burning at room temperature.

3.2. *Trap effect in hole burning*

In Sm^{2+}-doped crystals, Sm^{3+} ions generally act as principal electron traps which leads to hole refilling in hole burning process and this effect has been observed in SrFCl:Sm [9]. The evidence to verify that Sm^{3+} ions act as principal traps in SrFCl:Sm is that the spectral area of Sm^{2+} remains constant before and after hole burning at 77 K [9]. The same result is also obtained at room temperature. Fig. 3 shows the spectral distributions of Sm^{2+} before (solid) and after (broken) line bleaching at room temperature in SrFCl:Sm. There are two

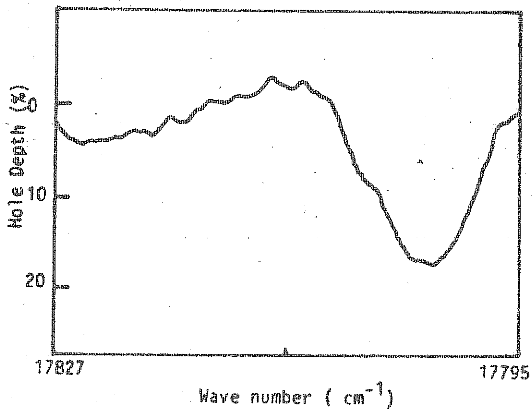


Fig. 2. Normalized hole shape burnt in the Sr_yBa_{1-y} series ($y = 0.5$) at room temperature.

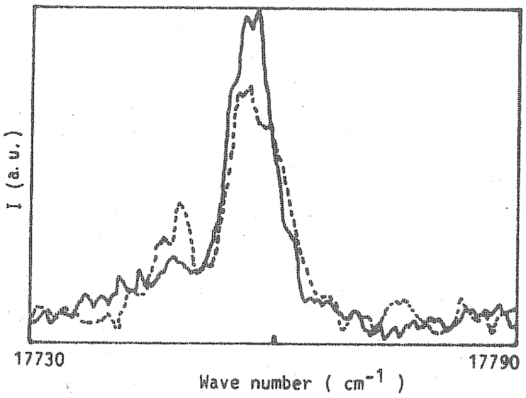


Fig. 3. The excitation spectra before (solid) and after (broken) bleaching the strong line in SrFCl:Sm at room temperature.

lines in the $^7F_0$–$^5D_2$ transition profile, which stem from two different Sm^{2+} centers. After burning at the peak of the strong line, no hole is found because hole width for this transition at room temperature approaches the inhomogeneous line width; instead the intensity of the strong line decreases following the increase of intensity of the weak line. This feature is interpreted as that the free electrons released from the photoionization of Sm^{2+} responsible for the strong line are captured by Sm^{3+} ions at the weak line site to generate Sm^{2+} ions distributing under the weak line. The Sm^{2+}-ion transfer

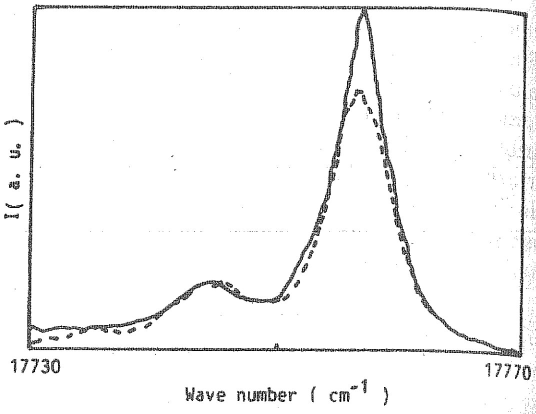


Fig. 4. The excitation spectra before (solid) and after (broken) bleaching the strong line in SrFCl: Sm, Yb at room temperature.

between the two different centers is essentially caused by the existence of the principal Sm^{3+} trap.

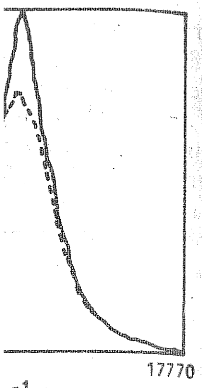
If the effective trap is different from Sm^{3+}, the spectral area should reduce. To introduce another trap, we dope Yb to SrFCl:Sm^{2+}. Fig. 4 shows the excitation spectra before (solid) and after (broken) bleaching the strong line in SrFCl:0.5% Sm, 2%Yb at room temperature. We see that the intensity of the strong line decreases and the intensity of the weak line keeps almost constant after bleaching the strong line. The result is because that almost no additional Sm^{2+} ions under the weak line are produced in the case of existence of new trap. The new trap in SrFCl:Sm, Yb is not understood very well. They probably have some connection with the Yb ions. For instance, Yb^{3+} and some unknown color centers due to the introducing of Yb can act as effective traps. Some trivalent rare earth ions such as Eu^{3+}, Tm^{3+}, Dy^{3+} and Ho^{3+}, etc., can probably act as trap if they are doped to the hole burning system. One of the reasons for this is that these ions in alkaline earth fluoride can convert to divalent ions by trapping electrons generated by radiation of X- or γ-rays [10,11]. Good selection of effective trap is useful not only to reduce the hole refilling effect but also to obtain the high temperature stable hole. The properties of a doubly doped hole burning system are currently under investigation.

4. Conclusion

High tempera
$M'_{1-y}FCl_{0.5}Br_{0.}$
prepared. In the
Sm^{2+} is broade
width of about 4
perature hole bu
$FCl_{0.5}Br_{0.5}:Sm^{2}$
homogeneous lir
mixing three sa
$y = 0, 0.25$ and (
burnt and probe
temperature. To
hole burning pro
tive trap differen
Yb doubly dope

Acknowledgemen

This work is
Excited State P
Physics, Chinese



›lid) and after (broken)
b at room temperature.

.ters is essentially
e principal Sm^{3+}

ıt from Sm^{3+}, the
introduce another
ı$^{2+}$. Fig. 4 shows
(solid) and after
ne in SrFCl:0.5%
e. We see that the
ases and the inten-
.ost constant after
result is because
$^{+}$ ions under the
ase of existence of
Cl:Sm, Yb is not
›bably have some
or instance, Yb^{3+}
s due to the intro-
:tive traps. Some
as Eu^{3+},Tm^{3+},
ably act as trap if
ng system. One of
e ions in alkaline
alent ions by trap-
ıdiation of X- or
›f effective trap is
ole refilling effect
:mperature stable
ubly doped hole
der investigation.

---

4. Conclusion

High temperature hole burning systems M_y-$M'_{1-y}FCl_{0.5}Br_{0.5}:Sm^{2+}$ (M, M′ = Ca, Sr, Ba) are prepared. In the system, the inhomogeneous line of Sm^{2+} is broadened greatly with a maximum line width of about 40 cm^{-1} for $y = 0.5$, and room temperature hole burning is performed in $Sr_{0.5}Ba_{0.5}$-$FCl_{0.5}Br_{0.5}:Sm^{2+}$. A mixture with the inhomogeneous line width of 65 cm^{-1} is obtained by mixing three samples of the Sr_yBa_{1-y} series for $y = 0, 0.25$ and 0.65, respectively. Three holes are burnt and probed in the mixture at liquid nitrogen temperature. To overcome hole refilling effect in hole burning process, the introducing of other effective trap different from Sm^{3+} is performed in Sm, Yb doubly doped SrFCl crystals.

Acknowledgement

This work is supported by the Laboratory of Excited State Processes, Changchun Institute of Physics, Chinese Academy of Sciences.

References

[1] A. Winnacker, R.M. Shelby and R.M. Macfarlane, Opt. Lett. 10 (1985) 350
[2] Changjiang Wei, Shihua Huang and Jiaqi Yu, J. Lumin. 43 (1989) 161
[3] Lingfen Zhang, Jiaqi Yu and Shihua Huang, J. Lumin. 45 (1990) 301
[4] A. Oppenlander, F. Madeore, J.-C. Vial and J.-P. Chaminade, J. Lumin. 50 (1991) 1
[5] C. Wei, K. Holliday, A.J. Meixner, M. Croci and U.P. Wild, J. Lumin. 50 (1991) 89.
[6] R. Jaaniso and H. Bill, Europhys. Lett. 16 (1991) 569
[7] K. Holliday, C. Wei, M. Croci and U.P. Wild, J. Lumin. 53 (1992) 227
[8] Jiahua Zhang, Shihua Huang and Jiaqi Yu, Opt. Lett. 17 (1992) 1146
[9] Jiahua Zhang, Shihua Huang, Weiping Qin, Diankun Gao and Jiaqi Yu, J. Lumin. 53 (1992) 275
[10] W. Hayes and J.W. Twidell, J. Chem. Phys. 35 (1961) 1521
[11] D.S. McClure and Z.J. Kiss, J. Chem. Phys. 39 (1963) 3251