Journal of Luminescence 43 (1989) 161–166
North-Holland, Amsterdam

TWO-PHOTON HOLE BURNING AND FLUORESCENCE-LINE-NARROWING STUDIES ON $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ AT 77 K

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Received 15 September 1988
Revised 1 February 1989
Accepted 7 February 1989

Persistent spectral hole burning (HB) and fluorescence-line-narrowing (FLN) were observed in $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ at 77 K. By adding Br^- to BaFCl, the linewidths of $^5D_J \rightarrow {}^7F_J$ transitions of Sm^{2+} were broadened by at least one order of magnitude due to the effect of disorder. As a result, tens of holes can potentially be burned in this material at 77 K. The results of FLN indicate that the random arrangement of Cl^- and Br^- around Sm^{2+} ions does not cause a detectable energy level splitting, but shifts the center of gravity of their energy levels. The unexpected two-line structure in FLN is interpreted as accidental coincidence of excitation energies.

1. Introduction

The optically active centers in solids at low temperature exhibit inhomogeneously broadened absorption lines due to their different local environment. When a subset of the centers is selectively pumped with a narrow bandwidth laser, the population depletion of the selected absorbers produces a spectral dip or a spectral peak according to the probing method; these are, respectively, spectral hole burning (HB) and fluorescence-line-narrowing (FLN). HB and FLN are, to some extent, complementary techniques, both of them have been used as tools for high-resolution spectroscopy [1,2]. This research has been stimulated by novel photo-induced phenomena as well as by the possible application of HB to frequency-domain optical storage [3,4].

In frequency-domain optical storage, a bit of stored data is associated with the presence or absence of a spectral hole at a given frequency location. Therefore, the storage capacity of this method at a laser beam spot is approximately determined by the ratio of inhomogeneous linewidth (Γ_i) to the homogeneous linewidth (Γ_h), Γ_i/Γ_h, which can be as high as 10^3–10^4 at low temperature. For a given material, the inhomogeneous linewidth changes only moderately with the temperature; on the other hand, the homogeneous linewidth, which is a consequence of dynamical perturbations such as various phonon-induced relaxation processes, will increase rapidly as the temperature rises. To maintain a high storage capacity, the temperature must be very low, usually at 4.2 K [5]; this limitation is one of the main obstacles to the practical application of HB.

The first observation of two-colour or photon-gated hole burning in $BaFCl:Sm^{2+}$ at 2 K was reported in 1985 by A. Winnacker et al. [6]. They found that the inhomogeneous linewidth of the $^5D_0 \rightarrow {}^7F_0$ transition was 16 GHz and the hole width was 25 MHz at 2 K. In this paper, we report the results of two-photon hole burning and FLN in $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ at 77 K. The inhomogeneous linewidths of the $^5D_J \rightarrow {}^7F_J$ transitions of Sm^{2+} ion were broadened significantly by adding Br ions to the BaFCl matrix. As a result, it was possible to study HB and FLN at quite a high

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0022-2313/89/$03.50

temperature (77 K). This might be important for the application of HB to frequency-domain optical storage.

2. Experimental

The measurements were performed on a $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ powder sample. The nominal molar concentration of Sm^{2+} was 1%. The sample was prepared by the method described below. Analytical grade barium fluoride (BaF_2), barium chloride ($BaCl_2$), barium bromide ($BaBr_2$) and samarium oxide (Sm_2O_3) were weighed according to desired stoichiometric ratios, ground together in an agate mortar and then placed in a Al_2O_3 crucible. The samples were heated in a furnace to 1100 °C for 1–2 h in a sealed quartz tube which contained an atmosphere of hydrogen and nitrogen (5%/95%). Then, the quartz tube was taken out of the furnace and cooled to room temperature. The reaction that occurred in the molten state was

$$BaF_2 + xBaCl_2 + (1-x)BaBr_2 \rightarrow 2BaFCl_xBr_{(1-x)}.$$

$BaFCl_xBr_{1-x}:Sm^{2+}$ samples have been prepared with different values of x ($x = 1$, 0.8, 0.5, 0.2, 0). In this paper, we report the results on $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ powder. Numerous results on the structure of mixed cation and anion fluoride halides have been reported [7,8]. MFX (M = Ca, Sr, Ba; X = Cl, Br, I) crystallizes in the tetragonal (P4/nmm), PbFCl-type structure with a layer sequence of $(F–M–X–X–M–)_n$ along the z axis, as shown in fig. 1. The cations and nonfluoride anions are located in position 2c, $\pm(1/4, 1/4, z)$, and the fluoride anions in position 2a, $\pm(3/4, 1/4, 0)$, corresponding to the setting of the space group P4/nmm with the origin at 2/m. For the structure of mixed cation and anion fluoride halides, it was found that when the ionic sizes were similar, the different cations randomly occupied the cation sites and the chloride, bromide and iodide ions randomly occupied the nonfluoride anion sites; the result was a PbFCl-type solid solution. PbFCl-type solid solutions were observed in the $BaFCl_xBr_{1-x}$ system for $0 \leqslant x \leqslant 1$ [8]. Our x-ray diffraction results also show that $BaFCl_{0.5}Br_{0.5}$ has a PbFCl-type structure and crystallizes in the tetragonal space group (P4/nmm). The same is true for BaFCl and BaFBr, with only small differences in lattice constants.

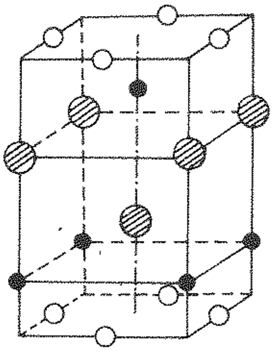

Fig. 1. Unit cell of MFX. Open circles: F^-; hatched circles: X^- (Cl^-, Br^-, I^-); black circles: M^{2+} (Ba^{2+}, Sr^{2+}, Ca^{2+}).

A Quanta-Ray PDL-2 tunable dye laser, pumped by a pulsed Quanta-Ray DCR-2A ND:YAG laser was used for HB and FLN studies. The laser linewidth was about 0.2 cm^{-1}, the pulse duration was 6–7 ns and the repetition rate was 20 Hz. For the FLN study, a Spex 1403 double grating spectrometer and an RCA C31034 photomultiplier were used to analyze the fluorescence. The data were processed by a microcomputer. The entrance and exit slit widths were both 0.1 mm. For the HB study, a D330 monochromator was used with the entrance and exit slits opened to 3 mm; the apparatus for HB is shown in fig. 2. To burn the hole, the $^5D_2 \leftarrow {}^7F_0$ transition of Sm^{2+} was irradiated by the laser for 5 min.

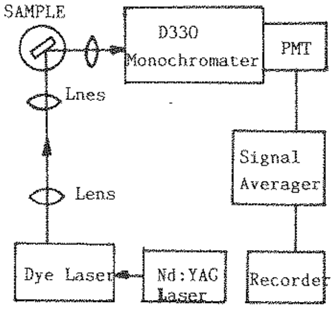

Fig. 2. Experimental setup for HB.

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Then, to detect the hole, the D330 spectrometer was set at 630 nm to monitor the $^5D_1 \rightarrow {}^7F_0$ fluorescence as the excitation spectrum was scanned with an attenuated laser. All measurements were carried out with the sample immersed in liquid nitrogen.

3. Results and discussions

3.1. *Fluorescence-line-narrowing*

The Sm^{2+} ion substitutes in the BaFX (X = Cl, Br) lattice at the Ba^{2+} sites. The symmetry of this site was presumed to be C_{4v}. The fluorescence is due to transitions from three metastable ^5D_J ($J = 0, 1, 2$) excited states to the ^7F_J ($J = 0, 1, 2, \ldots 6$) ground states of the $4f^6$ Sm^{2+} configuration. The Sm^{2+} site lacks an inversion center, so the $^5D_J \rightarrow {}^7F_J$ transition is now electric-dipole allowed and consequently quite intense transitions were expected. At higher energies there are broad absorption bands arising from transitions to $4f^5 5d^1$ states [9].

We have studied the different Sm^{2+} centers in BaFCl using the laser-selective-excitation technique [10]. It was found that the Sm^{2+} ions actually occupy two inequivalent lattice sites in either BaFCl or BaFBr, whose local symmetries are C_{4v} and C_s, respectively. The predominant Sm^{2+} sites have C_{4v} symmetries. The emission spectrum of the $^5D_0 \rightarrow {}^7F_0$ transition of BaFCl : Sm^{2+} resulting from nonselective excitation at 337.1 nm with a nitrogen laser is shown in fig. 3. The FWHM is about 1.3 cm^{-1}; the value for BaFBr : Sm^{2+} is about 3 cm^{-1} [11].

The same technique was used to obtain the emission spectrum of the $^5D_0 \rightarrow {}^7F_0$ transition of Sm^{2+} in $BaFCl_{0.5}Br_{0.5}$ (fig. 4). The FWHM is about 26 cm^{-1} at both 77 K and 300 K. We found, as was expected, that the linewidth in $BaFCl_{0.5}Br_{0.5}$: Sm^{2+} was much broader than that in BaFCl : Sm^{2+} or BaFBr : Sm^{2+}. In BaFCl : Sm^{2+} the linewidths of the $^5D_0 \rightarrow {}^7F_0$ transition at 77 K and 300 K are 1.3 cm^{-1} and 3.2 cm^{-1} [11] respectively; thus, it increases as the temperature rises. That means, at least at 77 K, that the main contribution to the measured linewidth comes from homogeneous broadening. In $BaFCl_{0.5}Br_{0.5}$: Sm^{2+}, the linewidths of $^5D_0 \rightarrow {}^7F_0$ transition at 77 K and 300 K are almost the same (fig. 4). This implies that the main contribution to it comes from the inhomogeneous broadening.

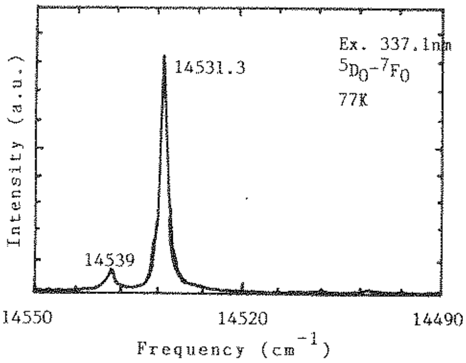

Fig. 3. Emission spectrum of BaFCl : Sm^{2+} ($^5D_0 \rightarrow {}^7F_0$ transition) at 77 K. Excitation: 337.1 nm.

In BaFCl, the Sm^{2+} ions fit into the lattice substitutionally at Ba^{2+} sites. The coordination polyhedron consists of four fluoride ions located in a plane perpendicular to the *c* axis, four chloride ions in a plane parallel to the fluoride plane, and one extra chloride ion on the *c* axis above the chloride plane. When one half of the chlorides were replaced by bromides, the chlorides and bromides surrounded the Sm^{2+} ions randomly; this affected both the local symmetry and the crystal field strength at the Sm^{2+} site. Later we will see that the effect on the local symmetry is not large enough to cause a detectable energy level splitting, but it does disturb the center of gravity

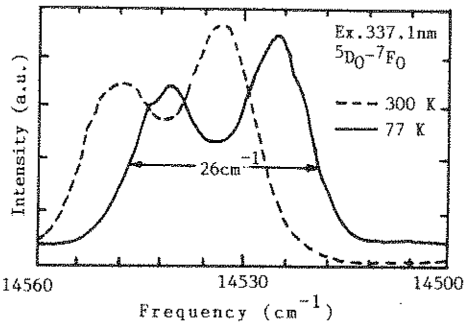

Fig. 4. Emission spectra of $BaFCl_{0.5}Br_{0.5}$: Sm^{2+} ($^5D_0 \rightarrow {}^7F_0$ transition) at (a) RT; (b) 77 K. Excitation 337.1 nm.

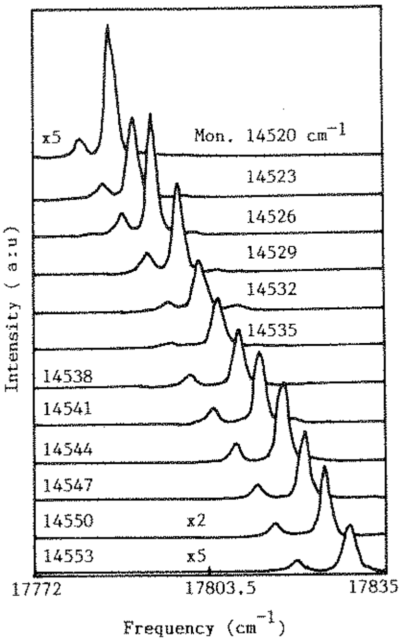

Fig. 5. Excitation spectra of $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ at 77 K monitored at different frequencies of the $^5D_0 \rightarrow {}^7F_0$ transition.

of Sm^{2+} ion energy levels and leads to broad band emission.

Fig. 5 shows the excitation spectra of $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$. They were obtained by monitoring different frequencies of $^5D_0 \rightarrow {}^7F_0$ fluorescence while the $^5D_2 \leftarrow {}^7F_0$ transition was scanned. All of the excitation spectra monitored at different frequencies are quite similar to each other and to the one obtained from $BaFCl:Sm^{2+}$ monitoring the C_{4v} center [10]; they consist of two peaks. This is in agreement with the fact that there are two electric-dipole allowed transitions for $^5D_2 \rightarrow {}^7F_0$, which are $E \rightarrow A_1$ and $A_1 \rightarrow A_1$, in a C_{4v} crystal field. We conclude, therefore, that the predominant Sm^{2+} center in $BaFCl_{0.5}Br_{0.5}$ probably still has C_{4v} symmetry. By tuning the laser frequency within lines in fig. 5 and measuring the fluorescence of $^5D_0 \rightarrow {}^7F_0$ we obtained the nonresonant FLN result shown in fig. 6. The resulting lines are much narrower and shift with the excitation wavelength. This contrasts with the laser-selective-excitation spectra of $BaFCl:Sm^{2+}$ in which there is only one peak in the $^5D_0 \rightarrow {}^7F_0$ spectrum if the C_{4v} center is selectively excited [12]. We think that the fact that there are two peaks in each FLN spectrum of $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ arises from the accidental coincidence of excitation energies of ions in different sites. As shown in fig. 7, ions at sites A, B C and D are all excited by the same laser frequency, but fluoresce to various terminal states at different frequencies. As a consequence, processes A, B and C caused residual broadening of the stronger peak and process D led to the weaker fluorescence peak.

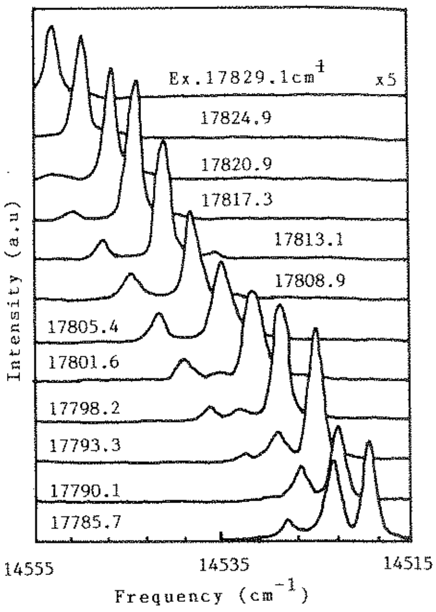

Fig. 6. FLN spectra of $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ at 77 K excited at different frequencies of $^5D_2 \leftarrow {}^7F_0$ transition.

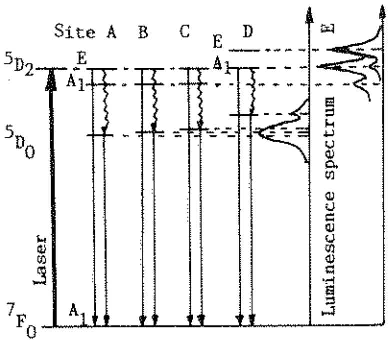

Fig. 7. Schematic representation of the "accidental coincidence" effect. Solid and wavy lines denote radiative and nonradiative transitions, respectively.

3.2. *Two-photon persistent hole burning*

The sample was immersed in liquid nitrogen and irradiated for 5 min with the dye laser tuned to the $^5D_2 \leftarrow {}^7F_0$ frequency. The burning intensity was about 10 kW/cm^2. Under such selective excitation, the subset of the Sm^{2+} ions resonant with the laser frequency was excited to the metastable excited state $^5D_2$ from the ground state $^7F_0$; subsequently, the Sm^{2+} ions excited to the $^5D_2$ state were photoionized to the conduction band by absorbing a second photon from the same laser beam. The electrons excited to the conduction band were captured by traps [6]. Consequently, a persistent hole in the absorption band at the spectral position of the laser frequency was produced. The schematic diagram of two-photon persistent hole burning in $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ is shown in fig. 8. Here, we use the term "two-photon" to emphasize that $\lambda_1 = \lambda_2$; the alternate phrase, "two-colour" or "photon-gated", often refers to cases where $\lambda_1 \neq \lambda_2$. In our experiment the hole was probed in a fluorescence excitation spectrum by monitoring the $^5D_1 \rightarrow {}^7F_0$ emission (at about 630 nm), which is the strongest of the three $^5D_J \rightarrow {}^7F_0$ ($J = 2, 1, 0$) fluorescence components at 77 K, while scanning $^5D_2 \leftarrow {}^7F_0$. The hole burning result is illustrated in fig. 9; it shows a hole with a 30% depth that was burned in 5 min. The hole width was about 1.4 cm^{-1}. At the lowest burning intensity, the hole width (Γ_{hole}) was about 1.14 cm^{-1}; thus, the homogeneous linewidth (Γ_h) is about 0.47 cm^{-1}, according to $\Gamma_h = (\Gamma_{hole} - \Gamma_{laser})/2$ [13], in which $\Gamma_{laser} = 0.2$ cm^{-1}. The inhomogeneous linewidth (Γ_i) of this band is about 40 cm^{-1} [12], so the ratio of Γ_i/Γ_h is on the order of 10^2. After 4 h we found that the hole became wider and a little shallower. This means the hole can be kept for at least several hours.

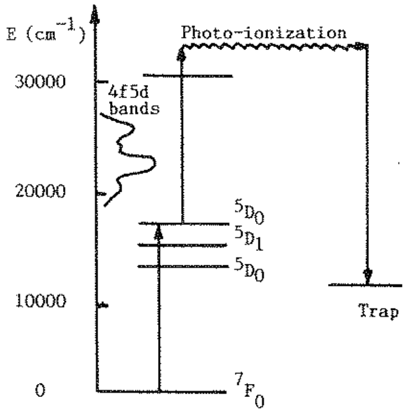

Fig. 8. Schematic diagram of two-photon hole burning in $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$.

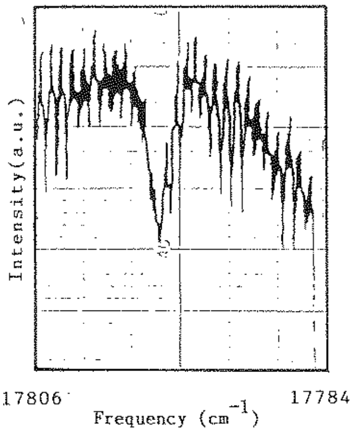

Fig. 9. Spectral hole observed in excitation spectrum at 77 K in $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$.

4. Conclusion

FLN and persistent hole-burning were studied in $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ at 77 K. The results show that it is possible to burn tens of holes at 77 K in this material. This has potential importance for the study on frequency domain optical storage.

Acknowledgements

The authors would like to thank Prof. Diankun Gao for his help with sample preparation. We are grateful to Mr. Weiping Qin and Yongrong Shen for their kind help with the experiments, to Professors L. Johnson and U.P. Wild for their careful proof reading.

References

[1] A. Szabo, Phys. Rev. Lett. 25 (1970) 924.
[2] A. Szabo, Phys. Rev. B11 (1975) 4512.

[3] G. Castro, D. Haarer, R.M. Macfarlane and H.P. Trommsdorff, U.S. Patent No. 4101976 (1978).

[4] A. Renn, R. Locher, A. Meixner and U.P. Wild, J. Lumin. 41 & 42 (1988) 823.

[5] F.M. Schellenberg, W. Length and G.C. Bjorklund, Appl. Opt. 25 (1986) 3207.

[6] A. Winnacker, R.M. Shelby and R.M. Macfarlane, Opt. Lett. 10 (1985) 350.

[7] S.A. Hodorowicz, E.K. Hodorowicz and H.A. Eick, J. Sol. St. Chem. 50 (1983) 180.

[8] Jianhua Lin and Mianzeng Su, Chem. J. Chinese Univ. 6 (1985) 957 (in Chinese).

[9] See e.g., J.C. Gacon, G. Grenet, J.C. Souillat and M. Kibler, J. Chem. Phys. 69 (1978) 868.

[10] Changjiang Wei, Shihua Huang and Jiaqi Yu, Proc. 3rd Asia Pacific Physics Conf. Hongkong, June 20–24, 1988.

[11] Changjiang Wei, unpublished.

[12] Changjiang Wei, Thesis (in Chinese), Changchun Inst. of Phys. (1987).

[13] A.A. Gorokhorskii, R.K. Kaarli and L.A. Rebane, Opt. Commun. 16 (1976) 282.

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