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$^5D_J \rightarrow {}^7F_0$ transition probability and hole burning quantum efficiency of Sm^{2+}

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Abstract

Along the $Sr_yBa_{1-y}FCl_{0.5}Br_{0.5}:Sm^{2+}$ series, the higher the Sr composition, the smaller the separation between the 4f5d band and the ^5D_J levels, the larger the $^7F_0 \rightarrow {}^5D_J$ absorption transition probabilities and the higher the hole-burning efficiencies. These results are attributed to admixtures of the 4f and 5d wave functions.

1. Introduction

Since photon-gated spectral hole burning in $BaFCl:Sm^{2+}$ was reported by Winnaker [1], divalent samarium-doped alkaline earth mixed halides have been widely investigated. Room temperature hole burning in this series has been reported [2, 3]. These materials have potential applications in frequency domain optical storage, but there are still some problems to be solved. One of the significant problems is how to increase the $^5D_J \rightarrow {}^7F_0$ transition probabilities, which are f–f electric dipole parity forbidden, so as to increase the hole burning efficiency. According to the Judd–Ofelt theory [4, 5], if the energy separation between the 4f5d band and the ^5D_J levels is reduced, the 4f and 5d wavefunctions mix more and the $^7F_0 \rightarrow {}^5D_J$ absorption transition probabilities increase. To this end we have studied the $BaFCl_xBr_{1-x}:Sm^{2+}$ series and found that, with increasing Br composition, the energy separation between the 4f5d band and the $^5D_2$ level became smaller and the $^7F_0 \rightarrow {}^5D_J$ absorption probabilities increased [6]. But the change in composition x also had a great effect on the inhomogeneous line widths which broadens as x approaches 0.5 along the series. Hence $BaFBr:Sm^{2+}$ is not the best material for hole burning. In this paper, we report a study of the $^7F_0 \rightarrow {}^5D_J$ transition probabilities and hole burning efficiencies for the $Sr_yBa_{1-y}FCl_{0.5}Br_{0.5}:Sm^{2+}$ series. Along this series, the composition y has only a minor effect on the inhomogeneous line widths.

2. Experimental

The powder samples of $Sr_yBa_{1-y}FCl_{0.5}Br_{0.5}:Sm^{2+}$ ($y = 0, 0.25, 0.5, 0.75, 1.0$) were prepared by the method described in Ref. [6]. The excitation spectra of Sm^{2+} were measured with a Hitachi F-4000 spectrometer by monitoring the $^5D_0 \rightarrow {}^7F_0$ emission. For measurements of the fluorescence spectra and the fluorescence decay curves, the samples were mounted in a helium gas closed-cycle cryostat and excited by a nitrogen laser. A D330

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monochromator, a boxcar averager and a Datemate microcomputer were used to detect and analyse the fluorescence of these samples. In the two photon hole burning experiments, the samples were excited by a 560 nm dye laser pumped by a YAG laser with pulse duration of 10 ns.

3. Results and discussion

3.1. The energy separations between the 4f5d band and the ^5D_J levels

The excitation spectra of the 4f5d bands of Sm^{2+} in $Sr_yBa_{1-y}FCl_{0.5}Br_{0.5}$ ($y = 0, 0.25, 0.5, 0.75, 1.0$) were measured by monitoring emission of the $^5D_0 \rightarrow {}^7F_0$ transition at 688 nm. With increasing Sr concentration, the position of the excitation peak nearest to the ^5D_J levels moves to lower energy by up to 8 nm (Fig. 1). With the same increase in Sr concentration, the positions of the ^5D_J levels also move to lower energies. Table 1 shows the energy position E_a (in cm^{-1}) of the 4f5d peak with the longest wavelength, the energy position E_J of the

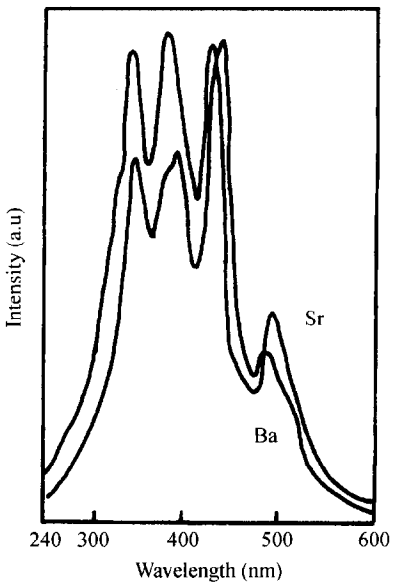

Fig. 1. Excitation spectra of $Sr_yBa_{1-y}FCl_{0.5}Br_{0.5}:Sm^{2+}$ measured by monitoring the $^5D_0 \rightarrow {}^7F_0$ emission and scanning the range of the 4f5d bands for (a) $y = 0$, and (b) $y = 1.0$.

Table 1
Energy position E_a (in cm^{-1}) of the peak with the longest wavelength of the 4f5d excitation band, emission peaks E_J (in cm^{-1}) ($J = 2, 1, 0$) of the ^5D_J levels and the energy separations E_{aJ} (in cm^{-1}) between E_a and the several E_J ($J = 2, 1, 0$) energies

E/y	1.0	0.75	0.5	0.25	0
E_a	20566	20640	20683	20790	20877
E_2	17757	17778	17787	17804	17818
E_1	15824	15844	15864	15872	15876
E_0	14478	14496	14516	14524	14531
E_{a2}	2809	2862	2905	2986	3059
E_{a1}	4742	4796	4819	4918	5001
E_{a0}	6088	6144	6167	6266	6346

$^5D_J \rightarrow {}^7F_0$ ($J = 0, 1, 2$) emission peaks, and the energy separation E_{aJ} between the 4f5d band and the ^5D_J levels. From Table 1 we can see that the 4f5d band and the ^5D_J levels all shift to lower energies, but the shift of the 4f5d band is larger than that of the ^5D_J levels. So, with increasing Sr concentration, the energy separations between the ^5D_J level and the 4f5d band becomes smaller.

3.2. The $^5D_J \rightarrow {}^7F_0$ radiative transition probability

According to the Judd–Ofelt theory, if $|\Psi' J' J'_z\rangle$ is a level of the ^5D_J multiplet, and $|\Psi''\rangle$ is a state of the 4f5d band, the mixed state $|B\rangle$ of this particular ^5D_J level is

$$|B\rangle = |\Psi' J' J'_z\rangle + \sum_{'} \frac{|\Psi''\rangle\langle\Psi''|H_C|\Psi' J' J'_z\rangle}{E(\Psi' J' J'_z) - E(\Psi'')},$$

where H_C is the interaction Hamiltonian mixing the wave functions. If $\langle A| = \langle \Psi J J_z|$ is a state of the $^7F_0$ multiplet, the matrix elements of the electric dipole operator P are given by

$$\langle A|P|B\rangle = \sum_{''} \frac{\langle \Psi J J_z|P|\Psi''\rangle\langle\Psi''|H_C|\Psi' J' J'_z\rangle}{E(\Psi' J' J'_z) - E(\Psi'')}.$$

Since $|\Psi''\rangle$ is a state of the 4f5d band, which has opposite parity to that of the $^7F_0$ state, $\langle \Psi J J_z|P|\Psi''\rangle$ is a parity-allowed matrix element. From the expression for $\langle A|P|B\rangle$, the smaller the energy separation $[E(\Psi' J' J'_z) - E(\Psi'')]$, the larger the $^5D_J \rightarrow {}^7F_0$ transition probability.

In order to obtain the $^5D_J \rightarrow {}^7F_0$ transition probability, we measured the temperature dependence of the $^5D_J \rightarrow {}^7F_0$ ($J = 0, 1, 2$) fluorescence

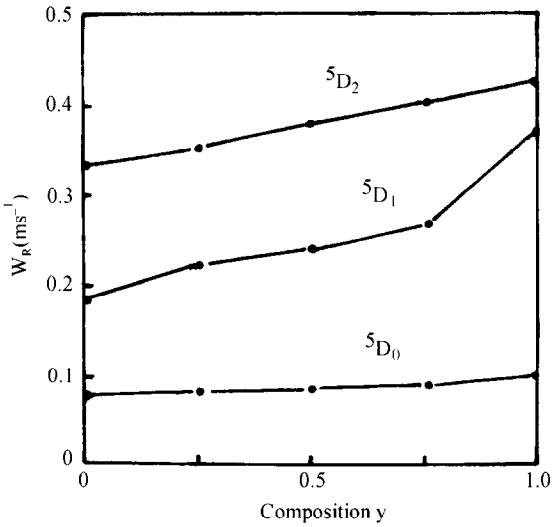

Fig. 2. The dependence of the $^5D_J \rightarrow {}^7F_0$ ($J = 0, 1, 2$) radiative transition probabilities W_R on y for $Sr_yBa_{1-y}FCl_{0.5}Br_{0.5}$: Sm^{2+}.

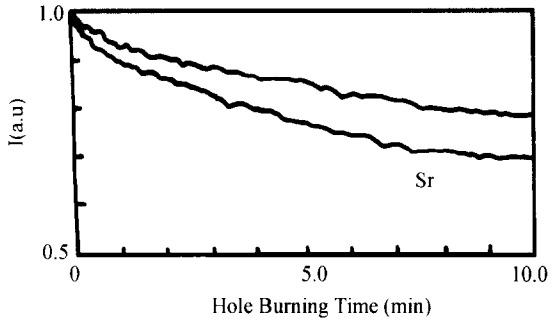

Fig. 3. The dependence of the 77 K $^5D_2 \rightarrow {}^7F_0$ fluorescence intensity I from Sm^{2+} ions located at the burning site on the hole burning time.

decays for temperatures between 16 and 275 K. The results show that the $^5D_J \rightarrow {}^7F_0$ fluorescence decay times increase with decreasing temperature. Below 30 K, they approach limiting values for the different samples. For multi-phonon relaxation, the non-radiative transition probability W_{NR} decreases with decreasing temperature while the radiative transition probability W_R does not change with temperature. At low temperatures, W_{NR} is much less than W_R and the $^5D_J \rightarrow \sum_{J'} {}^7F_{J'}$ total radiative transition probability W_R is the reciprocal of the $^5D_J \rightarrow {}^7F_0$ lifetime. As in our experiments, the relative strengths of the $^5D_J \rightarrow {}^7F_0$ transitions change very little with the change of composition y, the $^5D_J \rightarrow {}^7F_0$ radiative transition probability is proportional to the $^5D_J \rightarrow \sum_{J'} {}^7F_{J'}$ radiative transition probability. By measuring the luminescence spectra at 20 K for the series, we obtain the ratio ϕ of the fluorescence intensity of the $^5D_J \rightarrow {}^7F_0$ transition to that of $^5D_J \rightarrow \sum_{J'} {}^7F_{J'}$. From this analysis we obtain the $^5D_J \rightarrow {}^7F_0$ radiative transition probabilities and the dependence of these probabilities on the composition y (Fig. 2). Fig. 2 shows that the $^5D_J \rightarrow {}^7F_0$ radiative transition probability increases with increasing Sr concentration, with increases in W_R for the $^5D_2$, $^5D_1$ and $^5D_0$ multiplets of about 17%, 47% and 18%, respectively. In Fig. 2 the amount of increase in W_R for each ^5D_J ($J = 2, 1, 0$) level is different and this is attributed to differences in the ^5D_J wave functions. As the $^7F_0 \rightarrow {}^5D_J$ absorption probability is proportional to the $^5D_J \rightarrow {}^7F_0$ radiative transition probability, we can obtain the $^7F_0 \rightarrow {}^5D_J$ absorption transition probability, which is an important parameter for hole burning efficiency.

3.3. *Hole burning quantum efficiency along the* $Sr_yBa_{1-y}FCl_{0.5}Br_{0.5}:Sm^{2+}$ *series*

Based on the dynamical equations of motion of a three-level system, we derived the hole burning efficiency of Sm^{2+} under weak excitation by a gated pulsed laser, whose pulse width $\ll$ the ^5D_J lifetime $\ll$ the pulse interval. The theoretical result shows that the holeburning quantum efficiency is proportional to the $^7F_0 \rightarrow {}^5D_J$ absorption transition probability. From this result, the hole burning efficiency is expected to be enhanced with increasing Sr concentration.

In order to verify this theoretical prediction, hole burning experiments were performed at 77 K on $SrFCl_{0.5}Br_{0.5}:Sm^{2+}$ and on $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ samples using a 560 nm dye laser. Fig. 3 shows the dependence of the $^5D_2$ emission intensity I on the hole burning time under the same hole burning conditions for both crystals. As the hole depth is proportional to $[I_0(t = 0) - I(t)]$, these results show that, under identical hole burning conditions (80 mJ/pulse) and for the same hole burning time, a deeper hole can be obtained for $SrFCl_{0.5}Br_{0.5}:Sm^{2+}$.

Thus, we predict the hole burning quantum efficiency for $SrFCl_{0.5}Br_{0.5}:Sm^{2+}$ is larger than for $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$. Our experimental results are consistent with this theoretical prediction.

4. Conclusions

For the $Sr_yBa_{1-y}FCl_{0.5}Br_{0.5}:Sm^{2+}$ series, the higher the concentration of Sr, the smaller the energy separations between the ^5D_J levels and the 4f5d band and the larger the $^7F_0 \rightarrow {}^5D_J$ transition probabilities. In the process of photon-gated spectral hole burning by a gated pulsed laser, the hole burning quantum efficiency is theoretically proportional to the $^7F_0 \rightarrow {}^5D_J$ transition probability. The experimental results show that the hole burning efficiency increases with increasing Sr concentration along the series.

Acknowledgements

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