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Section 7. Holeburning

FLUORESCENCE LINE NARROWING AND INHOMOGENEOUS BROADENING OF Sm^{2+} IN $BaFCl_xBr_{1-x}$

Lingfen ZHANG, Jiaqi YU and Shihua HUANG

Changchun Institute of Physics, Academia Sinica, Changchun, China

The variation of inhomogeneous and homogeneous line width with x for Sm^{2+} ions in $BaFCl_xBr_{1-x}$ was studied by fluorescence line narrowing (FLN) and spectral hole-burning (HB). The ratios N of inhomogeneous width to homogeneous width approach a maximum for $x = 0.8$, 0.5. N is about 80 for transition from $^7F_0$ to $^5D_2$ of $BaFCl_{0.5}Br_{0.5}$ at 77 K. The inhomogeneous lines for transitions between ^5D_J and $^7F_0$ of Sm^{2+} ions in $BaFCl_xBr_{1-x}$ ($x = 0.8$, 0.5, 0.2) have novel double-peaked shape. According to the FLN study, these novel shapes are explained by different probabilities of Cl and Br ligand configurations around Sm^{2+}. These novel shapes significantly broaden the inhomogeneous line width of Sm^{2+} and make hole burning available at 77 K. This might have an important implication on frequency domain optical storage.

1. Introduction

The first observation of photon gated hole burning in $BaFCl:Sm^{2+}$ at 2 K was reported in 1985 by R.M. Macfarlane et al. [1]. In previous work [2], we have succeeded in raising the hole burning (HB) temperature to 77 K by adding Br ions to form $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$, which might be important for the application of HB to frequency domain optical storage.

In this paper, we report results on $BaFCl_xBr_{1-x}$. The origin of a novel double-peaked inhomogeneous line shape of $BaFCl_xBr_{1-x}$ ($x = 0.8$, 0.5, 0.2) was clarified by fluorescence line narrowing (FLN) study. The variation of inhomogeneous line width (Γ_i) and homogeneous line width (Γ_h) with x was studied by FLN and HB.

2. Results

Sm^{2+} ions have $4f^6$ configuration. Fluorescence is due to transition from three metastable ^5D_J ($J = 0$, 1, 2) excited states to the ^7F_J ($J = 0, 1, 2, \ldots, 6$) ground states.

The emission spectra of the $^5D_0$–$^7F_0$ transition of Sm^{2+} in BaFCl under nonselective excitation at 337.1 nm of a nitrogen laser is peaked at 14537.5 cm^{-1} with a Γ_i of 2.4 cm^{-1}, while that of $BaFBr:Sm^{2+}$ is peaked at 14551 cm^{-1} with a Γ_i of 2.6 cm^{-1}. However the emission lines of $BaFCl_xBr_{1-x}Sm^{2+}$ ($x = 0.8$, 0.5, 0.2) have a novel double-peaked shape as shown in fig. 1. Their Γ_i are much broader than that for $x = 1$ and $x = 0$ (25 cm^{-1} for $x = 0.8$, 26 cm^{-1} for $x = 0.5$). The line widths are almost the same at 77 K and 300 K. This implies that the main contribution comes from the inhomogeneous broadening for $x = 0.8$, 0.5, 0.2.

FLN spectra of $^5D_0$–$^7F_0$ of $BaFCl_{0.8}Br_{0.2}:Sm^{2+}$ at 77 K excited at different frequencies within the inhomogeneous line width of the $^7F_0$–$^5D_2$ transition, are shown in fig 2. The lines are much narrower and they shift with the excitation wavelength. The intensities of the FLN spectra ($x = 0.8$) reach their maximum at 14523 cm^{-1} and 14538 cm^{-1}. $BaFCl_{0.5}Br_{0.5}$ has similar FLN spectra. Based on the FLN data, we have plotted the inhomogeneous line shapes in fig. 1.

Homogeneous line widths of a transition from $^5D_0$, $^5D_1$ to $^7F_0$ were determined by the FLN method, exciting $^5D_2$. The homogeneous line width of a transition from $^7K_0$ to $^5D_2$ was determined by the HB method, exciting $^5D_2$ and then monitoring emission $^5D_0$–$^7F_0$ while scanning the persistent spectral hole in $^5D_2$. The results are shown in table 1. We can see that Γ_i and Γ_h

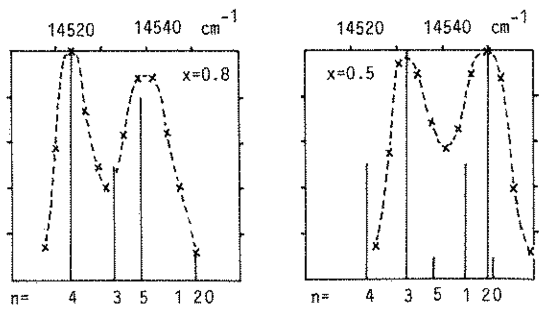

Fig. 1. Measured inhomogeneous line shapes of emission from $^5D_0$ to $^7F_0$ (broken line) and probabilities of ligand configuration Cl_nBr_{5-n} around the Sm^{2+} ion in $BaFCl_xBr_{1-x}$ (vertical line).

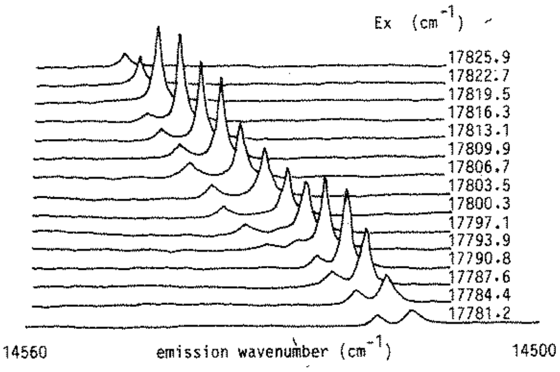

Fig. 2. FLN spectra of a transition from $^5D_0$ to $^7F_0$ of the Sm^{2+} ion in $BaFCl_{0.8}Br_{0.2}$ at 77 K, $^5D_2$ is excited.

reach their maximum at $x = 0.5$. N $(= \Gamma_i/\Gamma_h)$ reaches its maximum at $x = 0.8$ or 0.5. The maximum N is as large as 80 for $^5D_2$ with $x = 0.5$.

3. Discussion

In $BaFCl:Sm^{2+}$, the Sm^{2+} ions substitute at the Ba^{2+} ion sites. The coordination polyhedron of Sm^{2+} consists of four fluorine ions located in a plane perpendicular to the C axis, four chlorine ions in a plane parallel to the fluorine plane, and one extra chlorine ion on the C axis beyond the four chlorine ion planes. X-ray diffraction proves $BaFCl_xBr_{1-x}:Sm^{2+}$ to be a solid solution with the same structure of $BaFCl:Sm^{2+}$. Chlorine and bromine ions occupy the chlorine ion places of BaFCl randomly. This will affect local crystal field strength and symmetry at the Sm^{2+} site. It is expected that an inhomogeneous line width of $BaFCl_xBr_{1-x}:Sm^{2+}$ with $x = 0.8$, 0.5, 0.2 is much broader than that for $x = 1$ and 0. However a simple statistical factor should make a single peaked Gaussian line shape. The double-peaked shape as shown in fig. 1 is novel. The origin of this novel shape is discussed as follows.

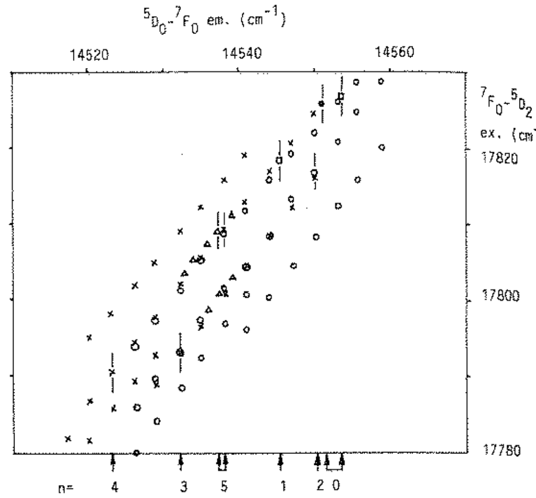

Fig. 3. Variations of the FLN peak of the transition from $^5D_0$ to $^7F_0$ with an excitation wavenumber of transition from $^7F_0$ to $^5D_2$ of Sm^{2+} in $BaFCl_xBr_{1-x}$ at 77 K. △, $x = 1$; ×, $x = 0.8$; ○, $x = 0.5$; □, $x = 0.2$; •, $x = 0$.

The FLN data for different x are shown in fig. 3. The bars indicate the maximum positions of emission intensity when the excitation wavelength varies.

From fig. 3, we see that there are two excitation lines for each emission wavelength of $BaFCl:Sm^{2+}$. This is easily understood. Sm^{2+} ions in BaFCl replace the Ba^{2+} ion surrounded by five Cl ions and has C_{4v} symmetry. The $^5D_2$ state splits into four sublevels in the C_{4v} crystal field, but only has two allowed transitions to the ground state $^7F_0$. The FLN spectra of $BaFCl:Sm^{2+}$ have their maximum at 14537.5 cm^{-1}. Naturally, 14537.5 cm^{-1} is assigned to an Sm^{2+} ion surrounded by five chlorine ions, we indicate this by an arrow with $n = 5$ in fig. 3.

For $x \neq 1$ or 0, the ligands Cl and Br around Sm^{2+} have different configurations with different probabili-

Table 1
Inhomogeneous line width (Γ_i), homogeneous line width (Γ_h) and ratio N $(= \Gamma_i/\Gamma_h)$ of Sm^{2+} in $BaFCl_xBr_{1-x}$ at 77 K

Transition	Parameter	$BaFCl_xBr_{1-x}:Sm^{2+}$ $x =$ 1	0.8	0.5	0.2	0	Measured by
$5D_0-^7F_0$	Γ_i (cm^{-1})	2.4	25	26	10	2.6	FLN
	Γ_h (cm^{-1})	0.23	0.66	0.78	0.36	0.29	
	$N = \Gamma_i/\Gamma_h$	10	38	33	28	9	
$^5D_0-^7F_1$	Γ_i	2.3	25	40	10	5	FLN
	Γ_h	0.42	0.78	1.3	1.0	0.36	
	N	5.5	38	30	10	14	
$^7F_0-^5D_2$	Γ_i	3.3	35	40	16	5	HB
	Γ_h		0.48	0.5	0.35		
	N		73	80	46		

Table 2
Probability of ligand configuration Cl_nBr_{5-n} around Sm^{2+} in $BaFCl_xBr_{1-x}$

	$x=1$	$x=0.8$	$x=0.5$
Cl_5	1	0.32768	0.03125
Cl_4Br	0	0.4096	0.15625
Cl_3Br_2	0	0.2048	0.3125
Cl_2Br_3	0	0.0512	0.3125
$ClBr_4$	0	0.0064	0.15625
Br_5	0	0.00032	0.03125

ties as shown in table 2. $BaFCl_{0.8}Br_{0.2}:Sm^{2+}$ has the most probable ligand configuration of Cl_5, Cl_4Br next. So we assign a maximum at 14538 cm^{-1} for $BaFCl_{0.8}Br_{0.2}:Sm^{2+}$ in fig. 3 to the ligand configuration Cl_5, since it nearly coincides with the 14537.5 cm^{-1} maximum of $BaFCl:Sm^{2+}$. Another maximum at 14523 cm^{-1} is assigned to the ligand configuration of Cl_4Br. For $x=0.5$, the most probable ligand configurations are Cl_3Br_2 and Cl_2Br_3, so the maximums at 14532 cm^{-1} and 14550 cm^{-1} are assigned to Cl_3Br_2 and Cl_2Br_3 respectively. The maximum at 14551 cm^{-1} of $BaFBr:Sm^{2+}$ is assigned to the Br_5 ligand configuration. Hence, the maximum at 14554 cm^{-1} of $BaFCl_{0.2}Br_{0.8}:Sm^{2+}$ is assigned to Br_5, and another maximum at 14545 cm^{-1} to $ClBr_4$. According to these assignments, the probabilities of different ligand configurations Cl_nBr_{5-n} are shown in fig. 1 using vertical lines with different heights. Comparing the measured inhomogeneous shape with envelope of probabilities of different ligand configurations and considering that each ligand configuration has its own Gaussian inhomogeneous line shape, we find that the double-peaked inhomogeneous shapes can be explained by envelopes over contributions from different ligand configurations.

From fig. 1, we estimate the inhomogeneous line width of each ligand configuration to be about 8 cm^{-1}, which are caused by strain in the solid solution $BaFCl_xBr_{1-x}$.

4. Conclusion

It is found that $BaFCl_xBr_{1-x}:Sm^{2+}$ ($x=0.8$, 0.5, 0.2) have novel double-peaked inhomogeneous line shapes for transitions between ^5D_J and $^7F_0$ of Sm^{2+}. According to the FLN study, these novel shapes are explained by different probabilities of ligand configuration Cl_nBr_{5-n} around Sm^{2+}. These novel shapes significantly broaden the inhomogeneous line widths of Sm^{2+} and make hole burning available at 77 K. The variation of inhomogeneous and homogeneous line widths with x was studied. The ratio N of inhomogeneous width to homogeneous width approached a maximum at $x=0.8$, 0.5. N is as large as 80 for the transition $^7F_0-^5D_2$ of $BaFCl_{0.5}Br_{0.5}$ at 77 K.

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