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# Configurational effects in the nonradiative $^5D_2$–$^5D_1$ transition processes of $Sm^{2+}$ in $BaFCl_xBr_{1-x}$ mixed crystals

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**Abstract**

The nonradiative $^5D_2$–$^5D_1$ transition processes of $Sm^{2+}$ in $BaFCl_xBr_{1-x}$ mixed crystals are investigated by using spectroscopic techniques in the thermal range 15–110 K. We found that the $Sm^{2+}$ centers in different local configurations have different nonradiative $^5D_2$–$^5D_1$ transition rates due to the indirect processes which occur through the $4f^55d$ band as intermediary. This characteristic leads to the fact that the inhomogeneous spectral distribution is strongly temperature dependent. It is observed that the different nonradiative rates are caused by the different positions of the low-lying $4f^55d$ states of the $Sm^{2+}$ ions in local configurations.

## 1. Introduction

Numerous papers have been devoted to the investigations on the nonradiative f–f transition processes of $Sm^{2+}$ in alkaline earth fluoride and halofluoride lattices [1–7]. The processes have been found to include a direct multiphonon f–f transition and an indirect multiphonon f–(d)–f transition which occurs through the $4f^55d$ band as intermediary. Gacon and co-workers [6,7] performed measurements of the temperature dependence of the nonradiative $^5D_2$–$^5D_1$ transition rates in BaFCl:$Sm^{2+}$ and obtained that the thermal activation upwards to the $4f^55d$ band is a dominant process causing thermal quenching of the $^5D_2$ level.

$BaFCl_xBr_{1-x}$:$Sm^{2+}$ mixed crystals were first prepared for high temperature spectral hole burning [8], which has a potential application in high density optical storage. The energy level scheme of $Sm^{2+}$ in this system was observed to be similar to that in BaFCl because $BaFCl_xBr_{1-x}$ has the same structure as BaFCl, which belongs to the PbFCl-type family, from the results of X-ray diffraction [9]. In $BaFCl_xBr_{1-x}$:$Sm^{2+}$ lattices, a $Sm^{2+}$ ion replacing a $Ba^{2+}$ ion is surrounded by five nearest halo-ligands $Cl^-$ and $Br^-$ ions which form 6 different clusters, $Cl_nBr_{5-n}$ ($n = 0, 1, \ldots, 5$) [10]. Recently, Jaaniso et al. [11] developed a model to describe the inhomogeneous broadening of optical spectra in substitutionally disordered crystals, which was compared to the experimental f–f fluorescence spectra of $Sm^{2+}$ in $SrFCl_xBr_{1-x}$ at 30 K. 12 different local configurations in the 6 clusters in $SrFCl_xBr_{1-x}$:$Sm^{2+}$ were observed in the fluorescence spectra and considered to describe the inhomogeneous spectral distributions.

We found in $BaFCl_xBr_{1-x}$:$Sm^{2+}$ that the $Sm^{2+}$


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ions in different local configurations have largely different nonradiative $^5D_2$–$^5D_1$ transition rates. This characteristic results in the inhomogeneous spectral distribution being strongly temperature dependent. An investigation of the configuration dependent nonradiative transition is important not only for understanding the fluorescence properties, but also for comprehending the spectral hole burning dynamics and spectral hole shape in this system. We have previously studied the temperature dependence of the fluorescence of $Sm^{2+}$ in $BaFCl_{0.5}Br_{0.5}$ [12]. This focused on the average effect of the fluorescence intensity. The variation in the inhomogeneous spectral distribution with temperature due to configurational effects was not investigated in detail. This Letter presents a study of the configurational dependent nonradiative $^5D_2$–$^5D_1$ transition processes in $BaFCl_xBr_{1-x}:Sm^{2+}$ using spectroscopic techniques.

## 2. Experimental

$BaFC_xBr_{1-x}:Sm^{2+}$ samples with different values of the composition $x$ were made by mixing different stoichiometric amounts of previously prepared $BaF_2$, $BaCl_2$ and $BaBr_2$ all doped nominally with 1% $SmF_3$. The ground mixtures were heated to 900°C under a $H_2$ reduction atmosphere and kept at this reaction condition for 2 h before being slowly cooled down. In measuring the fluorescence excitation spectra within the $^7F_0$–$^5D_2$ transition, a tunable dye laser with laser linewidth of 0.2 $cm^{-1}$, pumped by a pulsed Quanta-Ray DCR-2A Nd:YAG with a repetition frequency of 10 Hz, was used to scan the $^7F_0$–$^5D_2$ transition while the fluorescence from the $^5D_2$–$^7F_3$ or $^5D_1$–$^7F_0$ transition was monitored by a D330 spectrometer. The same dye laser was also used to perform two photon spectral hole burning. The duration of each pulse was 10 ns. In measuring the fluorescence spectra, a 337.1 nm line from a nitrogen laser or a 570 nm line from the dye laser was used as the excitation source. The fluorescence was detected by a Spex-1403 monochromator. In the measurements of both the excitation spectra and the fluorescence spectra, the signal was recorded 50 μs after each exciting pulse with a sampling time of 5 μs. Different temperatures were obtained by using a closed cycle refrigerator.

## 3. Results and discussion

It was in $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ that we first observed that $Sm^{2+}$ centers have different nonradiative $^5D_2$–$^5D_1$ transition rates. Fig. 1 shows the time decay patterns of the $^5D_2$–$^7F_3$ and $^5D_1$–$^7F_0$ transitions in $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ and $BaFCl:Sm^{2+}$ under selective excitation of the $^5D_2$ level at 77 K. Under these excitation conditions, the population of the $^5D_1$ level is completely from the $^5D_2$ level through nonradiative transition. Then an increase with a maximum occurring at time $t_{max} = [\tau_1\tau_2/(\tau_1 - \tau_2)]\ln(\tau_1/\tau_2)$ is expected and observed in $BaFCl:Sm^{2+}$ as shown in Fig. 1; The $\tau_1$ and $\tau_2$ are the lifetimes of the $^5D_1$ and $^5D_2$ levels, obtained from the tails of the decay patterns of the $^5D_1$ and $^5D_2$ levels, respectively. The obtained $\tau_1$ and $\tau_2$ in $BaFCl:Sm^{2+}$ at 77 K are 760 and 130 μs, respectively. They yield $t_{max} = 277$ μs, which is in agreement with the experimental result presented in Fig. 1. The obtained $\tau_1$ and $\tau_2$ in $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ at 77 K are 780 and 280 μs, respectively. They yield $t_{max} = 448$ μs. However, no increase was observed in the decay pattern of the $^5D_1$–$^7F_0$ transition in $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$. A reasonable explanation for this result is that the $Sm^{2+}$ centers have a different nonradiative $^5D_2$–$^5D_1$ transition rate due to an indirect process involving the $4f^55d$ band, and some $Sm^{2+}$ centers have fast indirect processes. This ex-

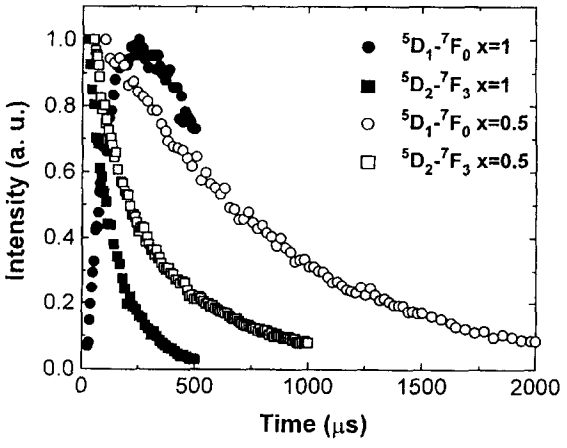


Fig. 1. The time decay patterns of the $^5D_2$–$^7F_3$ and $^5D_1$–$^7F_0$ transitions in $BaFCl:Sm^{2+}$ and $BaFCl_{0.5}Br_{0.5}:Sm^{2+}$ at 77 K under selective excitation of the $^5D_2$ level.

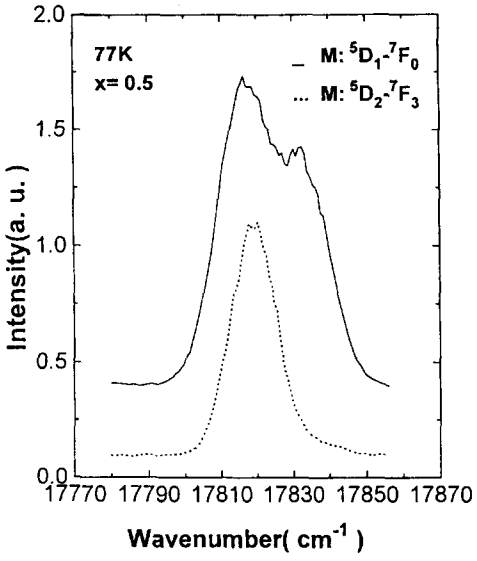


Fig. 2. Excitation spectra of the $^7F_0$–$^5D_2$ transitions by monitoring (M) the $^5D_2$–$^7F_3$ and $^5D_1$–$^7F_0$ emissions of $Sm^{2+}$ in $BaFCl_{0.5}Br_{0.5}$ at 77 K.

planation is based on the consideration that the $Sm^{2+}$ ions are surrounded by different local configurations in this system [10,11], the 5d Stark states are subject to considerably larger crystal field effects than the 4f states [1,3,4], and the $^5D_2$ level is in the proximity of the low-lying $4f^5 5d$ states [1,5–7]. In this case, the decay processes in $BaFCl_{0.5}Br_{0.5}$:$Sm^{2+}$ are described briefly as follows. The $Sm^{2+}$ centers having faster nonradiative processes quickly relax to the $^5D_1$ states and those having slower nonradiative processes remain in the $^5D_2$ states after excitation of the $^5D_2$ level. In this way, the fact that no increase is observed in the decay pattern of $^5D_1$ corresponds to the faster centers, and the obtained decay pattern of $^5D_2$ corresponds to the slower centers. Therefore, the fluorescence from the $^5D_2$ and $^5D_1$ states originate from the slower and faster $Sm^{2+}$ centers, respectively. These different $Sm^{2+}$ centers can be separated in the excitation spectra within the $^7F_0$–$^5D_2$ transitions when the $^5D_2$–$^7F_J$ and $^5D_1$–$^7F_J$ emissions are monitored, respectively. To separate these centers, we obtain the excitation spectra at 77 K by monitoring the $^5D_2$–$^7F_3$ and $^5D_1$–$^7F_0$ emissions, respectively, as shown in Fig. 2. The spectral distributions for $^5D_2$–$^7F_3$ and $^5D_1$–$^7F_0$ are clearly different. The spectrum for $^5D_2$–$^7F_3$ presents one band, while the spectrum for $^5D_1$–$^7F_0$ presents two broad bands. These bands are attributed to the different local configurations in the $Cl_nBr_{5-n}$ clusters formed by 5 nearest neighboring $Cl^-$ and $Br^-$ ions around a $Sm^{2+}$ ion according to an investigation of the inhomogeneous broadening of $Sm^{2+}$ in $MFCl_xBr_{1-x}$ mixed crystals (M = Ba, Sr) [10,11]. Hence, the different spectral distributions shown in Fig. 2 are caused by the different local configurations having different nonradiative $^5D_2$–$^5D_1$ transition rates. This assertion is also supported by the fact that no difference is observed between the excitation spectra of the $^5D_2$–$^7F_3$ and $^5D_1$–$^7F_0$ emissions in both the BaFCl:$Sm^{2+}$ and BaFBr:$Sm^{2+}$ systems.

In order to study the nonradiative processes of different local configurations, the excitation spectra are recorded at numerous temperatures between 15 and 110 K in $BaFCl_xBr_{1-x}$:$Sm^{2+}$ for $x = 0.8$ and

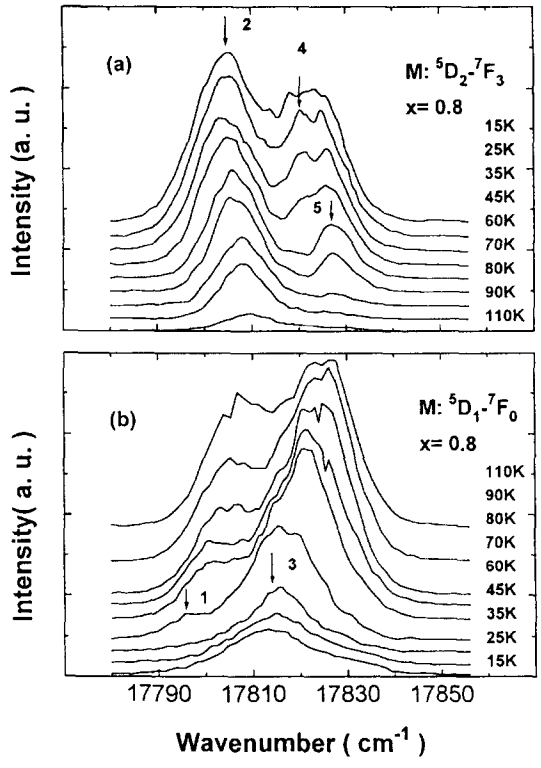


Fig. 3. Excitation spectra of the $^7F_0$–$^5D_2$ transitions by monitoring (M) the $^5D_2$–$^7F_3$ (a) and $^5D_1$–$^7F_0$ (b) emissions of $Sm^{2+}$ in $BaFCl_{0.8}Br_{0.2}$ at different temperatures. The cluster $Cl_nBr_{1-n}$ is labeled with '$n$'.

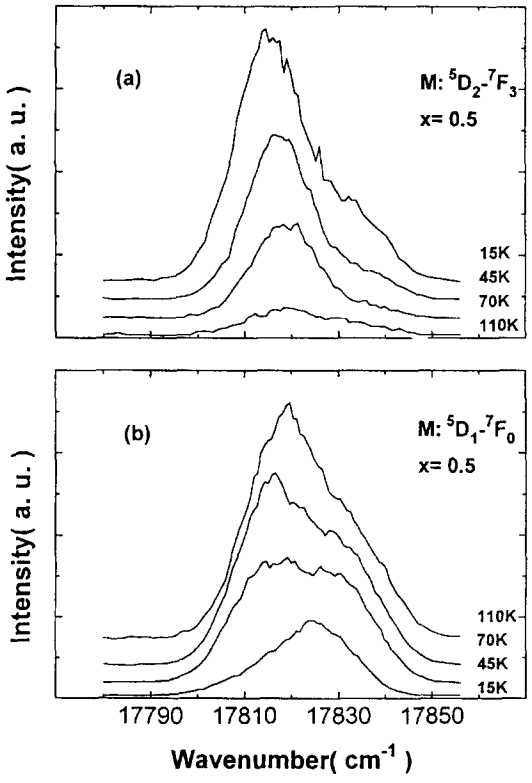


Fig. 4. Excitation spectra of the $^7F_0$–$^5D_2$ transitions by monitoring (M) the $^5D_2$–$^7F_3$ (a) and $^5D_1$–$^7F_0$ (b) emissions of $Sm^{2+}$ in $BaFCl_{0.5}Br_{0.5}$ at different temperatures.

0.5, respectively, as shown in Figs. 3 and 4. The spectra show that the fluorescence intensity of $^5D_2$–$^7F_3$ decreases following the growth of $^5D_1$–$^7F_0$ emissions with the increase in temperature. This feature results from the nonradiative $^5D_2$–$^5D_1$ transition process. The behavior that the excitation spectra of $^5D_2$–$^7F_3$ and $^5D_1$–$^7F_0$ are different for each $x$, and that the spectral distributions change considerably with variations in temperature indicates different nonradiative $^5D_2$–$^5D_1$ transition rates in different configurations, which are frequency dependent.

In Fig. 3 the excitation spectra of $^5D_2$–$^7F_3$ and $^5D_1$–$^7F_0$ in $BaFCl_{0.8}Br_{0.2}$:$Sm^{2+}$ totally consist of five resolvable bands. According to the results of the investigation on the inhomogeneous broadening of optical spectra in $SrFCl_xBr_{1-x}$:$Sm^{2+}$ [11], the five bands in the spectra from the high energy side to the low-energy side mainly correspond to the configurations in the clusters $Cl_nBr_{5-n}$ with $n = 5$, 4, 3, 2 and 1, respectively. The cluster with $n = 0$ is not observed at the low-energy side of the band $n = 1$ because of the small number of this cluster for $x = 0.8$. These different clusters are labeled with values of $n$, as shown in Fig. 3. In the spectra of $BaFCl_{0.5}Br_{0.5}$:$Sm^{2+}$ the different clusters cannot be resolved because the disorder of substitution reaches a maximum following the maximal band width for an individual configuration at $x = 0.5$ [10,11]. The spectra presented in Figs. 3 and 4 show that the differences in the nonradiative $^5D_2$–$^5D_1$ transition rates in different configurations for the same composition $x$ are large. Some configurations can completely relax from $^5D_2$ to $^5D_1$ and give fluorescence from $^5D_1$ even at 15 K, such as the $n = 3$ band in Fig. 3(b). Some configurations remain in the $^5D_2$ states until a sufficiently high temperature. For instance, the $n = 2$ band in Fig. 3(a) is quenched at 110 K. The different quenching temperatures of the $^5D_2$ levels may be due to the different positions of the low-lying $4f^55d$ states which are governed by local configurations. To examine this consideration, we measured the fluorescence spectra for different excitation wavelengths.

Fig. 5 shows the fluorescence spectra of the $^5D_2$–$^7F_0$ transition in $BaFCl_{0.8}Br_{0.2}$:$Sm^{2+}$ at 77 K on

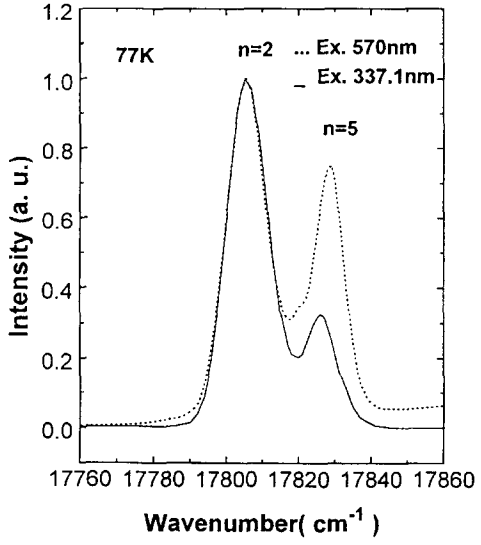


Fig. 5. Fluorescence spectra of the $^5D_2$–$^7F_0$ transitions in $BaFCl_{0.8}Br_{0.2}$:$Sm^{2+}$ at 77 K under 570 and 337.1 nm pulsed laser line excitations.

excitation of the $4f^5 5d$ band by 337.1 and 570 nm laser lines. The spectra exhibit a growth of the $n = 5$ band by using the 570 nm line instead of 337.1 nm line to excite the system. Considering that the 570 nm line excites the edge of the $4f^5 5d$ absorption band, the growth of the $n = 5$ band is interpreted as the low-lying $4f^5 5d$ states of the $Cl_5Br_0$ cluster being located at a lower position than the $Cl_2Br_3$ cluster. In this case, on one hand, the $Cl_5Br_0$ cluster is more effectively excited by the 570 nm line than the $Cl_2Br_3$ cluster, so the growth of the $n = 5$ band is expected; on the other hand, the $Cl_5Br_0$ cluster should have a smaller thermal activation energy than the $Cl_2Br_3$ cluster. This deduction has been supported by the fact that the quenching temperature of the $n = 5$ band is lower than that of the $n = 2$ band, as shown in Fig. 3(a). The fluorescence spectra for $x = 0.5$ and 0.25 are also measured under different excitation wavelengths. We obtain the same conclusion that the spectral distribution is dependent on the excitation wavelength, and the faster $Sm^{2+}$ centers are in favor of a longer excitation wavelength. As a result, the positions of the low-lying $4f^5 5d$ states of the $Sm^{2+}$ ions in different configurations are different, the faster centers have lower positions of the $4f^5 5d$ states.

To understand whether the configuration has an effect on the direct f–f transition rate of $Sm^{2+}$ in $BaFCl_xBr_{1-x}:Sm^{2+}$. We performed the following experiments. We measured the time resolved excitation spectra of the $^5D_1$–$^7F_0$ emission within the $^7F_0$–$^5D_2$ transition at 120 K. At this temperature the $^5D_2$ level is quenched, the nonradiative transition from $^5D_2$ to $^5D_1$ is rapidly finished after the exciting pulse. Subsequently the $^5D_1$ level begins to decay without feeding from $^5D_2$. We found that the spectral distributions do not vary with delay times for each $x$. The experiment shows that the different configurations have the same lifetime of the $^5D_1$ level, i.e. the same radiative transition rate from $^5D_1$ to the ground state and the same $^5D_1$–$^5D_0$ direct multiphonon transition rate. In the $^5D_1$–$^5D_0$ nonradiative processes, the upward nonradiative transitions from $^5D_1$ to $^5D_2$ and the $4f^5 5d$ band can be neglected in the range of temperatures investigated because the energy gap between $^5D_2$ and $^5D_1$ is around 1940 $cm^{-1}$ and that between the low-lying $4f^5 5d$ states and $^5D_1$ is larger than 1940 $cm^{-1}$. Hence, the nonradiative $^5D_1$–$5D_0$ process is determined by the direct process.

We have performed spectral hole burning in different configurations in the $^7F_0$–$^5D_2$ transitions under the same conditions. The same hole areas are probed in different configurations. This means that the radiative transition rate of the $^5D_2$ level is also configuration independent. The lifetimes of $^5D_2$, $^5D_1$ and $^5D_0$ for different $x$ are measured at 15 K when the system is excited into the $4f^5 5d$ band by the 337.1 nm laser line. We observed that the lifetimes are almost unchanged with different $x$. It is worth stressing that the obtained lifetimes of $^5D_2$ correspond to slow centers in which the indirect processes can be neglected at 15 K, although the fast $Sm^{2+}$ centers still have a large nonradiative $^5D_2$–$^5D_1$ transition rate at this temperature. From the experimental results mentioned above, we consider that the direct f–f transition rate is configuration and composition independent in $BaFCl_xBr_{1-x}:Sm^{2+}$. Under this condition, the fact that the excitation spectral distributions of $^5D_2$–$^7F_3$ and $^5D_1$–$^7F_0$ are different, as well as the spectral distribution being strongly temperature dependent definitely arises from the largely different indirect nonradiative $^5D_2$–$^5D_1$ transition rates for different local configurations.

## 4. Conclusions

The $Sm^{2+}$ centers in different local configurations in $BaFCl_xBr_{1-x}$ have largely different nonradiative $^5D_2$–$^5D_1$ transition rates due to the different positions of the low-lying $4f^5 5d$ states. This characteristic leads to the fact that the inhomogeneous spectral distribution is strongly temperature dependent. The results of this study are helpful for probing the local environments of $Sm^{2+}$ ions in $MFCl_xBr_{1-x}$ (M = Mg, Ca, Sr, Ba) mixed crystals and for comprehending the dephasing process and the spectral hole shape involved in the spectral hole burning of these systems.

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