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Importance of defect clustering in the analysis of $BaF_2:Er^{3+}$ optical spectra

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A description of the site distribution in rare-earth-doped BaF_2 crystals cannot be complete without the inclusion of cluster sites made up of two or more interacting dopant ions. Villermain-Lecolier *et al.* observed two transitions in the far-infrared spectrum of BaF_2:Er^{3+} which they assigned to two different sites, possibly the trigonal and tetragonal sites. They described the absorption band at 131 cm^{-1} considering contributions from only single Er^{3+}-F_I^- sites. An alternative explanation for their observations is presented considering the existence of cluster sites in the crystal and the validity of a description including only single pair sites is questioned.

Although numerous studies have been conducted on the BaF_2 lattice doped with low concentrations of Er^{3+}, a full understanding of the nature and concentration of the various charge-compensated sites that can be formed is far from being realized. Numerous experiments have permitted the identification of three inequivalent sites in which the compensating fluorine ion is in either tetragonal, or cubic symmetry relative to the Er^{3+} dopant ion.[1-6] On the basis of these experiments, it has long been assumed that these were the important sites at all concentration levels. In a previous paper[7] (hereafter referred to as I), we have used narrow-band laser excitation techniques to show that many other sites are present as well. These additional sites were found to consist of clusters of two or more Er^{3+} ions spatially located close together in the lattice and capable of undergoing rapid and efficient energy-transfer processes between the Er^{3+} ions spatially located close together in the lattice and capable of undergoing rapid and efficient energy-transfer processes between the Er^{3+} ions within the site. These sites probably correspond to the clustered fluoride interstitial ions observed by Steele *et al.*[8] and the dimers identified by Mustafa *et al.*[9] by NMR measurements. We believe that consideration of the high concentration of these cluster sites relative to that single Er^{3+}-F_I^- pair sites leads to an alternative explanation of the results reported by Villermain-Lecolier *et al.*[10,11] By studying the ground-state $^4I_{15/2}$ manifold of Er^{3+} in BaF_2 using far-infrared techniques, they observed two strong electronic transitions superimposed on the BaF_2 phonon spectrum at 69.2 and 70.3 cm^{-1}, which was stated to be in good agreement with the luminescence data of Aizenberg *et al.* for the trigonal site. They note also in Ref. 11 that the assumption made by Aizenberg *et al.* of one trigonal site with levels at 70 and 76 cm^{-1} might have to be revised because upon application of a magnetic field, the lines observed by Villermain-Lecolier *et al.* at 69.2 and 70.3 cm^{-1} split into four with two sets of inequivalent Landé g factors. This led them to believe that the two transitions were, in fact, arising from two different sites. In Ref. 10 they compared their lines at 69.2 and 70.3 cm^{-1} with the trigonal lines found by Aizenberg *et al.* at 70, 76, 80, and 88 cm^{-1} and the tetragonal line found by Zverev *et al.* at 70 cm^{-1} and speculated that the 70-cm^{-1} lines of the trigonal and tetragonal sites could be the two transitions they observed. They note, however, that the g factors they measure differ from those of the trigonal or cubic sites previously reported.[2] Our experiments confirm the assignments and energies of Aizenberg *et al.* for the trigonal site transitions and indicate that what Villermain-Lecolier *et al.* have perhaps observed is a cluster site, most likely one which we have arbitrarily designated as the J site. This site has a ground-state splitting that agrees very well with the splitting observed by Villermain-Lecolier *et al.* but the absolute energies do differ significantly. We also believe that our data invalidates their approach to deconvoluting the observed absorption band at 131 cm^{-1} into components arising from only single pair sites. At the concentrations of dopant used, our data indicates that the cluster site concentration is dominant. Any deconvolution, then, would require consideration from this source which can exist in a number of possible configurations.

The experimental apparatus and procedure used to selectively excite the individual charge compensated sites has been described in detail previously.[12-14] Our crystals are obtained from Optovac (North Brookfield, Mass.) and have shown identical spectra to those of all other workers for oxygen-free samples. Although there are changes in site distribution between crystals with different temperature histories, there are no changes in the types of sites or the fundamental defect chemistry that governs site concentrations. Figure 1 shows

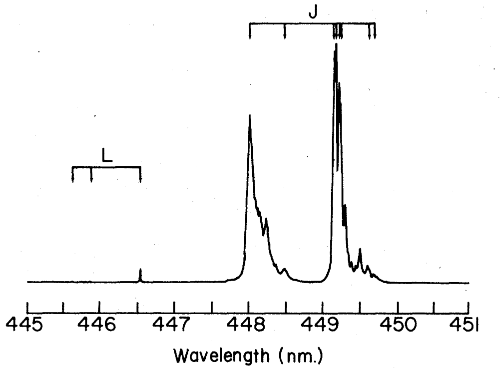

FIG. 1. $^4I_{15/2} \rightarrow {}^4F_{5/2}$ excitation spectra monitoring $^4S_{3/2} \rightarrow {}^4I_{15/2}$ fluorescence from all crystalline sites in BaF_2:0.20-mole%-Er^{3+}. The wavelength is that of the dye laser. The unidentified transitions arise from the remaining five cluster sites and are identified in Ref. 7.

the $^4F_{5/2}$ excitation spectrum obtained while monitoring fluorescence from all sites by using a broad 7-nm bandwidth in the BaF_2:0.20-mole%-Er^{3+} crystal, the same concentration of Er^{3+} examined by Villermain-Lecolier *et al.* The excitation spectra for each site is obtained by monitoring individual site fluorescence lines and scanning the dye laser over the excitation manifold. The $^4F_{5/2}$ excitation spectra for the sites we have designated as L and J are shown in Fig. 2(a) and 2(b) monitoring $^4S_{3/2}$ fluorescence. In I we have identified the L site as a single Er^{3+}-F_I^- pair site and J as a cluster site, based on the concentration dependences, the number of transitions, and the lack of or presence of energy transfer processes, since only clusters are capable of the efficient energy transfer observed. We have also identified five additional cluster sites which make up the remainder of the excitation spectrum shown in Fig. 1. These will not be discussed further here, but are described in detail in I.

By exciting a $^4I_{15/2} \rightarrow {}^4F_{5/2}$ transition characteristic of the L site, the $^4S_{3/2}$ fluorescence spectrum of the L site was obtained. It was found to be in excellent agreement with that of Aizenberg *et al.*[4] for the site they identified as trigonal. The comparison is shown in Table I. Our values for the first two excited Stark levels of the $^4I_{15/2}(Z)$ manifold agree well with Aizenberg *et al.*; i.e., $Z_2 = 70.0$ cm^{-1}, $Z_3 = 75.9$ cm^{-1} as compared with 70 and 76 cm^{-1}. In addition, excitation spectra taken monitoring any of the $E_1;E_2 \rightarrow Z_1;Z_2;Z_3$ lines are all identical, proving they all belong to one site. Careful study revealed no indication of any energy transfer processes or other cluster site behavior in this site. Thus, our studies confirm the transition frequencies given by Aizenberg *et al.* and show that all transitions result from one single Er^{3+}-F_I^- pair site.

When Villermain-Lecolier *et al.* applied a magnetic field, the Zeeman splitting of the two lines at 69.2 and 70.3 cm^{-1} showed different g factors for each line, with $g_\parallel = g_2 = 3.6$ and $g_\parallel = g_2 = 0.98$. They speculated that perhaps they were seeing one trigonal and one tetragonal site, but noted that their g factors disagreed considerably with those reported by Antipin *et al.*[2] for the trigonal ($g_\parallel = 6.734$) and cubic sites ($g_\parallel = 6.755$). Also, Zverev and Smirnov[1] have reported g factors of 5.908 ± 0.010 and 7.411 ± 0.010 for the tetragonal site, again in poor agreement. We believe that Villermain-Lecolier *et al.* observed two transitions in a dimer or cluster site, and the different g factors are the result of the different crystal fields felt by the two ions in the site. In I, we presented evidence that the cluster sites do, in general, give rise to more than $\frac{1}{2}(2J+1)$ lines, the maximum allowable for a single Er^{3+}-F_I^- pair. This indicates that the two ions present in the cluster are, in fact, under the influence of different crystal fields and the g factors would be expected to be inequivalent. The efficient energy transfer between ions

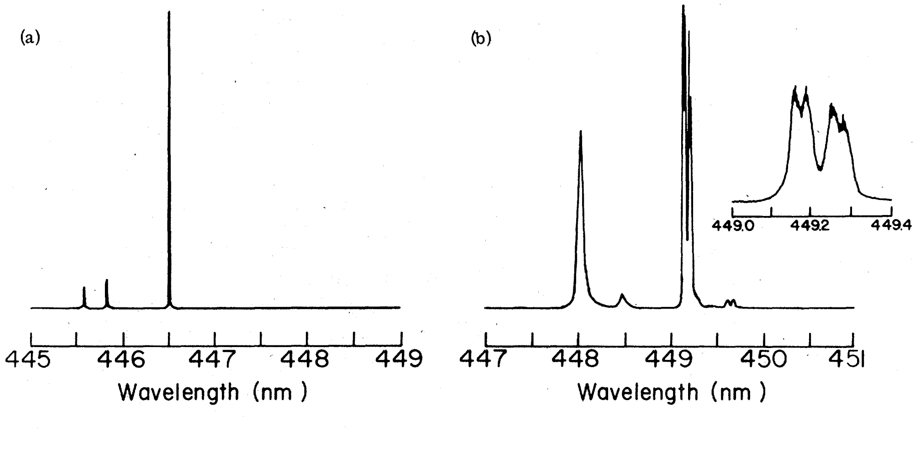

FIG. 2. $^4I_{15/2} \rightarrow {}^4F_{5/2}$ excitation spectra in BaF_2: 0.20-mole%-Er^{3+} monitoring fluorescence from $^5S_{3/2} \rightarrow {}^4I_{15/2}$ for the (a) L site, monitoring 540.49 nm; (b) J site, monitoring 545.05 nm.

TABLE I. ${}^4S_{3/2} \rightarrow {}^4I_{15/2}(E \rightarrow Z)$ transitions for the trigonal (L) site in BaF_2:Er^{3+}.

Aizenberg *et al.*[4]	Present study	Transition
5378.8	5378.4	$E_2 \rightarrow Z_1$
5384.6	5384.2	$E_1 \rightarrow Z_1$
5399.1	5398.6	$E_2 \rightarrow Z_2$
5401.2	5400.3	$E_2 \rightarrow Z_3$
5405.1	5404.9	$E_1 \rightarrow Z_2$
5406.8	5406.4	$E_1 \rightarrow Z_3$
	5418.4	
	5429.5	
	5433.8	
	5439.5	
	5461.8	
	5477.1	
	5483.1	
	5488.9	
5509.4	5509.2	$E_2 \rightarrow Z_4$
5514.4	5514.2	$E_2 \rightarrow Z_5$
5515.6	5515.2	$E_1 \rightarrow Z_4$
5520.7	5520.5	$E_1 \rightarrow Z_5$
	5531.4	$(E_2 \rightarrow Z_6)$
5539.0		$E_1 \rightarrow Z_6$
5542.7	5543.4	$E_1 \rightarrow Z_7$

causes the lines of one ion to appear in the spectrum of the second ion. Figure 1 shows that in the BaF_2:0.20-mole%-Er^{3+} crystal, the major contribution to the total fluorescence intensity arises from the J site, with that from the L site being much smaller. The excitation spectra of the ${}^4F_{9/2}$, ${}^4S_{3/2}$, and ${}^4F_{7/2}$ for the J site have all shown the existence of two closely spaced transitions, separated by ~ 1 cm^{-1}, as the lowest energy transitions. These arise from transitions from the Z_1 and Z_2 levels in the ${}^4I_{15/2}$ manifold, separated by 1 cm^{-1}, to the lowest energy Stark level of the excited manifold. Expansion of the J site ${}^4F_{5/2}$ excitation spectrum shown in Fig. 2(b) showed indication of splitting in the two weak lines at 449.66 and 449.74 nm, although they could not be resolved. The splitting shown in the inset in Fig. 2(b) for the higher Stark multiplets of the ${}^4F_{5/2}$ manifold is apparent and has an average value of 1.2 cm^{-1}. In addition, the ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ fluorescence spectrum of the J site was found to have a splitting of ~1 cm^{-1}, indicative of transitions from E_1 to Z_1 and Z_2 of the J site. We believe that the 1.1-cm^{-1} splitting attributed by Villermain-Lecolier *et al.* to excited levels of the ${}^4I_{15/2}$ manifold is actually the ground-state splitting of the J site. We have observed a transition in the ${}^4S_{3/2}$ fluorescence spectrum at 18 343 cm^{-1} which results from the $E_1 \rightarrow Z_3$ transition of the J site, placing Z_3 at 75 and 74 cm^{-1} above the Z_1 and Z_2 levels, respectively. Although the splitting we observed agrees very well with that of Villermain-Lecolier *et al.* (1.2 cm^{-1} as compared with 1.1 cm^{-1}), the transitions at 74 and 75 cm^{-1} do not agree with their reported values of 69.2 and 70.3 cm^{-1}. Our frequencies were calibrated by superimposing the spectrum of an iron hollow cathode lamp onto the fluorescence spectrum of the BaF_2:Er^{3+} crystal. The iron-neon lines are tabulated with an accuracy of ~ 0.002 nm and the fluorescence line frequencies can be calculated by linear interpolation with a reproducibility of ~0.25 cm^{-1}. Although modern far-infrared instruments allow measurement to 0.1 cm^{-1}, the absolute calibration of these instruments can vary with time. It is difficult to evaluate the accuracy of the values given by Villermain-Lecolier *et al.* since the calibration procedure used was not reported. We believe that neither of the two transitions observed by Villermain-Lecolier *et al.* arises from the trigonal site of Aizenberg *et al.* but instead from a cluster site; most likely from the J site identified in I.

Villermain-Lecolier *et al.* also reported the observation of an absorption band in BaF_2 doped with Nd^{3+} at 131 cm^{-1} and described it in terms of five Lorentzian oscillators. These five oscillators were required if the band was composed of contributions from cubic, tetragonal, and trigonal sites. The relative concentration of each of these single-pair sites was calculated by adjusting the relative contribution from each site. However, no contribution to this band profile was considered from cluster sites. Although the band they considered was observed in BaF_2 doped with 0.17-mole%-Nd^{3+}, a similar band was observed in BaF_2:Er^{3+}, as well as with other lanthanide ion dopants. Our experiments in CaF_2, SrF_2, and BaF_2 doped with Er^{3+} (Ref. 7, 12, 15) have shown that in all cases, the fluorescence intensity resulting from cluster sites is predominate at 0.20-mole% concentrations or less and absorption spectra have shown the cluster sites to have very large absorbances. Studies of the absolute site concentrations in the CaF_2:Er^{3+} system have shown that the concentration of clusters is at least as large as that of the single Er^{3+} - F_I^- pair sites at 0.20-% mole concentrations.[16] Considering the similar nature of the absorption bands at 131 cm^{-1} in the Nd^{3+}-and Er^{3+}-doped crystals, it is likely that a good fit to the Er^{3+} band could be found using five Lorentzian oscillators. We believe, however, that this process leads to an incorrect evaluation of the relative concentrations of the cubic, tetragonal, and trigonal sites. The very large contribution from the cluster sites, cannot be neglected since it would be expected to make up a considerable portion of this absorption band. A more reliable method of determining relative or absolute site concentrations has been reported[16] and should be used when measurements of this type are undertaken. This should not detract, however, from the significant experimental work of Villermain-Lecolier *et al.* who have observed the very interesting common absorption bands that all rare-earth dopants exhibit in BaF_2. These features may in fact be able to provide some basic information on the fluoride interstitial ions involved in the cluster sites. These fluoride interstitials may differ significantly from those of the single Er^{3+} ion sites because of the hypothesized scavenging effects of the cluster sites and the charge distribution changes that may result within cluster sites that have scavenged fluoride interstitials. It could prove quite interesting to study how these absorption features change as a function of dopant concentration in order to evaluate the contribution from the cluster sites.

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