

Quantum Efficiencies of Luminescent Eu^{3+} Centers in CaO

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The luminescence and quantum efficiency of the Eu^{3+} ion in $\text{CaO}:\text{Eu}^{3+},\text{Na}^+$ is reported. Center selective emission spectra provide information on the Eu^{3+} centers in CaO, which partly consist of associates of the Eu^{3+} ions with the available charge compensators, viz., calcium vacancies or Na^+ ions. The average quantum efficiency of the Eu^{3+} luminescence in CaO under charge-transfer excitation (q_{CT}) amounts to about 50%. The rocksalt lattice of CaO suppresses the radiationless relaxation rates in the charge-transfer state to a large extent, but not completely. The effectively positive charge of the Eu^{3+} ion in CaO (and other calcium compounds) seems to set an upper limit of about 50% to q_{CT} in calcium compounds. © 1992 Academic Press, Inc.

1. Introduction

Recently we have started a study on the luminescence of effectively charged rare-earth (RE) ions (1-3). The main interest concerns the influence of the effective charge of the RE ions in the lattice on the radiationless processes in the excited state. The nature of the opposite-parity excited state of the RE ion (charge-transfer of $f^{n-1}d$) appeared to be an important factor. Second, the charge-compensating mechanism influences the luminescence due to association of the charge compensator with the luminescent center. Third, the sign of the effective charge of the RE ion plays an important role in the understanding of the radiationless processes in the excited state.

Our previous studies (1-3) dealt with relatively complex, low-symmetrical systems for which it was difficult to relate the luminescence spectra in detail to the surroundings of the RE ion; it was not possible to

obtain structural information on the RE centers from the splittings of the observed transitions.

In this paper we report on the luminescence of CaO doped with Eu^{3+} . A previous study on the luminescence of the Eu^{3+} ion in CaO has revealed the presence of charge-compensating effects in the vicinity of the Eu^{3+} ion in the rocksalt lattice (4). These authors have reported three kinds of Eu^{3+} centers in CaO. The first one is a Eu^{3+} ion with a cubic surroundings pointing to a Eu^{3+} ion on a Ca^{2+} site without charge compensation in the surroundings (center A). A second center (B) consists of a Eu^{3+} ion on a Ca^{2+} site with a calcium vacancy (V_{Ca}') along the [110] direction in the lattice. A third center (C) gave only a very weak emission and was ascribed to a cluster of Eu^{3+} ions. Other authors have reported on $\text{CaO}:\text{Gd}^{3+}$ (5, 6) and obtained similar results. They observed one additional center, however, which was ascribed to a Gd^{3+} ion with a calcium va-

cancy along the [100] axis in the lattice. This gives rise to a Gd^{3+} ion with tetragonal symmetry. Other authors have studied the system $MgO:Cr^{3+}$ ((7) and further references therein) which is structurally comparable to $CaO:Eu^{3+}$. The observed Cr^{3+} centers in MgO are similar to those of the RE ions in CaO . In this paper additional information on the Eu^{3+} centers in CaO is reported, and the quantum efficiencies of the several Eu^{3+} centers under charge-transfer (CT) excitation will be discussed.

2. Experimental

The starting materials for the synthesis of $CaO:Eu^{3+}$ (Na^+) powders (0.1 and 0.3 mole%) were $CaCO_3$, Na_2CO_3 (both Merck, p.a.), and Eu_2O_3 (Highways Int., 99.999%). The required amounts of the starting materials were mixed and fired for 2 hr at $900^\circ C$. After profound grinding a refiring was carried out for 4 hr at $1100^\circ C$. The structure of the powders was checked with X-ray powder diffraction using $CuK\alpha$ radiation.

The equipment for the optical measurements has been described before (1) and consists mainly of an MPF 44B fluorescence spectrophotometer with a 150-W xenon lamp as a light source and a helium flow cryostat. High resolution spectra were recorded with a dye-laser pumped with a N_2 -laser. Digitalized luminescence spectra were obtained with a SPEX fluorolog spectrofluorometer equipped with two 0.22-m double grating monochromators and a 450-W xenon lamp as a light source. The luminescence spectra were recorded from 4.2 (LHeT) to 300 K (RT).

3. Results and Discussion

3.1. Nature of the Eu^{3+} Centers

Undoped CaO is a white material. Its diffusion reflection spectrum shows an optical absorption which starts at about 250 nm and

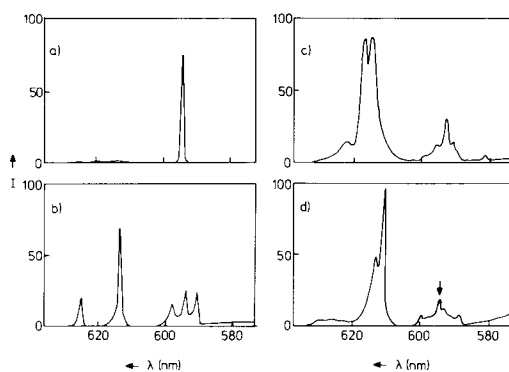


FIG. 1. Emission spectra of the several Eu^{3+} centers in $CaO:Eu^{3+}$ (0.1 mole%) in the ${}^5D_0 \rightarrow {}^7F_{0,1,2}$ region at LHeT under selective dye-laser excitation at LHeT: (a) center A ($\lambda_{exc} = 529.2$ nm); (b) center B ($\lambda_{exc} = 528.4$ nm); (c) center C ($\lambda_{exc} = 527.3$ nm); (d) center $D_{1,2}$ ($\lambda_{exc} = 526.3$ nm). The arrow in (d) indicates an emission line which originates from center A. See also text.

increases toward shorter wavelengths (8). $CaO:Eu^{3+}$ (Na^+) shows an intense luminescence under ultraviolet (UV) excitation. The diffuse reflection spectra of the $CaO:Eu^{3+}$ (Na^+) samples show an absorption band in the UV region, which is due to a CT transition of the Eu^{3+} centers and peaks at about 250 nm. The spectral features in the emission spectra of the Eu^{3+} ion in CaO depend strongly on the Eu^{3+} concentration and the addition of the charge compensator Na^+ .

For $CaO:Eu^{3+}$ (0.1 mole%) we could reproduce the spectra observed in Ref. (4) (see Fig. 1) under selective laser excitation in the ${}^7F_0 \rightarrow {}^5D_1$ transition of the Eu^{3+} ion. A schematic representation of the Eu^{3+} centers is given in Fig. 2. The cubic Eu^{3+} center (A) is the most pronounced, but the orthorhombic center (B) is also clearly observed. A much weaker emission is observed for center C, which was ascribed to a cluster of Eu^{3+} ions in Ref. (4). Decay time measurements confirm the agreement of our spectral observations with those in Ref. (4).

In addition to the earlier work on

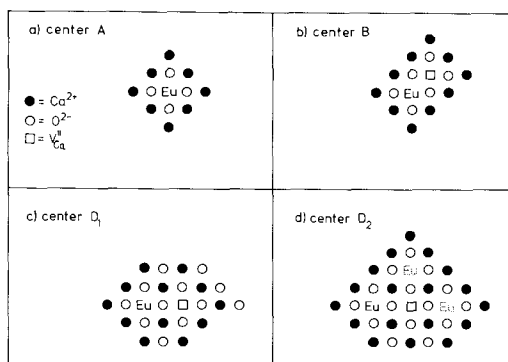


FIG. 2. Schematic representation of Eu^{3+} centers in $\text{CaO}:\text{Eu}^{3+}$ (0.1 mole%). The dotted Eu^{3+} ions (center D_2) indicate the two possible positions of the Eu^{3+} ions in the lattice relative to the other Eu^{3+} ion.

$\text{CaO}:\text{Eu}^{3+}$ we observed a fourth center in $\text{CaO}:\text{Eu}^{3+}$ (0.1%) (see Fig. 1d). Due to the weakness of this emission we were not able to excite this fourth center (denoted as center D) fully selectively. It is, therefore, not possible to derive the nature of this center from the number of observed emission lines. Especially the ${}^5D_0 \rightarrow {}^7F_1$ region remains unclear. One of the emission lines is probably due to another Eu^{3+} center (center A). The presence of this emission line originates from spectral overlap of the excitation lines of both centers. The excitation spectrum of this D emission in the ${}^7F_0 \rightarrow {}^5D_1$ region consists of four lines. Since the emission spectrum under excitation in these four lines shows hardly any change, we conclude that the D emission is due to at least two different Eu^{3+} centers with strongly overlapping emission spectra. We speculate that two centers are present, one consisting of a tetragonal $\text{Eu}_{\text{Ca}}-\text{V}_{\text{Ca}}''$ single associate directed along the [100] axis in the lattice (D_1 , see Fig. 2c), the other of an associate of two Eu^{3+} ions with a calcium vacancy (D_2 , see Fig. 2d). The relative orientation of the two Eu^{3+} ions in this center may be different for this D_2 center. This speculation is supported by the observations in Refs. (5, 6) of a tetrag-

onal Gd^{3+} center in CaO, a center which Porter and Wright (4) did not observe in their samples of $\text{CaO}:\text{Eu}^{3+}$. However, the presence of a D_2 center (a cluster center) includes a concentration dependence of this center. A possible explanation for the fact that this is not observed is that the Eu^{3+} centers with a calcium vacancy along the [100] direction are already very weak.

At higher Eu^{3+} concentrations in CaO (0.3%) the luminescence intensity of the centers A and B decreases, whereas the centers $D_{1,2}$ are no longer observed. The center C is dominant in agreement with the proposal of Porter and Wright (4) for a cluster center.

It remains to be explained what the exact nature of the cluster center C is. First we note the broad emission lines of the Eu^{3+} emission of center C (see Fig. 1c) pointing to an inhomogeneous distribution of the Eu^{3+} ions. A second observation is the absence of emission from higher 5D levels for excitation into these or higher levels ((4) and this work). Since the highest phonon frequency in the CaO lattice is about 500 cm^{-1} , emission from higher 5D levels is to be expected. For the centers A and B these higher 5D emission have been observed ((4) and this work). Center C shows no emission from higher 5D levels, which points to a fast relaxation from the higher 5D levels to 5D_0 . It is most likely that cross-relaxation induces this fast relaxation to the 5D_0 level. Cross-relaxation is strongly dependent on the distance between the Eu^{3+} ions involved. From this distance dependence a critical radius for cross-relaxation can be derived. This can be done by studying Gd^{3+} systems with different Eu^{3+} concentrations and measuring the ratio of the ${}^5D_1/{}^5D_0$ emission intensity as a function of Eu^{3+} concentration. We have done this at 300 K for two systems which have been investigated in our laboratory, viz., $\text{LiGd}_{1-x}\text{Eu}_x\text{F}_4$ (9) and $\text{Gd}_{2(1-x)}\text{Eu}_{2x}\text{ZnO}_5$ (10). It follows that the critical radius for cross-relaxation amounts to about

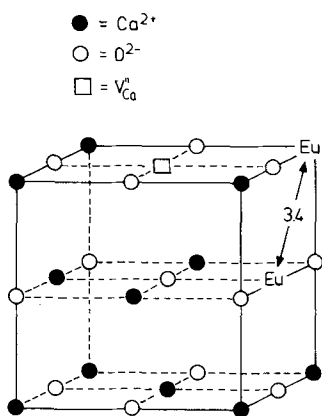


FIG. 3. Schematic representation of the suggestion for center C.

5 (± 0.5) Å. Therefore, the absence of emissions from higher 5D levels for center C points to a cluster of Eu^{3+} ions wherein their mutual distance is less than 5 Å. Since even at low temperatures no higher 5D emissions are observed, cross-relaxation is very effective. This points to a Eu–Eu distance which is much shorter than 5 Å. A proposal for center C is depicted in Fig. 3. From the figure it is clear that the relative position of the calcium vacancy toward both Eu^{3+} ions is along a $[110]$ direction in the lattice. This is in agreement with the most favorable alignment in the configuration for the single Eu^{3+} center (orthorhombic center B), where the calcium vacancy is also positioned along the $[110]$ axis. The inhomogeneous broadening of the emission lines of center C is probably due to the fact that the cluster center has other Eu^{3+} centers in its surroundings.

In the $\text{CaO}:\text{Eu}^{3+},\text{Na}^+$ samples the Eu^{3+} centers A, B, and C are also present, whereas the centers $D_{1,2}$ are only weakly observed. The occurrence of an extra Eu^{3+} center (E) must be due to the incorporation of the Na^+ ion in the lattice. Since the excitation lines of the several Eu^{3+} emissions in $\text{CaO}:\text{Eu}^{3+},\text{Na}^+$ show a considerable overlap, we were not able to make a fully selec-

tive excitation and monitor the emission of the extra Eu^{3+} center (E) exclusively. However, the Eu^{3+} emission reveals the presence of at least two lines in the region of the $^5D_0 \rightarrow ^7F_1$ transition and two lines in the region of the $^5D_0 \rightarrow ^7F_2$ transition (see Fig. 4) which were not observed for the other centers. In order to verify the presence of the Na^+ -induced center (E) in $\text{CaO}:\text{Eu}^{3+},\text{Na}^+$ (0.3 mole%), we measured the decay times of all emission lines in Fig. 4 and compared these values with those of the centers A, B, C, and $D_{1,2}$. The decay times of the several lines are given in Table I. The emission lines at 616.3 and 618.8, which have been assigned previously to center C, appear to contain a second component, since their decay is two-exponential. The emission line at 597.3 nm has also a two-exponential decay. It follows that three emission lines in the region of the $^5D_0 \rightarrow ^7F_1$ and four emission lines in the $^5D_0 \rightarrow ^7F_2$ region have a decay of about 5.2 msec. We conclude, therefore, that center E has three 7F_1 and four 7F_2 crystal-field components. The number of crystal-field components for center E points to an orthorhombically dis-

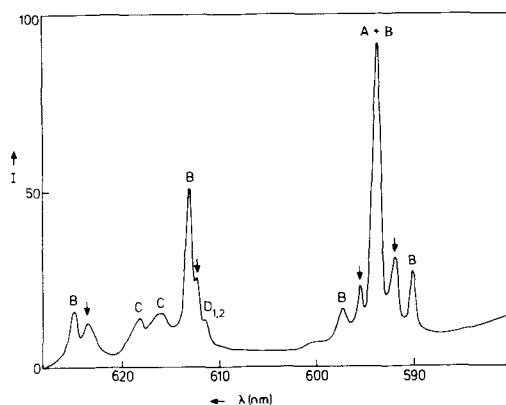


FIG. 4. Emission spectrum of $\text{CaO}:\text{Eu}^{3+},\text{Na}^+$ (0.3 mole%) in the $^5D_0 \rightarrow ^7F_{0,1,2}$ region at LHeT under dye-laser excitation in the $^7F_0 \rightarrow ^5D_1$ transition ($\lambda_{\text{exc}} = 529.0$ nm) with a center assignment. The arrows indicate the emission lines which were not observed in $\text{CaO}:\text{Eu}^{3+}$.

TABLE I

EMISSION LINES IN THE ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{0,1,2}$ REGION OF $\text{CaO}:\text{Eu}^{3+}, \text{Na}^+$ (0.3 mole%) AT RT WITH DECAY TIMES AND CENTER ASSIGNMENT

Wavelength (nm)	Decay time (msec)	Center
590.1	3.2	B
592.0	5.5	E
594.4	8.0	A
595.6	5.5	E
597.3	5.8 + 3.2	E + B
611.3	1.0	$\text{D}_{1,2}$
612.4	5.1	E
613.1	3.5	B
616.3	5.0 + 1.4	E + C
618.8	5.2 + 1.3	E + C
623.5	5.5	E
625.0	3.2	B

TABLE II

CHARACTERISTICS OF THE Eu^{3+} CENTERS IN CaO

Center	Symmetry	Decay time (msec)	CT band
A	cubic	8.0 ± 0.2	235
B	orthorhombic	3.1 ± 0.2	250
C	?	1.4 ± 0.1	250
$\text{D}_{1,2}$	tetragonal	1.0 ± 0.3	250
E	orthorhombic	5.3 ± 0.2	240

torted Eu^{3+} ion (site symmetry C_{2v}). Apparently the Na^+ ion is positioned at the same place in the lattice as the most favorable place for the calcium vacancy, viz., along the [110] axis (compare center B, Fig. 2b).

Another tool to characterize the Eu^{3+} centers in CaO is the position of the CT band. The values for the position of the CT maxima are derived from the excitation spectra of the relevant Eu^{3+} emission (see, for example, Fig. 5), and are tabulated in

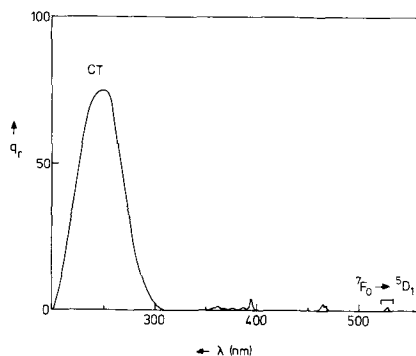


FIG. 5. Excitation spectrum of the Eu^{3+} emission of center B ($\lambda_{\text{em}} = 613.1$ nm) in $\text{CaO}:\text{Eu}^{3+}$ (0.1 mole%) at LHeT. q_r gives the relative quantum output in arbitrary units (a.u.).

Table II together with other characteristics of the Eu^{3+} centers in CaO . We note that all Eu^{3+} centers which contain a $\text{Eu}_{\text{Ca}}-\text{V}_{\text{Ca}}''$ associate have a CT band at 250 nm, whereas the Na^+ compensated (E) and the noncompensated center (A) have a CT band at shorter wavelengths, i.e., higher energies. This can be understood from the fact that the O^{2-} ion near a calcium vacancy is easier polarizable than an O^{2-} ion which is attached to cations alone (Eu^{3+} , Ca^{2+} , or Na^+). The fact that the CT band of center A is at higher energy than for center E shows that the O^{2-} ion near a Na^+ ion is easier polarizable than an O^{2-} ion near a Ca^{2+} ion, which is due to the lower charge of the Na^+ ion. The position of the CT bands of the Eu^{3+} ions supports the previous assignments for these centers.

3.2. Quantum Efficiency

In the previous section the nature of the Eu^{3+} centers in CaO was described and discussed. Now we try to correlate the nature of the Eu^{3+} centers with the quantum efficiency under CT excitation (q_{CT}).

The method which is used for the estimation of q_{CT} is based on the fact that the oscillator strength of the CT transition and the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$ magnetic-dipole transition are not strongly dependent on the surroundings of the Eu^{3+} ion. By calculating the intensity ratios $I(\text{CT})/I({}^7\text{F}_0 \rightarrow {}^5\text{D}_1)$ from the excitation spectra and comparing the values of these ratios with a standard phosphor with a

TABLE III

MEASURED q_{CT} VALUES OF THE Eu^{3+} CENTERS IN DIFFERENT CaO SAMPLES AT RT WITH AN INDICATION OF THEIR ABUNDANCE

Center	Samples		
	$\text{CaO}:\text{Eu}^{3+}$ (0.1%)	$\text{CaO}:\text{Eu}^{3+}$ (0.3%)	$\text{CaO}:\text{Eu}^{3+},\text{Na}^+$ (0.3%)
A	20 (s)	30 (m)	30 (m)
B	35 (s)	50 (m)	50 (m)
C	35 (m)	50 (s)	55 (w)
$\text{D}_{1,2}$	20 (w)	—	— (vw)
E	—	—	55 (s)

Note. In parentheses, s = strong, m = medium, w = weak, vw = very weak. See also text.

known q_{CT} value, an estimation of q_{CT} for the several Eu^{3+} centers can be made. The estimated absolute experimental error in the q_{CT} values is about $\pm 5\%$. However, a major problem in the estimation of q_{CT} is the competitive absorption of CaO itself in the region of the CT band of the Eu^{3+} ion. Due to the inaccuracy in the absorption of undoped CaO (from the diffuse reflection spectra) it is not possible to give a reliable estimate of the influence of the competitive absorption on the values of q_{CT} . It is clear that the influence is more pronounced for lower Eu^{3+} concentrations and for the Eu^{3+} centers with the higher CT bands.

In Table III the estimated values of q_{CT} for the several Eu^{3+} centers together with an indication of their abundance in the CaO samples are summarized. The q_{CT} values are independent of temperature. In view of the corrections to be made for the host absorption, the $\text{D}_{1,2}$ centers seem to have a q_{CT} which is lower than those of the other centers.

Recently we have presented a simple model which accounts for the influence on q_{CT} of an effective charge on the Eu^{3+} ion (3). For Eu^{3+} on Ca^{2+} sites the model predicts a low value of q_{CT} , unless the expansion in the excited state is counteracted as strongly as possible. In the rocksalt lattice this is realized, since the $\text{Eu}-\text{O}-\text{Ca}$ angle is

180° (Fig. 2). This explains immediately the lower q_{CT} for the $\text{D}_{1,2}$ centers: an oxygen ligand of the Eu^{3+} ion can expand into the direction of the vacancy. This is impossible in the case of the other centers. Nevertheless q_{CT} for these centers is still far from 100%, so that the rocksalt lattice of CaO is not yet stiff enough. However, the present q_{CT} values are considerably higher than those for other calcium compounds (1).

4. Conclusion

The Eu^{3+} ion shows an efficient luminescence in CaO under CT excitation. The luminescence consists of several emissions due to the occurrence of different Eu^{3+} centers in CaO .

The average q_{CT} value of the Eu^{3+} luminescence in CaO amounts to about 50%. The favorable orientation of the second coordination sphere of the Eu^{3+} ion in CaO is beneficial to the value of q_{CT} , but the effectively positive charge of the Eu^{3+} ion seems to set an upper limit of about 50% to q_{CT} in calcium compounds. This makes the realization of luminescent materials based on Eu^{3+} -doped calcium compounds doubtful.

Acknowledgments

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