

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

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The luminescence and quantum efficiency of the  $\text{Eu}^{3+}$  ion in  $\text{CaO}:\text{Eu}^{3+},\text{Na}^+$  is reported. Center selective emission spectra provide information on the  $\text{Eu}^{3+}$  centers in CaO, which partly consist of associates of the  $\text{Eu}^{3+}$  ions with the available charge compensators, viz., calcium vacancies or  $\text{Na}^+$  ions. The average quantum efficiency of the  $\text{Eu}^{3+}$  luminescence in CaO under charge-transfer excitation ( $q_{\text{CT}}$ ) 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  $\text{Eu}^{3+}$  ion in CaO (and other calcium compounds) seems to set an upper limit of about 50% to  $q_{\text{CT}}$  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  $\text{Eu}^{3+}$ . A previous study on the luminescence of the  $\text{Eu}^{3+}$  ion in CaO has revealed the presence of charge-compensating effects in the vicinity of the  $\text{Eu}^{3+}$  ion in the rocksalt lattice (4). These authors have reported three kinds of  $\text{Eu}^{3+}$  centers in CaO. The first one is a  $\text{Eu}^{3+}$  ion with a cubic surroundings pointing to a  $\text{Eu}^{3+}$  ion on a  $\text{Ca}^{2+}$  site without charge compensation in the surroundings (center A). A second center (B) consists of a  $\text{Eu}^{3+}$  ion on a  $\text{Ca}^{2+}$  site with a calcium vacancy ( $V''_{\text{Ca}}$ ) along the [110] direction in the lattice. A third center (C) gave only a very weak emission and was ascribed to a cluster of  $\text{Eu}^{3+}$  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  $\text{Gd}^{3+}$  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 refring 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

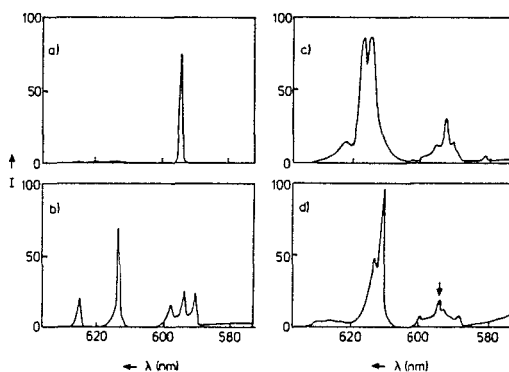


FIG. 1. Emission spectra of the several  $Eu^{3+}$  centers in  $CaO:Eu^{3+}$  (0.1 mole%) in the  ${}^5D_0 \rightarrow {}^7F_{0,1,2}$  region at LHeT under selective dye-laser excitation at LHeT: (a) center A ( $\lambda_{exc} = 529.2$  nm); (b) center B ( $\lambda_{exc} = 528.4$  nm); (c) center C ( $\lambda_{exc} = 527.3$  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

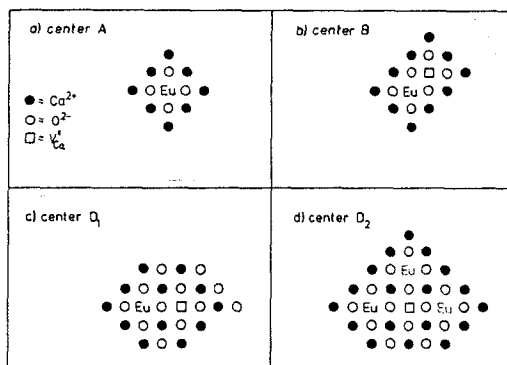


FIG. 2. Schematic representation of  $\text{Eu}^{3+}$  centers in  $\text{CaO}:\text{Eu}^{3+}$  (0.1 mole%). The dotted  $\text{Eu}^{3+}$  ions (center  $D_2$ ) indicate the two possible positions of the  $\text{Eu}^{3+}$  ions in the lattice relative to the other  $\text{Eu}^{3+}$  ion.

$\text{CaO}:\text{Eu}^{3+}$  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  $\text{Eu}^{3+}$  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  $\text{Eu}^{3+}$  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  $\text{Eu}^{3+}$  ions with a calcium vacancy ( $D_2$ , see Fig. 2d). The relative orientation of the two  $\text{Eu}^{3+}$  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  $\text{Gd}^{3+}$  center in  $\text{CaO}$ , 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  $\text{Eu}^{3+}$  centers with a calcium vacancy along the [100] direction are already very weak.

At higher  $\text{Eu}^{3+}$  concentrations in  $\text{CaO}$  (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  $\text{Eu}^{3+}$  emission of center C (see Fig. 1c) pointing to an inhomogeneous distribution of the  $\text{Eu}^{3+}$  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  $\text{CaO}$  lattice is about  $500\text{ cm}^{-1}$ , 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  $\text{Eu}^{3+}$  ions involved. From this distance dependence a critical radius for cross-relaxation can be derived. This can be done by studying  $\text{Gd}^{3+}$  systems with different  $\text{Eu}^{3+}$  concentrations and measuring the ratio of the  ${}^5D_1/{}^5D_0$  emission intensity as a function of  $\text{Eu}^{3+}$  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  $\text{Gd}_{2(1-x)}\text{Eu}_x\text{ZnO}_5$  (10). It follows that the critical radius for cross-relaxation amounts to about

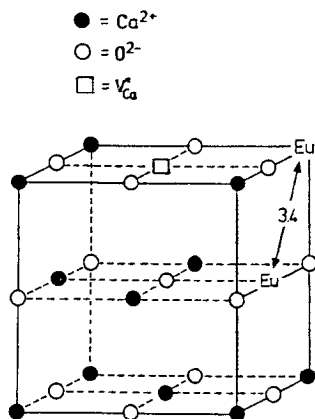


FIG. 3. Schematic representation of the suggestion for center C.

$5 (\pm 0.5) \text{ \AA}$ . Therefore, the absence of emissions from higher  $^5D$  levels for center C points to a cluster of  $\text{Eu}^{3+}$  ions wherein their mutual distance is less than  $5 \text{ \AA}$ . 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  $5 \text{ \AA}$ . 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  $\text{Eu}^{3+}$  ions is along a  $[110]$  direction in the lattice. This is in agreement with the most favorable alignment in the configuration for the single  $\text{Eu}^{3+}$  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  $\text{Eu}^{3+}$  centers in its surroundings.

In the  $\text{CaO}:\text{Eu}^{3+},\text{Na}^+$  samples the  $\text{Eu}^{3+}$  centers A, B, and C are also present, whereas the centers  $D_{1,2}$  are only weakly observed. The occurrence of an extra  $\text{Eu}^{3+}$  center (E) must be due to the incorporation of the  $\text{Na}^+$  ion in the lattice. Since the excitation lines of the several  $\text{Eu}^{3+}$  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  $\text{Eu}^{3+}$  center (E) exclusively. However, the  $\text{Eu}^{3+}$  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  $\text{Na}^+$ -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-

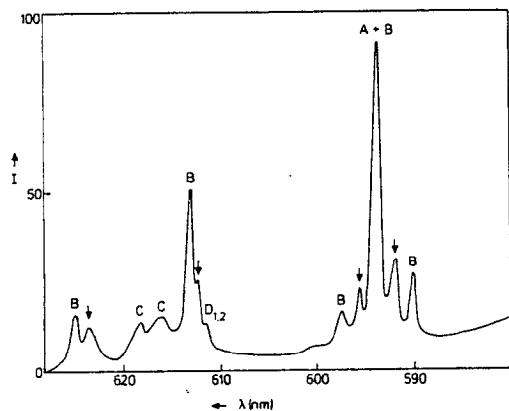


FIG. 4. Emission spectrum of  $\text{CaO}:\text{Eu}^{3+},\text{Na}^+$  (0.3 mole%) in the  $^5D_0 \rightarrow ^7F_{0,1,2}$  region at LHeT under dye-laser excitation in the  $^7F_0 \rightarrow ^5D_1$  transition ( $\lambda_{\text{exc}} = 529.0 \text{ nm}$ ) with a center assignment. The arrows indicate 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

torted  $\text{Eu}^{3+}$  ion (site symmetry  $C_{2v}$ ). Apparently the  $\text{Na}^+$  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  $\text{Eu}^{3+}$  centers in  $\text{CaO}$  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  $\text{Eu}^{3+}$  emission (see, for example, Fig. 5), and are tabulated in

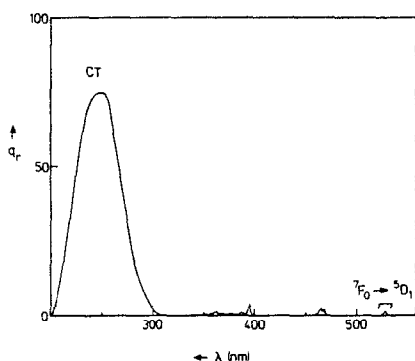


FIG. 5. Excitation spectrum of the  $\text{Eu}^{3+}$  emission of center B ( $\lambda_{em} = 613.1$  nm) in  $\text{CaO}:\text{Eu}^{3+}$  (0.1 mole%) at LHeT.  $q_r$  gives the relative quantum output in arbitrary units (a.u.).

TABLE II

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

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

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

### 3.2. Quantum Efficiency

In the previous section the nature of the  $\text{Eu}^{3+}$  centers in  $\text{CaO}$  was described and discussed. Now we try to correlate the nature of the  $\text{Eu}^{3+}$  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  $\text{Eu}^{3+}$  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  $\text{Eu}^{3+}$  CENTERS IN DIFFERENT  $\text{CaO}$  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)
$D_{1,2}$	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  $\text{Eu}^{3+}$  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  $\text{CaO}$  itself in the region of the CT band of the  $\text{Eu}^{3+}$  ion. Due to the inaccuracy in the absorption of undoped  $\text{CaO}$  (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  $\text{Eu}^{3+}$  concentrations and for the  $\text{Eu}^{3+}$  centers with the higher CT bands.

In Table III the estimated values of  $q_{CT}$  for the several  $\text{Eu}^{3+}$  centers together with an indication of their abundance in the  $\text{CaO}$  samples are summarized. The  $q_{CT}$  values are independent of temperature. In view of the corrections to be made for the host absorption, the  $D_{1,2}$  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  $\text{Eu}^{3+}$  ion (3). For  $\text{Eu}^{3+}$  on  $\text{Ca}^{2+}$  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

$180^\circ$  (Fig. 2). This explains immediately the lower  $q_{CT}$  for the  $D_{1,2}$  centers: an oxygen ligand of the  $\text{Eu}^{3+}$  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  $\text{CaO}$  is not yet stiff enough. However, the present  $q_{CT}$  values are considerably higher than those for other calcium compounds (1).

#### 4. Conclusion

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

The average  $q_{CT}$  value of the  $\text{Eu}^{3+}$  luminescence in  $\text{CaO}$  amounts to about 50%. The favorable orientation of the second coordination sphere of the  $\text{Eu}^{3+}$  ion in  $\text{CaO}$  is beneficial to the value of  $q_{CT}$ , but the effectively positive charge of the  $\text{Eu}^{3+}$  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  $\text{Eu}^{3+}$ -doped calcium compounds doubtful.

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