

Time-resolved spectroscopy of the  $\text{Eu}^{2+}$  luminescence in  $\text{KCl}:\text{Ba}^{2+}$ ,  $\text{Eu}^{2+}$   $\text{KCl}:\text{Sr}^{2+}$ ,  $\text{Eu}^{2+}$  and  $\text{KBr}:\text{Sr}^{2+}$ ,  $\text{Eu}^{2+}$

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## Time-resolved spectroscopy of the $\text{Eu}^{2+}$ luminescence in $\text{KCl}:\text{Ba}^{2+}$ , $\text{Eu}^{2+}$ , $\text{KCl}:\text{Sr}^{2+}$ , $\text{Eu}^{2+}$ and $\text{KBr}:\text{Sr}^{2+}$ , $\text{Eu}^{2+}$

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**Abstract.** In the present paper fluorescence kinetic studies of the  $\text{Eu}^{2+}$  luminescence in freshly quenched crystals of  $\text{KCl}:\text{Ba}^{2+}$ ,  $\text{Eu}^{2+}$ ,  $\text{KCl}:\text{Sr}^{2+}$ ,  $\text{Eu}^{2+}$  and  $\text{KBr}:\text{Sr}^{2+}$ ,  $\text{Eu}^{2+}$  are reported. The measurements were carried out at 300 K, at low concentrations of the dopants, and after the crystals were subjected to severe quenching treatments. The results obtained suggested that small complexes of  $\text{Ba}^{2+}-\text{Eu}^{2+}$  are preferentially formed in the lattice of potassium chloride. At variance with this situation, evidence for the preferential formation of  $\text{Sr}^{2+}-\text{Eu}^{2+}$  close pairs was not found in the doubly doped crystals of  $\text{KCl}:\text{Sr}$ ,  $\text{Eu}$  and  $\text{KBr}:\text{Sr}$ ,  $\text{Eu}$ . These results are in good agreement with the ionic radius criterion proposed by Rubio and co-workers several years ago to predict pairing between two impurity ions in a solid material.

### 1. Introduction

Recently, a detailed study dealing with the precipitation processes of  $\text{Ba}^{2+}$  ions in single-crystalline  $\text{KCl}$  using  $\text{Eu}^{2+}$  as an optical probe was performed by Verdiguél *et al* (1991). The spectroscopic data obtained by these workers suggested that the europium ions were associated with different barium aggregates in the lattice of potassium chloride. In particular, it was found that the emission spectrum of their freshly quenched crystals consisted of a broad band peaking at 417 nm which was very similar to that observed in quenched crystals of  $\text{KCl}:\text{Eu}^{2+}$ , although its peak position was slightly blue shifted. Since this band was the only one observed after quenching, Verdiguél *et al* (1991) concluded that the complexes responsible for this band were isolated  $\text{Eu}^{2+}$ -cation vacancy dipoles and small complexes of  $\text{Ba}^{2+}-\text{Eu}^{2+}$  which were preferentially formed in the lattice of  $\text{KCl}$ . However, spectroscopic evidence supporting the existence of the latter complexes was not presented by these workers.

The formation of  $\text{Ba}-\text{Eu}$  close pairs in quenched crystals of  $\text{KCl}:\text{Ba}^{2+}$ ,  $\text{Eu}^{2+}$  may be expected if one takes into consideration the ionic radius criterion proposed by Rubio *et al* (1985) to predict impurity pairing in a solid material. In fact, the average ionic radius of the  $\text{Ba}^{2+}$  and  $\text{Eu}^{2+}$  ions (1.23 Å) is similar to that of the host  $\text{K}^{+}$  ions (1.33 Å) for which they substitute in the lattice of  $\text{KCl}$ . Therefore, if the  $\text{Ba}^{2+}$  and  $\text{Eu}^{2+}$  ions couple through a  $\text{Cl}^{-}$  ion along a  $\langle 100 \rangle$  direction, then they must fit quite well into the allotted space in the lattice.

All the experimentally determined data obtained in our laboratory in the two-activator systems of  $\text{NaCl}:\text{Eu}$ ,  $\text{Mn}$ ,  $\text{NaBr}:\text{Eu}$ ,  $\text{Mn}$ ,  $\text{NaI}:\text{Eu}$ ,  $\text{Mn}$ ,  $\text{KCl}:\text{Eu}$ ,  $\text{Mn}$ ,  $\text{NaCl}:\text{Sn}$ ,  $\text{Mn}$ ,  $\text{NaCl}:\text{Cu}$ ,  $\text{Mn}$ ,  $\text{CaF}_2:\text{Eu}$ ,  $\text{Mn}$  and  $\text{CaCl}_2:\text{Eu}$ ,  $\text{Mn}$  give support to the applicability of this criterion which seems to provide a reasonable basis for selecting impurity ions and host crystals which might

be used for developing materials that are important for laser and phosphor applications and for optical wavelength conversion (Muñoz and Rubio 1988, Rubio *et al* 1985, 1987, 1988, Rubio and Camarillo 1989, Muñoz *et al* 1990, Caldiño *et al* 1990, 1993).

With the aim of obtaining spectroscopic evidence for the existence of barium and europium ions in close proximity in the lattice of potassium chloride, as expected by the ionic radius criterion, we carried out time-resolved spectroscopy measurements in acetone-quenched crystals of KCl:Ba, Eu and the results obtained are presented in this paper. The optical properties of KCl:Sr, Eu and KBr:Sr, Eu were also studied in order to compare the results obtained in these systems with those found in KCl:Ba:Eu. According to the ionic radius criterion, the formation of Sr–Eu close pairs is expected to be less favourable than that of Ba–Eu close pairs in the potassium halide lattices.

## 2. Experimental details

The single crystals of KCl:Eu<sup>2+</sup> (20 ppm), KCl:Ba (300 ppm), Eu (10 ppm), KCl:Sr (800 ppm), Eu (15 ppm), KBr:Eu (20 ppm) and KBr:Sr (800 ppm), Eu (20 ppm) employed in this investigation were grown by R Guerrero at the Crystal Growth Facility of the Institute of Physics, UNAM, using the Czochralski method under a controlled atmosphere of dry argon. All measurements were carried out in crystals with dimensions of about  $0.5 \times 0.5 \times 0.05$  cm<sup>3</sup> which were heated at 850 K for 6 h and then rapidly quenched into acetone in order to dissolve impurity aggregates and precipitates that might be present in the as-grown crystals.

Lifetime and laser time-resolved spectroscopy data were obtained using a PRA-LN 120-C pulsed nitrogen laser as the excitation source. This produced a pulse of about 10 ns in duration and 1 Å bandwidth at 3371 Å. The resulting transient fluorescence signal was analysed with a Pacific 0.45 m Czerny–Turner monochromator and detected with a cooled Hamamatsu R943-03 photomultiplier tube. Then, it was processed by a PAR 162 boxcar averager in combination with a PAR 165 gated integrator before it was presented on a strip chart recorder. Continuous fluorescence spectra were obtained with a Perkin–Elmer model 650-10S spectrofluorometer, equipped with a 150 W xenon lamp.

## 3. Results and discussion

Figure 1 displays the 300 K emission spectrum of an acetone-quenched crystal of KCl:Ba<sup>2+</sup>, Eu<sup>2+</sup> obtained under nitrogen-laser excitation at 100 ns after the pulse. A broad band with a peak at 417 nm is observed. This band is the same as that previously found by Verdigué *et al* (1991) using CW excitation light.

The emission spectra of acetone-quenched crystals of KCl:Sr, Eu and KBr:Sr, Eu are portrayed in figure 2. These spectra were obtained under the same experimental conditions as those employed to record the emission spectrum of KCl:Ba:Eu. For all systems, the observed emission band is due to the de-excitation of the doubly valent europium ions from the  $t_{2g}$  level of the  $4f^65d$  configuration to the ground state  $^8S_{7/2}$ . Values for the wavelength peak position and for the full width at half-maximum (FWHM) of each band are given in table 1. It is observed from the data presented in this table, that the FWHM value of the Eu<sup>2+</sup>-emission band peaking at 417 nm in KCl:Ba:Eu ( $1295$  cm<sup>-1</sup>) is larger than that of the emission band peaking at 419 nm in KCl:Eu ( $1267$  cm<sup>-1</sup>). This latter value is, however, quite similar to that measured for the FWHM of the Eu<sup>2+</sup> emission band in KCl:Sr, Eu ( $1263$  cm<sup>-1</sup>). On the other hand, the FWHM values for the bands associated with the de-excitation of the Eu<sup>2+</sup> ions in the systems KBr:Sr, Eu and KBr:Eu were found to be

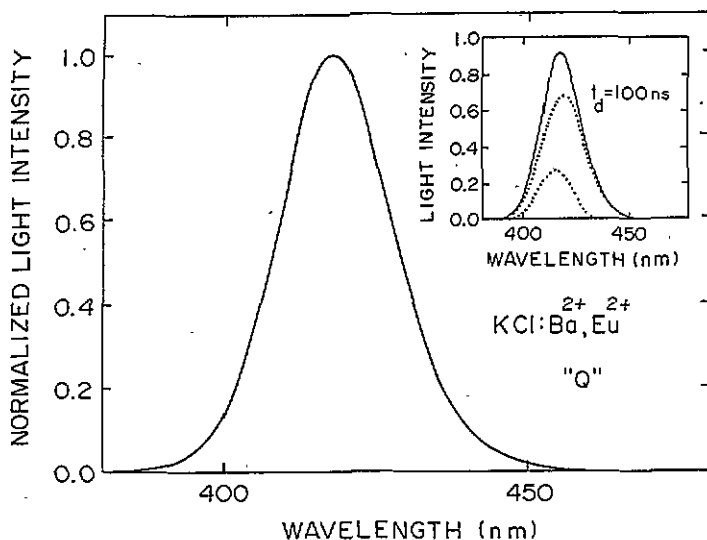


Figure 1. Room temperature time-resolved luminescence spectrum of an acetone-quenched sample of KCl:Ba<sup>2+</sup>, Eu<sup>2+</sup> recorded at 100 ns after the pulse excitation. The inset shows the decomposition of the emission band into two bands peaking at 415 and 419 nm.

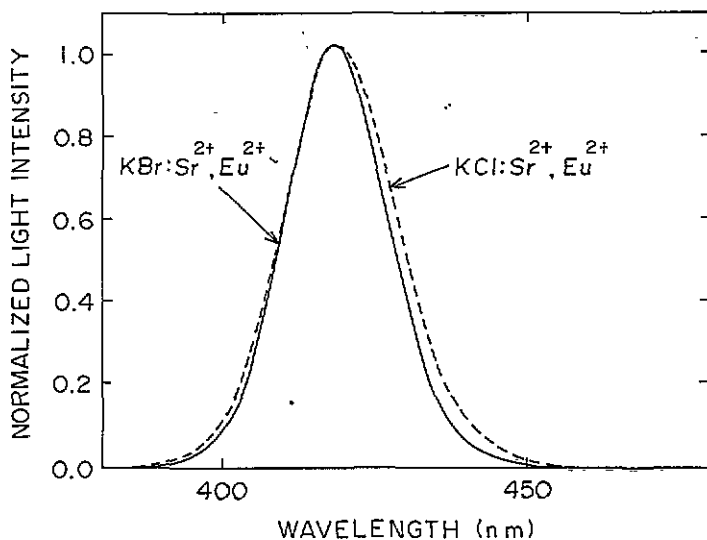


Figure 2. 300 K time-resolved luminescence spectra of acetone-quenched samples of KCl:Sr<sup>2+</sup>, Eu<sup>2+</sup> (---) and KBr:Sr<sup>2+</sup>, Eu<sup>2+</sup> (—) recorded at 100 ns after the pulse excitation.

nearly identical.

Lifetime measurements performed in the acetone-quenched crystals of KCl:Eu, KCl:Sr, Eu, KBr:Eu and KBr:Sr, Eu revealed that in all these systems, the decay scheme of the Eu<sup>2+</sup> emission consists of a pure exponential decay with decay constants displayed in table 1. Moreover, no difference was observed in the lifetime value between the low- and high-energy sides of the emission band, indicating that the Eu<sup>2+</sup> emission band in these doubly doped crystals does not consist of several bands with different lifetimes but is a single band.

**Table 1.** Values for the peak positions, full widths at half-maximum (FWHM) and lifetimes of the  $\text{Eu}^{2+}$  emission bands observed in the systems investigated in this work.

System	Emission band			
	Peak position		FWHM ( $\text{cm}^{-1}$ )	$\tau$ ( $\mu\text{s}$ )
	( $\text{cm}^{-1}$ )	(nm)		
KCL:Eu <sup>2+</sup>	23 866	419	1267	1.21
KCL:Ba <sup>2+</sup> , Eu <sup>2+</sup>	23 981	415	1295	1.16
		419		
KCL:Sr <sup>2+</sup> , Eu <sup>2+</sup>	23 866	419	1263	1.22
KBr:Eu <sup>2+</sup>	23 923	418	1201	1.13
KB:Sr <sup>2+</sup> , Eu <sup>2+</sup>	23 923	418	1204	1.15

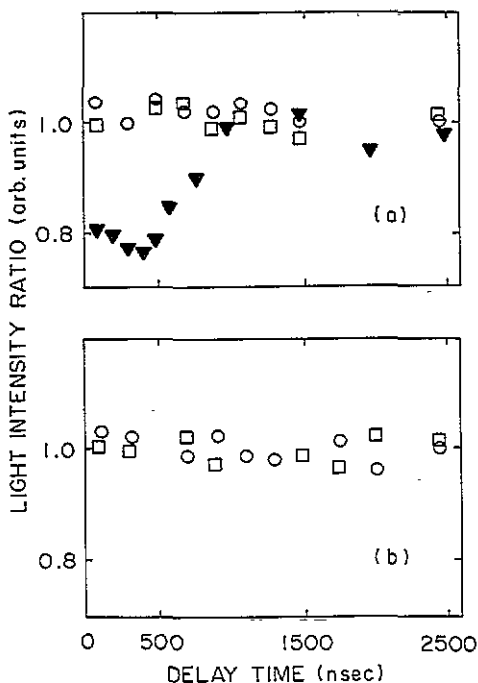
At variance with the results above, in the wide fluorescence spectrum between 390 and 470 nm, at any fluorescence wavelength, a nearly exponential decay was found for the Eu luminescence in the acetone quenched crystals of KCl:Ba, Eu under pulse nitrogen-laser excitation. The best exponential profile was observed on the long-wavelength side beyond 440 nm. The value for the first  $e^{-1}$  folding time was found to increase as the emission wavelength increased.

In order to gain a better insight into the nature of this band, the light intensity of the emission was measured at two selected fluorescence wavelengths, i.e. 410 and 440 nm, as a function of time after the nitrogen-laser excitation pulse. Then, the ratio  $I(440 \text{ nm})/I(410 \text{ nm})$  was calculated and the results obtained are portrayed in figure 3. The increase in the intensity ratios at long times is associated with the lifetime difference between the  $\text{Eu}^{2+}$  ions occupying violet and blue sites.

Different from the results above, the intensity ratios  $I(430 \text{ nm})/I(410 \text{ nm})$  calculated from the observed  $\text{Eu}^{2+}$  emission in quenched crystals of KCl:Eu, KCl:Sr, Eu, KBr:Sr, Eu and KBr:Eu were found to be independent of time after the nitrogen-laser excitation pulse, as can be appreciated from the results which are also displayed in figure 3.

All the spectroscopic data described above suggest that the  $\text{Eu}^{2+}$  emission band observed in our acetone-quenched doubly doped crystals of KCl:Ba, Eu is the result of superposition of several bands with different characteristic decay times. In fact, the 417 nm band could be resolved into two bands masked under it, as can be seen from the spectrum shown in the inset of figure 1. The peak positions of the resolved bands are at 415 and 419 nm. From the room-temperature time-resolved experiments, it was found that the band peaking at 415 nm has a lifetime of about  $1.0 \mu\text{s}$  while the lifetime of the 419 nm band is about  $1.25 \mu\text{s}$ . In the calculation of these values, care was taken to consider the overlap between the two bands.

It was also found that the ratio  $I(415 \text{ nm})/I(419 \text{ nm})$  of the intensity of the 415 nm band to that of the 419 nm emission band was dependent on the cooling procedure employed and increased with the use of the less efficient quenches. Moreover, the intensity of the 415 nm band was found to grow at the expense of that peaking at 419 nm when the acetone-quenched crystals were annealed at 300 K. For annealing times of about 50 min, another emission band peaking at 429 nm starts to grow and its intensity increases as a function of the annealing time. In figure 4, the evolution of the intensities of the 415, 419 and 429 nm bands as functions of the time elapsed at 300 K after quenching is presented. In order to obtain this information, the emission spectra were decomposed into symmetric



**Figure 3.** (a) Evolution of the light intensity ratio  $I(440 \text{ nm})/I(410 \text{ nm})$  for acetone-quenched samples of KCl:Sr, Eu ( $\square$ ) KCl:Ba:Eu ( $\blacktriangledown$ ) and KCl:Eu ( $\circ$ ) as a function of the time after the pulse excitation, with  $\lambda_{ex} = 337 \text{ nm}$ . (b) Evolution of the light intensity ratio  $I(430 \text{ nm})/I(410 \text{ nm})$  for acetone-quenched samples of KBr:Sr, Eu ( $\square$ ) and KBr:Eu ( $\circ$ ) as a function of the time after the pulse excitation at 337 nm.

Gaussian-shaped bands. A computer program was employed to change the peak position, intensity, band width and the number of the emission bands until a good fit (within 5%) to the experimental spectra was achieved. Figures 1 (inset) and 4(a) show examples of these fits. It should be pointed out that no attempt was made to perform the analysis mentioned above using asymmetric Gaussian-shaped bands. The reason for the latter is that a clear indication that this kind of curve should be involved in the analysis was not found in any of the spectra which were decomposed.

For a low concentration of impurities in our doubly doped crystals, a random distribution of the impurity ions is expected to occur in the acetone-quenched samples. In fact, Taylor *et al* (1981) found that one may obtain all the  $M^{2+}$  ions in solution at room temperature if sufficiently rapid quenches and low impurity concentrations are employed. According to these workers the acetone quench is capable of giving a fully efficient quench if the thickness of the crystals is about 0.5 mm.

The data described above suggest that the degree of association between  $\text{Eu}^{2+}$  and  $\text{Ba}^{2+}$  ions in the potassium halide lattices is different from that of  $\text{Eu}^{2+}$  and  $\text{Sr}^{2+}$ . In fact, the spectroscopic data obtained in KCl:Ba, Eu suggest that the bands peaking at 415 and 419 nm are due to the emission of europium ions forming different kinds of complexes in the lattice of KCl. The 419 nm band is due to the emission of  $\text{Eu}^{2+}$  ions forming ( $I-V$ ) dipolar complexes since the peak position, band width and lifetime of this band are nearly identical with those of the emission band which has been previously associated with europium ions in solution in the potassium chloride matrix (López *et al* 1980).

The emission at 415 nm may be associated with the de-excitation of europium ions

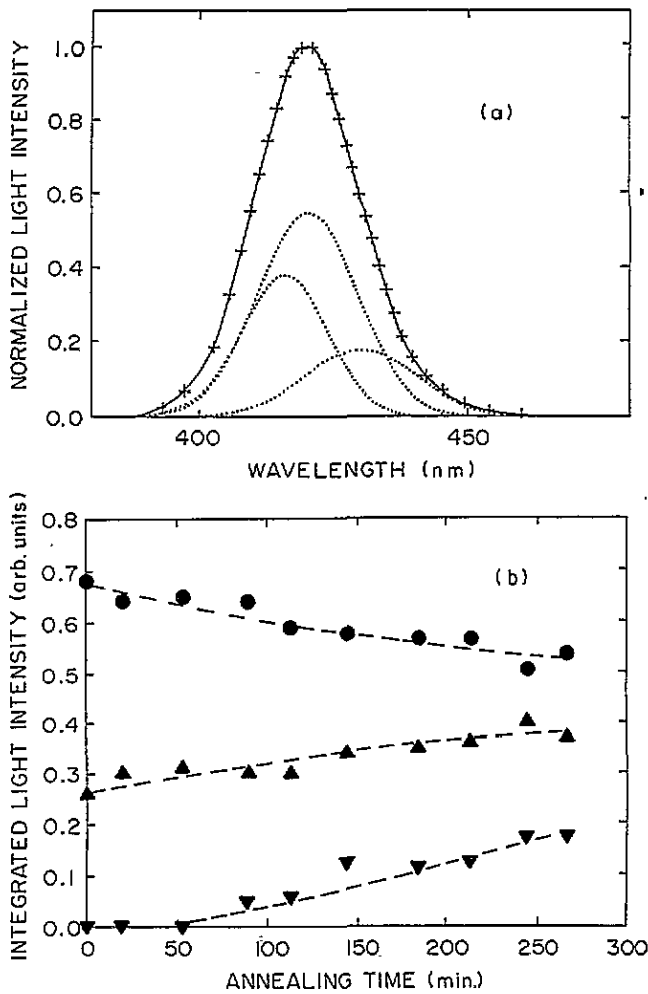


Figure 4. (a) 300 K emission spectrum of a KCl:Ba, Eu sample which had been annealed for 6 h at room temperature after quenching (this spectrum was obtained under CW excitation light (337 nm)): +, fit to the emission spectrum using symmetric Gaussian-shaped bands. (b) Evolution of the integrated intensities of the emission bands peaking at 419 nm (●), 415 nm (▲) and 429 nm (▼) as functions of the annealing time at room temperature: ---, guide to the eye.

forming small Ba–Eu aggregates (dimers, trimers, etc) which are preferentially formed in the lattice of KCl even after the crystals have been subjected to severe quenching treatments. The concentration of these aggregates increases as a function of the time elapsed at 300 K between quench and measurement, as well as with the use of the less efficient quenches. Unfortunately, the nature of these mixed complexes cannot be inferred from our experimentally determined data.

The 429 nm band has been previously ascribed (Verdiguel *et al* 1991) to the emission of  $\text{Eu}^{2+}$  ions embedded into barium precipitates possessing a cubic structure. Therefore, it appears from the data presented in figure 4 that the small clusters of Ba–Eu act during the precipitation processes as nucleation centres for the formation of larger barium aggregates in which some europium ions are embedded.

On the other hand, different from the results obtained for KCl:Ba, Eu, the spectroscopic data described above indicate that the observed emission in KCl:Sr, Eu and KBr:Sr, Eu is due to the de-excitation of europium ions which are not in close proximity to Sr ions. This suggests that Sr–Eu close pairs are not preferentially formed in our slightly doubly doped crystals after a severe quench into acetone.

The experimental findings described above are in good agreement with the expectations of the ionic radius criterion. In fact, according to this criterion the formation of Ba–Eu close pairs is more favourable than that of Sr–Eu close pairs in the potassium chloride lattice since the ionic radius of K<sup>+</sup> (1.33 Å) is more similar to the average ionic radius of the Ba<sup>2+</sup> and Eu<sup>2+</sup> ions (1.23 Å) than that of Sr<sup>2+</sup> and Eu<sup>2+</sup> (1.12 Å).

In conclusion, in the present paper the time-resolved spectroscopy technique has been employed to study the optical properties of KCl:Ba, Eu, KCl:Sr, Eu, KCl:Eu, KBr:Sr, Eu and KBr:Eu. This technique has proved to be quite useful for studying impurity clustering between two different ions, in particular when one of the ions is not optically active. The data obtained indicate that pairing of Ba<sup>2+</sup> and Eu<sup>2+</sup> ions is more favourable than that of Sr<sup>2+</sup>–Eu<sup>2+</sup> in the potassium halide lattices, in agreement with the expectation of the ionic radius criterion proposed by Rubio *et al* to predict impurity clustering in a solid material.

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