

Precipitation of Ba^{2+} ions in KCl using Eu^{2+} as an optical probe

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The results of the precipitation of Ba^{2+} ions in KCl crystals using Eu^{2+} as a probe are discussed. The Eu^{2+} -ion concentration used in these studies is about 10% of that of Ba^{2+} . Ionic-thermocurrent (ITC), EPR, and luminescence measurements were carried out in quenched and annealed samples. Quenched samples show one-emission-band peaking at 417 nm, which is characteristic of isolated- Eu^{2+} -vacancy complexes, while the ITC peak corresponds to isolated- Ba^{2+} -vacancy complexes. On the other hand, the EPR spectra correspond to Eu^{2+} -vacancy complexes, in agreement with the luminescence results. Annealing processes at temperatures below 400 K give rise to emission bands at 429 and 441 nm. This result, together with those of the ITC measurements, points out the presence of Eu^{2+} - Ba^{2+} complexes as well as barium precipitates. In particular, it is worth noting the presence of a cubic phase of $BaCl_2$, stable at room temperature, assigned to the band-emission peaking at 429 nm. This result is supported by EPR measurements that show a typical cubic spectrum. For annealing temperatures between 400 and 500 K, the nucleation of an orthorhombic phase is achieved, besides that of a cubic nature.

I. INTRODUCTION

Precipitation of a phase containing divalent ions from an alkali halide solid solution can take different structural forms. These have been investigated by different techniques such as electron paramagnetic resonance¹⁻³ (EPR), electron microscopy,^{4,5} x-ray diffraction,^{6,7} optical techniques,⁸⁻¹⁰ etc. The characteristic structures that have been identified are associated with the stable dihalide phase MX_2 (where $M = Ca^{2+}, Sr^{2+}, Ba^{2+}, Eu^{2+}$, etc; $X = Cl^-, Br^-, I^-$). Also depending on the impurity ion, the host, and the annealing temperature, another metastable phase, the so-called Suzuki phase, can take place. On the other hand, it is well known that the presence of these precipitates may influence considerably the physical properties of these crystals and it is for this reason that a lot of work has been done on this subject.

In the particular case of Eu^{2+} and Pb^{2+} as impurity ions in the above-mentioned crystals, the presence of precipitates and aggregates has been directly established from the analysis of the absorption and emission spectra, which are quite dependent on the aggregation-precipitation state of the impurity in the crystal lattice;¹⁰⁻¹² this fact has allowed the differentiation among the various aggregates and precipitates formed under different thermal treatments. Unfortunately for other divalent-cation impurities such as Mg^{2+} , Sr^{2+} , Ba^{2+} , etc., the presence of aggregates-precipitates in the samples cannot be directly obtained by means of such a simple technique. This difficulty, however, may be avoided by using adequate impurities to optically probe the pre-

cipitation processes of the impurity ions which do not present optical spectra. This technique has been proved to be very useful to study the precipitation processes with ions which are not optically active.¹³⁻¹⁵

In the present paper a detailed study dealing with the precipitation processes of Ba^{2+} ions in the KCl matrix, using Eu^{2+} as an optical probe, is reported.

II. EXPERIMENT

Single crystals of KCl doubly doped with Ba^{2+} and Eu^{2+} were grown from the melt by the Czochralski method under a controlled atmosphere of dry argon, the crystals being slowly cooled to room temperature in the furnace. The dopants were $BaCl_2$ and $EuCl_2$, the latter being previously reduced from $EuCl_3 \cdot 6H_2O$ with the use of standard techniques. The concentration of barium and europium ions was determined by atomic absorption spectrophotometry, the results being 30 ppm of Eu^{2+} and 300 ppm of Ba^{2+} ions. Thermal quenching was performed by heating the samples at 850 K for about 30 min and then dropping them onto a copper block at room temperature (300 K). Annealing treatments were carried out in a standard furnace with temperature control in the range ± 5 K.

The emission spectra were obtained at room temperature with a Perkin-Elmer model 650-10S fluorescence spectrophotometer with a resolution of 2 nm. The excitation source was a 150-W xenon lamp which was calibrated for intensity versus wavelength. All excitation spectra have been corrected for this effect and for the photomul-

plier response. A computer program was used to decompose the emission spectra into different Gaussian-shape bands.

Ionic thermocurrent (ITC) experiments were also performed in the 77–300-K temperature range using a setup described elsewhere.¹⁶ EPR data were obtained at 300 K using a Varian E-4 reflection-type X-band spectrometer with 100-kHz modulation.

III. EXPERIMENTAL RESULTS

Figure 1 shows the experimentally determined, ITC spectrum obtained from quenched samples of europium and barium doubly doped KCl crystals. Such ITC peaks allowed us to determine the activation energy for the reorientational jumps and the preexponential factor of the Ba^{2+} -vacancy complex in this host. To do that a least square fitting of $\ln[p_i^\infty/I(t)]$ versus T^{-1} was made. p_i^∞ and $I(t)$ are the residual polarization and the current at time t , respectively. The experimental data can be fitted with a monoenergetic model without taking into account any dipole-dipole interaction. The observed peak may be attributed then to a nearest-neighbor Ba^{2+} -vacancy complex reorientational process. Table I shows the fitting parameters which are in agreement with those reported in the literature.¹⁷ The Ba^{2+} dipole concentration obtained from the ITC peak of freshly quenched samples is within 10–15 % of the one determined from atomic absorption measurements; on the other hand, these results show a negligible contribution of the Eu^{2+} -vacancy complexes, to the depolarization current.

The inset in Fig. 1 shows the evolution of the intensity of the ITC peak as a function of time at an annealing

TABLE I. Values for the thermally stimulated depolarization parameters of Ba^{2+} -cation-vacancy dipoles in Eu-doped KCl single crystals.

System	T_m (K)	E (eV)	τ_0^{-1} (sec^{-1})	Reference
KCl:EuCl ₂	230	0.69 ± 0.02	$1.6 \times 10^{13 \pm 0.4}$	This work
KCl	233	0.71 ± 0.01	3.1×10^{13}	17

temperature of 340 K. The decrease in intensity is simply due to the aggregation process at this temperature. It should be noted that the time evolution of this peak could be fitted with the monoenergetic model for times up to 200 h. After such time this simple fitting procedure could not be made. This is probably due to the fact that the number of Ba^{2+} dipole complexes predominates at the beginning over that of isolated Eu^{2+} dipoles present in the lattice. Later on, other dipolar complexes formed during the aggregation process might also contribute to the ITC spectra making difficult the fitting procedure with just one interaction.

In order to have a better insight into the barium precipitation processes, luminescence and EPR studies of the Eu^{2+} ion were also performed. Immediately after quenching, the emission spectrum consists of only one symmetric band peaking at 417 nm; this peak is the characteristic isolated europium emission in KCl.¹⁰ Also, the EPR spectrum corresponds to isolated Eu^{2+} -vacancy complexes¹⁸ in orthorhombic symmetry. This spectrum consists of 14 groups of fine transitions with $\Delta M_s = \pm 1$ and each group consists of 12 hyperfine transitions, due to the isotopes ¹⁵¹Eu and ¹⁵³Eu with a nuclear spin of $\frac{5}{2}$

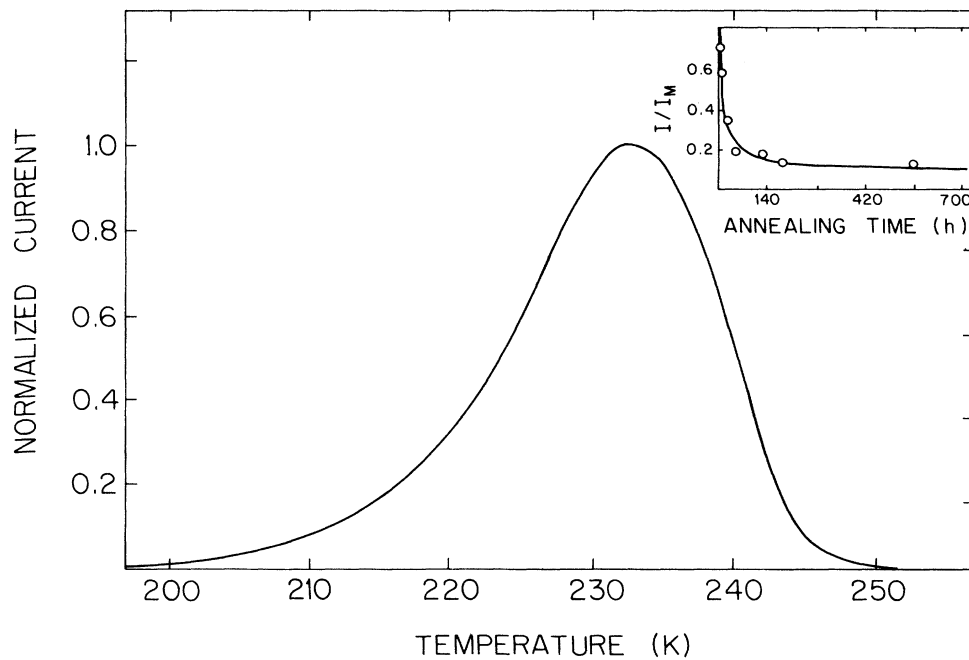


FIG. 1. ITC peak of a doubly doped sample $\text{KCl}:\text{Ba}^{2+}:\text{Eu}^{2+}$. This peak is due to the reorientational process of Ba^{2+} -vacancy complexes. The inset shows the intensity of this signal as a function of the annealing time at 340 K.

each. For the sake of brevity the spectra is not reproduced.

The time evolution of the emission spectra obtained from a crystal which has been annealed at 370 K is shown in Fig. 2(a). The spectrum consists of three emission bands peaking at 417, 429, and 441 nm. The half-intensity bandwidths of these bands obtained by decomposing the structured spectra in symmetric Gaussian-shape bands are 1210, 1307, and 2590 cm⁻¹, respectively. The integrated intensity of the bands peaking at 417, 429, and 441 nm is shown in Fig. 2(b) as a function of the annealing time at 370 K. The decrease of the former band is in the benefit of the growing of the latter two. It should be noted that the decrease of the intensity of this band, which, on the other hand, has been attributed to isolated europium dipoles, as mentioned above, is very

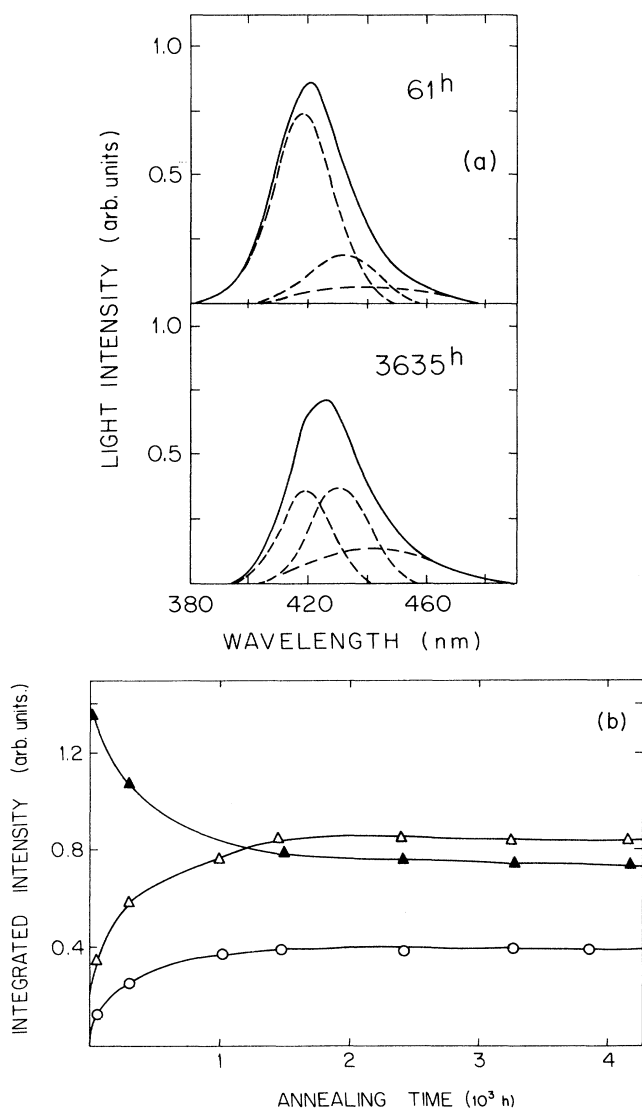


FIG. 2. Emission spectra of the Eu²⁺ ion in a KCl:Ba²⁺ sample. (a) The emission band consists of the superposition of three main bands peaking at 417, 429, and 441 nm. (b) Time evolution of these three bands at an annealing temperature of 370 K (▲, 417 nm; △, 429 nm; ○, 441 nm).

fast during the first 200 h of annealing, reaching a plateau at about 1000 h. The other two bands also stabilize their growth at about the same time. Additionally the ITC measurements could be fitted with a single process during the first 200 h. These two facts indicate the presence of dimers, trimers, or higher-order complexes.

The evolution of the emission spectra was also analyzed as a function of the annealing time at 330 and 340 K after the quenching treatment. The same emission bands mentioned above as well as the same behavior was observed for these temperatures.

The room-temperature EPR spectrum of the same sample from which the optical data described above were obtained is portrayed in Fig. 3. Reference to this figure shows that, in addition to the weak orthorhombic spectrum due to those europium ions still in solution in the KCl matrix, an intense spectrum consisting of the superposition of seven groups of hyperfine transitions is clearly distinguished. The spectrum was studied by observing its behavior as the crystal was rotated in either a (100) or a (110) plane. The observed behavior of the spectrum was the one expected for an *S* rare-earth impurity ion in a cubic crystalline field. Therefore the spectrum was fitted with the spin-Hamiltonian

$$H = g\mu_B \mathbf{H} \cdot \mathbf{S} + \frac{1}{60} b_4^0 (O_4^0 + 5O_4^4) + A \mathbf{I} \cdot \mathbf{S}$$

with $S = \frac{7}{2}$ and $I = \frac{5}{2}$. The sixth-order parameter b_6^0 was assumed to be very small and it was neglected. The values obtained for the spin-Hamiltonian parameters were $g = 1.996 \pm 0.002$, $b_4^0 = -3.6 \pm 0.1$ G, and $^{151}A = -33.8 \pm 0.1$ G.

On the other hand, annealing treatments of quenched samples at 440 and 470 K produce the same emission bands as those mentioned previously, although at variance with annealing at temperatures below 370 K, another band peaking at 392 nm, and 1170 cm⁻¹ bandwidth is obtained. Figure 4 shows the time evolution of the emission spectra and the evolution of the integrated intensity of each band plotted as a function of the annealing time at 440 K. As in the previous cases a decrease in the intensity of the band peaking at 417 nm which benefits the other bands is observed.

Figure 5 shows the excitation spectra of the different emission bands. There are significant differences among them, a fact that gives evidence of the different nature of the crystalline environments surrounding the Eu²⁺ ions. These spectra consists of two broad bands, the separation between them being a measure of the crystal-field splitting ($10Dq$) of the excited $5d$ europium orbital into its t_{2g} and e_g components. The values for the $10Dq$ splitting, calculated from the centers of gravity of the two broad bands in the excitation spectrum of each of the emission bands, are given in Table II. Due to the overlapping of the band peaking at 429 nm and the proximity of the 417-nm band, and its low intensity, its $10Dq$ value is not quite reliable; the uncertainty of this measurement is about 8%. For annealing temperatures at 470 K the same results are obtained.

The thermal stability of the emission bands was also investigated in the range of temperatures 300–800 K. To perform these measurements crystals showing an intense

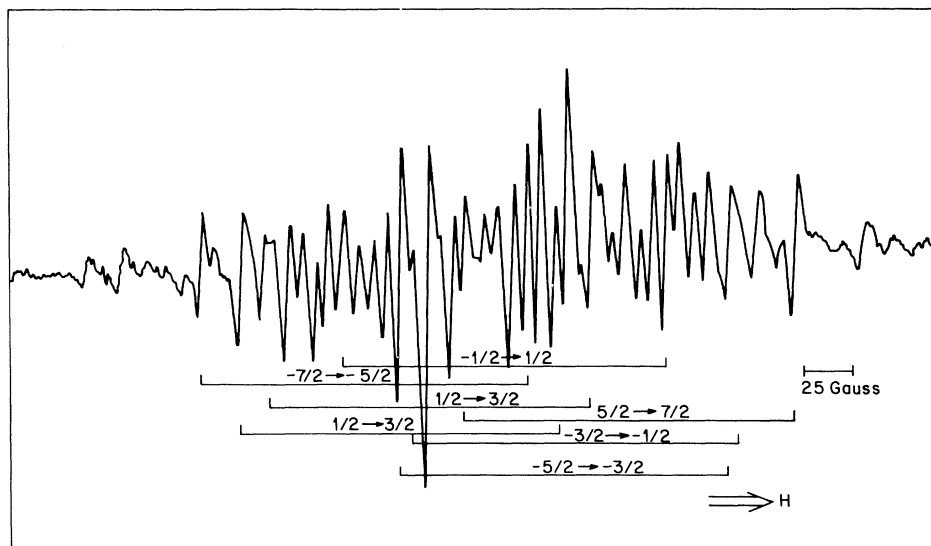


FIG. 3. Electron paramagnetic resonance spectrum of a crystal annealed at 370 K for about 2000 h. It corresponds to a Eu^{2+} ion in a cubic symmetry site of the BaCl_2 precipitates.

emission at 392 nm were heated at different temperatures for 10 min and then dropped onto a copper block at room temperature. Figure 6 shows the results of these experiments. As can be seen the emission at 392, 429, and 441 nm decrease while that at 417 nm increase, a fact due to the thermal dissolution of the different precipitates in which the Eu^{2+} ions were incorporated. The thermal stability of the emission bands occurring at 429 and 441 nm is particularly noticeable.

IV. DISCUSSION

The data presented above strongly suggest that the europium ions are associated with different barium aggregates and precipitates.

The results obtained from the ITC measurements clearly point out that the Ba^{2+} -vacancy complexes present immediately after quenching tend to form aggregates in a few hours. On the other hand, the emission band peaking at 417 nm is very similar to that previously reported in quenched samples of $\text{KCl}:\text{Eu}^{2+}$, although its peak position is slightly blue shifted. Since this band is the only one observed after quenching one can consider that the complexes responsible for this band are isolated

TABLE II. Values for the $10Dq$ splitting of the $5d$ orbitals of the europium ion obtained from the spectrum of each emission band observed in $\text{KCl}:\text{Ba}:\text{Eu}$ samples annealed at 470 K.

Emission band peak position (nm)	Bandwidth (cm^{-1})	Excitation spectrum $10Dq$ (cm^{-1})
392	1170	9 368
417	1210	11 997 ^a
429	1307	11 158
441	2590	11 225

^aReference 11.

Eu^{2+} -cation-vacancy dipoles, as well as possible mixed Ba-Eu centers. Now, the intensity of this band decreases very rapidly during the first 200 h of annealing at the temperatures used, while the ITO peak due to the Ba^{2+} -cation-vacancy dipolar complexes does the same. At the same time, the other bands start to increase. These facts can be correlated if one thinks that the barium ions start to form aggregated phases, in which some of the europium ions become incorporated. On the other hand, the band peaking at 417 nm reaches a stable value for times up to 5000 h of annealing. This might be an indication of the association of Eu^{2+} dipoles and Ba^{2+} dipoles into larger complexes. This effect can be supported by the suggestion of Rubio and co-workers¹⁹ that if the average radius of the two impurities is nearly identical to that of the host cation ion that they substitute in the lattice, there is a strong tendency to pair formation, probably to reduce the strain introduced in the lattice by the presence of each impurity alone. Once these pairs are formed they remain very stable in the lattice, which, on the other hand, is consistent with the experimental observation that the 417-nm band remains present for a long period of time, and that the other emission band associated with other aggregated or precipitated phases does not grow any more during this period of time.

It is a well-known fact, that the Eu^{2+} ion in KCl precipitates into a Suzuki-like phase for annealing temperatures of 400 K or below.¹⁰ Under such circumstances the corresponding emission band peaks at 427 nm. Additionally, according to Sors and Lilley,²⁰ when the ratio of the ionic radii of the impurity ion to that of the host cation is less than 1.2, the impurity ions can precipitate into the Suzuki phase.

Now, as this condition is satisfied in the present case for the Ba^{2+} ions, one might wonder if the 429-nm emission could be associated with the Eu^{2+} ion incorporated in the Ba^{2+} -Suzuki phase formed in the KCl lattice. In

order to check this possibility, the annealing treatments at temperatures between 370 and 470 K were carried out, since it is also known that at annealing temperatures about 470 K the Eu²⁺ ion precipitate in the stable EuCl₂ (Ref. 11) dihalide phase. Assuming that the Ba²⁺ ion behaves the same as Eu²⁺, one might expect to obtain a different aggregation process above 370 K and a different emission band under this thermal treatment. However, it was found that the band peaking at 429 nm appears for annealing temperatures of 370 K or below, as well as for temperatures of 470 K or below. This can be seen in Figs. 2(a) and 4(a).

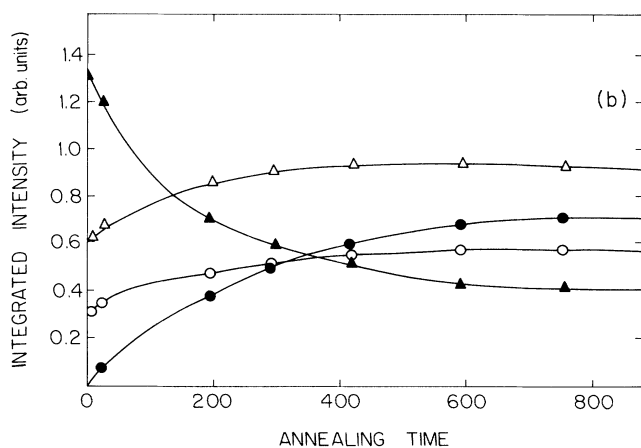
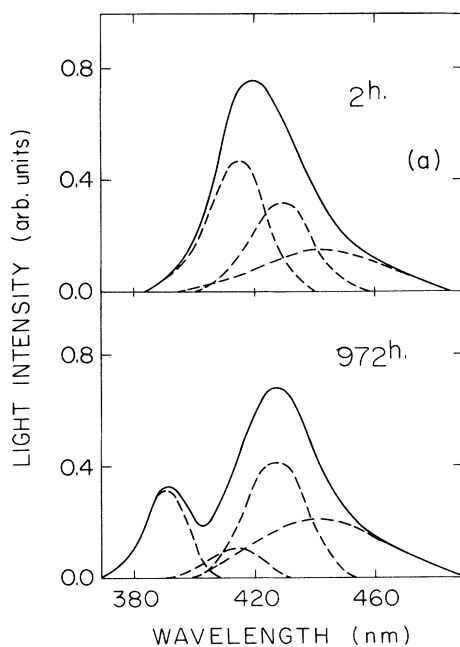


FIG. 4. Fluorescence spectra of Eu²⁺ in an annealed KCl:Ba²⁺ sample at 440 K. At variance with lower annealing temperatures there is a band peaking at 392 nm. (a) Decomposition into different contributions. (b) Integrated intensity as a function of the annealing time (●, 392 nm; ▲, 417 nm; △, 429 nm; ○, 441 nm).

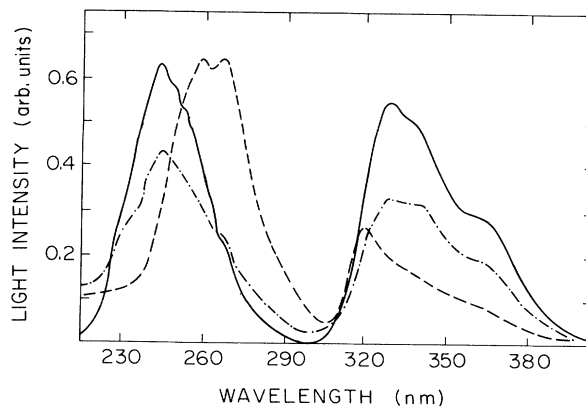


FIG. 5. Excitation spectra for the emission bands peaking at 392 nm (---), 429 nm (—), and 441 nm (-·-·-).

Also, it has been reported that the thermal resolution of the Suzuki phase occurs in a very narrow range of temperatures.^{21,22} In the present case, however, the dissolution of the phase that produces the emission band at 429 nm occurs over a wide range of temperatures. These facts suggest then that the precipitated phase of barium producing such an europium emission band must be associated with a different structure.

On the other hand, Swamy-Rao and Parasnis,²³ using optical microscopy and x-ray diffraction techniques, have described the morphology of BaCl₂ crystallites in the NaCl matrix. They reported that Ba²⁺ ions in NaCl precipitate into cubic and orthorhombic dichloride phases for annealing temperatures up to 600 K. The cubic phase precipitates have rod and platelet shapes and they are coherent with the matrix on the plane {111}. Additionally, Carrillo, Carrillo, and Rubio,²⁴ using a geometrical model to study the coherence between the matrix and precipitated phases, suggested active participation of nu-

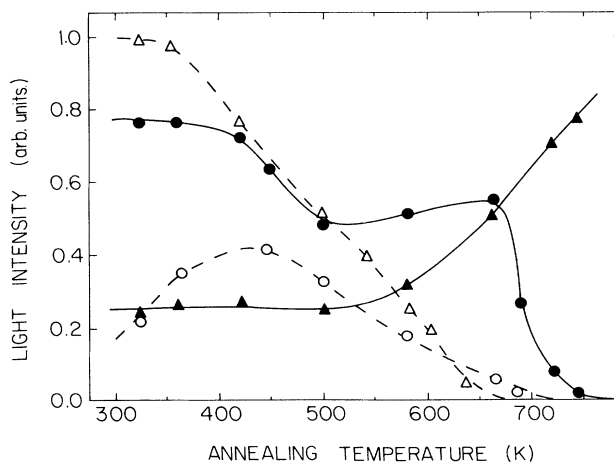


FIG. 6. Thermal stability of the emission bands. The stability of the emission bands peaking at 392 nm (●), 429 nm (△), and 441 nm (○) should be noticed.

cleation rods in the $\langle 220 \rangle$ direction, contained in an $\{111\}$ plane of the precipitate, as a generator of the platelets of cubic structure observed in this plane and limited by sides parallel to the $\langle 123 \rangle$ matrix directions. Unfortunately, there is no equivalent experimental study of the morphology of Ba precipitates in KCl, but in principle following the suggestion of Carrillo, Carrillo, and Rubio one may expect the easy growth of a cubic precipitate over the $\{110\}$ matrix plane and also on the $\{111\}$ plane. Moreover, the absence of nucleation rods in the $\langle 110 \rangle$ direction for this host can be considered as a restrictive condition for the precipitation of Ba ions into the Suzuki phase. One can then tentatively assign the europium emission bands peaking at 429 and 441 nm with barium precipitates of cubic structure growing in such planes as predicted by the geometric model of Carrillo, Carrillo, and Rubio. Additional information to reinforce this assignment can be gathered from the $10Dq$ values measured (Table II) in the excitation spectra for both emission bands. The $10Dq$ value represent the intensity of the crystalline field acting at the Eu^{2+} site; a similar value obtained for these bands gives evidence of a similar crystalline environment of the Eu^{2+} ion in the precipitates emitting in 427 and 441 nm. In addition, the thermal stability of these emission bands is also similar (Fig. 6). On the other hand, the above conclusions are confirmed by the EPR results which show spectra characteristic of a

cubic site for crystals annealed at temperatures below 370 K.

Brixner and Ferretti²⁵ performed an investigation dealing with the fluorescence emission of Eu^{2+} in BaCl_2 , which has an orthorhombic structure, and found that the fluorescence spectrum gives rise to a band peaking at 398 nm. Swamy-Rao and Parasnis also found platelets of orthorhombic structure in $\text{NaCl}:\text{Ba}^{2+}$. From these results it can be concluded that the band at 392 nm in $\text{KCl}:\text{Ba}:\text{Eu}$ system must be associated with precipitates of barium chloride of orthorhombic nature. Additionally, the thermal stability of this precipitate suggest some relationship with those precipitates of cubic nature which are emitting at 441 nm as can be seen from Fig. 6.

Finally, we may conclude that the europium ion is a very sensitive optical probe to follow precipitation processes in other ions that are not optically or magnetically active. On the other hand, our results show that in KCl matrix it is possible to stabilize at room temperature a cubic phase of BaCl_2 , while it is known that anhydrous barium chloride at room temperature is only stable in an orthorhombic phase.

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