OPTICAL STUDIES OF DIVALENT EUROPIUM DOPED MIXED KCl–KBr CRYSTALS

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A study about the aggregation–precipitation processes of divalent europium ions in mixed potassium halides (Cl/Br) has been carried out. Quenched samples lead to a single emission band at 418 nm, which compared with the emission observed in the corresponding europium doped non-mixed alkali halide crystals, appears perturbed by the presence of Cl or Br ions. This band has been ascribed to free europium–vacancy complexes. The annealing at 353 K produces an emission band composed of several contributions: (1) free dipoles, (2) an emission that might be attributed to a Suzuki type mixed phase containing chloride as well as bromide ions and (3) a band due to a metastable mixed phase peaking at around 450 nm. On the other hand, the annealing at 473 K induces metastable phases of the dihalide type emitting at 430, 448 and 474 nm. The intensity of these bands changes as a function of the content of halogen ions.

Keywords: Impurities; Luminescence; Second phase precipitation; Mixed crystals

INTRODUCTION

The alkali halide crystals, pure and doped, have been extensively studied because they posses a structure which allows for simple models that can be used for interpretation of physical phenomenon in other more complex crystalline systems. During the last years several works have

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been done on non-doped mixed alkali halide crystals due to the potential technological applications such as solid state lasers [1], but on divalent ion doped mixed crystals the information is scarce. There are some studies about the miscibility in KCl–KBr [2–4], establishing the range of anion concentration that can be mixed. The presence of these halogen impurity ions not only affects the physical properties of the crystal but also those of any divalent impurity ion [5,6].

On the other hand, much work has been done in order to characterize the optical and paramagnetic properties of divalent Eu doped alkali halide crystals [7–11]. Information has been gathered in these works concerning the above mentioned properties of the Eu^{2+}-cation vacancy complexes and about the aggregation–precipitation state of the impurity ion in those crystals. In particular for potassium and rubidium halides it has been observed that for annealing temperatures below 373 K the formation of the Suzuki [12] phase takes place, while for temperatures above 400 K the dihalide phase occurs [13,14]. Clark *et al.* [15] have studied quenched crystals of $KCl_{1-x}Br_x : Eu^{2+}$, finding that the halogen impurity ions occupy lattice sites which are very close to the Eu^{2+}-cation vacancy complexes (free dipoles), while Pedrero *et al.* [16] studied the precipitation processes in $NaBr_{1-x}Cl_x : Eu^{2+}$ mixed crystals. Their results point out that the dipoles act as nucleation centers producing mixed europium dihalide phases. In both works a remarkable difference has been found about the optical and paramagnetic response of this ion, with respect to the non-mixed alkali halide crystals. Pérez-Salas *et al.* [17] have recently performed a study about the precipitation processes of europium doped $KCl_{1-x}Br_x$ mixed crystals for an annealing temperature of 333 K. Their results point out the presence of free dipoles, a Suzuki-type phase and EuX_2 type aggregates. The former two occur as in the case of europium doped non-mixed alkali halide crystals, for this annealing temperature, while the latter are not expected to be formed at this temperature according to previous results [13].

In this paper we are reporting the results obtained by optical techniques about the thermally induced precipitation of the europium ion for different anion concentrations in the $KCl_{1-x}Br_x$ mixed crystals. The precipitation processes were studied at two annealing temperatures. The formation of the Suzuki phase in the divalent impurity doped alkali halide crystals is known to occur for temperatures up to 373 K [13], so in order to increase the temperature range used by Pérez-Salas *et al.* and

analyze the possible formation of this phase an annealing temperature of 353 K was used. On the other hand, studies on doped mixed crystals at higher annealing temperatures at which the EuX_2 type precipitates are expected to be formed have not yet been performed, so a study of the precipitation processes at 473 K has been carried out in this work.

EXPERIMENTAL

The $KCl_{1-x}Br_x$: Eu^{2+} crystals with variable x (KCl 99%, KBr 1%; KCl 95%, KBr 5%; KCl 85%, KBr 15%; KCl 60%, KBr 40%; KCl 50%, KBr 50%; KCl 30%, KBr 70%; KCl 15%, KBr 85%; KCl 5%, KBr 95%) were grown from the melt by the Czochralski method under a controlled atmosphere of dry argon and slowly cooled to room temperature (RT) in the furnace. An X-ray analysis showed monocrystalline samples. The doping material $EuCl_2$ was previously reduced from $EuCl_3$: $6H_2O$ by standard techniques. Atomic absorption was used to determine the europium concentration. Samples with a fixed concentration of about 100 ppm were selected for the experiments.

Thermal treatments were performed in standard furnaces with temperature control in the range ±3 K. Thermal quenching was done by heating the samples at 850 K for about 30 min and then dropping them onto a copper block at RT. Annealing treatments were done at 353 and 473 K for variable times. Luminescence measurements were made at RT using a Perkin-Elmer model 650-10S fluorescence spectrophotometer with a 150 W Xenon lamp. All excitation spectra were corrected for intensity and photomultiplier response. The deconvolution of the emission spectra into different Gaussian-shape bands was made with the computer program Origin.

RESULTS AND DISCUSSION

Figure 1 shows an example of the Eu^{2+} emission spectra for quenched mixed crystals with different concentrations of the halide ion, as it is indicated in the figure. As can be seen, they consist of a single emission band with the maximum around 418 nm. It is worth to note that the absorption spectrum, independently of the halide concentration,
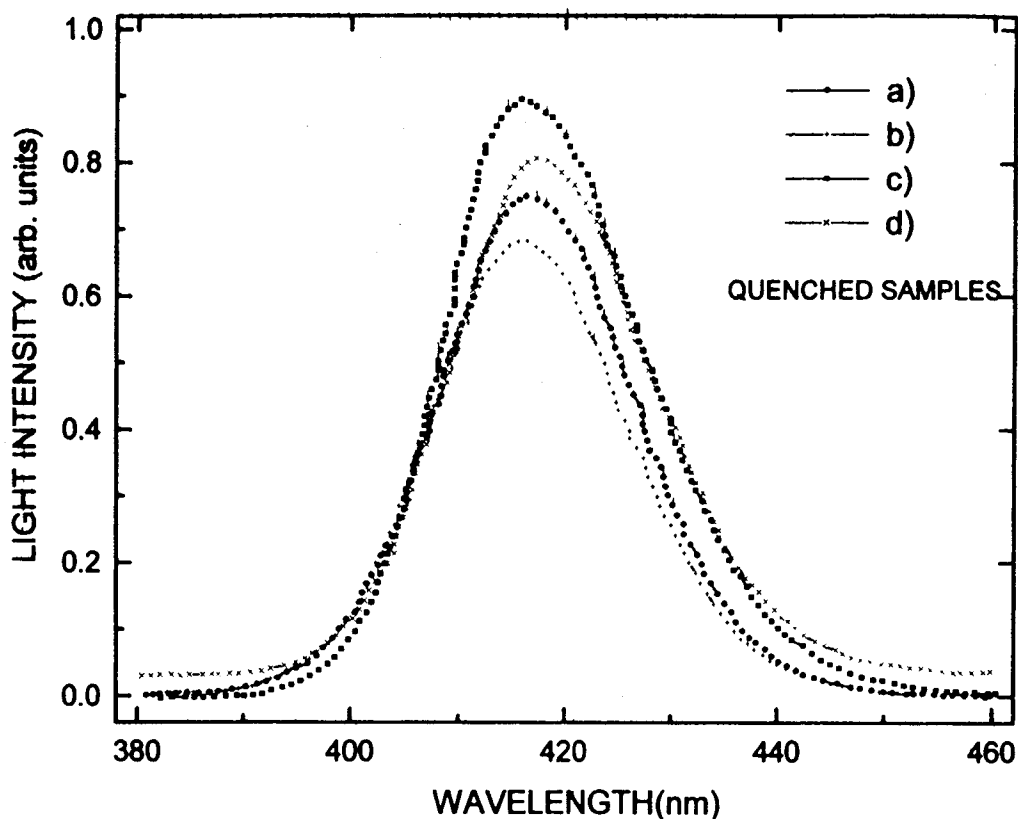
FIGURE 1 Eu^{2+} emission spectra for quenched mixed crystals: (a) KCl 5%, KBr 95%; (b) KCl 15%, KBr 85%; (c) KCl 85%, KBr 15%; and (d) KCl 95%, KBr 5%.

consists of the usual two broad bands peaking at around 245 and 350 nm, respectively. The emission spectrum consists of just one band either exciting with light lying in the high or low energy spectral absorption region. On the other hand, for divalent europium doped KCl and KBr quenched crystals the emission spectrum consists of a single band peaking at 418 and 421 nm [13,14]. These have been interpreted as emission bands due to isolated free dipoles. As mentioned above, Clark *et al.* [15] have found that the anion impurity is in a close lattice position to the divalent impurity ion. A similar situation seems to prevail in the present case with the anion impurity slightly perturbing the europium emission. Then, these similarities point out that the observed emission band in the mixed crystals corresponds to isolated Eu^{2+}–vacancy complexes, perturbed by the presence of an anion different to that of the crystal host.

To study the precipitation processes the crystals were annealed at 353 K during variable times. The evolution of the emission spectrum for

each halide concentration was monitored by measuring the position of the maximum of each peak. The crystals were annealed for two and a half years observing them periodically until the peak reached a stable position.

Figure 2 shows, for selected halide concentrations, the emission spectra of annealed crystals. As can be seen, the emission band presents a long tail towards long wavelengths as compared with the quenched case.

In the cases of non-mixed alkali halide crystals and in $NaBr_{1-x}Cl_x : Eu^{2+}$ this asymmetry has been interpreted as the contribution of different types of aggregates–precipitates [13,14,16]. Following this interpretation the best fit of the emission spectra was obtained with three Gaussian shape bands, as shown in Fig. 2. Table I summarizes the results.

It can be noticed that for the cases in which there is a larger content of Br ions, there is a contributing Gaussian band peaking at 422 nm, while for a larger content of Cl ions the peak appears at around 418 nm. These bands have a small relative intensity and they can be reasonably
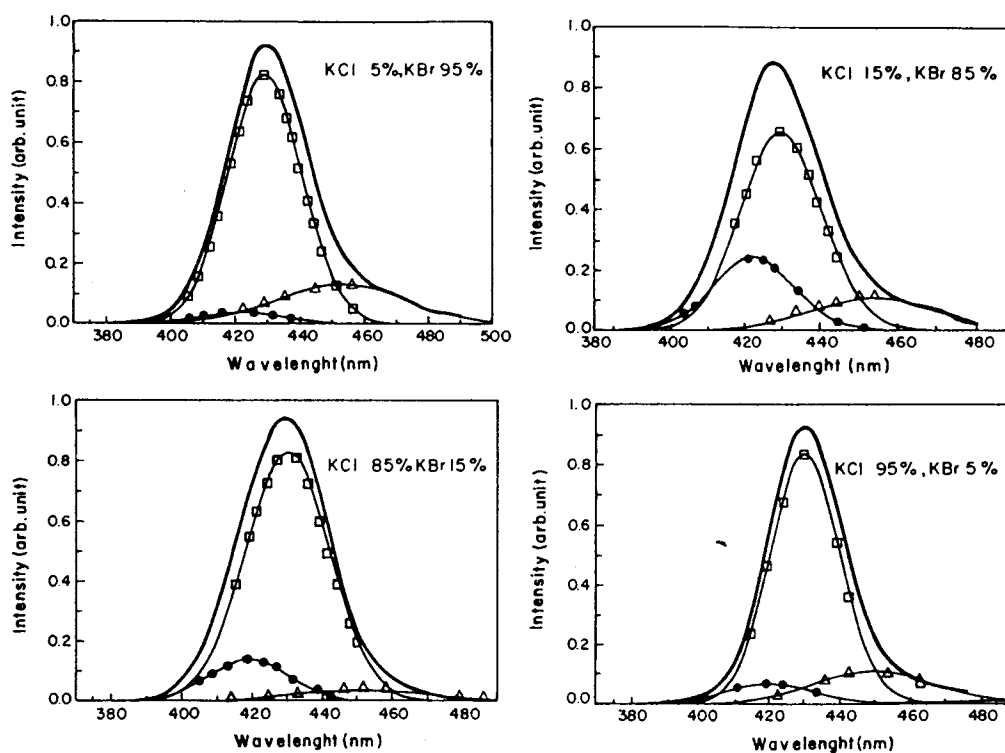

FIGURE 2   Emission spectra, $\lambda_{exc} = 340$ nm, of Eu doped mixed crystals with different anion concentrations and annealed at 353 K. The spectrum has been fitted with three Gaussian shape bands: (•) 422 nm, (□) 430 nm and (△) 454 nm.

TABLE I Peak position and halfwidth for the three gaussian shape components used to fit the experimental spectra

Crystal	Peak position (nm)	Halfwidth (nm)
KCl 5%, KBr 95%	422	23.95
	429	22.68
	452	30.30
KCl 15%, KBr 85%	422	21.81
	429	21.32
	452	31.12
KCl 85%, KBr 15%	419	23.10
	429	24.04
	452	42.79
KCl 95%, KBr 5%	420	23.62
	430	19.48
	449	31.31

ascribed to the respective free dipoles, as in $KBr:Eu^{2+}$ and $KCl:Eu^{2+}$ single crystals, since there is a larger content of one or another type of anion.

Now, taking into account that the annealing at 353 K induces the formation of the Suzuki phase in the single potassium and rubidium halides, as mentioned above, we used the same annealing temperature in order to see if it was possible to produce the same phase in mixed crystals. In $KCl:Eu^{2+}$ the maximum of the emission band corresponding to the Suzuki phase appears at 427 nm, while in $KBr:Eu^{2+}$ it peaks at 433 nm.

As can be seen in Table I, for all the samples studied and annealed at this temperature there is a second contributing band peaking at 430 nm. The fact that this peak appears at an intermediate position between 427 and 433 nm (emission bands for the Suzuki phase in Eu^{2+} doped KCl and KBr crystals, respectively) can be attributed to a Suzuki phase including chloride and bromide ions as well. It can be expected that the presence of a different anion (chloride or bromide) might produce significant changes in the crystal field splitting of the $4f^65d$ configuration. On the other hand, it has been shown that for the non-mixed doped alkali halide crystals, the Eu^{2+} ion is subjected to a more intense crystalline field when occupying lattice sites in the Suzuki phase [13], producing a large crystal field splitting of the 5d orbital. In our case this was confirmed by studying also the excitation spectra (see Fig. 3). The $10Dq$ values (calculated as the first moment of the intensity distribution
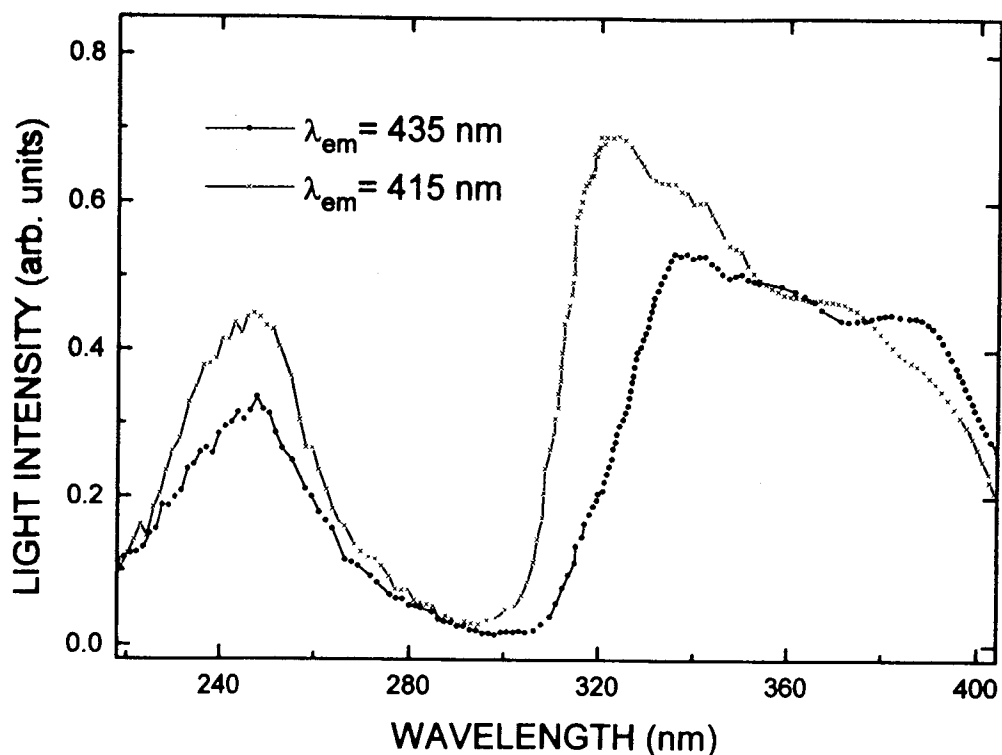
FIGURE 3   Excitation spectra obtained for two positions in the emission band: (●) at 435 nm associated to the metastable Suzuki phase and (×) the associated isolated dipole europium component.

of the excitation bands) are larger than those obtained for the isolated dipoles. As an example, the $10Dq$ values obtained for a KCl 85%, KBr 15% mixed crystal are $11695\,cm^{-1}$ for the annealed sample and $11280\,cm^{-1}$ for the quenched one. Then these aggregates–precipitates might be ascribed, as mentioned above, to a mixed Suzuki phase. These results are in agreement with those obtained by Pérez-Salas *et al.* [17].

There is a third band appearing at around 448 nm. This has been tentatively associated to metastable phases including both chloride and bromide ions. In the case of europium doped non-mixed alkali halides the emission bands associated to metastable phases of the dihalide type are usually found at long wavelengths. To support the previous assignment other samples were annealed at 473 K. This thermal treatment produces metastable dihalide phases for all the europium doped alkali halides [18].

As an example, the absorption spectrum of an europium doped KCl-85%, KBr-15% crystal, annealed 640 h at 473 K, is shown in Fig. 4. In
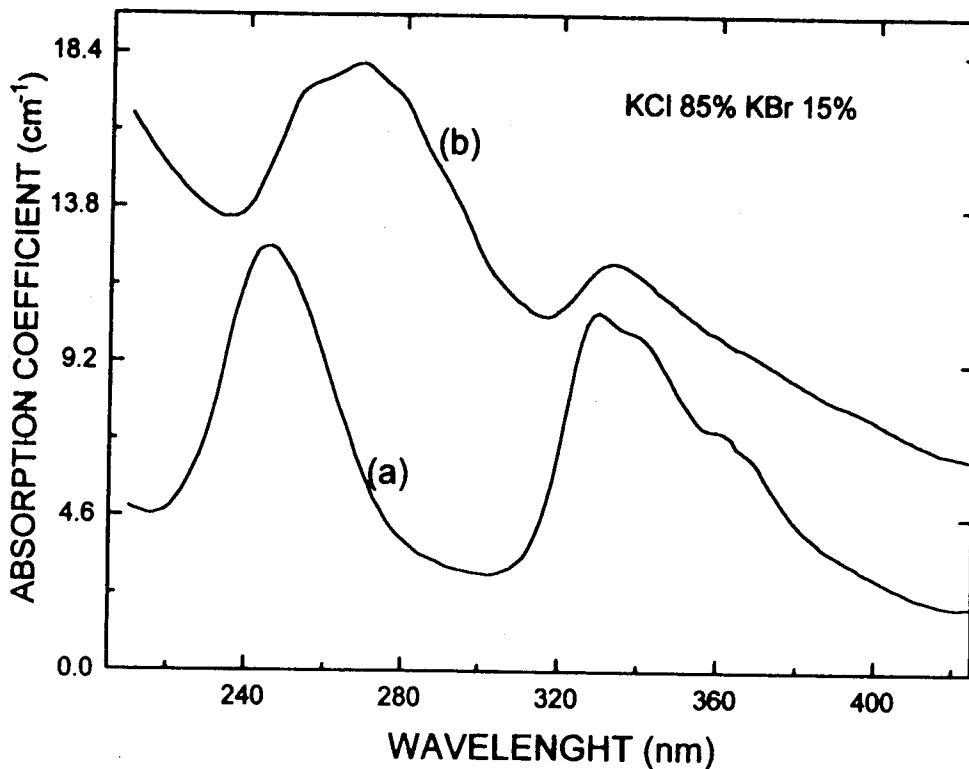
FIGURE 4   Absorption spectra of the Eu : KCl 85%, KBr 15% crystal: (a) quenched sample and (b) annealed 454 h at 473 K.

the same figure the spectrum obtained immediately after quenching from 773 K is included for the sake of comparison. The crystal field splitting of the 5d orbital is larger, as can be seen, in the quenched crystal. On the other hand, it is a well-known result that for the europium doped non-mixed alkali halide crystals the $10Dq$ value for the europium precipitates [13], of the dihalide type, decreases with respect to the free dipoles. Then, these spectra give evidence about the aggregation–precipitation state of the europium impurity ion when the crystals are annealed at this temperature. These states, as mentioned before, have been associated to chloride (bromide) type structures, called platelets, for which the high energy band shifts to the red decreasing the characteristic crystal field splitting $10Dq$. Figure 5 shows the excitation and emission spectra obtained for the annealed crystal. The emission spectrum, Fig. 5(a), consists two bands, one centered at around 420 nm and a broad one at 470 nm. On the other hand, the excitation spectrum of the band centered at 470 nm, Fig. 5(b), presents a smaller 5d splitting
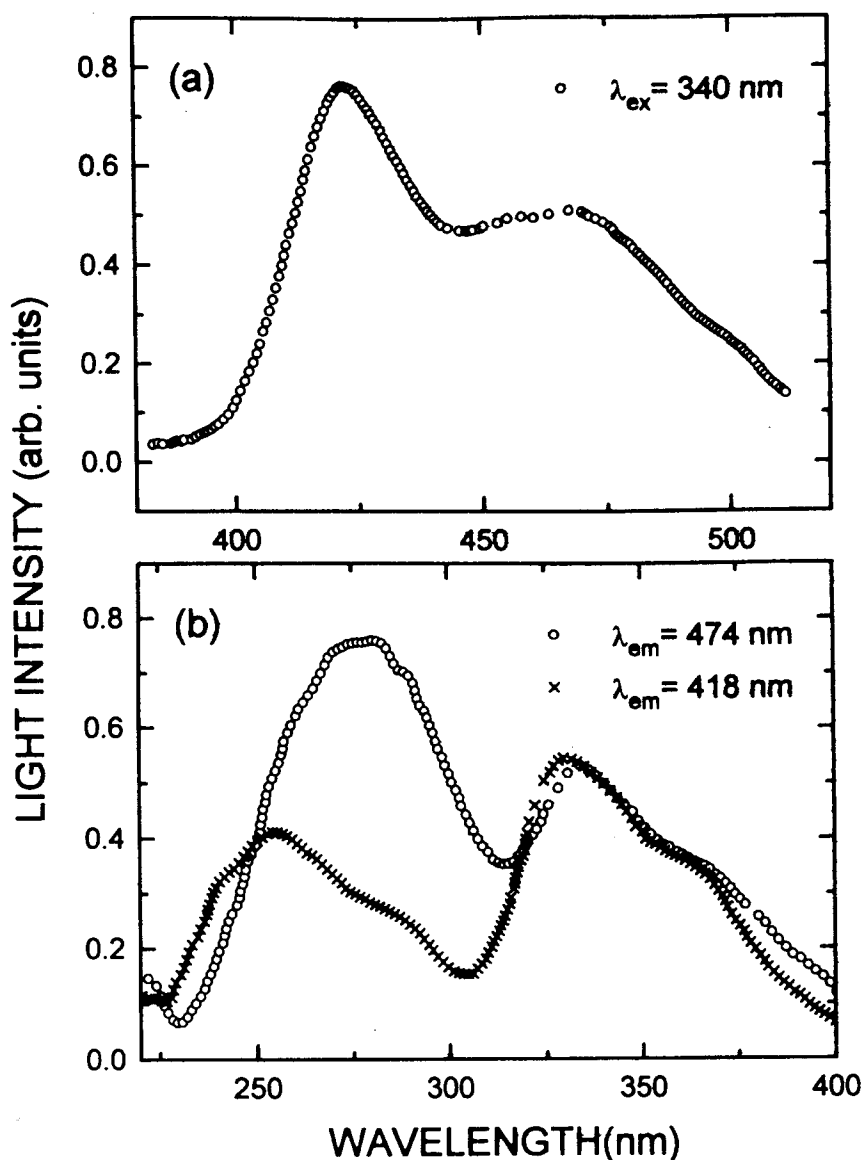
FIGURE 5   Optical response of the divalent europium ion in the KCl 85%, KBr 15% single crystal. (a) Emission spectrum under 340 nm excitation light. (b) Excitation spectra for dipolar europium 418 nm emission and the europium metastable phase at 474 nm.

than the one obtained from the excitation spectrum of the band at 420 nm, confirming then the presence of different aggregates as discussed above. The emission spectrum presented in Fig. 5(a) consists of several contributions. The band at 420 nm is the sum of two bands one peaking at 418 nm and the other at 430 nm. The former is ascribed to free dipoles while the latter can be associated to metastable precipitates. The broad band peaking at around 470 nm can be decomposed into two

contributing bands: one peaking at 448 nm, as the one found in the present study for the annealing at low temperature, and the other one at 474 nm, both of which can be attributed to metastable dihalide phases. The intensity of these bands changes accordingly to the halide concentration, as well as with the annealing time, as it will be discussed below.

The evolution of this type of structures has been followed through the emission spectrum as a function of the annealing time. Figure 6(a)
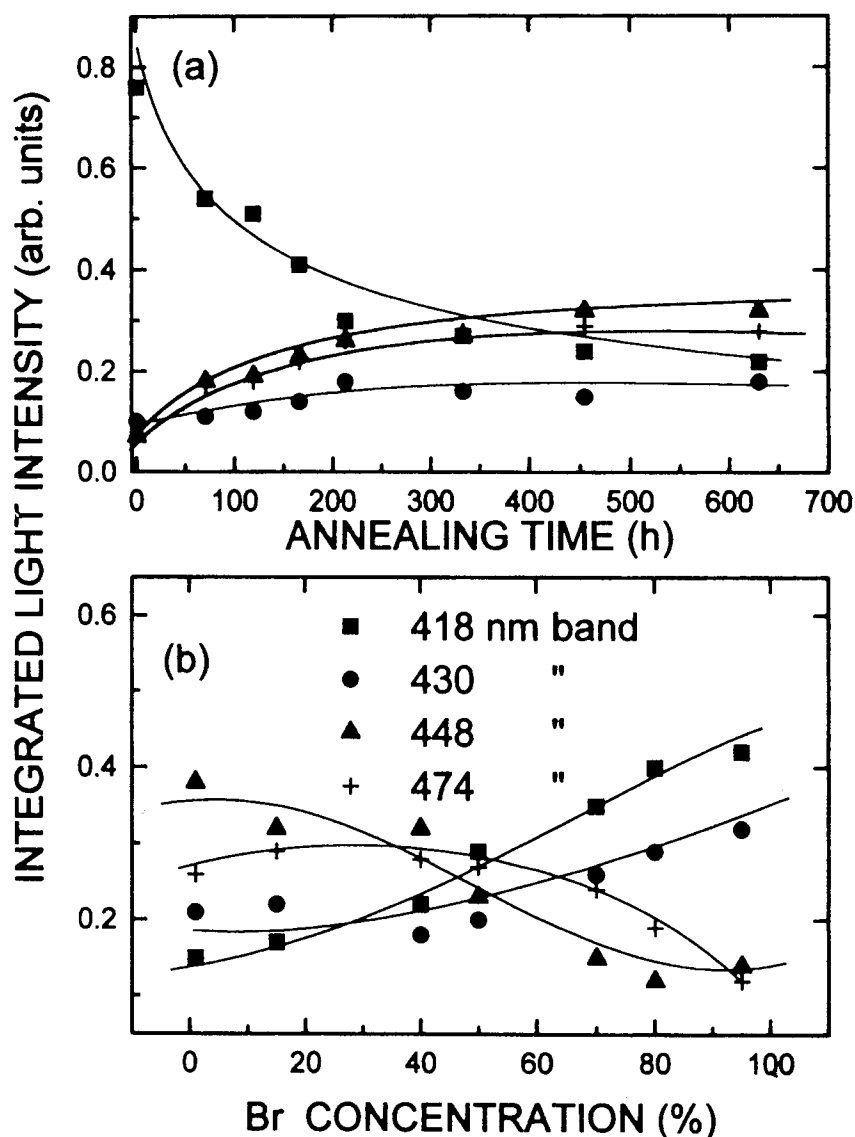

FIGURE 6   (a) Time evolution of the principal components of the emission spectrum for the mixed KCl 60%, KBr 40% crystal annealed at 473 K. (b) Dependence of the different europium complexes emission bands with the halide concentration. All samples were annealed for 630 h at 473 K.

shows the intensity variation of the emitted light, exciting with 350 nm, for a crystal KCl 60%, KBr 40%. As can be seen, it is very clear that the 418 nm (free dipoles) emission intensity decreases, while the other bands at 430, 448 and at 474 nm increase, reaching a plateau after about 300 h of annealing time. The same type of behavior has been observed in the non-mixed alkali halide crystals, confirming then the fact that the aggregation path followed by the europium ions in the mixed halide crystals is quite similar to that followed in the non-mixed alkali halide crystals for 473 K annealing temperatures.

Additionally, we have compared the efficiency of the formation of the precipitates emitting at 430, 448 and 474 nm regarding the anion mixture. This has been done by measuring the intensity of these emission bands at a fixed annealing time. Figure 6(b) shows the results for 630 h of annealing time. Crystals with a high content of chlorine ions show preferentially the band centered at 448 nm and few of the others. The behavior of this band as a function of the annealing time is quite similar to the one found for precipitates with the dihalide structure in KCl:Eu^{2+} [9]. As the bromide concentration is increased the intensity of the band at 474 nm also increases, reaching a maximum for about 40% of bromide ions, while the intensity of the band at 448 nm decreases. Finally, these types of precipitates for a high content of bromide ions are not preferentially formed, but instead a perturbed bromide second metastable phase precipitate, emitting at around 430 nm, is produced [14].

From the optical spectra it is not possible to know if the halide mixtures have the proportion of the characteristic halide of the initial mixture. However, evidently the halide content in the initial mixture influences the formation of the second phase in an efficient way.

CONCLUSIONS

The divalent europium ion has been usually considered as a good phosphor in the alkali halide crystals, possessing a reasonably quantum efficiency in the region of 420–450 nm. The present study on mixed alkali halide crystals has shown that the europium spectral response can be extended towards the green by an appropriate thermal annealing at 473 K. This produces an emission band at around 474 nm, whose

intensity also depends on the proportion of halide ions present in the initial mixture, besides other emission bands at lower wavelengths. On the other hand, the results point out that the optical properties of the europium ion are perturbed by the close presence of the minority anion and that Suzuki and dihalide type mixed phases can be induced with appropriate thermal annealings, in a similar way as they appear in the non-mixed alkali halide crystals.

Acknowledgment

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