

Cathodoluminescence and Optically Active Regions of Intrinsic and Induced Defects in Eu^{2+} -Doped KCl Crystals

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Cathodoluminescence (CL) spectra and images of $\text{KCl}:\text{Eu}^{2+}$ have been measured between 80 and 300 K. The CL broad band observed in the spectrum has been assigned to the well known $4f^65d \rightarrow 4f^7$ electronic transition of the Eu^{2+} ions and to the “off center” π luminescence (STE) modified by the F center absorption band (F center self-absorption). By studying the CL emissions at different temperatures it is found that the europium ions interfere the dynamics of the defect formation in KCl. In addition, the CL images have revealed the optically active zones in both the doped and pure samples.

1. Introduction

The origin of the induced luminescence by ionizing (X-, α -, β - and γ -rays) and non-ionizing (low energy UV) radiation in pure and doped alkali halide (AH) crystals has been studied extensively theoretically as well as experimentally during the past three decades. Actually, a great amount of radiation induced defects and its latter luminescent recombination processes have been identified and correlated to different lattice defects as electron and hole centers [1–4]. It is known that in pure AH crystals, these emissions are due to the recombination between the self-trapped holes and electrons [$(V_K + e^-)$] previously produced by X-rays [5–8], or by recombination of self-trapped excitons (STE) generated by direct stimulation in the excitonic region [9–12]. Due to the similarity of the energetic positions and the bandwidths of both the emissions, they are known to be the intrinsic luminescence of the material. This luminescence can be of σ , π or both in polarized state depending on the emitter level and material [13]. In fact, the STE luminescence is considered as a radiative “on center” [$(V_K + e^-)$, σ luminescence] and/or “off center” (STE, π luminescence) recombination [13]. In the case of mono- and divalent doped AH, the recombination process can produce the intrinsic luminescence perturbed by the dopant in addition to the emissions associated with the electronic transition of the impurity [14].

Recently, by CL and thermoluminescence (TL) studies in mixed $\text{KCl}:\text{KBr}$ crystals, three emission bands have been considered to be the intrinsic and perturbed STE ($\text{Br}_2^- + e^-$) π luminescence [15], and in KCl and KBr single crystals, the emission bands have been assigned to STE π and α center emissions [16]. In the case of doped

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crystals, i.e. KCl:Eu²⁺ samples, no CL studies have been performed until now, at least to our best knowledge, but several investigations by using different techniques and irradiation sources have been done to know the origin and processes involved in the luminescence of irradiated samples [17, 18]. The TL of room temperature (RT) β -rays and UV irradiated samples revealed the typical europium ion emission band and two shoulders located at both sides of the main emission. These two low intensity shoulders having maxima around 360 and 466 nm [19, 20]. In these studies, the authors did not associate these two emissions with the recombination of any defect produced by irradiation. Whereas, in pure KCl other authors [2, 16] have been assigned the band peaked at 460 nm as to an α center emission.

The sought objectives of this work are to present experimental evidence of the effect of europium on the formation and recombination processes of intrinsic and electron beam created defects in Eu²⁺ doped KCl, by measuring the CL spectra. Comparing the SEM and panchromatic CL images, it is also shown that the luminescence of recombination comes from specific regions of the material, placed favorably to accumulate intrinsic and electron beam induced defects.

2. Experimental

The KCl:Eu²⁺ single crystals were grown by the Czochralski technique under a controlled atmosphere of dry argon. For doping, 0.2% of EuCl₂ was added to the melt. Prior to any measurement, the KCl:Eu²⁺ crystals were annealed at 773 K for 30 min and quickly cooled to RT by contact with a copper plate to give a homogeneous distribution of Eu²⁺ ions. The crystals were observed in the secondary electron (SE) and CL modes of a scanning electron microscope (Hitachi S-2500) at temperatures between 80 and 300 K and beam energies in the range of 5–15 keV. The CL measurements were performed in the visible range with a photomultiplier tube (Hamamatsu R928). A computer controlled monochromator (Oriel 78215) coupled with a light guide was used for spectral analysis of the emission. The spectra and panchromatic images were collected in a slow sweep electron beam mode. The crystals were covered with a thin evaporated graphite layer to avoid the charge accumulation on the surfaces. The absorption measurements were done with a spectrophotometer (Perkin-Elmer Lambda 19) in the 200–800 nm spectral range.

3. Results

The CL spectra of KCl:Eu²⁺ crystals recorded at different temperatures are shown in Fig. 1. They consist of a very broad emission in the 320–700 nm range from 87 K to RT. The broad emission is overlapped with a strong emission band with maxima around 420 nm which shows different relative intensities depending on temperature. A minimum is shown in this CL spectra which is shifted from 550 nm at 300 K to 535 nm at 87 K. The intensity variation as a function of temperature of the main emission band (420 nm) and the shoulder around 455 nm is shown in Fig. 2. A minimum around 155 K is observed in the intensity versus temperature curve which is common for both bands. For comparison purposes the inset in Fig. 2 shows the same for pure KCl. A minimum around 220 K is shown. Considering that the CL signal is obtained during the electron beam irradiation and the electron beam current was constant for all the spectra re-

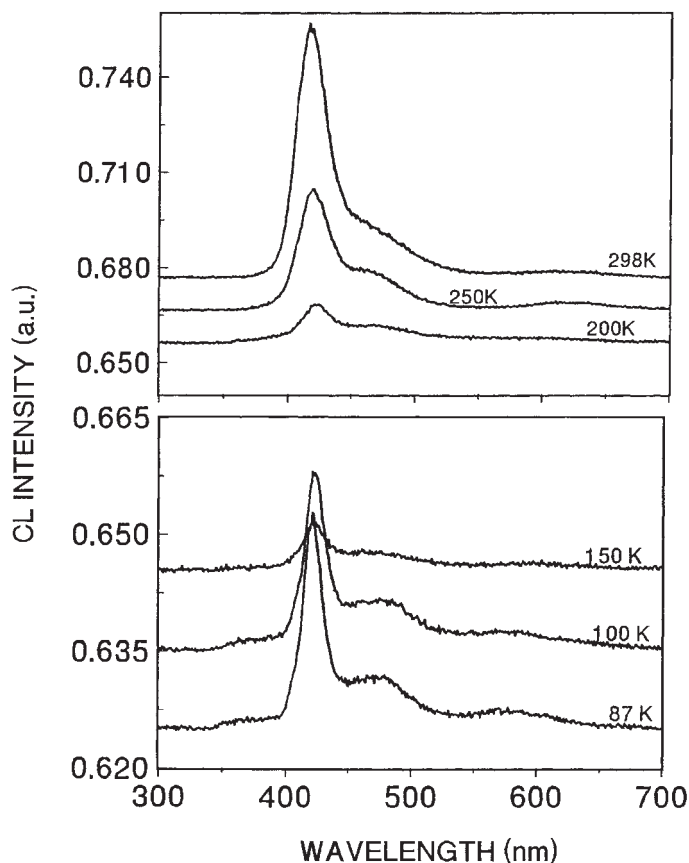


Fig. 1. CL spectra of $\text{KCl}:\text{Eu}^{2+}$ at different temperatures. Curves are shifted for clarity

corded at different temperatures, this result suggests the presence of a temperature dependent impurity induced trapping process, as is discussed latter.

Figure 3 shows that the CL emissions produced by the recombination of point defects induced during low energy electron irradiation originate from specific active regions instead of the whole surface. The secondary and panchromatic CL images of $\text{KCl}:\text{Eu}^{2+}$ crystal are presented in Figs. 3a and b, respectively. To compare, Figs. 3c and d show the secondary and panchromatic CL images of a pure KCl crystal. In $\text{KCl}:\text{Eu}^{2+}$ samples, the secondary image revealed a topography with a random distribution of grains (Fig. 3a), apparently of rounded shape, on the surface. The brighter grains clearly reveal optically active zones, as is shown on the corresponding CL image (Fig. 3b). In contrast, in pure KCl the surface looks irregular with grains of parallelepiped shape and canals arranged on a linear way (Fig. 3c). The panchromatic CL image shows the optically active zones as bright regions (Fig. 3d). The brightest emission coming from the two grains placed together almost at the center region of the SEM image.

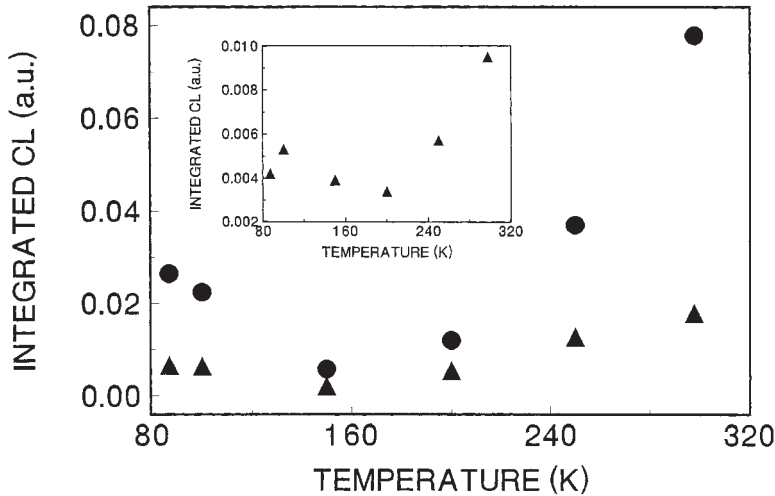


Fig. 2. Maxima of intensity versus temperature for the KCl:Eu²⁺ CL emission bands as obtained from a fitting process. Solid circle, 420 nm; solid triangle, 460 nm. Inset: 460 nm CL emission in pure KCl

4. Discussion

The main feature in the CL spectra of europium doped KCl is the very strong emission band with a maximum at about 420 nm. Based on the photoluminescence (PL) studies [21], this band can be ascribed to the $4f^65d(t_{2g}) \rightarrow 4f^7(^8S_{7/2})$ electronic transition of Eu²⁺ ions in the KCl matrix. The position of the maximum suggests that the emission is due to free dipoles (Eu²⁺-V_C) and/or first aggregation products (dimers, trimers). As in the studies of Yang et al. [16], our pure KCl samples also show an emission band with maximum around 450 nm but it is overlapped due to the presence of the higher intensity europium emission (420 nm). This europium related emission band can be induced by a nonradiative energy transfer process after electron irradiation. The process to produce defects of type H, F, V_K, etc. as well as optical transitions causing the luminescence in HA single crystals by electron beam, have been explained by considering the adiabatic potential surface (APS) diagram as proposed by Kayanuma [22]. After electron irradiation, the produced electron-hole pairs relax to form self-trapped excitons of type (V_K + e⁻) (on-center) and/or STE (off-center). In KCl, the V_K + e⁻ centers are unstable and evolve to different STE excited states. In these single crystals, the energy difference (ΔE) between the "on center" and "off center" symmetries is about 2.6 eV [23]. Relative to the STE ground state (i.e. perfect crystal), the absorption bands of the europium ions are overlaid in this energy interval ΔE . So, if the V_K + e⁻ → STE evolution is produced in the vicinity of the europium ions, then it is possible to have a nonradiative energy transfer process from some levels in the continuous ΔE interval to the Eu²⁺ ions. As the "on-center" to "off-center" relaxation is completed in a time as short as picoseconds (ps) [10], then the energy transfer process must be completed in ps or less time. It is important to mention that this energy transfer process is without charge migration and assuming the electron-hole pairs localized only on halogen sites. This process is shown in Fig. 4.

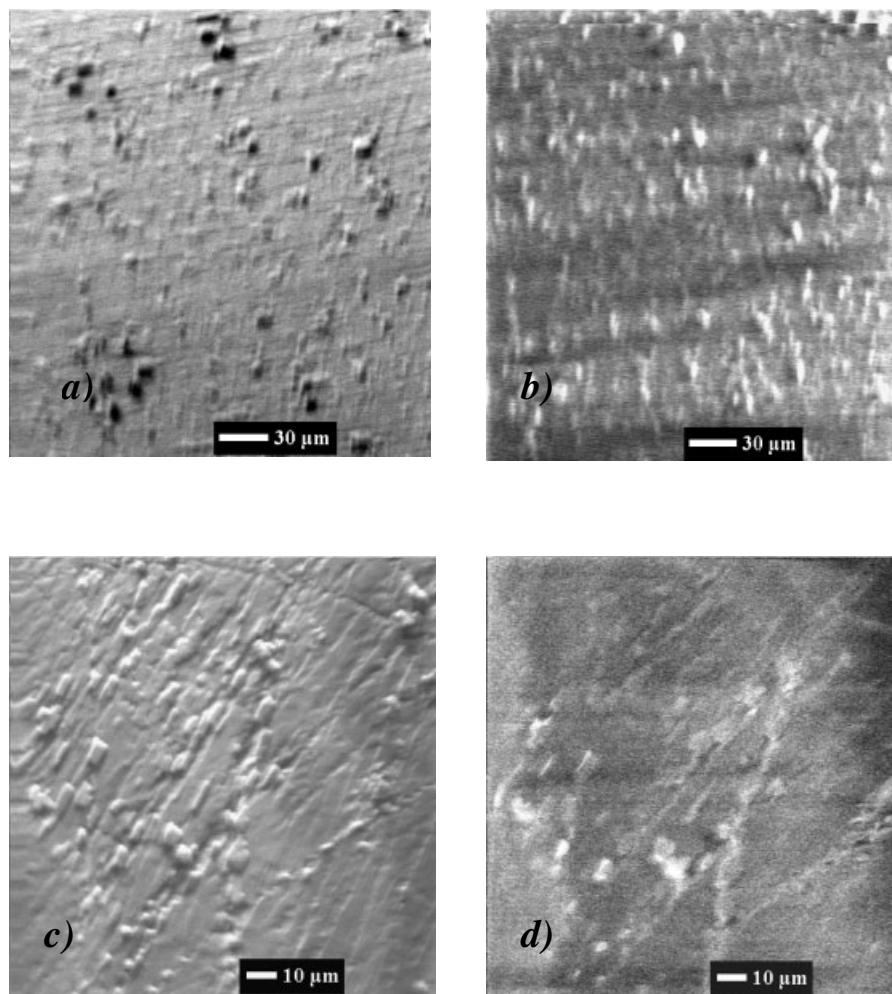


Fig. 3. Room temperature SEM micrographs and corresponding panchromatic CL images for a), b) $\text{KCl}:\text{Eu}^{2+}$; c), d) pure KCl crystals. The brighter points in the CL images b), d) correspond to optically active regions

On the other hand, the valley with minimum around 535 nm shown in Fig. 1, has been considered to be the F center self-absorption because the coincidence between the “off center” STE π luminescence at 534 nm (2.32 eV) [13] and the absorption band at 536 nm in X-irradiated pure KCl at 4 K [24]. Yang et al. [16] has supported this assignment by CL studies in pure KCl. This coincidence is also shown in our pure and Eu^{2+} -doped KCl samples, as it is shown in Fig. 5. In addition, there is no evidence of the presence of another kind of induced defect, like F_2 centers due to presence of europium ions in the doped samples, as it is shown in the inset of the same figure. So, the minimum in the CL emission broad band of Eu^{2+} -doped KCl corresponds to the π luminescence modified by the F center absorption band.

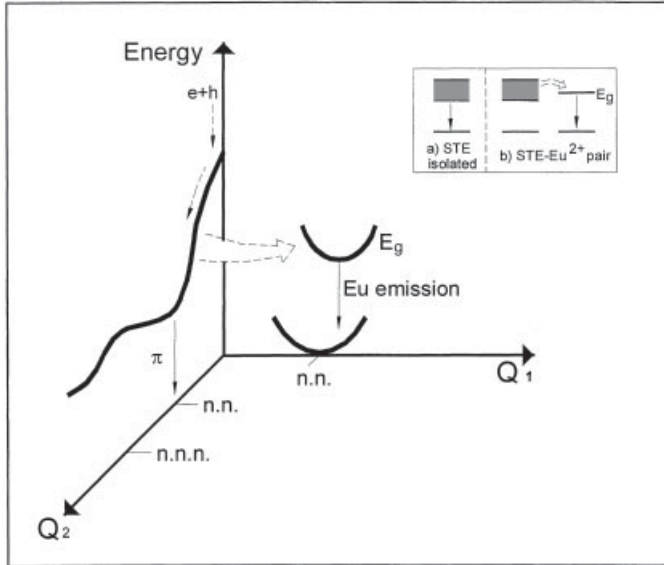


Fig. 4. Schematic configuration coordinate diagram proposed to explain the energy transfer process. The Q_2 coordinate represents the translational mode in the “on-to-off-center” relaxation along the $\langle 110 \rangle$ direction as discussed in [13]. In this axis the solid curve is the adiabatic potential surface as proposed by Kayanuma [22] for pure KCl. The electron-hole pair and the “on-center” defect coincide with the origin which is assumed on a halogen ion. The Q_1 axis represents the configuration coordinate of the Eu ions in the $\langle 100 \rangle$ direction. The parabolic curves are the five-fold orbital degeneracy d level splitted by the crystal field in cubic symmetry of the europium ions. Inset: energy level diagram to describe the feature of the energy transfer process. The shaded region represents the continuous ΔE energy difference between the “on-center” to “off-center” relaxation; a) insulated STE, b) STE-Eu²⁺ pair. The optical transition for π and Eu²⁺ luminescence are denoted by vertical arrows and nonradiative paths are denoted by dashed arrows. Block arrows denote energy transfer rate

Yang et al. [16] noted a minimum at 50–90 K range in the STE CL emission intensity versus temperature of pure KCl. They gave two possible reasons for this behavior. One of them is associated with the shortening of the lifetime of the STE and the other with the thermal decay of the H centres. In our case, a similar minimum is observed in the STE CL signal of KCl:Eu²⁺ but in the 150–170 K temperature range (Fig. 2) and at 190–210 K in pure KCl (inset Fig. 2). These results suggest a process of quenching of STE and Eu²⁺ CL emissions to be different to that proposed by Yang et al. As it was previously mentioned, the unstable $V_K + e^-$ defect evolved to a STE. This evolution process can be influenced by impurities trapping electrons and/or holes preventing the formation of excited STEs responsible for the π luminescence and consequently the CL intensity becomes smaller. In KCl:Eu²⁺ the europium-vacancy (Eu²⁺-V_C) dipoles act as traps to the V_K holes and form V_Z centers (V_K centers being trapped on the cation vacancy of the dipole complex). In fact, in doped KCl (KCl:X, X = Pb²⁺, Na⁺, Li⁺) these V_K-type centers have been reported to be as V_K, V_{KA}(Na⁺), V_{KAA}(Na⁺) and V_F centers [25]. The trapping process inhibits the formation of the “on-center” self-trapped excitons and consequentially the CL signal. Because the Eu²⁺ luminescence is obtained as a consequence of the energy transfer process, as it is discussed earlier, the V_K + e⁻

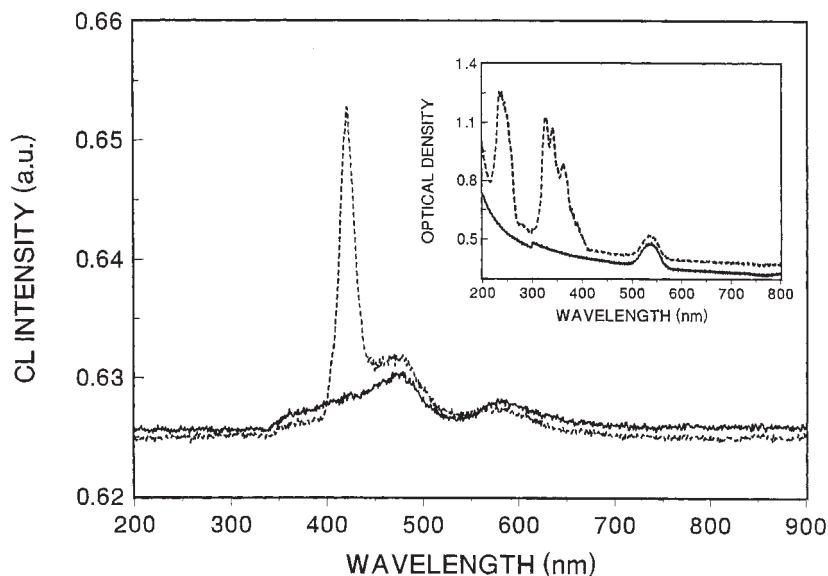


Fig. 5. CL spectra of pure KCl (solid curve) and KCl:Eu²⁺ (dashed curve) crystals taken at 87 K. The inset presents the absorption spectra of pure KCl (solid curve) and KCl:Eu²⁺ (dashed curve) samples measured after exposing the samples to an electron beam of 15 keV (at RT) for 600 s

trapping process reduces the available defects involved in the energy transfer process decreasing the Eu²⁺ emission. In our pure KCl samples, this trapping process by unknown impurities can explain the minima around 220 K in the CL emission vs. temperature curve (inset Fig. 2). Actually, by fluorescence measurements traces of lead have been detected in our nominally pure samples. Temperature dependence of emission intensity associated with the radiative recombination of the self-trapped excitons of type $V_K + e^-$ perturbed by divalent impurities $[(V_K + e^-)_Z]$ has been reported in KCl:Y²⁺ (Y = Pb, Ca) [4]. In this material, the temperature dependence of emission intensity revealed a minimum around 200 K.

By inspection of Fig. 2 a small decrease in the CL intensity is observed for the 87 K point. Maybe, this decrease reveals the beginning of a CL thermal quenching as it is proposed by Yang et al. [16]. Unfortunately, we were unable to study this possibility because our experimental set up only allow us cold down up to liquid nitrogen temperatures.

Finally, it is necessary to comment about the optically active regions of both the pure and doped samples. As it is shown in Fig. 3, the inclusion of Eu²⁺ ions in KCl modified the topography of the surface and consequently the CL emission. At the same amplification, the secondary image revealed a relatively flat and regular surface of pure KCl (Fig. 3c) compared to the corresponding image of the europium doped KCl crystal (Fig. 3a). Also, the CL emission intensity is very low in pure KCl (Fig. 3d) compared to that of the doped sample (Fig. 3b). These findings along with the CL spectroscopic results allowed us to consider different optically active regions responsible for the CL emission in the two samples (pure and doped). In both cases the brighter regions in the CL images (active regions) mainly come from the several sizes and shapes of grains. In

pure KCl crystals, it seems that the light in the brighter regions comes from the borders of the grains and in Eu-doped KCl from the inside. That the luminescence came from the borders is more or less clear because regions as grain frontiers, dislocations, etc. are energetically more favorable to trap defects. But, that the emission in KCl:Eu²⁺ samples came from the inside from these randomly distributed grains is a question that it is not possible to answer with the results presented here.

It is important to note that metallic clusters (colloids) induced by low temperature electron irradiation with average size around 20 nm have been reported on LiF [26]. As the experimental conditions used in that paper are similar to ours, it could be that the nodular particles on Fig. 3 were colloids induced by the electron irradiation. However, the nodular particles on this figure are clearly larger to this average size, so maybe they are not alkali metal but some EuCl₂-type aggregate phase. Unfortunately, the results presented here are not enough to clear this point and it is necessary to do further and more careful experimental work on this matter.

5. Summary

KCl:Eu²⁺ crystals have been studied by both microscopic and spectroscopic CL techniques. The origin of the several CL emission bands have been identified and the possible mechanisms responsible for them have been explained.

The CL emission in KCl:Eu²⁺ samples is composed mainly of two emission bands associated with the radiative electronic transitions of the Eu²⁺ ions involving a previous radiationless energy transfer process between some levels of the ΔE continuum and europium ions ($V_K + e^- \rightarrow$ STE conversion), and to the STE recombination modified by the self-absorption of F and F_Z centers.

The interference of the Eu²⁺ ions in the dynamics of electron beam induced defect formation in KCl is explained as a trapping process of V_K holes by cation vacancies. The presence of Eu²⁺ ions produce a shift in the thermal stability curve passing from 220 K in pure KCl to 155 K in KCl:Eu²⁺.

The optically active regions are considered different in both samples. In pure KCl it seems that the CL comes from the borders of the grains. In Eu²⁺-doped KCl the CL looks like coming from the inside of the grains containing europium ions.

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