Luminescent quantum efficiency of Eu^{2+} ions in mixed $KCl_{1-x}Br_x$ crystals

Luminescent quantum efficiency of Eu^{2+} ions in mixed $KCl_{1-x}Br_x$ crystals

J A Muñoz†, R di Paolo†‖, J O Tocho†‖, F Cussó†, B Castañeda‡, R Pérez-Salas§, R Aceves§ and M Barboza-Flores§

† Departamento Física de Materiales, C-IV, Universidad Autónoma de Madrid, 28049 Madrid, Spain
‡ Departamento de Investigación en Física, Universidad de Sonora, PO Box 1626, Hermosillo, Sonora 83000, Mexico
§ Centro de Investigación en Física, Universidad de Sonora, PO Box 5-088, Hermosillo, Sonora 83190, Mexico

Abstract. In this work, the luminescent quantum efficiency of Eu^{2+} ions in mixed $KCl_{1-x}Br_x$ crystals is determined by using simultaneous and multiwavelength measurement of photoacoustic and luminescent signals after pulsed laser excitation. This method, which was first demonstrated in Eu^{2+} doped alkali halides (NaCl, KCl, KBr and KI) is now extended to mixed crystals. It is found that the quantum efficiency is reduced for mixed $KCl_{1-x}Br_x$ crystals from $\Phi \approx 100\%$, in pure alkali halides (KCl and KBr), to a value $\Phi \approx 60\%$ for $x \approx 0.6$.

1. Introduction

Alkali halides doped with Eu^{2+} ions are well known luminescent phosphors which have been recently proposed as candidates for a variety of applications including UV detectors and thermoluminescent dosimeters appropriate for the actinic region (200–320 nm), where skin burn and erythema are produced [1–3].

The use of mixed crystals may be interesting for several reasons. It provides the possibility of a continuous variation of compositions, provided that the $KCl_{1-x}Br_x$ mixed systems form a solid solution for all concentrations [4], and it has been recently found that the detection sensitivity for UV radiation is enhanced at middle compositions comparatively to pure KCl and KBr end components [5].

For a luminescent material the quantum efficiency (Φ) is one of the most relevant parameters for any practical application. While this magnitude is known for several pure alkali halides, it is unknown for the mixed crystals. In the present work the luminescent quantum efficiency of Eu^{2+} ions in mixed $KCl_{1-x}Br_x$ crystals is investigated in order to confirm their possibilities as active ions in luminescent applications. It has been found that while a high quantum efficiency ($\Phi \approx 100\%$) is obtained for Eu^{2+} ions in pure alkali halides (KCl and KBr) it is reduced for mixed $KCl_{1-x}Br_x$ crystals, down to a value $\Phi \approx 60\%$ for $x \approx 0.6$.

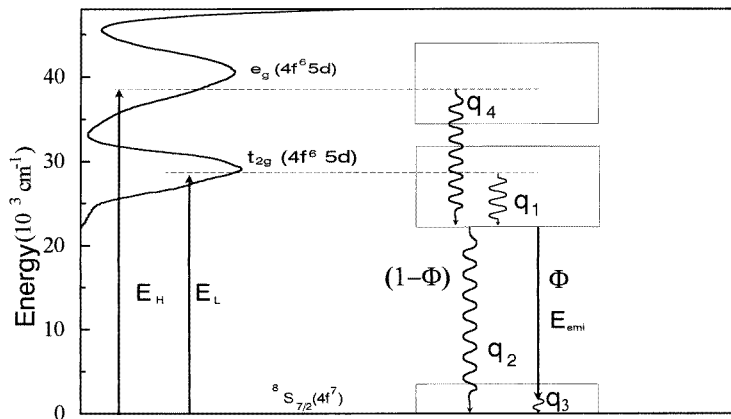‖ Permanent address: Centro de Investigaciones Opticas, La Plata, Argentina.

Figure 1. Absorption bands of Eu^{2+} in alkali halides, showing the coincidence with the $(3\omega_0)$ and fourth $(4\omega_0)$ harmonics of the Nd:YAG laser, and schematic energy diagram indicating the different contributions (q_i) to the photoacoustic signal.

2. Experimental setup

Single crystals of KCl and KBr and seven different compositions of $KCl_{1-x}Br_x$ ($x = 0.99$, 0.80, 0.60, 0.50, 0.40, 0.15 and 0.01) mixed crystals, containing 0.1 wt% of divalent europium, were grown under a controlled atmosphere of dry argon, at the Crystal Growth Laboratory of the Institute of Physics of the Universidad Nacional Autónoma de México (IFUNAM), using the Czochralski technique. The divalent europium was added to the melt in the form of EuX_2 (X = halogen component) which was previously reduced from EuX_3.

Optical absorption and luminescence measurements were performed by using a Hitachi spectrophotometer and a Jobin–Yvon JY3CS spectrofluorimeter.

Pulsed excitation, at different wavelengths, is achieved by using a Nd:YAG laser (Quanta Ray DCR-2) linked to a harmonics generator. The laser gives 10 ns pulses with energies ranging from 300 mJ in the infrared (1.064 μm) to 20 mJ in the ultraviolet (266 nm).

Photoacoustic and luminescence signals were detected using the configuration described elsewhere [6]. The signals, taken from a resonant piezoelectric transducer [7] and an EMI 9558QB photomultiplier tube respectively, were suitably amplified and finally averaged and recorded using a digital oscilloscope.

3. Experimental results and discussion

The absorption spectrum of Eu^{2+} ions in mixed alkali halides is similar to that found in single crystals and consists of two broad absorption bands attributed to transitions from the $^8S_{7/2}$ ground state of the $4f^7$ configuration to the $4f^65d$ configuration. In cubic symmetry, the crystal field splits the d-electron state into two components, e_g and t_{2g}, which correspond to the observed absorption bands (figure 1). For sixfold coordination, which is the case for Eu^{2+} ions entering substitutionally for the alkali ions, the t_{2g} is the lower lying level [8].

As indicated in figure 1, the two Eu^{2+} absorption bands can be excited with the third $(3\omega_0)$ and fourth $(4\omega_0)$ harmonics of the Nd:YAG laser at $\lambda = 355$ nm and $\lambda = 266$ nm respectively. After excitation within either of these two bands a single luminescence band is observed, corresponding to the $t_{2g} \rightarrow 4f^7$ transition. The changes in the peak position

for different compositions are smaller than 2 nm.

The different contributions to the luminescent or photoacoustic signals are also indicated in figure 1. Considering first the excitation to the lower excited state (t$_{2g}$ level) at a frequency $\omega_L = 3\omega_0$, the non-radiative relaxation within this level gives a thermal contribution q_1. The relaxation from the bottom of this lower excited state to the 4f^7 level is partially luminescent with a quantum efficiency Φ, and partially non-radiative with efficiency $(1 - \Phi)$. The radiative channel gives a thermal contribution Φq_3 which corresponds to the non-radiative relaxation within the ground state, while the non-radiative channel gives a contribution $(1 - \Phi)q_2$.

In the case of excitation to the upper excited state (e$_g$ level) at a frequency $\omega_H = 4\omega_0$, a non-radiative relaxation to the lower lying excited state (t$_{2g}$ level) takes place, with a thermal contribution q_4. Then the next steps in the de-excitation are similar to those already described above.

The luminescent quantum efficiency can be obtained by comparing the photoacoustic (PAS) and luminescent (LUM) signals generated at different excitation powers for each excitation wavelength, as described elsewhere [6].

In terms of the energies involved in the process (see figure 1), E_H, E_L, E_{emi} we obtained:

$$\text{PAS}(\omega_L, \omega_H) = \left(\frac{K_P}{K_L}\right)\frac{E_L - E_{emi}\Phi}{\Phi}\text{LUM}(\omega_L, \omega_H) \qquad (1)$$

where (K_P/K_L) includes the instrumental responses of photoacoustic and luminescence detection. These constants are independent of the excitation wavelength, and they can be eliminated by comparing the slopes of PAS against LUM at excitations ω_L and ω_H:

$$\Lambda = \frac{\partial\text{PAS}(\omega_H)/\partial\text{LUM}(\omega_H)}{\partial\text{PAS}(\omega_L)/\partial\text{LUM}(\omega_L)}. \qquad (2)$$

In terms of that ratio, which is the quantity to be determined experimentally, the quantum efficiency is given explicitly by:

$$\Phi = \frac{\omega_L}{\omega_{emi}}\frac{\Lambda - (\omega_H/\omega_L)}{\Lambda - 1}. \qquad (3)$$

Figure 2 shows the comparison of photoacoustic versus luminescence signals for KCl$_{1-x}$Br$_x$ crystals with three different compositions ($x = 0, 0.6, 1$). A linear dependence, as expected from equation (1), is observed in all cases, and the difference in slope between ω_H and ω_L excitations is apparent.

It can be observed that pure KCl and KBr crystals ($x = 0$ and 1) are coincident and exhibit a maximum difference in slope (Λ) between the two excitations (ω_H and ω_L). At the intermediate concentration ($x = 0.6$) the slope difference is reduced, which is a clear indication of a reduction in the luminescent quantum efficiency.

With the values of Λ obtained from the least squares fitting of slopes of PAS against LUM for ω_H and ω_L, the luminescent quantum efficiency (Φ) is calculated and shown (open circles) in figure 3 as function of the composition. The line corresponds to a least squares fitting assuming a Gaussian dependence on composition. From this figure it can be observed that the quantum efficiencies of Eu^{2+} ions are close to 100% for extreme x values but suffer a noticeable reduction at intermediate compositions.

The fact that the intermediate compositions in mixed alkali halides exhibit maximum deviation from the values of pure end components is common to a variety of physical processes. For instance there is a maximum in the value of the dielectric constant [9];
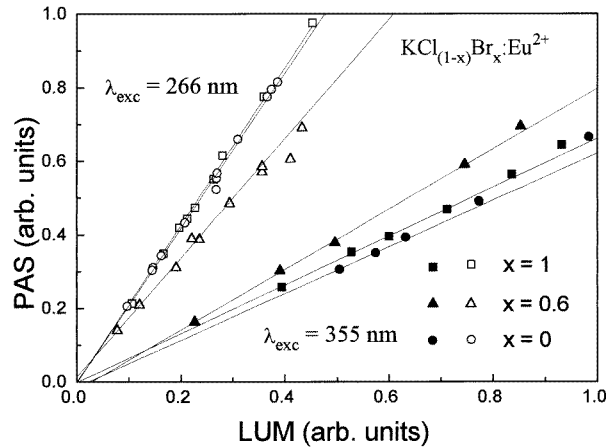
Figure 2. Comparison of the photoacoustic (PAS) and luminescent (LUM) signals simultaneously generated after $3\omega_0$ ($\lambda_{exc} = 355$ nm, full symbols) and $4\omega_0$ ($\lambda_{exc} = 266$ nm, open symbols) excitation of Eu^{2+} in $KCl_{1-x}Br_x$ crystals for different compositions.

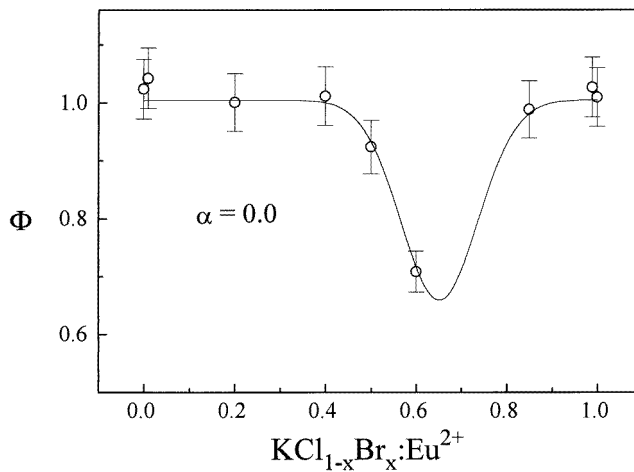**Figure 3.** Luminescent quantum efficiency of Eu^{2+} in $KCl_{1-x}Br_x$ crystals for different compositions.

and colour centre production or thermoluminescence efficiency also exhibit singularities for intermediate compositions [4, 5, 10].

In order to understand the origin of this reduction in luminescent quantum efficiency of Eu^{2+} ions, it should be considered which is the main effect of the mixture of compositions in the crystal structure. It is well established that there is an increase in the atomic diffusion coefficients (either self- and heterodiffusion) which has been attributed to an increase in the cation and anion vacancy content in the crystals. Such an increase is found to be maximum for intermediate ($x \approx 0.6$) compositions [11].

It is not surprising therefore that the appearance of a large number of vacancies in the crystals had implications for the optical properties of ions in these crystals. In fact, such an effect has been found in electronic excitations of defects (F centres) where the Stokes shift
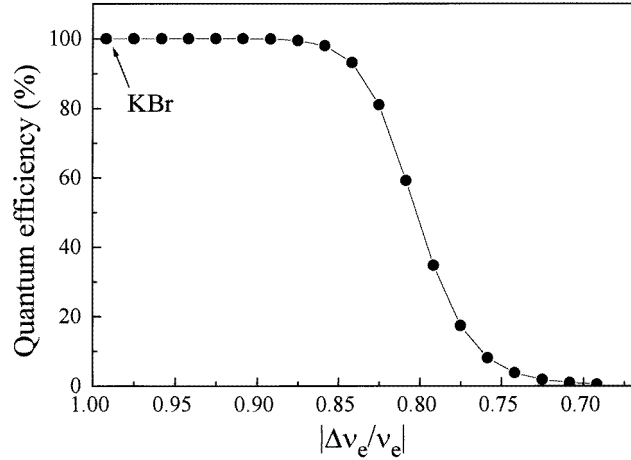
Figure 4. Calculated quantum efficiency of Eu^{2+} ions (equations (4) and (5)), assuming a configurational coordinate model with vibrational frequency shifted ($\Delta\nu_e/\nu_e$) from that of pure KBr.

in additively coloured KCl$_{1-x}$Br$_x$ mixed crystals is strongly influenced by the composition [10].

In the present case, it seems also plausible that the increase in the number of vacancies could affect the Eu^{2+} optical properties, particularly in relation to the local vibrations, and therefore the relaxation properties. In fact, it has been already established, for pure crystals, that the changes in the local environment of the impurities caused by aggregation/precipitation processes have a strong effect on the Eu^{2+} luminescent quantum efficiency [12, 13].

An order-of-magnitude estimation of the effects expected can be made using a simple configurational coordinate model. In fact, the activation energy for thermal quenching (E_Q) of Eu^{2+} ions and the vibrational frequency (ν_e) of the system in the excited state have been reported for a number of pure alkali halides, including KCl and KBr [14].

With this information and the radiative lifetime (τ_{rad}), the probability for non-radiative relaxation (W_{nr}), and then the quantum efficiency, can be calculated straightforwardly:

$$W_{nr} = \nu_e \exp\left(-E_Q/KT\right) \tag{4}$$

$$\Phi = \tau_{rad}^{-1}/\left(\tau_{rad}^{-1} + W_{nr}\right). \tag{5}$$

Using the reported quenching energies and vibration frequencies [14], a quantum efficiency of 100% for Eu^{2+} ions in pure KCl and KBr at room temperature is obtained, in agreement with the values determined experimentally by photoacoustic measurements [15], and consistent with the observation of a temperature independent lifetime in the range 77–300 K. It is also reported that the lifetime (and then, the luminescent efficiency) drops abruptly a few degrees above room temperature [14]. This indicates that small changes in the relaxation characteristics may change strongly the quantum efficiency.

Although a fully quantitative approach cannot be made, provided that there is no information about the local vibrational properties of the lattice around Eu^{2+} ions in mixed crystals, it is possible to make an estimation of the changes needed to explain the observed quantum efficiency variations. Figure 4 shows the calculated quantum efficiency using a configurational coordinate model and the reported values for KBr ($\nu_e = 119$ cm^{-1}), and

then allowing the change in the vibrational frequency (ν_e) while having fixed absorption and emission energy values for the Eu^{2+} ions, as is the experimental evidence in the mixed $KCl_{1-x}Br_x$ crystals [16]. It can be seen from this calculation that with a reduction in the vibrational frequency of only 20% from the value in pure KBr, it would be possible to explain the observed reduction in the quantum efficiency of Eu^{2+} ions. This reduction is much smaller than that found in precipitaed Eu^{2+} phases, and it still remains high enough to be considered of interest for luminescent applications.

In summary, it has been found that the luminescent quantum efficiency of Eu^{2+} ions in mixed $KCl_{1-x}Br_x$ crystals is reduced at intermediate compositions ($x \approx 0.6$) in comparison to pure KCl or KBr crystals. The observed reduction is compatible with slight variations in the relaxation properties, which could be caused by local changes in the Eu^{2+} environment, possibly associated with production of an excess of vacancies in the mixed crystals.

References

[1] Aguirre de Cárcer I, Lifante G, Cussó F, Jaque F and Calderón T 1991 *Appl. Phys. Lett.* **58** 1825
[2] Nanto H, Murayama K, Usuda T, Endo F and Hirai Y 1993 *J. Appl. Phys.* **74** 1445
[3] Barboza-Flores M, Pérez-Salas R, Aceves R, Pashchenko L P, Medvedev L L and Pitters T M 1994 *Appl. Phys. Lett.* **64** 1789
[4] Smakula A, Maynard N and Repucci A 1962 *J. Appl. Phys.* **33** 453
[5] Castañeda B, Aceves R, Pitters T M, Barboza-Flores M, Meléndrez R and Pérez-Salas R 1996 *Appl. Phys. Lett.* **69** 1388
[6] Rodríguez E, Tocho J O and Cussó F 1993 *Phys. Rev.* B **47** 14 049
[7] Braslavsky S E and Heihoff K 1989 *Handbook of Organic Photochemistry* vol 1, ed J C Scaiano (Boca Raton, FL: Chemical Rubber Company) pp 327–54
[8] Rubio O J 1991 *J. Phys. Chem. Solids* **52** 101
[9] Hari Babu V, Subba Rao U V and Venkata Ramiah K 1975 *Phys. Status Solidi* a **28** 269
[10] Rodríguez-Mijangos R, Pérez-Salas R, Muñoz-Sandoval E and Barboza-Flores M 1996 *Radiat. Eff.* **138** 153
[11] Benière F, Benière M, Hari Babu V and Reddy K V J 1994 *Phys. Chem. Solids* **55** 595
[12] Muñoz-Santiuste J E, García-Solé J and Manfredi M 1990 *Phys. Rev.* B **42** 11 339
[13] Muñoz J A, Rodríguez E, Tocho J O and Cussó F 1997 *J. Lumin.* **72–74** 233
[14] Jaque F, Hernández J, Murrieta H and Rubio J 1982 *J. Phys. Soc. Japan* **51** 249
[15] Rodríguez E, Muñoz J A, Tocho J O and Cussó F 1994 *J. Phys.: Condens. Matter* **6** 10 625
[16] Pérez-Salas R, Pitters T M, Aceves R, Rodriguez-Mijangos R and Barboza-Flores M 1996 *J. Phys. Chem. Solids* **58** 1027