

A generalized rule of average for glow peak temperature of ternary alkali halide systems

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The anion composition dependence of the characteristic glow peak temperature of europium doped $\text{KCl}_{0.50}\text{KBr}_{0.25}\text{RbX}_{0.25}:\text{Eu}^{2+}$ ($X=\text{Cl}, \text{Br}$) mixed crystals are studied. Each material shows a thermoluminescence glow curve consisting of two main glow peaks with a temperature is between $\text{KCl}:\text{Eu}^{2+}$ and $\text{KBr}:\text{Eu}^{2+}$. The most intense is related to the F center destruction as occur in the case of $\text{KCl}:\text{Eu}^{2+}$ crystals and its characteristic temperature depends strongly on the halogen composition. This behavior confirms that the temperature of the F-H centers recombination in this type of materials depends more on the proportion of anions. From these results, a generalized rule to obtain the temperature from averaging the characteristic temperature as function of the composition is discussed.

Keywords: Defects in solids; ternary solid solutions; thermoluminescence; color centers.

Se estudia la dependencia de la temperatura en la curva de brillo con la composición de los aniones en mezclas cristalinas impurificadas con Europio: $\text{KCl}_{0.5}:\text{KBr}_{0.25}:\text{RbX}_{0.25}:\text{Eu}^{2+}$ ($X = \text{Cl}, \text{Br}$). Cada material muestra una curva de brillo termoluminiscente consistente en dos picos de brillo principales con temperatura entre la del $\text{KCl}:\text{Eu}^{2+}$ y la del $\text{KBr}:\text{Eu}^{2+}$. El pico más intenso está relacionado con la destrucción del centro F, como ocurre en el caso de cristales de $\text{KCl}:\text{Eu}^{2+}$ y su temperatura característica depende fuertemente de la composición del halógeno. El comportamiento confirma que la temperatura de la recombinación de los centros F-H en este tipo de materiales depende en gran medida de la proporción de los aniones. De estos resultados se propone una regla generalizada para obtener la temperatura, promediando la temperatura característica en función de la composición.

Descriptores: Defectos en sólidos; soluciones sólidas ternarias; termoluminiscencia; centros de color.

PACS: 78.20 Nv; 78.40 Ha; 78.60 Kn; 78.90 +t

1. Introduction

Recently, the problem of finding a relationship which predict or give an idea of the temperature of recombination of the main defects induced by ionizing radiation in europium doped alkali halide has been discussed in the literature [1-3]. Some results obtained for the $\text{KCl}_x\text{Br}_{1-x}:\text{Eu}^{2+}$ system indicated that the temperature of the main glow peak could be expressed as a function of the composition x by means of a linear relation

$$T(x) = xT_1 + (1 - x)T_2, \quad (1)$$

where T_1 and T_2 are the temperatures of the ends, in this case $\text{KCl}:\text{Eu}$ and $\text{KBr}:\text{Eu}$. However, since it has the same form of the Vegard's law, the temperature was lead to a dependence with the lattice constant of the mixed crystal. In this case the larger shift of temperature was observed to be about 100°C . However, in mixed crystals $\text{K}_x\text{Rb}_{1-x}\text{Cl}:\text{Eu}$, the maximum shift resulted to be about 20°C , a lower shift that in the case of $\text{KCl}_x\text{Br}_{1-x}:\text{Eu}^{2+}$. This led us to think that halogens influence more the temperature of recombination, and maybe the temperature would be better managed through an ion-size dependence. The comparison of the above results has been done assuming that the main glow peak has a common origin: the recombination of H centers and F centers (H-F recombination). As is well known, the color centers [4] are defects generated when an alkali halide crystal is exposed to ionizing

radiation. They consist of F center aggregates or F centers associated with impurities. The most simple and the most abundant of defects created are the F centers, the following is the F^{2+} center, which consists of an electron trapped in two adjacent vacancies. Recently, a theoretical study has been carried out to explain its electronic energies, by working the defect as a confined system [5]. Another defect, widely studied is the F_A center, which consists of an F center next to an alkali ion impurity. The proximity of an alkali ion impurity affects the absorption spectrum of the F center easily detected, however, the effect of an anion impurity on the spectrum of the F center is not detected. A very detailed theoretical study concludes that anion impurity effect on the absorption of the F center is not detectable because it is very small. Another very interesting related defect is the so-called F_Z center, which consists of an F center next to a divalent cation impurity-cation vacancy dipole (I-V_C), a system being electrically neutral. A divalent impurity of interest in the study of induced defects in solids is Eu^{+2} ion, an absorber with high quantum efficiency. There are theoretical models for explaining the optical absorption of the F_Z centers [6] The optical properties of F centers have been studied in several mixed alkali halide crystals. The results show that the absorption energy has a dependence on the lattice constant. In particular, the explanation of the shift of the F center optical absorption band as function of the binary composition has received a lot of attention [7].

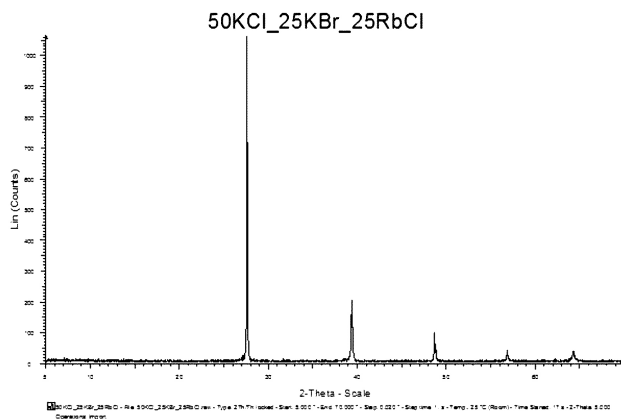


FIGURE 1. X-ray diffraction spectrum of a $\text{KCl}_{0.50}\text{KBr}_{0.25}\text{RbCl}_{0.25}:\text{Eu}^{2+}$ ternary crystal.

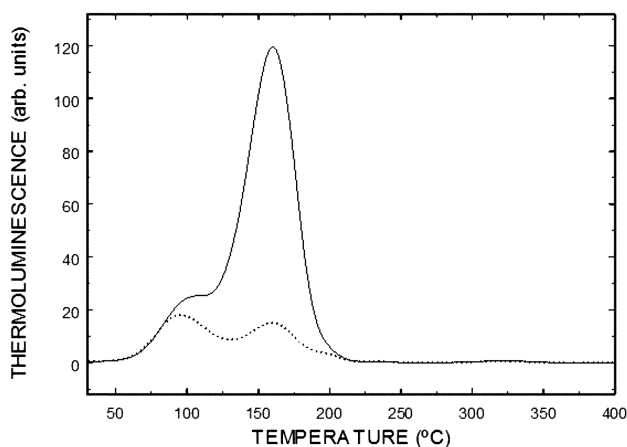


FIGURE 2. Thermoluminescence glow curves of a quenched $\text{KCl}_{0.50}\text{KBr}_{0.25}\text{RbCl}_{0.25}:\text{Eu}^{2+}$ crystal: (full line) immediately after 5 s of beta-irradiation and (dashed line) after 5 s of beta irradiation and 20 s of illumination with 630 nm light.

Until the late 90's, color centers were studied in binary mixtures; however, at the end of that decade, the F band of an irradiated ternary mixed crystal in solid solution was reported [8]. This was the beginning of a systematic study of defects induced by irradiation in alkali halide solid solutions with more than two components. They were related to the lattice constant of the mixed system for which the Vegard's law, [9] established for the lattice of a binary solid solution, was generalized to multicomponent systems.

Thermoluminescence (TL) is an experimental technique to detect the light emitted during the F-H centers recombination when the crystal is heated in a certain range of temperature. TL spectra of alkali halide doped with divalent Europium ions (optical sensors), previously subjected to ionizing radiation, can be very complex, however, the luminescence during this process can be identified [10] and seen that it is realized at well defined characteristic temperatures (CT) of the crystal. Being this effect related to the thermal properties of the material, it would be expected that a significant population of F centers and interstitial atoms have some influence on the thermal properties of an ionic crystal. But recent

calculations indicated that its influence at least on the heat capacity of an alkali halide crystal is negligible [11]. Therefore, the problem of making the temperature of the thermoluminescent signal predictable through a certain model remains as a challenge. So far only empirical values have been obtained by handling experimental spectra [12]. Recent advances on phenomenological models for these temperatures in alkali halides have been only given for binary systems. In those systems, the characteristic temperatures behave linearly with concentration x (similarly to the Vegard's law) [13,3]. In addition to this rule, the study reveals the main factor for the shift in the CT of TL is the mixture of halogen ions, which in turn is associated with the creation and destruction of F centers. In this report, the CT of the electron-hole recombination of europium doped ternary alkali halide crystals β -irradiated is investigated and compared with the corresponding CT's of europium doped alkali halide crystals of one and two components.

2. Experimental

The ternary crystals were grown using the Czochralski method. A mixture of salts (50%) KCl, (25%) KBr, (25%) RbCl (RbBr) with 0.1% of EuCl_2 was added in the melt. The crystal growing started from a seed of KCl because it has the highest melting point. For obtaining the lattice constant of the ternary crystal, powder diffractometry has been used. Diffraction spectra were obtained by using an advanced Bruker Analytical Diffraction X-ray diffractometer with Cu-radiation. Samples were irradiated with a $^{90}\text{Sr}/\text{Y}$ β -ray source providing a dose rate of 5 Gy min^{-1} approximately. TL intensity was measured from room temperature (RT) to 400°C in a RISO TL/OSL-DA-15 system with a linear heating rate of 5°C s^{-1} .

3. Results

The diffractogram of a $\text{KCl}_{0.50}\text{KBr}_{0.25}\text{RbCl}_{0.25}:\text{Eu}^{2+}$ sample is shown in Fig. 1. It indicates that the material is a solid solution with a NaCl type structure. By applying the Bragg law a lattice constant of 0.647nm is obtained, which is approximated to the value obtained by a generalized average formula $a = xa_1 + ya_2 + (1-x-y)a_3$, where a_1 , a_2 and a_3 are the lattice constants of the KCl, KBr and RbCl, respectively, and x , y and $(1-x-y)$ their respective concentrations in the ternary crystal. The glow curve of a sample of this crystal is shown in Fig. 2 (solid line). It consists of two intense emissions, the most intense peak is found about 160°C while the weaker appears about 96°C . A similar glow curve is found for the $\text{KCl}_{0.50}\text{KBr}_{0.25}\text{RbBr}_{0.25}:\text{Eu}^{2+}$ crystal for which the characteristic glow peak is found about 138°C . The relation between the glow peaks and the light dependence has been investigated by irradiated sample through the TL measurements. For a given dose of beta irradiation, a characteristic effect of the 630 nm light during 20 s on the

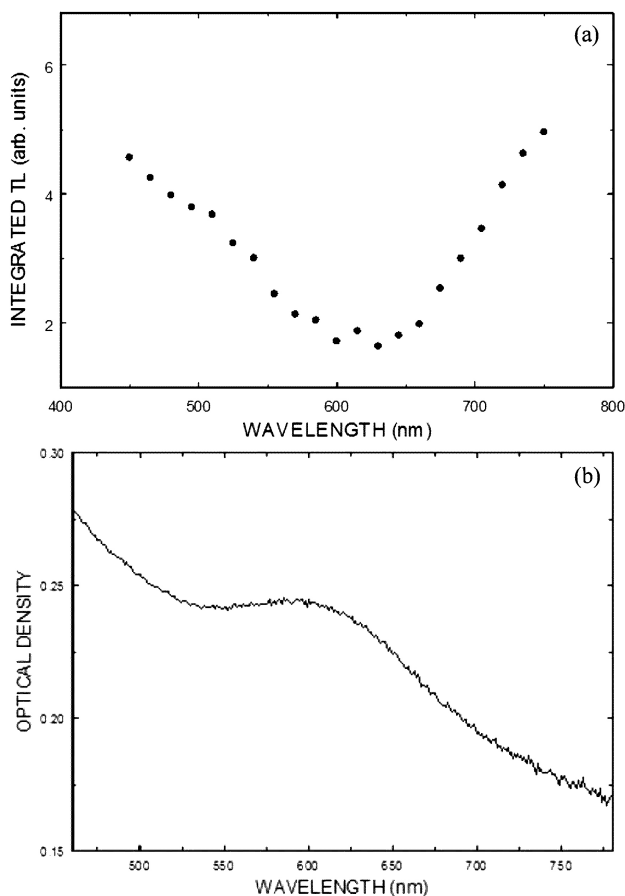


FIGURE 3. (a) Thermoluminescence total intensity as function of the wavelength of illumination light with exposures of 20 s on a $\text{KCl}_{0.50}\text{KBr}_{0.25}\text{RbCl}_{0.25}:\text{Eu}^{2+}$ sample beta-irradiated 5 s. This bleaching spectrum is not corrected by the lamp emission spectrum which is more or less constant in the working region. (b). Optical absorption spectrum of defects induced by 1800 s of beta irradiation in the $\text{KCl}_{0.50}\text{KBr}_{0.25}\text{RbCl}_{0.25}:\text{Eu}^{2+}$ crystal at room temperature.

$\text{KCl}_{0.50}\text{KBr}_{0.25}\text{RbCl}_{0.25}:\text{Eu}^{2+}$ sample can be seen in Fig. 2. The result indicates that the most intense glow peak is reduced (bleached) by more than 60% while its glow peak temperature remains almost constant and the small glow peaks around 160°C are also affected by the 630 nm light. The effects on the 160°C glow peak due to different wavelengths in the region of 450-750 nm are displayed in Fig. 3a. The higher effect of bleaching of this peak is obtained with 620 nm light, approximately. The absorption spectrum (Fig. 3b) of irradiated crystals shows the typical broad bands of Eu^{2+} in the region of 200-420 $^\circ\text{C}$ and a broad band from 450 to 700 nm with maximum at 620 nm. When the absorption spectrum is compared with the photobleaching spectrum a good correlation is found. This behavior is very similar to that found in beta irradiated $\text{KCl}:\text{Eu}^{2+}$ crystals [10]. From these results it can be seen that the glow peaks observed in the TL of the ternary crystals have a similar origin as the main glow peaks observed in other alkali halide crystals. These evidences allow us to compare the CT observed in the ternary crystals

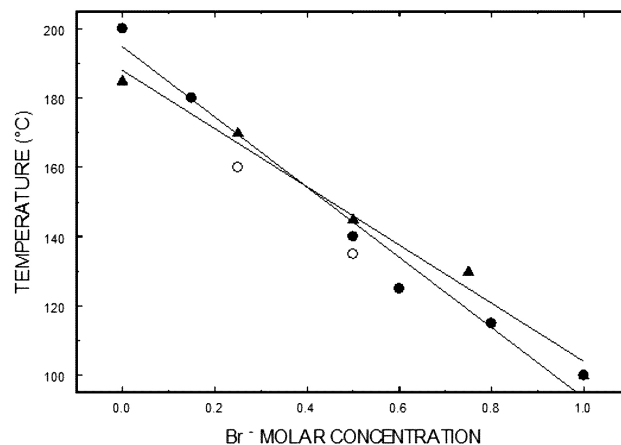


FIGURE 4. Br^- concentration dependence of the characteristic glow peak temperature (full circles) $\text{KCl}_x\text{KBr}_{1-x}$, (full triangles) $\text{RbCl}_x\text{KBr}_{1-x}$, and (empty circles) $\text{KCl}_{0.50}\text{KBr}_{0.25}\text{RbCl}_{0.25}:\text{Eu}^{2+}$ and $\text{KCl}_{0.50}\text{KBr}_{0.25}\text{RbBr}_{0.25}:\text{Eu}^{2+}$ ternary systems.

with those of $\text{KCl}_x\text{Br}_{1-x}:\text{Eu}^{2+}$, $\text{K}_x\text{Rb}_{1-x}\text{Cl}:\text{Eu}^{2+}$ and $\text{RbCl}_x\text{KBr}_{1-x}:\text{Eu}^{2+}$ mixed crystals. The CT of these crystals as function of the Br^- concentration is displayed in Fig. 4. The points corresponding to the ternary crystals follow the behavior of the other materials, so their CT shifts depend on the Br^- concentration.

4. Discussion

Besides the mentioned above, we can mention that the temperature values, obtained from an extension of the relation (1) to three components, resulted 10°C higher than the experimental ones, which could be due to the change of ion size of the alkali composition and maybe also to non-identified structural defects. Although the lattice constant of the ternary crystals follow a linear composition dependence according to the diffraction results, the rule applied to the CT gives values over the experimental ones. Such discrepancy with the generalized rule of average could be the effect of the mixing which can produce a loose in the symmetry requiring less thermal energy to allow the releasing of the hole. However, the initial process for the recombination of an interstitial halogen with an F center is the mobility of the hole from its trap to the recombination center through the halogen lines. The hole carrier is an interstitial halogen which is released from its trap when the amplitude of oscillation of the anions achieves certain temperature value as the temperature increases.

5. Conclusions

In summary, the diffractometry and thermoluminescence results of $\text{KCl}_{0.50}\text{KBr}_{0.25}\text{RbX}_{0.25}:\text{Eu}^{2+}$ ($X=\text{Cl}, \text{Br}$) ternary mixed crystals behave as the other alkali halide crystals of one and two components. After being β -irradiated, a characteristic glow peak whose temperature is found between those of $\text{KBr}:\text{Eu}$ and $\text{KCl}:\text{Eu}$ crystals. In addition, it has been seen

that the shift in the temperature of the electron-hole recombination in this type of crystals depends on the anion composition but seems affected by the alkali composition. It is found that its lattice constant obeys a rule of average which can be considered as a generalization of the rule applied to binary crystals, but in the case of the CT, a rule of this type is not clearly followed. Additional experiments are in progress to confirm this behavior, using the empirical method to obtain novel ternary alkali halide crystals from the Mollwo-Ivey law of F centers [14].

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1. M. Niki *et al.*, *Phys. Rev. B* **51** (1995) 5192.
 2. F.C. Brown, *The physics of solids c.* (Benjamin. N.Y. 1969).
 3. R. Rodríguez-Mijangos and R. Perez-Salas, *Physica Status Solidi* **4** (2007) 954.
 4. W.B. Fowler, *Physics of color centers* (Academic Press N.Y. 1968).
 5. J.L. Marin, R. Aceves, R.A. Rosas, and S. Grijalva, *Rev. Mex. de Fis E.* **54** (2008) 25.
 6. R. Rodríguez-Mijangos and C. Ruíz Mejía, *Rev. Mex. de Fís.* **39** (1993) 77.
 7. R. Rodríguez-Mijangos and C. Ruiz Mejía, *Phys Rev B* **39** (1989) 11120.
 8. R.R. Mijangos, A. Cordero-Borboa, E. Camarillo, H. Riveros, and V. Castaño, *Phys, Letters A* **245** (1998) 123.
 9. L. Vegard and H. Schjeklerup, *Z. Phys.* **18** (1917) 93.
 10. R. Aceves, R. Perez-Salas, and M. Barboza-Flores, *J. Phys. Condens. Matter* **6** (1994) 10397.
 11. R. Rodríguez-Mijangos, G. Moyoroqui-Estrella, G. Vázquez-Polo, and R. Perez-Salas, *Rev. Mex. de Fis.* **51** (2005) 149.
 12. S.W. Mc Keever, *Thermoluminescence in solids* (Cambridge University Press, 1985).
 13. R. Perez-Salas, R. Aceves, R. Rodríguez-Mijangos, H.G. Riveros and C. Duarte, *J. Phys. Condens. Matter* **16** (2004) 491.
 14. R. Rodríguez-Mijangos, G. Vázquez-Polo, J.J. Palafox, and R. Pérez-Salas, *Rev. Mex. de Fís.* **54** (2008) 15.