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Composition dependence of glow peak temperature in $KCl_{1-x}Br_x$ doped with divalent cations

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Abstract

Thermoluminescence measurements of β-irradiated Eu^{2+}- and Ca^{2+}-doped $KCl_{1-x}KBr_x$ solid solutions excited at room temperature have been carried out to identify the effect of composition on the glow peaks. A typical glow peak has been distinguished for each composition. A linear dependence of its temperature on the composition x has been found. These results indicate that for divalent impurity-doped alkali halide solid solutions these glow peak temperatures are mostly dependent on the lattice constant of the host than on the size of the anion or impurity cation.

1. Introduction

As is well known, thermoluminescence (TL) is a luminescent phenomenon observed in thermally stimulated materials exposed to ionizing radiation and giving rise to a glow curve. The TL response of a material depends on the nature of traps and recombination centres which can be modified by changing aspects such as the impurity or host ionic radii, radiation-induced trap transformations, ion aggregates, dislocations, etc. A correlation between the glow peak temperature (GPT) and the ionic radii of impurities has been investigated recently in LaF_3 (Yang *et al* 1998), $Bi_4Ge_3O_{12}$ (Raymond and Townsend 2000), $CaSO_4$ (Karali *et al* 1998), zircon (Karali *et al* 2000) and alkaline earth fluorides (Maghrabi and Townsend 2001) doped with trivalent rare earth ions. Only in the first three cases has an appreciable shift of the GPT been found. In alkaline earth fluorides, a shift is noticeable only with changes in the impurity concentration. On the other hand, a great deal of work on TL has been carried out on alkali halides with different extrinsic and intrinsic defects. In particular, TL observed from alkali halides doped with divalent impurities has been explained as light emission emanating from

the recombination process of electron–hole (e–h) pairs previously produced under exposure of the crystal to ionizing radiation (x-, β-, α-, γ-rays). Electrons are trapped by anion vacancies forming F centres (Aceves *et al* 1994) and holes at interstitial sites, producing H centres. Results on the efficiency of F-centre formation in x-irradiated KCl:Eu^{2+} crystals indicate a higher efficiency with increasing Eu^{2+}-ion concentration which is explained by assuming that divalent impurity–cation vacancy (I–V_C) dipoles act as interstitial traps (Rubio *et al* 1982) enhancing their sensitivity to ionizing radiation.

TL of Eu^{2+}-doped alkali halides exposed to ionizing radiation at room temperature (RT) shows several glow peaks at different temperatures. Two groups of peaks have been related to F- and F_Z-centre destruction while others were related to some traps of aggregates in KCl:Eu^{2+} crystals (Aceves *et al* 1994). Furthermore, F-centre destruction has also been found but the F_Z centre has not been detected in KBr:Eu^{2+} crystals (Pérez-Salas *et al* 1996). During thermally stimulated recombination processes in these materials an emission spectrum which resembles that of Eu^{2+} ions is produced, which makes it more difficult to explain the radiative recombination mechanism. Thus, in KCl:Eu^{2+} as well as in KBr:Eu^{2+} the same types of defects participate in the recombination processes; however, the glow peaks appear at different temperatures, which could be related to the difference in size between the hole carriers. Recently, in a dosimetric study carried out in mixed $KCl_{1-x}KBr_x$:Eu^{2+} crystals, Barboza-Flores *et al* (1998) observed that the GPT of an intense glow peak is shifted on changing the composition x. This draws attention to a lattice constant effect on the GPT.

It can be observed from published data on the GPT for some divalent impurity-doped alkali halide crystals (Sirdeshmukh *et al* 2001) that the GPT could be more a host than a cation divalent impurity effect, i.e. the temperature of some glow peaks seems to be mostly related to the lattice constant than to the other parameters involved. In order to study this relation, $KCl_{1-x}Br_x$ crystals doped with Eu^{2+} and Ca^{2+} ions have been chosen, taking into account the composition dependence of the lattice constant, according to Vegard's law, and that the temperature of the most intense glow peak reported for the pure ends lies within the working thermal limits of the TL dosimetry equipment (303–703 K). The GPT is around 470 K in Eu^{2+}- and Ca^{2+}-doped KCl crystals irradiated with different ionizing radiation (Aceves *et al* 1994, Meléndrez *et al* 1996, Deshmukh *et al* 1988) and 383 K for Eu^{2+}-doped KBr in x-irradiated crystals (Pérez-Salas *et al* 1996).

2. Experimental details

Crystals were grown in the Crystal Growth Laboratory of the IFUNAM, México, by the Czochralski technique in an Ar atmosphere. $EuCl_2$ was added to the melt at a molar concentration of 0.1%. A β-ray ^{90}Sr source at 5 Gy min^{-1} was used to irradiate the samples. The irradiation time in all cases was 5 s to avoid induced defect aggregates. Molar composition x was verified by x-ray diffractometry using a Bruker advanced x-ray diffractometer. TL measurements were carried out with a TL-DA-15 system at 5 K s^{-1} from 313 to 723 K, in an N_2 atmosphere. The crystals used were stored for more than two years. Two readouts were obtained on each sample, the former on irradiated as-grown samples and the latter on the same sample after a new exposure to irradiation at RT.

3. Results and discussion

Figure 1 shows the diffraction pattern of a crystal with a nominal composition $x = 0.5$. A diffractogram of the database for $x = 0.5$ has been included in figure 1 (vertical curves) in

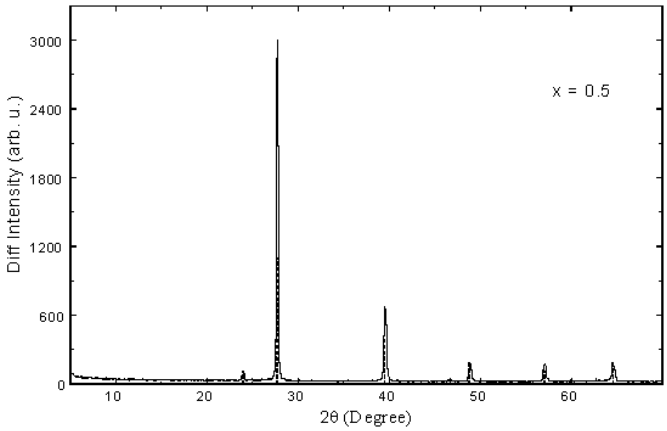

Figure 1. Diffractograms of a crystal with composition $x = 0.50$. Vertical curves correspond to the diffractogram database of the same composition.

order to verify by comparison the molar composition of our material. From the figure it can be seen that the diffraction patterns are in good agreement with the diffractogram of the database. Similar results were obtained for all the other compositions. This also confirms that these materials are crystalline solid solutions and not mixed crystals.

A TL readout was obtained for irradiated as-grown samples in order to determine the β-irradiation effects on existing defects since, prior to the TL measurements, all these materials had been exposed to environmental light. The TL response of as-grown samples is a parallel process to the thermally induced dissolution effect of impurity aggregates, which was verified by photoluminescence measurements under 350 nm excitation light. The emission spectra measured before and after the first readout indicated that the dissolution of aggregates produced an increase in free dipoles and first aggregation products according to Rubio (1991).

Figure 2 shows the TL glow curves obtained from 303 to 723 K in $KCl_{0.5}KBr_{0.5}$:Eu^{2+} crystals for as-grown crystals (solid curve) and after the first cycle readout (dotted curve). In this first readout intense emission is observed at temperatures greater than 473 K, which is absent in the second readout. This emission could be produced from the recombination of defect aggregates which cannot be formed during the short time of irradiation on the annealed crystal. In addition to the thermal bleaching effect, during the first readout a large number of I–V_C dipoles are released from the aggregates and converted to free dipoles. The glow peak observed at 424 K is a result of the β-irradiation. Its low relative intensity shows the magnitude of the effect that the aggregates of defects have on defect formation and the stabilization of radiation-induced defects. According to the glow curve of the second readout (solid curve), with short irradiation doses the traps emptied during the first heating cycle are not filled, but the formation of the glow peak at 413 K at a little higher intensity is induced and appears shifted to lower temperature. The higher intensity of this glow peak suggests that a higher efficiency in defect trapping may be due to an increase in the number of free dipoles or conversion of the high-temperature traps. These results suggest that the TL glow peak located at 413 K is a characteristic emission for this composition. The characteristic glow peak has been identified in a similar form for each composition analysed. Figure 3 shows the composition effect on the GPT. In spite of the annealing during the first readout, additional emissions at temperatures higher than 473 K were obtained for some compositions, as can be seen in figure 3. In these cases we believe that aggregates of defects may even be induced by the low dose of radiation

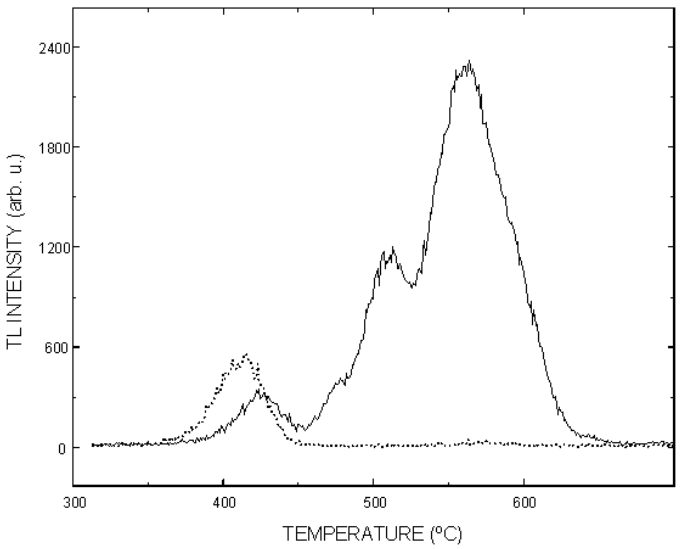

Figure 2. Glow curves obtained from the first (solid curve) and second readouts (dotted curve) of $KCl_{0.5}KBr_{0.5}$:Eu^{2+} crystals.

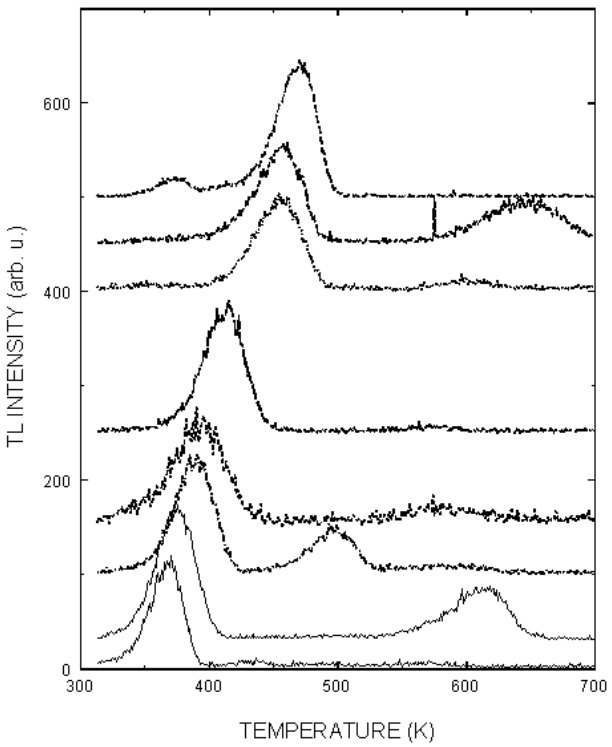

Figure 3. Glow curves of $KCl_{1-x}KBr_x$:Eu^{2+} solid solution. From top to bottom, $x = 0.01$, 0.10, 0.15, 0.50, 0.60, 0.80, 0.90 and 0.99.

Table 1. GPT for several compositions x in the first (as-grown samples) and second readouts (heated samples).

KBr molar composition x	Temperature (K) of glow peaks			
	First readout		Second readout	
	Eu^{2+}		Eu^{2+}	Ca^{2+}
1.00	368		368	
0.99	379		368	
0.90	382	613	373	
0.80	398	495	388	
0.60	416	573	398	394
0.50	424	572	413	410
0.40				417
0.25				434
0.15	457	603	453	
0.10	442	643	455	
0.01	468	373	471	
0.00	473		473	463

exposure. The temperatures of these and the most intense glow peaks in both readouts are listed in table 1.

Similar measurements were carried out on $KCl_{1-x}KBr_x$:Ca^{2+} crystals. The results are also listed in table 1. These measurements were obtained for compositions x different from that of Eu^{2+}-doped crystals, though the characteristic glow peaks were also found. Their temperature corresponds to the series of intermediate values of the composition x of the solid solution.

Since the characteristic emissions of KCl:Eu^{2+} and KBr:Eu^{2+} crystals appear around 473 and 373 K, respectively, it was expected that in crystals containing KCl and KBr at different compositions, the same glow peaks should occur around 473 and 373 K with relative intensities in the same ratio x. However, the TL results do not correspond to this situation. The crystalline system behaves as a solid solution with a unique type of simple traps whose release temperature depends directly on the composition. The values of the GPT obtained in this work confirm the assumption made above in the sense that there are GPTs related to the lattice constant of the host which are less dependent on the ionic radii of divalent cationic impurities or halogen ions. Figure 4 shows the composition dependence of the GPT. From the linear fit the temperature $T(x)$ behaves as $T(x) = 469 - 104x$. It can be written as

$$T(x) = (1 - x)T_1 + xT_2 \tag{1}$$

as in the form of Vegard's law $a(x) = (1 - x)a_1 + xa_2$, where T_1, a_1 and T_2, a_2 are the corresponding values of the GPT and lattice constant of the pure ends. Therefore the GPT can be related to the lattice constant as

$$T = T_1 + \frac{T_2 - T_1}{a_2 - a_1}(a - a_1). \tag{2}$$

An increase in the lattice constant leads to a decrease in the GPT. Similar analyses of the temperature shift of the glow peaks were carried out by Townsend *et al* (1967) for non-doped alkali halide crystals in the thermal range from 20 to 300 K where a different trend, similar to the Mollwo–Ivey relation, was found between the temperature of intense emissions and the lattice constant for three groups of glow peaks.

Our result might be extrapolated in a way to Eu^{2+}-doped one-component crystals (KCl, KBr, NaCl, etc) since such behaviour is observed in a comparison of the GPT in Eu^{2+}-doped

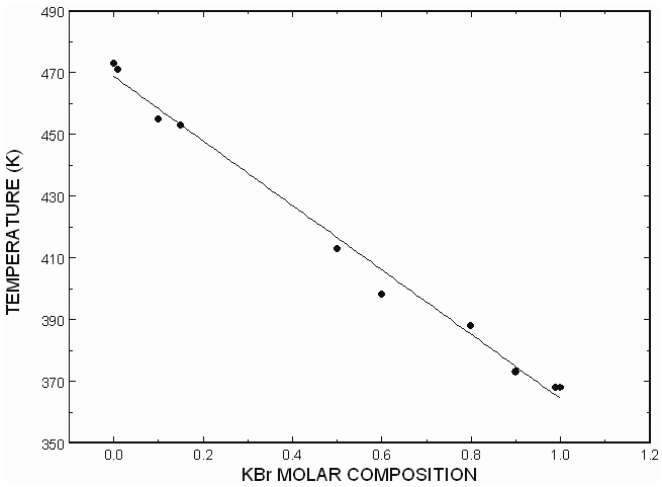

Figure 4. Temperature dependence of molar composition x in $KCl_{1-x}KBr_x:Eu^{2+}$ crystals.

KCl and KBr with that reported in the TL results of Aguirre de Cárcer *et al* (1999) for KI:Eu^{2+} crystals irradiated at 233 K where an intense glow peak at 278 K was found.

Finally, as the results obtained in rare-earth-doped crystalline materials indicate an impurity ion size effect on the GPT, and our results suggest that the shift of the GPT is not a local but a collective effect based on the lattice parameter, we consider that, to determine the most important parameter for the prediction of the GPT in different materials, further investigation is required.

4. Conclusion

In conclusion, a typical glow peak for divalent impurity-doped alkali halide solid solutions has been found. A linear dependence of the GPT on the composition x is observed which leads us to propose that the temperatures of characteristic glow peaks are mainly dependent on the lattice constant of the host and less dependent on the size of the anion or impurity cation. However, for a general prediction, further investigation is required.

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