



Influence of Thallium Co-Doped Luminescence characteristics of $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}$ Mixed Crystals

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ABSTRACT

The photoluminescence (PL) spectrum of $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}$ (0.05mol %) mixed crystal gives emission of europium at 420nm. This 420nm emission is due to the transition from T^{2g} component of $4f^6 5d$ configuration to the ground state $8s$ of europium. When adding Tl^+ ion as co-activator in $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}$ (0.05mol %) mixed crystal the same PL emission observed and enhanced their PL intensity. This enhancement is attributed to the energy transfer from $\text{Tl}^+ \rightarrow \text{Eu}^{2+}$ ions. Photo stimulated luminescence (PSL) studies on γ -irradiated $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}$, Tl^+ mixed crystal is discussed and tentative mechanism in the present study is reported.

Keywords: Mixed crystals, Tl^+ ion; Eu^{2+} ion, co-doped Mixed crystals, PL, PSL, Co-doped $\text{KBr-KI}:\text{Eu}^{2+}$

1. INTRODUCTION

Materials capable of storing images, produced by the absorption of X-rays (X-ray storage phosphors) because of the radiation induced defect formation. Generally electron and hole trap centers are involved in the image formation. In the Photostimulated luminescence (PSL) imaging process, the phosphor-imaging screen is first exposed to a dose of ionizing radiation. The ionizing radiation creates free electrons and holes, which are trapped at the crystals lattice site or impurities in the phosphor materials. Usually the F-centres are the electron trapped centres detrapping of these charge carriers requires energy. Upon photostimulation at the wavelengths corresponding to F-centre absorption, electrons are released from the F-centres and they recombine with the hole centres resulting in the emission of visible photons. Mostly this PSL phenomenon is proportional to the dose of ionizing radiation, and can serve as an alternate to conventional imaging technology involving the ionizing radiation.

Extensive studies have been made on the luminescence of ns^2 ion in alkali halides particularly thallium ions in alkali halides such as potassium halides, sodium halides have been studied thoroughly [1-3]. Thallium doped alkali halides exhibits excellent scintillation properties and is therefore used in the field of high energy radiation detection. However, reports on luminescence studies on thallium doped rubidium mixed halides is still meager. Recently new system to radiographic imaging, which are based on the conversion of X-ray imaging pattern into digital signals utilizing a laser beam scanning of the imaging plate have been studied in the field of medical diagnosis and radiation dosimetry. The most advanced one among the several digital radiography systems is based on the photostimulated luminescence (PSL) phenomenon in a laser stimuable Eu^{2+} -doped BaFBr phosphor powder screen imaging plate [4].

To the best of our knowledge there is no report on PL and PSL studies of thallium as co-doped with $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}$, Tl^+ mixed crystals. An attempt has been made to explore the possibility of $\text{KBr-KI}:\text{Eu}^{2+}$, Tl^+ to be used as X-ray storage phosphor for Imaging Plate (IP). Results of PL and PSL investigation carried out on $\text{KBr-KI}:\text{Eu}^{2+}$, Tl^+ mixed crystals are reported and discussed in this paper.

2. EXPERIMENTAL

The systems studied in the present work are $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}$, Tl^+ (0.05, 0.01mol %) mixed crystals grown in vacuum by slow cooling from its melt. Analytical Reagent grade KBr and KBI (99.9%) and the dopant in the form of TlBr and EuCl (99.99%) taken in the required stoichiometric proportions. The method of growth is briefly described in an earlier work [5] The Photostimulated luminescence (PSL) measurements were carried out using a JOBIN YVON – Spex Spectrofluorometer (FL3-11 Modell spectrofluorometer).

3. RESULTS AND DISCUSSIONS

The PL emission spectra of $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}$ (0.05mol %) mixed crystals observed around 2.91eV under different wavelengths of excitation are shown in Figure.1 curve (a) 250 (b) 262 (c) 274 (d) 332 (e) 365 (f) 371nm respectively.

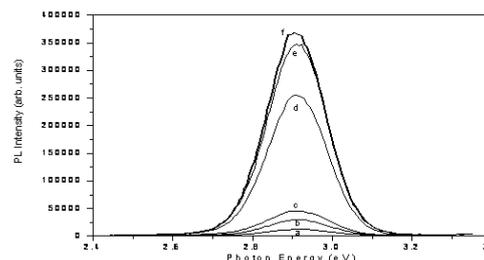


Figure 1: PL Emission spectra of $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}$ (0.05mol %) mixed crystals excited at (a) 250 (b) 262 (c) 274 (d) 332 (e) 365 (f) 371nm

The 2.91eV PL emission band is the well known characteristic of Eu^{2+} emission due to the transition from Sf^6 5d level to $4f^7$ [6-9]. However, their peak intensity increases with increasing excitation sources. Interestingly, the intensity of emission for main peak of 371nm excitation is higher than the emission of other excitations may be related to the overlapping of different excitation bands figure not shown.

Figure 2 shows the PL emission spectra of co-doped $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Ti}^+,\text{Eu}^{2+}$ (0.01, 0.05mol %) mixed crystal appear to be similar to those observed in $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}$ (0.05mol %) crystals for excitation at the same corresponding wavelengths.

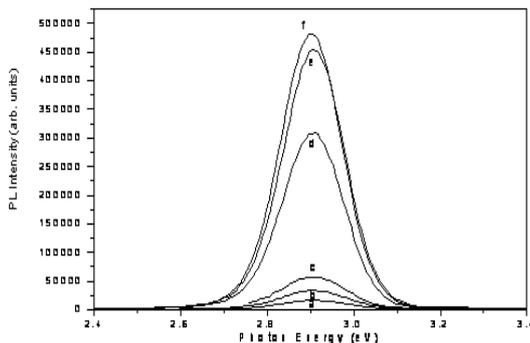


Figure 2: PL Emission spectra of $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}, \text{Ti}^+$ (0.05, 0.01mol %) mixed crystals excited at (a) 250 (b) 262 (c) 274 (d) 332 (e) 365 (f) 371nm

In this spectrum, there is an enhancement in the intensity of PL emission when compared to $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}$ (0.05mol %) mixed crystal due to overlapping between the excitation bands of europium ions 332-373nm, the excitation by radiation of any wavelength between 250-274nm would excite both the types of impurity ions in the $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Ti}^+,\text{Eu}^{2+}$ resulting in the 2.91eV Eu^{2+} emission. Thus an energy transfer between $\text{Ti}^+ - \text{Eu}^{2+}$ in $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Ti}^+,\text{Eu}^{2+}$ is expected to produce an enhancement in the 2.91eV emission [9-12].

The photostimulated luminescence of gamma irradiated $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}$ (0.05mol %) mixed crystal grown in vacuum shows a single emission band around 2.95eV under stimulated at 620nm F- absorption band (Fig.3.).

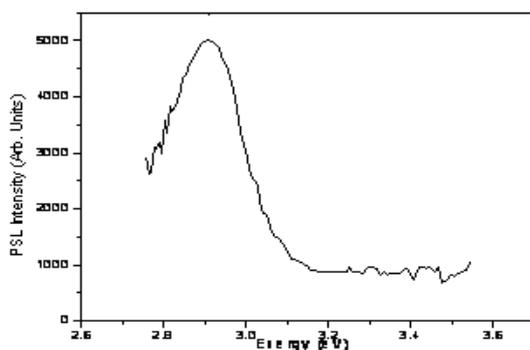


Figure 3: PSL emission spectrum of $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}$ (0.05mol %) mixed crystal.

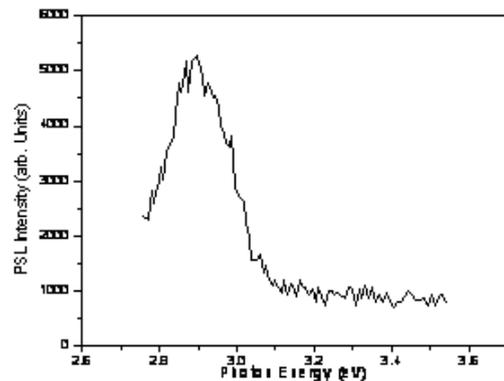


Figure 4: PSL emission spectrum of $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}, \text{Ti}^+$ (0.05, 0.01mol %) mixed crystal.

PSL emission of $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}, \text{Ti}^+$ showed similar spectrum as that of $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}$ but with slightly increased in intensity shown in Fig.4. The PSL and PL emissions at 2.95eV (420nm) due to the Eu^{2+} ions are similar, suggesting the involvement of Eu^{2+} ions in the PSL process. The stimulation spectrum for this emission observed a broad band around 630nm (Figure not shown).

The stimulation band clearly resembles the F-band absorption in KBr crystals and hence the F-centered are suggested to be the electron-trapped centres involved in the PSL process [13]. Further the intensity of PSL emission slightly increases when added thallium as co doping in $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}$ mixed crystals attributed to the energy transfer from Ti^+ to Eu^{2+} ions in double doped mixed crystals [11, 14]. The PSL emission of gamma irradiated $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}, \text{Ti}^+$ mixed crystals phosphors do not show any emission band attributed to the centers involving thallium ions. It is known that in alkali halides doped with Eu^{2+} ions, a part of the free electrons and free holes generated upon irradiation are trapped by anion vacancies and Eu^{2+} ions forming F-centres and Eu^{3+} ions respectively [13, 15]. Subsequent photostimulation in the F-band releases electrons from F-center traps into the conduction band and when some of these free electrons recombine with Eu^{3+} ions, the characteristic Eu^{2+} emission (around 420 nm) results. On the other hand, in alkali halides doped with Ti^+ ions, upon irradiation, different types of thallium centers have been reported to be formed depending upon several factors such as concentration of Ti^+ ions, temperature of irradiation etc. [15].

The enhancement of PSL emission in $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}, \text{Ti}^+$ phosphors containing higher concentration of Ti^+ ions may be related to the formation of hole trapped thallium centres in large numbers which would cause an enhancement in the concentration of F-centres formed [16]. While a part of the electrons released from F-centres by photostimulation in the F-band recombine with Eu^{3+} ions, another part of them may recombine with hole trapped thallium centres resulting in their characteristic emission bands. Further study is required to confirm the exact mechanism.



CONCLUSION

PSL emission of Eu^{2+} ions in $\text{KBr}_{0.95}\text{I}_{0.05}:\text{Eu}^{2+}$, phosphors are enhanced by adding appropriate amounts of Tl^+ ions as co-activator. This enhancement is attributed to the energy transfer from $\text{Tl}^+ \rightarrow \text{Eu}^{2+}$ ions.

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REFERENCES

- [1] Fukuda, A., 1964. *Sci. Light*, 13: 64.
- [2] Edgerton, R., and K. Teegarden, 1963. *Phy. Rev.*, 129: 160
- [3] Delbecq, C. J., Ghose, A. K and Yuster, P. H, 1966. *Phys. Rev*, 151: 599.
- [4] Von Seggern, H., Voigt, T, Knupfer, W and Lange, G, 1988. *J. Appl. Phys*, 45: 1405.
- [5] Eswaran, P., Ravisankar, R and Nagarajan, S, 2009. *Nucl Sci Tech*, 20: 208.
- [6] Ganpathi Subramaniam, N., Selvasekarandia, S and Pal, H, 2003. *J Lum*, 102/103: 807.
- [7] Ganpathi Subramaniam, N., Selvasekarandia, S and Pal, H, 2003. *Mat Letters*, 57: 2021.
- [8] Ganpathi Subramaniam, N., Selvasekarandia, S, G. Bhavan, Tae Won Kang and H. Pal, 2004. *Optical Mat*, 27: 515.
- [9] Nagarajan, S and Suderkodi R, 2009. *J Alloys Compd*, 468: 558.
- [10] Nagarajan S, Suderkodi R, 2009. *Luminescence*, 24: 162.
- [11] Nagarajan, S and Suderkodi R, 2008. *Radiation Effects and Defects in Solids*, 163: 915.
- [12] Nagarajan, S., and Suderkodi R, 2008. *Nucl Inst Meth Res B*, 266: 3595.
- [13] Nanto, H., M. Miyaski, M. Imai, A. Komori, 2000. *IEEE Trans. Nucl. Sci*, 47: 1620.
- [14] Eswaran, P., S. Nagarajan and R. Ravisankar, 2011. *Recent Research science and Technology*, 3 (4): 114.
- [15] Roth, M and A. Halperin, 1982. *J. Phys. Chem. Solids*, 43: 609.
- [16] Agullo-Lopez, F., F. J. Lopez and F. Jaque, 1982. *Cryst. Latt. Def. and Amorp. Mat*, 9, 227.