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Optical studies on $RbBr_{1-X}I_X$:TlI mixed crystals

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ABSTRACT

Photo-stimulated luminescence (PSL) induced in thallium doped $RbBr_{1-x}I_x$ mixed crystals grown under vacuum (x = 0.00, 0.05 and 0.10) by irradiated with ionizing radiation such as γ- ray is studied at room temperature. Photo-stimulated luminescence observed in mixed crystals by Photostimulation at F-band resulted in emission spectra appeared to be broad and slightly shifted towards low energy side with increasing of iodine content of x. The mechanism of PSL is suggested.

Keywords: PSL, Stimulation band, RbBr-RbI mixed crystals, Tl^+ ions, γ- ray irradiation, Tl^+ impurity, ionizing radiation.

INTRODUCTION

Photo-stimulated luminescence (PSL) phenomenon in alkali halides and other phosphors doped with impurities such as Eu^{2+}, Tl^+ ions has gained momentum due to its application in the field of high energy radiation detection, imaging plate for X-ray radiography etc [1-4]. A number of alkali halide phosphors doped with impurities such as Eu^{2+}, Tl^+, Ga^{2+}, etc. have been investigated for their suitability as X-ray storage phosphors employed in X-ray imaging plates [5-8].

X-ray storage phosphor materials based on photostimulated luminescence (PSL) are capable of storing images produced by the absorption of X-rays and they offer a number of advantages such as high sensitivity, low fading, a higher dynamical range, linear dose response and so on when compared to conventional X-ray films. Commercial X-ray storage phosphor BaFBr:Eu^{2+} has excellent PSL characteristics. However the problems associated with this phosphor are related to the poor spatial resolution of the stored image and scattering effects during the read-out process due to the birefringence of BaFBr crystallites [9]. Hence a need for the development of new transparent or translucent phosphor which has a higher resolution raised. Thus transparent alkali halides such as rubidium single and mixed halides doped with suitable activators have been proposed as new storage phosphors. After surveying many alkali halide phosphors it was found that impurity doped rubidium halides exhibit very good PSL characteristics for computed radiography. Currently, new systems of computerized digital radiography utilizing the photostimulated luminescence (PSL) phenomenon in He-Ne laser-stimulable $CsBr:Eu^{2+}$ phosphor imaging plates or semiconductor laser-stimulable $RbBr:Tl^{+}$ film type imaging plates are commercially available for such applications [5,7]. RbBr-RbI mixed system seems to be attractive in view of the spectral position of F-band in RbBr (around 630nm) as it lies close to the He-Ne laser wavelength (633nm) that is used for photostimulation in some commercial X-ray radiography.

Recently, a number of workers are studying the PSL characteristics of mixed alkali halides doped with activator ions [10-12]. However, a luminescence study on Tl^{+} doped mixed alkali halides is still meager. In this context, Thallium doped RbBr-RbI mixed crystals have been chosen for studying their luminescence behavior.

MATERIALS AND METHODS

$RbBr_{1-x}\,I_x$:TlI (0.1mol%) mixed crystals grown in vacuum with x = 0.00, 0.05 and 0.10 by slow cooling from its melt. Analytical Reagent grade RbBr and RbI (99.9%) and the dopant in the form of TlI (99.99%) taken in the required stoichiometric proportions described in our earlier work [13]. The Photostimulated Luminescence (PSL) measurements were carried out using a JOBIN YVON – Spex Spectro- fluorometer (FL3-11 Modell spectrofluorometer).

RESULTS AND DISCUSSION

Figure.1. (curve a) shows the PSL emission spectrum of gamma-irradiated single crystal of RbBr:TlI (0.1mol%), photostimulated in the F-band absorption subsequent to irradiation. It shows an emission band around 370nm (3.34eV) which is comparable to the PL emission band, when the specimen was excited with 260nm light [shown in inset of Fig.1. (Communicated)], which corresponds to the characteristic of Tl^{+} ions. The PSL

emission results of $RbBr:Tl^{+}$ crystals agree with earlier reports by Von Seggern [6]. The PSL emission spectra of $RbBr_{0.95}\,I_{0.05}$: TlI mixed crystals appear to have slightly shifted towards low energy side when compared to the crystals added with RbI in the melt. However, the 2.9eV shoulder observed in the PL emission is not seen prominently (communicated). Similar results are observed for $RbBr_{0.9}\,I_{0.10}$: TlI mixed crystals phosphors. The intensity of the PSL emission in $RbBr_{0.95}\,I_{0.05}$: TlI is higher than that in $RbBr:Tl^{+}$ single crystals. However, the intensity decreased significantly with further increase in iodine composition.

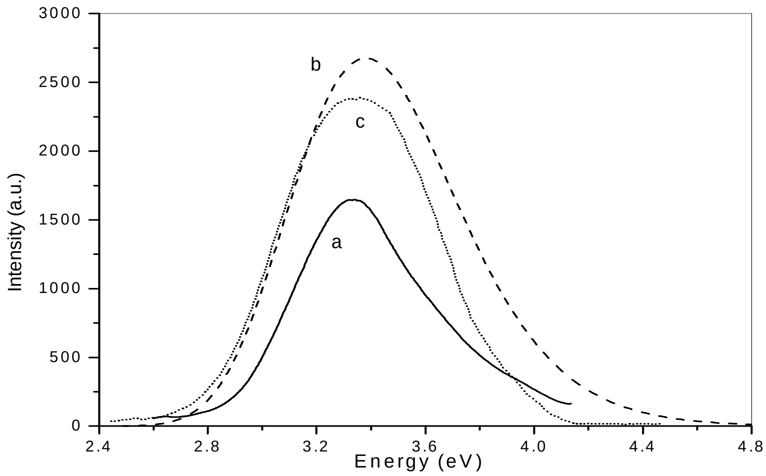

Figure.1. PSL emission spectra of $RbBr_{1-x}I_x$: TlI (0.1 mol %) with a) x = 0.00, b) 0.05 and c) 0.10 stimulation in the F-band.

Photostimulation spectra of $RbBr_{1-x}I_x$:TlI (0.1mol%) mixed crystal with x = 0.00, 0.05 and 0.10 exhibit stimulation bands located around 1.783eV for RbBr:TlI. In the case of $RbBr_{1-x}I_x$:TlI mixed crystals with x = 0.05 and 0.10, the observed stimulation band (around 1.772 and 1.764eV respectively) appeared to be broad with its peak position shifted towards low energy side as shown in Figure. 2. The broad stimulation band position shifts towards the lower energy side with composition of iodine similar to that of the F-band absorption peak (communicated). This is probably due to the combined effect of increase in lattice parameter with composition of iodine.

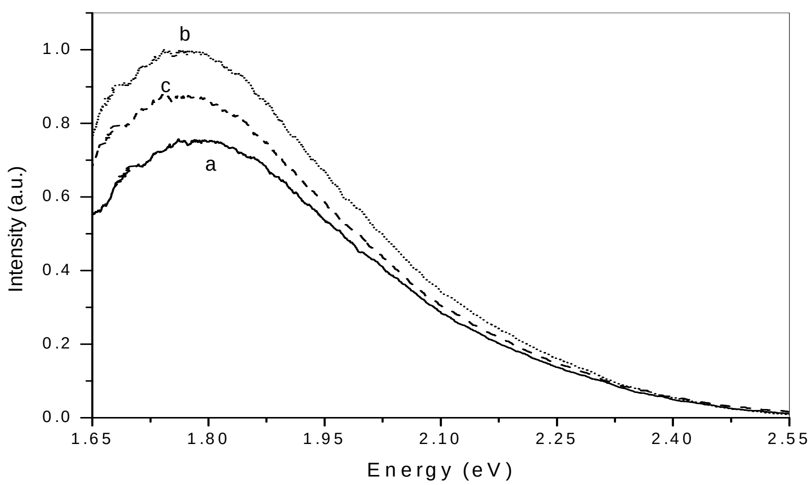

Figure.2. Photostimulation spectra of $RbBr_{1-x}I_x$: TlI (0.1 mol %) with a) x = 0.00, b) 0.05 and c) 0.10 emission at 3.34eV.

Mixed crystals of alkali halides acquire less coloration compared to single crystal components when exposed to ionizing radiation [14]. However, the intensity of stimulation band is slightly higher in the case of $RbBr_{1-x}I_x$:TlI mixed crystals than RbBr:TlI single crystals. This may be due to effect of I^- involved in these mixed crystals.

It is well known that, during irradiation free electrons and holes are generated in the crystal. Most of these free electrons and holes recombine immediately emitting radiation. However, a part of the free electrons are trapped at anion vacancies forming F-centers while corresponding number of holes are trapped by Tl^+ ions forming Tl^{++} ions. However it is worth mentioning that Tl^+ ions in alkali halides can trap electrons or holes during irradiation [15]. When the gamma irradiated crystal is photostimulated in the F- band, the electrons trapped in some of the F-centers are liberated to the conduction band again. Some of these free electrons recombine with Tl^{++} ions converting them into Tl+ ions in the excited state. When these ions relax to their ground state, the characteristic Tl^+ emission (PSL) results. However, it should be mentioned that, from their life time studies of PSL at low temperature and at room temperature, Von Seggern et al proposed a tunneling mechanism [6] which was similar to a tunneling mechanism proposed in BaFBr: Eu [16-18].

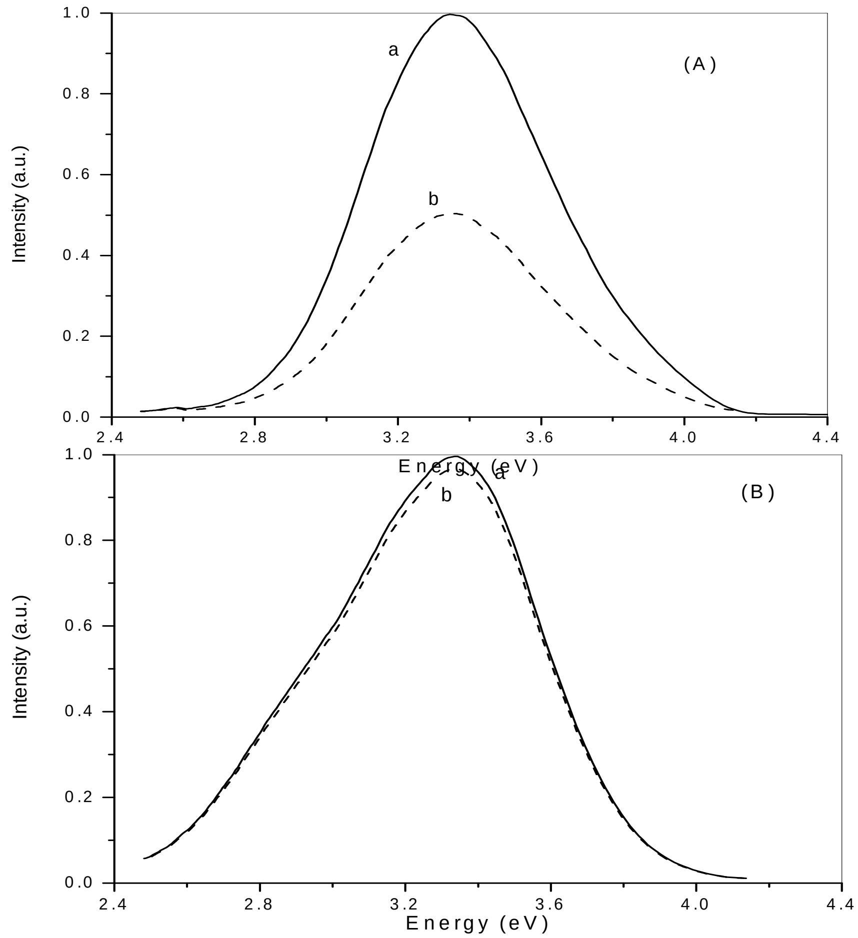

Figure 3. (A), (B). PL emission spectra of RbBr $_{0.9}$ I$_{0.10}$: TlI (0.1mol %) grown in vacuum for excitation wavelengths λ_{ex} = 260nm, λ_{ex} = 280nm (a) Before irradiation (b) after irradiation.

According to their model, X-ray irradiation of the RbBr:Tl^+ crystals leads to the formation of Tl^+ - H complex and F-centers. The Tl^+-H complex was reported to act as the recombination centre while the F- centers as the occupied electron traps. Upon photostimulation of the F-centers, the electron of F-centre is excited. The electron from the relaxed excited state of the F-centre recombines with a nearby tunneling which results in the Tl^+-H complex emission of the characteristic Tl^+ spectrum. P L emission spectra of gamma irradiated $RbBr_{1-x}$ I_x :TlI (with x = 0.05 and 0.10) samples obtained by exciting them in the A-band (around 260nm) show a considerable decrease in emission intensity while the intensity of the PL emission for excitation in the long wavelength band (around 280nm) shows only a very small decrease in intensity (Fig.3. A and B).

The large reduction in the intensity of PL emission intensity for λ_{ex} = 260nm band after irradiation implies that the concentration of these centers is considerably reduced on irradiation while that of the complex thallium centers responsible for 2.9eV emission is not reduced significantly.

Usually, coloration is poor in alkali iodides when compared to that in other alkali halides. In the case of an alkali halide doped with foreign halogen ions (such as KCl- KI, KBr- KI), generally, F-centre production yield is significantly reduced [17]. The presence of a foreign halogen ion distorts the lattice and it defocuses the primary collision chain during irradiation resulting in poor coloration. PL measurements of $RbBr_{1-x}$ I_x:TlI mixed crystals have indicated the formation of complex Tl^+ centers involving Br- and I- ions as nearest neighbors to Tl^+ ions (communicated). Since the ionic radius of I- ion is larger than that of Br- ion, the lattice surrounding the Tl^+ impurity ion will be distorted. The lattice distortion and the strain field around the Tl^+ ions is expected to be high if these centers involve a relatively large number of I- ions. Hence due to the abovementioned defocusing effect, the free electrons and holes generated during irradiation are not stabilized (i.e trapped) efficiently at the defect sites in the crystal resulting in a poor color-centre production. Hence the change of valence state of the Tl^+ ions in such complex centers in RbBr-RbI: (Tl^+) mixed crystals may not occur efficiently upon irradiation. This implies that hole centers involving thallium ions are not formed in large numbers on irradiation if the complex thallium centre involves a relatively large number of I- ions surrounding a Tl^+ ion as its nearest neighbors. On the other hand, it is speculated that, in complex Tl^+ centers involving no or relatively less number of I- ions, the conversion of Tl^+ ions to Tl^{++} or (Tl^+-V centers) on irradiation may be relatively more efficient. Hence a relatively large number of Tl^+ ions in such thallium centers may undergo valence change by trapping holes during irradiation. Thus, the larger reduction in the intensity of the PL emission for λ_{ex} = 260nm (4.78eV) after irradiation may be related to the efficient trapping of holes by Tl^+ ions. This tentative suggestion requires further confirmation. However, the absence of the 2.9-3.0eV emission shoulder (observed in the PL emission) in the PSL emission may be considered as a supporting evidence for the above view.

The plot of PSL emission intensity (370nm emission) of $RbBr_{1-x}$ I_x:TlI (0.1mol%) mixed crystals against radiation dose is shown in Figure.4. The intensity of PSL emission of gamma irradiated $RbBr_{1-x}$ I_x:TlI (0.1mol%) increase with increasing gamma ray dose in two stages.

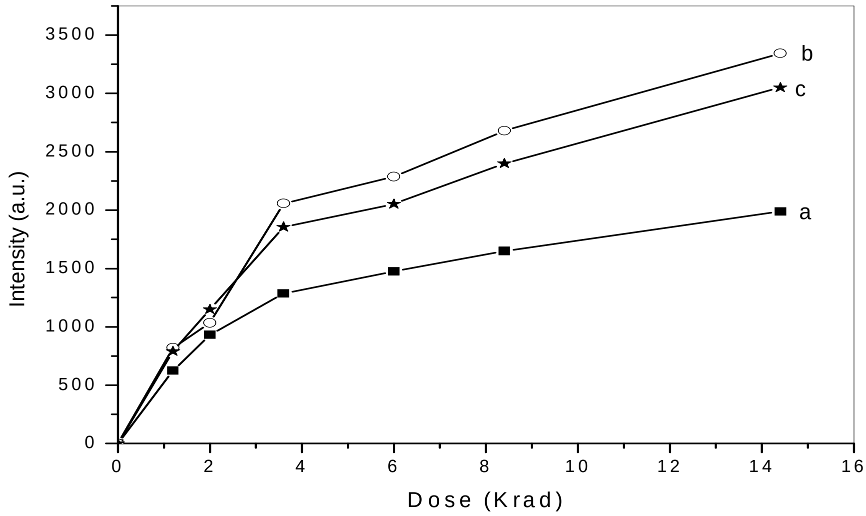

Figure.4. PSL emission intensities of $RbBr_{1-x}\,I_x$:TlI (0.1mol%) with a) x = 0.00, b) 0.05 and c) 0.10 mixed crystals as a function of gamma dose.

The optical absorption spectra of $RbBr_{1-x}\,I_x$:TlI (0.1mol%) mixed crystals exhibited an inhomogeneous broadening of the A-band towards low energy side with increases of I- ion composition. Compared with the absorption spectra of RbBr:TlBr single crystals and RbBr:TlI crystals, the changes in the absorption spectra of $RbBr_{1-x}\,I_x$:TlI mixed crystals are due to some complex Tl^+ centers involving Br- and I- ions formed in the mixed crystals [13,19, communicated].

When the RbBr:TlBr single crystals are excited at different wavelengths in A- band same asymmetric emission band (3.34eV) is observed. When $RbBr_{1-x}\,I_x$:TlI mixed crystals are excited at different wavelengths in the A-band absorption, an additional emission band around 2.9eV is also observed. Comparing with earlier results, the observed changes in the emission in $RbBr_{1-x}\,I_x$:TlI mixed crystals are attributed to the formation of complex Tl^+ centers of the type $TlBr_6$-n In involving both Br- and I- ions as nearest neighbours to the Tl^+ ions [11, 19, communicated].

PSL emission spectra of gamma irradiated $RbBr_{1-x}\,I_x$:TlI mixed crystals under band stimulation show PSL emission band around 370nm (3.35eV) The PSL emission bands are comparable to the PL emission bands observed in them. Comparing the results with earlier reports, a mechanism for PSL emission is suggested.

CONCLUSIONS

PSL emission spectra of gamma irradiated $RbBr_{1-x}\,I_x$:TlI mixed crystals under F-band stimulation show PSL emission band around 370nm (3.35eV) The spectral peak position of PSL emission of RbBr-RbI mixed crystals doped with Tl^+ ions slightly shift towards low energy side when compared to that observed in RbBr: Tl^+ single crystals. The intensity of the PSL emission in $RbBr_{0.95}\,I_{0.05}$: TlI is higher than that in RbBr:Tl^+ single crystals. However, the intensity decreased significantly with further increase in iodine composition. The PSL intensity increases with increasing gamma dose. Comparing the results with earlier reports, a mechanism for PSL emission is suggested.

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REFERENCES

[1] J. O. Rubio, *Phys. Chem. Solids*., **1991,** 52, 101.
[2] A. Ranfagni, D. Mugnai, M. Bacci, *Adv.Phys*., **1983,** 32, 823.
[3] H. Nanto, M. Miyazaki, A. Imai, *IEEE. Trans. Nucl. Sci.*, **2000,** 47, 1620.
[4] M. Sonoda, J. Takano, H. Miyahara, *Radiology*., **1983**, 148, 833.
[5] M. Weidner, M. Batentschuk, F. Meister, *Radiat. Measur*., **2007,** 42, 661.
[6] H. Von Seggern, A. Meijerink, T. Voigt, *J. Appl. Phys*., **1998,** 66, 4418.
[7] U. Rogulis, S. Schweizer, S. Assmann, *J. Appl. Phys.*, **1998,** 84, 4537.
[8] H. Nanto, K. Murayama, T. Usuda, *Radiat. Prot. Dosim.*, **1983,** 47, 281.
[9] K. Takahashi, K. Kodha, J. Miyahara, *J. Lumin*., **1984,** 31/32, 266.
[10] N. Ganapathi Subramaniam, S. Selvasekarapandian, H. Pal, *J. Lumin*.,**2003,** 102/103, 807.
[11] S. Nagarajan, P. Eswaran, *Nucl. Instr. Meth. Phys. Res* (B)., **2009,** 267,800.
[12] S. Nagrajan, R. Suderkodi, *Luminescence*., **2009,** 24, 162.
[13] P. Eswaran, S. Nagarajan, *Nucl. Sci. Tech.*, **2009,** 20, 208.
[14] K. Brinda Subramanium, G. Bansigir *Pramana*., **1981,** 17, 445.
[15] M. Roth, A. Halperin, *J. Phys. Chem. Solid*., **1982,** 43, 609.
[16] H. Vonseggern, T. Voigt, W. Knupfer, *Appl. Phys.*, **1988,** 64, 1405.
[17] H. Vonseggern, T. Voigt, K. Schwarzmichel, *Siemens Res. Develop.Rep.*, **1988,** 17, 124.
[18] D. M. Deleeuw, T. Kovats, S. P. Herko, *J. Electrochem. Soc*., **1984,** 134,491.
[19] W. Kleemann, *Z. Fischer Physik*., **1966,** 197, 75.