Lyoluminescence in Ce^{3+} activated (KNa)Br phosphor for ionizing radiation dosimetry

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Abstract. The lyoluminescence (LL) in γ-ray irradiated (KNa)Br : Ce^{3+} phosphors are reported in this paper. LL of (KNa)Br : Ce^{3+} have been recorded for different γ-ray doses. The nature of variations of LL peak intensities is found to be linear with γ-ray irradiation dose and LL peak intensity is found to be dependent on concentrations ($0\cdot1$–10 mol%) of added Ce^{3+} ions in the (KNa)Br host lattice. Negligible fading in the prepared sample is observed.

Keywords. Lyoluminescence; γ-ray dose; radiation dosimetry; phosphor; (KNa)Br.

1. Introduction

The measurement of radiation dose has become a science of ever increasing importance due to the estimation of risk and benefits inherent to the uses and to the exposure of ionizing radiation. When strongly energized, crystals are dissolved in a liquid solvent like water and light is emitted because of recombination of hydrated electrons with holes on the surface of crystallites. This phenomenon is called lyoluminescence (Harvey 1957) and has been investigated by many workers for use in dosimetry application. Ahnstrom (1965) and Arnikar and co-workers (1972) support the formation of hydrated electron (e_{aq}^{-}) as the prerequisite for emission of light. The work in this field appears to deal more with the improvement of techniques, both for detection and preparation of materials, aimed at achieving more reliable dosimetry (Ettinger and Puite 1982). However, there are a number of factors that influence the light yield during dissolution of γ-irradiated alkali halides in water, and which have not been investigated in detail. Various studies have been undertaken to understand the mechanism of LL (Reynolds 1992). The parameters that influence the LL intensity are, for example, grain size, mass of the irradiated alkali halide, pH of the solvent, temperature of the solvent, irradiation dose, type of impurity etc and requires detailed investigation for the development of LL dosimetric materials (Chandra *et al* 1997).

Colour centres in alkali halides have been studied for many years. Moharil and Deshmukh (1978) had shown that the colouration in microcrystalline powders obtained by crushing the electrolytically coloured single crystal is not stable. It is known that the electrolytically produced colouration in potassium halides is lost within a day (Moharil and Deshmukh 1978). The colour centres have mostly been studied in single crystals, while applications such as dosimetry of the ionizing radiation using thermoluminescence (TL) and lyoluminescence (LL) more often involves measurements on powders. Ettinger (1966) initiated the application of LL to radiation dosimetry. It is generally believed that the mechanism of colour centres production is similar for single crystals and microcrystalline powder. Production of colour centres by γ-irradiation in NaCl, KCl and KBr is reported by Deshmukh and co-workers (1985a,b, 1986, 1988), in crystal and microcrystalline powder. For development of LL dosimetry materials, researchers concentrated on an enhancement in LL intensity, observed in certain fluorescent (Atari and Ettinger 1974; Kalkar 1983), chemiluminescent solutions (Atari 1980; Chazhoor and Mishra 1982) and dye lasers (Schafer 1972).

Recently, Sahu and co-workers (2009) studied particle size effect of KCl : Sr and concluded that the lyoluminescence intensity cannot be directly correlated to the radiolysis product (colour centre concentration) or the dissolution rate but it depends on both factors simultaneously. Such studies would be helpful in providing information for lyoluminescence dosimetry and a better insight into the kinetics of reactions responsible for LL emission. It would definitely add to our knowledge of defect interactions in general and particularly in solids. Kher *et al* (2010) and Puppalwar *et al* (2011) prepared phosphors for measurement of radiation dose based on ML and LL technique, respectively by using the rare earth materials as dopant. Bangaru and co-workers (Bangaru and Muralidharan 2009; Bangaru *et al* 2010) also reported the enhanced luminescent properties and thermoluminescence studies in alkali halides by doping rare earth materials. Many alkali halide based materials like LiF exhibit important dosimetric properties. The study of luminescence properties in alkali halides is a challenging task to find out the possible dosimetric material by using lyoluminescence technique in the development of radiation dosimetry.

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In this paper, we report the dependence of the nature of the radiolysis products, LL in $(K_{0.5}Na_{0.5})Br:Ce$ phosphor (considered as (KNa)Br : Ce for convenience, throughout the paper) in powder form and comparison of it with LL characteristics of KBr : Ce and NaBr : Ce materials.

2. Experimental

All phosphors containing different concentrations of $Ce^{3+}(0.1–10$ mol%) were prepared by a wet chemical method. For the preparation of $(K_{1−x}Na_x)Br$ material equimolar mass of KBr and NaBr materials were dissolved in distilled water. The prepared material was $(K_{0.5}Na_{0.5})Br$, but for convenience it is referred to as (KNa)Br in this paper. For preparation of (KNa)Br : Ce, KBr : Ce and NaBr : Ce, the required concentrations of Ce were added in the solution of (KNa)Br, KBr and NaBr, respectively. Then the solutions were evaporated at 80°C in an oven for about 4–5 days in a controlled manner. The recrystallized residues were normally crushed to powder, and then heated at 500°C in a furnace for 1 h and quenched. Analytical reagent grade chemicals were used in the present investigation. The samples were exposed to γ-rays dose from a ^{60}Co source having a dose rate of 0.50 kGy/h.

Lyoluminescence was studied with the usual set up consisting of LL cell, photomultiplier tube (RCA 931), amplifier and recorder at room temperature (Dhoble *et al* 2002; Dahikar *et al* 2008). Distilled water containing $7 \times 10^{−4}$ mol% luminol was used as solvent. For recording the LL, 5 mg sample was dissolved in 2 ml solvent, injected by syringe into a test tube having high transparency placed close to the window of PMT.

All samples were stored in the dark at room temperature during experiments. All experiments were performed under identical conditions for many times to ensure reproducibility.

3. Results and discussion

3.1 *Lyoluminescence studies*

The irradiation of alkali halides produces both trapped electron colour centres and a trapped hole colour centre. According to the mechanism described by Atari (1980) when an energized alkali halide crystal is dissolved, the entire process of LL takes place in two stages: one in the solid phase of the sample when it is irradiated with γ-rays or X-rays and the other in the liquid phase when it undergoes dissolution. When an alkali halide crystal dissolved in water, the two effects occur simultaneously. An electron is released from an *F* centre and a hydrated electron $(e^{−}_{aq})$ is formed. The large quenching effect of the hydrated electron acceptors indicates that the released *F*-centre undergoes hydration before its recombination with a V_2 centre. The rapid recombination of the hydrated electron with a V_2 centre at the water–solid interphase gives luminescence. The hydration process takes place in a very short time. The rate at which light is

produced depends on the diffusion constant of the hydrated electron and the availability of its counterpart (the V_2 centre) at the water–solid interphase. The presence of both *F* and V_2 centres together is essential for exhibition of the LL phenomenon. Schematically the process can be written as follows:

$$e^{−}_{trapped} + H_2O \rightarrow e^{−}_{aq}, \tag{1}$$

$$e^{−}_{aq} + X \rightarrow X^{*}_{aq}, \tag{2}$$

$$X^{*}_{aq} \rightarrow X_{aq} + h\nu, \tag{3}$$

where $X = Cl^{−}$, $Br^{−}$ and $I^{−}$ etc. It is possible that steps (2) and (3) can occur together without the intermediate state, i.e. the formation of X^{*}_{aq}. A similar mechanism was also suggested by Ahnstrom (1965).

Ettinger and Puite (1982) investigated typical applications of LL material in dosimetry. 20–30 mg of irradiated LL material was dissolved in suitable solvents and the LL yield was measured in terms of the investigated light intensity per mg. However, in intercavity gamma radiation therapy only about 5 mg of the sample is recommended to avoid degradation. However, to avoid the role of mass effect in LL yield a small amount of prepared phosphor, i.e. 5 mg, was taken for each measurement of LL intensity and the results are shown for LL intensity per mg, in this investigation. Consistent with the observations of Atari (1980), it was found that addition of a small quantity of luminol increased LL intensity by orders of magnitude. It was found that the optimum luminol concentration was $7 \times 10^{−4}$ mol % and pH of the solvent was 12.

Lyoluminescence, using water containing luminol as a solvent, in (KNa)Br(pure) and (KNa)Br : Ce(0.1–10 mol%) is shown in figure 1. LL glow curves show isolated single peak indicating that only one type of luminescence centre is formed during irradiation by γ-rays in each sample. For all (KNa)Br : Ce samples the LL intensity is more than (KNa)Br(pure) sample. Specifically for (KNa)Br : Ce(0.5 mol%), LL intensity peak height is two times higher as compared to pure (KNa)Br material. The observed LL is due to the dissolution of materials in water containing $7 \times 10^{−4}$ mol% luminol as solvent traps are released. The enhancement of LL intensity in Ce doped (KNa)Br samples indicates that more trapping centres are formed during irradiation. This characteristic is very applicable for development of LL dosimetric material.

3.2 *Effect of dopant concentrations on LL intensity*

Significant enhancement of the lyoluminescence light yield in amino acids are obtained if terbium ions are present in the solution, i.e. addition of rare earth ions to solvent used in lyoluminescence results in an increase of light intensity (Ettinger and Anunuso 1981). In the present investigation, rare earth material (i.e. Ce ion) is present in the solutes, i.e. in the prepared materials. The enhancement of the lyoluminescence intensity is also observed.
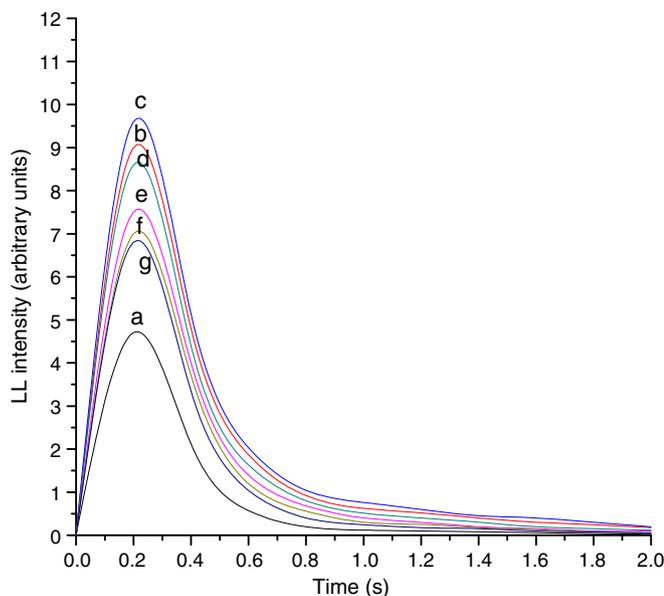
Figure 1. LL glow curve of (KNa)Br(pure) and (KNa)Br : Ce (0·1–10 mol%), dissolved in water containing luminol, exposed to a gamma dose of 0·50 kGy. (a) (KNa)Br(pure), (b) (KNa)Br : Ce(0·1 mol%), (c) (KNa)Br : Ce(0·5 mol%), (d) (KNa)Br : Ce (1 mol%), (e) (KNa)Br : Ce(2 mol%), (f) (KNa)Br : Ce(5 mol%) and (g) (KNa)Br : Ce(10 mol%).
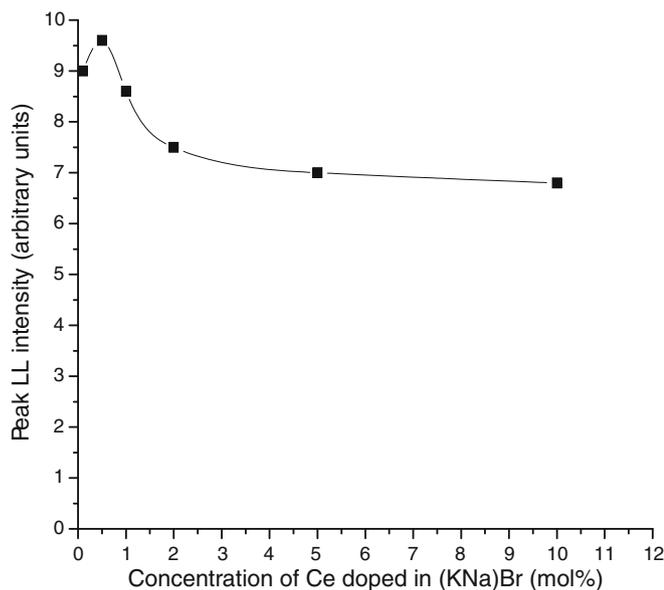

Figure 2. Variation of peak LL intensity with different concentrations of Ce doped in (KNa)Br, exposed to a gamma dose of 0·50 kGy.

Figure 2 shows variation of peak LL intensity with different concentrations of Ce doped in (KNa)Br. LL intensity is found to be dependent on the concentration of Ce impurity ions in the host material. LL intensity becomes saturated at 0·5 mol% of Ce doped in (KNa)Br due to concentration quenching and LL intensity decreases above 0·5 mol% due

to aggregation of impurity ions. Low concentration of impurity ions shows maximum lyoluminescence intensity and cost-wise is a desirable characteristic for the development of materials for radiation dosimetry.

Figure 3 shows comparison of variation of LL intensity with dopant concentrations. LL intensity for NaBr : Ce material is more than KBr : Ce sample and the LL intensity of (KNa)Br : Ce material is in between the LL intensities of KBr : Ce and NaBr : Ce materials. LL intensity of (KNa)Br : Ce is more than KBr : Ce sample and nearer to it. In the (KNa)Br : Ce materials, LL intensity decreases as compared to NaBr : Ce powder. This may be due to interaction or orientation of ionic radius of K^+ ion with the ionic radius of Na^+ ion in the (KNa)Br : Ce materials, since the ionic radius of K^+ ion is 152 pm and Na^+ ion is 116 pm, i.e. the ionic radius of both the ions is different. Formation of colour centres in this interaction as well as the release of luminescence centres during dissolution are responsible for LL intensity of (KNa)Br : Ce materials.

3.3 *Dependence of LL on radiation dose*

Figure 4 shows variation of peak LL intensity with γ-rays exposure of (KNa)Br(pure) and (KNa)Br : Ce (0·5 mol%). LL intensity linearly increases with γ-rays exposure up to 2·5 kGy high exposure. For the (KNa)Br(pure) material, the LL intensity also linearly increases up to 2.5 kGy γ-rays dose. But for Ce-doped sample, the comparative increase in LL intensity is found to be more. When alkali halide crystal is exposed to high energy radiation like γ-rays or X-rays, it results into excitation of electrons of halide atoms from valence band to conduction band. Some of the excited
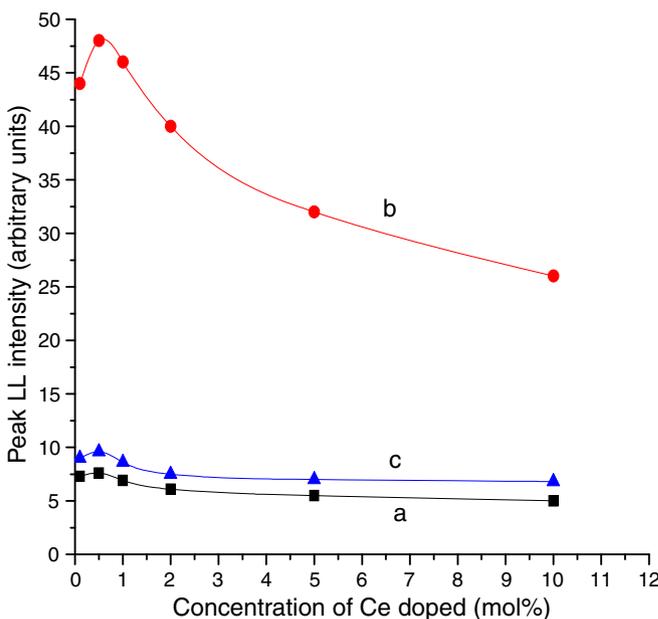

Figure 3. Comparison of variation of peak LL intensity with different concentrations of Ce doped in (a) KBr, (b) NaBr and (c) (KNa)Br, exposed to a gamma dose of 0·50 kGy.
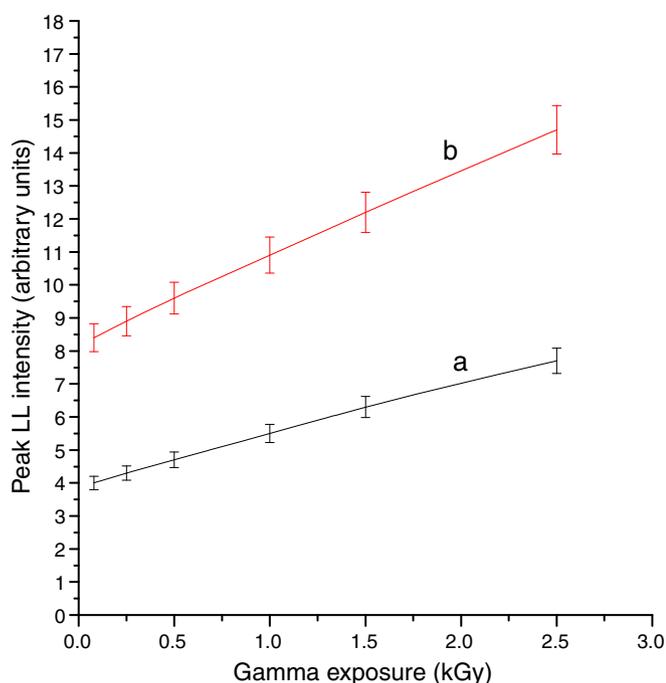
Figure 4. Variation of peak LL intensity with different gamma exposures of (a) (KNa)Br(pure) and (b) (KNa)Br : Ce (0·5 mol%).

Figure 5. Comparison of variation of peak LL intensity with different gamma exposure of (a) KBr : Ce(0·5 mol%), (b) NaBr : Ce(0·5 mol%) and (c) (KNa)Br : Ce(0·5 mol%).

electrons return immediately from the conduction band to the valence band. However, some of the electrons in the conduction band get trapped in the negative ion vacancies during their movement and consequently, the formation of colour centres takes place. Initially the number of colour centres increases with the radiation doses given to the crystals and thereby, LL intensity increases. However, if the crystals are irradiated for a long duration, the recombination between electrons and holes takes place and consequently, the density of colour centres in the crystals attains a saturation value. In fact, LL intensity attains a saturation value for high radiation doses given to the crystallites (Chandra *et al* 1997).

In figure 5, a comparison of variation of LL peak intensity with different gamma exposures is shown. From our results it is seen that the peak LL intensity of KBr : Ce(0·5 mol%) sample increased sublinearly up to 1·5 kGy and then it became saturated. For the NaBr : Ce(0·5 mol%) material, LL peak intensity increased sublinearly up to 2·5 kGy. But for (KNa)Br : Ce(0·5 mol%) material, the peak intensity increased linearly up to 2·5 kGy. Though the LL intensity for (KNa)Br : Ce(0·5 mol%) sample is found to be weak in comparison to that of NaBr : Ce(0·5 mol%) sample, but it increases linearly with gamma exposure. This response curve may play an important role for ionizing radiation dosimetry.

3.4 *Fading*

Figure 6 shows effect of storage of (KNa)Br : Ce(0·5 mol%) sample in dark at room temperature on the peak LL intensity and figure 7 shows comparison of fading in LL intensities in
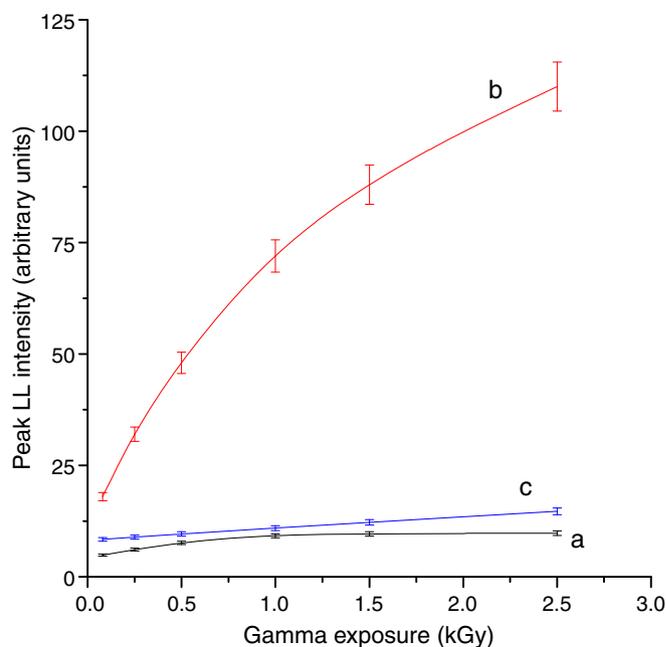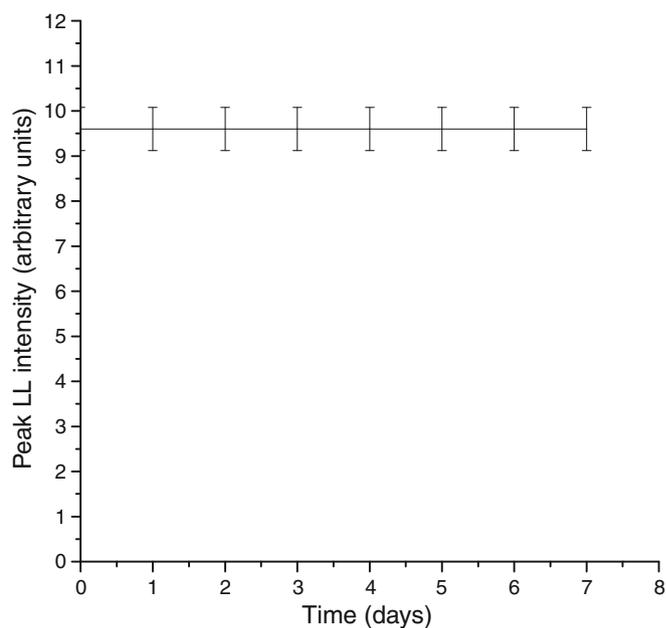

Figure 6. Effect of storage on LL glow peak in (KNa)Br : Ce(0·5 mol%), exposed to a gamma dose of 0·50 kGy.

the samples viz. KBr : Ce(0·5 mol%), NaBr(0·5 mol%) and (KNa)Br : Ce(0·5 mol%). From these graphs, it is seen that the LL peak intensity of the samples is quite stable since there is not much fading of intensities as the loss of colouration is less in dark (Hersh 1957a,b; Arnikar *et al* 1975; Moharil 1976).
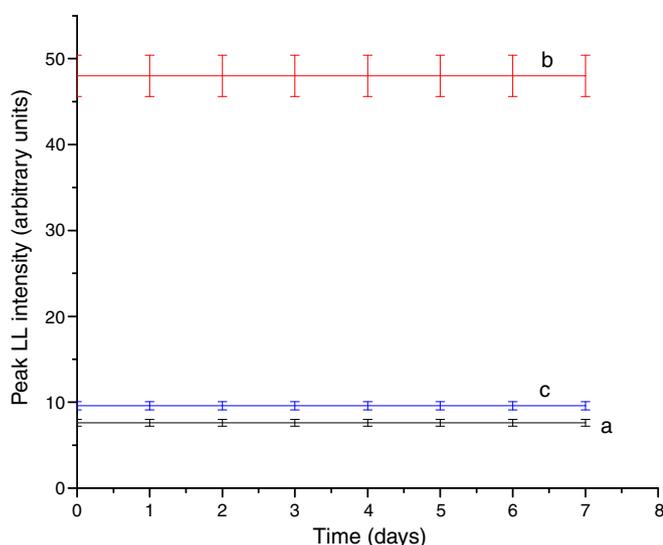
Figure 7. Comparison of effect of storage on LL glow peak in (a) KBr : Ce(0·5 mol%), (b) NaBr : Ce(0·5 mol%) and (c) (KNa)Br : Ce(0·5 mol%), exposed to a gamma dose of 0·50 kGy.

Today the measurement of high dose radiation is a challenging task and it is required for accidental dosimetry. The prepared (KNa)Br : Ce(0·5 mol%) phosphor shows dose measurements possible up to 2·5 kGy gamma exposure using lyoluminescence technique and therefore, the prepared (KNa)Br : Ce(0·5 mol%) phosphor may be useful for accidental dosimetry.

4. Conclusions

Lyoluminescence in (KNa)Br : Ce, KBr : Ce and NaBr : Ce materials are reported. LL in these materials shows single isolated LL peak due to the formation of only one type of luminescence centre. LL peak intensity is dependent on concentration of Ce^{3+} doping in the host material in all the samples. LL peak intensity increases linearly with γ-ray exposure up to 2·5 kGy high dose for (KNa)Br : Ce(0·5 mol%) material. For KBr : Ce(0·5 mol%) and NaBr : Ce(0·5 mol%) samples the peak intensity increases sublinearly up to 1·5 kGy and 2·5 kGy, respectively.

Fading in the prepared samples is also minimal. These characteristics show that the prepared (KNa)Br : Ce(0·5 mol%) phosphor may be applicable for LL dosimetry for high dose measurement, i. e. for the case of accidental ionizing radiation dosimetry.

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