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Preparation and Thermoluminescence Glow Curves of Novel Phosphors

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Abstract

The mixed and impurity added doped crystals of alkali halides are found to be harder than the end members and so they are more useful. In view of this, it becomes necessary and useful to prepare binary and ternary- mixed crystals regardless of miscibility problem and characterize them by measuring their physical properties. In the present work we have grown $(KCl)_{0.333}$ $(KBr)_{0.333}(NaI)_{0.333}$ ternary alkali halide crystals with and without $La(NO_3)_3$ dopant by the melt method and physically characterized. Crystals were γ- irradiated. For the irradiated crystals, Thermoluminescence studies have been made. Thermoluminescence glow curves were analysed as function of irradiation strength. A thermoluminescen enhancement, relative to the pure end components is found and mixed crystal presents a significant increase in thermoluminescence efficiency.

Keywords: Colour centers, Mixed alkali halide crystals, Microhardness, Thermoluminescence, γ- irradiation

1. 0 INTRODUCTION

The alkali halide crystals have always been at the center state of solid state physics. They have been "model crystals for testing many solid state theories. In recent decades, they have also proved useful in several applications ranging from X-ray monochromators to tunable lasers [1].

The use of pure simple alkali halides is limited by the mechanical systems and hence there exist the need to strengthen them. The mixed and doped crystals of alkali halides are found to be harder than the end members and so they become more useful in these applications. Also it is a known fact that alloys are more useful than the pure simple metals in device fabrications. In addition, mixed alkali halides find their applications in optical, opto-electronic and electronic devices. For these reasons, it becomes necessary and useful to prepare binary and mixed crystals regardless of miscibility problem and characterize them by measuring their physical properties.

Alkali halide mixed crystals are of the completely disordered substitutional type. Haribabu and Subbarao [2] have reviewed the aspects of the growth and characterization of alkali halide mixed crystals. Sirdeshmukh and Srinivas have reviewed the physical properties. Several more reports are available on binary-mixed crystals of alkali halides [3,4,5]. Some reports are also available on ternary and quaternary mixed crystals of alkali halides [6,7,8,9].

In the present investigation, Studies on $(KCl)_{0.333}(KBr)_{0.333}(NaI)_{0.333}$ with Lanthanum Nitrate dopant have been considered. On the prepared mixed crystals, refractive index measurements, determination of lattice parameters, Microhardness studies, Dielectric measurement, Thermoluminescence and optical Absorption studies have been done. Results of Microhardness and Thermoluminescence are reported in this paper.

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1.1 EXPERIMENTAL

$(KCl)_{0.333}(KBr)_{0.333}(NaI)_{0.333}$ mixed crystals with $La(NO_3)_3$ dopant were prepared by melt method (slow cooling) using AR grade chemicals of KCl, KBr, NaI and $La(NO_3)_3$. The elemental analysis of the grown crystals was carried out by an energy dispersive X-ray (EDAX) spectroscopy. It is observed that the composition of the mixed crystal is not very different from the actual composition determined on the basis of the initial weights of the salts. The crystals of small sizes were cleaved from the large grown blocks and were annealed at 500 ^{0}C for about 3 hours and cooled to room temperature very slowly. Annealed samples were exposed to γ- irradiation to strength of 50, 100, 150 and 200 KGrey using a ^{60}Co Gamma source having beam energy 1.17 Mev and 1.27 Mev. γ-Irradiated mixed crystals were subjected to the TL studies.

1.2 RESULTS AND DISCUSSIONS

1.2.1 MICROHARDNESS STUDIES

Microhardness measurements were carried out on unirradiated samples using Zwick 3212 hardness tester fitted with a Vicker's diamond pyramidal indenter. All the indentation measurements were carried out on the freshly cleaved samples. The indentation was made at a load of 10, 25, 50 and 100P and the time of indentation was kept at 10 sec. The indentated impressions were approximately square. Diagonal lengths of the indented impression were measured using calibrated micrometer attached to the eyepiece of the microscope. Several indentations were made on each sample. The average value of the diagonal lengths of the indentation mark was used to calculate the hardness.

The Microhardness is calculated using the expression [10]

$$H=1.8544P/d^2 \ \ Kg\ mm^{-2}$$

where P is the applied load in Kg and d the average diagonal length of the Vickers impression in mm after unloading.

Figure 1. shows the variation of microhardness with load for undoped and La^{3+} doped $(KCl)_{0.333}(KBr)_{0.333}(NaI)_{0.333}$ mixed crystals. It is observed that the formation of a mixed crystal is accompanied by an increase in hardness compared to the end members and microhardness varies non-linearly with load. The increased microhardness in the mixed crystals is due to the presence of imperfections. These imperfections can be vacancies, impurity – vacancy pairs, dislocations, low – angle grain boundaries etc. The studies made by others on ionic conductivity of mixed crystals [11] shows that conductivity is high for mixed crystals as compared to the end crystals. Since ionic

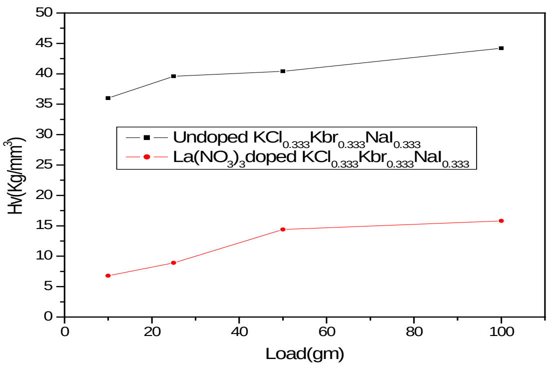

Fig. 1: Variation of Microhardness with Load in undoped and $La(NO_3)_3$ doped $(KCl)_{0.333}(KBr)_{0.333}(NaI)_{0.333}$ mixed crystals

conductivity is solely due to the presence of charged vacancies, these results therefore indicate that mixed crystals contain excess of vacancies. The results on dislocation morphology [12] shows that the low – angle grain boundaries and dislocations are more in mixed crystals compared to pure crystals. Also Tiller's eutectic crystallization mechanism may be responsible for the origin of low – angle grain boundaries in mixed crystals [13]. Thus vacancies, dislocations and grain boundaries appear to be the dominant imperfections in mixed crystals and these may be responsible for the observed increased microhardness in them.

It is well known that lattice strains are developed in mixed crystals due to the difference in the size of the atoms or ions. The size of different ions is shown in the table below.

PAULING IONIC RADII IN Å

Ion	Ionic size Å
Cl^-	1.81
Br^-	1.95
I^-	2.16
K^+	1.33
Na^+	0.95

Therefore internal strain arising out of the difference in ionic sizes may be responsible for the formation of various types of imperfections such as vacancies, dislocations, low angle grain boundaries and other defects, which in turn were responsible for the increased microhardness in the mixed crystals compared to the end members. The results also suggest that the microhardness in mixed crystals depends upon the difference in the size of the ions and not on the nature of the ions substituted.

Microhardness of La^{3+} doped crystals is less than the undoped one. It implies that the trivalent impurity ions (La^{3+}ions) are not favoring the hardness.

1.2.2 THERMOLUMINESCECE STUDIES

γ-Irradiated La^{3+} doped mixed crystals were subjected to the TL studies. In this study a previously excited sample is heated at a uniform rate from low temperature to high temperature and the luminescent intensity emitted by the sample is recorded using PC based TL reader. TL glow curves were recorded at constant heating rate of 2°C/s & 5°C/s.

Figures 2 and 3 shows the TL glow curves of annealed and as prepared Lanthanum Nitrate doped KCl $_{0.333}$ KBr $_{0.333}$ NaI $_{0.333}$ mixed samples irradiated to strength of 50, 100, 150 and 200 KGrey for the heating rate of 2°C/s & 5°C/s. In the irradiated samples glow curve structure appears in the 400-460 K temperature interval. The glow peak shifts towards high energy side with the increase in the heating rate. The thermoluinescence behavior of mixed crystals subjected to γ-irradiation has been associated with trapped electrons in the form of F and Fz centers [14]. The significant enhancement effect observed in doped mixed crystals, could be understood in terms of the vacancy concentration variation with composition. In fact, the effect of mixing pure alkali halides on the Schottky defect concentration has been investigated in some mixed systems [15]. Invariably these results have established an enhancement of self- and heterodiffusion coefficients in the crystalline solid solutions, and the enhancement has been attributed to an increase of the vacancy concentration of the mixed alkali halides relative to the pure end component. It is well known that thermoluminescence is produced while trapped carriers are thermally released and recombined with carriers of the opposite sign; the intensity of the TL glow peaks is proportional to the number of trapped carriers. Therefore, an increase of trapped carriers and in the TL efficiency should be expected for the mixed crystals. The prepared $(KCl)_{0.333}(KBr)_{0.333}(NaI)_{0.333}:La^{3+}$ materials have negligible fading on storage in TL intensity. These characteristics show that the prepared $(KCl)_{0.333}(KBr)_{0.333}(NaI)_{0.333}:La^{3+}$ phosphors may be suitable for application in TL dosimetry for high dose measurement.

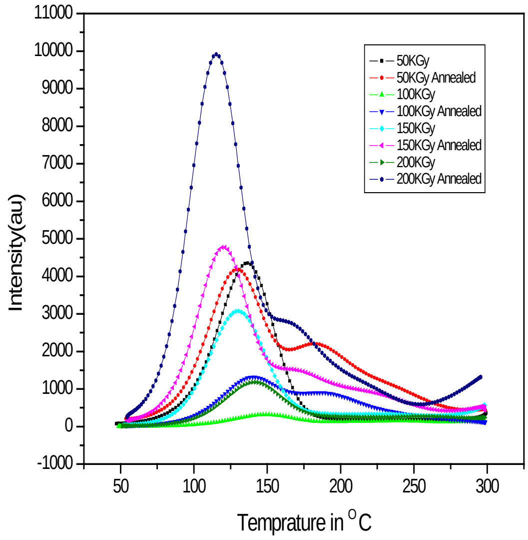

Fig. 2: Thermoluminescence glow curves of $(KCl)_{0.333}(KBr)_{0.333}(NaI)_{0.333}:La^{3+}$ Crystals in the annealed and as prepared samples irradiated to different dosages for the heating rate of 2°C/s

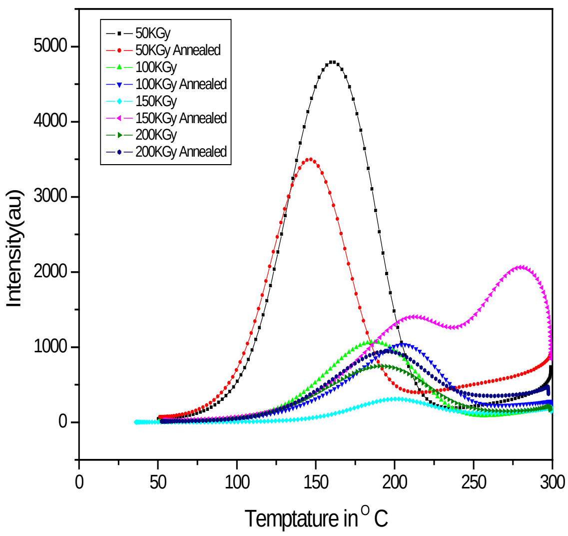

Fig. 3: Thermoluminescence glow curves of $(KCl)_{0.333}(KBr)_{0.333}(NaI)_{0.333}:La^{3+}$ Crystals in the annealed and as prepared samples irradiated to different dosages for the heating rate of 5°C/s

Table 1: Trap Depth and Glow peak Temperature of $KCl_{0.333} KBr_{0.333} NaI_{0.333}$ crystals doped with Lanthanum Nitrate for the heating rate of 2°C/S

Irradiation Dose	Concentration	Tg(K)	Intensity (AU)	Activation Energy(ev)
50KGY	$KCl_{0.333} KBr_{0.333} NaI_{0.333}$	409.75	4348.45	1.08607
	$KCl_{0.333} KBr_{0.333} NaI_{0.333}$ annealed	401.86	4182.23	1.06487
100KGy	$KCl_{0.333} KBr_{0.333} NaI_{0.333}$	422.14 512.78	318.53 152.41	1.12020 1.36934
	$KCl_{0.333} KBr_{0.333} NaI_{0.333}$ annealed	412.99	1315.85	1.09530
150KGY	$KCl_{0.333} KBr_{0.333} NaI_{0.333}$	403.45 499.69	3073.06 332.61	1.069108 1.333362
	$KCl_{0.333} KBr_{0.333} NaI_{0.333}$ annealed	392.28	4768.83	1.038632
200KGy	$KCl_{0.333} KBr_{0.333} NaI_{0.333}$	414.77 529.86	1176.45 269.28	1.100129 1.416590
	$KCl_{0.333} KBr_{0.333} NaI_{0.333}$ annealed	388.25	9917.05	1.027748

Table 2: Trap Depth and Glow peak Temperature of $KCl_{0.333} KBr_{0.333} NaI_{0.333}$ crystals doped with Lanthanum Nitrate for the heating rate of 5°C/S

Irradiation Dose	Concentration	Tg(K)	Intensity (AU)	Activation Energy(ev)
50KGy	$KCl_{0.333} KBr_{0.333} NaI_{0.333}$	434.83	4790.81	1.12054
	$KCl_{0.333} KBr_{0.333} NaI_{0.333}$ annealed	419.91	3494.93	1.08080
100KGy	$KCl_{0.333} KBr_{0.333} NaI_{0.333}$	460.46	1067.74	1.18882
	$KCl_{0.333} KBr_{0.333} NaI_{0.333}$ annealed	477.26	1031.72	1.23357
150KGy	$KCl_{0.333} KBr_{0.333} NaI_{0.333}$	473.20	308.99	1.22274
	$KCl_{0.333} KBr_{0.333} NaI_{0.333}$ annealed	486.82 554.3	1400.61 2058.12	1.25919 1.43994
200KGy	$KCl_{0.333} KBr_{0.333} NaI_{0.333}$	465.34	745.66	1.20188
	$KCl_{0.333} KBr_{0.333} NaI_{0.333}$ annealed	469	942.43	1.21185

The glow curves obtained for all the combinations of mixed crystals were analyzed by numerical curve fitting [16,17] and the trap depth (activation energy) has been calculated. Computed values of the activation energies are given in tables 1 and 2.

2. CONCLUSION

Good optically transparent $(KCl)_{0.333}(KBr)_{0.333}(NaI)_{0.333}$ mixed crystals with $La(NO_3)_3$ dopant were grown from the melt. Elemental analysis has been confirmed by EDAX. Microhardness is more in mixed crystals than in the pure components. The increased hardness in mixed crystals has been attributed to the internal strains arising out of the difference in ionic sizes, which is responsible for the formation of dislocations, low-angle grain boundaries and other defects. Trivalent La^{3+} impurity ions are not favoring the hardness. The glow peaks observed mixed crystal are mainly due to the destruction of the F- centers

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