Thermoluminescence, optical absorption and ESR studies in $(\text{KCl})_{1-x}(\text{KBr})_x$ mixed alkali halide crystals doped with gold

R. Ananda Kumari^{a,*}, R. Chandramani^b

^a*Sree Siddaganga Women's College, Tumkur, Karnataka, India*

^b*Bangalore University, Bangalore, Karnataka, India*

Received 13 August 2007; received in revised form 4 November 2007; accepted 29 November 2007

Abstract

Mixed crystals of KCl–KBr of different compositions were grown with Czochralski technique. Crystals were doped with gold. Both the undoped and gold doped crystals were γ -irradiated using ^{60}Co source. All the irradiated samples were subjected to thermoluminescence, optical absorption and ESR studies. The present study shows the composition dependence of the parameters and enhancement in the luminescence intensity as well as the absorption coefficient with gold doping. Non-linear variation of color center peak position and half band width of F-center with composition has been observed. The results of the above studies are presented in this paper.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Color centers; Mixed alkali halide crystals; Thermoluminescence; Optical absorption; Electron spin resonance

1. Introduction

Mixed crystals have aroused considerable interest, curiosity and have motivated extensive investigations because of wide applications. Sixteen pairs of mixed alkali halides are completely miscible at room temperature and several have limited miscibility. The solid solutions of alkali halides indeed constitute a very interesting study. There are several reasons for this choice. The location of the maxima of various color center electronic bands for the mixed crystals depends on the composition. Hence composition can be varied to suit any available laser wavelength in the appropriate region. In recent years, attempts have been made to use these crystals for optical information storage processes (Prasad, 1981). Some of the mixed crystals find application as Laser window materials (Sahagian and Pitha, 1971; Shrivastava, 1980) and as neutron monochromators (Freund et al., 1972).

In view of this, in the present study alkali halide mixed crystals $(\text{KCl})_{1-x}(\text{KBr})_x$ of a different composition was grown by

Czochralski technique and various studies like thermoluminescence, optical absorption and electron spin resonance has been carried out on the grown mixed crystals.

2. Experimental

Mixed crystals of $(\text{KCl})_{1-x}(\text{KBr})_x$ were grown by Czochralski technique using AR grade chemicals as starting materials. The weighed salts were first grounded separately to form fine powder and then mixed, so that the two salts would melt together uniformly. Large completely transparent crystals without any cracks and free from strain were grown. Using the gold solution all the combinations of mixed crystals were doped with Au^+ by diffusion method (Tuck, 1974; Fair, 1981). The elemental analyses of the grown crystals were carried out by an energy dispersive X-ray (EDAX) spectroscopy. It is observed that the compositions of the mixed crystals were not very different from the actual compositions determined on the basis of the initial weights of the salts. The crystals obtained were checked using the XRD pattern. The lattice parameters of the crystals were determined by powder diffraction method.

Grown crystals were cleaved and were subjected to γ -irradiation to a strength of 2.5, 5 and 10 Mrads using ^{60}Co Gamma

* Corresponding author.

E-mail address: ranandakumari61@yahoo.com (R. Ananda Kumari).

source having beam energy 1.17 and 1.27 MeV to a dosage of 2.5, 3, 5, 7.5, 10, 12.5 and 20 Mrads. Irradiated samples were preserved in black paper before subjecting them to optical absorption, ESR and Thermoluminescence studies.

3. Results and discussion

3.1. Thermoluminescence studies

γ -irradiated undoped/ Au-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 home made experimental set up where the radiation was converted to electric current by a 931A photo multiplier tube.

In KCl–KBr mixed crystals grown by Czochralski technique three glow peaks (around 350, 410 and 450 K) were observed for the higher concentration of KBr and with decrease in concentration of KBr, peak around 410 K diminishes. The 450 K glow peak shifts towards the higher temperature with the increase in concentration of KCl i.e. towards the characteristic glow peak of KCl. Appreciable shift in the peak position with change in composition is depicted in Figs. 1 and 2. All the observed glow peaks are mainly due to the destruction of F centers. The trap depth increases with decrease in the concentration of KBr. Non-linear variation of trap depth with composition is observed.

Similar pattern of the glow peaks were observed in both the undoped and Au doped mixed crystals in all the combinations for all the irradiation doses whereas the thermoluminescent intensity is more in gold-doped mixed crystals (Numan and Sahare, 2006).

Fig. 1. Thermoluminescence glow curves of undoped $(\text{KCl})_{1-x}(\text{KBr})_x$ mixed crystals irradiated with a dose of 10 Mrads.

Fig. 2. Thermoluminescence glow curves of Au^+ doped $(\text{KCl})_{1-x}(\text{KBr})_x$ mixed crystals irradiated with a dose of 10 Mrads.

Table 1

Estimated values of trap depth of undoped $(\text{KCl})_{1-x}(\text{KBr})_x$ mixed crystals irradiated with a dose of 10 Mrads

Concentration (x)	Glow peak	T _g (K)	Trap depth (eV)
$(\text{KCl})_{1-x}(\text{KBr})_x$ $x = 0.1$	Weak	368	1.022
	Weak	401	1.117
	Strong	451	1.261
$x = 0.3$	Weak	345	0.959
	Strong	457	1.281
$x = 0.5$	Weak	444	1.239
	Strong	463	1.294
$x = 0.7$	Strong	438	1.238
$x = 0.9$	Weak	363	1.015
	Strong	443	1.246

The glow curves obtained for all the combinations of KCl–KBr mixed crystals which originated from the recombination of thermally released charge carriers from the trap at luminescent centers were analyzed by numerical curve fitting (Halperin, 1960; Halperin and Braner, 1961) and the trap depth (activation energy) has been calculated. Computed values of the activation energies are given in Tables 1 and 2 and the glow curves are shown in Figs. 1 and 2.

3.2. Optical absorption

Optical absorption spectra of the irradiated crystals were recorded using the Hitachi U-3200 spectrophotometer in the range 200–800 nm at room temperature. The sample holder in the spectrophotometer, originally designed for liquids, was modified to accommodate thin plates of crystals. The accuracy in the measurement of the absorption coefficient was 0.001.

Table 2
Estimated values of trap depth of Au^+ doped $(\text{KCl})_{1-x}(\text{KBr})_x$ mixed crystals irradiated with a dose of 10 Mrads

Concentration (x)	Glow peak	T _g (K)	Trap depth (eV)
Au^+ doped $(\text{KCl})_{1-x}(\text{KBr})_x$	Weak	346	0.961
	Strong	447	1.252
$x = 0.1$			
$x = 0.3$	Weak	411	1.167
	Strong	443	1.261
$x = 0.5$	Strong	467	1.316
$x = 0.7$	Strong	467	1.243
$x = 0.9$	Weak	362	1.004
	Strong	488	1.366

Fig. 3. Variation of F-band peak position with composition in $(\text{KCl})_{1-x}(\text{KBr})_x$ mixed crystals. Solid circles represent the experimental values while the line is drawn through the calculated values.

Using Abbe's refractometer, n , the refractive index has been determined accurately for all the combinations.

Mixed crystals were subjected to optical absorption before irradiation. No absorption was observed before irradiation which is in agreement with the fact that alkali halides being transparent from far UV through IR region.

The absorption spectra of the KCl–KBr mixed crystals irradiated to different dosages showed one absorption band corresponding to F centers in the range 560 and 620 nm. The absorption coefficient however was found to increase with duration of irradiation. Fig. 3 shows the variation of F band peak position against composition. Replacing anions produces shift in F-band peak position and it shifts towards the lower energy that is towards longer wavelength as the concentration of KBr in KCl increases. The half bandwidth has varied non-linearly with the composition and has attained the maximum value for the composition 90 mol% of KCl in KBr.

In the Au-doped mixed crystals of all combinations, similar absorption band pattern is observed as in the undoped one. But the absorption coefficient of doped one was observed to be more than in undoped one.

Fig. 4. Optical absorption spectra of undoped $(\text{KCl})_{1-x}(\text{KBr})_x$ mixed crystals irradiated with a dosage 10 Mrads. (1) $x = 0.1$, (2) $x = 0.3$, (3) $x = 0.5$, (4) $x = 0.7$, (5) $x = 0.9$.

Fig. 5. Optical absorption spectra of Au^+ doped $(\text{KCl})_{1-x}(\text{KBr})_x$ mixed crystals irradiated with a dosage 10 Mrads. (1) $x = 0.1$, (2) $x = 0.3$, (3) $x = 0.5$, (4) $x = 0.7$, (5) $x = 0.9$.

F-band width and half bandwidth are observed to be greater in mixed crystals than in the pure components. The broadening of the F-band may be due to the superposition of seven elementary bands corresponding to seven different combinations of the two cations which surround the F-center octahedrally (Ananda Kumari and Chandramani, 2003). Also it is due to the additional effect of Schottky defects (Melik-Gaikazyan and Zavodskaya, 1960). The increased half width of the F-band in the mixed crystals may be due to the result of superposition of the absorption due to the centers having different number of anions bordering the F-center.

The observed absorption spectra of the irradiated mixed crystals are shown in Figs. 4 and 5. The computed F-center density

Table 3
Half band width and color center density of $(\text{KCl})_{1-x}(\text{KBr})_x$ mixed crystals irradiated with a dosage 10 Mrads

Sample	Refractive index	Peak position (nm)	Absorption coefficient	Half band width (eV)	Density of defects (10^{17} cm^{-3})
Undoped $(\text{KCl})_{1-x}(\text{KBr})_x$					
$x = 0.1$	1.479	563	1.746	12.44	2.6797
$x = 0.3$	1.493	582	1.4146	4.638	0.8115
$x = 0.5$	1.507	599	1.8100	2.115	0.4760
$x = 0.7$	1.519	608	1.1524	6.823	0.9858
$x = 0.9$	1.529	619	2.2621	4.2698	1.2213
Au^+ doped $(\text{KCl})_{1-x}(\text{KBr})_x$					
$x = 0.1$	1.479	566	1.7985	4.723	0.860
$x = 0.3$	1.491	582	1.4652	3.675	0.254
$x = 0.5$	1.504	599	1.7932	6.823	0.679
$x = 0.7$	1.518	608	2.1234	4.265	0.537
$x = 0.9$	1.529	621	3.2100	7.4041	3.0431

Table 4
Estimated 'g' value from the ESR Spectra

Sample	Composition	'g' value
$(\text{KCl})_{1-x}(\text{KBr})_x$	$x = 0.9$	2.218
	$x = 0.7$	2.079
	$x = 0.5$	2.084
	$x = 0.3$	2.153
	$x = 0.1$	2.138
Au^+ doped $(\text{KCl})_{1-x}(\text{KBr})_x$	$x = 0.9$	2.133
	$x = 0.7$	2.081
	$x = 0.5$	2.101
	$x = 0.1$	2.054

Fig. 6. ESR spectra of undoped $\text{KCl}_{0.1}\text{KBr}_{0.9}$ mixed crystal irradiated with a dosage 10 Mrads.

calculated using Smakula's equation (Smakula et al., 1963) is around 10^{17} centers/ cm^3 and is tabulated in Table 3.

3.3. ESR Study

The ESR spectra were recorded using the Bruker X-band ESR (ER200D) spectrometer. All the irradiated samples were

Fig. 7. ESR spectra of undoped $\text{KCl}_{0.7}\text{KBr}_{0.3}$ mixed crystal irradiated with a dosage 10 Mrads.

subjected to ESR study. Samples possessing paramagnetic property have given rise to good ESR derivative. ESR chart has shown two or three derivatives in some combinations of undoped crystals corresponding to different types of centers indicating the paramagnetic property. These may be due to hole center or electron center. Au-doped samples have answered for a Single derivative depicting the Au^+ ions effect in the sample. From the resonance signal, 'g' values have been calculated which gives information regarding the chemical environment. The results are tabulated in Table 4. The ESR spectra are shown in Figs. 6 and 7.

4. Conclusions

- Good optically transparent mixed alkali halide crystals $(\text{KCl})_{1-x}(\text{KBr})_x$ of different compositions were grown by Czochralski technique. All grown mixed crystals were gold-doped. Compositions of the mixed crystals have been confirmed by EDAX.
- The glow peaks observed in all the combinations of mixed crystals are mainly due to the (i) destruction of the F- centers

(ii) Z_1 centers or impurity centers or complexes in dislocation regions.

- The non-linear variation of trap depth and glow peak temperature with composition is thought of as due to high disorder present in the mixed crystals.
- Shift in the glow peak position and more deformation has resulted due to higher dosages of irradiation. Results of more deformation, further affects the glow peak position. Due to this cumulative effect there is an appreciable shift in the TL glow peak position that has been revealed in figures. Thermoluminescence intensity is more in the gold-doped mixed crystals.
- F-band peak position of the F-center varies linearly with the composition. Broadening of F-band is observed in the KCl–KBr mixed crystals compared to end components. Lower coloration is observed in mixed crystals as compared to their end components.
- Samples possessing paramagnetic property have given rise to good ESR derivative.

Acknowledgement

We thank Professor S.V. Bhat, Department of Physics, Indian Institute of Science, Bangalore for providing the facilities to get ESR Spectra of Crystals.

References

- Ananda Kumari, R., Chandramani, R., 2003. Indian J. Phys. 77A (3), 219–224.
- Fair, R.B., 1981. Concentration profiles of diffused dopants in Silicon. In: Wang, F.F.V. (Ed.), Impurity Doping Processes in Silicon. North-Holland, New York.
- Freund, A., Guinet, P., Mareschal, J., Rustichelli, F., Vanoni, F., 1972. J. Cryst. Growth 13/14, 726.
- Halperin, A., 1960. Phys. Rev. 177, 408.
- Halperin, A., Braner, A.A., 1961. Proc. Int. Conf. Phys. Semiconductors, 724.
- Melik-Gaikazyan, I.Ya., Zavodskaya, E.K., 1960. Opt. Spectr. (USSR) 9, 268.
- Numan, S., Sahare, P.D., 2006. J. Phys. D: Appl. Phys. 39, 2684–2691.
- Prasad, K.L.N., 1981. Thesis, I.I.T, Madras.
- Sahagian, C.S., Pitha, C.A., 1971. Tech. Rep AFCRL 71, 592.
- Shrivastava, U.C., 1980. J. Appl. Phys. 51, 1510.
- Smakula, A., Maynard, N.C., Rapucci, A., 1963. Phys. Rev. 130, 113.
- Tuck, B., 1974. Introduction to Diffusion in Semiconductors. IEE Monoser, London.