Glow curves and the emission of flux-grown BaFCl : Na crystals

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The thermoluminescence glow curves and the emission spectra of flux-grown BaFCl : Na crystals were recorded. An additional TL peak at 320 K, an optical absorption band at 570 nm and an emission peak at 490 nm have been seen in X/γ-irradiated crystals. Bleaching, room-temperature annealing and high-temperature emission results led us to conclude that the sodium impurity is responsible for the additional glow peak, optical absorption band and emission peak.

1. Introduction

Although the flux technique has been recognized as an established technique for the growth of mixed dihalides [1–3], the unreacted mass may be present as a major impurity in the crystals thus grown. Bhat and Narayanan [2] have grown SrFCl crystals by the reacted flux technique using $SrCl_2$ and NaF as starting materials and found that sodium is the highest impurity present in the crystals. Corsmit and Dirksen [4] synthesized PbFCl crystals by the slow cooling of a molten equimolar mixture of PbF_2 and $PbCl_2$. It is observed that this type of growth leads, in general, to the compositions $PbF_{1-x}Cl_{1+x}$ or $PbF_{1+x}Cl_{1-x}$, affecting the molecularity of the crystals which, in turn, affects the concentrations of the ionic point defects and hence ionic conductivity, etc. In our earlier paper [5] we reported that the perfection of the BaFCl crystals, which were grown by the flux technique using $BaCl_2$ and NaF, was improved by adding 10 mol% excess NaF. It was supported by dislocation etch pit density, rocking curves and luminescence output. We described these crystals as sodium-doped BaFCl crystals [6], because the sodium content is extremely high in the crystals.

Thermoluminescence (TL) dosimetry is an economical method widely used in personal monitoring and radiation therapy. Many phosphors are known at present, but there is a trend to use special luminophors for application in different fields of dosimetry. In the course of testing several materials such as $CaSO_4$, $MgSiO_4$, LiF, CaF_2 for their TL characteristics, BaFCl crystals also showed interesting features [7, 8].

In view of structure sensitivity of the TL phenomena, the impurity may either enhance TL yield or inhibit it, depending on the concentration and also on the temperature at which the crystals were exposed to ionizing radiation. In order to know more about the radiation-induced defects and recombination centres that are responsible for TL, information about spectral distribution of TL emission is necessary. Thus we report here the results of some experiments on the TL glow and TL emission of irradiated BaFCl : Na crystals in the temperature range 300 to ~ 500 K. A mechanism for the radiative recombination processes is suggested.

2. Experimental procedure

The sodium-doped BaFCl crystals were grown by the flux method using $BaCl_2$ and NaF (BDH AR) as starting materials. The details of the growth process were published elsewhere [3]. X-rays from an iron target operated at 30 kV and 15 mA and γ-rays from a ^{60}Co source were used for irradiation The TL output was recorded using conventional apparatus described elsewhere [5]; the photomultiplier tube was EMI6256S. The irradiated crystals were heated at a constant rate of 25 K min^{-1}. The optical absorption spectra were

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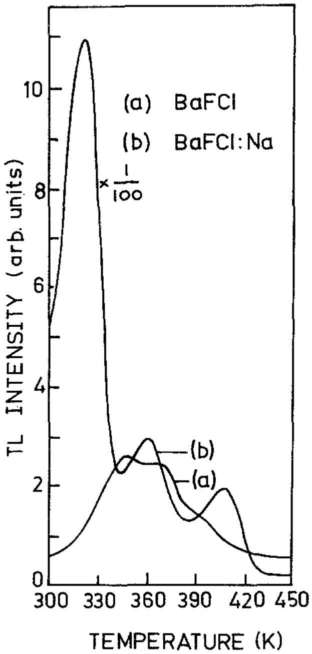

Figure 1 Glow curves of (a) BaFCl, (b) BaFCl: Na.

recorded on a Cary 14R spectrophotometer at room temperature and the emission spectra with a 0.25 m Jarell-Ash monochromator.

3. Results

3.1. Thermoluminescence

Fig. 1 shows the glow curve pattern of pure BaFCl and non-stoichiometric BaFCl in which 10 mol% excess NaF is present, the irradiation time being 10 min. In curve (a), which is recorded for pure BaFCl, two peaks at 345 and 365 K and a shoulder at about 390 K can be seen. Curve (b) is obtained for BaFCl: Na crystal. Here three prominent peaks at 320, 355 and 400 K can be seen. The low-temperature peak at 320 K is found to be more intense than the other two peaks. The figure also indicates that the luminescence output in a crystal having excess sodium is nearly ten times lower than that of undoped BaFCl.

The glow curves obtained by exposing the crystal to X-rays for different times are shown in Fig. 2. In general, three peaks in the temperature ranges 310 to ~ 320 K, 350 to ~ 355 K and 390 to ~ 400 K have been observed. The intensity of these peaks is found to increase with irradiation time up to 15 min, and decreased after that The first low-temperature peak at 315 K is found to bleach rapidly after irradiation at room tempera-

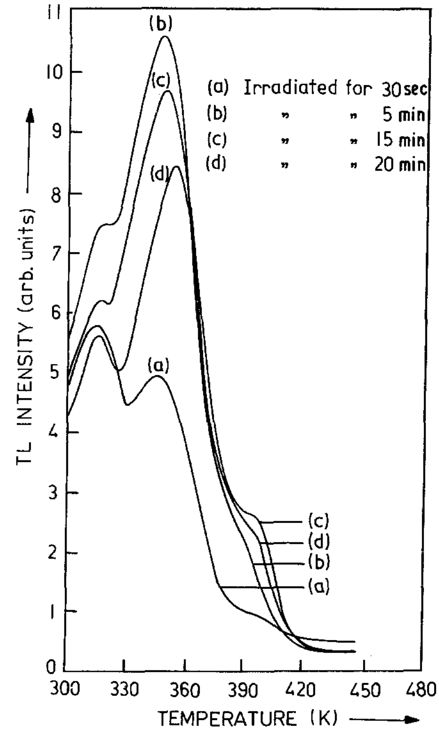

Figure 2 Effect of irradiation time on glow curve of BaFCl: Na.

ture. Hence the glow curves were recorded immediately after irradiation.

The optical absorption spectra of γ-irradiated BaFCl: Na showed two prominent bands at 440

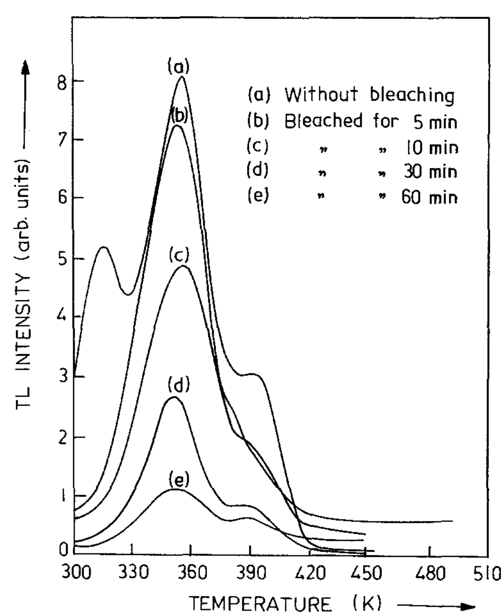

Figure 3 Effect of bleaching with 455 nm unpolarized light on glow curve of BaFCl: Na.

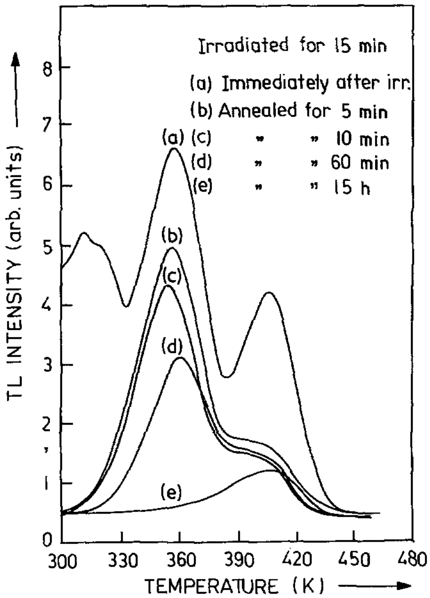

Figure 4 Effect of room temperature annealing on glow curve of BaFCl:Na.

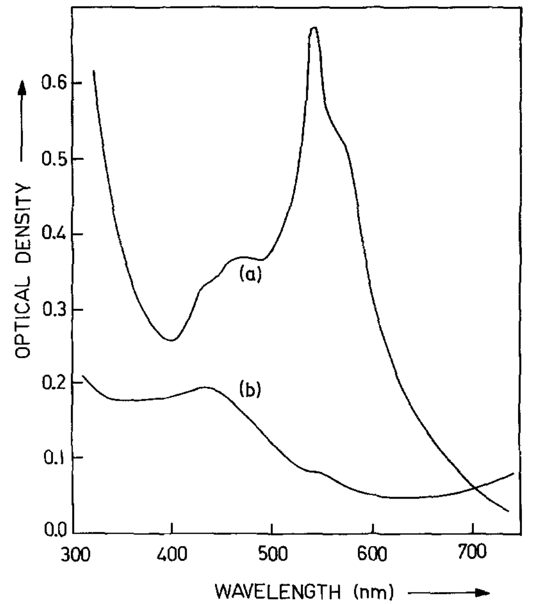

Figure 5 Optical absorption spectra of γ-irradiated BaFCl:Na crystal; (a) immediately after irradiation, (b) annealed at room temperature for 90 days.

to ~460 nm and 540 nm. Hence a systematic study of the bleaching effect on glow curves was made with these two energies. The glow curves obtained in bleached and unbleached crystals are shown in Fig. 3. Curve (a) is recorded on an unbleached crystal while others are obtained after bleaching with 455 nm unpolarized light. On bleaching for 5, 10, 30 and 60 min the peaks at 355 and 400 K bleach gradually, whereas the low-temperature peak at 315 K disappeared by bleaching for only 5 min. The peak at 400 K also shifted towards low temperature. Bleaching studies with 540 nm unpolarized light also gave similar results.

Since BaFCl:Na crystal exhibited phosphorescence decay at room temperature after X-irradiation, thermoluminescence has been studied after different annealing times at room temperature and the curves obtained are shown in Fig. 4. Curve (a) is recorded immediately after irradiation, while curves (b), (c), and (d) are recorded after annealing for 5, 10 and 60 min. From these curves it may be observed that the low-temperature peak at 310 K has bleached away immediately, whereas the other two peaks at 355 and 400 K were suppressed slowly. On annealing for a longer time, i.e. 15 h, the peak at 355 K disappeared and only a broad peak at 400 K resulted. This is shown in curve (e).

3.2. Optical absorption

Fig. 5 shows the optical absorption spectra of BaFCl:Na after irradiating for 20 h with γ-rays. Curve (a), which was recorded immediately after irradiation, consists of two well-defined bands. The band at 440 nm has a double band structure with a separation of 20 nm whereas the other band at 545 nm is well resolved. In addition to these two, a small shoulder at 570 nm can also be seen. Curve (b), which was recorded after 90 days, shows two bands at 440 and 550 nm with less intensity. However, the band at 440 nm is relatively more prominent than that at 550 nm.

3.3. Thermoluminescence emission

Fig. 6 shows the emission spectra of a 10 min γ-irradiated BaFCl:Na at room temperature and higher. Curve (a), which is recorded at room temperature shows two well-developed bands centred at 400 nm (3.00 eV) and 490 nm (2.53 eV). The band at 490 nm completely disappears and that at 400 nm is enhanced when the emission spectra is recorded at 350 K. This is seen in curve (b). Curve (c), which is recorded at 393 K, does not show any change except an increase in intensity. Further increase in temperature results in decrease in intensity of the 400 nm band (curve d).

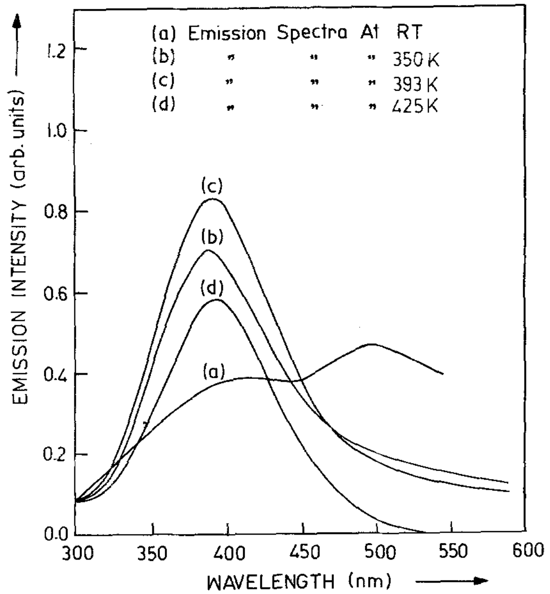

Figure 6 Emission spectra of BaFCl:Na (γ-irradiated).

4. Discussion

In our earlier work [7] we reported four glow peaks occurring at 345, 365, 385 and 415 K in undoped BaFCl crystals. From the thermoluminescence and optical absorption studies of irradiated and annealed crystals the first low-temperature peaks are attributed to the detrapping of elecrtrons from impurities and subsequent recombination with holes, whereas the other two peaks at 385 and 415 K are associated with $F(\bar{Cl})$ and $F(\bar{F})$ centres, respectively.

In the present investigation on BaFCl:Na crystals, three glow peaks at 320, 355 and 400 K were seen. Growth curves, bleaching and room-temperature annealing studies have clearly shown that the peak at 320 K is less stable compared to others. Optical obsorption studies have revealed an additional shoulder at 570 nm as the other two were also present in undoped BaFCl [7]. This also disappears on room-temperature annealing. Thermoluminescence emission spectra showed two emission bands at 400 and 490 nm. The band at 400 nm was attributed to radiative recombination centres in undoped BaFCl [8]. Hence the other band at 490 nm is an additional emission band which disappears just below 350 K.

It is known that X/γ-irradiation notably produces F-centres in BaFCl crystals. When such crystals are heated at constant rate the F-centre electrons may be excited to the conduction band and may recombine the V-centres emitting the usual TL glow. Impurities and other imperfections also give rise to traps of different trap depths in the forbidden region. On irradiation electrons may be trapped at these shallow traps. It is also generally expected that these electrons will be released and combine radiatively with holes, when the crystals are heated. At some stage in this recombination process light is emitted. Thus in the present investigation, the low-temperature glow peak at 320 K is attributed to the colour centres being formed due to the sodium impurity, in view of its close resemblance in annealing bleaching and emission studies. The high-temperature glow peak which appeared at 400 K is considered to be the 415 K peak in undoped BaFCl. This slight shift towards low temperature is attributed to the perturbation of the F-centre by the aggregated centres, which are formed due to sodium impurity and cause the 570 nm shoulder in the optical absorption spectra. These aggregated centres perhaps change the configuration coordinate of the $F(\bar{F})$ centre, resulting in a shift.

5. Conclusion

1. Basically the same type of colour centres are formed by X/γ-irradiation in BaFCl:Na as in undoped BaFCl, but only the equilibrium of the $F(\bar{F})$ centres is changed by sodium doping.
2. Compared with undoped BaFCl, the colour centre formation is less in BaFCl:Na. TL results show that sodium stabilizes the shallower traps.
3. The 490 nm emission in the TL spectra of BaFCl:Na is attributed to the presence of sodium.

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