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# Thermoluminescence spectra and X-ray luminescence spectra of $CaF_2$–Nd single crystals

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X-ray luminescence measurements are an important tool in the study of the optical properties of a fluorite system. In the case of $CaF_2$–Nd the major emission under X-ray excitation is in the infrared region, which has been studied extensively. In this paper emission in the ultraviolet and visible range under X-ray excitation is reported. Thermoluminescence (TL) and TL spectra in the same region have also been measured. The similarities in the peak emission wavelengths in the two processes show that the emission centres involved are the same.

## 1. Introduction

Luminescence measurements are very important because sometimes they show the presence of some new centres which are not detected by absorption measurements. The mechanism of X-ray luminescence in rare-earth (RE) doped $CaF_2$ is identical with the thermoluminescence (TL) mechanism of a previously irradiated $CaF_2$–RE crystal and involves recombination [1]. Since both cubic and tetragonal symmetry of $RE^{3+}$ ions is possible depending on the location of the compensating $F^-$ interstitial ions, the X-ray luminescence of $RE^{3+}$ ions may basically originate from various optical centres. However, the excitation of non-cubic centres related to ionization–recombination processes has much smaller capture and recombination cross-sections than in the cubic centres [2]. The following equations represent the X-ray luminescence excitation mechanisms of two types of $Nd^{3+}$ centres in $CaF_2$:

(a) In the case of cubic centres

$$Nd^{3+}_{ca} \xrightarrow{+e} Nd^{2+}_{ca} \xrightarrow{+h} (Nd^{3+}_{ca})^*$$

(b) In the case of tetragonal centres

$$Nd^{3+}_{ca}F^-_i \xrightarrow{+e} Nd^{2+}_{ca}F^-_i \xrightarrow{+h} (Nd^{3+}_{ca}F^-_i)^*$$

where $Nd^{3+}_{ca}$ denotes the $Nd^{3+}$ ion replacing a doubly charged $Ca^{2+}$ ion in the fluorite lattice; $F^-_i$ denotes an interstitial fluorine ion; e denotes an electron; h denotes a hole; and the asterisk denotes an excited state.

Since the capture and recombination cross-sections of the cubic centres are very high as compared to those of the tetragonal centres, mechanism (a) will be mainly operative in the X-ray luminescence of $CaF_2$–$RE^{3+}$ crystals.

Vakhidov *et al.* [3] have observed an intense visible phosphorescence spectrum similar to the gamma luminescence spectrum for $CaF_2$–$NdF_3$ samples, but they did not report any detailed results of the luminescence in the visible region. Voron'ko *et al.* [2] have studied the infrared luminescence spectra of $CaF_2$–$Nd^{3+}$ crystals and represented schematically the X-ray luminescence excitation mechanism of various $Nd^{3+}$ centres in a fluorite crystal.

In the present work, the TL spectra around the glow peak temperature (340° C) and X-ray luminescence spectra at various temperatures between liquid nitrogen temperature (LNT) and 400° C for $CaF_2$–Nd crystals have been analysed in the 200 to 900 nm range. The temperature variation of X-ray luminescence intensity and the concentration dependence have also been studied at peak emission wavelengths.

## 2. Experimental procedure

A detailed description of the set-up used here is given elsewhere [4]. For measuring the TL spectra, the $CaF_2$–Nd (0.049 wt %) crystal was irradiated by X-rays (30 kV, 10 mA) for 30 min at room temperature (RT). The coloured sample was then quickly heated to the desired temperature (around the peak temperature) and keeping this temperature constant, the TL output was scanned by a monochromator and the spectra were recorded. The monochromator was set to low-blaze (3000 lines $cm^{-1}$) for measurements in the region 200 to 400 nm and to high blaze (6000 lines $cm^{-1}$) for the 400 to 900 nm range measurements. The photomultiplier (PM) tube used was R-456. All the emission spectra were corrected for PM tube efficiency and the monochromator grating dispersion.

For the measurement of X-ray luminescence spectra the sample was kept at an angle of 45° to the direction of the X-ray beam and the emissions were simultaneously recorded after scanning. The measurements were carried out at different temperatures between LNT and 400° C.

For the measurement of the temperature variation of X-ray luminescence, the sample was kept in the same position (45° to X-ray beam) and heated to 400° C. Then the X-rays were switched on and the sample was gradually cooled to RT. The emission from the sample was filtered at a particular wavelength before entering the PM tube. The output intensity was recorded with respect to temperature. Here the samples studied were single crystals of $CaF_2$–Nd(I)

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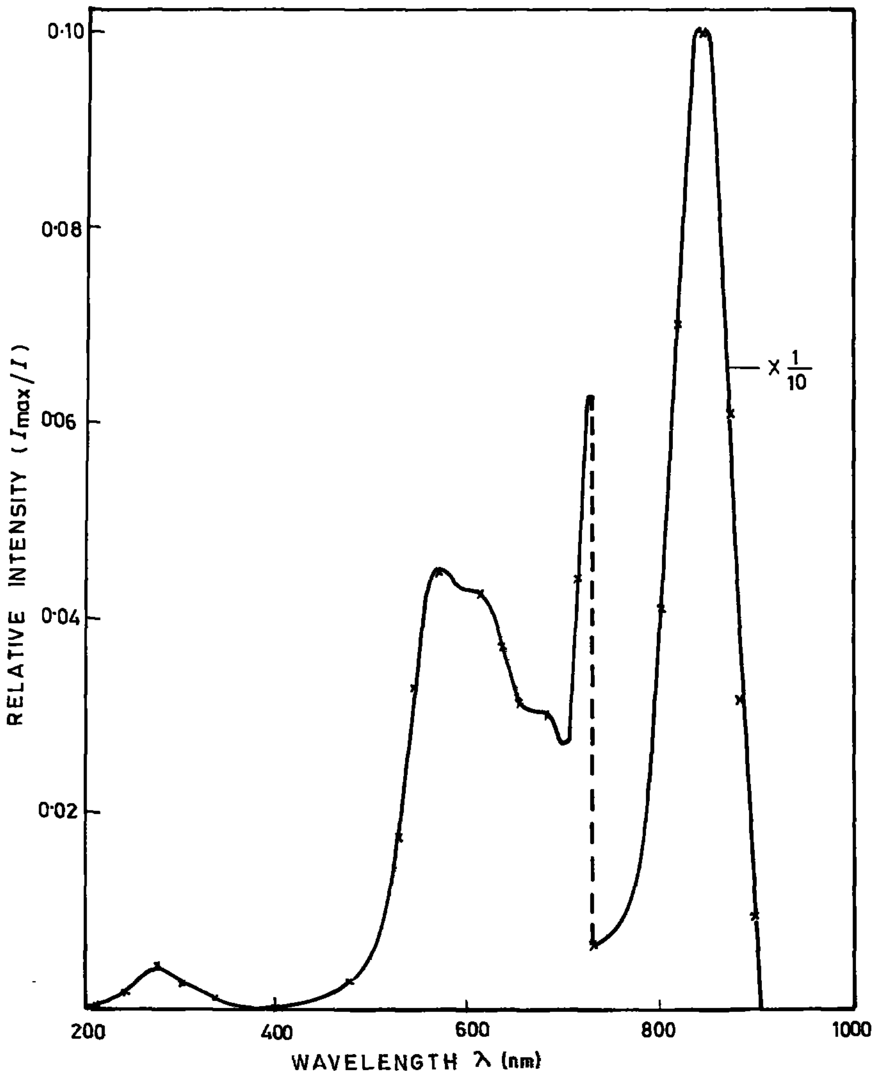

*Figure 1* TL spectra at 340° C of $CaF_2$–Nd (0.049 wt %) crystal X-ray irradiated at RT for 30 min.

(0.0078 wt %); $CaF_2$–Nd(II) (0.049 wt %); and $CaF_2$–Nd(III) (0.089 wt %).

## 3. Results

In order to study the emission mechanisms during TL, the TL spectrum of $CaF_2$–Nd was studied (Fig. 1). Essentially three emission wavelength peaks are obtained ; two broad peaks located around 275 nm and 600 nm and a third sharp peak at about 830 nm whose intensity could not be determined accurately because of the uncertain correction factor involved.

Fig. 2 represents the X-ray luminescence spectra of $CaF_2$–Nd single crystal measured at different temperatures between RT and LNT. It may be pointed out here that in earlier measurements [2, 3, 5] on $CaF_2$–Nd attention has been given to the emission in the infrared region and no data for emission in the visible are available. The present measurements have been carried out in the UV and visible range only. It is observed that the emission peaks are around 300, 600 and 830 nm and their intensity increases as the temperature decreases from RT to LNT.

Fig. 3 gives the X-ray luminescence spectra of $CaF_2$–Nd measured at different temperatures between RT and 400° C in vacuum. There are three main emission peaks around 300 and 600 and 830 nm at all temperatures. At 126 and 203° C the luminescence intensity diminishes, while at 357° C it increases again, but still it is much less than that at RT. TL spectra and X-ray luminescence spectra for $CaF_2$–Nd(II) are given in Table I.

Fig. 4 shows the X-ray luminescence spectra of $CaF_2$–Nd(I), $CaF_2$–Nd(II) and $CaF_2$–Nd(III) measured at RT. It is found that with an increase of dopant concentration the intensities of all three peaks increase, reaching a maximum for $CaF_2$–Nd(II) and then decreasing with a further increase in neodymium concentration.

In Fig. 5, Curves (1) and (2) represent the temperature variation of X-ray luminescence intensity for 300 nm and 600 nm peaks, respectively, measured from RT to 400° C. In both cases the intensity decreases as the temperature rises from RT to around 235° C, then increases till 325° C and again decreases on further increase of temperature. This intensity peak occurs nearly around the same glow peak temperature

TABLE I TL spectra and X-ray luminescence spectra for $CaF_2$–Nd (0.049 wt %)

| TL peak at 340° C (nm) | X-luminescence peak at 351° C (nm) | X-luminescence peak at RT (nm) | X-luminescence peak at LNT (nm) |
|---|---|---|---|
| 275 | 295 | 285 | 285 |
| 600 | 615 | 600 | 585 |
| 830 | 840 | 825 | 827 |

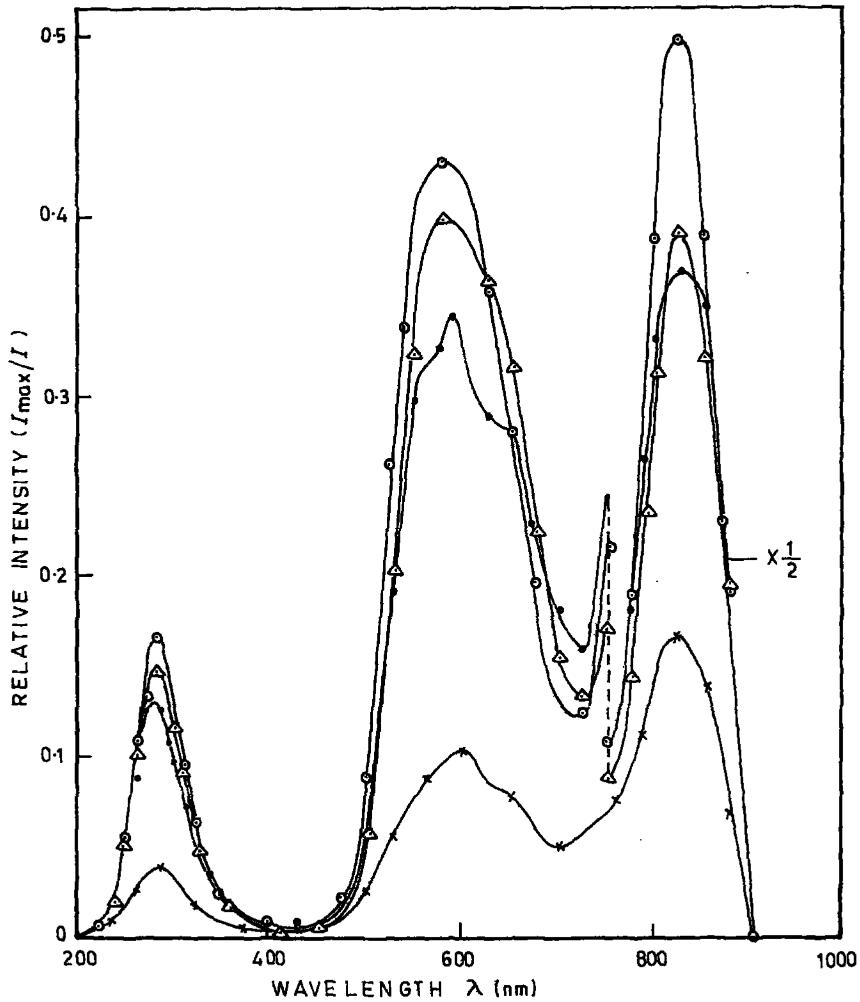

*Figure 2* X-ray luminescence spectra of $CaF_2$–Nd (0.049 wt %) crystal at various temperatures from LNT to RT: (⊙) LNT, (△) −110° C, (●) −31° C, (×) RT.

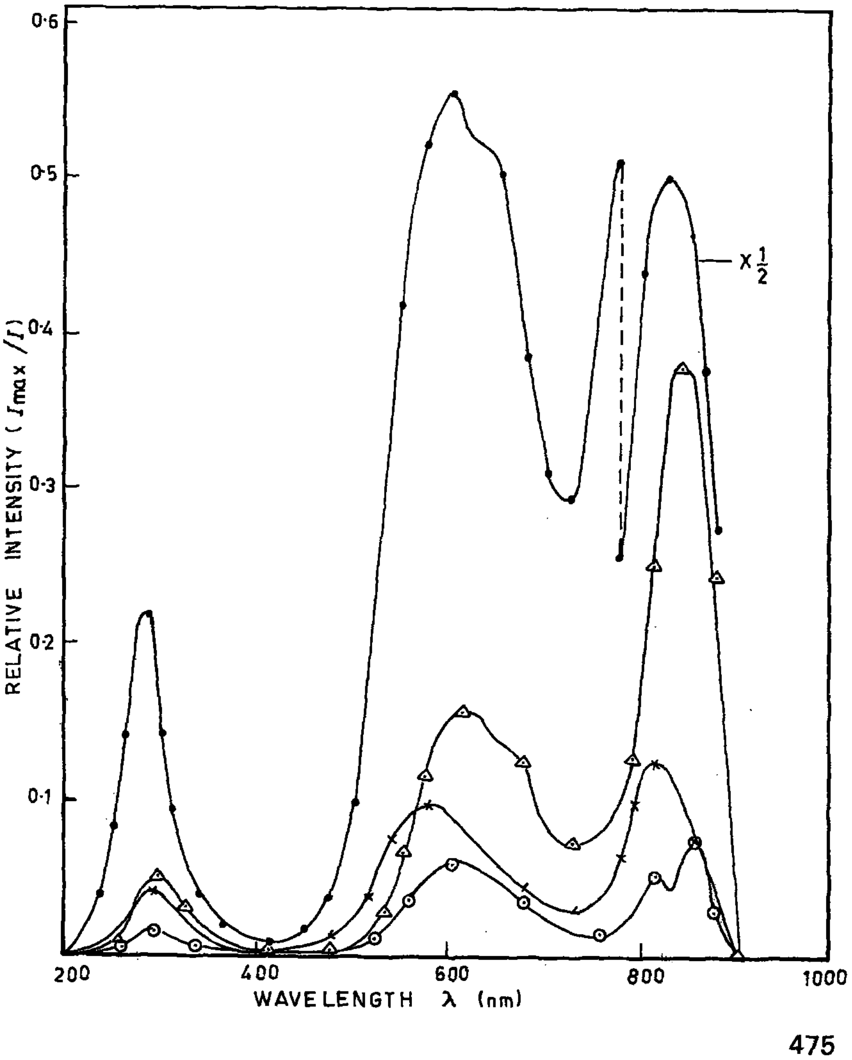

*Figure 3* X-ray luminescence spectra of $CaF_2$–Nd (0.049 wt %) crystal at various temperatures between RT and 400° C: (●) RT (30° C), (×) 126° C, (⊙) 203° C, (△) 351° C.

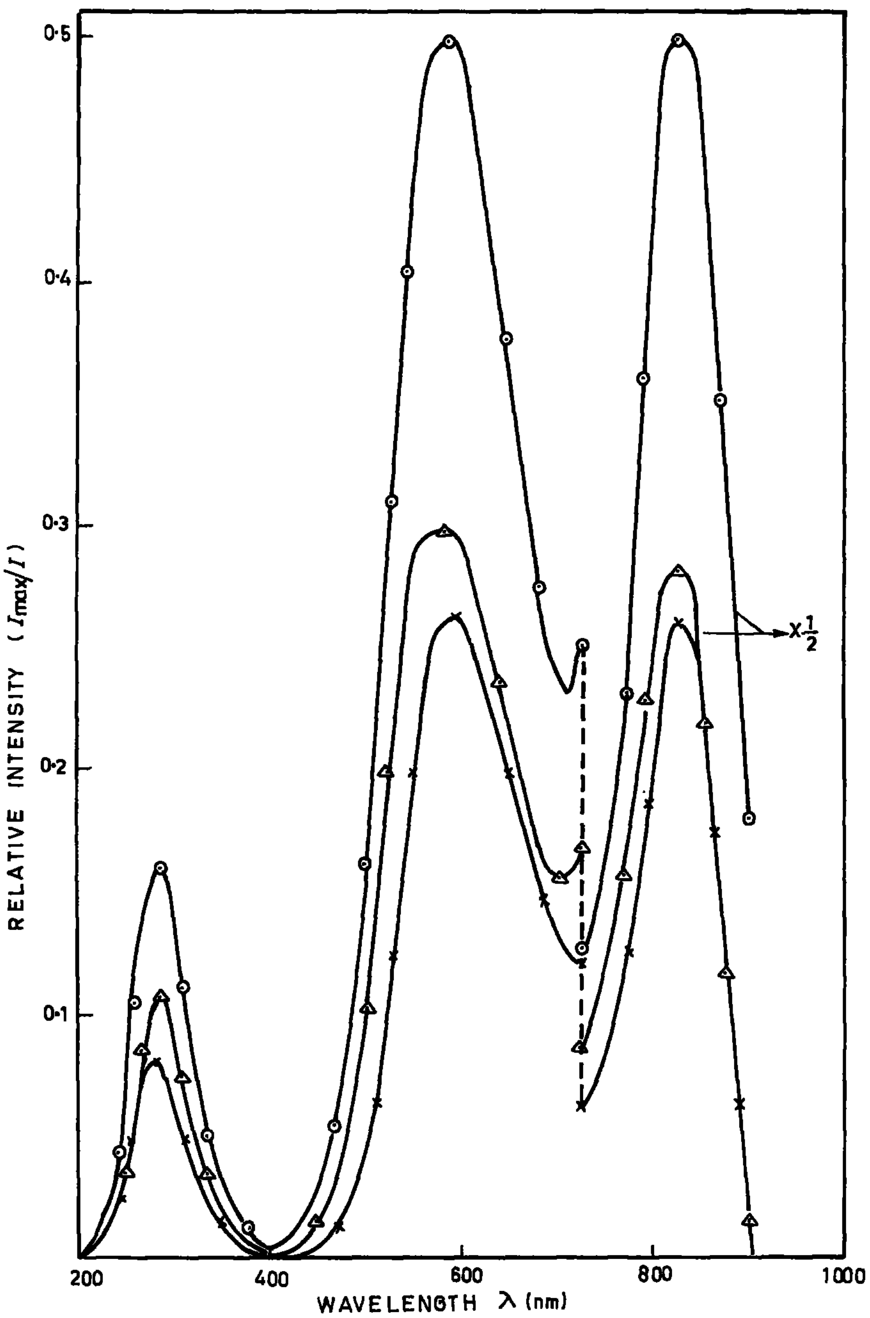

*Figure 4* X-ray luminescence spectra of $CaF_2$–Nd crystals at RT: (△) 0.0078 wt % Nd, (⊙) 0.049%, (×) 0.089%.

obtained in the case of TL measurements. It is clearly seen from this figure that the 600 nm emission is nearly four times stronger than the 300 nm emission.

## 4. Discussion

The mechanism of X-ray luminescence emission in the case of $CaF_2$–RE is that X-irradiation reduces the trivalent RE ion to a divalent state, along with counterparts in the form of $F^0$ interstitials. These reduced rare earths capture holes from mobile hole-trapped centres giving rise to $RE^{3+}$ in the excited state. Subsequently, de-excitation of these centres yields luminescence. Although it is well known that neodymium emission has prominent lines in the infrared, it has been reported that it has strong visible emission under gamma irradiation [3]. According to the radiative scheme of $Nd^{3+}$ [6] there may be emission in the region of 606 nm and 833 nm due to $^4d_{3/2}$ to $^4f_{3/2}$ and $^4d_{3/2}$ to $^2h_{11/2}$ transitions, respectively.

The peak emission wavelengths of X-ray luminescence spectra are located around 300, 600 and 830 nm (Figs 2 and 3). While the origin of the 300 nm peak is completely uncertain, the other two peaks may be related to the emissions connected to some excited states of neodymium. It is interesting to note that the same emission peaks occur in the TL spectra at 340° C (Fig. 1). This indicates that the electronic transitions involved in the TL emission and X-ray luminescence are identical.

Again, it is clearly seen from Figs 2 and 3 that the X-ray luminescence is greatly enhanced as the temperature is lowered. The enhancement of luminescence with the lowering of temperature is due to the fact that at high temperatures the larger amplitudes of lattice vibrations interfere with the excited electrons in the impurity ions, thereby increasing the probability of internal conversion as compared to that of luminescence [7].

X-ray luminescence intensity decreases with increase in temperature as seen in Fig. 3. However, there is a characteristic marginal increase in X-ray luminescence intensity at 351° C. This increase in

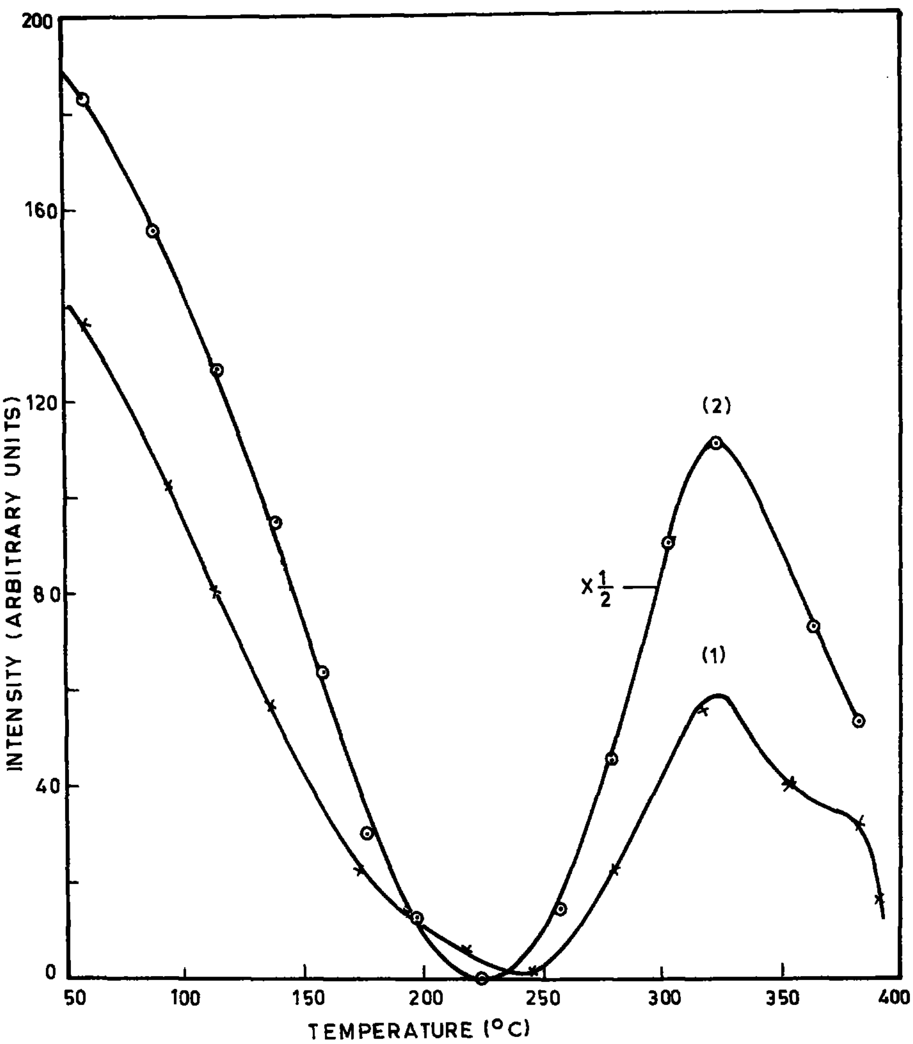

*Figure 5* Variation of X-ray luminescence intensity with temperature (RT to 400° C) at different peak emission wavelengths for $CaF_2$–Nd (0.049 wt %) crystals: (×) 300 nm, (⊙) 600 nm.

luminescence intensity is possibly due to thermal ionization of electrons from deeper traps which were responsible for the 350° C TL peak observed in normal TL glow curves.

Fig. 4 gives the intensity variation of X-ray luminescence spectra with the concentration of impurity content (neodymium) present in the system. It shows that intermediate doping gives the maximum intensity of emission, through the range of 200 to 900 nm; while the heavily doped sample gives the minimum intensity. For heavy doping, it is possible that a part of the dopant remains in the separate aggregated phase resulting in the reduction of emitting centres. This is similar to the "concentration quenching" frequently found in heavily doped alkali halides.

In Fig. 5, the intensity peak located around 330° C for both the emission wavelengths at 300 and 600 nm indicates detrapping of electrons from deeper traps, probably associated with vacancies which have captured electrons forming $\alpha$ and $\beta$ bands. (It may be mentioned that X-ray irradiation in the temperature range of 180 to 250° C produces $\alpha$, $\beta$ bands in $CaF_2$ as reported by Ratnam [8].) The fact that the TL peak also occurs around the same temperature (i.e. 330° C) indicates that the X-ray luminescence process is similar to the TL process in this temperature region. It is to be remembered that X-irradiation reduces the $Nd^{3+}$ ions to $Nd^{2+}$ ions which on heating are reconverted to the trivalent excited state and TL is emitted. Since the prompt emission is expected to be proportional to the number of $Nd^{3+}$ emitting centres, it will increase with the temperature in the range where the divalent to trivalent conversion takes place, which is the TL glow peak temperature region.

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