Thermoluminescence of calcium flouride doped with neodymium

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Abstract. Thermoluminescence (TL) and radioluminescence (RL) spectra have been recorded from a set of calcium flouride samples doped with Neodymium. The dopant levels used were 1.0, 0.1 and 0.0130 and 400 °C, with spectra being taken both prior to heat treatments, and after heating to 500 °C for one hour and cooling at different rates. For the RL, each sample gave a UV/blue emission band near 300 nm which decreased with increasing Nd concentration. During thermoluminescence the Nd is the main recombination centre and shows characteristic line emission. However the spectra vary with concentration and thermal treatments. Models for the changes involve Nd defect clustering with non-radiative decay paths. At high temperature the TL spectra include other emission bands attributed to relaxed exciton decay.

1. Introduction

The thermoluminescence (TL) of calcium fluoride has been intensively studied as the presence of rare earth (RE) impurity ions provides a very bright phosphor. The TL signals from natural minerals of fluorite (Bill and Calas, 1978, Calderon *et al* 1990, 1992) have been linked to varying concentrations of RE ions. Earlier TL studies of CaF_2 doped with Mn, Dy, Tb, Ce etc were reviewed by Sunta (1984) and, as a result of the high sensitivity to radiation dose, the material has been exploited in the form of a commercial CaF_2:Dy TL dosimeter. In addition to the TL studies there have been many efforts to determine the detailed structure of the RE sites in the fluorite lattice and examples of defect structures are discussed by Hayes (1975) and Hayes and Stoneham (1985). The simple point defect model of a RE ion substituted on to a calcium site is inadequate for charge compensation and therefore alternative associations of the RE^{3+} with charge compensators such as interstitial F-ions have been considered for pure material or compensation by substitutional $O^=$ which enters the crystal during growth in air. The RE impurities have a tendency to pair so once lattice distortions are introduced it is energetically favourable to form larger defect complexes with, for example, pairs of substitutional impurities with charge compensators and off-site neighbours. Variations on this pattern mean that the 'simple' RE defects in CaF_2 frequently involve ten or more lattice sites.

By analogy with the early alkali halide nomenclature the presence of clusters involving one, two three or four RE impurities have been variously labelled L, M, and N or, more informatively, by a notation of (2,2,2) etc which emphasizes the relative number of component anion interstitials, impurities and vacancies.

One consequence of the presence of multiple constituent complexes is that the defect sites, and of course the TL signal, are sensitive to thermal treatments and previous irradiation

history. For TL radiation dosimeters the possibility of sensitization by factors of up to 500 have been recorded. Note however that such sensitization steps may be unfavourable in material which is to be reused. Some dramatic examples of thermally induced TL defects and their consequent changes in the sensitivity and number of glow peaks were included in work by Bangert *et al* (1982).

Neodymium does not seem to have featured in many of the natural fluorite or dosimeter studies although it can be incorporated in the lattice in a number of site symmetries (Vakhidov *et al*, 1972, Subramanian and Mukherjee, 1987, Han *et al* 1993, Can *et al* 1994). In these examples it is clear that the spectra and the overall intensity of the Nd related emission can change with Nd concentration, and further data will be reported here for effects of thermal treatments.

In this present paper we have recorded the emission spectra during x-ray irradiation radio-luminescence (RL) between 200 and 800 nm, and the TL spectra both at room temperature and after heat treatments consisting of heating at 500 °C for one hour and cooling at two different rates. We have addressed two main areas, namely the possibility of there being concentration effects in both the RL and TL spectra of our three different samples, and whether we can influence clustering of the Nd ions present using different heat treatments. In addition, changes occur during storage time after heat treatment of a sample, and the intensity and spectra of the TL signal.

An attempt to match the line spectra results with the transitions responsible for them using the Nd data of Dieke and Crosswhite (1963) was successful over the temperature range 20 to 250 °C, but additional broad band features occur for the 350 °C glow peak.

2. Experimental methods

For the RL measurements a simple system was initially used which includes a scanning monochromator and a red sensitive photomultiplier tube. Whilst the system also allowed recording of TL spectra it had the weakness of all TL scanning systems of being inefficient and also, even during one wavelength scan, of obtaining the data over a range of temperatures. With the development of a wavelength multiplexed system (Luff and Townsend, 1993), with an efficiency improvement of some 500 times compared with their scanning monochromator, the later data were recorded on the new equipment. The spectra were recorded between 200 and 800 nm with a typical resolution of 5 nm. The heating rate was 2.5 °C s^{-1}. All spectra were corrected for the spectral response of the system. Data near 800 nm are less accurate as they include a component from second-order 400 nm emission as well as that from Nd. Note earlier Nd data include strong emission peaking variously near 830 nm. Data were acquired at 1 s intervals. X-ray excitation was made *in situ* with a 15 kV x-ray beam delivering 0.7 Gy per minute.

Measurements were made for three different doping levels of Neodymium in calcium flouride, namely 1.0%, 0.1%, and 0.01% Nd.

The heat treatments consisted of heating samples to 500 °C in air for one hour and either cooling slowly (pulling the sample gradually from the furnace over a further period of one hour) or quenching i.e. the sample was pulled straight out of the furnace and left to cool on the bench. Normally, TL experiments were conducted on the same day the heat treatment was performed, while in others the sample was stored at room temperature for several days before TL measurements were taken. Note the two procedures produce different results.

3. Results and comments

3.1. Radioluminescence

In order to gain some idea of the influence of an increasing amount of Nd in the samples, RL spectra were recorded at room temperature for all three doping concentrations. Figure 1(a) shows the results. Three broad peaks are seen: in the UV, green and red at approximately 285 nm, 525 nm and 700 nm. It is also quite clear that for all wavelengths, the intensity of the peak decreases with increasing Nd concentration. Further, it is worth noting that the peaks as well as being broad are also featureless.
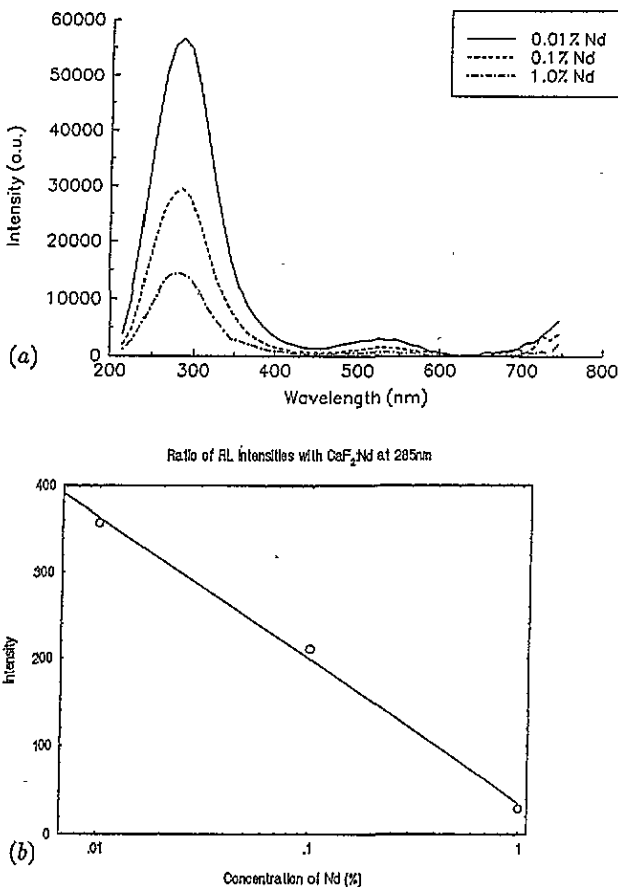

Figure 1. (a) Radioluminescence spectra of CaF$_2$ with three Nd doping levels. (b) Nd induced quenching of the 285 nm signal.

Turning to figure 1(b) a clear inverse log relationship can be seen between the RL intensity and Nd doping concentration of the peak at 285 nm. This relationship is given by the equation

$$y = -170 \log(0.61x) + \text{constant} \tag{1}$$

The intensity relationships at both the 525 nm and 700 nm peaks followed the same pattern. A simple model predicts the shape of this line as follows. We can see from figure 1(a) that an increase in the Nd concentration is reducing the luminescence intensity, i.e. there is a quenching factor Q scaling with n where n is the concentration of Nd ions. For the intensity to be decreasing, the Nd ions must be interacting in such a way as to produce non-radiative transitions. Thus Q may be expressed in the form

$$Q = A \exp(-E^*/kT) \tag{2}$$

which is merely a constant times the non-radiative transition probability, and E^* is the energy required for a non-radiative transition to take place. Therefore we can write

$$A \exp(-E^*/kT) = n \tag{3}$$

which converts to

$$0.43(-E^*/kT) + \log B = \log n \tag{4}$$

which is in the same basic form as equation (1).

Note that in a parallel set of cathodoluminescence (CL) measurements on the same samples there is a somewhat similar quenching behaviour for broad bands centred near 340 and 650 nm. However in the CL data Nd line emission was apparent on the side of the UV band (at 363, 384 and 415 nm) for the heavily doped samples. The fact that this description covers the dopant concentration range from 0.01 to 1.0% can be interpreted to mean that the RE cluster defects are in equilibrium. This suggestion is partially supported by the earlier data of Subramanian and Mukherjee (1987) in which they noted their RL signals from Nd doped CaF_2 peaked at 0.049% in their set of three samples with Nd at 0.0078, 0.049 and 0.089 wt %. The present samples are thus above this critical limit and hence one assumes this is a consequence of Nd multiple ion defect sites. Nevertheless, the form of their spectra differ from the present work. In their data all the emission features were broad bands with peaks near 285, 600 and 825 nm. The former two thus resemble, in wavelength, those seen in CL (but inversely so in intensity). They assigned their strongest signal at 825 nm as arising from Nd ions.

One should contrast the preceding data with the photostimulated luminescence of CaF_2:Nd of Bausa *et al* (1991). They excited with an argon 514 nm laser and recorded the emission from 850 to 1100 nm. Lines characteristic of the single, double and triple Nd sites were identified with the relative importance of multiple sites increasing over the concentration range up to 4 wt % Nd. The main 1047 nm line increased linearly with Nd concentration. In particular it should be noted that their samples were probably oxygen free as they were grown as thin films under ultra high vacuum by molecular beam epitaxy.

3.2. Thermoluminescence

Figures 2, 3 and 4 show examples of the isometric plots of the TL spectra (intensity versus wavelength and temperature) of the three Nd concentrations after x-ray doses of 14 Gy at room temperature. In order to view the line features of the weaker low temperature peaks, the high intensity signals are truncated on these plots. Black body radiation dominates the red corner of the plot at high temperature. One must be slightly cautious in interpreting signals beyond 780 nm, as these include some second order signals from 390–400 nm when
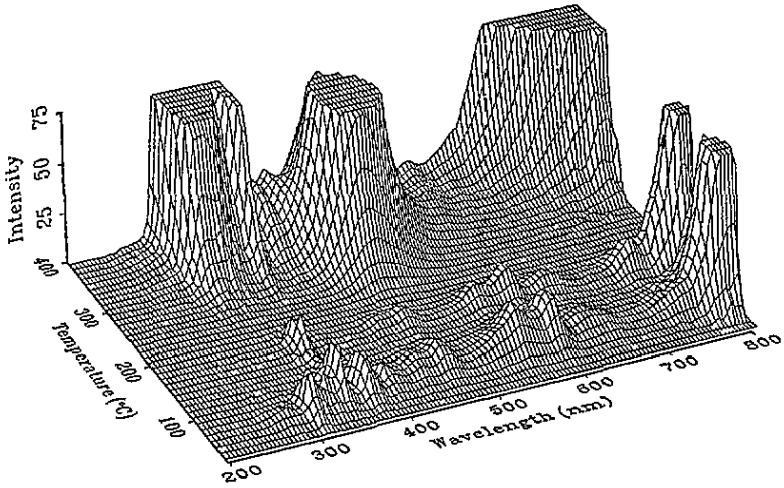
CaF$_2$:Nd 0.01%
After 14Gy

Figure 2. Thermoluminescence after x-ray irradiation of CaF$_2$:Nd. The doping level is 0.01% Nd.
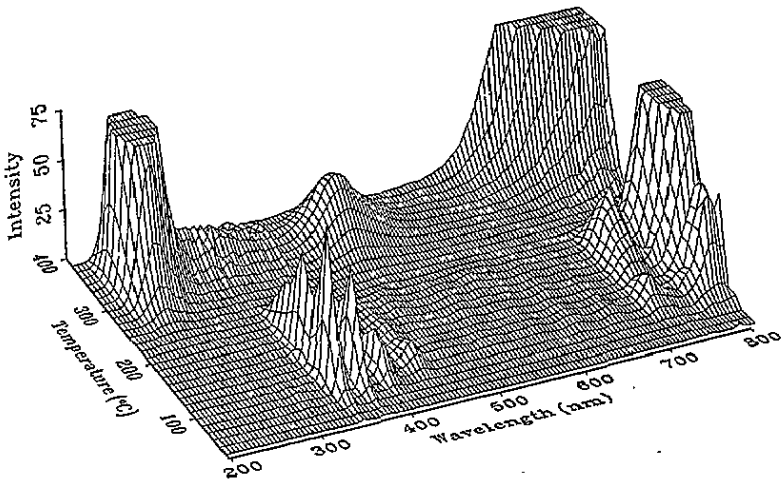
CaF$_2$:Nd 0.1%
After 14Gy

Figure 3. As figure 2 for 0.1% Nd.

short wavelength emission is present. However, for the CaF$_2$:Nd there is a strong signal close to 800 nm.

If one nominally separates the glow peaks into emission near 100, 200 and 350 °C then, ignoring changes in relative intensity, the lower two peaks comprise a similar set of line like emission bands. The relative intensities of the UV, green and infra-red groups of bands
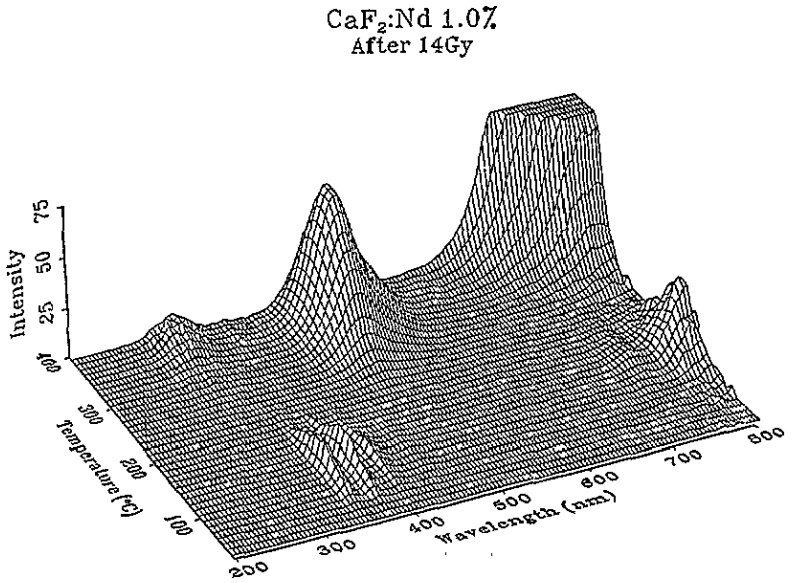
CaF$_2$:Nd 1.0%
After 14Gy

Figure 4. As figure 2 for 1.0% Nd.

are strongly concentration dependent. By contrast, the 350°C emission is quite different. Some line features are preserved; a totally new peak near 490 nm occurs in each case, but in the UV region there is no obvious pattern between the samples as a function of Nd concentration. Indeed for the 0.1% sample there is a large peak at 240 nm which is not present for either of the other concentrations: 0.01% has a large peak at 325 nm, while 1.0% has a low intensity peak at around 300 nm. In addition the high temperature peak at 490 nm shows no obvious correlation with Nd concentration either, as for 0.01% it is at it's largest, followed by the 1.0% case, and decreasing to a fraction of the latter for 0.1%. In all cases, including after heat treatments (see later) there are features adjoining the black body emission both around 600 nm at 350°C and towards 750 nm at around 300°C. These features differ slightly from sample to sample, but the peaks would have to be better resolved to determine if any concentration or heat treatment dependencies existed. Figure 5, showing a temperature slice at 350°C for each sample, clarifies some of these points.

Figure 6, showing the Nd energy scheme, clarifies the identification of the lines from the lower temperature glow peaks. It can be seen that the UV, green, and infra-red groups of lines in our data come from the 4D, 2D to 4G, and 4F levels respectively. One may further suggest how the intensity pattern varies with Nd concentration. If we assume that at higher Nd concentration the Nd–Nd interactions favour non-radiative decay through each manifold of levels, this can explain why the features between 400 and 700 nm at low temperature decrease with increasing Nd concentration. At all concentrations charge moves down to the energetically well isolated $^4D_{3/2}$ level. Decay down to the lower ^4I states provides the observed blue/UV light at the 450, 413, 382 and 356 nm lines. However, within the next set of levels the interactions caused by increasing Nd content generate non-radiative decay down to the lowest G level (i.e. this suppresses the green decay events). Exit from the lowest state generates infra-red signals. To be consistent with this pattern one assumes that there should be an emission line near 870 nm where the $^4I_{15/2}$ is the end state. Indeed, in a subsequent search for this emission it was detected.
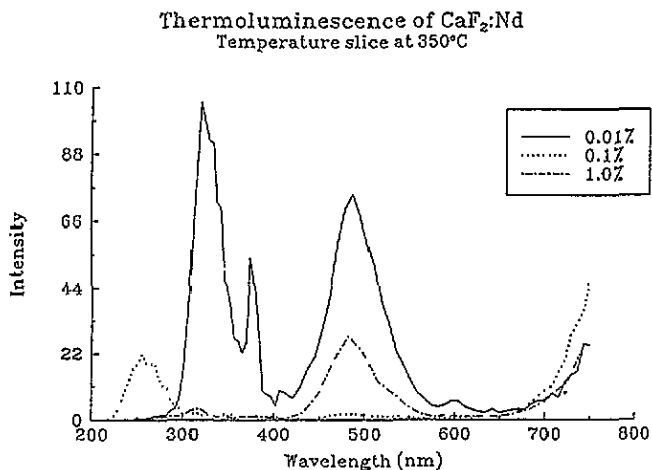
Thermoluminescence of CaF$_2$:Nd
Temperature slice at 350°C

Figure 5. Comparisons of spectra taken at 350 °C for the three Nd dopant levels.

3.3. Thermal treatments

It is evident from the figures that the TL spectra are sensitive to the Nd doping level. In such a situation the signals may also respond to changes in Nd clustering, even for the same total impurity content. In order to test this, samples were variously annealed and either slow cooled or quenched. Figure 7 shows the TL spectra of 0.01% Nd doped CaF$_2$ after heating to 500 °C and cooling slowly for approximately one hour. The emission region between 400 and 700 nm for the 100 and 200 °C peaks is reduced in intensity relative to that of figure 2, making it more similar to the spectra of the high Nd concentration sample shown in figure 3. Thus there is a change induced by slow cooling which might be explained by the Nd ion complexes having time to cluster. It is assumed that, as in the case of high Nd concentration, when the Nd states are thus arranged, non-radiative decay occurs in the 400–700 nm regions.

A reversal of this implied Nd precipitation was attempted by re-heating the same sample to 500 °C and rapidly quenching. The results showed an approximate doubling of the blue/green emission but not a complete reversal to that of Figure 2, which we had assumed to be produced when the Nd (and their charge compensators) are in their dispersed state. The 490 nm peak at high temperature also increases again bringing the intensity nearer to that of figure 2, but features to the left of this peak have changed greatly. Note in this discussion 'isolated' Nd defects could include the RE pair defects, and so clustering or dispersion phenomena relate to larger scale aggregation of the defects. Also note that at 0.01% Nd dopant level prior to any clustering the typical defect–defect distance will be some 20 lattice spacings but only 10 for the 0.1% doping. Since the colour centre studies already indicate that the RE ions influence some 10 or so neighbouring lattice sites then the 0.01% Nd level is on the borderline of behaving as though the defects are non-interacting. Hence it is only for this lowest Nd concentration we can easily detect that the cooling speed can influence the state of Nd clustering seen in the 400–700 nm low temperature region. The second fast cooling cycle has partially reversed the precipitation of the Nd ions. Since the nature of the defect cluster is highly speculative one should also note that there is the possibility of the formation of a RE fluoride precipitate phase NdF$_{2+x}$ ($x < 1$) (Hayes and Stoneham, 1985).
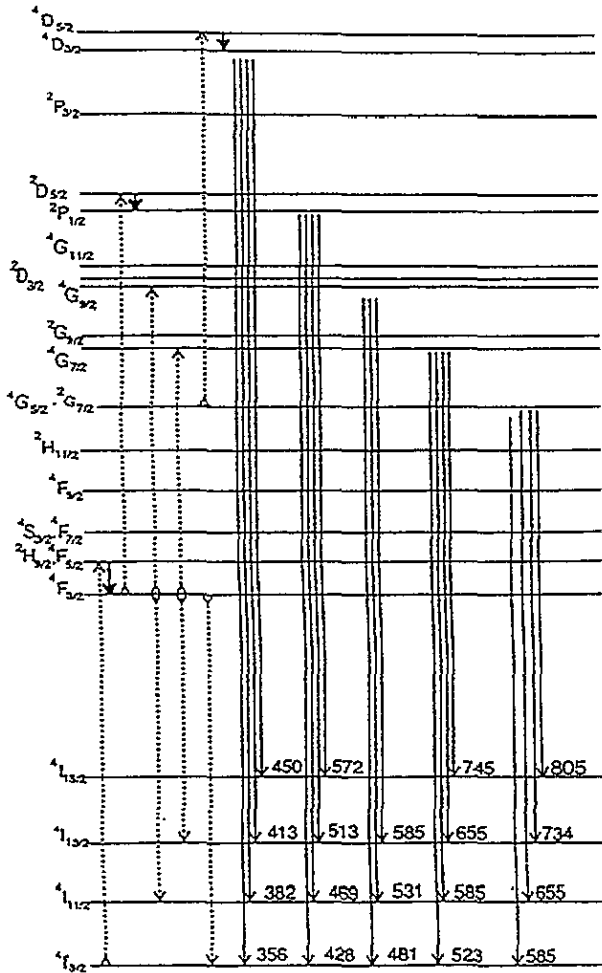
Figure 6. The energy level scheme of Nd (after Dieke and Crosswhite).

Thermal treatments for the higher Nd concentrations show somewhat similar features but the changes are less pronounced. For example, as shown on comparing figure 4 with figure 8, for the spectra for 0.1% Nd dopant after a slow cool heat treatment. It should be noted that the 490 nm peak at high temperature follows the same pattern as the blue/green emission at lower temperatures for both the 0.01% and 0.1%Nd samples, but in the 1.0% doping case this pattern is reversed. Thus more complicated effects than the formation of clusters are suspected to be coming into play in this case.

Interpretation of the signals from the 350 °C peak are more difficult since, as is obvious from figures 2, 3 and 4 the only common feature is the emission band near 490 nm. The intensity of this is quite sensitive to thermal treatment and for example with the 1.0% dopant level it is reduced by a third on fast cooling. Figure 8 shows that this can be the only remaining high temperature peak and the UV emission near 300 nm (seen in figure 4) has disappeared.

It should also be mentioned that the fast or slow cooling used here does not necessarily establish a stable defect distribution. Indeed storage of the samples for several days after
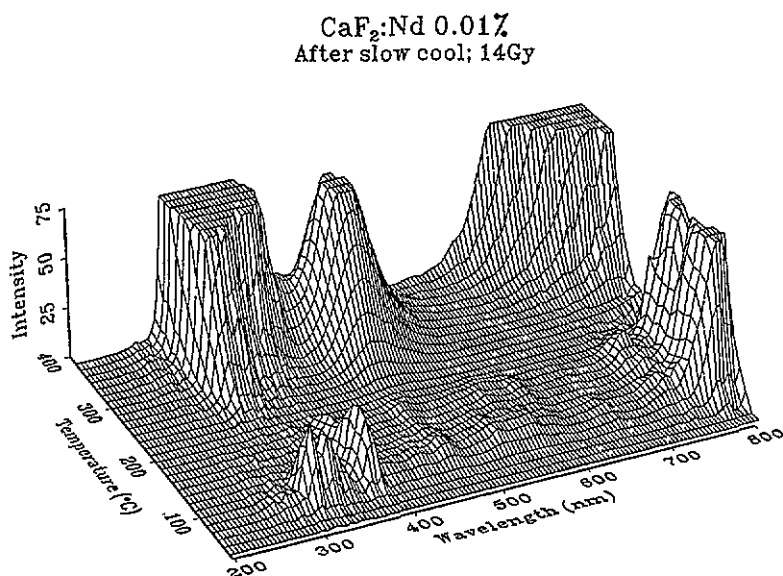
CaF$_2$:Nd 0.01%
After slow cool; 14Gy

Figure 7. TL spectra taken with CaF$_2$:Nd (0.01%) after slow cooling.
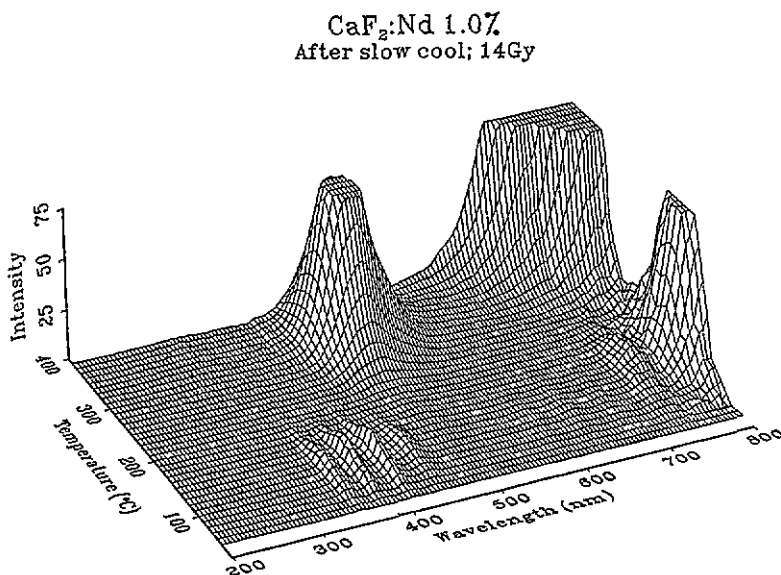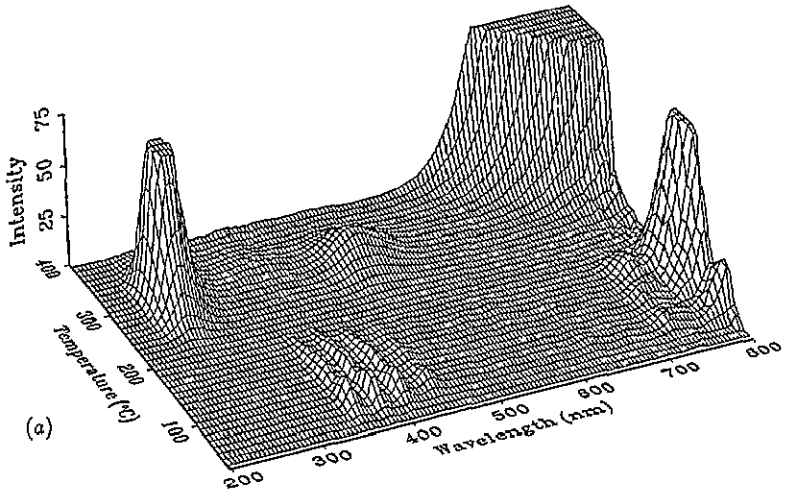
CaF$_2$:Nd 1.0%
After slow cool; 14Gy

Figure 8. As figure 7 but for a 1.0% Nd dopant level.

the heat treatment can cause spectral changes partially consistent with breakup of clusters. See figures 9(a) and 9(b). All that can be conclusively said is that the results produced by thermal treatments are not in equilibrium, and that the differences in emission spectra are both concentration and clustering dependent.

Referring back to figure 5, on comparing the emission spectra for the 350 °C region for the three types of sample, none of the 250, 300 or 490 nm emission bands exactly

CaF$_2$:Nd 0.1%
After slow cool same day; 14Gy

(a)

CaF$_2$:Nd 0.1%
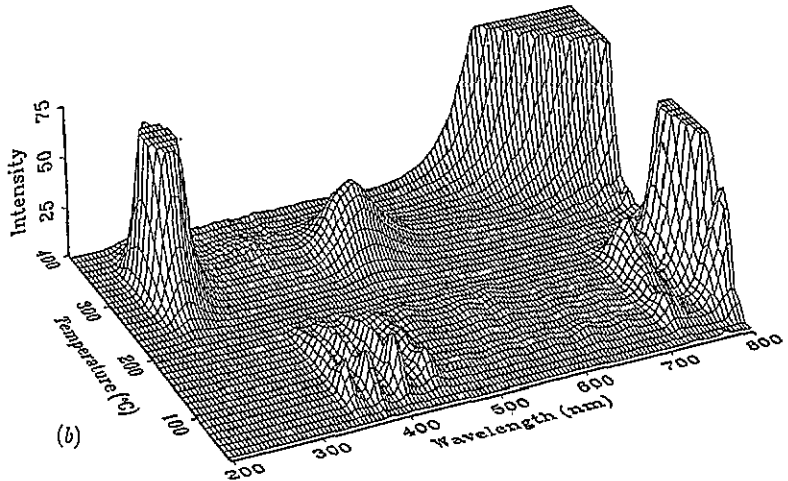After slow cool 3 days ago; 14 Gy

(b)

Figure 9. (a) As figure 7 but for the 0.1% Nd level. The TL experiment was made on the same day. (b) As (a) but a three day storage was made prior to the TL experiment.

correspond to previously described luminescence bands from intrinsic or Nd doped CaF$_2$. The closest UV peak is the emission from self trapped excitons, which is quoted as being at 280 nm for measurements near 80 K. In the TL and RL data of Subramanian and Mukherjee, (1987) there is a peak at either 275 or 295 nm for the two types of excitation in lightly doped material at 340°C. Hence the bands are not specific to the present crystals although their origin is far from clear.

3.4. TL mechanisms

The standard model of RE ions in the TL of CaF_2 (e.g. Sunta, 1984) is that the RE^{3+} ion is charge stabilized by an interstitial fluorine ion (or a substitutional oxygen). Therefore on irradiation the RE^{3+} converts to RE^{2+} by gaining an electron and the F moves off to form a V_k centre. During the TL heating stage the model assumes the V_k emits a hole so V_k converts to $F^- + F^- + h^+$ and $RE^{2+} + h^+$ goes to RE^{2+} (excited), relaxing to give $RE^{3+} +$ TL.

Whilst the 3+ assignment of the lines is satisfactory in all the RE cases reported, and whilst optical absorption studies have confirmed this mechanism to be taking place (Lakshmanan and Tiwari, 1993, Merz and Pershan, 1967), there is however a problem in understanding how capture of a hole, (i.e. the transfer of an electron from the Nd^{2+} ion) can lead to high level excited states of Nd^{3+}. Note in particular that Nd lines of up to 4 eV energy are clearly detected. Excitation of such high level states seems unlikely on this standard model.

Alternative routes which package the energy via an exciton that dissociates at the Nd complex could offer one solution as even the relaxed exciton emits with some 4.4 eV. Certainly the exciton decay process is strongly influenced by the presence of the Nd defects and figures 1 and 2 emphasize that the exciton emission is quenched by the Nd sites. However figure 1 is not consistent with an alternative decay route in which exciton energy is emitted at the Nd sites. Hence a simple exciton absorption at the Nd site does not explain why the TL spectra are characteristic of Nd. More complex steps therefore seem to be needed but at this stage are only speculation. Nevertheless the TL process implies both separation of electrons and holes and relaxation from the original atomic structures. One may speculate that these two elements of the TL are spatially linked.

4. Conclusions

The presence of Nd impurity ions in CaF_2 results in TL emission spectra which are characteristic of the Nd^{3+} transitions for the 100 and 200 °C glow peaks. Other defect structures are involved in the emission spectra of the higher temperature, 350 °C, peak. The possibility of Nd cluster type defects can be used to explain the quenching of the green emission lines. Nd ions also quench the intrinsic luminescence but do not become the alternative radiative decay route, hence a variety of processes are revealed by comparison of the RL and TL data. Despite the clear assignment of the emission spectra to Nd sites it is less clear how the trapping and energy transport processes operate.

Acknowledgments

References

Bangert U, Thiel K, Ahmed K and Townsend P D 1982 *Radiat. Effect.* **64** 153–60
Bausa L E, Legros R and Munoz-Yague A 1991 *J. Appl. Phys.* **70** 4485–9
Bill H and Calas G 1978 *Phys. Chem. Minerals* **3** 117–31
Calderon T, Khanlary M R, Rendell H M and Townsend P D 1992 *Nucl. Tracks. Radiat. Meas.* **20** 475–85
Calderon T, Millan A, Jaque F and Sole J G 1990 *Nucl. Tracks Radiat. Meas.* **17** 557–61

Can N, Kazanci N, Townsend P D and Chadwick A V *Phys. Status Solidi* submitted

Dieke G H and Crosswhite H M 1963 *Appl. Opt.* **2** 675–86

Han T P J, Jones G D and Syme R W G 1993 *Phys. Rev.* B **47** 14706–23

Hayes W (ed) 1975 *Crystals with the fluorite structure* (Oxford: Oxford University Press)

Hayes W and Stoneham A M 1985 *Defects and defect processes in non-metallic solids* (New York: Wiley)

Lakshmanan A R and Tiwari S S 1993 *Radiat. Protect. Dosimetry* **47** 243–6

Luff B J and Townsend P D 1993 *Meas. Sci. Technol.* **4** 65–71

Merz J L and Pershan P S 1967 *Phys. Rev.* **162** 217–35

Subramanian M A and Mukherjee M L 1987 *J. Mater. Sci.* **22** 473–7

Sunta C M 1984 *Radiat. Protect. Dosimetry* **8** 25–44

Vakhidov Sh A, Kaipov B and Tavshunskii G A 1972 *Opt. Spectrosc.* **33** 431