Thermoluminescence spectra of rare earth doped Ca, Sr and Ba fluorides

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Abstract
The low temperature TL spectra of undoped alkaline earth fluorides consistently show a continuous broad band emission around 280–300 nm. The origin of this emission is related to the relaxation of the self-trapped exciton (STE) in the form of an F–H pair. In doped samples, the broad emission is quenched in favour of emissions from the rare earth (RE) impurity sites. The degree of quenching varies between the REs. The spectral measurements showed that the temperature of the glow peaks below room temperature is to a large extent independent of the RE impurity, although some effects are related to the concentration. Additionally, the host material has minimal effect on the glow peak temperatures, T_{max}. The scale of the observed differences in T_{max} between the three hosts is similar to the differences in annealing temperatures of the V_k and H centres in these hosts. Above room temperature, the glow peaks are specific to the added RE ions and do not show common peaks.

1. Introduction

Alkaline earth fluorides (AEF) were widely investigated in the early 1960s and 1970s to characterize the lattice defects associated with them. Their relatively simple structure, the ease with which they can accept large concentrations of interstitial defects and the ease with which rare earth elements can be incorporated in the lattice are among the main motivating factors for those studies. Within this context, several experimental techniques had been applied, which include electron paramagnetic resonance (EPR), electron nuclear double resonance (ENDOR), optical absorption (OA) and luminescence techniques [1, 2]. Such studies resulted in a large volume of data about the structure of the intrinsic colour centres and their properties.

Among all of the alkaline earth fluorides, CaF_2 doped with rare earth impurity ions was extensively studied because of its high sensitivity and its ability to store the incident energy [3, 4]

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giving it suitability for radiation dosimetry. The material has been marketed as a commercial TL dosimeter, CaF_2:Dy, under the commercial name TLD200. On the other hand, luminescence studies of SrF_2 and BaF_2 [5–8] doped with rare earths have received much less attention, despite their intense luminescence. For BaF_2 Lucas and Kapsar [9] studied the luminescence properties of BaF_2:Dy and the possibility of using this material in radiation measurements. Their results show that the BaF_2:Dy system exhibits intense thermoluminescence. Compared to the most commonly used TL dosimeter, it is 20 times more sensitive than TLD100 and twice as sensitive as TLD200. However, the problems of supralinearity and high fading preclude using this material in radiation dosimetry. Nevertheless, the material was successfully used as a scintillator for gamma ray detection after the discovery of the fast luminescence component at 220 nm [10]. Doping with rare earths to improve its scintillation properties has also received considerable attention from the workers in this field [11–16]. The researches on SrF_2:RE system for the application in radiation dosimetry are very scarce and its radiation properties are little documented.

Earlier TL models in fluorides at low temperature [17–19] are usually built on the inherent assumption of separated traps (intrinsic defects) and recombination centres (RE sites). This conclusion is mainly based on the observation that the glow peaks in the fluorite structure occur, more or less, at the same temperature irrespective of the RE dopant. Such models assume that the irradiation at low temperature reduces the RE^{3+} in cubic sites to RE^{2+}. In the readout stage the trapped holes are released to recombine with the electrons trapped at the RE site resulting in light emission or glow peaks at temperatures determined by the annealing temperatures of the various hole traps. However, the actual situation may not be as simple as this, especially at high doping levels, which put the RE ions in the immediate neighbourhood of each other. The low temperature TL data presented here indicate that the RE ions have some influence on the charge trapping and the intrinsic luminescence, although there is no major effect on the peak maximum positions. Experimental observations (including current data) suggest the RE ions influence the TL kinetics, since the following are seen.

 (i) The intrinsic luminescence of fluorides shows two maxima occurring at the same wavelength, whereas in doped samples the intrinsic peaks, if they were present, usually suffer from wavelength shifts with temperature.

 (ii) There are large variations in peak intensities between the various REs, where in some cases one glow peak is dominant with a certain RE, but is only just detectable, or missing, with others.

(iii) The emission solely occurs via the RE^{3+} sites and the RE^{2+} emission is lacking even in the RL spectra.

(iv) Lower pre-exponential factors are derived from kinetic analyses for the heavily doped samples.

 (v) In addition, the accommodation of RE^{2+} in the lattice would create an unacceptably large volume distortion from the ion size considerations, as discussed in [4] and [20].

The objective of this research is therefore to study the TL in Sr and Ba fluorides doped with rare earth ions. The study has been extended to include samples of Ca, Sr and Ba fluorides doped with Ho in order to study the effect of the host lattice on the glow peak positions. This should enable an assessment of any relation between the lattice constants and the peak maxima in these hosts.

Table 1. The concentration of the rare earth doped Ba and Sr fluorides.

	RE dopants and their concentration (wt%)						
	Ce	Gd	Tb	Dy	Ho	Er	Tm
BaF_2	0.1	1.0	1.0	1.0	0.1 & 1.0	0.1 & 1.0	1.0
SrF_2	0.1 & 1.0	1.0	—	0.01	0.2	0.01 & 0.2	—

Table 2. The concentration of Ho doped Ca, Sr and Ba fluorides.

	Ho Concentration (wt%)	
CaF_2	0.1	0.2
SrF_2	0.1	0.2
BaF_2	0.01	0.1

2. Experiment

A selection of RE^{3+} doped BaF_2 and SrF_2 were obtained from Optovac, a part of the Advanced Chemicals Division of EM Industries, Inc. Samples were in the form of discs, which have a 1 cm diameter and a thickness of 1–2 mm. Table 1 shows the dopants used in this study and their nominal concentrations. All measurements were carried out on the high sensitivity wavelength multiplexed spectrometer at Sussex [21]. The low temperature (25–280 K) TL spectra were recorded at a heating rate of 0.1 K s^{-1} whereas those above room temperature (300–673 K) were recorded at a heating rate of 1 K s^{-1}.

Another set of Ca, Sr and Ba fluorides doped with Ho was included to study the effect of the host material. The Ho concentration is shown in table 2.

3. Results

Radioluminescence (RL) of pure AEF show a continuous broad band emission in the UV/blue region. Figure 1(a) shows an RL example of undoped BaF_2. In addition to AEF, many materials are found to emit in this region, which include alkali halides, sulphates, quartz, silica etc. In all cases this emission is assumed to result from a defect linked to a relaxed exciton or recombination at lattice defects. The effect of temperature on this emission is evident from figure 1(a), where the intensity at room temperature is less than one half that at 25 K.

In all doped samples the intrinsic emission is retained but suppressed in intensity and the amount of suppression varies between the RE's. Examples of RL in doped samples are shown in figures 1(b) and 1(c). Terbium seems to be more efficient in suppressing this emission than Dy. It is also to be noted that the suppression in the intrinsic emission intensity is accompanied with an enhancement in the intensity of the impurity lines. Changes in the relative intensity of the lines with temperature are observed for most of the dopants as seen in figure 1(b) for BaF_2:Dy.

The low temperature TL spectra of undoped BaF_2 and SrF_2 are shown in figure 2. The TL spectrum of BaF_2 is typical of that observed in alkali halides or LaF_3 [22, 23] in that it consists of one major peak and another smaller one. By contrast, SrF_2 shows four or five glow peaks with line emissions superimposed on the continuous band suggesting that the undoped SrF_2 is contaminated with RE impurities, most probably by Ce and Gd. The intrinsic emission of the doped samples is largely suppressed, especially in the SrF_2 host, and the impurity lines mainly define the emission.
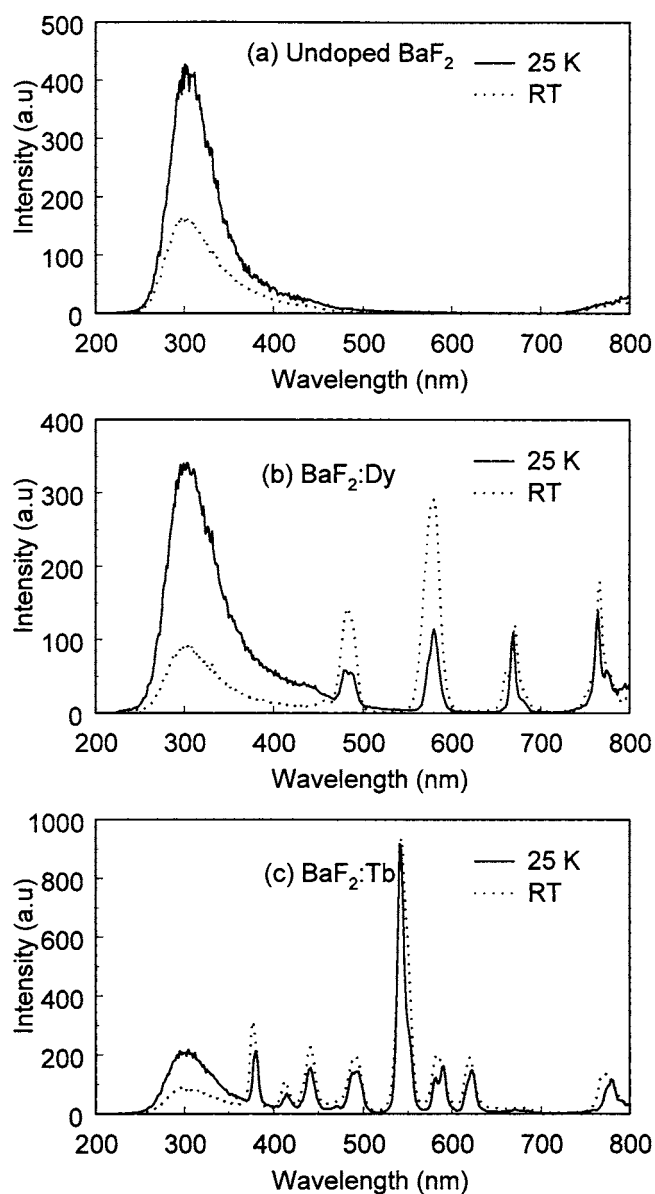
Figure 1. Radioluminescence (RL) of BaF$_2$ at 25 K and room temperature: (a) undoped, (b) doped with Dy and (c) doped with Tb.

The effect of concentration (to be commented on later) on the resultant glow curves is evident in figure 3. Examples of lightly doped (0.01 wt%), intermediate (0.2 wt%) and heavily doped (1 wt%) SrF$_2$ samples are shown in this figure. It is obvious from the figure that on increasing the RE concentration the glow peaks become broader and overlap with each other, especially at the higher temperatures. An example of the wavelength shift of the intrinsic emission with temperature is shown in figure 4 for BaF$_2$:Er (1 wt%) (e.g. near 300 to 320 nm for the peaks at 108 and 141 K).
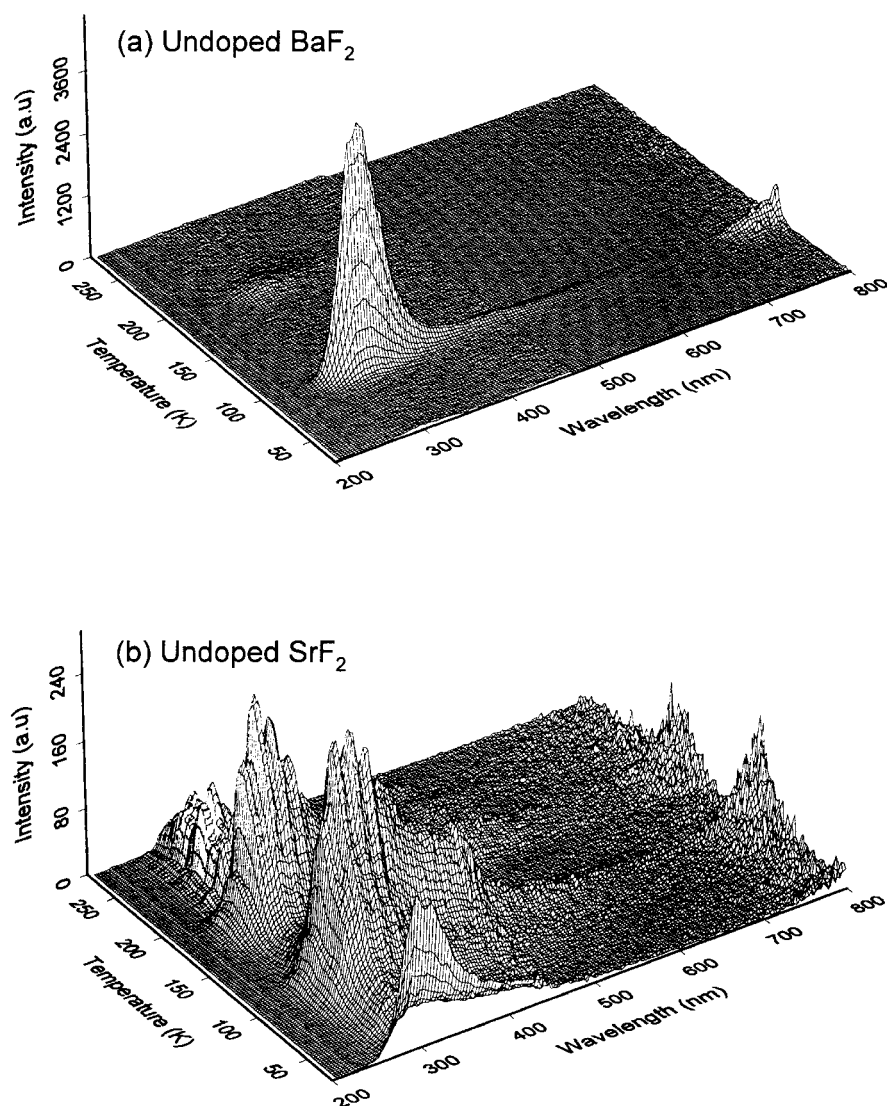
Figure 2. Thermoluminescence (TL) spectra of (a) undoped BaF_2 and (b) undoped SrF_2.

In order to determine the positions of the glow peaks, the glow curves were integrated along the main emission line of each dopant, with data taken directly from the 3D isometric plots. Results are displayed in figures 5 and 6 for BaF_2:RE and SrF_2:RE respectively. The temperatures of peak maxima are summarized in tables 3 and 4.

The set of data (Ca, Sr and Ba fluorides doped with Ho) were fitted to the general order kinetic equation using a peak fit programme, and the data shown in figure 7 are for the 0.1% Ho concentration. The fitting has two objectives. The first is to resolve the strongly overlapped peaks, as in the case of CaF_2:Ho. Secondly, this might reveal a more accurate relation between the peak maxima and the lattice constant, as shown in figure 8.

Finally, the TL spectra observed above room temperature (not included here) did not show the common peaks between rare earths. Instead, each dopant shows its own characteristic glow
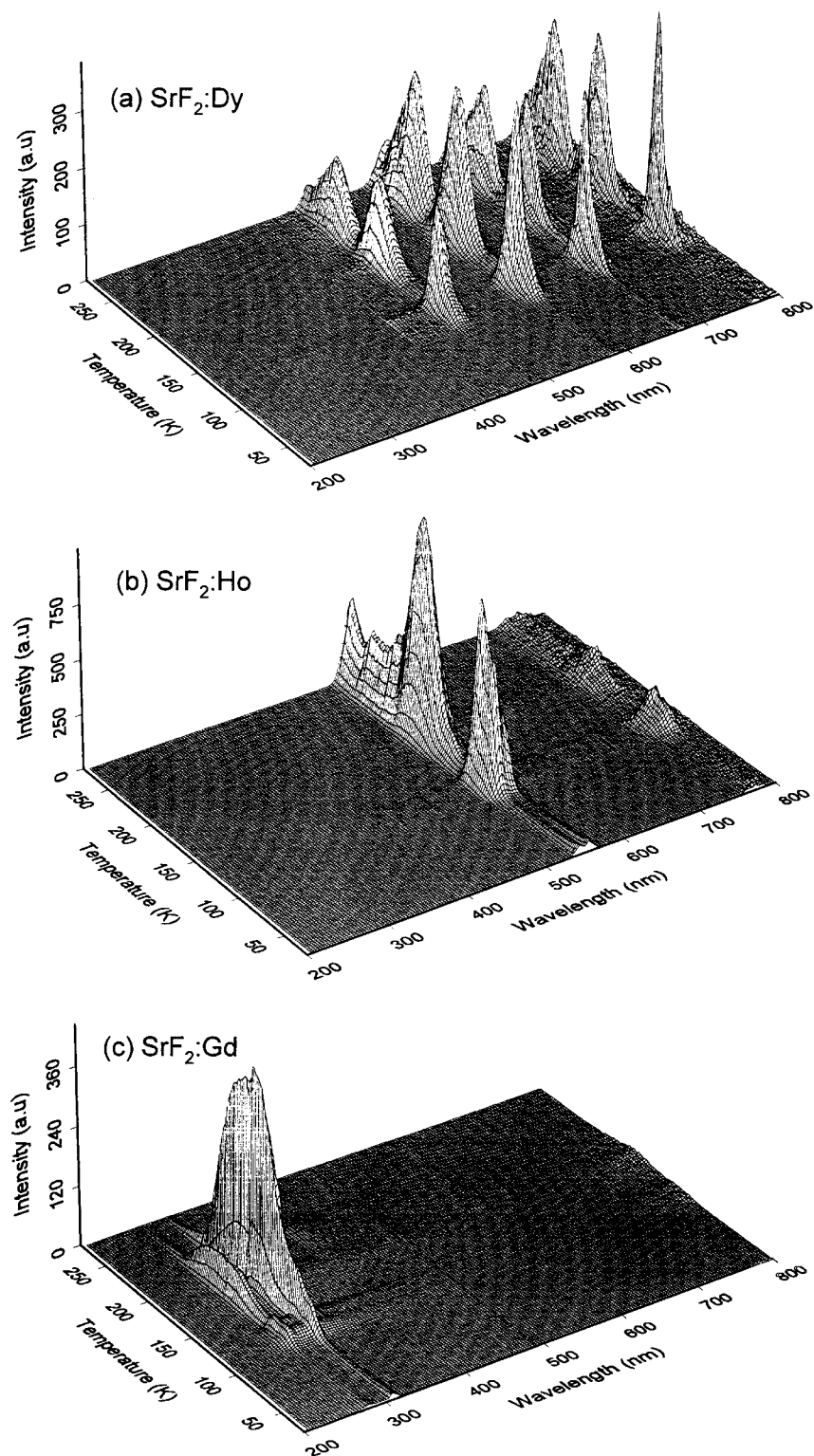
Figure 3. TL spectra of SrF$_2$ doped with (a) 0.01 wt% Dy, (b) 0.2 wt% Ho and (c) 1.0 wt% Gd.
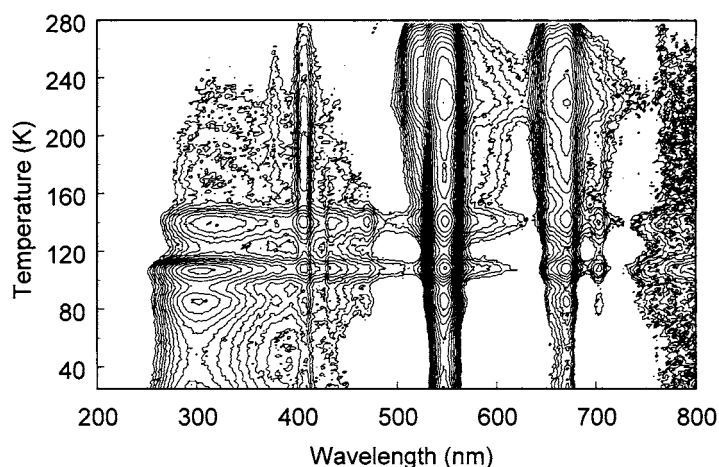
Figure 4. Logarithmic contour map of the TL data of BaF$_2$:Er (1.0 wt%).

Table 3. Low temperature TL peak maxima in BaF$_2$:RE. Italic numbers refer to uncertainty in determining the maxima of the broad peaks. ** refers to unresolved broad peaks. Er 1% has an extra peak at 194 K.

Ion	Conc. (wt%)	Temperatures (K) of peak maxima in BaF$_2$						
Ce	0.1	63	94	105, 117	144	—	178	205	—
Gd	1.0	—	—	108	142	—	—	212	249
Tb	1.0	—	88	108	*140*	154	—	—	240
Dy	1.0	66	89	—	*140*	162	—	210	—
Ho	0.1	72	—	102	—	*160*	179	217	—
Ho	1.0	79	—	102	**	**	**	220	252
Er	0.1	—	87	113	143	*165*	180	221	*253*
Er	1.0	—	86	108	141	—	173	224	*250*
Tm	1.0	—	91	—	—	*160*	—	213	251
	Average	70	89	108	142	160	177	215	249

Table 4. Low temperature TL peak maxima in SrF$_2$:RE. Italic numbers refer to uncertainty in determining the maxima of the broad peaks. Er (0.01%) has an extra peak at 257 K.

Ion	Conc. (wt%)	Temperatures (K) of peak maxima in SrF$_2$					
Ce	0.1	116	—	156	—	*210*	242
Ce	1.0	*124*	—	—	—	210	—
Gd	1.0	118	130	170, 184	—	—	—
Dy	0.01	*115*	133	—	197	—	242
Ho	0.2	120	132	—	195	—	*250*
Er	0.01	*113*	134	—	—	210	245
Er	0.2	110, 124	—	—	198	—	240
	Average	117	132		197	210	244

peaks. Further, Ho shows its first peak around 333 K, Gd does not show any maxima until temperatures up to 623 K. Note that such wide differences in temperature have previously been interpreted as evidence that the REs are strongly present in both the trapping and recombination centres [24–26], and/or that they have separated out as microphase precipitates [24]. Consequently the temperature of the glow peaks are determined by the structure of the specific rare earth complex, rather than the host lattice.
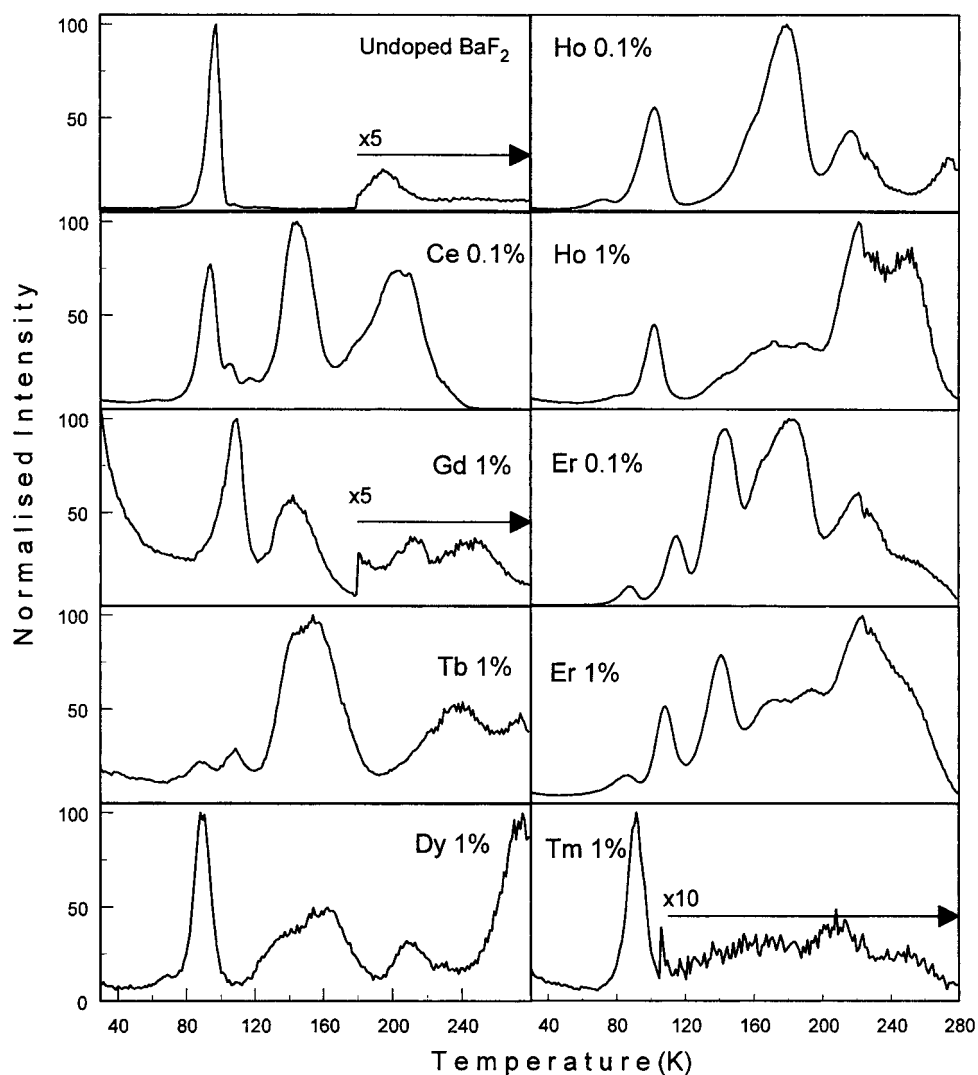
Figure 5. Wavelength slices of the TL data of undoped and RE doped BaF$_2$.

4. Discussion

4.1. Intrinsic luminescence

Alkaline earth fluorides, either pure or doped with rare earth impurity ions, show broad band emission centred at 280–300 nm. The origin of this emission is related to the relaxation of a self-trapped exciton (STE). Unlike the alkali halides, the structure of the STE in the fluorite lattice is of the form of an F–H pair rather than the V$_k$ + e$^-$ form [2]. The formation of the F and H centres is stimulated by capturing the freed electrons and holes by a fluorine vacancy and by fluorine interstitial respectively. The energy of recombination of the nearest F–H pair is emitted as light in the UV/blue region.

In all spectra, the emission via the STEs show some quenching as either the temperature is raised or the concentration of the RE's is increased. The precise nature of luminescence
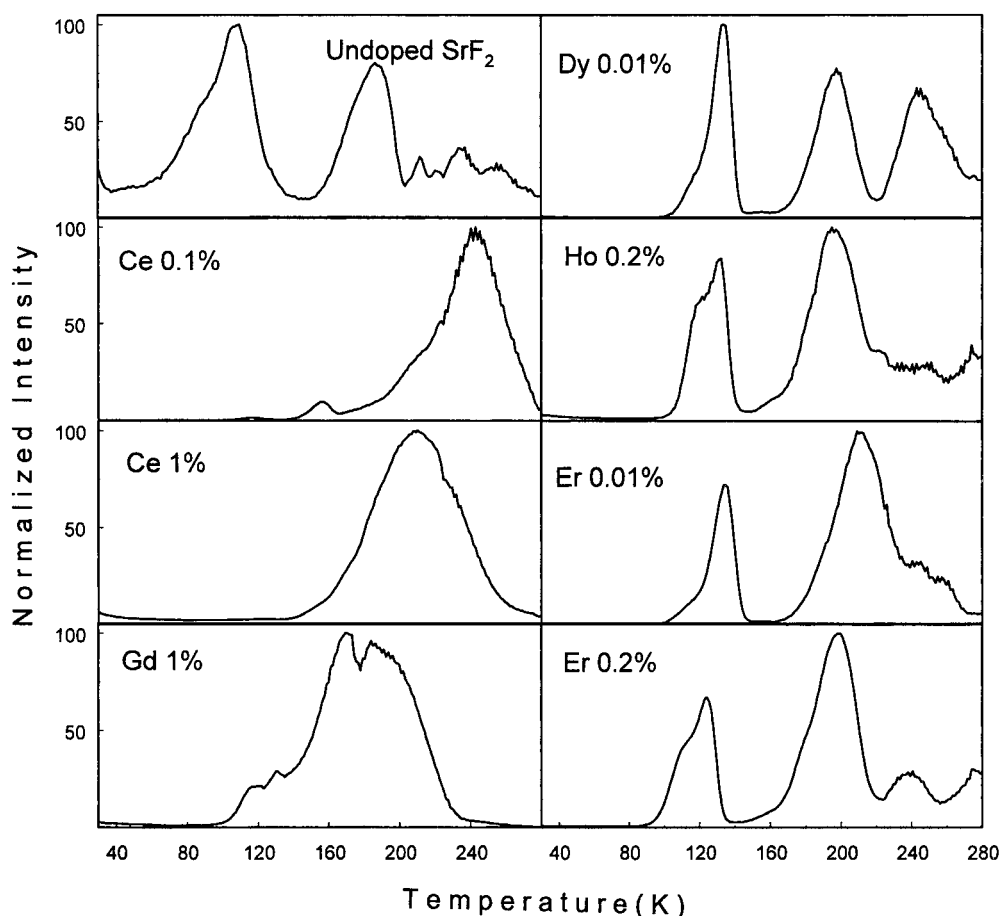
Figure 6. Wavelength slices of the TL data of undoped and RE doped SrF_2.

quenching is not fully understood till now. Nevertheless, two approaches are usually discussed in the literature to account for this phenomenon. In doped material the decay of the STE non-radiatively due to the presence of some kind of quenching centres in the crystal comprise the first approach [11]. The other approach [15, 16] relies on the RE charge conversion, which assumes that rare earth ions introduce extra electron traps that compete with the trapping of electrons by holes. In effect, fewer STE's are then formed, which eventually suppresses the STE luminescence. By contrast to the intrinsic emission, the general trend of rare earth ions in these hosts is to show an increase in intensity at room temperature compared to the ones at 25 K. Only BaF_2 doped with either Ce or Tm does not follow this trend.

4.2. Concentration effects

The effect of concentration on the resultant intensity is not straightforward. In general at high concentration the RE ions tend to associate in pairs or larger clusters to minimize the lattice strain. The consequence is that non-radiative pathways become more probable, reducing the TL efficiency per RE ion. Of equal importance for the alkaline earth fluorides is that a mechanism is required to charge compensate for the trivalent rare earth impurity ions. Possible routes are
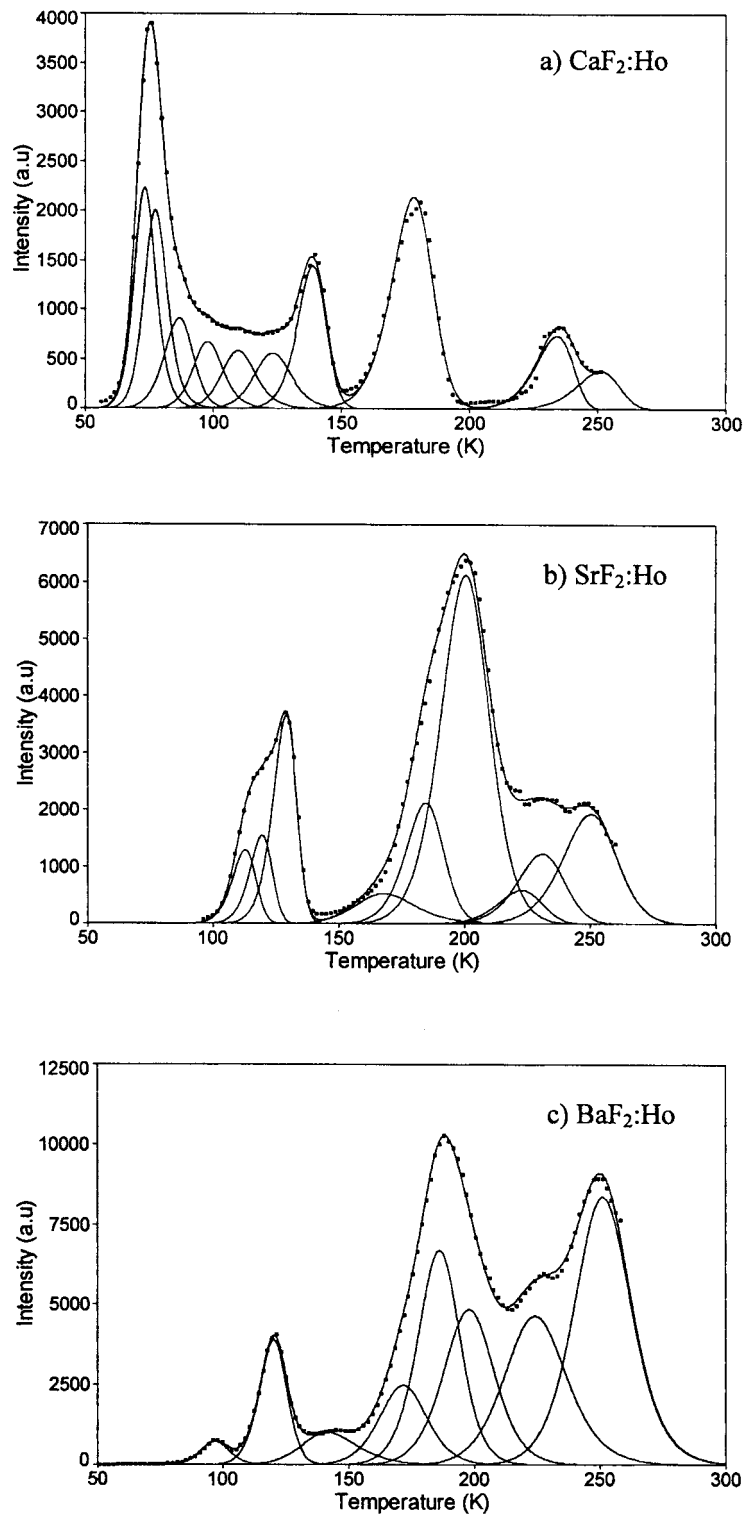
Figure 7. Examples of the curve fitting of the TL data of the 0.1% Ho doped (a) CaF_2, (b) SrF_2 and (c) BaF_2.
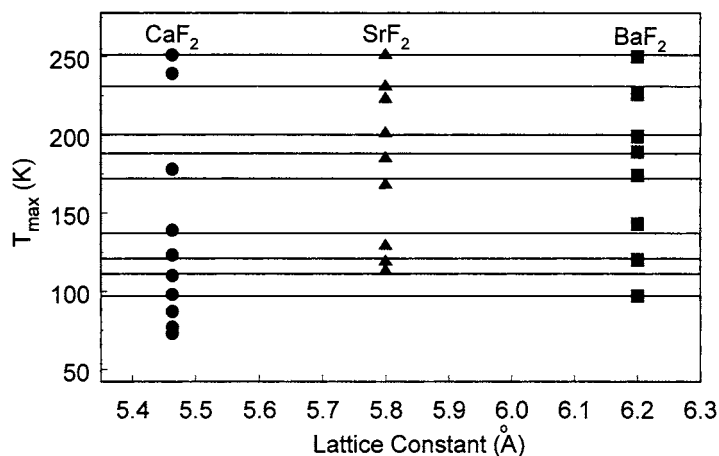
Figure 8. The temperatures of peak maxima versus the lattice constant of the host. The horizontal lines are merely visual aids.

to associate pairs of RE ions within an extended region of modified lattice, which includes both intrinsic defects and lattice distortions [27].

Even at very low dopant concentrations the mechanisms of charge compensation for the trivalent rare earth ions substituted on alkaline earth sites may result in pairs of RE ions within an extended region of modified, or distorted host lattice. This has an interesting consequence that the local atomic structure of the complex may be relatively insensitive to the lattice parameter of the Ca, Sr or BaF_2 (i.e. in complete contrast with the situation for RE ions in LaF_3 [22, 23]). The extreme case is that the RE halide structure precipitates out of the host to form a new phase. This situation definitely exists for the Suzuki phase of LiF:Mg [28], and has been considered in the more speculative interpretation of RE effects on TL in synthetic zircon [24].

Light doping minimizes the tendency of the RE's to associate in even larger complexes, which significantly simplifies the situation for the discussion of TL mechanisms. At higher concentrations, on the other hand, there are several consequences for the resultant glow curve. First, it alters the relative intensity of the peaks. This effect is clearly observed in figure 6, where the increase in the RE content between Dy, Ho and Er change the relative intensity of the peaks between 115 and 125 K. Second, it alters the shape of the glow peaks. This is more evident in Ho or Er doped BaF_2 (figure 5) where the glow peak (peaks) in the temperature range 140–180 K are reduced in intensity, become broader and strongly overlap with each other on increasing the impurity content. This effect can also be seen in Tb or Dy doped BaF_2, where the peaks in the same temperature range are broad and overlap well with each other. The latter observation suggests that the glow peaks in this region are concentration dependent. Furthermore, the higher concentration is always accompanied by the appearance of broad peaks probably due to the formation of larger clusters or aggregates, which alter the recombination processes. This is most obvious in SrF_2 doped with Ce or Gd (figure 6). Third, the higher concentration alters the position of some glow peaks. Example of this are observed in BaF_2:Ho, where the first peak occurs at 72 K for the 0.1% and at 79 K for the 1% sample. Although small, these temperature shifts exceed the experimental and sample variations. Fourth, the higher concentration is frequently accompanied by the appearance of new glow peaks or shoulders. In BaF_2:Er the 1% sample shows a new peak at 194 K, which was not observed for the same dopant at 0.1% concentration.

A closer look at table 4 shows that the first peak variously moves between 115 and 125 K. All the temperature values quoted in tables 3 and 4 are taken directly from the glow curves. However, the curve fitting procedure may be more accurate, especially for the overlapping peaks. Curve fitting for SrF_2:Dy showed that the estimated peak at 115 K is in fact two overlapping peaks at 115 and 123 K. Therefore, one could conclude that this peak is truly two overlapping peaks and the estimated figure around either 115 or 125 K depends on which one is the dominant peak.

From table 3 it is apparent that the higher temperature peaks of Ce and Tb do not match well with other impurities. For the Ce case, it is observed that the clustering effects dominate in SrF_2 at the higher concentration. Such effects may be present in BaF_2; this was not verified due to the lack of different Ce concentrations in BaF_2. Nevertheless, the appearance of broad peaks at higher temperatures shifted to lower temperature relative to other RE's indicate that the RE–RE clustering may alter the recombination kinetics, presumably by changing the recombination process in this temperature region. Similar remarks can be made for the Tb data, but the presence of only one Tb concentration precludes the examination of the effect of its concentration on the resulting spectra.

It is argued [29] that the recombination processes via a highly localized defect might lead to broad peaks with a lower frequency factor compared with that of isolated traps. In order to check for this, the glow curves of BaF_2:Ce, BaF_2:Tb and SrF_2:Dy were fitted to the general order kinetic equation using the peak fit programme. The procedure of fitting is to assign initial values for the kinetic parameters for each peak. The programme after that will vary these values in an iterative manner to minimize the differences between the experimental and the theoretical curves. The iterative procedure will continue until self-consistency is reached. The fitted curves and their deconvoluted peaks showed that most of the peaks are of mixed order ($1 < b < 2$). As discussed by Chen and McKeever [29] mixed order kinetics disguise the actual frequency factor but nonetheless changes in the computed value still indicate different situations. Terbium (1%) shows the lowest effective frequency factor, $\sim 10^6$ s^{-1}, and this value enhanced to $\sim 10^9$ or $\sim 10^{12}$ s^{-1} for Ce and Dy respectively as the concentration decreased by a factor of ten. In other words the increase in the RE concentration by a factor of 10 decreases the frequency factor by a factor of 10^3. For first order kinetics the expected frequency factor from isolated traps is of the order of lattice vibration (10^{13} s^{-1}) as in the case of SrF_2:Dy, where most of the peaks have a frequency factor of the same order. The low values of the frequency factors for Ce and Tb are consistent with the energy transfer model [26] in that the emission from RE–RE clusters dominates over the emission from direct charge recombination within the defect complex.

4.3. TL mechanism

From figures 5, 6 and 8 it is apparent that the temperatures at which low temperature TL maxima occur are essentially independent of a specific RE. Although the emission spectra are characteristic of the introduced RE^{3+} ion, the relative intensities of the peaks differ significantly between the various RE's or between the peaks of the same RE as in the case of Tm doped BaF_2. The occurrence of the glow peaks more or less at the same temperature is again evident in the lightly doped samples, as seen in figure 6 for SrF_2 doped with either Dy or Ho or Er.

As previously stated the light emission is stimulated by the release of trapped holes and their subsequent recombination at the RE site. Therefore, the presence of the RE ions has minimal or no effect on the relative population of these traps or their thermal stability. Clearly this situation is not in full agreement with the data presented here, where there are large differences in peaks intensities between the various RE ions. This indicates that the RE ions

have some effect on the relative population of the various hole traps, instead of their having a passive role in the TL process. Thus a more complex model would be needed to explain all the details of the present data. One simple view is to have closely linked traps and recombination sites within a larger complex defect.

As already mentioned, colour centre studies showed that the incorporation of the trivalent RE^{3+} substitutionally for the divalent metal ion forms the site with a surplus positive charge. Compensation of this extra charge can be attained in several ways. Variants proposed include an insertion of an interstitial fluoride ion; substitution of a divalent ion such as O^{2-} for the monovalent ion etc [27]. The consequence of this is that the RE's are normally associated in pairs or clusters to preserve the overall electrical charge neutrality and to minimize the lattice strain resulting from the difference in ionic radii between the RE's and the metal ions. Clusters involving impurities, interstitials and vacancies are normal entities occurring in the fluorite structure, and clusters containing up to ten components have been noted. A recent study on CaF_2:RE [30] showed that concentrations well below 0.01% have profound effects on the absorption spectra, and the variations are attributed to the formation of complex clusters. For the present discussion this has an interesting consequence that the internal ionic spacing within the complex, of RE ions plus charge compensator and intrinsic defects, may be insensitive to the host lattice spacing. Hence the associated glow peaks will be at similar temperatures not only for different RE ions within a single host but will not differ greatly for the variants of Ca, Sr and Ba fluorides. This feature is in distinct contrast with the observations of ionic size dependence for RE ions in LaF_3.

Despite this degree of complexity in charge compensation, it seems that below room temperature the RE ions only have a modest effect on the peak positions. The situation above room temperature is completely different, where the peak positions are specific to the added RE ion indicating that the RE ions are present in the trapping and recombination processes. No clear pattern is observed between the peak positions and the increase in the RE volume.

In most cases of TL spectra of CaF_2, BaF_2 and SrF_2 doped with rare earths, the intrinsic emission is largely quenched. As previously stated this emission originates from a self-trapped exciton in the form of an F–H pair. The decay temperature of the H-centre in AEF is around 175 K. Therefore it is unlikely to observe excitonic emission beyond this temperature due to thermal quenching. At temperatures below 175 K the excitonic emission competes with the line spectra from rare earths. In most cases the emission occurs mainly from the RE with the suppression of the intrinsic emission. The proposed mechanism [4] for this suppression is that in doped materials the exciton decay route occurs at the RE site. Energy transfer between the excited electron hole pair and the RE site gives emission mainly from the RE, if the RE can relax faster than the exciton. The lifetime of the exciton in wide band gap materials such as fluorides is relatively long, resulting in a broad band emission. In Er doped BaF_2 (figure 4) the intrinsic emission is clearly observed and competes with the Er lines, suggesting a relatively long lifetime of the excited states of erbium (as is well documented).

4.4. Lattice effect

The low temperature glow peaks in the fluorite lattice occur more or less at the same temperature irrespective of the RE dopant, although some variations are observed as a result of different concentrations. Results indicate that the host material has minimal effect on the temperature positions of the glow peaks, which may suggest that the same traps exist in these hosts. The small differences observed here in T_{max} as a function of lattice constants reflect the small differences in the annealing temperatures of V_k and H centres in these hosts. The nature of the extended complex RE sites, which even for the simplest of complexes will involve distortions

on perhaps six to ten immediate lattice sites, may minimize the differences in T_{max} between hosts of the AEF series. The agreement between the glow peaks positions in these hosts is good, especially in the temperature range 120–250 K. This is in sharp contrast with the data reported for materials such as LaF$_3$ [22, 23], Bi$_4$Ge$_3$O$_{12}$ [31, 32] or sulphates and borates [25, 33, 34].

5. Conclusions

The data of this study emphasize the close interaction between the trapping and the luminescent sites. The fact that the low temperature glow peak positions are relatively independent of the RE impurity, as opposed to those above room temperature, simply implies that such interactions are very small below room temperature. Changes in the RE concentration alter the glow peaks in several ways. The effect of the host material on T_{max} is minimal and the scale of differences in T_{max} is on the same scale of differences in the annealing temperatures of the V_k and H centres in these hosts.

Acknowledgment

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