Low-temperature thermoluminescence spectra of rare-earth-doped lanthanum fluoride

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Lanthanum fluoride consistently shows two strong thermoluminescence glow peaks at low temperature in pure material near 90 and 128 K. A model is proposed in which these thermoluminescence peaks arise from the annealing of halogen defect sites, similar to the H and V_k centers of the alkali halides. Relaxation and decay of these defects in the pure LaF_3 lattice results in broad-band intrinsic luminescence. Addition of rare-earth-impurity ions has two effects. First, the broad-band emission is replaced by narrow-band line emission defined by the trivalent rare-earth dopants. Second, it preferentially determines the formation of the halogen defect sites at impurity lattice sites and such sites appear to increase in thermal stability since the glow peak temperature increases from 128 K in the intrinsic material up to 141 K through the sequence of rare-earth dopants from La to Er. The temperature movement directly correlates with the changes in ionic size of the rare-earth ions, when allowance is made for differences in effective coordination number of the impurity ions. The data suggest two alternative lattice sites can be occupied. The model emphasizes that the intense thermoluminescence signals arise from internal charge rearrangements and annealing of defect complexes, rather than through the more conventional model of separated charge traps and recombination centers. At higher temperatures there is a complex array of glow peaks which depend not only on the dopant concentration but also are specific to each rare earth. Such effects imply defect models giving thermoluminescence within localized complexes and possible reasons are mentioned. [S0163-1829(98)04701-8]

I. INTRODUCTION

Lanthanum halides have played a central role as the host material for the characterization of the emission spectra of rare-earth ions in solids.[1–3] The rare-earth dopants have the same valence, and very similar ionic radii, to the lanthanum ions, therefore they are expected to occupy normal lattice sites, without excessive lattice distortion or the need for charge compensators. For the purposes of color center studies this provides a simplified situation for analysis of impurity and intrinsic lattice defect interactions which are here explored using one of the most sensitive techniques for the detection of lattice imperfections in insulators, namely thermoluminescence (TL). This type of analysis has an extensive literature associated with the presence of rare-earth ions, and their influence on TL, particularly in the highly sensitive radiation dosimeters such as $CaSO_4$ or MgB_4O_7 doped with Dy or Tm.[4,5] Many similar dosimetry examples of rare-earth (RE) ions in alkaline earth fluorides, e.g., CaF_2 or BaF_2, have been widely documented.[5–9] In all these examples the need for charge compensation of the impurity site results in complex defect sites which are variously thought to influence between 5 and 50 normal lattice sites. Interpretation and analysis of such ''point'' defects is thus difficult and most radiation dosimeters using thermoluminescence have been developed from a semiempirical basis. Dosimetry optimization invariably includes addition of secondary or tertiary dopants and thermal treatments to sensitize the material.[5,10] There are many factors still poorly understood, not least of which are the reasons why there are orders of magnitude difference between the sensitization produced by different rare-earth ions in the same host. Current discussions recognize that the inclusion of impurity ions introduce lattice distortions and also need charge compensators. This results in

structural instabilities. One consequence of which is that the rare-earth impurity ions in the dosimeters often associate in pairs or form cluster type sites involving several components (impurities, vacancies, off-axis ions, interstitials, etc.).[11–13] Fortunately, the presence of the narrow emission lines resulting from screened shell transitions of rare-earth impurity ions offers a probe of the geometry and crystal field near the impurity sites so, in principle, high-resolution spectroscopy of the rare-earth-ion transitions can reveal small wavelength shifts associated with changes in the site structure. More dramatic changes in the emission pattern may occur as the result of changing the fraction of single, pairs, or higher-order rare-earth cluster sites, by altering the dopant concentration or applying thermal treatments.[14–16] Spectral analysis of the various TL glow peaks clearly indicates where rare-earth ions are active in the luminescence, but even when just broad-band spectra are recorded the emission bands can differ significantly between the glow peaks[17] linked to different defect types. For radiation dosimetry the variations are undesirable, but for more fundamental studies of the lattice imperfections the spectral changes offer useful data. Because of the inherent complications of interpretation of the majority of thermoluminescence studies using rare-earth activators (i.e., with compensators and impurity-intrinsic complexes), the present study was undertaken to benefit from the simpler defect situation which is expected for rare-earth-doped LaF_3, where the trivalent impurities should merely substitute for the La ions. Thermoluminescence data have excellent sensitivity and are widely used to separate the charge detrapping processes from different imperfections as a function of temperature. In this study the power of the technique is greatly increased by inclusion of spectrally resolved TL, a method which is much less widely used for reasons of experimental difficulty.

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II. EXPERIMENTAL DETAILS

The RE-doped lanthanum fluoride samples were obtained from Optovac with nominal dopant levels from 0.1 to 2.0 % of the dopant fluoride. The original crystal boules were sectioned for the TL measurements and it was noted that in many cases the dopant, and trace impurity levels, varied between successive slices. A ''high-purity'' sample was provided by Professor Rutt of Southampton University. The various crystals were grown with nominally only one rare-earth dopant but, as will be noted, several crystals were contaminated by other rare-earth ions. This was most apparent for the heavily doped samples. Thermoluminescence was primarily made at low temperature in the range 20 to 300 K following x-ray excitation at 20 K, but some data were also collected for irradiations above room temperature. The low-temperature heating ramp of a Cryophysics closed cycle cooler was driven by a Lakeshore controller. Heating rates were typically 6 K/min. Above room temperature a heater strip was controlled by a Eurotherm controller at rates of 50 to 150 °C/min. A key feature of the analysis was the spectral information and this was obtained on a high sensitivity spectral apparatus with f/2.2 optics.[18] This employs two Photek (formerly ITL) imaging photomultiplier tubes giving UV/blue (200–440 nm) and blue/green/red (380–800 nm) coverage, respectively. The wavelength dispersion is achieved by grating spectrometers blazed for each region. All spectra were corrected for the wavelength dependent efficiency of the double spectrometer system. Two experimental artifacts are noted. First, as collected, the data frequently display a mismatch intensity step at the interface (420 nm) between the two systems. Second, the low-detection efficiency for wavelengths longer than 780 nm can result in a false signal from second-order diffraction of strong emission near 390 nm and these signals have not been suppressed. The matching step has been minimized by scaling for most of the figures shown here, but the second-order signals shown above 780 nm remain, however, for the present purposes they do not introduce any interpretive problems.

The TL spectra system is designed for weak light collection, not high resolution, such that resolution is ∼5 nm. A major benefit of this wavelength multiplexed method of data collection is that an entire spectrum is recorded every second. Thus in principle, any differences in emission spectra as a function of temperature can be directly observed with a temperature resolution of ∼0.25 K. This proved to be highly desirable in the present work, and for example some of the smaller temperature differences between emission lines from different RE ions would probably have been overlooked with scanning monochromator spectral recording of the TL, even though a scanning system might have offered higher spectral resolution. The temperature measurements, in absolute terms, are limited by experimental factors such as the variations between samples as the result of different thermal coupling between the control stage and the sample, and as a result of temperature gradients through the samples.[19] At the low heating rates, and by using thin samples, these variations were minimized to typically about one degree at low temperatures.

III. RESULTS AND COMMENTS

The TL of pure and RE-doped LaF_3 at low temperatures is relatively intense and comparable glow curves were recorded for nominally pure material from different sources. In thermoluminescence terms the highest purity material came from Southampton and this gave a small phosphorescence decay near 20 K and two intense glow peaks near 90 and 128 K. The spectral image of these features is shown in Fig. 1(a) and wavelength slices of the spectra are displayed in Fig. 1(b). The wavelengths of the peak maxima at 20, 90, and 130 K were near 305, 328, and 319 nm, respectively. Figure 1(c) shows that at higher temperatures there were other glow peaks with a totally different spectra which are characteristic of rare-earth dopants. Note that the intensity scales of Figs. 1(a) and 1(c) are very different, by ∼1000 times. Figure 1(d) records wavelength slices at 205 and 270 K from which it is apparent that different narrow line features, and hence different rare-earth impurities, define the spectra. Overall the figure indicates that the TL spectra can reveal trace impurities of rare-earth ions and even the best samples are contaminated. Other nominally pure samples showed weaker, but still strong, main peaks, plus additional UV features below 90 K, and longer wavelength line features above 130 K.

The addition of rare-earth impurities has several effects which are immediately apparent in Figs. 2(a)–2(f) for the dopant concentrations of ∼0.1 to 0.3 % for the sequence of lanthanides of Pr, Nd, Sm, Tb, Ho, and Er. In all cases the original broad band intrinsic features are retained but greatly suppressed in intensity. The dopant ions appear to be efficient recombination sites since there are line-type emission bands which are characteristic of the well documented transitions of the dopants. Above the 130 K region these are the predominate source of TL emission. For the glow peaks nominally at 90 and 128 K the dopants are in competition with the intrinsic bands. At lower temperatures some lines are apparent, not in the form of glow peaks, but as athermal emission of relatively constant density [e.g., Fig. 2(c) for Sm dopants]. The intensity scales are in arbitrary units but are consistent for the spectrometer and data sets. Neutral density filters were used during recording and their transmission factors have been included in the calculations of the intensities. It is apparent that the intrinsic signals for the Pr, Nd, and Ho samples are approximately half as intense as for the pure samples, the signals from Tb- and Er-doped samples are reduced a further 50% and the Sm broad-band signals are the weakest. However, all samples produce comparable brightness per unit radiation dose, if one integrates across the entire spectrum. For these specimens the Er, Tb, and Sm dopants are particularly effective at reducing the intrinsic emission in favor of light generation at the impurity sites.

On increasing the concentration of the dopant ions the spectral components change in a number of ways. In general there is a suppression of the intrinsic signals, as is seen by comparing Figs. 3 and 4 with data of Fig. 2. Signals from high concentration boules of from 1.0 to 2.0 % dopant levels for Pr, Sm, Tb, and Er are shown in Fig. 3. For the Pr dopant, Fig. 3(a) the spectral components are nominally the same as for Fig. 2, but there are small changes in their relative intensities. The number and relative intensities of the higher temperature parts of the glow curves obviously differ, and on closer inspection there are many more features apparent even in the 90 to 150 K region, as shown in Fig. 5(a). Below 90 K
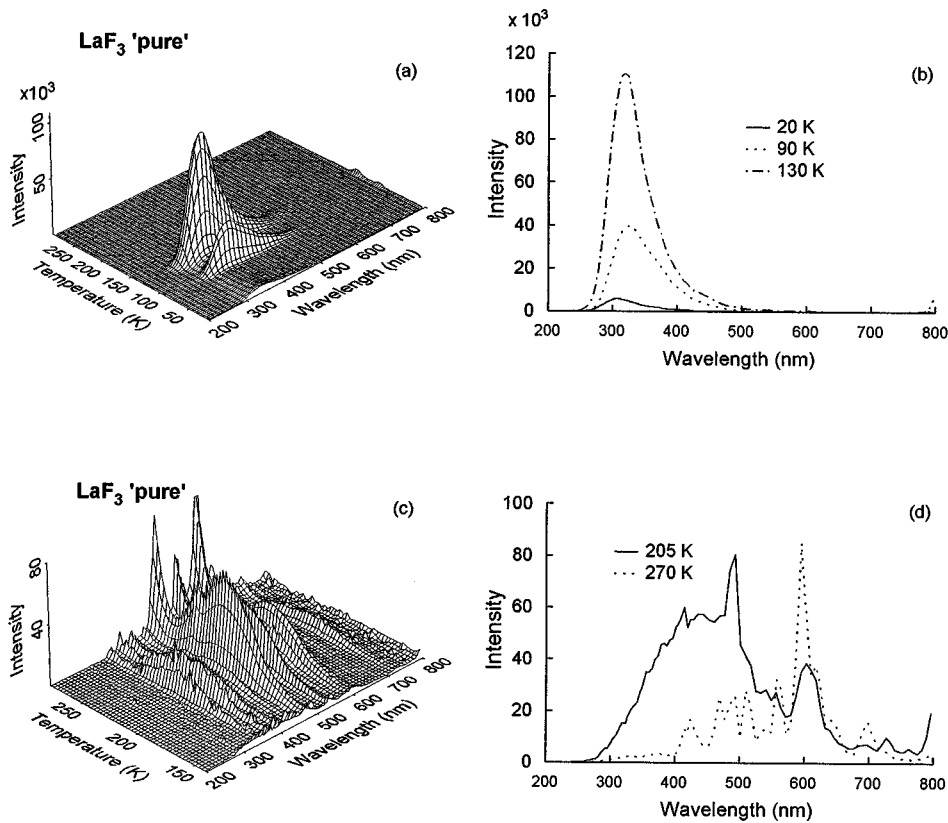
FIG. 1. Low-temperature wavelength multiplexed TL spectra of a sample of "pure" LaF$_3$ after x-ray excitation at 20 K. The heating rate was 6 K/min. Spectra were recorded at 1 sec intervals and are corrected for the performance of the system. (a) An isometric view of the data set, (b) spectral slices taken at 20, 90, and 130 K, (c) a magnified view of the high-temperature signals, and (d) spectral slices at 205 and 270 K.

the athermal signals are more pronounced. Figure 3(b) displays the TL from LaF$_3$ with 1.0% SmF$_3$ but because the intrinsic signals are so weak relative to those from Sm the data are shown with a 10^3 times higher magnification for the UV/blue region. This magnification emphasizes the presence of two further TL peaks with broad emission bands near 160 and 270 K. Comparing Figs. 3(b) and 2(c) for the Sm peaks near 200 and 250 K it is noted that these have inverted in terms of relative intensity, as have those near 90 and 128 K. A highly doped NdF$_3$ sample was not available for comparison with Fig. 2. The Tb data of Fig. 3(c) has also required higher magnification of the UV/blue signals, where the data resemble the Sm pattern of peaks. Similarly the intensities of the lower temperature Tb glow peaks are more equal than for the lower concentration data of Fig. 2(d). Finally, Fig. 3(d) provides TL data for the doping with 2.0% ErF$_3$. The signals at 90 K and lower are enhanced relative to those near 128 K and further strong peaks emerge at higher temperatures. The only sample of Eu was at the 0.5% dopant level and this is included on Fig. 4 with various examples of nominally 1.0% Ho doping. High concentrations of holmium produce data, Figs. 4(c) and 4(d), which show the pattern of raising the intensity of the 90 K peak relative to that of the one near 128 K. At higher temperatures the spectra of the different peaks clearly differ, an effect which is apparent from Figs. 3 and 4(a), but as will be discussed later, some of the lines can be attributed to a second dopant of Pr. These differences in spectra as a function of temperature, and the variations between various samples from the Ho boule are emphasized by the contour plots shown in Fig. 6. Because of the large dynamic range of signal intensities the contour maps are of the logarithm of the intensity. Figure 6 contrasts the log contour

maps of two 1% Ho-doped samples [Figs. 6(a) and 6(b)] with the lightly doped 0.1% Ho boule [Fig. 6(c)] and a 1% Pr-doped sample [Fig. 6(d)]. In all cases there is some evidence of cross contamination but the majority of the Ho and Pr lines are separable.

The mixed Ho/Pr samples show high-temperature glow peaks via emission bands that are almost entirely characterized by only one or other of these two elements. To assess if this is a feature of the TL process or a temperature-dependent anomaly of the emission efficiency several experiments were made using the temperature ramp whilst continuously exciting with x rays. Figure 4(b) shows one such RL/TL contour plot. All the line features, from both dopants, persist at a roughly constant intensity level throughout the temperature range from 20 to 300 K. However, because this is a dynamic situation there are TL signals superposed on the constant RL background. Hence the RL stimulated Ho and Pr emissions are not temperature sensitive and separation of high-temperature glow peaks by emission spectrum is a phenomenon related to the TL traps. The figure also indicates a strongly temperature-dependent intrinsic background near 310 nm which falls smoothly in intensity from 20 K down to only trace signals by ~200 K.

The data are representative of the general trends seen in the RE-doped LaF$_3$, despite the fact that the original boules were nonuniformly doped. Whilst the isometric plots indicate considerable complexity in the TL spectra at various temperatures, they require processing into contour maps and spectral slices taken at fixed temperatures or wavelengths, in order to emphasize and quantify the changes between the glow curve patterns. Figure 7(a) presents four examples of spectra from a 1.0% Ho-doped sample, for the peak regions
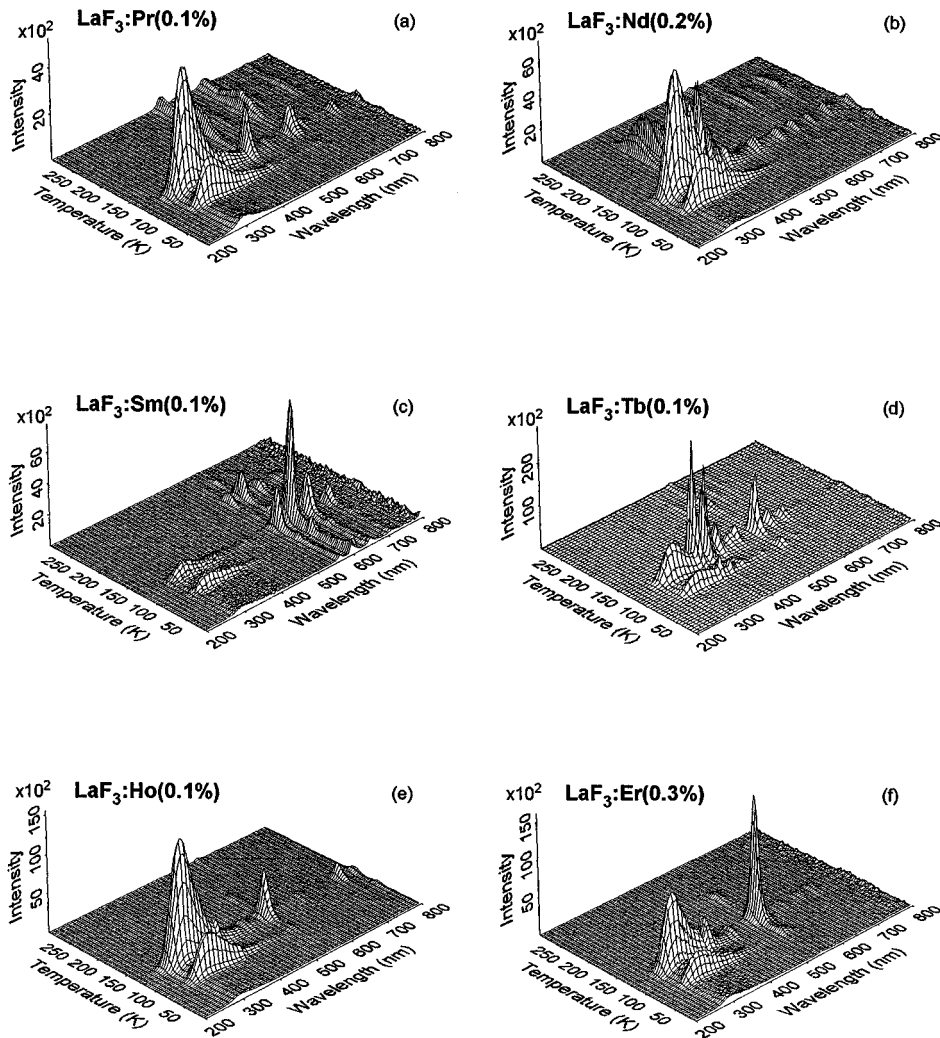
FIG. 2. (a)–(f) show isometric plots of the TL spectra for low-dopant concentrations in the range of ~0.1 to 0.3 % for the sequence of lanthanides of Pr, Nd, Sm, Tb, Ho, and Er.

at 85, 125, 190, and 225 K. The latter spectral slices have been magnified by 3 and 10 times because of the large dynamic range in signals. The figure emphasizes that the emission pattern differs for the various glow peak regions. A further example, Fig. 7(b) contrasts the radioluminescence spectra at 20 and 280 K. In RL the 20 K emission contains not only the intrinsic emission in the UV but also a set of line features from Ho, and trace impurities, whereas at 280 K only the RE signals are intense. The situation is in fact not quite so straightforward as the relative intensities of the RE line features altered with temperature, some lines have become displaced (e.g., from 500 and 560 nm to shorter wavelengths), whilst others have appeared at the high temperature (at ~620 and 740 nm). The line changes may reflect the results of several RE dopants.

Finally, Figs. 7(c) and 7(d) are particularly instructive as they plot the conventional type of TL curve abstracted from the isometric data set for a variety of wavelengths and the two concentration levels of Ho of nominally 0.1 and 1.0 %. The wavelengths chosen are at 310 nm for the intrinsic signals, whereas the 761-nm data are mostly from Ho and 486 nm is from Pr sites. The strong Ho signals near 650 nm match those at 761 nm but, as indicated in Fig. 5(b), the TL slices of the contour maps for the 550 maximum disguise overlapping signals which differ in their temperature dependence. Overall, not only do these curves differ in terms of the number of glow peaks, but more significantly the peak positions are variously shifted in temperature, with clear changes between the intrinsic, Ho and Pr peak temperatures for the nominal 128 feature. Particularly from the high Ho concentration sample it is apparent that for a signal near 550 nm there are at least three overlapping glow peaks in the 130 to 150 K region.

Experimental systematic problems of differences between the recorded heater stage temperature and that of the emitting sample are inevitable in TL because of difficulties of thermal contact and heat conductivity in insulators. Such differences are reduced for low heating rates (e.g., 6 K/min) but nevertheless some sample, and run, dependent *absolute* errors are inevitable. However, the detection of temperature *shifts* between the emission signals recorded here between intrinsic and dopant sites separated by different wavelengths are both real and reproducible using this wavelength multiplexed system.

Some measurements were made of the TL above room temperature. In these examples the emission bands were almost totally characteristic of the dopant RE ions. Indeed, this was also the case even for many ''pure'' samples. An example of the high-temperature TL is given in Fig. 8. Note
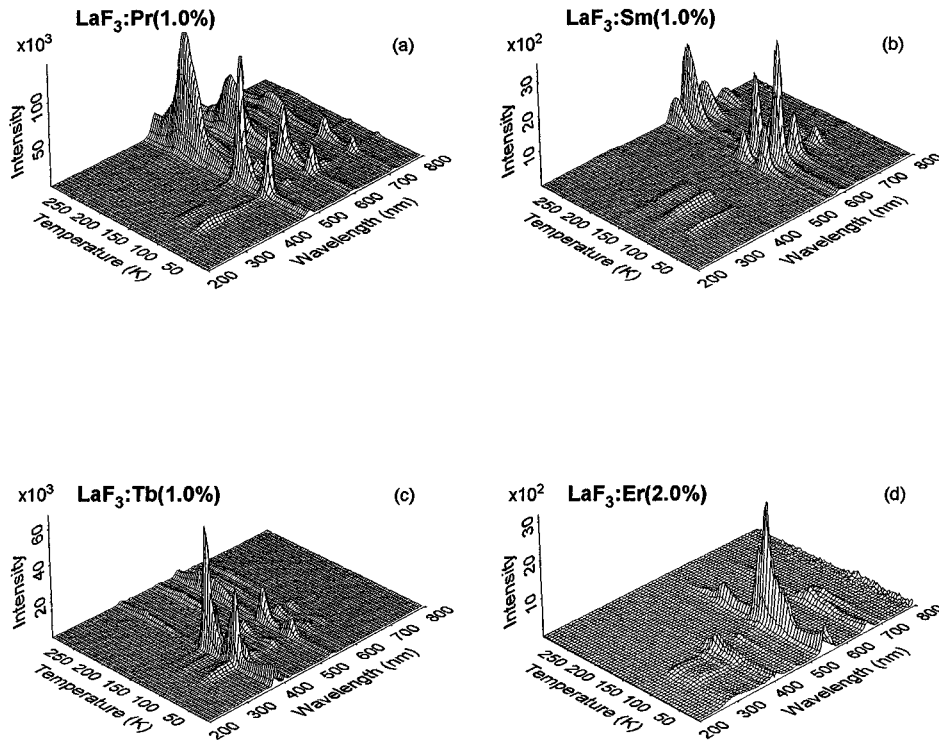
FIG. 3. TL spectra for heavily doped LaF_3 crystal with (a) 1.0% PrF_3, (b) 1.0% SmF_3, (c) 1.0% TbF_3, and (d) 2.0% ErF_3. The UV/blue signals are magnified by 10^3 times for the Sm data and by 20 for the Er results.

that the glow peak intensities are several orders of magnitude weaker than those recorded at lower temperature.

IV. DISCUSSION

Intrinsic emission spectra. The low-temperature TL of undoped lanthanum fluoride crystals is typical of that observed in many halide crystals and glass (CaF_2, BaF_2, NaF, LiF, ZBLAN, etc.) in that it consists of just one or two glow peaks, below about 150 K, with emission bands in the near UV region of the spectrum. The component luminescence signals can often be stimulated by other routes such as radioluminescence or optical band gap excitation. This general pattern of behavior can be interpreted as the result of electron hole recombination which is, either directly or indirectly, the result of the formation of an excitonic type state with a long
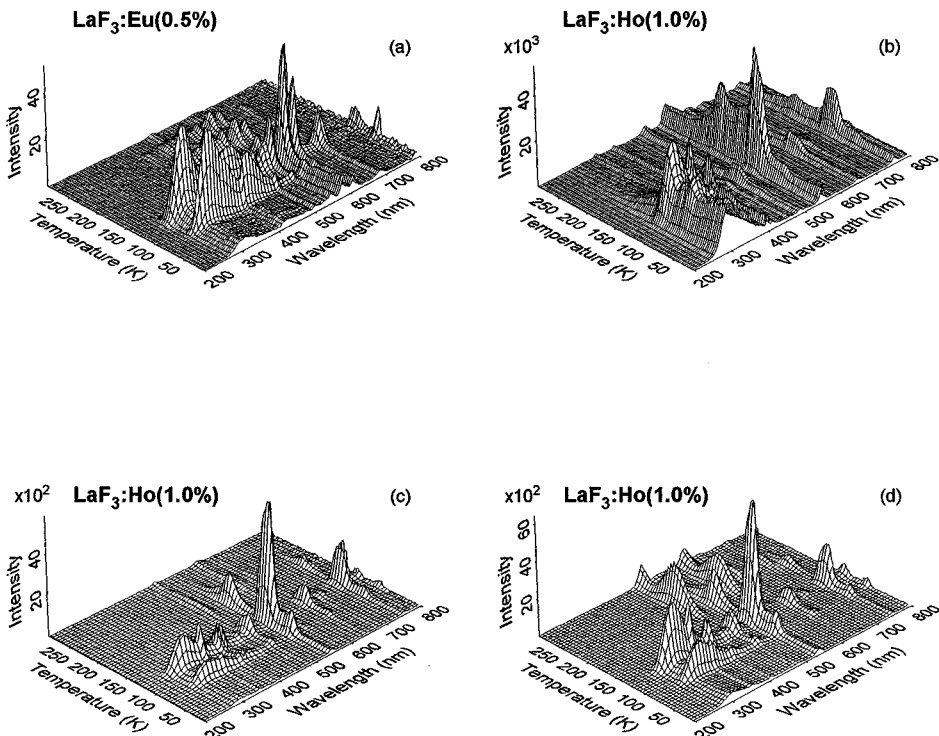

FIG. 4. Examples of spectra from more heavily doped LaF_3 crystals. (a) contains 0.5% Eu, (b)–(d) are all for 1.0% Ho doping. Note, however, that there is some Pr within these Ho samples. Data of (a), (c), and (d) are for TL whereas curve (b) is for a combined RL/TL excitation.
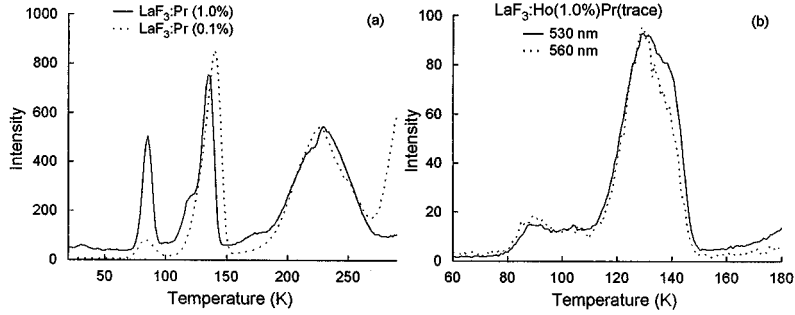
FIG. 5. (a) Examples of TL slices from data sets for Pr-doped crystals. The slices were chosen at 478 nm. The intensity of the signal from the 0.1% sample has been multiplied by 4 times for ease of comparison of the signals. (b) Normalized slices for a Ho-doped sample from the region of the 550 nm peak, for the 530 and 560 nm sides of the peak. The contour map of this example is shown in Fig. 6(b).

lifetime. Relaxation of the exciton then provides broad emission bands corresponding to singlet or triplet states. Since the central feature is the relaxation of the bound electron-hole pair the emission energy is only slightly modified by the dielectric constant and the details of the local lattice structure. Hence many wide band gap insulators, oxides as well as halides, have characteristic emission decay of excitons, or electron-hole recombination at defect sites, that is apparent in the near UV/blue spectral region. For the alkali halides commonly observed defects are the V_k or H centers which involve either self-trapping of a hole on a pair of adjacent halide ions (V_k), or a hole trapped on the larger unit of four halide ions spread over three lattice sites (H).[12,13,20,21] The thermal stability of these structures in the alkali halides is such that they typically dissociate in the temperature range of 80–100 and 130–150 K (e.g., as in LiF for the H and V_k

centers). Detailed examination shows that the temperature for dissociation, and the precise emission spectrum are sensitive to impurities associated with the lattice sites. In crystalline and glass oxides, such as silicates, silicate fibers, sapphire, MgO, or BGO, the recombination sites are normally discussed in terms of variants of oxygen vacancy centers, however, they behave similarly in that the emission bands are sensitive to association with impurities. For example, luminescence signals shift through the 380 to 500 nm region in silicates such as quartz, on varying the dopant ions from H to Ge or Al.[22,23] Glow peaks with these intrinsic type emission bands are variously dominant to about 150 K.[24] At higher temperatures in all these examples the signals are much more strongly influenced in temperature and spectra by the impurities and stable defect complexes. These well documented examples are closely analogous to the present observations
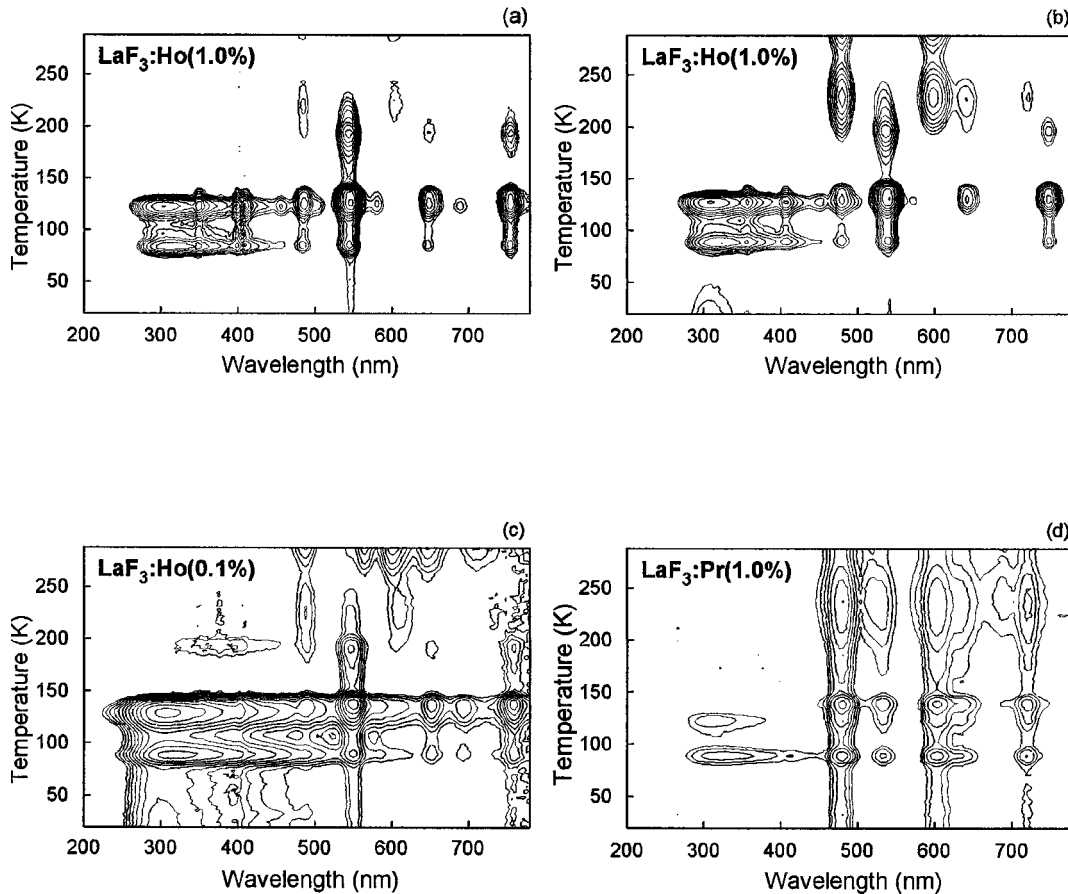

FIG. 6. Logarithmic contour maps of the TL from (a) and (b) 1.0% Ho-doped samples, (c) 0.1% Ho, and (d) 1.0% Pr.
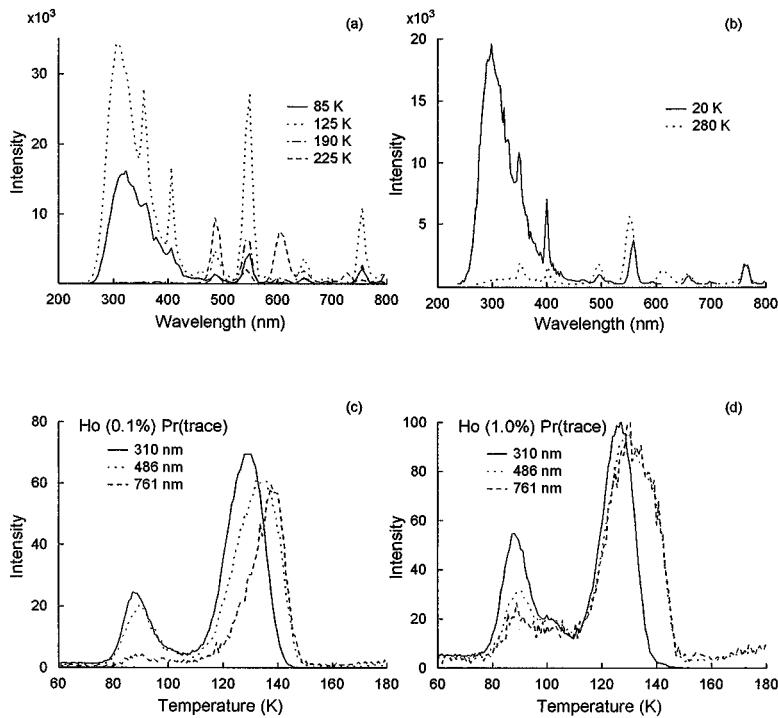
FIG. 7. Emission spectra slices taken for Ho samples. (a) during TL of a 1.0% sample, (b) during RL of a 1.0% crystal. Sets of glow curve slices taken at three wavelengths showing intrinsic behavior at 310 nm, Pr emission at 486 nm, and Ho emission at 761 nm for (c) 0.1% Ho with Pr and (d) 1.0% Ho with Pr.

of LaF_3 and the conclusion is that the broad emission bands near 300–400 nm which show glow peaks near 90 and 128 K are also the result of electron-hole pair recombination at intrinsic halide lattice sites. The more speculative, but not unreasonable, suggestion from the comparisons is that the lower temperature band is from the LaF_3 equivalent of a fluorine H center and that at 128 K is from the V_k self-trapped structure. The presence of a fluoride type interstitial center (the I center in alkali halides) may be proposed as a first guess as a model for the signals at 20 K but currently the data are experimentally limited for LaF_3 as they commence at too high a temperature to record this feature as a resolved glow peak.

Linkages between trapping and recombination centers. It is tempting to draw similar conclusions from the LaF_3 data as have been made from the very similar type of observation recorded for the case of the BGO.[25,26] The common features are (i) in pure material there is broad band emission typical of relaxed electron-hole pair recombination, (ii) with increasing RE content the intrinsic emission is suppressed in favor of the RE emission, (iii) the temperature of the intrinsic process alter with ionic radius of the dopant, and (iv) at higher temperatures and high dopant levels the glow peaks vary and emission is almost entirely via the RE transitions. For LaF_3 exciton trapping, either by migration of free excitons, or via the presence of H- or V_k-type centers can generate the two intrinsic glow peaks with strong broad UV/blue emission bands. Small impurity sites in alkali halides introduce distortions which can favor charge trapping at the expense of perfect lattice sites. Hence, by analogy, a competition between intrinsic and impurity sites will favor the V_k- and H-type centers in LaF_3 which are in close proximity to the RE dopants, which are all smaller than the host lanthanum ions. The impurity stabilized sites will (as for H or V_k centers in alkali halides) dissociate at higher temperatures than in the perfect

lattice. The fact that not only do the glow peaks move with dopant inclusion, but also that the emission spectrum is characteristic of the impurity, implies that the trapping and recombination sites are spatially linked. In other words, the impurities distort the lattice to stabilize a neighboring V_k-type center, and when this thermally dissociates, the energy release drives the excitation of light from the RE dopant stabilizer.

Effects of ionic radius on the lattice sites. Comparison with the low-temperature TL data for RE-doped LaF_3 and BGO ($Bi_4Ge_3O_{12}$) data[26] shows considerable similarities. In the BGO results there are broad band emissions from pure material (ascribed to electron hole recombination at vacancy sites) but addition of rare-earth dopants quenched these signals above ~ 75 K and replaced them with TL emission characteristic of the rare-earth dopant. For the high-temperature glow peaks the precise glow peak temperatures deviated from that of the pure material as a linear function of the ionic radius of the dopant ion for RE ions which have radii smaller than the Bi^{3+} ion, which they were assumed to replace in the
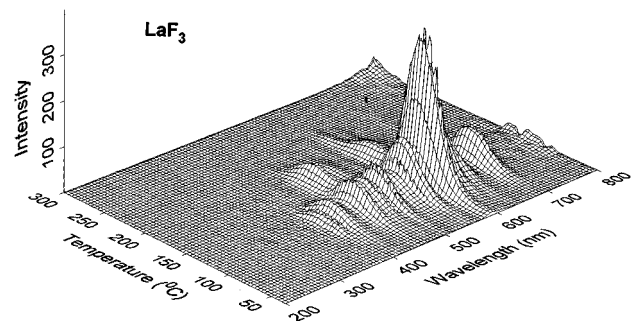

FIG. 8. An example of the high-temperature TL for nominally pure LaF_3.

lattice.[25] No obvious pattern was apparent for oversize RE ions. The activation energies were the same in each case and the peak temperature variation could be described as a result of mass-dependent changes in the vibrational frequency of the defect site. More recent data for $CaSO_4$:Dy:Tm (Ref. 30) also indicate temperature shifts of $\sim 10\,°C$, between the emission of nominally the same dosimetry glow peaks recorded at Dy or Tm emission wavelengths. These differences in peak temperature are perhaps more surprising as they are apparent for the glow peaks above room temperature near 220 °C. For the LaF_3 the movement of the ''128 K'' glow peak is much greater than for the BGO and $CaSO_4$ examples and is as much as 13 K in the case of Er where the peak occurs at 141 K. Inspection of the entire set of data from numerous runs emphasizes a consistent pattern of peak shift with dopant ion. In view of the known tendency for pairing and clustering of RE dopants in many crystals, the simplest analysis is attempted for the lightly doped samples (e.g., with TL as seen in Fig. 2). For the higher dopant levels (Figs. 3 and 4, etc.) additional glow peaks or shoulders appear which may result from RE-intrinsic complexes, or at least in the case of the Ho samples which are contaminated with Pr, from Ho-Pr complexes. The presence of a wider range of RE defect sites is inevitable at higher RE-doping levels since at high dopant concentrations there will be increasingly greater formation of impurity pairs or clusters from statistically random lattice dopants; as well as preferential strain induced impurity pairing. The main advantage of LaF_3 as the host for the RE dopants is that charge compensators are not required, so that the large lattice distortions from a combination of impurity and compensator are avoided. Strain induced concentration pairing is well documented for Cr luminescence changes in the ruby structure of Al_2O_3:Cr where new Cr pair emission bands are generated. In the TL radiation dosimeters of CaF_2:RE, $CaSO_4$:RE, $CaCO_3$:Mn, or MgB_4O_7:RE the effect of raising the dopant levels is to rapidly quench the luminescence efficiency for dopant concentrations above about 0.1%. This same pattern of behavior has already been mentioned in detailed spectroscopic studies of the energy levels of Pr^{3+} in LaF_3 where the changes have been reported as evidence for the formation of impurity ion pairs and clusters.[27,28] For LaF_3 the interpretation of lattice distortions on the defect stability of adjacent V_k-type sites may therefore be simplified by concentrating on the effects at low-dopant concentration.

The pattern of glow peak shift can be partially rationalized by a plot of the movement of the nominal ''128 K'' peak relative to the intrinsic signal at 310 nm as a function of RE ionic radius, as is shown in Fig. 9. It is recognized that the concept of an ionic radius is very simplistic, but nevertheless in order to summarize the large amount of data on the shifts in glow peak temperature with RE-doped LaF_3 such a parameter offers a first-order simplification to reveal trends. The spectra for the samples doped with Er, Tb, Nd, Eu, and Sm are clearly identifiable with the chosen dopant but for some of the boules containing Ho or Pr there appears to be cross contamination, and both boules contain traces of the other dopant. This is in fact fortuitous, as they offer within a single sample unequivocal evidence that the glow peak temperatures from the different dopants are displaced. From the boule with a low-Pr concentration the glow peak position
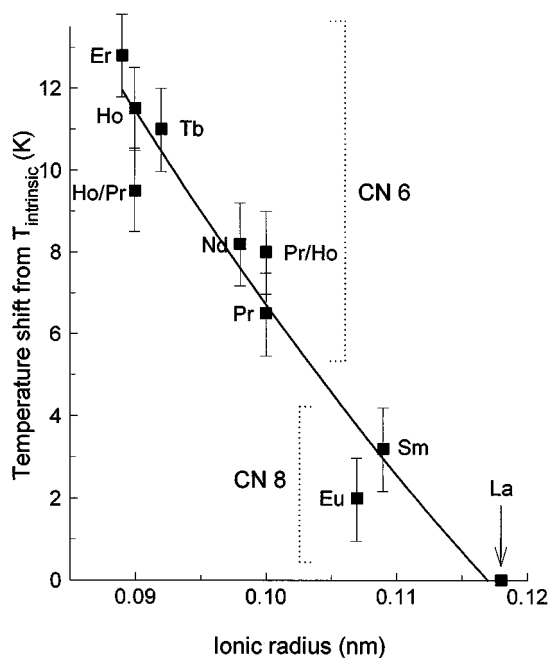

FIG. 9. A plot of the temperature shifts for the RE emission signals relative to the intrinsic glow peak near 128 K as a function of RE ionic radius. Note for the ions of Er to Pr the radii are for sixfold coordination but for Eu, Sm, and La the eightfold values are used (see text). Also note that the Ho/Pr and Pr/Ho values refer to cross contaminated samples.

occurs near 134.5 K, but in double doped samples the Pr peak position is increased to ~ 136 K. All the Ho samples were contaminated with Pr to some extent. A few samples showed weak contamination and the larger temperature shifts for these examples are indicated on Fig. 9 just as Ho. However, inspection of many sets of data from these samples suggests that the composite Ho/Pr glow peaks have a maximum value which often occurs at too low a temperature relative to the other data. The influence of double doping seems to lower the value for Ho/Pr peaks and raise that for the Pr/Ho signals, therefore one may infer that the dopant rare earths are not necessarily entering the LaF_3 lattice as single dopants, but rather as larger units or clusters. Association of two different dopants would then lead to the displacement of signals from those expected for singly doped material. However, if only simple Ho-Pr pairs were involved then the peak would occur at the same temperature in the Ho/Pr and the Pr/Ho cases. This is clearly not the case so it either implies that the two components are not equally effective in the TL site complex, or that more than two impurities are required and the involvement of say Ho-Ho-Pr would then differ from a Pr-Pr-Ho site.

It is noticeable that the Eu data do not fit particularly well on the trend described by the other examples and on closer inspection the Eu data are seen to be even more difficult to interpret since there are quite different temperature shifts for the various Eu transitions. To some extent this effect is seen in several of the heavily doped samples and, as already mentioned, the relative intensities of the lines from the same dopants often alternate between glow peaks. Such variations may be understood in terms of the electron orbital patterns

where the more extensive orbits (typically from the higher excited states) will interact differently with neighboring ions and, although all the doped crystals showed line spectra which are attributed to trivalent RE-dopant ions, this is not a guarantee that the RE recombination ions occupy identical site symmetry in the lattice. The observation that different transitions emit at slightly different temperatures offers some indication as to how the rare-earth ions might become excited within the defect-RE complex. Simple configurational coordinate diagrams of the complex will have branches which differ for charge transfer into different excited states and intuitively one might expect that the higher-energy states may involve longer-range interactions and so would allow charge transfer at slightly lower temperatures. Such an effect has been noted earlier in the TL of calcite where at high temperature the Mn line emission of higher photon energies (blue lines) occurs at slightly lower temperature than for the lower levels (orange emission lines).[28]

It is also noted that there is considerable disagreement in the literature regarding the precise structure of LaF_3. It is generally quoted as being of a Tysonite structure[29] but there are small differences and conflicts in interpretation which may result either from twinning or variations between different conditions of sample preparation. Nevertheless, the fluorine has been shown to have four chemically different sites and the lanthanum has three alternative sites. Consequently the addition of rare-earth dopants and the formation of directly associated V_k- or H-like halogen defects offers considerable scope for diversity, and indeed not all RE ions may have the same preferred substitutional site. This possibility is reflected in the construction of Fig. 9. In order to plot the displacement of the ''128 K'' glow peak as a smooth function of the sequence of RE ions in the data on Fig. 9 it was necessary to use the ionic radii of Er, Ho, Tb, Nd, and Pr cited from tables for a sixfold coordination number. These values define a clear pattern of temperature shift with ionic radius. However, in order to also include the data for Eu and Sm the latter ions are included with radii appropriate for eightfold coordination. An alternative of 12-fold coordination was discarded since these values would be much larger at ~0.125 nm. Europium and samarium ions frequently behave somewhat differently from the remainder of the other rare-earth ions, for example, they routinely show divalent properties, but the use of ionic radii of divalent ions seems inappropriate, since the spectra are indicative of trivalent sites. It should be noted that the trend line of Fig. 9 includes a zero temperature shift for the pure lattice for the La^{3+} radius in the eightfold coordination. Alternative estimates of 6 or 12 coordinated La ionic radii were considered but one notes that the radius of the six coordinated La is much smaller at ~0.1 nm, and the 12-fold value is much greater. Overall, the need to use two different types of RE local lattice configurations to simplify the pattern of the TL peak shift suggests that there is the strong possibility that two of the alternative types of La site are involved, and doping with RE ions can be selective in the way in which they become occupied. With these caveats, a pattern of glow peak shift with ionic radius has emerged.

Data for highly doped material is more difficult to interpret because of the presence of additional TL peaks and shoulders. The figures demonstrated the presence of different trapping sites as a function of doping level. These may be from pairing, clustering, or just general lattice distortions caused by the high dopant concentration since with a 1% dopant level a uniform distribution of the impurities would result in an average impurity to impurity distance of only ~5 metal ions. Hence, pairs and clusters, etc., are certain to exist. To some extent these may be the origin of the subpeaks in the 130 to 150 K region, or may be the basis of the defects which produce the glow peaks at higher temperatures. It must be recognized that while increasing the dopant concentration will add new types of defect it will also quench the TL emission intensity and reduce the concentration of isolated defect sites. For improved separation of single and higher order impurity effects a study is required with a much wider range of rare-earth dopant concentrations. Experimentally it should not pose detection problems even for levels down to ppm dopant concentrations as the TL signals are intense and were in fact attenuated in the present work.

Models for the defect sites which cause the higher temperature glow peaks, from 150 to 300 K, are problematic. The fact that the peak temperatures differ between the differently doped samples implies that the charge trapping sites are not independent of the impurity ions. If the dopants merely introduced a lattice strain and stabilization of common defect structures then one might expect a pattern of peak shifts related to the size of the rare earth (as for the 128 K peak) but no such pattern has yet emerged. The double doped specimens containing Ho and Pr are particularly surprising in that, as seen from Figs. 4, 6, and 7, there is a complete separation of glow peaks by emission temperature with for example an intense Ho glow peak near 190 K and a totally independent Pr peak at 230 K. Stabilization of the same defect structure is feasible but seems unlikely since the sequence of peaks are in the opposite sense to those seen for the 128 K variants. The only clear feature is that the absence of significant emission from the other dopant means that the entire TL mechanism for these glow peaks must be operating within a closed complex in which the emitting rare earth is an integral part of the structure. The failure to see intermediate variants in which both Ho and Pr signals are emitted further suggests that Ho-Pr pair sites are not readily formed.

In more general terms the classic model of TL, initially modeled in terms of isolated single lattice site defects, assumed the charge trapping site and the recombination center are totally independent. Whereas, for the examples cited here for LaF_3, the earlier work with BGO, as well as very recent data for $CaSO_4$:Dy:Tm (Ref. 30), all suggest that independent site models are not appropriate for these examples. Instead, one must consider that a dominant process in TL is driven by charge or energy transfer between different parts of a single complex defect center involving a number of lattice sites within a single ''point'' defect.[8]

Activation energies and pre-exponential factors. For the lightly doped materials, where the glow peaks seem to be relatively cleanly isolated, it is possible to estimate the energy required for stimulation of the glow peak by an Arrhenius plot of ln (intensity) versus $1/T$. This activation energy (E) can then be used to derive a pre-exponential factor (Y) which, for TL is often viewed as a local vibrational frequency factor. Values so obtained are included on Table I and are reliable to ~5%, but this assumes there are no over-

TABLE I. Examples of activation energies and glow peak temperatures in RE-doped LaF_3.

Sample	Pure LaF_3	LaF_3:Sm	LaF_3:Eu	LaF_3:Pr	LaF_3:Pr/Ho	LaF_3:Nd	LaF_3:Tb	LaF_3:Ho/Pr	LaF_3:Er
E, eV	0.232	0.239		0.23		0.234	0.24	0.239	0.214
T_{max} K	128	131.2	130	134.5	136	136.2	139	137.5	140.8

lapping glow peaks. The activation energies appear to be in the expected energy range which, for TL this can often be approximated by the simple estimate of assuming it is $\sim 25kT_{max}$, where k is the Boltzmann constant and T_{max} is the peak temperature and the implied Y value is that of the lattice vibrational frequency. For a 128 K peak the $25kT_{max}$ value is ~ 0.28 eV. There is not a clear pattern of variation in the values for E with the sequence of RE ions and the numbers are constant within $\sim 10\%$. Indeed, a constant value would be expected on a purely classical model in which the glow peak is defined by charge release from a trapping site which is unconnected with the recombination center. For separated trap and recombination sites the emission spectra would be characteristic of the recombination site. However, in the classical model the glow peak temperature, and by definition the pre-exponential factor, would be invariant. This is clearly not the situation here for, as shown in Fig. 9, the peak temperature is a function of the ionic radii of the dopants. If the activation energy is assumed to be a constant at 0.232 eV then the pre-exponential factor Y spans the range from 2.53×10^7 s^{-1} for the pure LaF_3 to 2.06×10^7 s^{-1} for the Er-doped material. There is thus a 25% change in the frequency term required to compensate for the RE-dependent peak shift. On moving through the lanthanide series to increasing mass one would expect that a vibrational frequency involving the RE ion would decrease, hence the glow peaks would shift to higher temperatures. By analogy with the earlier BGO result[25] one should consider if this could be related to the mass of the dopants. The mass changes from La to Er are only from 139 to 167 atomic mass units and, for equal force constants, this would only imply vibrational changes on the scale of $(167/139)^{0.5}$ at most (i.e., a factor of just 10%), which is insufficient to account for the observed glow peak movement. However, if not only is there a mass dependence but also a change in coupling constant because of lattice distortion then the observed 25% change might be explicable.

Despite the uncertainties in the precise mechanism for the peak shift it is still clear that the observed peak movement and emission features can only be generated if the TL process involves a single complex which contains the source of charge release and also the possibility of releasing the energy via excited rare-earth ions. The proposed model of a V_k-like fluoride structure stabilized by the RE dopant, which both self-traps a hole and is directly associated to the RE dopant,

satisfies this condition. The energy associated with the relaxation and annealing of the V_k fraction of the complex can be resonantly transferred to the RE^{3+} part, and hence give the characteristic emission of the dopant. It should be noted from Figs. 2 and 3 that the emission contains relatively energetic photons of up to ~ 3.5 eV.

V. CONCLUSION

The low-temperature data of rare-earth-doped LaF_3 can be interpreted in terms of charge trapping at classical type halogen defect sites, similar to the H and V_k centers of the alkali halides. It appears that such defects are directly linked and stabilized by the rare-earth impurities, and as a consequence, the TL produced during their decay, excites the rare-earth dopant ions and gives the luminescence characteristic of the impurity site. The strong coupling between impurity and the fluoride charge trap results in changes in the glow peak temperature, primarily through a reduction of the pre-exponential factor. The shift in glow peak temperature scales directly with the ionic radii of the lanthanide ions in the lattice, however, this latter simplification is only possible if different rare-earth ions occupy different nonequivalent lanthanum ion sites which differ in their local coordination number. While the ionic radius is a useful guide to estimating the influence of the rare-earth distortions on the lattice and defect complexes, the more subtle changes in relative intensities of the transition intensities and their glow peak temperatures implies that much more detailed orbital effects must be considered. In heavily doped material there is evidence for more complex defect sites which are thought to involve pairs or clusters of impurity ions but the reasons why some glow peaks are specific to a particular dopant are not yet understood.

The interpretation does not immediately agree with those examples of TL which also display thermally stimulated conductivity since in the current model for LaF_3 there would not be free carriers for charge transfer within the sites involving the rare-earth ions. Future work might explore this and also attempt to use more structurally specific techniques such as electron spin resonance and electron nuclear double resonance.

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