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Abstract.   Thermoluminescence from alkaline-earth halides with rare-earth ions shows emission signals from both the host and the dopants. In many cases each glow peak contains a complete set of emission lines from the rare-earth dopant, but in the case of Er in SrF_2 the spectra change significantly with temperature. In part this is interpreted as evidence for a range of erbium sites, and in part as evidence for energy transfer between erbium states. Near 200 °C the conversion between the 545 and 525 nm emission lines follows a thermally activated pattern consistent with the differences in their initial energy states. This pair of transitions define more glow peaks than signals from the other Er lines. Spectrally analysed recording of the thermoluminescence is thus essential to separate the closely spaced glow peaks.

1. Background

Rare-earth ions are effective activators of intense thermoluminescence in a wide range of insulators and there have been numerous attempts to study the way in which such ions are incorporated into the various host lattices. In many cases analysis of the spectra allows identification of the rare-earth signals and the separation of their characteristic line spectra from the broad-band luminescence which is typical of the host lattice. Several general trends have emerged. For wide-band-gap insulators the host emission is typically centred near 350 to 450 nm, and has been attributed to electron–hole recombination leading to a decay which is similar to a relaxed exciton luminescence. The positions of the luminescence bands are consistently in this range because the screening from the dielectric constants of the host tend to be similar in each case. Rare-earth (RE) ions do not require charge compensation if incorporated at trivalent host sites, as for example in LaF_3 or the Bi site in $Bi_4Ge_3O_{12}$, but compensation is needed in materials such as $CaSO_4$, MgB_4O_7 and zircon. Independently of the charge compensation the rare-earth ions introduce varying degrees of lattice distortion according to their size misfit into the host lattice. The consequences of these two main considerations are that although RE sites might exist as isolated ions when the dopant concentration is very low, there is formation of complexes with several RE ions at higher concentrations. In very heavily doped material there may even be precipitation into new phases.

In materials where the charge-trapping and recombination luminescence sites are closely interacting the RE volume-dependent distortions from the various dopant ions result in

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thermoluminescence (TL) peaks which are temperature shifted according to the rare-earth size. Very clear examples have been discussed for LaF_3 (Yang *et al* 1998, Yang and Townsend 2000), $Bi_4Ge_3O_{12}$ (Raymond *et al* 1994, Raymond and Townsend 2000), $CaSO_4$ (Karali *et al* 1998, 1999, Maghrabi *et al* 2000), MgB_4O_7 (Karali *et al* 1999) and zircon (Karali *et al* 2000). The TL peak temperatures move relative to the intrinsic signals in proportion to the distortions caused by changes in the ionic radii of the RE dopants. The range of TL peak shifts typically spans up to ∼20 degrees as a smooth function of RE radii. In each of these examples the shifts are to higher temperature than that for the intrinsic broad emission band (when an intrinsic signal is also present). The low-temperature TL peaks move to higher temperatures for the smaller ions. Extreme examples of up to ∼200 degree shifts have also been cited for zircon, but these are less well defined and have a more speculative attribution to phase precipitates. By contrast, in the zircon example the higher temperatures are linked to larger ion sizes. A different behaviour is noted for the TL emission spectra of alkaline-earth fluorides (BaF_2, CaF_2 and SrF_2) (Arkhangelskaya 1965, Merz and Pershan 1967, Drozdowski *et al* 1999) which show very minor variations in temperature with RE-ion size, implying that the TL charge-trapping sites are separated from the RE sites.

The emission spectra are sensitive to the crystal field at the RE site and, whilst the line wavelengths appear stable (after resolving component fine-structure lines) (Holgate *et al* 1994, Barriere *et al* 1994), their relative intensities vary quite considerably between different temperature glow peaks and respond to changes in clustering or dopant dispersion. With careful inspection of the temperature dependence of the TL emission lines from a single dopant species a number of the earlier examples also indicate that different emission lines can occur at slightly different temperatures, with changes on the scale of one or two degrees. For all the materials cited so far there are additional smaller peak temperature movements caused by varying the dopant concentration, and/or by thermal treatments which modify the equilibrium between small and larger cluster defect sites. The general interpretation of these small variations is that there are long-range defect interactions between luminescent sites. By contrast, the data presented here describe an apparently highly atypical situation for lightly doped Er in SrF_2 in which the various Er lines define glow curves in the region of 200 °C that appear shifted by up to 30 degrees as a function of wavelength.

2. Experimental conditions

The samples were obtained from Optovac and the unusual results described here came from crystals with 0.01 mol% Er in SrF_2. The experimental system for collection of spectral data during TL has been described many times in previous work (Luff and Townsend 1993, Yang *et al* 1998, Yang and Townsend 2000, Raymond *et al* 1994, Raymond and Townsend 2000). The main feature is that the system has high sensitivity and is wavelength multiplexed so that spectra are recorded in parallel, normally every second. Irradiation was provided by *in situ* x-irradiation and the heating rates used here were 0.25 or 1 deg s^{-1}. Note that intensity matching between the two detector regions can introduce uncertainties in the strength of signals near 440 nm.

3. Results

The TL of x-ray-irradiated SrF_2:Er crystals produces a variety of emission features with broad-band emission near 300 nm and Er line signals spread across the spectrum over the measurement range up to 800 nm. The signals differ greatly in relative intensity with temperature. Figure 1
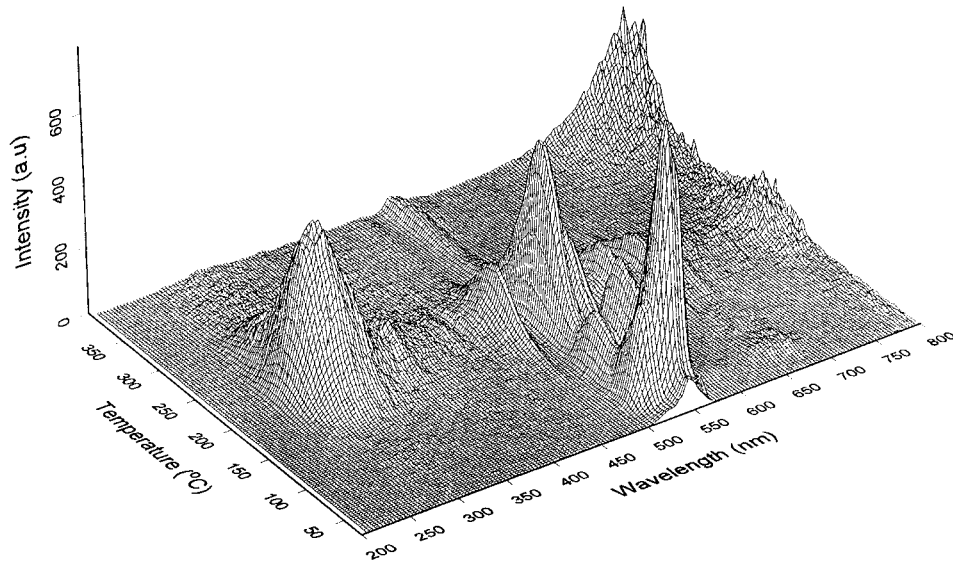
Figure 1. Thermoluminescence spectra obtained from SrF_2 containing 0.01 mol% Er.

displays an isometric plot of the TL above room temperature. Figure 2 presents a contour map of the intensity in the region near 200 °C. The absolute temperature is defined by the heating rate and the pattern moves to lower temperatures by $\sim$25 °C on lowering the heating rate from 1 to 0.25 deg s^{-1}. Different samples show basically the same pattern, although there are differences in the number of broad-band components near 300 nm. Note that most of the
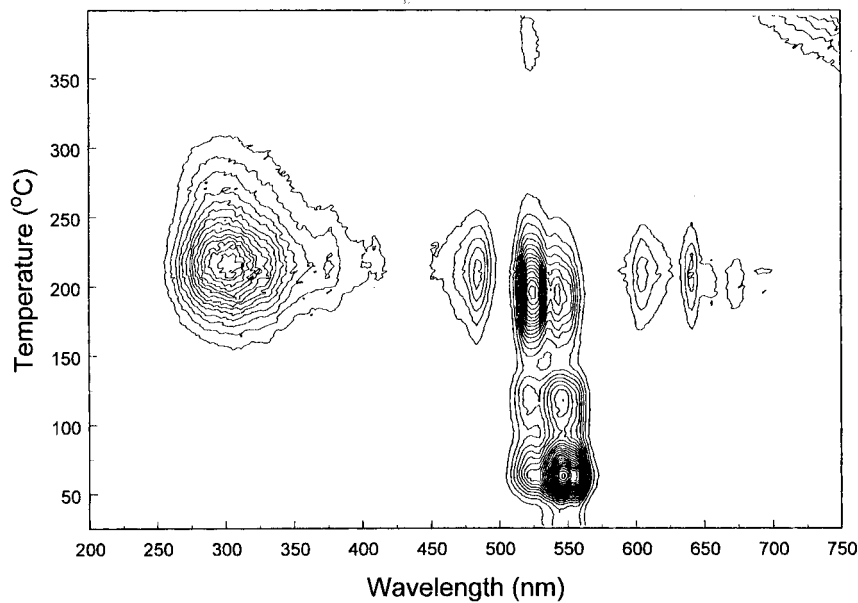

Figure 2. A contour plot of data from figure 1.

features are at lower temperatures than the intrinsic broad-band signal, in contrast to the case for the examples discussed above.

Since in experiments with higher RE concentrations it has been possible to modify the TL response by heat treatments (i.e. to assist cluster formation or to rapidly quench to increase the fraction of isolated ions) some thermal treatments were also carried out on these samples. The experiments included heating to 600 °C for three hours and quenching to room temperature. No major effects were noted for these low-Er-concentration doped samples. However, some minor changes are observed, which include the appearance of new small peaks for the main emission lines and changes in the relative intensity of the glow peaks near 54, 120, 192, 195 °C.

4. Discussion

There are apparently glow peak shifts of up to 28 degrees on recording the signals near 200 °C at different wavelengths. There is no precedent for such an effect from a single recombination site, although rare-earth line shifts on the scale of one degree have been noted in the examples cited earlier. As seen in figure 1, and emphasized strongly with the low-temperature TL measured from 25 K, figure 3, the lower-temperature signals are dominated by emission near 550 nm. Some of the other lines are apparent at the lowest temperatures, below about 120 K. A similar low-temperature pattern is seen for other alkaline-earth fluorides and data for Er-doped BaF_2 are included in figure 4, since this shows rather more clearly the presence of the multiple line emissions, plus intrinsic signals at the lowest temperatures. The balance between the intensities of the 525 and 545 nm Er lines varies with temperature with a decrease of the lower-energy signal (545 nm) at higher temperatures. This changing balance between these line intensities for SrF_2 has been monitored during radioluminescence excitation and it is described by a thermally activated process with an energy of 0.097 eV $\pm$ 0.015 eV. This energy matches the energy difference between the 525 and 545 nm emission (i.e. 0.087 eV)
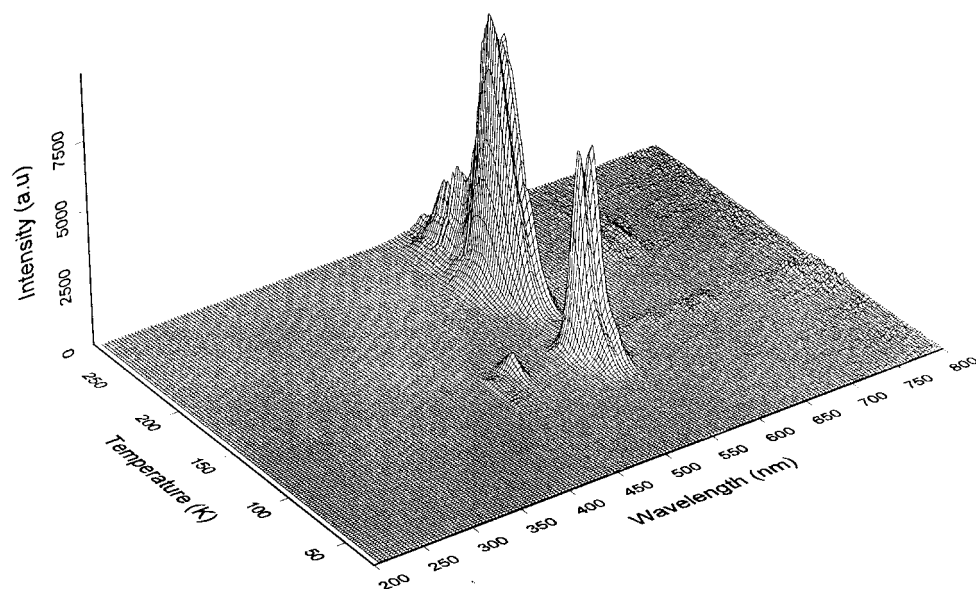

Figure 3. Low-temperature TL from a crystal of SrF_2 containing 0.01 mol% Er.
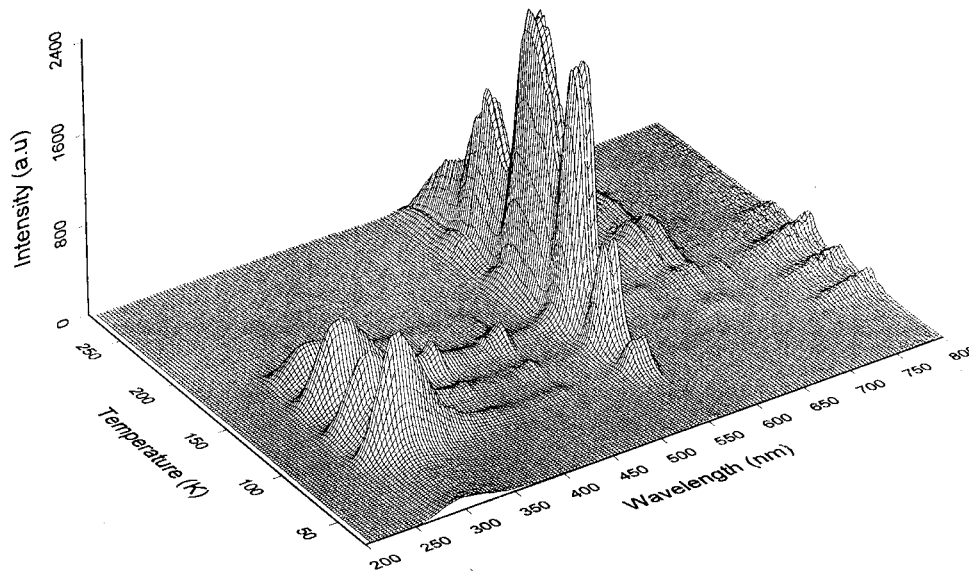
Figure 4. An example of low-temperature TL from 0.1 mol% Er in BaF$_2$.

Overall, such considerations suggest that a possible explanation of the apparent wavelength-dependent peak shift is that there are several overlapping features from different types of defect site. In one case the TL is primarily in the green 525/545 nm region, whereas a second peak is emitted at a multiplicity of wavelengths. Both these peak temperatures differ from the intrinsic emission broad-band UV signals.

In order to test this model experimentally, further samples were used to take TL curves in two steps. In the first part the samples were irradiated and heated to either 185 or 195 °C, then cooled and reheated over the full range to 400 °C. The objective was to test whether any lower-temperature peaks could be removed, or reduced, in the initial heating. Figure 5 compares the wavelength-defined TL curves for the normal TL runs and samples which were subjected to the 195 °C limits. The data are normalized for clarity. For the rare-earth emission lines it is apparent that the first heating step removes a strong signal near 195 °C and then reveals a clean 215 °C signal which is relatively insensitive to the wavelength. The broad bands, corresponding to intrinsic emission, peak at a higher temperature, and almost certainly contain a further component near 275 °C.

An alternative and complementary route to discriminating between the signals is to seek more information about the recombination process from the kinetic parameters. Curve fitting of the original TL data was attempted to determine the kinetic parameters. The results are summarized in table 1. Analyses were attempted using both simple and general order kinetics (Chen and McKeever 1997) and successful curve analysis was achieved in the case of general order kinetics with matching between experimental data and the simulations giving 'coefficients of determination' (r^2) in excess of 0.99 (where $r^2 = 1 -$ [sum of squares due to error]/[sum of squares about the mean]). Such clean fits to the data imply that the activation energy analyses are consistent to within $\sim$0.01 eV. The secondary parameter of order kinetics, b, and the S-value (with dimensions of a frequency factor) are less helpful. The b-value merely underlines differences between the various temperature peaks and indicates that the mechanisms are not direct. The S-parameter is a modified version of
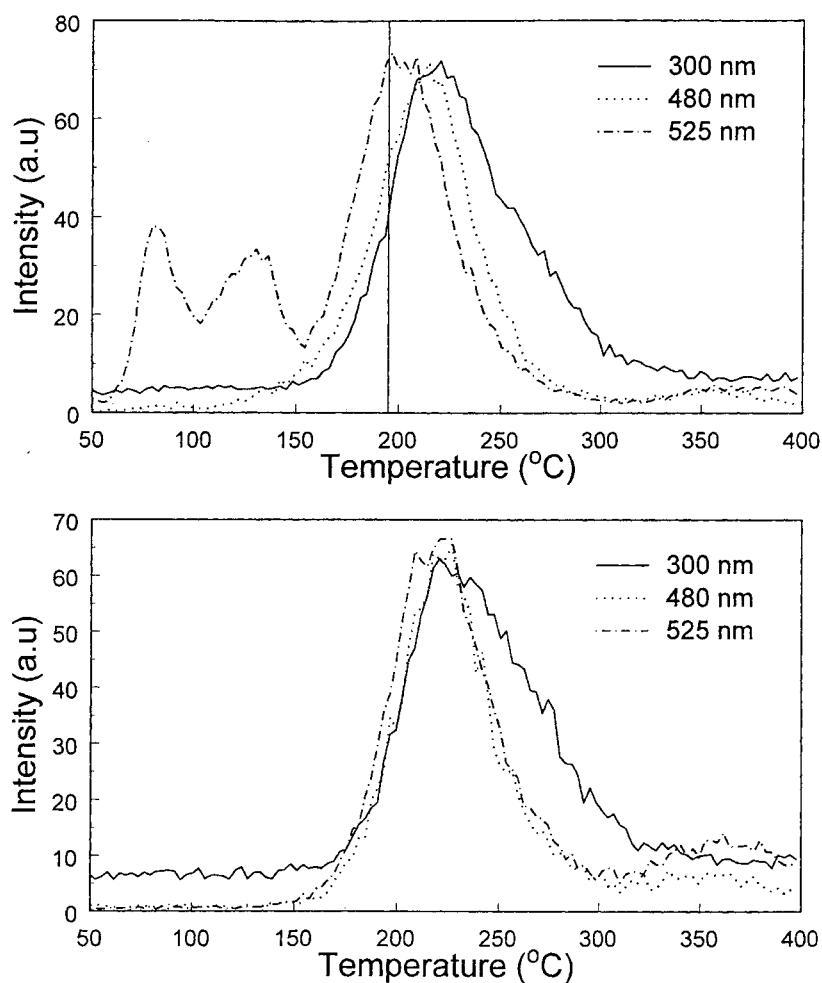
Figure 5. Wavelength-resolved TL for SrF$_2$ samples after room temperature x-ray irradiation (upper figure) and after an initial heating to 195 °C to remove the lower-temperature features (lower figure).

the pre-exponential factor, s, where $S = sn_0^{(b-1)}$. The s-value in the equation governing the TL intensity is given by $I = -dn/dt = s\exp(-E/kT)n^b$ and has unusual dimensions for the general order case. As discussed in Chen and McKeever (1997) this dimensional problem can be avoided by using the modified expression $I = (n^b/N^{b-1})s\exp(-E/kT)$, where N is the total number of traps. However, for the present purposes the S-parameter just indicates consistency between the various groups of values shown in table 1.

The various emissions can be divided into at least three groups, labelled as A, B and C. The most intense emission lines near 525 and 545 nm define group A and have a peak near 187 °C. The signals at 480, 605 and 640 nm comprise group B and occur at 208 °C. Group C includes the broad-band emissions from the lattice, which peak some ~30 degrees higher in temperature when compared with group A. Results indicate that the variations in temperature between the various glow peaks did not appreciably influence the activation energy, although the frequency factor spanned the range ~10^{10}–10^{13} s^{-1}. Group B lines have the lowest frequency factor

Table 1. The fitting parameters for Er glow peaks.

Intrinsic band	Er lines (nm)	T_{max} (K)	T_{max} (°C)	E (eV)	S	b
A						
	525	468	195	1.09	7.89×10^{13}	1.92
	545	465	192	0.94	1.80×10^{13}	1.74
	670	474	201	0.98	7.79×10^{12}	1.83
B						
	480	482	209	0.92	3.00×10^{10}	1.46
	605	481	208	0.92	2.30×10^{10}	1.45
	640	481	208	0.93	2.73×10^{10}	1.47
C						
	280	493	220	1.05		

$\sim 10^{10}$ s^{-1} and the same kinetic order of ~ 1.46, whereas the A group of green lines have the highest frequency factor of $\sim 10^{13}$ s^{-1}, and also a higher kinetic order of 1.74 to 1.92. The broad-band signal has a leading edge approximated by a slightly higher energy. Even such simplistic attempts at analysis indicate that it is unlikely that all lines originate from the same type of site, and separations implied by the analysis agree well with those seen from the thermal cleaning experiments.

The data obtained by thermal cleaning and analysis of the overall original signal both strongly indicate that the only anomaly in these data is that the emission spectra change dramatically between three closely spaced glow peaks. The highest-temperature example is from an intrinsic process, such as electron–hole recombination which, as is generally observed (e.g. McKeever *et al* 1995), gives broad-UV-band emissions. The fact that the components of the band differ between samples also indicates that it involves alternative intrinsic lattice defects. Considering the relatively high temperature involved, these are likely to be vacancy sites, either in isolation or in larger clusters or complexes.

The early literature on the inclusion of rare-earth ions into alkaline-earth fluorides summarizes the problem (Hayes 1974, Hayes and Stoneham 1985) of distortion and charge compensation by discussion of impurity pairs (or larger groups) coupled to intrinsic defects and localized distortions. Historically such arguments focused on a relatively small distortion zone, whereas later discussions reviewing these problems emphasize the need to include interactions with much longer ranges (Rowlands *et al* 1999, Townsend and Rowlands 1999, Townsend 2000). At the relatively low dopant concentration used here, it is probable that the simplest defects predominate. However, it is still unclear whether these involve isolated Er ions or Er pairs.

There are a range of competing conditions which include (a) high densities of imperfections where Er sites are interacting either with intrinsic defects, or at high dopant concentrations, with other Er sites; (b) Er sites that are relatively isolated and (c) thermally activated coupling between neighbouring Er sites. Both cases (a) and (c) can result in stimulation of higher energy states and thus a more complex emission pattern. At the lowest temperatures there will be a high concentration of the intrinsic hole defects such as the H or the V centres (i.e. below about 150 K for most halide insulators); hence the Er levels can couple to these sites. Consequently the emission appears not only with a multiplicity of Er transition lines, but also with the broad-band emission characteristic of the host lattice defects. This situation is consistent with the Er patterns seen for samples of Sr, Ba and Ca fluoride doped with higher levels of Er and the data shown in figures 1, 3 and 4. In any situation where the defect concentration is low, and

so there are minor long-range interactions, the thermoluminescence emission proceeds from the dominant closely spaced pair of energy levels labelled $^4S_{3/2}$ and $^2H_{11/2}$ to give the 545 and 525 nm emissions. The balance between the intensities within the pair is merely controlled by thermal activation between them, as exemplified by the current radioluminescence temperature and TL data. However, for more complex defects incorporating several Er ions, or those which are energy coupled via long-range interactions, less direct processes are possible. The energy levels of Er are noted for a variety of long lifetimes that are frequently exploited to give up-conversion emission. Coupled Er ions, within a single defect, can thus provide an emission pattern with a wealth of lines, as seen for the higher-temperature set of B signals above 200 °C.

5. Summary

Spectrally resolved thermoluminescence of Er in SrF_2 indicates that there are both isolated and coupled Er defect sites. When several Er ions are involved then energy transfer within the Er energy levels leads to emission from numerous excited states. Equally, there can be coupling to intrinsic defects, as seen at low temperature. Similarities in TL signal energies produce an apparently anomalous situation in which the integrated signals from several glow peaks appear to give wavelength-dependent TL. The TL kinetic parameters of the various defects can be analysed in the present wavelength-resolved example, but clearly the normal TL detection systems (which use polychromatic signals) would generate erroneous kinetic parameters.

Acknowledgments

References

Arkhangelskaya V 1965 Thermal bleaching of subtractive coloring due to divalent rare earths in fluorite-type crystals *Opt. Spectrosc.* **18** 46–9
Barriere A S, Raoux S, Garcia A, l'Haridon H, Lambert B and Moutonnet D 1994 Intra-4f-shell transitions at room temperature of Er^{3+} ions in $Ca_{1-x}Er_xF_{2+x}$ thin films grown on Si(100) *J. Appl. Phys.* **75** 1133–7
Chen R and McKeever S W S 1997 *Theory of Thermoluminescence and Related Phenomena* (Singapore: World Scientific) pp 29–35
Drozdowski W, Przegietka K, Wojtowicz A and Oczkowski H 1999 Charge traps in Ce doped CaF_2 and BaF_2 *Acta Phys. Pol.* A **95** 251–8
Hayes W (ed) 1974 *Crystals with the Fluorite Structure* (Oxford: Oxford University Press)
Hayes W and Stoneham A M 1985 *Defects and Defect Processes in Nonmetallic Solids* (New York: Wiley)
Holgate S A, Sloane T H, Townsend P D, White D R and Chadwick A V 1994 Thermoluminescence of calcium fluoride doped with neodymium *J. Phys.: Condens. Matter* **6** 9255–66
Karali T, Can N, Townsend P D, Rowlands A P and Hanchar J 2000 Radioluminescence and thermoluminescence of rare earth element and phosphorus-doped zircon *Am. Mineral.* **85** 668–81
Karali T, Rowlands A P, Townsend P D, Prokic M and Olivares J 1998 Spectral comparison of Dy, Tm and Dy/Tm in $CaSO_4$ thermoluminescent dosimeters *J. Phys. D: Appl. Phys.* **31** 754–65
Karali T, Townsend P D, Prokic M and Rowlands A P 1999 Comparison of the thermally stimulated luminescence spectra of codoped dosimetric materials *Radiat. Protect. Dosim.* **84** 281–4
Luff B J and Townsend P D 1993 High sensitivity thermoluminescence spectrometer *Meas. Sci. Technol.* **4** 65–71
Maghrabi M, Karali T, Townsend P D and Lakshmanan A R 2000 Luminescence spectra of $CaSO_4$ with Ce, Dy, Mn and Ag codopants *J. Phys. D: Appl. Phys.* **33** 477–84
McKeever S W S, Moscovitch M and Townsend P D 1995 *Thermoluminescence Dosimetry Materials: Properties and Uses* (Ashford: Nuclear Technology Publishing)
Merz J and Pershan P 1967 Charge conversion of irradiated rare earth ions in calcium fluorides *Phys. Rev.* **162** 217–35
Raymond S G, Luff B J, Townsend P D, Feng Xiqi and Hu Guanqing 1994 Thermoluminescence spectra of doped $Bi_4Ge_3O_{12}$ *Radiat. Meas.* **23** 195–202

Raymond S G and Townsend P D 2000 The influence of rare earth ions on the low temperature thermoluminescence of $Bi_4Ge_3O_{12}$ *J. Phys.: Condens. Matter* **12** 2103–22

Rowlands A P, Karali T, Townsend P D and Yang B 1999 Thermoluminescence from within large defect complexes *Radiat. Eff.* **149** 167–73

Townsend P D 2000 How big is a point defect? *Radiat. Eff.* at press

Townsend P D and Rowlands A P 1999 Extended defect models for thermoluminescence *Radiat. Protect. Dosim.* **84** 7–12

Yang B and Townsend P D 2000 Patterns of glow peak movement in rare earth doped LaF_3 *J. Appl. Phys.* at press

Yang B, Townsend P D and Rowlands A P 1998 Thermoluminescence of LaF_3 *Phys. Rev.* B **57** 178–88