

Thermoluminescence spectra of minerals

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Abstract

Thermoluminescence (TL) studies of insulators, including crystals of minerals such as calcite, quartz or zircon, have resulted in the development of a wider range of applications in the fields of radiation dosimetry and archaeological and geological dating. Most conventional TL measurements are made by recording light emission during heating by means of broad-band optical filters and blue-sensitive photomultiplier tubes. Much more information may be gained by monitoring the details of the emission spectrum during thermoluminescence. TL spectra of minerals exhibit changes as a result of crystal purity, radiation dose, dose rate and thermal history. This paper exemplifies the additional information available as a result of spectral studies, and focuses on investigations undertaken by the University of Sussex TL group. Examples include work on calcite, fluorite, zircon and feldspars.

KEYWORDS: thermoluminescence, insulators, dating, calcite, zircon, fluorite, feldspar.

Introduction

THERMOLUMINESCENCE (TL) is a sensitive technique for studying defects and defect concentrations in insulators. Naturally-occurring crystals of rock-forming minerals contain both intrinsic defects and extrinsic impurities. The presence of impurities in concentrations of the order of p.p.b. to p.p.m. is, for example, responsible for the colours exhibited by natural forms of transparent minerals such as quartz and fluorite. TL spectra provide important information on the nature of both intrinsic and extrinsic defects, and on their spatial relationships within crystals, by allowing both temperature-dispersive separation of different traps (defects) and wavelength-dispersive separation of radiative recombination centres. A review of the potential information that can be deduced from TL spectra is given by Townsend and Kirsh (1989). There is a variety of techniques for studying defects and not all methods reveal the same defects. Luminescence methods of TL, CL (cathodoluminescence) and PL (photoluminescence) are complementary in that TL records metastable defects, dispersed throughout the bulk of the material, with charge states within the band gap. By contrast, CL provides data from transient defects, in a thin surface layer, after ionisation within the lattice.

Experimental methods

Conventional TL measurements are relatively simple to make. An irradiated sample is placed on a heater strip, in an inert atmosphere or under vacuum, the temperature is then raised at a constant rate (e.g. $150^\circ \text{ min}^{-1}$) and the emitted light is detected by a photomultiplier tube with either current or photon counting electronics. In principle, different depth traps release charge at different temperatures so that the TL signal gives a temperature-dispersive measure of the trap population. This in turn relates to the irradiation history of the sample, and TL is therefore a sensitive radiation dosimetric method. In reality, the processes are not so simple, and one requires a more complete understanding of the possible processes involved, as discussed by McKeever (1985), Horowitz (1984) and Aitken (1985). To obtain maximum signal, most simple TL systems use a broad band filter, which rejects both short wavelength UV and the longer wavelength red signals. The latter are rejected in order to reduce saturation from black body emission. Blue-sensitive photomultiplier tubes also limit the spectral range, but are used because they have a low dark current. With these experimental constraints, one typically detects between 1% and 20% of the available signal. The simple filter plus blue PM

tube systems do not offer any information on the spectra of the emitted light, and so automatically reject a wealth of information from the recombination sites. Although these simplified TL measurements are often made for reasons of cost, the measurement of transient emission spectra at the relatively low intensities provided by TL is a difficult experiment. Several different strategies have been employed to measure TL spectra including a rotating set of broad band filters, scanning monochromators, a Fourier transform spectrometer, commercial optical multi-channel analysers (OMA) and, most recently a new Sussex system employing a pair of high aperture spectrometers coupled to position sensitive photomultiplier tubes. Some of the relative advantages of these different experimental approaches are discussed by Luff and Townsend (1992). The TL spectra discussed in this paper were almost all obtained using a scanning monochromator system over a wavelength range of 300–800 nm with a bandpass of 10 nm and heating rates of the order of 20–30 °C min⁻¹. The new spectral system at the University of Sussex, mentioned above, used two position-sensitive photomultipliers to record the spectrum simultaneously throughout the wavelength range 200–800 nm, achieving a sensitivity at least 200 times greater than the earlier Sussex monochromator system. All the spectra presented here are corrected for the wavelength dependence of the sensitivity of the spectrometer. This is an essential requirement because neither the diffraction grating nor the detector perform equally efficiently at all wavelengths. The scale of the corrections can be very large. For example, in the Sussex scanning monochromator system, the efficiency varies by a factor of almost 200 within

the region scanned. Further signal manipulation is also required as the system has a fixed entrance slit defining a fixed wavelength spread ($\Delta\lambda$), but spectra need conversion to the physically more meaningful photon energy axis and hence require adjustment to equivalent ΔE apertures. Failure to observe these essential corrections results in a very distorted view of the data but, nevertheless, the need for corrections is not universally appreciated in descriptions of TL, photoluminescence or cathodoluminescence data.

Experimental Results and Discussion

TL spectra of minerals exhibit changes as a result of crystal purity (Chee *et al.*, 1988; Down *et al.*, 1985), radiation dose (Rendell *et al.*, 1985), dose rate and thermal history (Strain *et al.*, 1985). In the following section we present results for a number of different rock-forming minerals. These results exemplify the potential value of TL spectra for provenance studies, in the case of minerals like fluorite and zircon, and for studies of impurities within minerals.

Calcite. Calcite is a bright TL phosphor which emits strongly in the orange portion of the visible spectrum (*ca.* 550–650 nm) when doped with manganese. TL spectra of natural Mn-rich calcite (Joplin, USA) and pure synthetic Iceland spar show pronounced differences. After X-ray irradiation the natural calcite sample showed a broad peaks at 150 °C and near 400 °C (Fig. 1a). The spectrum for synthetic Iceland spar under identical experimental conditions exhibited line spectra (Fig. 1b). The wavelength region of the emission confirms that light is emitted at Mn sites (Medlin, 1968), but to understand why the spectrum has line features or is broad band requires an

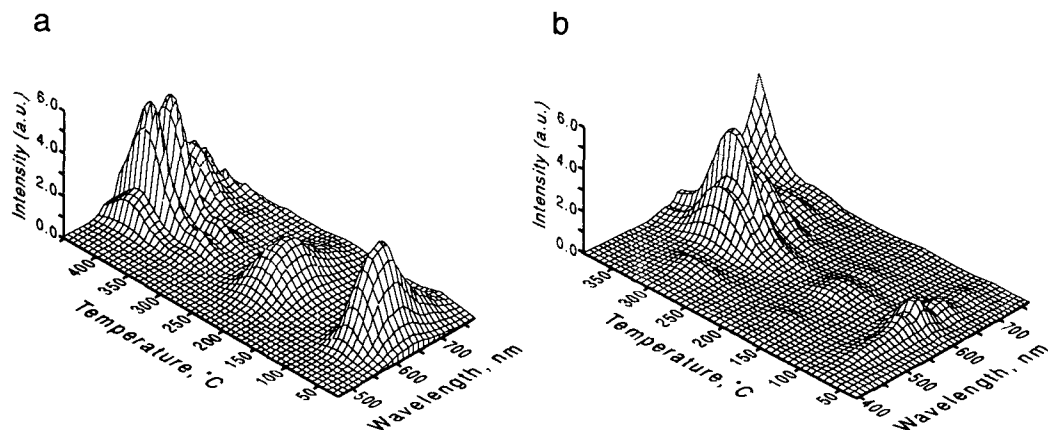


FIG. 1(a). X-ray irradiated calcite (Joplin, U.S.A.) (b) X-ray irradiated synthetic Iceland spar.

explanation of the alternative Mn-related recombination sites. These differences are interpreted in the detailed study by Down *et al.* (1985) in terms of the concentration and solubility of Mn impurity ions. At low concentrations Mn ions exist as isolated defects within the crystal lattice. At higher concentrations, of the order of 1000 ppm, the solubility limit is exceeded and Mn precipitates in clusters. But solubility is temperature dependent, and as the material is heated Mn clusters dissolve and the number of isolated Mn defects increases. Consequently the line features from isolated Mn sites are apparent at all temperatures in the purer Iceland spar crystals, whereas in the heavily doped calcite, line features only emerge at high temperature, and at low temperature the Mn exists as clusters which give broad emission bands. Thermal processing of samples has been used to modify the dynamics of the clustering process (Down *et al.*, 1985). Crushing the calcite also produces changes in intensity of emission which appear to be related to Mn-migration (Khanlary and Townsend, 1991).

Fluorite. Studies of thermoluminescence, photoluminescence and optical absorption of natural fluorites from Spain (M1, M2) and USA (M3) (Calderon *et al.*, 1992) have demonstrated that different colour fluorites are characterised by different combinations of rare earth impurities. A key observation is that all three techniques are required, as separately they each only detect a selection of the impurities, despite the fact that the impurities are all rare earth ions. One obvious reason for this is that naturally acquired radiation doses or laboratory experiments using X-ray irradiation can alter the charge state of the RE ion from RE^{2+} to RE^{3+} . The sample of green fluorite (M1) exhibited optical absorption charac-

teristic of samarium (Sm^{2+}) and photoluminescence peaks characteristic of samarium and europium (Eu^{2+}). The spectrum of the natural TL showed a mixture of broad peaks and line features from 300–700 nm (Fig. 2a). When the same sample was cooled, irradiated with X-rays and then reheated, a series of line features, characteristic of Dy^{3+} transitions, was present at 50°C together with a series of broad peaks in the blue region at higher temperatures (Fig. 2b). By contrast, the sample of yellow fluorite (M2) showed optical absorption characteristic of O^{3-} substitution for two adjacent F^- ions, and photoluminescence characteristic of cerium (Ce^{3+}) and Eu^{2+} . The spectrum of the natural TL shows a well defined broad peak at 380 nm at high temperature but no clearly defined line features (Fig. 3a) After X-ray irradiation, line features were revealed at low temperatures in the wavelength range 480–680 nm (Fig. 3b). The majority of these features are at wavelengths characteristic of dysprosium (Dy^{3+}). The dark-blue fluorite (M3) showed optical absorption characteristic of aggregated colloids of atoms of calcium and no photoluminescence. The spectrum of natural TL is dominated by line spectra at high temperature (Fig. 4a). After X-ray irradiation, the line features reappear at low temperatures and are again characteristic of Dy^{3+} (Fig. 4b). In all three cases the spectra from the natural and the annealed and X-ray irradiated samples allow the samples to be distinguished from each other. In addition, the roles played by the rare earth impurities appear complex and they may be varied by thermal and/or radiation treatments. All three techniques give information on the REE impurities but, in the case of TL, Dy^{3+} appears to dominate emission of the line spectra.

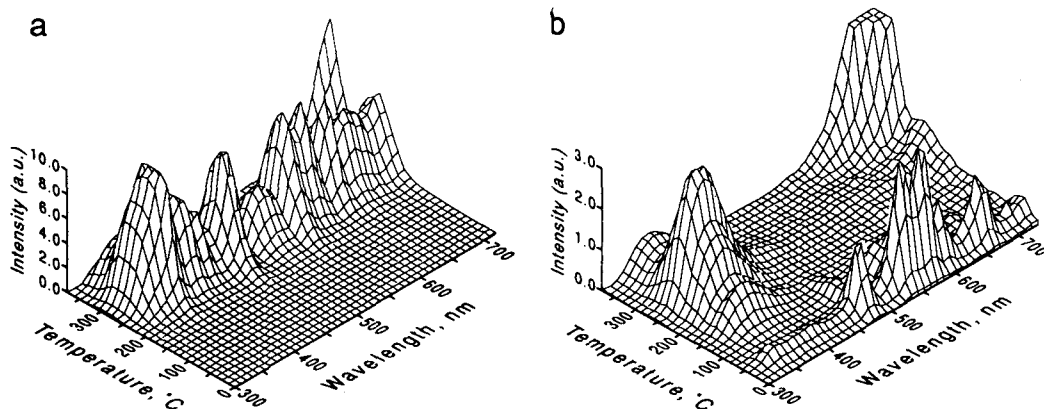


FIG. 2(a). Natural TL of green fluorite (Spain) (b) X-ray irradiated green fluorite.

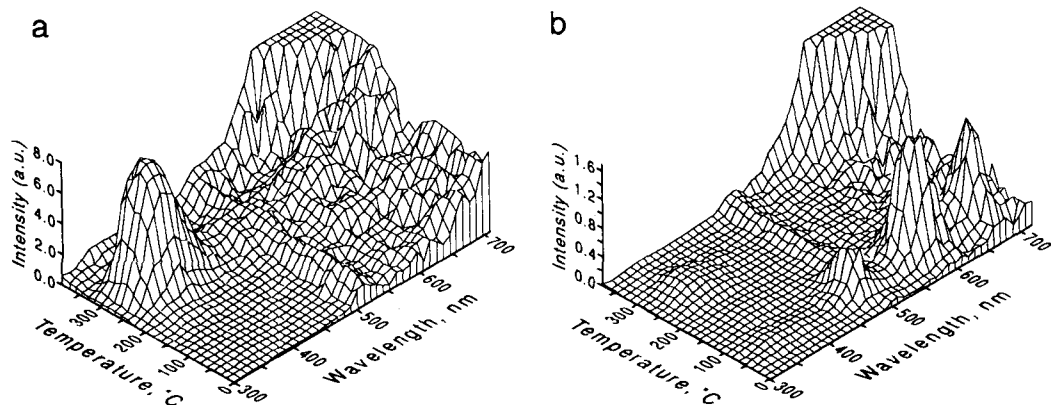


FIG. 3(a). Natural TL of yellow fluorite (Spain) (b) X-ray irradiated yellow fluorite.

Zircon. Zircon is a common component of heavy mineral suites, and fission track dating of zircons is now a widely-accepted dating technique. TL spectra of natural zircons are dominated by the line spectra characteristic of the rare earth Tb^{3+} and/or Dy^{3+} (Chee *et al.*, 1988). The emission spectra of two samples of natural zircon show broad features in the blue region (300–480 nm) and a series of line spectra in the region 480–750 nm (Fig. 5a and b). Both spectra were recorded after 750 Gy X-ray irradiation and at heating rates of $20^{\circ}C\ min^{-1}$. The Sri Lankan zircon sample shown in Fig. 5a shows a strong emission at the red end of the spectrum which is characteristic of Eu^{3+} whereas the Mexican zircon sample shown in Fig. 5b exhibits strong line features characteristic of Dy^{3+} at $100^{\circ}C$ and of Tb^{3+} at higher temperatures. Both spectra contain a broad feature at about $100^{\circ}C$ with a peak at 385 nm. This broad spectral feature is characteristic of minerals containing SiO_4 groups, including

quartz and feldspars, and may be related to defective Si–O bonds (Chee *et al.*, 1988). As in the case of the fluorite samples discussed above, it is apparent that while several rare earth impurity ions may be present in a zircon crystal, the ions contribute to the TL signal in different ways. The low-temperature signals tend to be dominated by Dy^{3+} , but storage after irradiation and before heating can result in the growth of Tb^{3+} related emission features at the expense of the Dy^{3+} ones. Such conversions can take place at unexpectedly low temperatures, and we have monitored the growth of $90^{\circ}C$ 630 nm Tb^{3+} line, at the expense of the Dy^{3+} lines. This work has served to underline the importance of rare earth impurities as radiative recombination centres as well as the complexity of such centres.

The feldspar group. In contrast to the sharp, clearly defined spectral features exhibited by fluorites, TL emissions from the feldspar group are dominated by broad band emissions. All the

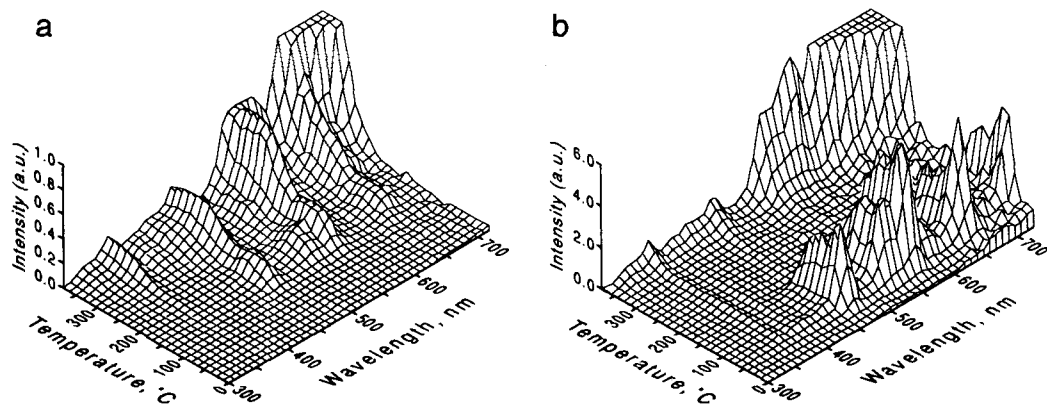


FIG. 4(a). Natural TL of dark-blue fluorite (U.S.A.) (b) X-ray irradiated dark-blue fluorite.

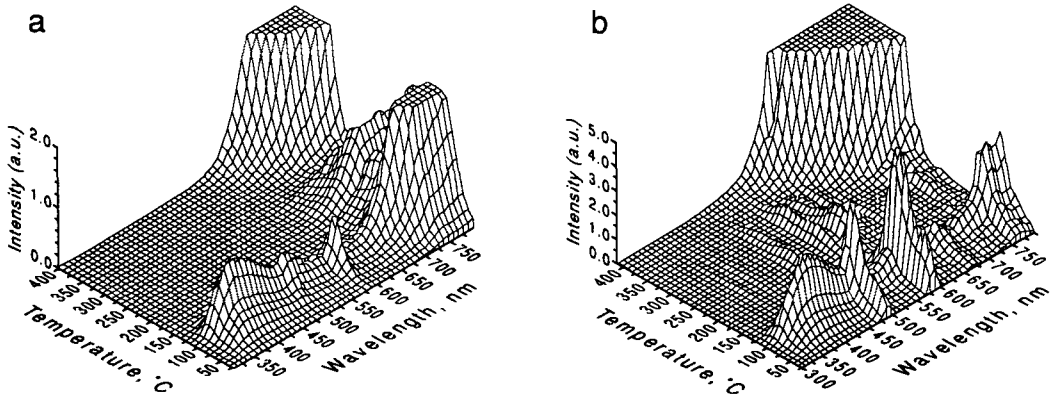


FIG. 5(a). X-ray irradiated zircon (Sri Lanka) (b) X-ray irradiated zircon (Mexico).

feldspars show strong emission at the red end of the spectrum (680–730 nm), and this emission has generally been attributed to conversion between Fe^{2+} and Fe^{3+} impurities that act as recombination sites for either holes or electrons, depending on valency. In contrast to albite, microcline and orthoclase, the samples of plagioclase studied by the Sussex group have shown no strong emissions in the blue spectral region (Dalal *et al.*, 1988; Kirsh and Townsend, 1988) (Fig. 6a, b). Broad emissions in the blue spectral region appear characteristic of intrinsic defects modified by association with impurities such as an Al–O–Al group (Kirsh and Townsend, 1988). If the blue emission is caused by electron-hole recombination then defect sites can influence the fraction of the recombinations which are radiative, for example emission intensity may be enhanced where the defects become more complex (e.g. by the presence of Cu^{2+} impurities near to the hole trap). Data from cathodoluminescence studies of

feldspars indicate that emission bands in the blue region may be enhanced by the presence of Cu^{2+} ($420 \text{ nm} \pm 5 \text{ nm}$) and Ti^{4+} ($460 \text{ nm} \pm 10 \text{ nm}$) (Marshall, 1988). The relative strength of the blue and red emissions varies, with the particular feldspar samples measured, but no line spectra, characteristic of rare earth impurity ions, have been detected in any of the spectra that we have examined. There is some evidence from CL studies of natural and synthetic feldspars that RE ions rarely if ever occur in sufficient concentrations in natural feldspars to be effective activators (Marshall, 1988).

Conclusions

The examples given above have served to emphasise the value of TL spectral studies of minerals. TL is a very sensitive tool for probing defects within crystals and the spectra allow both the nature of the electron and hole traps and of

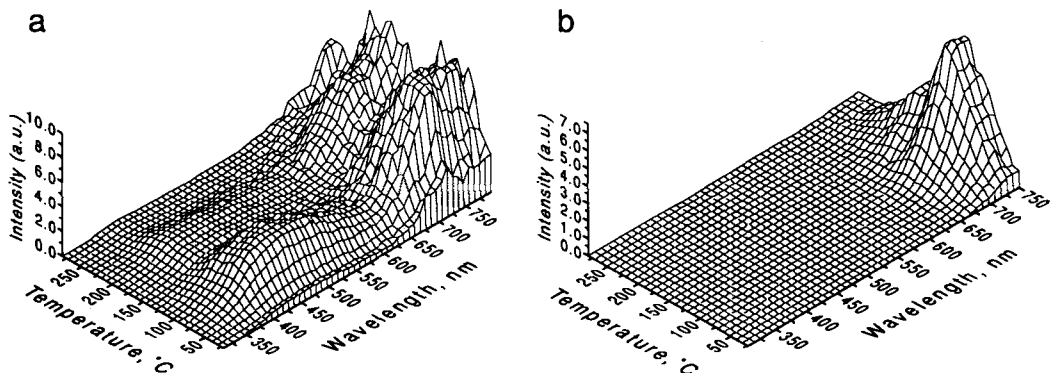


FIG. 6(a). X-ray irradiated orthoclase feldspar (b) X-ray irradiated plagioclase feldspar.

the radiative recombination centres to be explored. The ability to detect low concentrations of impurity ions is of value in its own right, and of potential value for provenance studies.

Acknowledgements

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