Journal of Luminescence 192 (2017) 574–581

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Spectral changes and wavelength dependent thermoluminescence of rare earth ions after X-ray irradiation

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ARTICLE INFO

Keywords:
Thermoluminescence
Model
Wavelength dependent

ABSTRACT

The thermoluminescence spectra of rare earth doped materials after X-ray irradiation typically vary with the glow peak temperature. Additionally, there are many examples where, for the same dopant ion, the expected component emission lines peak, but at different temperatures. This unusual behaviour is discussed in terms of changes in proximity of coupling between trapping and recombination sites. Changes in the energy barriers for recombination influence alternative routes for charge transfer to rare earth sites which can involve different higher energy states of the rare earth dopants. Proposed mechanisms include selective tunnelling, or barrier crossing, in addition to normal charge transfer from remote trapping sites. The model successfully describes numerous examples in terms of the energy scheme for the rare earth ions. Whilst the standard emission lines are recorded in the glow curve spectra they do not always occur at the same temperature, and, even for the same rare earth dopant, they can differ by as much as 30 °C. These wavelength dependent variations in peak temperature not only offer information on the proximity of trap and recombination sites, but also introduce issues in conventional activation energy analysis when recording is with polychromatic light. The concepts are relevant for related types of measurement, such as optically stimulated thermoluminescence.

1. Introduction

Luminescence studies offer a highly sensitive probe of defect structures in insulating materials with techniques such as photoluminescence (PL), cathodoluminescence (CL), radioluminescence (RL) and thermoluminescence (TL), etc. Each technique has a vast literature with data from hundreds of materials. It is thus surprising to find a phenomenon that had not previously been noted in the last 60 years of TL data. Nevertheless, the current observations of differences between the TL peak temperatures of a set of emission lines, from the same rare earth dopants, has remained unnoticed. This article summarises these unfamiliar features that have been observed from several types of material with the same high sensitivity spectrally resolved TL equipment.

Thermoluminescence is of particular importance because of its applications in radiation dosimetry, as well as the ability to thermally separate different features from trapping and luminescence sites [e.g. [1–3]]. Polychromatic recording is invariably used for dosimetry, but for more fundamental analyses the TL heating data require detailed spectral recording. Broad band luminescence spectra are common features linked to intrinsic defect sites; by contrast, signals from rare earth dopants are characterised by narrower bands, or line spectra. In each case, there can be both changes in the overall emission pattern with temperature and movements of the peak wavelengths. Major spectral changes are normally considered to be evidence of different defect sites. In continuously excited signals (PL, CL or RL) steady spectral movements as a function of temperature can indicate that the relevant defect sites are basically unchanged. By contrast TL signals occur over limited temperature ranges resulting from charge transfer between trapping and recombination sites. Here the temperature monitors the transfer barrier, even if the emission site is common to many TL peaks. The TL spectra from rare earth sites can vary significantly in terms of the number of lines, and their relative intensities. Such differences are

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http://dx.doi.org/10.1016/j.jlumin.2017.07.041
Received 20 January 2017; Received in revised form 10 June 2017; Accepted 21 July 2017
Available online 22 July 2017
0022-2313/

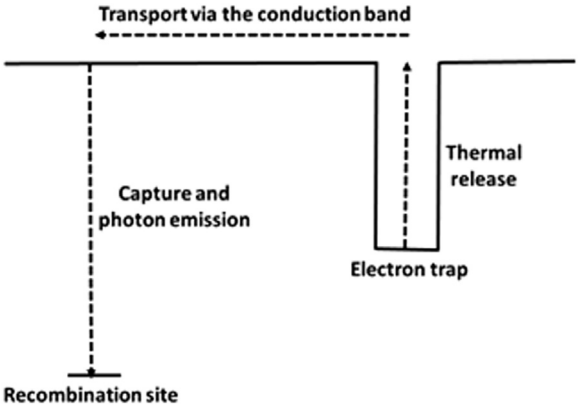

Fig. 1. An early simplistic model for thermoluminescence with totally independent trapping and recombination sites and charge transport via the conduction band.

unlikely if there is separation of the traps and the rare earth (RE) recombination sites, thus close links between traps and the rare earth sites must be considered.

2. Evolution of thermoluminescence models

Thermoluminescence (TL) is a simple process in which exposure to ionizing radiation, or UV light, can produce free electrons and/or holes. These become trapped at imperfections. Subsequent heating releases the charges and, during their recombination and return to a ground state, the energy release is in the form of light. This is a potential dosimeter for ionizing and UV radiation, as in favourable conditions the trapping sites are stable at ambient temperature, and eventually the read-out stage offers an integrated signal proportional to the radiation exposure. A high percentage of insulating materials display TL; the personnel dosimetry market is large, and so there have been hundreds of publications proposing new, or better, dosimeters. In the initial idealised models, Fig. 1, the trapping and recombination sites were assumed to be separate and it was then simple to model the processes in terms of a trap depth (E) and an attempt to escape frequency (ν). For applications, the progress has been with a mixture of understanding the complex properties of imperfections and intelligent empirical experimentation. The requirements are a material that is stable during storage, produces a high light output for a small radiation exposure, and emits strongly in the frequency range where photomultiplier tubes are efficient. High heating rates improve dosimetry analysis by reducing background noise, although they compromise accurate temperature measurements.

Even by the 1960s it was apparent that for successful dosimeters, such as TLD100, the simplistic model was inappropriate. This material is doped LiF, which is a favourable equivalent for radiation absorption in tissue. The TLD 100 includes Mg^{2+} ions located on Li^+ lattice sites, with size and charge compensation of the Mg^{2+} via an adjacent Li vacancy. For thermal stability of storage, the site is heat treated to form a ring of three units. A closely linked trapping site means the trap to luminescence pathway is very efficient, and this is provided with Ti^{4+} ions directly associated with the ring of Mg-$Li_{vacancy}$ units. Further charge compensation (for Ti^{4+} ions on Li^+ sites) is needed in the form of O^{2-} ions on fluorine sites. In reality, this package is totally different from the idealised model of well separated independent trapping and luminescent sites. Many other dosimeter models have been cited [e.g. [1–3]].

Advances in understanding impurity sites show that charge compensation, and minimisation of lattice strain energy, invariably cause close association of impurities and compensators, and, in extreme cases, precipitation of dopants into new phases. Hence, there can be a multiplicity of very similar traps and luminescence sites. Many rare earth (RE) examples are documented via techniques such as site selective spectroscopy [4,5] in which scanning with high resolution excitation spectra reveal equally detailed changes in the emission from nominally the same type of rare earth site. Luminescence does not provide lattice structure details, but in paramagnetic resonance studies of RE ions, such as ENDOR (electron nuclear double resonance) [6], the local distortions of the lattice are observable over many neighbouring atoms. Even more distant trap/recombination site interactions have been monitored. For example, at low temperature, a shifting pattern of exciton emission data from GaP [7] was modelled to confirm that pair-related exciton line spectra from electron/hole binding were measurable up to separations of some 50 neighbouring ionic shells.

The long-range interactions between rare earth dopants and structural defects are also evident in technological applications, such as rare earth laser systems, where the impurity clustering as a function of dopant concentration, and interactions with defects (from surfaces, dislocations, and intrinsic defects) all change the luminescence properties of relative intensity of emission lines, excited state lifetimes and laser performance [8].

Overall, the defect literature indicates considerable complexity, and distortions in the imperfections and these are apparent in a sensitive technique such as TL. In reality it also implies non-unique activation energies if there are a range of similar sites with small changes in local distortions. TL kinetics of a band of activation energies have similarly been discussed in mineral systems where there are structural variations between different ordered and disordered phases [9]. Such subtle site variations are obscured in polychromatic TL recording, and irrelevant for dosimetry applications. However, addition of good resolution spectral detail offers many insights into the many defect interactions, especially from rare earth sites. For precise temperature analysis both low heating rates, in order to have accurate temperature control [10], and high sensitivity wavelength multiplexed spectral acquisition are essential. This precision can separate the many defect processes which are present. Successes with the present system are many (e.g. as reviewed in reference [11]). For example, in numerous host lattices the rare earth dopants show displacement of the TL peak temperature in a systematic pattern depending on the size of the impurity ion relative to the host site. Particularly clear examples were reported for RE-doped LaF_3 and $Bi_4Ge_3O_{12}$ in which the changes in TL peak temperature are a smooth function of the ionic size. The LaF_3 data also indicate that the RE ions are clustered into groups of at least three dopants (i.e. a similar pattern to that of TLD 100). Dopant clustering and association with intrinsic defects was exemplified by changes in the spectra and peak temperatures of Nd-doped CaF_2 where changing Nd concentrations and/or thermal treatments, totally modify the TL spectral data and generate different balances between the Nd line spectra, as well as changes in band width, plus intrinsic broad band emission. Extreme examples of clustering revealed by TL data include impurity phase precipitation of rare earth dopants in zircon [12] and impurity nanoparticle precipitates [13].

Overall the improvements in understanding the complexity of defect structures, and their influence on TL has moved a long way from the simplistic original thoughts on isolated unique-valued parameters of TL, as envisioned in the historic models. These did not consider the present thoughts on changing rare earth emission spectra with glow peak temperature, nor the possibility that, from the same rare earth dopant, the emission wavelengths could differ in their TL temperature. However, in hindsight, one can sense these features in earlier publications. Defect models now require the realisation that many of the sites are complexes of dopants and impurity sites, and indeed the traps and recombination sites may be intimately linked.

3. Experimental background

The thermoluminescence data discussed here were collected with a sensitive wavelength multiplexed spectrometer system [14]. Collection spans temperature ranges from 20 to 673 K. (Note, however, that