Introduction

Many key and current technologies are based on optical properties for production, control and detection of light from areas such as lasers to optical processing and communication. In parallel with the development of such techniques, there is an ongoing stimulus to find new optical materials and/or new phases with improved optical responses. Therefore, detection of structural changes or phase transitions within materials becomes essential for material scientists and technicians. Phase changes are characterised by discontinuity of thermodynamic properties around the transition of long-range structural order, crystal structure, enthalpy and heat capacity. However, the transitions are potentially sensitive to external conditions, not only temperature but also pressure and electric or magnetic fields. Sensitivity to optical illumination, sound, ionization or radiation damage is also feasible. Many of these more subtle influences have not been explored by standard techniques available for characterisation that include X-ray, electron or neutron crystallography. Nevertheless, besides the standard crystallography, there are wide ranges of optical methods that can be very rapid, clean, lossless and provide a high level of sensitivity. They potentially also respond to phase transitions of inclusions. We will briefly review some optical methods and examples that can be used to indicate the structural or phase changes within insulating materials and show how they lead to new ideas for using these techniques. Emphasis will be on less utilised temperature scanning methods, phase transition signatures and newly reported unexpected features.

Experimental techniques

General

There are a variety of ways to excite luminescence and each approach has different advantages and problems. Photoluminescence (PL) can be wavelength selective in the choice of site that is stimulated (e.g., intrinsic defects or nanoparticles). PL can therefore couple to the sample via specific optical absorption bands. PL of the internal transitions as seen for rare earth ions offers a probe of local environment via changes in wavelength defined by site-symmetry as perturbed by local distortions, including phase changes. PL depth penetration is defined by optical absorption whereas using excitation with X-ray irradiation (RL), one can sample the bulk material. For surfaces, there is partial control of excitation depth by PL with strongly absorbed light or by varying the electron energy in cathodoluminescence (CL). Ion beam luminescence (IL) with light ions generates similar ionisation events as CL but with a different depth distribution. IL has some attractive alternative features since one can change the depth and rate of energy transfer by varying the ion energy and implant species (1). Less obvious for phase transition studies is to use thermoluminescence (TL). This approach monitors the efficiency of charge release with temperature caused by previous irradiation (e.g., with X-ray or other sources). Phase changes can perturb TL both by variations in emission spectra and discontinuities in luminescence efficiency.

No region of a crystal is truly perfect and free from influence of imperfections (2,3) and our understanding and acceptance of long-range interactions has increased over time. This is...
particularly important for studies of phase transitions where there are inclusions and nanoparticles, since the apparently localized changes at the inclusion regions influence large volumes of the host material and vice versa. For example, the influence of phase changes at inclusions on host signals was clearly apparent for garnets (4) or zircon (5). Spectral changes in the host lattice from inclusions could also be seen for both narrow and broadband transitions with rare earth ions or Cr dopant probes (6). In some cases, the spectrum remained nominally the same but with discrete changes in emission lifetime. Lifetime discrimination of different emission sites including phase changes is well established (7,8) and one notes that in the rapidly developing field of optical biopsy, fluorescence lifetime imaging is a particularly powerful method to resolve differences between healthy and diseased tissue (9) (i.e., effectively a phase change). This biological difference between healthy and modified tissue has similarities in that the intensity, emission spectra, lifetime, etc. of the signals differ between the variants and the signals are sensitive to long-range effects. Similarly, botanical examples of water content in a leaf showed changes in emission spectral components; for example, with different lifetimes and intensity for wet and dry leaves.

The luminescence techniques needed to detect phase changes are simple since different phases of a crystal structure demonstrate changes in emission spectra, different decay lifetimes and changes in efficiency of the luminescence process. These suggest that there are intensity steps when changing phase even if the spectral differences are hard to discern. A final and clear signature of a phase transition is often that, at the transition temperature, the luminescence efficiency is greatly increased so that there is an intensity spike on heating or cooling through the phase transition temperature. In our studies, we used wavelength multiplexed signal recording and low heating or cooling rates of $10^{-3}$ per/min. These conditions offered high sensitivity detection of bulk and inclusion phases as well as evidence of hysteresis and provided a rapid survey for new materials.

An example of sensitive equipment design

Conventional luminescence systems can offer high sensitivity via monochromatic signal recording with photomultiplier (PM) or CCD detectors but normally, the wavelength multiplexed versions rely on CCD arrays. The CCD detectors were convenient but lacked the sensitivity and signal gain of the PM tube; further, they were less suitable for lifetime resolved processing (e.g., as often used with CL recording). PM tubes also had a wide dynamic intensity response, which was particularly valuable in recording both thermoluminescence (TL) and signals with a combination of broadband and rare earth line signals. For measurement of emission spectra during thermoluminescence and the current search for phase transition effects, one experimentally needs a parallel input at all wavelengths, rapid response and high sensitivity. The equipment used was at the University of Sussex (10) and now at the University of St. Andrews achieved these objectives with a pair of f/2 grating spectrometers. Two separate gratings allowed high diffraction efficiency in both the UV/blue region and in visible/NIR spectral ranges. Signals were then detected by a pair of photon imaging tubes (Photek Ltd, UK) with responses chosen for the two spectral regions. Overall, this offered peak PM sensitivity and simultaneous wavelength multiplexed signal collection. The sample geometry allowed excitations with electrons, X-rays or light while retaining the heating or cooling requirements of thermoluminescence over the range of 25 K to $\sim$575 K (300 °C). Further, high sensitivity meant that low heating rates could be used so that accurate temperature data were feasible without normal TL problems of sample temperature gradients (11).

Examples of phase changes detected by luminescence

Bulk phase changes detected by luminescence

As expected, luminescence detection of different phases of insulating crystals was typified by changes in intensity, emission spectra and decay lifetimes. There was also a strong signature in our data of an intensity spike since we scanned through the temperature range of the phase transition. Spikes are particularly valuable markers when there is hysteresis. Luminescence from impurities was affected by transitions of the host and an interesting example was the detection of superconducting transitions. To emphasise that the concept was not limited to insulating materials, we performed a CL study of a superconducting tape of Bi/Pb –2223 Ag. It was possible to sense luminescence from impurities such as surface oxides or sulphides (12) and the temperature response is shown in Figure 1. The signal vanished on cooling through the superconducting temperature near 90 K. We proposed that this was feasible since in the superconducting state, magnetic flux was excluded from the superconductor and hence the electron beam could not enter the surface. The signals offered interesting insights into the host material as we observed that there were higher temperature spikes than just the 90 K event. This suggests that some grains of the material could demonstrate even higher transition temperatures up to 120 K instead of $\sim$90 K. It is therefore advantageous to modify the fabrication process to increase the...
fraction of the grains that will show higher temperature performance. Bi/Pb – 2223 Ag is not the only example and luminescence data for PbF₂ has also been recorded (13). Those studies showed that there were spectral changes at the transition temperature but not as obvious as for the Bi/Pb samples. Similarly, a fullerene phase transition was shown via surface solvents.

**Lattice changes detected by impurity probe ions**

Many studies have exploited the site-sensitive transition energies and lifetimes of rare earth ions embedded in lattice and when there are phase transitions of the host, these are normally reflected by discrete shifts in these rare earth emission and absorption properties with early examples such as (14–16). Rare earth signals are sharply defined and well documented in terms of their transitions; for example, as shown by recent absorption, luminescence and Raman spectra for RE doped Al₂O₃ (17,18). Note that the presence of the rare earth probes can themselves modify lattice stability. Luminescence emission lines of other dopants such as chromium have equally been useful as in ruby to characterize temperature and pressure changes in host materials. The inherent distortions and stresses caused by impurity inclusions resulted in association of dopants and impurities into clusters or complexes often with intrinsic defects. This implies that, particularly with high dopant concentrations, it can be inappropriate to consider the signals from original host material and instead one should consider the possibility of new compounds either based on the original host material or as a completely new phase separation of precipitates.

The Eu³⁺ ion had a relatively simple energy level diagram and was sensitive to the local environment. As a result, it was favoured for laser excited site-selective spectroscopy to analyse changes from site to site in the energy level diagram, lifetime, line widths and energy transfer processes between ions in sites that were close in energy but spectrally different (19–22). PL of Eu³⁺ ions in (Eu₂–(CH₂(COO)₂)₃(H₂O)₆) crystals demonstrated a structural phase transition at ~ 240 K. PL spectra change with temperature and there were energy transfer processes between Eu³⁺ ions in two local sites at the low temperature range (23). The ⁴F₃/₂ → ⁴I₉/₂ single excitation line split into two at the 240 K, which indicated that two different Eu³⁺ sites existed in the low temperature caused by the phase changes of the host. The temperature dependence of the energy transfer could be explained by a non-radiative two phonon-assisted process. The implication was that there are two closely spaced Eu sites that can relax and couple together, in essence, a micro-phase transition. A phase transition process of GdVO₄:Eu³⁺ microcrystal with high pressure was monitored by the Raman and PL spectra (24). The Eu³⁺ ion is not the only rare earth ion that can probe structure changes from host materials. PL and Raman spectra from Sm³⁺ have been reported to detect the anatase–to-rutile phase transition of TiO₂ powder material (25).

**Phase changes from nanoparticles, inclusions and surface impurities**

Nanoparticle inclusions may represent a tiny percentage of the total volume. As a result, for many classical techniques, any phase change within the inclusions are extremely difficult to detect. This is certainly not the situation for the luminescence data since the long-range effects of the nanoparticle phase transitions could modify bulk lattice signals. The reverse is of course also true, but that is intuitively more acceptable. Note that even for isolated “point defects”, we could observe luminescence perturbations over perhaps 50 shells of surrounding ions. Therefore, for the more stressful factors of nanoparticle inclusions, the volume of perturbed host lattice would be even greater. For example, the presence of water nanoparticles in the form of inclusions and/or surface or grain boundary layers has been inferred from many of our sample types since RL and CL signals of the host lattice undergo a major intensity step near 170 K, which corresponds to the cubic to hexagonal phase transition of ice (4,5,26). Water nanoparticle could be immediately at the surface, in the near surface by ingress along grain boundaries and dislocations or embedded within the material. Each type of feature could be addressed by choice of excitation; for example, strongly absorbed energy deposition for CL or low energy IL emphasized near surface features whereas bulk features were addressed by RL. We noted many examples of water/ice phase transitions, particularly for the cubic to hexagonal ice transition near 170 K. Figure 2 shows CL isometric signals from Sm doped zircon and a contour map for the mineral spodumene. The huge change with a host signal intensity step was surprising. If water was present as a trace impurity then it must have been associated into sufficiently large clusters that it behaved as water rather than impurity trapped OH ions. For CL, the first assumption was that the water was at the surface or within surface emergent dislocations. If there were sufficiently long-range interactions with the distorted lattice adjacent to the water and the Sm sites in the zircon, then changes in the phase of the ice influenced the luminescence efficiency. The model
was not unreasonable but the scale of the luminescence quenching was surprising. For RL examples, water particles needed to be distributed throughout the bulk of the material since similar quenching events occurred at 170 K. A weaker event near 230 K was noted and was probably due to a surface phase of water ice in a vacuum system. The role of near surface water on host luminescence has been clearly demonstrated (26–29). Nd:YAG displayed an intensity step at 170K. However, heating at 100°C drove off any near surface water and the luminescence intensity step was removed but could be reintroduced by a brief exposure to steam. The process was repeatable (27). Depth information could be probed by varying the energy of the electron beam in CL excitation (28).

A consequence of what may be extremely small contaminant concentrations is that it implies that standard analytical methods could be inadequate in many cases, and even IR detection of OH bonding could be misinterpreted in terms of isolated OH radicals rather than water nanoparticles. One should note that luminescence could respond to changes close to the ppb level whereas analyses for water inclusions would normally be at 10 to 100 ppm concentrations. The trapped impurity signals were not confined to the surface and many examples were seen with RL, implying that they were from bulk material. A series of intensity discontinuities was noted with crystals of MgO doped with Cr in which the red chromium emission band underwent both intensity steps and wavelength displacements at a number of temperatures (6). The temperature values were tentatively linked to phase transitions of trapped gases such as N2 and O2 since the event lines matched their solid/liquid and liquid/gas phase transitions. For the same samples, there were differences in the direction of the wavelength shifts from RL and CL data. This is not unreasonable, since within the bulk, these phase changes involved expansions and increased in pressure with compression of the neighbouring MgO lattice. By contrast, CL probed the surface where the pressure change could result in a surface expansion of the lattice and a corresponding lattice expansion. Trapped gas signals were similarly noted from alumina samples prepared by pulse laser deposition in an argon atmosphere (29,30). The intensity steps matched the phase transition temperature of argon.

**Bulk structural changes and relaxation caused by ion implantation**

Normally, one assumes that ion implantation is a surface effect in which there is doping of the host material and for high doses some sputtering and changes in composition of the implanted layer. This was certainly the initial response but there were additional stresses that modified the lattice structure deeper into the implanted crystal. Stress fields were not confined to the implant zone and early experiments suggested that stress extended maybe 10 times deeper than the implant. In addition, at very high implant concentrations, the lattice was no longer thermodynamically stable and standard behaviour included relaxation into new structures, new compounds and/or precipitation of sub-phases or nanoparticles. Indeed, such events are well documented in the ion implantation literature and in the case of luminescent nanoparticles in semiconductors and silica, the emission spectra changed progressively with the size of the nanoparticles. The interpretations of the changes in signal are often controversial at the detailed level but the signals are monitors of the implanted volume. In the case of optical waveguides formed by ion implantation of light ions, there was a low refractive index damage layer that separated the waveguide from the bulk; the guide was stressed relative to the bulk material (1,31). Hence, in waveguides formed in Nd:YAG, Nd emission spectra, relative line intensities, transition probabilities and emission wavelengths were all perturbed compared to those of the bulk material. Such changes were to be expected and are well documented for a range of ion implanted laser waveguides (31).

An unexpected outcome of the surface implantation was that the stress fields could extend much further into the substrate and even induce phase transitions. The assumption was that surface stresses propagated throughout the bulk material. Spectra shown in Figure 3 compare RL signals (i.e., bulk responses) of pure and ion implanted samples (32). It is obvious that in material implanted at room temperature, there were changes in subsequent low temperature data. For the implanted material, the intense red emission was quenched at low temperature and a number of strong shorter wavelength emission bands appeared. The implant depth was merely ~ 100nm whereas the bulk material excited by the X rays was ~ 1 mm thick. Thus, the optical signals revealed the result of bulk relaxation as a consequence of surface stress and radiation damage. More detailed analysis of the lower temperature intensity steps showed that they matched known phase transitions of SrTiO3 which are typically listed near 105, 65, 35, 25 and 16 K while the detailed results differed between samples of different purity. They were insensitive to the choice of implant as noted in a more recent article for copper implanted SrTiO3 (33). The example is for SrTiO3 but zinc oxide, bismuth germinate or silicon carbide could follow similar trends since in each case structural analyses revealed that these materials can vary in their stoichiometry, including a number of

![Figure 3. Contrast of changes in the original (top) bulk radioluminescence of strontium titanate to that observed (bottom) caused by surface induced stress from ion implantation.](image-url)
and a consequent distortion of the intrinsic vacancy sites. Reduced by high dose surface implants. The new TL responses are strikingly large changes in the TL signals from the bulk material in Cu implanted ZnO is shown in contrast of isometric TL data for a pure German ZnO sample and a one suspects that this is a far more general occurrence. The con-trast of isometric TL data for a pure German ZnO sample and a Cu implanted ZnO is shown in figure 4 (36). There were surprisingly large changes in the TL signals from the bulk induced by high dose surface implants. The new TL responses were consistent with a model as above whereby the stress induced by the implants caused a relaxation of the bulk material and a consequent distortion of the intrinsic vacancy sites.

Conclusions and future directions

The data presented here and elsewhere (37) indicate that luminescence recorded during heating and cooling cycles of many types of materials could uniquely and readily resolve the presence of phase transitions. In some examples (RTP and KTP), the phase changes were irreversible except by using high temperature annealing, so the currently measured properties might not be truly representative of the full potential of the materials. Luminescence has a strong future role in any study of structural changes or relaxations in insulating materials. Additionally, there were indirect processes that allowed recording of phase changes in other types of materials (e.g., the super-conductor and fullerene examples) and here, the luminescence clearly indicated that higher superconductivity phases exist which with better sample preparation, could raise the transition temperature from 90 to 120 K. We concentrated on phase detection via luminescence spectra but in other system changes in line widths, lifetime or polarisation might be preferable. It must be noted that the unique signatures of intensity spikes at phase transitions required both temperature scanning and wavelength multiplexing.

There were two areas where the luminescence technique was both powerful and revealed unexpected behaviour. The first was that phase changes of inclusions were readily detectable not just from luminescence at the included nanoparticles but instead via dramatic changes in the luminescence efficiency of the host. The second major novelty was that high dose surface implants caused structural relaxations and phase changes of the underlying bulk material. This was so unexpected that few experiments have been considered to test the possibility. New factors that have emerged from the current study are that phase transitions of inclusions (e.g., trapped water, CO2 or other background gases) indicate hidden problems from sample preparation and that these factors are currently overlooked. Again, this suggests that the luminescence probes could offer key information on material quality. For example, the ice phase changes almost suppressed host luminescence in some of the examples.

Unexplored territory arises from the observations that surface ion implantation could generate stresses that propagate through the entire crystal. The possibility of such events would not have been considered, so there is a major reason to expand this area of observation to assess how general are such changes, not least because many materials are non-stoichiometric or have added impurities and stress induced by the growth techniques or may exist in several phases that are stabilised by the impurities. A wider view of phase transitions could include biological difference between healthy and modified tissues and these could be detected by variants of intensity, emission spectra, lifetime, etc., of the signals since they are also sensitive to long-range effects. This aspect of optical biopsy is of increasing importance. Other biological examples exist in phase transition and optical properties of DNA-gold nanoparticle assemblies (38). The changes in optical property due to self-assembly of DNA-linked nanoparticle assemblies differed from that of free DNA. The phase transitions were influenced by many parameters such as nanoparticle size, DNA sequence, density, length, antiparticle distance and electrolyte concentration. The change in optical property due to self-assembly of DNA linked nanoparticle demonstrated that the system had potential to be used as a novel technology for DNA detection. Overall, this is an area that is poised for rapid expansion and valuable output in many disciplines.

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References


