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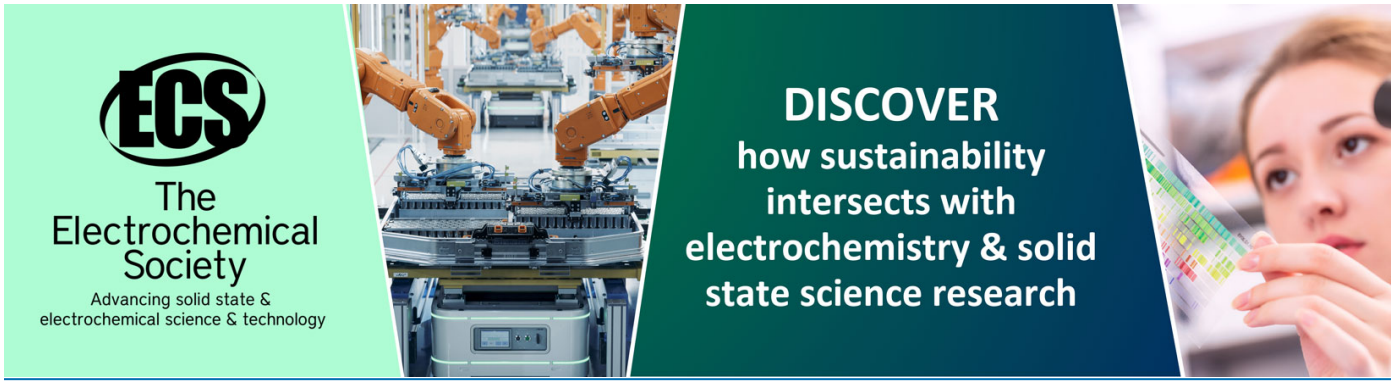

Common mistakes in luminescence analysis

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Abstract. Luminescence techniques are powerful and sensitive probes to study imperfections, impurities and modifications of insulating materials. They are used in a wide range of disciplines from condensed matter physics to archaeology and mineralogy and the methods have developed over nearly a century. Early equipment was often not quantitative and data were collected in formats that were difficult to process and manipulate, and so signals were frequently presented in terms of the initial signals without corrections for equipment spectral sensitivity. Unfortunately not only did this distort the information but often it resulted in incorrect interpretations. Further, the incorrect data handling has persisted into modern usage both by physicists and those in other fields who merely use luminescence as a sensitive technique. Several main types of problem are considered. These include temperature errors in thermoluminescence dosimetry; subtleties in the signal intensity corrections for the responses of both the spectrometer and detectors; grating polarization effects; sample anisotropy; and common errors in spectral deconvolution, especially failure to transform from wavelength to energy plots.

1. Introduction

Luminescence signals provide information on relaxation processes in both inorganic and biological materials and the photon energy of the transition is primarily defined by the electronic structure around the emission site. Subtle variations in the structure will then influence the transition energy and excited state lifetime. Such variations have been successfully used to track changes over volumes as large as 50 neighbouring shells. Luminescence is therefore a powerful probe of defect structures in insulators, as well as responding to impurities, phase changes and distortions such as those caused by stress or nanoparticle inclusions. Equally, the changes induced by local distortion make luminescence a useful probe to distinguish between healthy and diseased biological material and it is used in the emerging field of Optical Biopsy.

Luminescence signals have been studied for more than a century with techniques from simple visual observation to black and white or colour photography. By the 1960s more quantitative detectors, such as photomultiplier tubes became available. However the spectral information was generally displayed on a chart recording as a monochromator swept through the wavelength range of the system. Such raw data were then published and used as the basis for discussion and interpretation of the luminescence. For some applications this was acceptable, for example in mineralogical applications changes in spectra revealed different component materials and the presence of rare earth ions were easily identified by characteristic line spectra. It must be recalled that in the 1960s attempts to remove the background dark current, and then scale the signals to correct for the transmission efficiency of the monochromator and sensitivity of the PM tube involved tedious manual processing (N.B. on line computer processing was not available).

The sensitivity of luminescence was still attractive and widely used both by physicists and those from other disciplines who were expert in their own fields, but not necessarily in luminescence. In

this context there are many examples of the problems from those based in semiconductor science and materials modifications. This situation has unfortunately resulted in many errors in signal processing and discussion which have persisted to the present day. In part this is because data are compared with earlier work and in part because different communities of research areas handle signals in similar manners, often with identical recording equipment. Overall, systematic errors have become established. Three examples of these problems will now be discussed.

2. Thermoluminescence dosimetry

Radiation dosimetry evolved in the 1950s for health reasons for those working in the nuclear industries. Rather than use photographic film badges it was found that many materials (such as LiF with added impurities) could both respond similarly to body tissue and also offer an extremely sensitive and reliable radiation dosimeter. The science of thermoluminescence (TL) is that in an insulating material exposure to ionising radiation releases electrons which can become trapped at impurity/defect sites. Subsequently the material can be heated and during the heating the electrons are released, move through the material to more stable sites, and finally emit luminescence as they drop into the lower energy states. For dosimetry this is excellent as the total emitted signal is proportional to the original irradiation dose. Radiation dose measurements by TL are valuable not only for personnel dosimetry but also for archaeological dating of materials which had been heated at some time in their history (i.e. to offer a time zero). Consequently dosimetry signals from pottery can be linked to age, and the information is helpful both for historic reasons and for sensing fakes or later copies of a particular style of ceramic.

Experimentally the signal rises through a peak (called a glow curve) as the rate of charge release increases exponentially with sample temperature, but the signal then falls as the number of trapped charges become exhausted [1]. The peak temperature Tm is related to the activation energy or trapping (E) and the attempt to escape frequency (υ), with other factors influencing the detailed shape of the glow peak. In order to see a weak signal against the background noise of the PM tube detector it became fashionable to use very high heating rates. The temperature that was measured was taken with a thermocouple on a heater strip and this was controlled to give a rapid linear heating ramp. The dosimeters are by definition insulating materials, and hence poor thermal conductors. This means there is a changing temperature gradient dT between the heater strip and the emitting face of the dosimeter. For *dosimetry* this error between the true sample temperature and the heater is irrelevant as one is only concerned with the integrated signal. Further, most research groups tend to use very similar equipment so there is the same systematic error between different workers in the field and there is no confusion in discussions within the community.

The dT problem becomes apparent once one attempts to move to a more scientific analysis of the data, as the error dT will change with heating rate (β) and the entire curve shape is distorted. Therefore the dosimetry community may discuss a feature at say 250^{o}C but, as recorded, their estimates of E and υ will be wrong, as will be temperature of the glow peak. More critically is that comparison of a glow peak temperature with literature data obtained via other techniques, such as isothermal annealing of absorption or ESR signals, will not match. Hence neither the TL experts, nor those in other fields, will realise they are discussing the same process. Dosimetry heating rates can run to more than 100 degrees per second so the dT values are very significant. Figure 1 indicates the scale of the errors that can accrue. It contrasts the glow peak for a theoretical glow curve, where the true surface temperature is rising at 50 degrees per second, with the measured curve where the signals are plotted in terms of the heater temperature and there is a typical thermal temperature lag developing. Even for this modest heating rate the recorded signal is wrong by some 50 degrees.

As already mentioned, this systematic error is not critical for dosimetry, but it is a major error in terms of modelling of the processes. Nevertheless many journal articles continue to appear with modelling based on the heater temperature, despite a number of publications which have given detailed indications of the errors involved, or empirical suggestions as to how to minimise them [2-5].

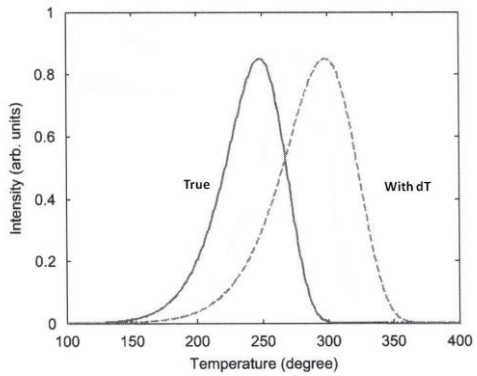

Figure 1. The solid line shows a true glow curve of a sample heated at 50 degrees per second and the dashed line is typical of recorded data based on the thermocouple temperature of the heater strip. The thermal gradient across the insulating sample introduces a variable lag of dT which is ~50 degrees at the peak value in this example.

3. Errors in corrections of the instrument sensitivity

3.1 Diffraction grating effects

The initial step in correcting the spectral data is to remove the dark current or other sample independent signals that are produced by the detector. Signal to noise can be excellent for strong signals and PM tubes but the linear dynamic range of CCD detectors is often far less than the range for the PM tubes. The next step is to correct the measured spectral intensity for distortions introduced by the transmission characteristics of any optics, filters and polarizers etc in the system. Polarizers are often used in data recorded from anisotropic crystals but their spectral response is rarely flat across the spectra. Similarly with diffraction grating monochromators (and spectrometers) one must avoid the problems of second or third order diffraction and so blocking filters are required at longer wavelengths to remove higher order spectra. Note for a grating the dispersion is given by $n\lambda = 2d \sin\theta$ so at a nominal setting of say 800 nm the unfiltered signal will contain not only 800 nm light but also second order from 400 nm and third order from 266 nm etc. Since the grating performance is far better at 400 nm than at 800 nm (as seen in figure 2). Similarly with PM tubes the efficiency of detecting the second order 400 nm signal will be superior to that of detection of the real 800 nm signal. In one sensitive system used in Sussex the overall efficiency at 400 nm was 200 times greater than at 800 nm so the second order terms swamped the true signals unless filters were added.

For steady persistent signals there is no difficulty in acquiring spectra with and without the second order filters but in measurement of transient luminescence signals, or those that are time dependent, this is a serious problem. In one of the Sussex systems designed to record the emission spectra during thermoluminescence the problem was avoided by the use of a pair of diffraction grating spectrometers, each with its own photon imaging PM tube [6]. This has an additional benefit that the red region could use a diffraction grating blazed for long wavelengths (i.e. giving higher efficiency) and a second order filter was permanently installed on the red system.

Intensity correction of the signal requires knowledge of the spectral response of both the monochromator and detector. Often the calibration is made for the package but, as will be mentioned, this can be deceptive if the signals are polarized. Typical grating sensitivities are sketched in figure 2 [7, 8]. The transmission efficiency is strongly dependent on whether the light is polarized parallel to the rulings on the grating (P type) or normal to them (S type). For nominally unpolarized light the net sensitivity is a mixture of the two responses. For any system that is intended to record the full spectral range from say 200 to 900 nm the peak will always be near 400 nm, and sensitivity falls steeply in the UV and less rapidly at the red end of the spectrum.

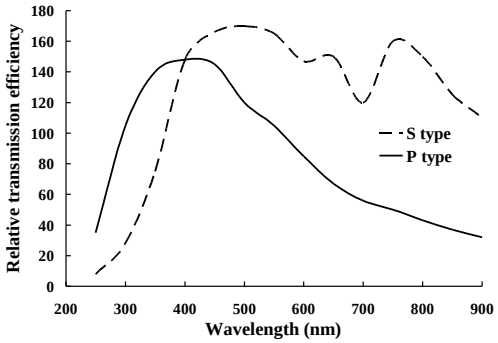

Figure 2. Relative transmission efficiency of a diffraction grating spectrometer for light polarized parallel (P) and perpendicular (S) to the grating lines.

For luminescence studies of anisotropic crystalline material figure 2 indicates there is an unexpected problem. If the different emission bands have a polarized component then across the range of the spectrum the transmission characteristics differ by a factor of 8. This strongly distorts the relative intensities of the components. Some experimentalists introduce a polarizer in front of the spectrometer to select one view of the emission, but because in many configurations (e.g. in a cryostat) it is not possible to rotate the sample. The temptation is to rotate the polarizer by 90 degrees to record the other polarized view. Quite clearly this gives a completely different response and generates false data. Correct solutions would be to select a polarizer orientation, and have a sensitivity calibration for this setting, and then rotate the sample. A simpler option is to choose the polarizer orientation relative to the sample and use an optical fibre link which randomises the polarized signal before it enters the spectrometer. This is preferable as the same grating response applies to each polarizer setting as well as for an unpolarized input.

An additional word of caution is that for some anisotropic materials the emission not only depends on the face that is viewed but also on the axis along which it has been excited. Examples of such phenomena exist for ion implanted crystals.

3.2 Spectral response of the detector

For a wide spectral coverage of luminescence the preferred PM tube has invariably been a multi-alkali photocathode (termed S20). The response of such tubes can be quite variable at the long wavelength end of the spectrum so they need individual calibration [9, 10]. They may also vary with age and, more critically, with exposure to light. The sensitivity changes are apparent in variations in the dark current and in monochromatic systems the red response can be enhanced by exposure to short wavelength light. Hence a spectral scan from short to long wavelengths can differ from scans made in the reverse direction. In recent years various ways of coupling the light to the PM tube have offered enhanced red performance [10-13]. Some of these same enhancements can be achieved with S20 cathode photon imaging tubes as are used in spectrometer systems.

For spectrometer systems there are geometric advantages in using CCD detector arrays, not least because they have greater red coverage. Once again they are very variable and depend on the manufacturer, whether or not they are designed to be illuminated on the front or rear face, and features such as anti-reflective coatings to enhance performance. In general they have a limited dynamic range, so caution is needed if the spectrum has a mixture of weak and strong signals. Coated, or thinned detectors, may display thin film interference effects which can appear as real sample data. This is problematic if the samples are thin films which may also generate signal oscillations with wavelength. For time resolved measurements of luminescence the CCD response is considerably slower than from a PM tube and PM tubes are compatible with lock-in amplifier detection.

The main feature to note is that it is essential to derive a spectral calibration curve for the entire system in order to correctly process the raw data. Over a wide spectral range this implies the use of a detection system which includes long wavelength data that have been filtered to remove high order spectral overlap with the true long wavelength signal. Not all systems automatically include this feature and for equipment used as a general tool (e.g. not by specialists in luminescence) this can (and does) generate misleading data.

4. Errors in data processing

The ubiquitous use of diffraction gratings means that the emission spectra are obtained as intensity as a function of wavelength. The monochromator has a fixed bandwidth entrance slit so the collected data after processing and correcting for the system response appear as a display of intensity versus wavelength {I(λ)dλ versus λ}. If there are many overlapping feature then some peak deconvolution is necessary. Unfortunately many people using luminescence fail to recognise that such deconvolution cannot be made with the wavelength data. Instead the signals *must* be transformed into an energy plot of {I(E)dE versus E}. There are basically two common errors in this attempt at signal deconvolution. The first is to feed the wavelength data into a curve fitting package but unfortunately the analysis is not just incorrect in terms of the physics, but it is totally misleading. The second incorrect approach is to transform only the wavelength axis into photon energy ($E = hc/\lambda$). Such a transformation is immediately apparent as the intensities of the peaks are the same as in the wavelength view of the signals. The correct route requires adjustment of the intensity data from a fixed dλ to a fixed dE. Mathematically this is trivial as $dE = -hc/\lambda^2$. However the λ^2 term has a major influence on the intensities. Less obvious is that the energy of the peak taken from a wavelength plot does not match the peak energy of the correctly transformed data. More obvious is that the intensity changes can strongly influence our discussions as to which are the major features.

The normal assumption is that luminescence processes of emission sites in solids result in Gaussian or Lorentzian line shapes [14-16]. Figure 3 therefore shows how a set of symmetric Gaussian bands (in energy) would have appeared on the wavelength version of the data. In wavelength plots the peak shifts as a function of full width half maximum and the value is only correct as the bandwidth approaches zero. This is of course why such errors are not obvious when recording line spectra, as from rare earth ions. The current example has considered a red emission band centred at 2.0eV, since for the longer wavelength signals one can sense more clearly why the apparent wavelength data are so sensitive to bandwidth. In this example the change from a narrow to a wide FWHM shifts the wavelength peak by nearly 200 nm!

To emphasise the scale of the changes that have occurred along the processing route figure 4 displays the data sets that would have been recorded by a grating spectrometer with either a red sensitive PM tube or two different types of CCD detector. Figure 4 is the view that would appear before the signals were corrected for the responses of the collection systems. Whilst it is evident that with UV sensitive detectors there are probably 4 emission bands present, it is very tempting to assume that with the CCD detector there are probably some minor bands in addition to the 4 main ones. It is also clear that the PM and CCD do not define the peak values at the same wavelengths. Certainly one could not assume that after the spectrometer corrections and a transformation into an energy plot the spectrum is actually comprised of four Gaussian features of equal intensity of equal bandwidth (0.8 eV) centred at 1.50. 2.03, 4.16 and 5.50 eV. In true wavelength terms these peaks are near 826, 438, 299 and 225 nm.

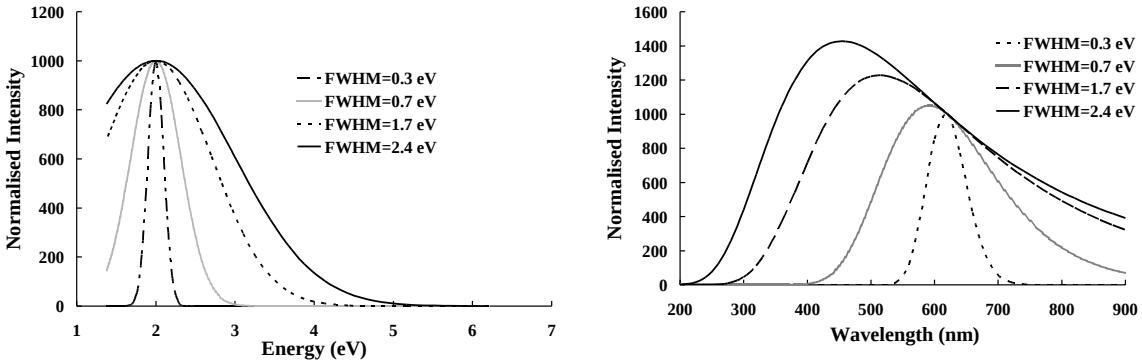

Figure 3. Equivalent wavelength and energy plots of a set of Gaussian luminescence bands centred at the same photon energy but different FWHM values

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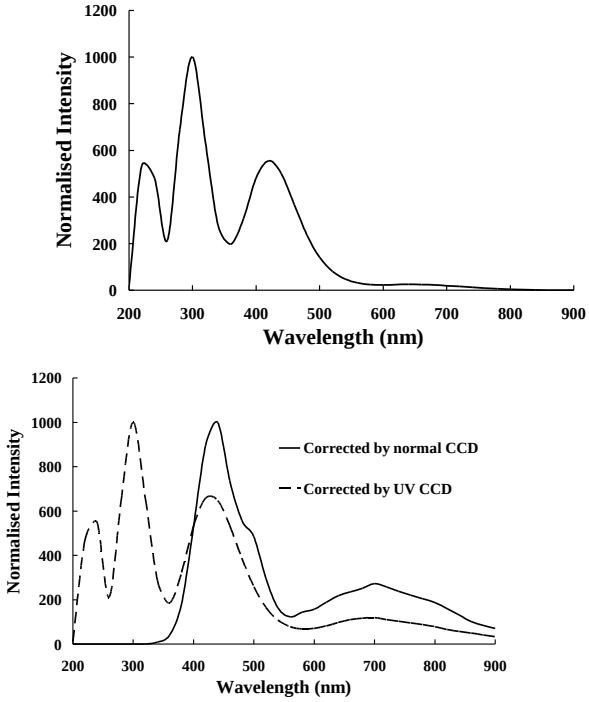

Figure 4. The spectra that would initially be collected by a spectrometer and PM tube (left) and the same signal as sensed by two different types of CCD detector (right). Note that after spectrometer correction and

transformation to an energy plot there are just 4 Gaussian emission bands of equal intensity and bandwidth.

5. Final comments

The examples presented here emphasise that because of the long history of luminescence techniques much of the early literature did not take into account all the factors which cause signal distortion as the data were collected. Further, many of the users of luminescence are experts in different disciplines and so the luminescence technology is used merely as a tool without a full appreciation of the problems. Overall this has resulted in a literature in which many signal processing errors are either not appreciated or not mentioned in the publications. It is then difficult to guess whether system corrections have been applied and, for energy plots, if both intensity and energy axes have been transformed from the wavelength recorded data. Unfortunately the current literature of luminescence data, even in physics based areas such as semiconductor physics, is rarely explicit in the type of corrections which have been made, and the trend is to show and discuss data presented on a wavelength axis. The reader must then guess which, or if, detector corrections were applied. For the examples used in this article it is apparent that such problems lead to errors in the data collection as well as subsequent signal processing and interpretation. One ongoing problem is that publications often show data in ways which match, or can be compared with earlier articles. There is thus inertia in attempting to move all the luminescence literature towards clearly stated and properly corrected signals.

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