Triboluminescent materials for structural damage monitoring†

Ian Sage and Grant Bourhill*

*Defence Evaluation and Research Agency, St. Andrews Rd, Malvern, Worcs, UK WR14 3PS.
E-mail: gbourhill@dera.gov.uk*

Triboluminescent materials have been known for at least four centuries. The majority of work to date has been academic in nature – reporting a new triboluminescent material and/or presenting a spectroscopic study in an effort to explain the mechanism underlying the fracture-induced light emission. Recently, the advantages of triboluminescent materials as real-time structural damage sensors have been highlighted. These sensors can be exploited in both commercial and military markets. In addition to covering some of the recent advances in the field, this paper aims to provide a timely overview of those triboluminescent materials which may be suitable as structural damage sensors.

1. Introduction

It may at first appear almost fanciful that light is emitted when certain materials are fractured. That this is science-fact and not science-fiction can be readily demonstrated, however, by crushing crystalline sugar in a darkened room, after allowing an appropriate time for dark adaptation of the eyes, and observing the resulting bluish-white light.[1] This fracture-induced light emission, referred to here as triboluminescence, but elsewhere as fracto-[2] or mechano-luminescence,[3] has in fact been known for almost 400 years,[4] with one of the earliest references, again to sugar, appearing in Francis Bacon's "The advancement of learning" in 1605. Indeed, given the requirement for visual observation and, in the majority of cases, dark-adaptation, it is remarkable that by the turn of the previous century reviews were appearing which listed hundreds of known triboluminescent materials.[4]

Quantitative analysis of the triboluminescent spectral content and intensity was made possible firstly through photographic techniques,[5] but secondly and more importantly, through the use of photoelectronic detectors.[6] Indeed, since 1950, a large number of reports have appeared which, based in part on a spectral analysis, attempt to detail firstly the nature of the excited states responsible for triboluminescence and secondly the underlying triboluminescent mechanism itself. It soon becomes evident from these reports however that no single mechanism is common to all triboluminescent substances and it is therefore convenient to class materials according to both their chemical nature and the type of triboluminescence observed.[4]

In spite of the work carried out to date, it is clear that triboluminescence is not as widely known, or as widely studied, in the scientific community as other luminescent phenomena such as photoluminescence, electroluminescence or chemi-luminescence. The reason for this may be due, in part, to the lack of any application requiring triboluminescent materials and so, to date, there has been no commercial requirement to both support and drive basic research in this area. Recently however, reports have appeared suggesting the use of triboluminescent materials as smart sensors of structural damage.[7,8] The concept is that triboluminescent materials either attached to, or embedded within, a host material can indicate the occurrence of structural damage by emitting light upon fracture. In addition to indicating the onset of damage, it is proposed that the severity of damage can be extracted from the intensity of the triboluminescent light emission. Further-more, by utilising an array of triboluminescent sensors, where each sensor in the array emits a different triboluminescent wavelength upon fracture, simply monitoring the colour of the light emission allows the damage location to be ascertained. These structural damage sensors have application ranging from prosthetic composite limbs to modern military platforms.

Given the newly proposed application for triboluminescence, it is timely therefore that a review appear highlighting both recent advances in the field and the current range of triboluminescent materials which may be suitable for damage monitoring. It is hoped that this review will, in part, encourage research allowing a better understanding of the current materials, resulting in a rational design of more efficient compounds.[9] The aim of this paper therefore is not to provide an extensive review of triboluminescence, as this can be found elsewhere,[4,10] but to give a flavour for the various types of triboluminescent compounds currently known, their properties and associated (proposed) triboluminescent mechanisms. Furthermore, although materials are known which emit light when elastically or plastically deformed,[11] given the proposed application, this paper will focus on the more prevalent triboluminescent compounds – those that emit light only upon crystalline fracture.

Section 2 will discuss briefly the methods which have been used to both generate and measure triboluminescence. Section 3 will discuss the various common types of materials which emit light upon fracture and section 4 will discuss efforts to provide quantitative comparisons of triboluminescence efficiency. Section 5 will discuss the material and sensor requirements for the recently proposed application of tribo-luminescent compounds as smart structural damage sensors and will highlight potential areas for future research. Throughout the paper, an italicised material name denotes that the structure of the triboluminescent compound is included in the Appendix.

2. Techniques for inducing and measuring triboluminescence

2.1 Methods for generating triboluminescence

An in-depth analysis of how crystal structure influences triboluminescent intensity would involve positioning a single crystal in a particular orientation and monitoring the light intensity when a stress is applied in a given direction.

DOI: 10.1039/b007029g

J. Mater. Chem., 2001, **11**, 231–245   **231**
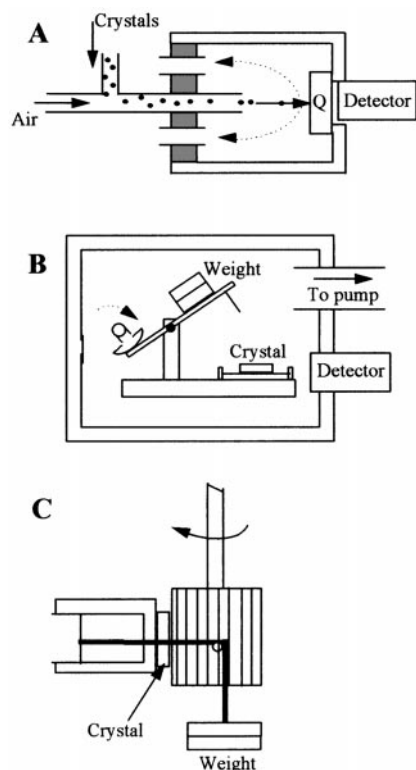
This journal is © The Royal Society of Chemistry 2001

Fig. 1 Methods for inducing triboluminescence: **A** – the air-driven technique;[14,15] **B** – the impacting needle technique;[16,17] **C** – the crystal milling technique.[17,18]

Fig. 2 Modern techniques for inducing triboluminescence: **A** – the air-driven piston;[20] **B** – the falling weight technique;[21] **C** – variant of the falling weight technique.[22]

Unfortunately, crystal size, crystal quality and/or triboluminescent intensity is generally insufficient to allow this and a more random approach has been adopted, such as crushing a material in transparent holders with a variety of crushing implements.[12,13] Of course, random crushing does not yield any information on the applied mechanical energy. This situation has been resolved in a number of ways (Fig. 1).

Fig. 1**A** illustrates that particles of the triboluminescent material under investigation are introduced into an air stream which propels them onto a quartz screen, positioned just in front of the entrance slit of a spectrometer. Great care must be taken however to ensure that no powdered material is deposited on the quartz plate, which would act to scatter and/or absorb part of the triboluminescence occurring in later impacts. The impacting needle technique (Fig. 1**B**) has the advantage that: (i) the load upon impact can be varied and controlled by the weight applied to the lever; (ii) the impact is periodic, the frequency of which is controlled by the speed of the rotating cam, and so fresh material can be moved into position prior to every impact event; (iii) the apparatus can be operated under different atmospheric conditions and (iv) a hot
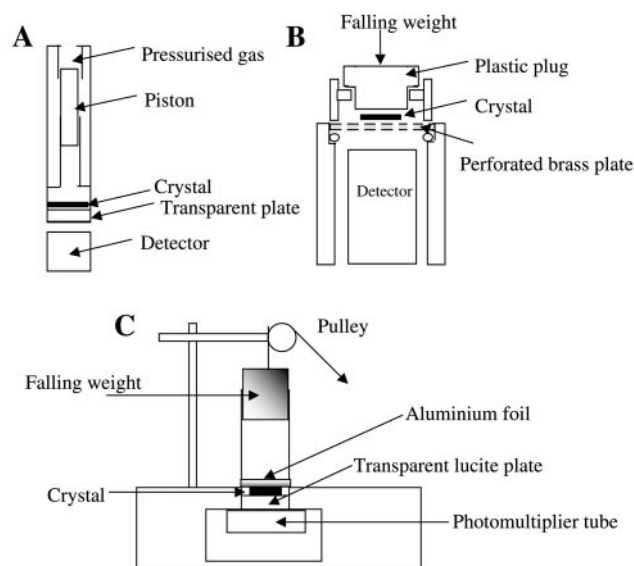
plate positioned under the crystal allows the triboluminescent intensity to be determined as a function of temperature. Fig. 1**C** on the other hand is useful where thick, transparent crystals are available since the surface of the crystal being milled can be imaged onto the entrance slit of a spectrometer. A modification of this apparatus has been used by others.[19]

The apparatus in Fig. 1 for inducing triboluminescence with a known amount of mechanical energy is now infrequently used. The more common techniques prevalent today are illustrated in Fig. 2. In Fig. 2**A**, an air-driven piston is used to crush the material under investigation, with the impact energy controlled in part by the velocity of the piston at impact.[20] A related technique is shown in Fig. 2**B** where a falling weight is used to impact a plastic stopper which distributes the load across the sample.[21] Again the impact energy is controlled in part by the velocity of the falling weight upon impact. In the design shown in Fig. 2**B**, a perforated brass plate situated beneath the sample is used to allow the emitted photons to reach the detector. In other designs[20,23] a simple transparent plate is sufficient. Fig. 2**C** represents a variant of the falling weight design.[22]

During the course of our studies on triboluminescence,[8,24] either a commercial drop tower (Fig. 3**A**), which offers the advantages that a wide range of impact energies can be accessed and also that secondary impact events due to the bounce of the falling weight can be eliminated, or a home-built drop tower (Fig. 3**B**) were used. In the latter case, the triboluminescent material under investigation was doped into
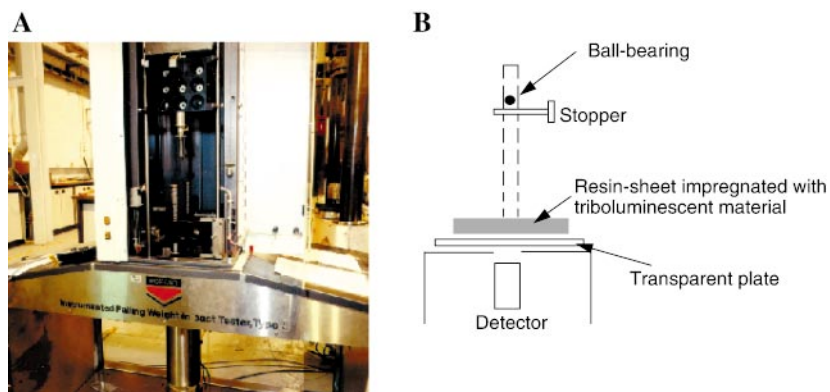

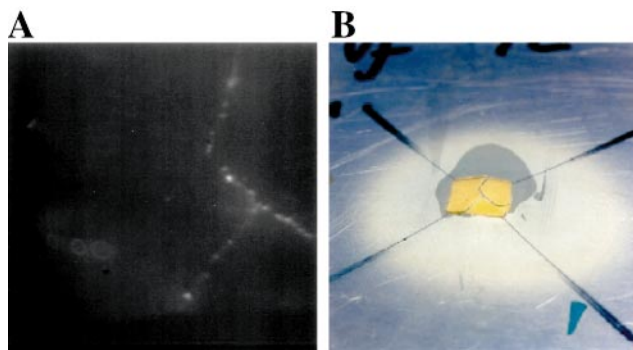Fig. 3 Apparatus used[8,24] to induce triboluminescence: **A** – commercial drop tower; **B** – home-built drop tower.

Fig. 4 **A** – Light emission from a resin doped with a triboluminescent material upon impact (using apparatus in Fig. 3**A**) as imaged by a monochrome CCD camera; **B** – the resulting fracture pattern. Both images are taken from reference 8.

a resin, with the resin sheet placed on top of a transparent plate and impacted directly by a falling ball-bearing.

A number of more exotic methods have also been used for generating triboluminescent emission, including high peak-power laser pulses[25] and thermal-shock-induced-tribolumines-cence using liquid nitrogen.[26–28] Use of these techniques has been limited however.

2.2 Measuring the triboluminescent emission

The simplest method to measure the triboluminescent output intensity is *via* a high-gain detector, such as a photomultiplier tube or semiconductor diode.[29,30] Other authors[8,21,24,31] have utilised a CCD camera to capture the triboluminescent emission. While this technique offers the advantages that an image of the sample under stress is obtained (Fig. 4) and that a sum of the charge on each pixel comprising the CCD array can be made to obtain an overall (detected) light intensity, care has to be taken to account for the wavelength sensitivity of the CCD before meaningful comparisons between the efficiencies of different materials can be made. This is similar to the corrections made when determining, in an absolute manner, the photoluminescent quantum yield of thin films.[32,33]

While photomultiplier tubes, semiconductor diodes and CCD cameras generate information regarding the emitted light intensity, they do not directly yield information as regards the spectral content (*i.e.* intensity *versus* wavelength) of the triboluminescent emission. This problem was first addressed in 1922 when Longchambon[5] succeeded in measuring the spectral content of the triboluminescence from sugar using a spectrograph and a photographic film. While this technique was effective in determining the spectral content, the exposure time was four hours, due to the weak triboluminescent output, and the amount of material required to generate the spectrum was 5 kg. This photographic technique was evolved further[34–36] with the use of an image-intensifier to amplify the tribolumi-nescent emission, with the output phosphor screen of the image intensifier being imaged onto a photographic film (Fig. 5**A**), with the resulting image developed and densitometered to yield the intensity *versus* wavelength information. Due to the use of the image-intensifier, a significantly shorter exposure time and thus a smaller amount of material is required. However, the use of the photographic film still made the technique relatively insensitive *e.g.* hundreds of grammes of material being required, with an exposure time of approximately one minute,[35] and the data analysis was time consuming. This problem was overcome in 1985[6] by the use of an array of diodes positioned at the phosphor screen which converted the optical image at the phosphor screen into an electronic signal (Fig. 5**B**), eliminating the need for photographic imaging and densitometry. This technique allows triboluminescent spectra to be collected, using approximately 100 mg of material, with exposure times of tens of milliseconds (depending of course on the efficiency of the material being examined) and with a typical resolution of 1–2 nm.

Another technique commonly used[37,38] has similarities to a dual-beam spectrometer (Fig. 5**C**). Here, the triboluminescence generated by a sample is efficiently collected by a condensing lens and focused through the entrance slit of a monochro-mator. The triboluminescent light is subsequently split by a quartz beamsplitter positioned within the monochromator. The reflected beam passes directly into a photomultiplier tube which yields a signal proportional to the overall intensity (I_T) for that particular triboluminescent emissive event. The light
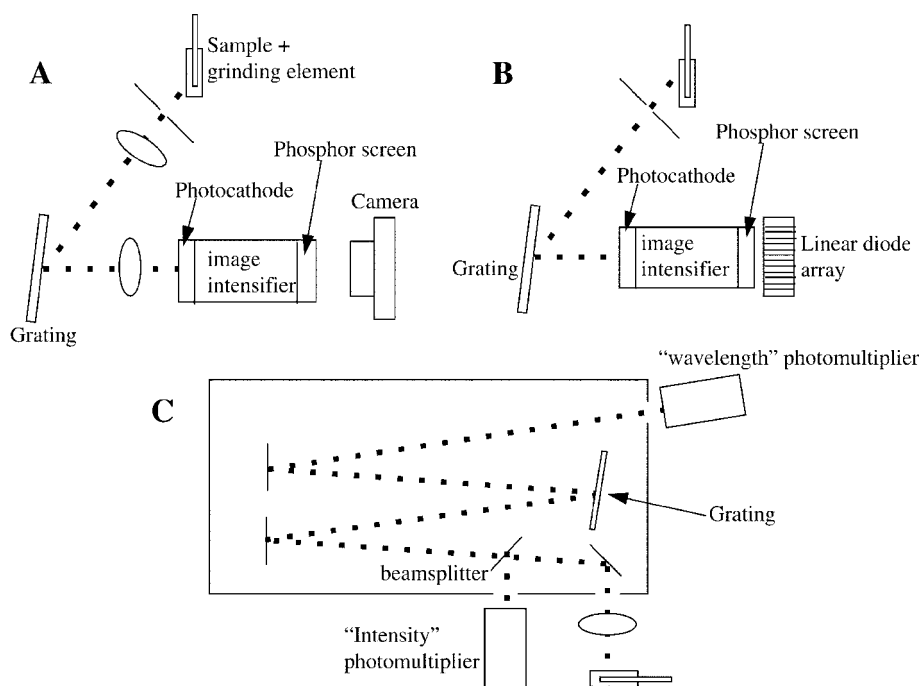

Fig. 5 Various techniques to determine the spectral content of the triboluminescent emission: **A** – photographic measurement of the intensity of the image-intensifier phosphor screen;[34–36] **B** – electronic measurement of the intensity of the image-intensifier phosphor screen;[6] **C** – dual detector spectrometer.[37,38]
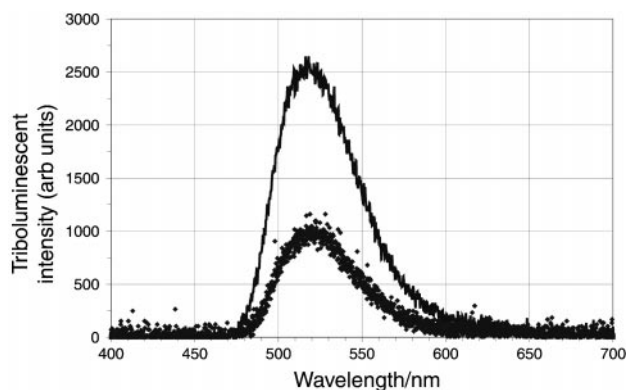
Fig. 6 Triboluminescent spectrum of *dibromobis(triphenylphosphine oxide)manganese* **9** as collected by a fibre-coupled miniature non-intensified optical multichannel analyser.[41] The lower curve (data points) was recorded with a resolution of 1.3 nm whereas the upper curve (solid line) was collected at 2.5 nm resolution.

transmitted by the beamsplitter is diffracted by a grating, with the intensity at a selected wavelength (I_λ) measured by a second photomultiplier. Taking a ratio of I_λ/I_T and then repeating the measurement over a range of wavelengths allows the triboluminescent spectrum to be constructed. Despite this technique having been used extensively in the past, only low resolution spectra (typically 5–10 nm) have typically been recorded due to the relatively time consuming data collection and the small signal intensity at high resolution. Furthermore, it has been noted that great care has to be taken to ensure that each photomultiplier tube accesses light from the same fracture volume in the sample to ensure a correct I_λ/I_T ratio. This is important if the spectral shape and position of the triboluminescent emission is to be compared with, for example, solid-state photoluminescence or electroluminescence spectra.[4,39]

Recent advances in both silicon sensitivity and miniaturisation of optical components have allowed the apparatus in Fig. 5B to be evolved to the level where an image-intensifier is no longer required to determine the spectral output from materials with moderate triboluminescent efficiencies *i.e.* the triboluminescent emission is diffracted by the grating and detected without signal amplification by the linear diode array. These miniature spectrometers, or non-intensified optical multichannel analysers, are now widespread within the spectroscopy community since they are significantly less expensive than systems incorporating an image-intensifier

tube. The spectra in Fig. 6 are single frame images (*i.e.* no averaging), with 0.3 seconds integration time, of the triboluminescent emission from *dibromobis(triphenylphosphine oxide)manganese* **9**[40] recorded with a fibre-coupled miniaturised non-intensified optical multichannel analyser (Ocean Optics SD2000).[41] This apparatus offers advantages of speed of collection, cost, portability, ease of use and fibre-optic delivery of the triboluminescent emission to the spectrometer. However, compromise has to be made in terms of both resolution and sensitivity compared to an image-intensified system.

3. Triboluminescent materials

Of the vast number of triboluminescent materials known, the majority emit light only upon fracture.[42,43] This fracture-induced light emission holds for the material tested in Fig. 4, where it can be seen that the strongest light emission occurred in the region corresponding to the major crack. The remaining less intense light away from this major crack line has presumably arisen due to either microcracks formed during the impact event and/or triboluminescence caused by the sample (triboluminescent material doped into an epoxy resin) peeling from the metal substrate. To study whether materials emit in their elastic, plastic or fracture regimes, Chandra[20] has developed an experimental technique which measures the triboluminescence intensity as a function of applied stress and deformation. A number of materials have been tested and been shown to triboluminesce only upon fracture. We have examined a number of compounds, using apparatus similar to that of Chandra. Fig. 7**A** shows the results obtained for a material emitting light only upon fracture whereas Fig. 7**B** shows a material emitting light during elastic/plastic deformation in addition to fracture.[44]

Triboluminescent damage sensors should only emit light when structural fracture/damage to the host has occurred and should not emit when elastically or plastically strained during the normal flexures and strains experienced by the host structure. In other words there should be a 1:1 correlation between host fracture and fracture of the triboluminescent sensor. In this paper we focus therefore on materials that are triboluminescent only upon fracture. It is convenient to class the various triboluminescent materials into categories representing both the nature of the triboluminescence and/or the material type.[4] Sub-sections 3.1–3.3 have classified materials according to the nature of the light emission – either a gas discharge, a luminescence similar to the solid-state photoluminescence or a combination of both. Sub-section 3.4 has
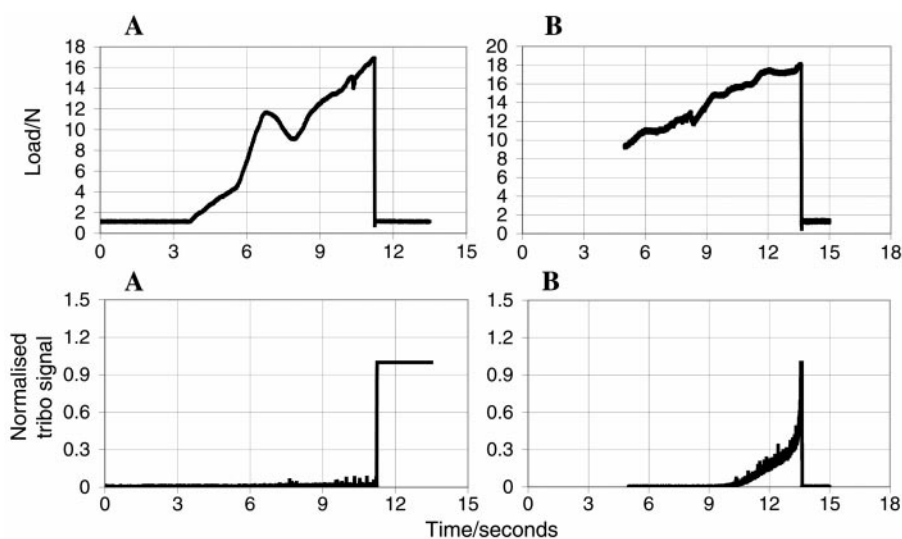

Fig. 7 The triboluminescent light emission as a function of the applied load for *europium tetrakis(dibenzoylmethide)triethylammonium* **1** (**A**) and Mn-doped ZnS **8** (**B**) incorporated into an epoxy resin and being subjected to deflection.[44]
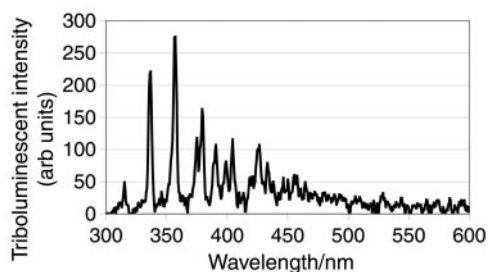
Fig. 8 Triboluminescence spectrum of sucrose.[41]

been added to discuss the triboluminescence of metal complexes as materials of this type are among the brightest triboluminescent compounds currently known.

3.1 Gas discharge

The most common material which exhibits a gas discharge upon fracture is sucrose. In air, the spectrum of the fracture-induced emission from this material (Fig. 8) is identical to that of a nitrogen discharge,[12,26] identified as a $^3\Pi_u \rightarrow ^3\Pi_g$ transition.[12,38] That this transition is the origin of the emitted light is supported by reports that vacuum degassed samples of sucrose do not exhibit triboluminescence when fractured under a nitrogen-free solvent.[12]

The generally accepted mechanism for gas-discharge triboluminescence is crystalline fracture resulting in piezoelectric charging of the newly created surfaces[45] of sufficient magnitude to cause gas breakdown and/or gas excitation *via* electron bombardment. The crucial role of a piezoelectric charge is evident since sucrose does not triboluminesce when cleaved in a plane parallel to the unique axis since, by symmetry, this does not generate a piezoelectric charge, whereas cleavage in any other plane results in the triboluminescent gas discharge spectrum.[4] In addition, it has been shown that the intensity of the nitrogen discharge is directly proportional to the charge generated during fracture for crystals of rochelle salt.[46] Additional support for a piezoelectricity-induced gas breakdown comes from statistical studies of the occurrence of triboluminescence in acentric (and thus piezoelectric) crystals,[47] as well as spectroscopic studies of the triboluminescence generated when sucrose is fractured in different gaseous environments.[4]

Additional materials which triboluminesce with a spectrum characteristic of a nitrogen discharge include: saccharides,[12]

menthol,[6] lithium sulfate,[45] aniline hydrochloride,[48] tartaric acid,[10] D-camphoric acid[49] and copper sulfate.[43]

3.2 Fracture-induced triboluminescence–photoluminescence

There are many examples in the literature of materials which triboluminesce with a spectrum very similar to, or identical with, their solid-state photoluminescence spectrum. Fig. 9A for example shows the triboluminescence and solid-state photo-luminescence from *salicylsalicylic acid*,[39] **17**, a little known but highly triboluminescent material.[50] The close overlap between the triboluminescent and solid-state photoluminescent spectra does not always hold true however. For example, *N-acetylanthranilic acid* **16** (Fig. 9B) and *menthyl-9-anthracene-carboxylate* **18** (Fig. 9C) show a significant spectral difference between the two emission maxima,[39,51] even when both luminescent spectra are recorded on the same apparatus at an identical resolution. It has been suggested that, generally, a spectral shift between the triboluminescence and solid-state photoluminescence spectra may arise from:

(1) Pressure-induced changes in Franck–Condon factors controlling the spectral location, shape and intensity of the light emission[52,53]

(2) Self-absorption of the triboluminescence. Generally, photoluminescence from a solid sample is a surface effect whereas triboluminescence is typically generated within the bulk of a sample and the emitted triboluminescent light may suffer absorptive attenuation when propagating through the material towards the detector[51]

(3) Symmetry changes to emitting centres close to the face of the freshly-formed fracture[54]

Assuming that a crack propagates at close to the speed of sound (approximately 1000 m per second) and that the crack front has a diameter of a few nanometres, molecules will only be under significant pressures for a few picoseconds.[54] Indeed, the pressure at the emitting centre has been estimated for several materials[52,55] and found to be close to atmospheric pressure. However the materials typically examined have had long solid-state photoluminescent lifetimes (10's to 100's of microseconds), sufficiently long for the crack-front to have propagated away from the emitting site and for the local pressure at the emitting site to have reduced. Given that molecules are only under pressure for a few picoseconds, observation of pressure-induced changes to Franck–Condon factors is more likely therefore with fluorescent rather than phosphorescent materials due to the (generally) shorter
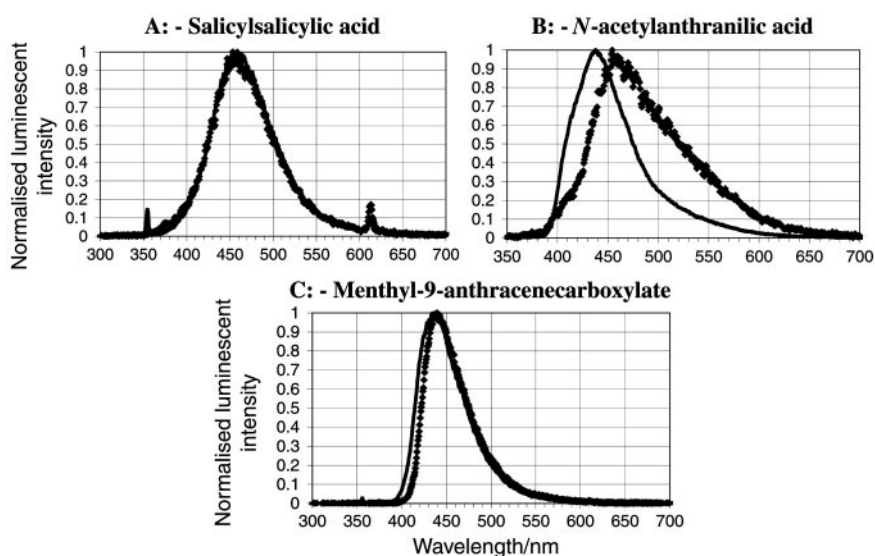

Fig. 9 Normalised solid-state photoluminescence (solid line) and triboluminescence (data points) from: **A** – *salicylsalicylic acid* **17**; **B** – *N-acetylanthranilic acid* **16** and **C** – *menthyl-9-anthracenecarboxylate* **18**. All data from reference 39.
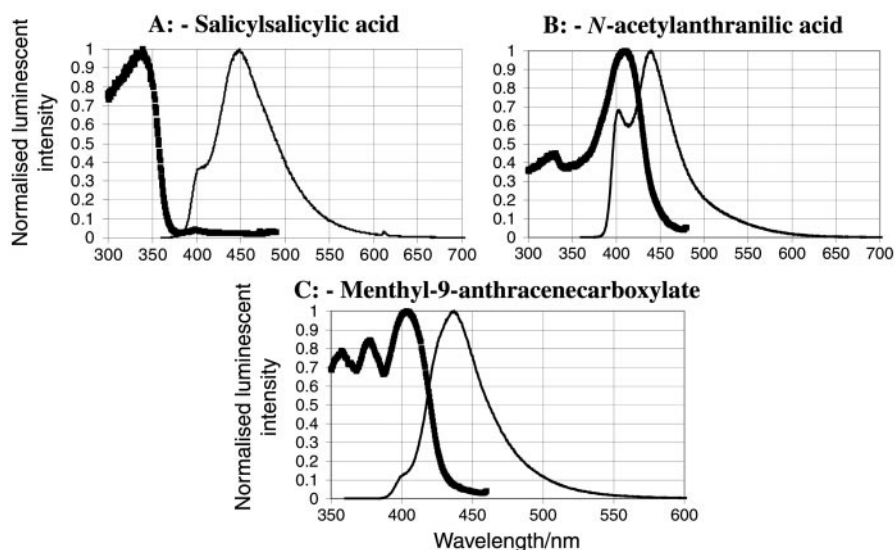
Fig. 10 Normalised solid-state photoluminescent excitation and emission spectra from: **A** – *salicylsalicylic acid* **17**; **B** – *N-acetylanthranilic acid* **16** and **C** – *menthyl-9-anthracenecarboxylate* **18**. All data from reference 39.

radiative lifetime of the fluorescent compound.[53] It is still unlikely however that this effect would be observed for the materials in Fig. 9A–C, which have solid-state photoluminescent lifetimes of approximately 4 ns.[39] Therefore the spectral shifts observed in Figs. 9**B** and 9**C** require an alternative explanation.

Solid-state excitation and emission fluorescence spectroscopy has revealed[39] that there is a significant spectral overlap between the solid-state excitation (absorption) spectrum and the solid-state emission spectrum for *N-acetylanthranilic acid* **16** (Fig. 10**B**) and *menthyl-9-anthracenecarboxylate* **18** (Fig. 10**C**) but not for *salicylsalicylic acid* **17** (Fig. 10**A**). This result is consistent with self-absorption of the triboluminescent emission being responsible for the spectral shifts observed in Fig. 9**B** and 9**C**.

Hexacelsians are rare-earth doped $BaAl_2Si_2O_8$ crystals, with the rare-earth atom occupying Ba sites in the solid lattice.[31,56] The triboluminescence and solid-state photoluminescence spectra of hexacelsians doped with Eu^{2+}, Yb^{2+}, Ce^{3+} or Sm^{2+}/Sm^{3+} have been recorded on the same apparatus at an identical resolution.[39] Fig. 11 shows the luminescence spectra whereas Fig. 12 shows the solid-state excitation (absorption) and emission photoluminescence spectra from these samples. It

is clear from Fig. 11 that radiative transitions involving rare-earths in the +2 oxidation state exhibit a spectral difference between the triboluminescence and photoluminescence spectra, whereas no significant difference is observed for the Ce^{3+} hexacelsian **12**. Fig. 12A reveals that self-absorption can explain the spectral difference for the Eu^{2+} hexacelsian **10**. However, the spectral differences for the Yb^{2+} and Sm^{2+} transitions can not be due to self-absorption and given the long solid-state photoluminescent lifetimes of these materials (of the order of tens to hundreds of microseconds[39]), it is unlikely that pressure-induced changes to Franck–Condon factors are important. Instead, it is suggested[39] that symmetry changes to the ligand field, caused by the creation of fracture surfaces, are responsible for the difference in the two luminescent emissions. This suggestion is consistent with f–d transitions in divalent rare-earths being more sensitive to ligand field perturbations than the f–f transitions in trivalent lanthanides.

It is clear that when the triboluminescent and solid-state photoluminescent spectra are identical, the emitting excited state in both cases must also be the same. What is not certain however is the mechanism by which the excited state becomes populated during fracture. Statistical studies[10,42] have revealed a significant correlation between piezoelectric space groups and
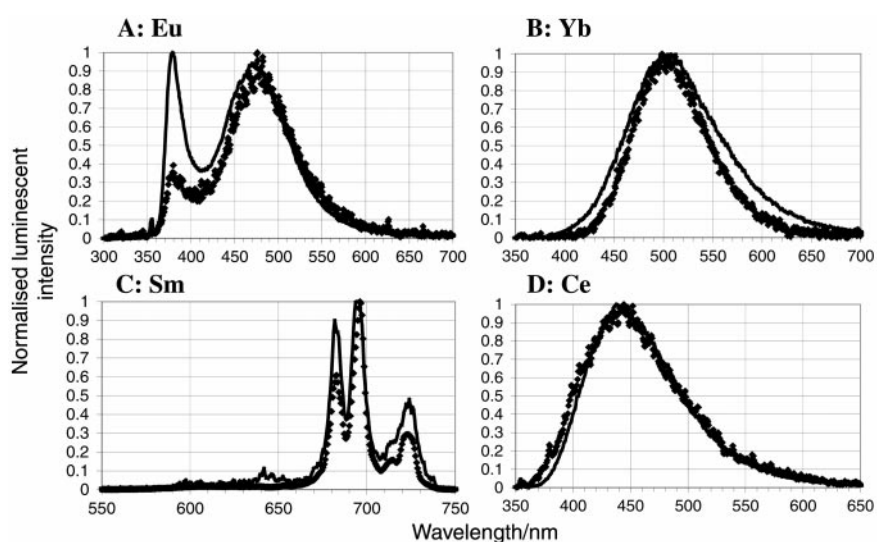

Fig. 11 Normalised solid-state photoluminescence (solid line) and triboluminescence (data points) from: **A** – Eu^{2+} hexacelsian **10**; **B** – Yb^{2+} hexacelsian; **C** – Sm^{2+}/Sm^{3+} hexacelsian **11** and **D** – Ce^{3+} hexacelsian **12**. All data from reference 39.
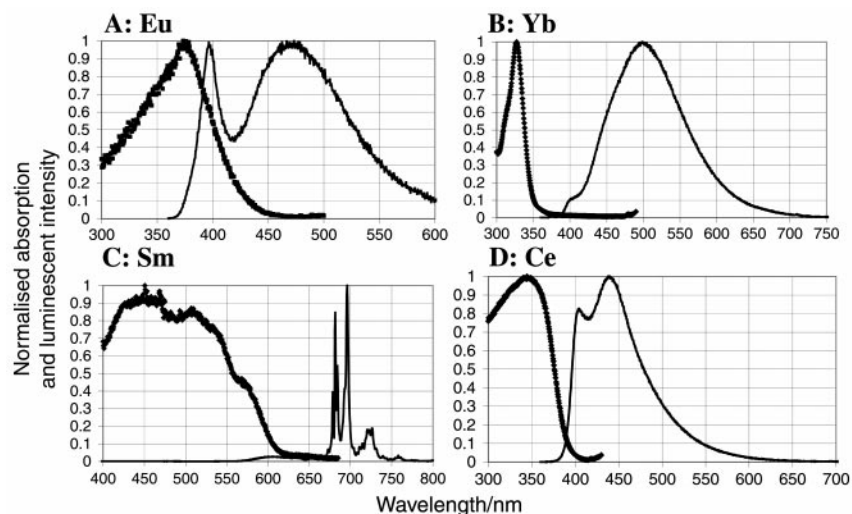
Fig. 12 Normalised solid-state photoluminescent excitation and emission spectra from **A** – Eu^{2+} hexacelsian **10**; **B** – Yb^{2+} hexacelsian; **C** – Sm^{2+}/Sm^{3+} hexacelsian **11** and **D** – Ce^{3+} hexacelsian **12**. All data from reference 39.

triboluminescent activity indicative of the role of a piezoelectric charge in the creation of excited molecular species. Further strong evidence for the participation of a piezoelectric charge[47] comes from studies of two separate polymorphic systems. In both cases, the polymorphic form which is triboluminescent also crystallises in a non-centrosymmetric structure, whereas the non-triboluminescent forms crystallise in a centric manner. Further evidence for the requirement of an acentric structure arose from studies of *saccharin*,[47] **20**, which in its pure form is non-triboluminescent and resides in a non-piezoelectric space group. Commercially obtained *saccharin* **20**, however, is highly triboluminescent. Successive purification leads to a diminution and subsequent elimination of the triboluminescence, indicative of an impurity being responsible for the triboluminescent activity.[47] It has been postulated that the impurity causes sites of local acentricity, sufficient to generate a piezoelectric charge upon fracture.[10,47] The preponderance for triboluminescent active molecules to crystallise in an acentric manner has been successfully exploited by Sweeting to engineer triboluminescent materials[51] based upon a chiral moiety, ensuring crystallisation in an acentric manner.

In general, despite evidence indicative of the necessity for a piezoelectric structure, it is still not clear whether the piezoelectric charge excites nitrogen which then transfers energy to the luminescent species, whether a gas discharge occurs which is effectively absorbed by the luminescent species, whether excitation of the luminescent species is *via* electron-bombardment or whether excitation occurs *via* a combination of all processes.[57]

Additional molecules which triboluminesce with a spectrum similar to, or identical with, their solid-state photoluminescence spectrum include: *cholesteryl salicylate*[39,42] **15**, *nicotinium salicylate*[58] **21**, carbazole derivatives,[59] triphenylphosphole[60] and fluorites.[54]

3.3 Fracture-induced triboluminescence – gas discharge and photoluminescence

A number of materials are known whose triboluminescence in air consists of both a nitrogen discharge and a triboluminescence emission spectrum similar to the solid-state photoluminescence. This has been reported for coumarin,[13] resorcinol,[13] triphenylmethane,[61] chlorotriphenylmethane,[61] cholesterol,[42] uranyl nitrate[28,62] and sulfanilic acid.[58] This dual emission also occurs for wintergreen candy, which is sucrose (nitrogen emission) doped with methyl salicylate (photoluminescence). It has been shown[62] that with increasing concentration of methyl salicylate, the intensity of particular nitrogen discharge lines

decreased while the photoluminescent intensity increased, consistent with the triboluminescence consisting of an initial nitrogen discharge, some of which is absorbed by methyl salicylate to result in a photoluminescent emission.

For other materials where a dual emission is observed, great care has to be taken not to assign the photoluminescent-like emission as arising exclusively from a nitrogen discharge excitation,[13,58] as the nitrogen lines could result from an entirely separate process *e.g.* an electric discharge caused by grinding the material to induce the triboluminescence. Alternatively, the nitrogen discharge could result from a piezoelectric-induced breakdown of the nitrogen absorbed or adsorbed on the surface of the crystals,[12] with the photoluminescence-like emission arising *via* a separate excitation pathway.[58] It has been suggested[58] that if the discrete lines in the nitrogen discharge spectrum are present in the normal relative intensities, the part of the triboluminescence spectrum resembling the solid-state photoluminescence does not originate *via* gas discharge excitation. However, if some of the nitrogen lines are either absent or present at reduced intensities, the photoluminescent-like emission contains at least a contribution arising from a nitrogen discharge excitation. Degassing and fracturing crystals in a nitrogen free environment can reveal the extent to which the photoluminescent-like emission originates *via* excited nitrogen.
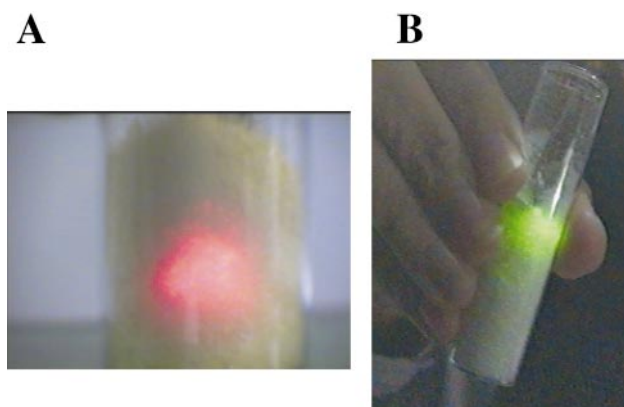
A   **B**

Fig. 13 The triboluminescence observed from: **A** – *europium tetrakis(dibenzoylmethide)triethylammonium* **1** and **B** – *tris(1,3-di-tert-butyl-β-propanedione)terbium-p-dimethylaminopyridine* **4**.
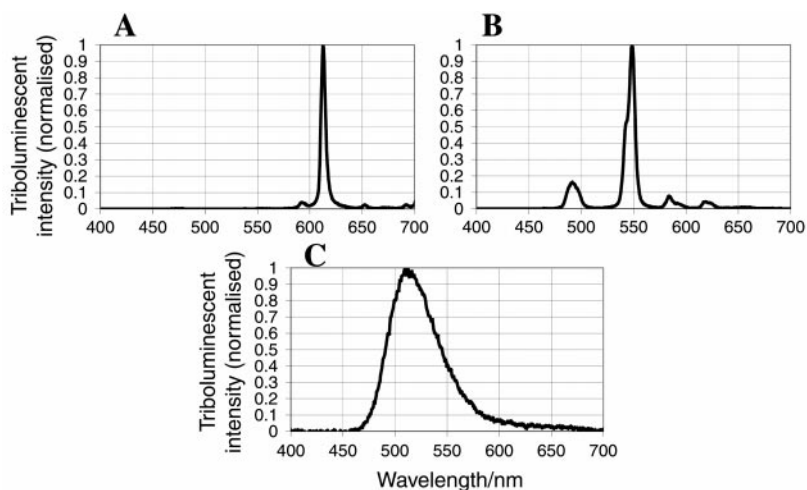
Fig. 14 The triboluminescent spectra of various metal complexes measured using an image-intensified spectrometer similar to that in Fig. 5B: A – *europium tetrakis(dibenzoylmethide)triethylammonium* **1**; B – *tris(1,3-di-tert-butyl-β-propanedione)terbium-p-dimethylaminopyridine* **4**; C – *dibromobis(triphenylphosphine oxide)manganese* **9**. All data from reference 39. All spectra have been recorded on the same instrument at an identical resolution of 1.75 nm.

3.4 Fracture-induced triboluminescence – metal complexes

Some of the most intense triboluminescent materials known are metal complexes (Fig. 13). One of the brightest from this category is *europium tetrakis(dibenzoylmethide)triethylammonium*,[63] **1**, whose triboluminescence and triboluminescence spectrum are shown in Figs. 13**A** and 14**A** respectively. Other intense triboluminescent metal complexes include *tris(1,3-di-tert-butyl-β-propanedione)terbium-p-dimethylaminopyridine*,[64] **4**, (Figs. 13**B** and 14**B**) and *dibromobis(triphenylphosphine oxide)manganese*,[40,65] **9**, (Fig. 14**C**).

The vast majority of all currently known metal complexes triboluminesce with a spectrum which is very similar to the solid-state photoluminescence spectrum, with no associated gas discharge being detected.[39,58] The spectral agreement between the triboluminescence and solid-state photoluminescence spectra may not be surprising since the majority of triboluminescent metal complexes contain a trivalent lanthanide as the emitting centre. The radiative lifetime of the f–f transition responsible for the triboluminescence is typically 10's to 100's of microseconds,[39] orders of magnitude larger than the lifetimes required to observe the influence of pressure-induced changes to Franck–Condon factors (section 3.2). Additionally, the Stokes shift between the solid-state absorption and emission spectra with these lanthanide complexes is typically very large, of the order of 100's of nm.[9] Self-absorption of the triboluminescent light is therefore not expected. Finally, the intra-f-shell transition is relatively insensitive to crystal field effects and so symmetry changes due to the creation of fracture surfaces are expected to play, at best, only a minor role in modifying the triboluminescent emission spectrum relative to the solid-state photoluminescence spectrum.

To our knowledge, the only reported metal complex to triboluminesce with both a gas discharge and an emission similar to the solid-state photoluminescent spectrum is *europium tris(2-thenoyltrifluoroacetone)phenanthroline*,[66] **2**. However, it is not clear whether the gas discharge is responsible for the photoluminescent-like emission or is a separate, independent process. For some manganese-centred materials, it has been reported that a nitrogen discharge is emitted along with the solid-state photoluminescence-like emission.[48] However, vacuum-degassed samples when fractured under inert atmospheres only exhibit the solid-state photoluminescent-like triboluminescence,[38,48] indicative that the nitrogen discharge plays only, at best, a minor role in generating the photoluminescence-like light emission.

It appears then that a general feature of metal complexes is

that they triboluminesce with no evidence of a gas discharge. Furthermore, certain highly triboluminescent metal complexes containing chelated lanthanides, such as *europium tetrakis(dibenzoylmethide)triethylammonium*, **1**, have been reported to crystallise in a centrosymmetric manner,[67,68] precluding the possibility of triboluminescence excitation *via* a piezoelectric mechanism, assuming that the symmetry of the crystalline material is not lowered upon stressing to fracture, which may not be a valid assumption.[54,60] Doubts have arisen however about the assignment of the centrosymmetric structure for, at least, **1** based upon the quality of the X-ray diffraction data.[69] Due to this uncertainty, we conducted second harmonic generation experiments based on the Kurtz and Perry powder test,[70] which is a sensitive probe for non-centrosymmetric structures, on this and other highly efficient triboluminescent compounds (Table 1). *Europium tetrakis(dibenzoylmethide)triethylammonium*, **1**, exhibited a significant second harmonic signal,[71] indicative of non-centrosymmetry. Single crystals of sufficient quality for X-ray analysis were subsequently grown *via* slow evaporation of a supersaturated ethanol solution. The X-ray analysis assigned the crystalline symmetry to the asymmetric $P2_1$ space group,[72] consistent with the non-zero second harmonic signal. It appears then, at least for this material, excitation *via* a piezoelectric charge is possible. The highly efficient *tris(1,3 di-tert-butyl-β-propanedione)terbium-p-dimethylaminopyridine* **4** and samarium analogue **5** also exhibited a non-negligible second harmonic signal (Table 1). X-Ray analysis of these compounds[73] revealed the molecules also reside in the $P2_1$ space group. Again, it appears that the triboluminescence may result from a piezoelectric charging of the freshly cleaved surfaces. An unambiguous piezoelectric origin for the triboluminescence has been demonstrated recently[74] for *europium tris(2-thenoyltrifluoroacetone)phenanthroline*, **2**, which crystallises in the acentric orthorhombic *Pca*21 space group. The reason why no nitrogen discharge is observed with the majority of these compounds could be that: (i) electron bombardment leads to direct ligand/lanthanide excitation; (ii) excitation involves energy transfer from excited nitrogen or (iii) the metal complex is too optically dense in the ultraviolet–violet portion of the electromagnetic spectrum to allow a nitrogen discharge of sufficient magnitude to be detected.

Suggesting a triboluminescence excitation mechanism for *hexakis(antipyrine)terbium triiodide*,[68] **3**, and *dibromobis(triphenylphosphine oxide)manganese*,[40] **9**, is slightly more complicated. The reported crystalline structure[68] for the terbium-

Table 1 Observation of a second harmonic signal at 532 nm from a number of triboluminescent materials[71]

Compound	Name	SHG signal
1	*Europium tetrakis(dibenzoylmethide)triethylammonium*	Y
2	*Europium tris(2-thenoyltrifluoroacetone)phenanthroline*	Y
3	*Hexakis(antipyrine)terbium triiodide*	N
4	*Tris(1,3-di-tert-butyl-β-propanedione)terbium-p-dimethylaminopyridine*	Y
5	*Tris(1,3-di-tert-butyl-β-propanedione)samarium-p-dimethylaminopyridine*	Y
6	*Tris(1,3-di-tert-butyl-β-propanedione)dysprosium-p-dimethylaminopyridine*	Y
7	Terbium trichloride hexahydrate	N
8	Mn:ZnS	Y
9	*Dibromobis(triphenylphosphine oxide)manganese*	N
10	Europium(2+) hexacelsian	N
11	Samarium(2+ and 3+) hexacelsian	N
12	Cerium(3+) hexacelsian	N
13	Terbium(3+) hexacelsian	N
14	Dysprosium(3+) hexacelsian	N
15	*Cholesteryl salicylate*	Y
16	*N-Acetylanthranilic acid*	Y
17	*Salicylsalicylic acid*	Y
18	*Menthyl-9-anthracenecarboxylate*	Y
19	9-Isopropylcarbazole	Y

containing material is centrosymmetric rhombohedral $R\bar{3}$. This result has been confirmed by our group[75] and is consistent with no measurable second harmonic generation signal (Table 1). It has been suggested[60,76] that impurities and/or disorder may lead to small localised acentric areas capable of piezoelectric charging. This situation is not consistent however with the crystallography and second harmonic generation results. It has also been reported that *hexakis(antipyrine)terbium triiodide* **3** exhibits no emission when grown and cleaved under a helium atmosphere, but almost full activity is observed when the crystals are grown under nitrogen and cleaved under helium.[68] It is clear therefore that nitrogen trapped within the crystal structure is intimately involved in generating the triboluminescence. It is difficult to tell whether the excitation occurs due to: (i) the stresses necessary for fracture inducing an acentric structure;[54] (ii) the centric ionic crystal fracturing in a direction which actually generates charged surfaces[60] or (iii) the trapped nitrogen causing very localised acentric structures, although it is surprising that the presence of these would not have been identified *via* the second harmonic generation experiments. It is highlighted once again that when attempting to ascertain the excitation mechanism either (i) vacuum degassing and cleavage of the crystals under an inert atmosphere or (ii) growth and cleavage of the crystals under an inert atmosphere, are key experiments to assess the role of trapped nitrogen.

To our knowledge, no structural data is available for *dibromobis(triphenylphosphine oxide)manganese* **9**, however tetrahedral manganese(II) complexes are known to crystallise in a centrosymmetric point group.[38] Furthermore, no charge has been measured upon fracture of this material[76] and no discernible second harmonic signal has been measurable (Table 1). While these latter two tests are not definitive of a centrosymmetric structure, they do support the possibility. It has been suggested again that the triboluminescence results from impurities leading to small localised areas of acentric structure[76] but this is unlikely given the lack of charge upon fracture and a measurable second harmonic signal. Furthermore, the compound still exhibits the solid-state photoluminescent-like emission, with no nitrogen discharge, when crystals are vacuum-degassed and cleaved under an inert atmosphere,[38,76] consistent with a minor role, at best, of nitrogen in the excitation mechanism for this compound. Other possible triboluminescent excitation mechanisms in centrosymmetric materials have been proposed[60,77] but it is uncertain at present which, if any, is responsible for the triboluminescence in tetrahedral manganese(II) complexes.

4. Relative triboluminescent efficiency

Even the most cursory examination of the literature reveals that studies comparing the triboluminescent efficiency of various materials are lacking. There are qualitative statements such as:

●"*ditriphenylphosphine oxide manganese bromide* **9** exhibits mechanoluminescence whose intensity is highest among all the crystals"[76]

●"the most intensely triboluminescent substance recorded to date is *cholesteryl salicylate* **15**"[45]

●"*tetrakis(dibenzoylmethanato)europate*, **1**, is of unrivalled triboluminescent activity"[68]

●"the mechanoluminescence of impure *saccharin* **20** can be seen in daylight"[10]

●"The mechanoluminescence of *ditriphenylphosphine oxide manganese bromide* **9** is so intense that it can be seen in daylight"[10]

●"*triethylammonium tetrakis(dibenzoylmethide)europate*, **1**, is the brightest known triboluminescent material"[6]

●"*nicotinium salicylate* **21** can produce emissions bright enough to be seen at the back of a dark lecture hall"[58]

●"The light emission from *N-acetylanthranilic acid* **16** is readily observed in a darkened room"[78]

but few quantitative studies to grade materials in terms of efficiency. From an applications perspective, this lack of comparative studies is a drawback since the most efficient materials are not obvious.

Table 2 Relative intensities of triboluminescent emissions. Data collated from references 18, 42, 43, 47, 61 and 79

Triboluminescent material	Intensity normalised to sucrose
Cholesteryl salicylate **15**	56
N-Isopropylcarbazole **19**	22
Cinchonine sulfate	7.3
Acenaphthene	4.1
$Ce_2(SO_4)_3 \cdot 8H_2O$	2.6
Cholesterol	2.5
Resorcinol	2.4
Phenanthrene	1.5
Sucrose	1.0
Uranyl nitrate·6H$_2$O	0.78
Tartaric acid	0.57
Uranyl disalicylate	0.49
Nicotinium salicylate **21**	0.25
$Li_2SO_4 \cdot H_2O$	0.06
Triphenylamine	0.06
Triphenylphosphine oxide	0.02

Table 3 Solid-state photoluminescent quantum yields of a number of triboluminescent compounds.[9] Partial self-absorption of the solid-state photoluminescent emission explains the lower bound values for **10**, **16** and **18**

Compound	Name	Φ
1	*Europium tetrakis(dibenzoylmethide)triethylammonium*	0.75
2	*Europium tris(2-thenoyltrifluoroacetone)-phenanthroline*	0.85
3	*Hexakis(antipyrine)terbium triiodide*	0.53
4	*Tris(1,3-di-tert-butyl-β-propanedione)terbium-p-dimethylaminopyridine*	0.71
5	*Tris(1,3-di-tert-butyl-β-propanedione)samarium-p-dimethylaminopyridine*	0.04
6	*Tris(1,3-di-tert-butyl-β-propanedione)dysprosium-p-dimethylaminopyridine*	0.07
7	Terbium trichloride hexahydrate	0.33
8	Mn : ZnS	1.00
9	*Dibromobis(triphenylphosphine oxide)manganese*	0.19
10	Europium(2+) hexacelsian	>0.57
11	Samarium(2+ and 3+) hexacelsian	0.62
12	Cerium(3+) hexacelsian	0.44
15	*Cholesteryl salicylate*	0.13
16	*N-Acetylanthranilic acid*	>0.28
17	*Salicylsalicylic acid*	0.17
18	*Menthyl-9-anthracenecarboxylate*	>0.43

Chandra and Zink have reported comparative studies of a range of materials using the air-driven piston in Fig. 2A.[42,43,47,61,79] Table 2 summarises the relative intensities for some of the more highly efficient materials reported. Zink has also compared the triboluminescent efficiency of several materials using an actinometric technique,[80] yielding ratios very similar to those given in Table 2. The comparisons in Table 2, while useful, are not exhaustive of the better known bright triboluminescent materials. For example no comparison has been made, to date, between *cholesteryl salicylate* **15**, *europium tetrakis(dibenzoylmethide)triethylammonium* **1**, *dibromobis(triphenylphosphine oxide)manganese* **9**, impure *saccharin* **20** and *tris(1,3-di-tert-butyl-β-propanedione)terbium-p-dimethylaminopyridine* **4**. It is surprising that *nicotinium salicylate* **21**, which some authors describe as being highly triboluminescent,[58] appears towards the bottom of Table 2. Possible reasons for this include: (i) *nicotinium salicylate* **21** is known to be chemically unstable;[69] (ii) two polymorphic forms of the compound are known – one is triboluminescent active whereas the other is triboluminescent inactive;[81] (iii) impurities could have quenched the triboluminescence; (iv) no correction being made for the wavelength response of the photomultiplier tube; (v) significant self-absorption of the triboluminescence and (vi) the detected triboluminescent signal may have been sensitive to the actual particle size distribution after fracture. The detector only monitors a finite solid emission angle, but the angular distribution of scattered light depends on the particle size.

Structural design guidelines for highly efficient triboluminescent materials are also lacking. This is due to the overall triboluminescent efficiency depending on both the efficiency with which the emitting excited state is generated during fracture and the efficiency by which this excited state undergoes radiative relaxation. It would be extremely beneficial if the efficiencies of these two processes could be de-coupled and quantified separately as this may eventually lead to an insight into the triboluminescent mechanism and thus design guidelines for optimised materials. Exploiting techniques used to characterise organic light emitting polymers,[32,33] we measured the solid-state photoluminescent quantum yield of a number of triboluminescent compounds in powder form.[9] Assuming that the triboluminescence and solid-state photoluminescence originate from the same excited state, which is a valid assumption for the compounds studied,[39] the solid-state photoluminescent quantum yield indicates the efficiency with which the excited state undergoes radiative relaxation during triboluminescence. Table 3 summarises the results obtained.

The salient points are:

• There are a number of triboluminescent materials (**1**, **2**, **4** and **8**) with near optimised solid-state photoluminescent quantum yields.

• The triboluminescence from morpholinium tetrakis(dibenzoylmethide)europate has been reported[82] to be 8 times more intense than that from the structurally similar *europium tetrakis(dibenzoylmethide)triethylammonium* **1**, despite the latter possessing a solid-state photoluminescent quantum yield of 0.75. To explain the large enhancement in triboluminescence, the difference between the two materials must be how efficiently excited-states are populated during fracture. Closer examination of these two compounds may therefore lead to insight into the underlying triboluminescent mechanism.

• Structurally similar compounds (*e.g.* **4–6**) can exhibit significantly different solid-state photoluminescent quantum yields. It has been suggested[9] that this difference is due to a significant non-radiative decay for **5** and **6** shortening the excited state lifetime. Energy transfer from the lanthanide to vibrational overtones of the ligand may cause this non-radiative decay.[83–85] Chemical modifications to the ligands may reduce this non-radiative decay and increase the triboluminescent efficiency of **5** and **6**.

• A number of triboluminescent compounds (**5**, **6**, **9**, **15–17**) which appear relatively bright to the eye, possess quite low solid-state photoluminescent quantum yields, highlighting the fact that the triboluminescence could be enhanced if the radiative quantum yield was increased.

Solid-state photoluminescent quantum yield measurements should be carried out therefore in addition to actinometric measurements of the triboluminescent efficiency to quantify separately the efficiency of each process involved in triboluminescence. This may result eventually in structural design guidelines and truly optimised triboluminescent materials.

5. Triboluminescent damage sensors: requirements and future research

It has been proposed that triboluminescent materials can act as structural damage sensors, in the form of a surface patch on all materials, or embedded within polymeric composite host structures.[7,8] Upon impact, the onset of structural damage is indicated by a light emission; the severity of damage is indicated by the overall light intensity and the location of damage is obtained by the wavelength of the emitted light. Using embedded triboluminescent sensors, we have recently successfully demonstrated real-time structural damage monitoring in both glass-fibre and (optically black) carbon-fibre composites.[86]

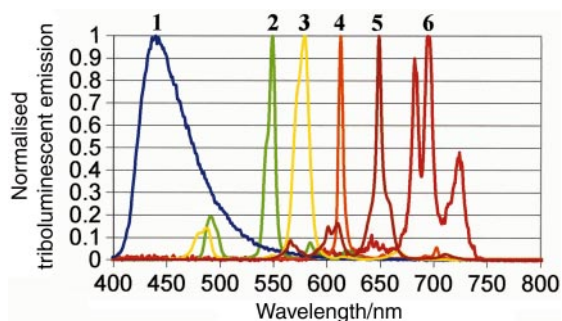Widespread adoption of triboluminescent structural damage

Fig. 15 The triboluminescence emission spectra of six different triboluminescent materials.[41]

sensors however requires that:

● The sensor should incorporate highly triboluminescent material. Use of high efficiency material results in a sensor containing less triboluminescent compound which (i) reduces the sensor cost, minimises the overall added weight and reduces the influence of the sensor on the mechanical properties of the host and/or (ii) allows less sensitive detectors to be used which minimises the cost, size and weight of the integrated sensor system.

● The triboluminescent material should luminesce over a narrow bandwidth consistent with using different triboluminescent materials in a sensor array, with the emission colour indicating the location of structural damage. Fig. 15 shows the emission from six different highly triboluminescent materials, indicating the degree of spectral separation that can currently be achieved.[41] Fig. 15 illustrates also that materials with a narrow bandwidth emission in the spectral region between 400 and 500 nm are currently lacking.

● The triboluminescent material should only emit light when fractured and not when elastically or plastically deformed. This avoids sensor output during the normal flexures and strains experienced by the host structure.

● The triboluminescent material should be chemically compatible with the polymeric composite host.

● The triboluminescent material should not melt below the cure temperature of the composite.

● The triboluminescent material should be inexpensive *i.e.* both cheap raw materials and a straightforward synthetic route.

● The mechanical properties of the triboluminescent material should closely match that of the host structure.

● The sensor light emission should be optimised for a particular fracture area.

● The integrated sensor should not adversely affect the mechanical properties of the host structure.

● For embedded sensors, the light emitted by a triboluminescent material upon fracture should be efficiently coupled to the waveguide connecting the sensor with the detection unit. Furthermore the waveguide should exhibit low propagation losses for the "light damage signal".

● The integrated sensor should function over the full operating envelope of the host structure *e.g.* temperature, moisture.

● The integrated sensor should be inexpensive *i.e.* easily fabricated, handled and integrated.

To address these requirements, research is required to:

(1) Understand the mechanism underlying current triboluminescent materials. For example: (i) why are many esters of salicylic acid triboluminescent? (ii) why is the triboluminescence efficiency of metal complexes so dependent on the choice of ligand and/or counterion? (iii) all organic triboluminescent materials emit light in the ultraviolet or in the violet-blue portion of the electromagnetic spectrum – is it possible to synthesise organic triboluminescent materials that luminesce

green or red? (iv) the dependence of the triboluminescent emission on a nitrogen discharge should be investigated for a number of the highly efficient metal complexes.

(2) Adopt a rational approach to study and improve the triboluminescence of current materials. For example, use of highly fluorinated ligands in materials **5** and **6** in Table 3 may reduce the non-radiative decay, enhancing both the excited state lifetime and the triboluminescent efficiency. Furthermore, the triboluminescence of metal complexes that require ligand excitation prior to metal emission may be improved by optimising the rate of intramolecular energy transfer from ligand to metal.[87]

(3) Investigate a number of materials using both actinometric and solid-state photoluminescent quantum yield measurements to develop structural design guidelines for efficient triboluminescent materials (section 4).

(4) Identify efficient materials with narrow bandwidth triboluminescent emissions, especially those with emissions between 400–500 nm.

(5) Investigate the mechanical properties of triboluminescent crystals as a function of, for example, material type and particle size.

(6) Investigate the relationship between the: (i) sensor signal; (ii) triboluminescent particle size and loading volume fraction and (iii) degradation in the mechanical properties of the host structure.

(7) Investigate novel methods to efficiently couple light from embedded triboluminescent crystals into an optical waveguide.

(8) Understand the sensor performance under different operating environments (*e.g.* temperature and moisture) and investigate the effect of fatigue on the long-term sensor performance.

Since the proposed application for triboluminescent materials, there has been a significant increase of interest in this luminescent phenomenon by research groups worldwide. However, much work remains to be done by the Chemistry, Physics, Materials and Engineering communities before we both fully understand the fracture-induced light emission from these compounds and see widespread use of triboluminescent damage sensors.

6. Summary

Triboluminescent materials have been known for at least four centuries. The majority of work to date has been academic in nature – reporting a new triboluminescent material and/or presenting a spectroscopic study in an effort to explain the mechanism underlying the fracture-induced light emission. Recently, the advantages of triboluminescent materials as real-time structural damage sensors have been highlighted. These sensors can be exploited in both commercial and military markets. In addition to covering some of the recent advances in the field, this review aims to provide a timely overview of those triboluminescent materials which may be suitable as structural damage sensors.

Methods for measuring triboluminescence with a known input mechanical energy and apparatus to monitor the light intensity and spectral content have been reviewed in section 2. Materials suitable for structural damage sensing should emit light only upon fracture and not upon elastic or plastic deformation. Triboluminescent materials emitting light solely upon crystalline fracture are by far the most prevalent and are discussed in section 3. The materials have been primarily classified according to the nature of the triboluminescence. However metal complexes are discussed in their own right since materials of this type are among the brightest known triboluminescent compounds. The salient points from section 3 include: (i) it is generally accepted that triboluminescence resembling a gas discharge has a piezoelectric origin; (ii) many

materials are known whose triboluminescence spectrum resembles the solid-state photoluminescence spectrum. Examples are given where there is a spectral shift between the two luminescent spectra and these differences have been explained by either self-absorption of the triboluminescent light or by ligand field changes during fracture; (iii) there is strong supportive evidence for many materials exhibiting triboluminescence similar to the solid-state photoluminescence spectrum that the triboluminescent mechanism has a piezoelectric origin. However, the actual mechanism is unclear; (iv) some materials emit both a gas discharge and a solid-state photoluminescent-like emission. When this is the case, if the gas discharge lines are all present with intensities in the expected ratio, it is suggested that the gas discharge plays little part in generating the photoluminescent-like emission. However if the gas discharge spectrum exhibits evidence of absorptive losses, then the gas discharge will contribute, to some extent, to the photoluminescent-like emission and (v) the vast majority of metal complexes do not show evidence for a gas discharge. Some materials clearly rely on a gas discharge for their triboluminescence, whereas others do not.

It appears therefore that no one triboluminescent mechanism can explain the fracture-induced light emission in all materials. The importance of degassing and fracturing the materials under an inert atmosphere is stressed as this is the key experiment in demonstrating the necessity of a gas discharge for triboluminescent activity.

From an applications perspective, a drawback is the lack of studies comparing triboluminescent efficiency. The studies that do exist do not cover the better known efficient triboluminescent crystals. Furthermore, structural guidelines covering the synthesis of highly efficient materials are lacking. This is due to the triboluminescent efficiency depending on the efficiency of excited state generation during fracture and the efficiency by which the excited state undergoes radiative relaxation.
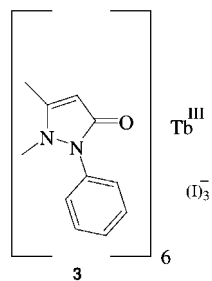
Recently, the use of solid-state photoluminescent quantum yield measurements have quantified the latter efficiency for a wide number of highly triboluminescent materials. This study identified that: (i) some materials already possess near unity radiative quantum yields; (ii) structurally similar materials can exhibit widely varying quantum yields and (iii) some materials which appear to the eye as being reasonably bright possess relatively small photoluminescent quantum yields, allowing the possibility to design more efficient compounds. Combining the solid-state photoluminescent quantum yield measurements with the actinometric measurement of the triboluminescent efficiency allows the efficiency of both processes involved in triboluminescence to be quantified. It is hoped that this will lead to insight into the triboluminescent mechanism and eventually to design guidelines for highly efficient triboluminescent compounds.

Section 5 has defined the main material and sensor requirements which must be addressed prior to widespread adoption of triboluminescent damage sensors. Although much research remains to be done to meet all of these requirements, it is clear that triboluminescent materials and sensors have a very bright future indeed.

Appendix

Chemical structures of some highly triboluminescent materials

Table 4 Triboluminescent materials

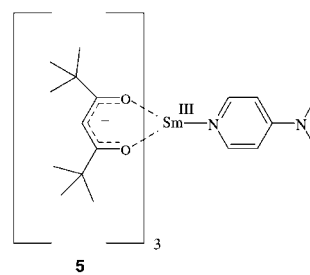| Compound	Name	Structure
1	*Europium tetrakis(dibenzoylmethide)triethylammonium*	
2	*Europium tris(2-thenoyltrifluoroacetone)phenanthroline*	

3   *Hexakis(antipyrine)terbium triiodide*
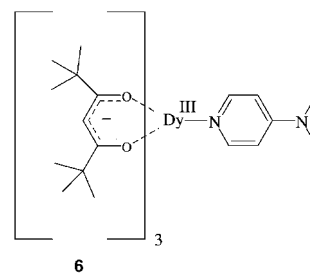

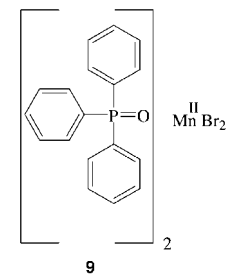**4**   *Tris(1,3-di-tert-butyl-β-propanedione)terbium-p-dimethylaminopyridine*
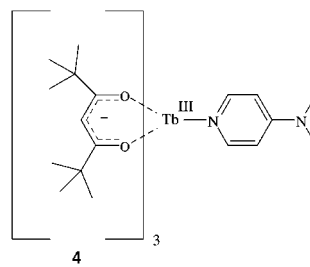
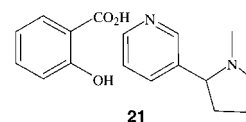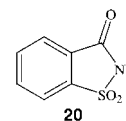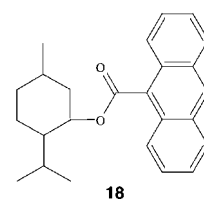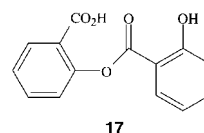**5**   *Tris(1,3-di-tert-butyl-β-propanedione)samarium-p-dimethylaminopyridine*

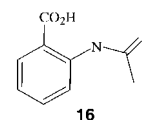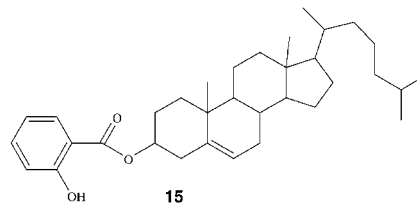**6**   *Tris(1,3-di-tert-butyl-β-propanedione)dysprosium-p-dimethylaminopyridine*

9   *Dibromobis(triphenylphosphine oxide)manganese*

15	*Cholesteryl salicylate*	

15

16	*N-Acetylanthranilic acid*	

16

17	*Salicylsalicylic acid*	

17

18	*Menthyl-9-anthracenecarboxylate*	

18

20	*Saccharin*	

20

21	*Nicotinium salicylate*	

21

References

1 L. M. Sweeting, *Chem. Mater.*, 1990, 10.
2 Y. Kawaguchi, *Jpn. J. Appl. Phys.*, 1998, **37**, 1892.
3 B. P. Chandra, M. Elyas and B. Majumdar, *Solid State Commun.*, 1982, **42**, 753.
4 A. J. Walton, *Adv. Phys.*, 1977, **26**, 887.
5 H. Longchambon, *Comptes rendus*, 1922, **174**, 1633.
6 L. M. Sweeting and J. L. Guido, *J. Lumin.*, 1985, **33**, 167.
7 I. Sage and N. Geddes, Patent 5905260, 1999.
8 I. Sage, R. Badcock, L. Humberstone, N. Geddes, M. Kemp and G. Bourhill, *Smart Mater. Struct.*, 1999, **8**, 504.
9 G. Bourhill, L. O. Pålsson, I. D. W. Samuel, I. C. Sage, I. D. H. Oswald and J. P. Duignan, *Chem. Phys. Lett.*, in press.
10 B. P. Chandra, *Nucl. Tracks.*, 1985, **10**, 225.
11 G. Alzetta, I. Chudáček and R. Scarmozzino, *Phys. Status Solidi A*, 1970, **1**, 775.
12 J. I. Zink, G. E. Hardy and J. E. Sutton, *J. Phys. Chem.*, 1976, **80**, 248.
13 L. M. Sweeting, M. L. Cashel and M. M. Rosenblatt, *J. Lumin.*, 1992, **52**, 281.
14 H. Longchambon, *Bull. Soc. Fr. Miner.*, 1925, **48**, 130.
15 L. Sodomka , *Phys. Status Solidi A*, 1971, **7**, K65.
16 K. Meyer and F. Polly, *Phys. Status Solidi*, 1965, **8**, 441.
17 K. Meyer, D. Obrikat and M. Rossberg, *Krist. Tech.*, 1970, **5**, 181.
18 R. Nowak, A. Krajewska and M. Samoć, *Chem. Phys. Lett.*, 1983, **94**, 270.
19 A. T. Tokhmetov and V. I. Vettegren, *Sov. Phys. Sol. State*, 1989, **31**, 2125.
20 B. P. Chandra and J. I. Zink, *Phys. Rev. B: Solid State*, 1980, **21**, 816.
21 G. T. Reynolds, *J. Lumin.*, 1997, **75**, 295.
22 S. T. Shikha, S. Tiwari, B. K. Sahu and B. P. Chandra, *Bull. Mater. Sci.*, 1995, **18**, 503.
23 B. P. Chandra, N. G. Deshmukh and A. K. Jaiswal, *Mol. Cryst. Liq. Cryst.*, 1987, **142**, 157.
24 I. Sage, R. Badcock, L. Humberstone, N. Geddes, M. Kemp, S. Bishop and G. Bourhill, *Proc. SPIE–Int. Soc. Opt. Eng.*, 1999, **3675**, 169.
25 G. E. Hardy, B. P. Chandra, J. I. Zink, A. W. Adamson, R. C. Fukuda and R. T. Walters, *J. Am. Chem. Soc.*, 1979, **101**, 4554.
26 F. G. Wick, *J. Opt. Soc. Am. A*, 1940, **30**, 302.
27 R. A. Angelos, J. I. Zink and G. E. Hardy, *J. Chem. Educ.*, 1979, **56**, 413.
28 J. I. Zink, *Inorg. Chem.*, 1975, **14**, 555.
29 B. P. Chandra, N. G. Deshmukh, R. B. Sahu and A. K. Verma, *Cryst. Res. Technol.*, 1986, **21**, 1559.

30 B. P. Chandra and A. K. Khare, *Indian J. Cryog.*, 1983, **8**, 282.
31 T. Ishihara, K. Tanaka, K. Fujita, K. Hirao and N. Soga, *Solid State Commun.*, 1998, **107**, 763.
32 N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Phillips, Y. A. R. R. Kessener, S. C. Moratti, A. B. Holmes and R. H. Friend, *Chem. Phys. Lett.*, 1995, **241**, 89.
33 J. C. de Mello, H. F. Wittmann and R. H. Friend, *Adv. Mater.*, 1997, **9**, 230.
34 G. T. Reynolds and S. Gruner, *IEEE Trans. Nucl. Sci.*, 1975, **22**, 404.
35 A. J. Walton and P. Botos, *J. Phys. E: Sci. Instrum.*, 1978, **11**, 513.
36 G. N. Chapman, J. C. Ramage and A. J. Walton, *J. Phys. E: Sci. Instrum.*, 1982, **15**, 181.
37 L. M. Belyaev and N. Y. Martyshev, *Phys. Status Solidi*, 1969, **34**, 57.
38 G. E. Hardy and J. I. Zink, *Inorg. Chem.*, 1976, **15**, 3061.
39 J. P. Duignan, I. D. H. Oswald, I. C. Sage, L. M. Sweeting, K. Tanaka, T. Ishihara, K. Hirao and G. Bourhill, *J. Lumin.*, in press.
40 D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 1961, 3735.
41 I. Sage and G. Bourhill, unpublished data.
42 B. P. Chandra and J. I. Zink, *J. Lumin.*, 1981, **23**, 363.
43 B. P. Chandra and J. I. Zink, *Inorg. Chem.*, 1980, **19**, 3098.
44 G. Bourhill, N. J. Geddes, I. Sage, I. Oswald, L. Humberstone, R. Badcock, P. Lloyd, N. Williamson and M. Kemp, *J. Def. Sci.*, 2000, **5**, 433.
45 J. I. Zink, *Naturwissenschaften*, 1981, **68**, 507.
46 B. P. Chandra and K. K. Shrivastava, *J. Phys. Chem. Solids*, 1978, **39**, 939.
47 G. E. Hardy, W. C. Kaska, B. P. Chandra and J. I. Zink, *J. Am. Chem. Soc.*, 1981, **103**, 1074.
48 G. E. Hardy, J. C. Baldwin, J. I. Zink, W. C. Kaska, P. Liu and L. Dubois, *J. Am. Chem. Soc.*, 1977, **99**, 3552.
49 B. P. Chandra and B. Majumdar, *Z. Phys. B: Condens. Matter Quanta*, 1983, **52**, 277.
50 S. R. Byrn, R. R. Pfeiffer, G. Stephenson, D. J. W. Grant and W. B. Gleason, *Chem. Mater.*, 1994, **6**, 1148.
51 L. M. Sweeting, A. L. Rheingold, J. M. Gingerich, A. W. Rutter, R. A. Spence, C. D. Cox and T. J. Kim, *Chem. Mater.*, 1997, **9**, 1103.
52 E. Leyrer, F. Zimmermann, J. I. Zink and G. Gliemann, *Inorg. Chem.*, 1985, **24**, 102.
53 J. I. Zink and W. Klimt, *J. Am. Chem. Soc.*, 1974, **96**, 4690.
54 G. N. Chapman and A. J. Walton, *J. Phys. C*, 1983, **16**, 5543.
55 J. I. Zink, G. E. Hardy and G. Gliemann, *Inorg. Chem.*, 1980, **19**, 488.
56 T. Ishihara, K. Tanaka, K. Hirao and N. Soga, *Jpn. J. Appl. Phys.*, 1997, **36**, L781.
57 B. P. Chandra and J. I. Zink, *J. Chem. Phys.*, 1980, **73**, 5933.
58 L. M. Sweeting, M. L. Cashel, M. Dott, J. M. Gingerich, J. L. Guido, J. A. Kling, R. F. Pippin, M. M. Rosenblatt, M. Rutter and R. A. Spence, *Mol. Cryst. Liq. Cryst.*, 1992, **211**, 389.
59 N. Kitamura, O. Saravari, H.-B. Kim and S. Tazuke, *Chem. Phys. Lett.*, 1986, **125**, 360.
60 M. B. Hocking, D. M. Preston and J. I. Zink, *J. Lumin.*, 1989, **43**, 309.
61 B. P. Chandra and J. I. Zink, *J. Phys. Chem.*, 1982, **86**, 4138.
62 L. M. Sweeting, in *Spectroscopic characterization of minerals and their surfaces*, L. M. Coyne, S. W. S. McKeever and D. F. Blake, eds., (ACS Symposium series 415), Washington DC, 1990, pp. 245–260.
63 C. R. Hurt, N. McAvoy, S. Bjorklund and N. Filipescu, *Nature*, 1966, **212**, 179.
64 V. Goulle, patent WO 96/20942, 1996.
65 F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc.*, 1962, **84**, 167.
66 N. Takada, J. Sugiyama, R. Katoh, N. Minami and S. Hieda, *Synth. Met.*, 1997, **91**, 351.
67 L. M. Sweeting and A. L. Rheingold, *J. Am. Chem. Soc.*, 1987, **109**, 2652.
68 A. L. Rheingold and W. King, *Inorg. Chem.*, 1989, **28**, 1715.
69 L. M. Sweeting, personal communication.
70 S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, 1968, **39**, 3798.
71 K. Wilkinson, J. Robertson, L. Humberstone, S. Drake, I. Sage and G. Bourhill, unpublished data.
72 W. Clegg, I. Sage, I. Oswald, K. Wilkinson, J. Robertson and G. Bourhill, *J. Mater. Chem.*, to be submitted.
73 W. Clegg, I. Sage, I. Oswald, P. Brough and G. Bourhill, *Acta Crystallogr., Sect. C*, 2000, **56**, 1323.
74 N. Takada, S. Hieda, J. Sugiyama, R. Katoh and N. Minami, *Synth. Met.*, 2000, **111**, 587.
75 W. Clegg, I. Sage and G. Bourhill, unpublished data.
76 B. P. Chandra, M. S. K. Khokhar, R. S. Gupta and B. Majumdar, *J. Phys.*, 1987, **29**, 399.
77 B. P. Chandra, S. Tiwari, M. Ramrakhiani and M. H. Ansari, *Cryst. Res. Technol.*, 1991, **26**, 767.
78 J. Erikson, *J. Chem. Educ.*, 1972, **49**, 688.
79 B. P. Chandra and J. I. Zink, *J. Phys. Chem. Solids*, 1981, **42**, 529.
80 W. Beese and J. I. Zink, *J. Lumin.*, 1984, **29**, 119.
81 G. Weitz, *Naturwissenschaften*, 1969, **56**, 325.
82 X. Zeng, R. Xiong, X. You and K. Cheung, *Inorg. Chem. Commun.*, 2000, **3**, 341.
83 M. Iwamuro, Y. Hasegawa, Y. Wada, K. Murakoshi, N. Nakashima, T. Yamanaka and S. Yanagida, *J. Lumin.*, 1998, **79**, 29.
84 S. I. Klink, G. A. Hebbink, L. Grave, F. C. Van Veggel, D. N. Reinhoudt, L. H. Slooff, A. Polman and J. W. Hofstraat, *J. Appl. Phys.*, 1999, **86**, 1181.
85 W. P. Gillin and R. J. Curry, *Appl. Phys. Lett.*, 1999, **74**, 798.
86 I. Sage, L. Humberstone, I. Oswald, P. Lloyd and G. Bourhill, *Smart Mater. Struct.*, accepted.
87 S. Sato and M. Wada, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 1955.