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Trapped charge migration in BaFBr:Eu^{2+}: The recuperation of photostimulated luminescence

Andrew Harrison*
Department of Chemistry, University of Edinburgh, The King's Buildings, Edinburgh, EH9 3JJ, United Kingdom

Michael T. Harrison
Inorganic Chemistry Laboratory, University of Oxford, South Parks Road., Oxford, OX1 3QR, United Kingdom

Gary P. Keogh and Richard H. Templer*
Department of Chemistry, Imperial College, University of London, SW7 2AY, United Kingdom

Andrew S. Wills
Department of Chemistry, University of Edinburgh, The King's Buildings, Edinburgh, EH9 3JJ, United Kingdom

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We present a model of the photostimulated luminescence (PSL) in BaFBr:Eu^{2+} in which the trapped charge defects are mobile, rather than static. The PSL occurs when trapped electrons and holes migrate together to form loose clusters around Eu^{2+}, and recombine after photostimulation. The model predicts that if one measures the PSL for some time and then stops the photostimulation, the PSL measured some time later will be enhanced. We have recorded this effect and present the results as strong evidence in support of our hypothesis.

BaFBr doped with approximately 0.1 mol % Eu^{2+} (henceforth BaFBr:Eu $^{2+}$) may be used to store images of ionizing radiation in the form of trapped electrons and holes. The image may subsequently be read out by recording the blue emission which can be stimulated with a red light source (generally a HeNe laser).[1] The wide dynamic range, good sensitivity, and reusability of films made of BaFBr:Eu^{2+} have led to their widespread use as radiation imagers.[2] Despite the practical importance of this phosphor, the mechanism of the storage and stimulation process is still not fully understood. Indeed, it is not clear why BaFX:RE compounds in general (where X is a halide ion and RE is a rare-earth ion) are particularly efficient PSL phosphors. In this work we present experimental results that indicate that the migration of charged defects plays a fundamental role in the behavior of this system, and in the light of this observation, we hypothesize that there are some general physical features which characterize technologically useful PSL materials.

BaFBr:Eu^{2+} has the PbFCl structure in which layers of F^{-} ions and double layers of Br^{-} ions are separated by Ba^{2+} ions,[3] and Eu^{2+} ions substitute for Ba^{2+} ions. When this material is exposed to ionizing radiation, electrons are excited across the conduction band to leave holes. A proportion of these electrons are trapped at Br^{-} and F^{-} vacancies to produce F centers denoted F(Br^{-}) and F(F^{-}), respectively. Holes are trapped as Br$_2^{-}$ V$_k$ centers at low temperatures,[4] but these are thought to decay on warming to room temperature. Some of the holes recombine with F centers to produce luminescence, while others diffuse to oxide impurities which are present even in crystals which have been grown with great care to exclude oxygen and water.[5,6] Such impurities lie on the fluoride sublattice, are denoted O$_F^{2-}$ and at low temperatures their charge is compensated locally by a bromide ion vacancy. The combination of the V$_k$ center with O$_F^{2-}$ produces O$_F^{-}$ as well as a bromide-ion vacancy, V$_{\mathrm{Br}^-}$, which may diffuse away from O$_F^{-}$ at temperatures above 200 K. Thus, at room temperature, charge is stored in F(Br^{-}) and F(F^{-}) centers, on O$_F^{-}$ sites, and possibly on other sites which have not yet been identified.

The first model to explain the photostimulated recombination of the stored charge, due to Takahashi and his co-workers,[7] involved the promotion of electrons from the F centers into the conduction band followed by diffusion until they found a Eu^{3+} hole site where they recombined radiatively. Subsequently von Seggern and co-workers[4,8] proposed that the PSL occurred when electrons on $F(Br^-)$ centers were promoted to an excited state from which they tunneled to an adjacent hole which was complexed with a Eu^{2+} ion in a loosely defined entity called a photostimulable luminescence complex (PSLC) [electrons at $F(F^-)$ centers are bound too deeply to be stimulated in this way by the HeNe laser[9]]. The energy released in this process excites Eu^{2+} to the $4f^65d^7$ state with subsequent radiative decay to the $4f^7$ ground state. Although direct evidence for PSLC's has been produced,[5,6] recent work by Iwabuchi and co-workers[10] favors Takahashi's original bimolecular kinetic scheme and shows that the PSL in $BaFBr:Eu^{2+}$ is accompanied by photostimulated conductivity (PSC). This is interpreted as evidence for electronic diffusion through the conduction band, an effect which is explicitly forbidden in von Seggern's model.

The charge stored in $BaFBr:Eu^{2+}$ may also be detrapped by heating the material to produce thermostimulated luminescence (TL). Using TL methods Templer[11] has measured the trap depths which are filled during room-temperature irradiation, the shallowest being 0.89±0.2 eV. The equivalent trap depth for photostimulation is greater,[12] because of the Franck-Condon principle, and has been calculated to be between 2.7 and 2.9 eV.[11] Since a HeNe photon has an energy of 1.96 eV it appears that even the shallowest traps are too deep to enable direct photostimulation into the conduction band. Indeed even if one heats $BaFBr:Eu^{2+}$ to 698 °C prior to measurement at room temperature there remains a measurable PSL signal.[11] By this stage there is no reasonable chance of there being any direct photoexcitation into the conduction band with red light since the traps which remain filled have an optical trap depth of at least 6.3 eV.

Templer also recorded the room temperature PSL as a function of time after annealing to a variety of temperatures.[11] The shape of the PSL decay curve was unaffected by the anneal after the first 10–20 s. Figure 1 shows the PSL curves measured after annealing to 182, 262, and 351 °C and then divided by the PSL signal measured after a 122 °C anneal. This result is remarkable because, as the annealing temperature is increased, we would expect to be successively emptying deeper and deeper traps and hence, in the case of both models, we would be progressively etching away the faster temporal components from the PSL.

Attempting to rationalize the above observations has led us to the following model of the PSL in $BaFBr:Eu^{2+}$. At least one of the species of trapped charge is able to migrate about its two-dimensional sublattice, both by thermal[5,6] and photostimulation. The lowest activation energies for vacancy migration are 0.5–0.6 and 0.8–0.9 eV within the Br^- and F^- layers, respectively,[13] while the lowest interplane migration energy has been calculated to be 1.1–1.2 eV for migration from Br to F vacancies. However, electrons in F centers are trapped too deeply to allow direct excitation by red light into the conduction band; only when an electron and hole come into proximity during the random walk are they able to recombine via a thermally or photostimulated subconduction band transition. The PSC in $BaFBr:Eu^{2+}$ can then be explained in terms of optically stimulated diffusion of trapped charge on a two-dimensional lattice without the need for any electronic diffusion in the conduction band. Since our model also predicts that the rate limiting step in the PSL process is the trapped charge migration, we would also expect the PSC and PSL excitation spectra to have the same appearance, which is found to be the case. It also explains why PSL is still observed after high-temperature annealing. This is simply due to charge remaining in deep traps which have yet to form a PSLC. By extension the data in Fig. 1 can be explained in a similar manner. After a 10–20 s settling time, of which more later, we are simply observing the kinetics of charge migration in samples with increasingly diminished levels of trapped charge. The time dependence of the charge migration is independent of the trapped charge population and therefore the curves appear similar.

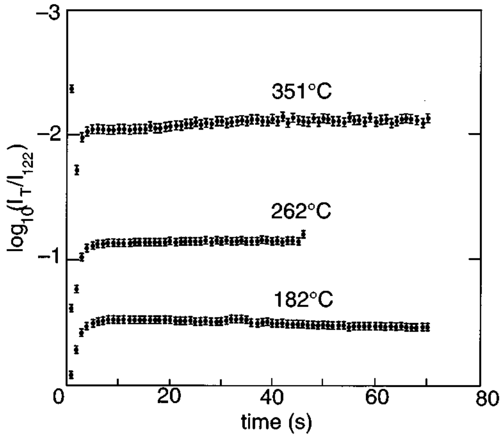

FIG. 1. Decay of the PSL from $BaFBr:Eu^{2+}$ after the sample has been annealed at temperatures of 182 °C, 262 °C, and 351 °C; all the curves have been divided by the decay curve measured after annealing at 122 °C.

The model is also consistent with other salient features of the PSL response of $BaFBr:Eu^{2+}$. At very short times $t(<10$ μs) the PSL signal decays exponentially. This represents the recombination of charge in PSLC's which are already formed, via a single energetic pathway. At longer times (>100 s) the decay of PSL intensity goes as t^{-n}, with n ranging from 1.16 to 1.22 to 1.33 as the temperature is raised from 5 to 45 to 80 °C, respectively. Power-law decays of this form are predicted for random walks on a periodic lattice[14] although in the simplest model involving the hopping of an initially random distribution of electrons and holes on a two-dimensional lattice, the decay exponent would be 1.5 and would not have an explicit temperature dependence. We have not pursued more sophisticated kinetic models for the PSL, since it is evident that a random hopping model can always be devised to match the desired temporal response, but, without additional, nonkinetic data this does not provide particularly compelling evidence to support the model. It is also well known that the initial PSL signal rises linearly with the applied dose, up to saturation. This is consistent with the model, because the PSL only occurs when spatially localized trap pairs are formed. This means that although there may be significant retrapping of photostimulated charge, the charge is retrapped at its original trap site which results in first-order behavior.[15]

Our model is not only capable of qualitatively rationalizing what previously appeared to be conflicting observations but also predicts a rather startling kinetic effect which cannot be explained if one assumes that charge is trapped at static locations. Suppose a sample is illuminated up to a time t_1 and then the source of stimulation is switched off. The formation of PSLC's will continue in the dark, so that if the laser is switched on again at a time t_2 the PSL signal should be higher compared with that at t_1. We call this effect *recuperation*. Of course we would also predict that the rate of recuperation would increase as we increase the temperature at which we store the sample, until the storage temperature itself was high enough to stimulate appreciable electron-hole recombination. In what follows we demonstrate exactly this sort of recuperation in BaFBr:Eu^{2+}. Aspects of thermally stimulated signal recovery have been reported before:[5,6] the photostimulated signal observed at 10 K was exhausted by continuous stimulation, but could be restored by warming the sample to room temperature, the effect being particularly marked above about 200 K. Here we look at this phenomenon in greater depth and produce a self-consistent microscopic model for the recovery.

In the experiments we report in this letter the phosphor samples were cut from a commercial plate manufactured by the Fuji Film Company, comprising powdered BaFBr:Eu^{2+} bound in an organic material and set on a plastic plate. The sample was in the form of a square of edge 5 mm. All irradiation was performed in the dark for 30 min at room temperature with a ^{90}Sr β source of 30 mCi activity. After irradiation, the sample was stuck to an aluminum pin with silicone vacuum grease and transferred in the dark to a light-tight box containing apparatus for PSL measurements. The pin was slotted into an aluminum block equipped with a heater coil and thermocouple and bathed in a stream of cooled nitrogen gas so that the temperature of the sample could be maintained between 5 °C (when ice started to form) and 85 °C. At a selected time, the microcomputer that controlled the instrument opened a shutter and exposed the entire sample to light from a 4 mW HeNe laser (Laser Lines 1124P). A notch filter rejected light other than the harmonic at 632.8 nm. The PSL passed through an interference filter to be detected by a photomultiplier tube (PMT, Thorn EMI 9558QA). The interference filter had a typical bandpass of 40 nm centered at 400 nm and filtered out all light away from the pass region by a factor of 10^4. The PSL signal was measured with Keithley 195A digital ammeter and transferred to a microcomputer at rates of up to 60 Hz.

After the PSL had been measured, the sample was exposed to a 16W UV lamp with a peak wavelength of 350 nm for approximately 1 h, at which point the residual PSL activity was negligible by comparison with the previous PSL measurement, and the background signal was measured. For the recuperation measurements reported here, the computer was programmed to close and open the shutter at times t_1 and t_2, respectively. t_1 was fixed at 116 s and t_2 was varied from 1 min after t_1 to 17 h and measurements were made with the sample temperature set at 45, 65, and 85 °C.

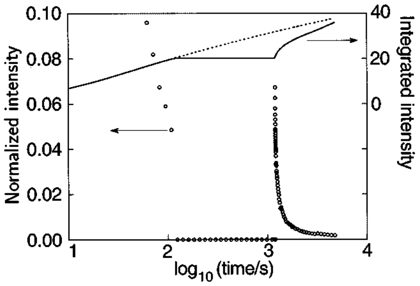

FIG. 2. Recuperation of the PSL from BaFBr:Eu^{2+} at a temperature of 45 °C. The lines at the top of the figure depict the integrated intensity, with the solid line representing the measured intensity and the dotted line the integrated signal that we might expect if the laser had not been switched off then on again. The scale of the measured signal is defined relative to a value of 1.0 when the laser is first switched on.

The phenomenon of recuperation is demonstrated clearly in Fig. 2 which shows data taken at 45 °C with $t_1 = 116$ s and $t_2 = 1075$ s. We also display the integrated signal at the top of Fig. 2, both for the actual light measured and for the extrapolation of the luminescence measured before the laser was switched off at t_1. The curve used in this integration was obtained by extrapolating a least-squares fit to the power-law decay of the stimulated emission measured before t_1. The fact that the actual integrated signal is less than the extrapolated signal is evidence to support our contention that the rate at which the trapped charge hops is enhanced during photostimulation. In Fig. 3 we have plotted the recuperation, defined as $R = [I(t_2) - I(t_1)]/I(t_1)$, where $I(t_n)$ is the PSL intensity at time t_n, as a function of the recuperation period $(t_2 - t_1)$. It is clear that the rate of recuperation is greatest at the highest temperature, as we would predict, but that it also decays at longer times at this temperature, presumably due to thermally stimulated charge recombination.

If we concentrate on the initial growth of our recuperation plots we can extract the hopping energy for the mobile trapped charge. We assume that only the F(Br$^-$) species are mobile, since it is this ionic vacancy that has the lowest hopping energy (for the moment there is insufficient data to give us any hints as to the mobility of the trapped hole). The recuperation is then associated with the build up of PSLC's when F(Br$^-$) species become loosely bound to Eu^{2+} sites during the period $t_1 - t_2$. Those F(Br$^-$) species not yet in a PSLC will execute a random migration across the two-

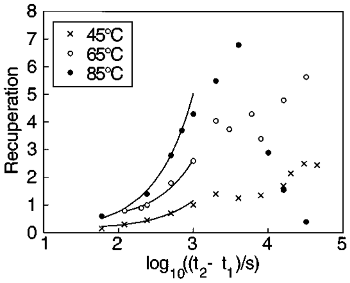

FIG. 3. The dependence on temperature of the recuperation (that is the PSL intensity at t_2 relative to the PSL intensity at t_1), measured at 45 °C, 65 °C, and 85 °C. The lines through the experimental points represent least-squares fits of the recuperation expression (discussed in the text) to the data taken during the initial rise time.

dimensional bromine sublattice. At short times there will be little or no competition amongst the mobile $\mathrm{F(Br^-)}$ species for a specific $\mathrm{Eu^{2+}}$ site and the recuperation will simply be proportional to the number of independent lattice sites, n_s, which have been visited. To first order this is given by $n_s = \pi n_h/\ln(n_h)$,[16] where n_h is the number of hops. The number of hops made in a time t during the recuperation period is simply given by $n_h = st\exp(-E_h/kT)$, where s is the crystal vibration frequency, E_h is the hopping energy, k is the Boltzmann constant, and T is the temperature. This gives the following expression for the recuperation:

$$R = A\frac{ste^{-E_h/kT}}{[\ln(st) - E_h/kT]}, \qquad (1)$$

where A is a constant of proportionality. The crystal vibration frequency has been derived independently[11] and is $10^{13}\ \mathrm{s}^{-1}$. Using this value we have fitted the initial rise in the recuperated PSL with the above formula and found E_h to be 0.89 ±0.01 eV at 45 °C, 0.95±0.01 eV at 65 °C, and 0.95±0.05 eV at 85 °C. It is likely that the rate-determining step for this process is the migration of $\mathrm{F(Br^-)}$, in which case we expect E_h to be larger than the activation energy of 0.5–0.6 eV for the corresponding vacancy.[13] Within experimental error E_h is the same as that measured for the first TL peak in $\mathrm{BaFBr{:}Eu^{2+}}$ (0.89±0.2 eV) though the implications of this are unclear to us. This analysis only applies to the initial state of the recuperation; at longer times factors such as the decay in the population of active migrating species lead to the power-law dependence of growth of PSLC's on time that characterized the decay of the PSL. R will then depend on t_1 and t_2 as $R \propto [1 - (t_1/t_2)^n]$, where n is the power-law exponent. The time at which the transition to this temporal decay occurs will be much longer in the dark compared with that for PSL.

The phenomenon of recuperation also hints at the reason for the initial differences in PSL decay curve shape seen in annealed samples, Fig. 1. Heating the phosphor enables the recombination of charge trapped in PSLC's and alters the form of the radial distribution function for trapped charge in a manner that will depend on the annealing temperature. Recuperation will start as soon as the heat treatment has ended, but there will still be differences in radial distribution functions between the different samples until the laser-induced hopping returns the system to its dynamic equilibrium distribution.

Finally, what can we say about the design of better phosphors? One reason why Ba*FX*:RE is a particularly efficient material appears to arise from its particular form of layered structure. Charge is transferred between the different halide layers so that holes accumulate in the fluorine layers and electrons accumulate in the bromine layers. This partitioning of charge means that it is possible to store electrons in F centers for a long time despite the fact that they are free to migrate over many neighboring sites, and provides traps that are sufficiently deep to store charge efficiently at room temperature, yet not so deep that migration and recombination cannot be stimulated by the relatively modest energy provided by the HeNe laser. The movement of different charge defects is then restricted to different sublattices, and it is likely that it will be hindered only when such defects become pinned at lattice imperfections, some of which may lead to the formation of PSLC's. The general requirement for a good storage phosphor of this type is a layered or chainlike structure with a wide bandgap in which two sublattices of atoms with different electronegativities, or molecules with different electron affinities, are isolated from one another by a third type of atom or molecule. It may also be necessary to introduce a low concentration of impurities to act as charge traps and nuclei for PSLC formation. The resulting defect charge-transfer material is exemplified by Ba*X*:RE salts and may also be sought among its isomorphs and other ternary layered salts; alternatively, such activity may be engineered by epitaxial growth of suitable atomic or molecular multilayers.

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[*] Authors to whom correspondence should be addressed.

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