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Luminescent properties of fluoride phosphate glass for radiation dosimetry

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Abstract: Fluoride phosphate glass has the ability to detect ionizing radiation, and thus can be utilized in various forms for the purposes of dosimetry. To further understand the potential of this material, the luminescence properties have been studied using techniques such as thermoluminescence (TL) and optically stimulated luminescence (OSL). Short luminescent lifetimes and shallow electron trap depths were measured. At the main TL peak at 60 ℃, the activation energy was calculated to be 0.5 eV with a frequency factor of 1.9×10^6 s^{-1} and lifetime of 2.1×10^2 s at 293 K. Fast timing results yield an OSL rise-time of 12.2 μs. Results indicate the material studied is well suited for monitoring applications where the time between radiation exposure and OSL read-out is in the order of several minutes.

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1. Introduction

Fluoride phosphate glass has been previously studied for the purposes of radiation dosimetry [1, 2]. In previous work this material was fabricated into optical fibers to create a fiber based radiation dosimeter, where the optical fiber itself acts as the radiation sensing component [2]. Determining the depth and structure of traps provides an insight into the suitability of the material for various dosimetry applications, such as applications that require continuous monitoring, in contrast to applications that require cumulative measurements over weeks or months. In previous studies, it was found that a brief optical stimulation was sufficient to completely bleach the material [2]. This result suggested the presence of shallow trap depths, and short trap lifetimes, prompting further investigation into the detail of these traps. Therefore, to further understand the behaviour of these fibers with respect to their luminescence properties additional investigations were performed, focusing on the properties of electron traps, and how they affect the luminescence signal.

In addition to the properties of traps and their associated luminescence characteristics, the luminescence kinetics of the material during optical stimulation was also studied. Using pulsed OSL in the micro-second time scale the detrapping and relaxation efficiency can be measured. This was done to determine the time period from initial stimulation to luminescence photon production, a parameter that becomes relevant we seek to make measurements indicating the spatial position of a signal along the fibre length, such as optical time domain reflectometry (OTDR).

In this paper we study the luminescent properties of commercially available Schott N-FK51A fluoride phosphate glass, a material that has previously been identified as a suitable material for an OSL-based fiber dosimeter [1, 2]. The material is a low index (1.49 at 405 nm), low dispersion glass, and has a transmission window extending into the UV to 360 nm. The composition in atomic weight percent is 18(Mg, Ca, Sr, Ba) - 11 Al - 6 P - 23 O - 43 F.

2. Thermoluminescence experiments

Thermoluminescence (TL) allows us to examine the properties of electron traps within the material. A detailed explanation of the application of TL to dosimetry can be found in Ref. [3, 4]. The important parameters for this study are the trap depths (E), frequency factors (s) and lifetimes (τ). These parameters allow us to establish the capabilities of the material in a practical dosimetry application, indicating the temperatures and time-scales in which a device made from this material would be most effective.

TL and initial rise measurements were performed on a Risø TL/OSL DA-20 Reader, which incorporates a ^{90}Sr/^{90}Y beta source, gas-cooled heating plate, optical stimulation using an LED module at 470 nm and an optically filtered EMI 9235QB photomultiplier tube for luminescence detection. TL emission spectra measurements were performed on a 3D TL spectrometer [5]. Samples of fluoride phosphate glass were ground into grains with diameters from 150 to 250 µm. Several samples were used, where the mass of material was approximately 12-14 mg per sample. All experiments were performed following a dose of 1 Gy delivered at ambient temperature.

2.1. Thermoluminescence

TL measurements were performed between 0 - 300 ºC at a heating rate of 1 ºC/s under a nitrogen atmosphere. No filters were used here, the light sum (luminescence intensity) is the total detected signal collected over the sensitive range of the photomultiplier tube. The experiment was also run on an un-irradiated sample to provide a background measurement to subtract the incandescence detected at higher temperatures. TL results are shown in Fig. 1. The peak at 65 ºC indicates the presence of a population of shallow traps, while the lack of any peaks at higher temperatures indicates that no deeper traps producing TL are present. The falling edge found between 0 - 30 ºC is due to shallow traps for which the ambient room temperature is sufficient to rapidly excite electrons into the conduction band.

   Following the results shown in Section 2.2, which shows TL emission centered at 400 nm, further TL measurements were performed using filters to isolate a waveband centered at 400 nm which contains the principal TL emission band. This was done using Schott BG39 (3 mm thick) and Corning 7-59 (4 mm thick) coloured glass filters, the transmission at 400 nm of this composite filter is 40%. Results can be seen in Fig. 1.
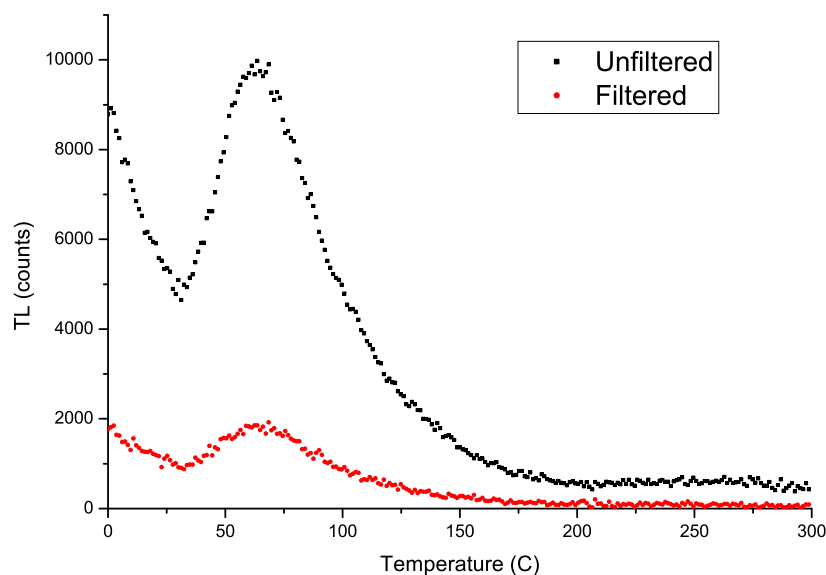

Fig. 1. Thermoluminescence of fluoride phosphate glass. Filtered data was taken using Schott BG39 and Corning 7-59 filters, and therefore shows the thermoluminescence emission centered at 400 nm. Transmission window FWHM = 100 nm.

2.2. Thermoluminescence emission spectra

Spectral information on the thermoluminescence was obtained using a thermoluminescence emission spectrometer [5]. As this is a separate instrument to the Risø Reader, it is important to note the radiation source was also different. This radiation source, although also ^{90}Sr/^{90}Y, has a different activity, and hence dose rate, which means an applied dosage of 1 Gy requires more time. Given the short luminescent lifetime of this material, as is reported here, this difference in irradiation time may affect the total light-sum in comparison to experiments performed in the Risø instrument. It is also important to note the heating rate required was 5 K/s, causing the TL

peak to appear at a higher temperature than the 1 K/s heating rate used for other TL experiments in this study. The results are shown in Fig. 2. The low-temperature TL peak is again seen, with a broad emission peak centered at 400 nm. This emission, centered in the violet, prompted further TL analysis using filters, shown in Section 2.1.
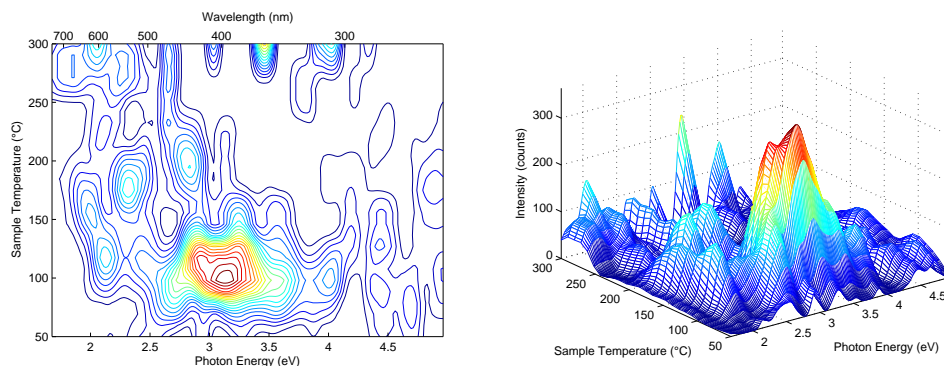

Fig. 2. Thermoluminescence emission spectra of fluoride phosphate glass, measured after administering a 1 Gy dose.

2.3. Initial rise method

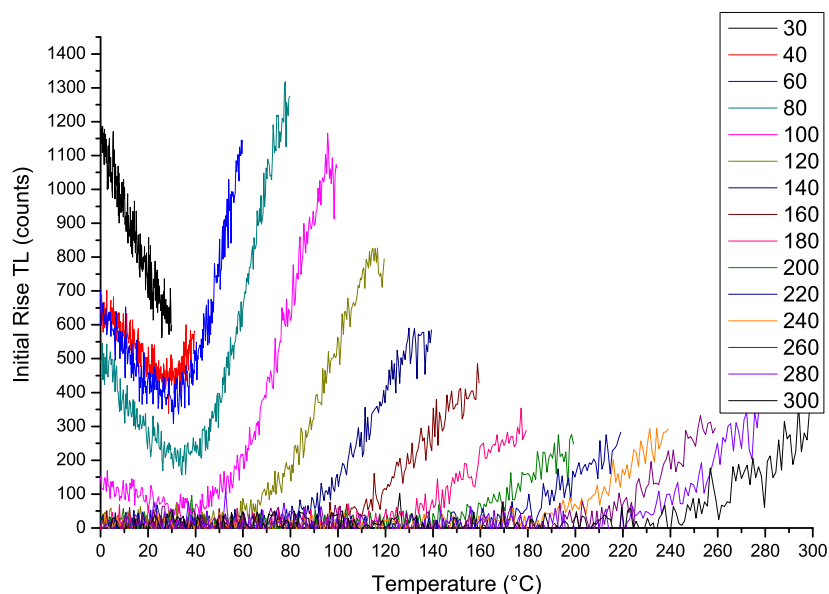Fig. 3. Initial rise thermoluminescence of fluoride phosphate glass for successive heating to the temperatures (in °C) as shown.

Determining the activation energy of traps can be achieved using the initial rise TL method described in McKeever [4]. In summary, following radiation exposure, TL is measured to a certain temperature, then cooled to room temperature. TL is again measured to a temperature slightly

higher than the initial measurement, and this process repeated up to the chosen temperature. For this study, this process was repeated at 20 ℃ increments up to a temperature of 300 ℃ using a heating rate of 1 K/s. 300 ℃ is high enough to resolve the TL peak, without going to a temperature where incandescence introduces unnecessary background. The measurement was also done with an un-irradiated sample to obtain a background measurement. The data can be seen in Fig. 3. Calculation of the activation energy is performed using the relation given in McKeever [4]:

$$I_t = c.\exp\left[\frac{-E}{kT}\right] \tag{1}$$

where I_t is the thermoluminescence intensity, c is a constant, E is the activation energy, k is Boltzmann's constant and T is temperature. A plot of $ln(I)$ vs. $1/T$ over the initial rise region will yield a linear relationship with a slope of $-E/k$ which can be used to calculate the activation energy. Calculation of the frequency factor, s, is achieved using the relation

$$\frac{\beta E}{kT_m^2} = s\exp\left[\frac{-E}{kT_m}\right] \tag{2}$$

where β is the heating rate and T_m is the maximum temperature of the thermoluminescence peak. The trap lifetimes are also calculated using the equation:

$$\tau = \frac{1}{s}\exp\left[\frac{E}{kT}\right] \tag{3}$$

The activation energy, frequency factors and lifetimes calculated from the data shown in Fig. 3 are listed in Table 1. The data shows shallow trap energies, and the resulting short lifetimes derived for electron retention in these traps.

Table 1. Activation Energy (E), Frequency Factor (s) and Lifetimes at T = 293 K (τ) for Fluoride Phosphate Glass Using Initial Rise Data

T_m (℃)	E (eV)	s (s^{-1})	τ (s)
60	0.50 ± 0.039	1.9×10^6	2.1×10^2
80	0.63 ± 0.041	5.1×10^7	1.2×10^3
100	0.69 ± 0.016	1.4×10^8	6.4×10^3
120	0.76 ± 0.027	2.9×10^8	3.7×10^4
140	0.89 ± 0.030	5.1×10^9	5.0×10^5

3. Isothermal decay

Isothermal decay was performed on the glass using a method similar to that outlined by McKeever [4]. This measurement gives information on the decay kinetics of the population of trapped electrons over time at varying temperatures. The change in luminescence intensity with time is monitored at a constant temperature, measurements were taken at room temperature, 40, 50, 60, 70 and 80 ℃. At successively higher temperatures, the shallower components of the excited population are removed before measurements commence, hence decay is observed only from successively deeper traps. To avoid excessive depletion of the excited population, short, low-power pulses of stimulation were used for the measurements. Optical stimulation was performed at 470 nm. Measurements were taken at 10, 17, 26, 42, 78, 184, 490 and 1496 s. All values have been adjusted to account for the duty cycle times of components within the Risø instrument.

In the case where a material has an exponential decay, a plot of $ln(I/I_0)$ vs. t will produce a linear relationship, where I is the intensity, I_0 is the initial intensity and t is time. Figure
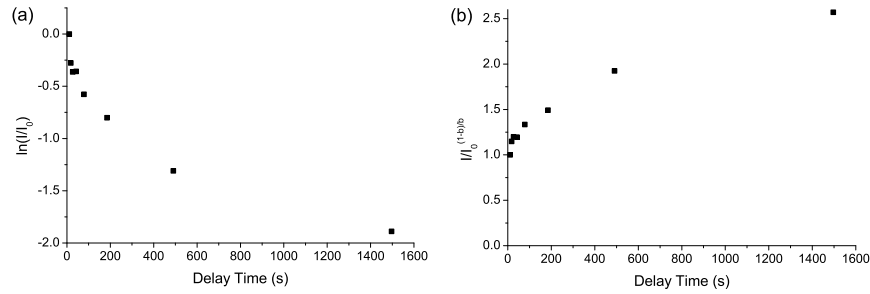
Fig. 4. Fit of optically stimulated isothermal decay data to (a) $ln(I/I_0)$ vs. t and (b) $(I/I_0)^{(1-b)/b}$ vs. t. Data shown is for measurements taken at ambient temperature.

4(a) shows this material does not produce a linear trend, and does not have first order kinetics. For materials with higher order kinetics, a plot of $(I/I_0)^{(1-b)/b}$ vs. t can be used, substituting an appropriate value of b. This can be used to establish the kinetic order of the decay. This was attempted for second order kinetics ($b = 2$), and as indicated by Fig. 4(b), the relationship is not linear. The kinetic order was not obtained for any value where $b \to \infty$, indicating we cannot assume any simple model such as de-trapping from a broad distribution of traps. It is also possible that a combination of re-trapping, tunnelling and a broad range of energy levels associated with a given defect, due to the amorphous structure of glass all contribute to the complex behaviour measured, this will be discussed in Section 5.

4. Photon arrival time

Depending on the application, the decay kinetics of the OSL can be important. In systems where gated or pulsed timing is used the production time of the luminescence - the time elapsing between the absorption of the stimulation photon and the emission of the luminescence photon - is important. Likewise, for optical fiber applications utilizing optical time domain reflectometry, this parameter is also relevant. Measurements were conducted to determine this parameter. Decay kinetics were analyzed using the pulsed optically stimulated luminescence function on the Risø instrument. Following irradiation, samples were exposed to microsecond pulses of stimulation at 470 nm, data was collected using the photomultiplier during both the on and off periods of optical stimulation. A Hoya U-340 UV-pass filter was used to isolate the signal from any stimulation light.

Results can be seen in Fig. 5, where data for optical stimulation pulse widths of 50, 100 and 200 μs are shown. The data was fitted with a sum of two exponential functions and used to calculate a luminescence production lifetime photon arrival time of 12.2 ± 1.3 μs, when the photon intensity reached the 1/e value of 682 counts.

5. Discussion

The measurements shown here explain the behavior found in previous studies of this material [2], where a short optical stimulation of five seconds was found to efficiently remove the population of trapped electrons. Electrons in low temperature traps are released very quickly, and the lack of deeper traps removes any long-lifetime component that would require substantial bleaching. TL, TL emission spectrometry and TL initial rise data all indicate shallow traps with low activation energies and consequently short lifetimes at ambient temperatures.

Isothermal decay results indicate complex de-trapping and recombination pathways. Based
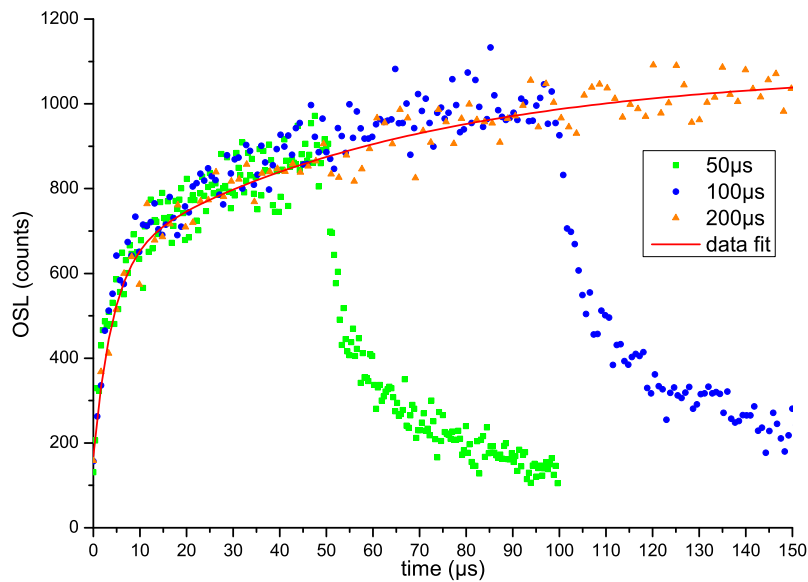
Fig. 5. Fast-timing decay kinetics of fluoride phosphate glass. The pulse width of the optical stimulation for each measurement is shown.

on the complex kinetics measured, re-trapping of excited charge is most likely occurring. Tunnelling of charge between adjacent traps may also be contributing to this behavior [3, 6], but is yet to be confirmed. The interaction between defect sites as addressed by Townsend et. al [7] possibly has merit as an explanation for the processes occurring within this material, given the number of elements from which the glass is formed. A complex network of lattice distortions, all interacting and not independent, could provide the opportunity for several effects. Tunnelling between adjacent sites, a complex path back to recombination sites and the opportunity for re-trapping of free charge. In addition, the amorphous lattice structure of a glass material creates a wide distribution of trap energies.

Various models for trap distribution have been addressed in the past [8–10]. Calculations have been made for materials where the distributions follow 'top-hat', decreasing and increasing exponential functions [8]. Results calculated for the 'top-hat' model are not dissimilar to the results measured here at room temperature for fluoride phosphate glass, however it is not enough to adequately describe the trap structure of this material. It is likely the fluoride phosphate glass has a distribution of traps loosely following a top-hat function, but with some slight variation.

Measurements using the TL emission spectrometer show luminescence occurring over a wide range of wavelengths centered at 400 nm. This region is at the edge of the transmission spectrum for this glass, but it is a useful region for practical device design due to the high detection efficiency of photomultiplier tubes, as well as the variety of filters available to isolate luminescence signals at these wavelengths. There exists the possibility of introducing dopant ions to tailor the emission of these glasses, such as using transition metal or rare earth ions [1].

Pulsed optically stimulated luminescence results show that the material has a luminescence production time of 12.2 ± 1.3 μs. Where spatially resolved measurements and optical time-domain reflectometry techniques are used, this value will need to be taken into account. The

delay in time between stimulation and luminescence emission may be due to re-trapping and the complex recombination path discussed above.

It is interesting to compare fluoride phosphate glass with other dosimeter materials. The extensively-used Al_2O_3:C has a high sensitivity for both OSL and TL compared with most other luminescent materials, for OSL the intensity is approximately 10^3 higher than for fluoride phosphate glass. However, it suffers from its efficient signal-retention, i.e. the difficulty of fully resetting it during readout. For very low-dose applications (mGy) Al_2O_3:C shows efficient signal bleaching and re-usability [11], however for higher dosages the material requires long stimulation periods to largely drain the population of excited electrons [12]. If repeated measurements are required, dose information carried over from a previous measurement will frequently affect subsequent measurements. This has been addressed through various methods, such as only measuring the fast and medium components of the OSL curve and applying appropriate correction values [13]. Another method involves applying a 20 Gy pre-dose before commencing measurements [14]. In comparison, fluoride phosphate glass has particularly efficient bleaching characteristics: a short pulse of stimulation is sufficient to revert the material back to its pre-irradiated state.

From these results, we can establish this glass is suitable for a certain range of applications, and unsuitable for others. Due to its shallow traps and short lifetime at ambient temperature, this material is suitable for applications where interrogation of the material occurs on a rapid duty cycle, or where the material does not need to sit in a passive environment for time periods longer than several minutes. This also makes the material ideal for applications where fast and efficient bleaching is required, and/or where repeatability from one measurement to the next is necessary. Applications for which this material would not be suitable include environments where there is a significant delay between radiation exposure and interrogation.

6. Conclusion

Fluoride phosphate glass, N-FK51A purchased from Schott Glass Company, was studied for its luminescence characteristics, and its response to various TL and OSL measurements. Very shallow electron traps were measured with an activation energy of approximately 0.5 eV, with a median lifetime of 2.1×10^2 s at 293 K. A broad TL emission peak was measured, centered at 400 nm. The trap distribution was found to be complex, with the decay kinetics possibly attributed also to re-trapping and tunnelling. The luminescence production mechanism was measured to have a time-constant of 12.2 μs between stimulation photon incidence and luminescence photon emission. The material was found to be suitable for short-lifetime dosimetry measurements where efficient and complete bleaching of the dosimeter is required. The potential suitability of this material for spatially resolved dosimetry in real time is identified.