Published in final edited form as:

Nucl Instrum Methods Phys Res B. 2014 May 1; 326: 182–184. doi:10.1016/j.nimb.2013.09.031.

Temperature dependence of the photostimulated luminescence in KCl:Eu²⁺

Zhiyan Xiao, Rachael Hansel, Lei Zhang, and H. Harold Li

Center of Materials Innovation, and Medical Physics Division, Department of Radiation Oncology, Washington University in St. Louis, 4921 Parkview Place, Campus Box 8224, St. Louis, MO 63110

Abstract

The goal of this work is to understand the physical mechanism behind the signal stabilization process in KCl:Eu²⁺, a storage phosphor material that has generated renewed interest due to its potential in radiation therapy dosimetry application. The temperature dependency of the photostimulated luminescence (PSL) spectra and intensity vs. time post x ray irradiation was measured. Commercial BaFBr:Eu²⁺ materials were included in this study for comparison. Unlike BaFBr:Eu²⁺, broadening of the F(Cl⁻) stimulation band and red-shift of the peak were observed for KCl:Eu²⁺ with increasing temperature. For irradiations at temperatures lower than 200 K, PSL intensity of KCl:Eu²⁺ showed recuperation behavior in the first 2 hrs post-irradiation and stayed almost constant with time thereafter. Moreover, spatially-correlated storage centers increased from 24% for irradiation at 50 K to 31% at 195 K and almost 100% at room temperature. The data suggest that certain types of charge storage-centers were mobile and contribute to the fast fading in PSL.

Keywords

storage phosphor; photostimulated luminescence; temporal stability

1. Introduction

With the increased complexity in radiation therapy treatment planning and delivery, there is a pressing need for advanced dosimetry tools that can accurately characterize delivered dose to a cancer patient [1, 2]. A recent suggestion that europium doped potassium chloride (KCl:Eu²⁺) has the potential to significantly advance the state-of-the-art in radiation therapy dosimetry has generated a renewed interest in a classic storage phosphor material [3, 4].

An important property of storage phosphors is the stability of the information stored in the phosphor after irradiation. Previous results have shown that the PSL intensity decreases with

© 2014 Elsevier B.V. All rights reserved.

Corresponding Author: hli@radonc.wustl.edu.

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

storage time between irradiation and PSL readout, typically consisting of a fast component after irradiation and a much slower component afterward [4]. In order to avoid having to apply a large time-dependent correction, dosimeters should be readout the day after irradiation so that the delay time difference between calibration and measurement dosimeters will be negligible. For example, a 30 minute delay time difference will lead to a small correction factor of approximately 0.2%. Although irradiating the dosimeters in the evening and reading on the following day works well in the clinical schedule, reducing the wait time to few hours is desirable. However, the shorter the wait time, the larger the uncertainty will be. This may not be a concern for diagnostic computed radiography [5]; however, large uncertainty associated with fast decay at the time of readout could be critical for quantitative, absolute radiation therapy dosimetry purposes where an accuracy of better than 3% is required. Ideally the materials should be engineered in such a way that they exhibit clinically insignificant fading, *i.e.* the time to reach equilibrium shortens to a few seconds or minutes.

The ultimate goal of this work is to understand the physical mechanism behind the signal stabilization process in KCl:Eu^{2+} . KCl:Eu^{2+} along with commercially available BaFBr:Eu^{2+} were irradiated by a medical linear accelerator at temperatures ranging from room temperature (RT) down to 50 K. The temperature dependences of both the PSL stimulation spectra and PSL intensity versus time post irradiation were measured.

2. Experimental

High purity KCl (99.995%, Sigma-Aldrich) particles and reagent grade $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ particles were mixed at a 500 ppm Eu^{2+} concentration. Powders were pressed at 2200 lbs force in a hydraulic press (Carver Inc., Wabash, IN) using an evaluable pressing die to 6 mm in diameter and 1 mm thick. The pellets were sintered at 710 °C for 3 h in air and allowed to cool naturally to 300 °C followed by a rapid cooling to room temperature. Commercial BaFBr:Eu^{2+} storage phosphor panels (Agfa DS4000 and Fuji STVI) were cut into same diameters as KCl:Eu^{2+} x ray detectors.

Detectors were placed in a temperature-controlled cryostat (Model CCS 450, Janis, MA) and irradiated to 8 Gy using a 6 MV beam from a Varian medical linear accelerator (Varian, Palo Alto, CA). The 6 MV beam is a polyenergetic bremsstrahlung radiation with a maximum photon energy of 6 MeV and an average photon energy of 2 MeV. The readout light source consisted of a 150 W, UV enhanced Xe arc lamp (Newport, Stratford, CT). Wavelength selection for the Xe source was provided by a motorized monochromator (Cornerstone 130, Newport) with a grating of 1200 lines/mm and a combination of optical filters. PSL signals were separated from the readout light by using narrow bandpass filters (FB420-10 or FB390-10, Thorlabs, Newton, NJ) and detected by a photomultiplier tube (R1924A, Hamamatsu, Bridgewater, NJ) connected to a lock-in amplifier (Model SR830, Stanford Research Systems). PSL temporal stability was monitored by probing the signal at various times post-irradiation.

3. Results and Discussion

3.1 Temperature dependence of PSL stimulation spectra

As shown in Figure 1a, there was almost no changes in stimulation peak and FWHM (full width at half maximum) for BaFBr:Eu²⁺, which is consistent with the literature [6–8]. For KCl:Eu²⁺, however, the F(Cl⁻) band stimulation peak red-shifted by about 15 nm and FWHM broadened by 21 nm (Figure 1b). The changes in the F- band peak and FWHM could be a result of electron-phonon interaction [9]. An increase in FWHM with increasing temperature could be related to the growing phonon frequency while the thermal shift in peak position could be due to a frequency change between the ground and excited states [10]. Figure 1(b) suggests that different stimulation wavelength should be used at different measuring temperature in order to obtain comparable PSL intensities and sufficient signal-to-noise-ratios.

3.2 Temperature dependence of fading characteristics

Figure 2 shows the PSL intensity vs. time post-irradiation at RT and 50K for both KCl:Eu²⁺ and BaFBr:Eu²⁺. The PSL intensity was monitored at the corresponding irradiation temperature for about 20 hrs. For irradiations at RT, the PSL faded with time for all samples with Fuji samples showing the least fading (Figure 2a). The fast fading with time is likely due to unstable electron or hole- storage centers, or both in the material. It is generally accepted that a number of factors affect the shape of the fast fading curve, including thermal stimulation of stored charges from the shallow traps, re-trapping at the dosimetric trap, and photo transfer of charges from deep to the dosimetric and shallow energy levels [10]. Therefore, the decay curve was multi-exponential.

When the samples were irradiated at 50 K, both BaFBr:Eu²⁺ samples fade with time (Figure 2b). Surprisingly, KCl:Eu²⁺ showed an initial increase (i.e. recuperation according to Harrison [8]) in the first 4 hours before reaching a plateau. Similar initial increases in the PSL have been reported for Al₂O₃:C materials [10]. Intrinsic traps, especially shallow traps, may exist in the polycrystalline KCl:Eu²⁺ samples. These traps may not be photostimulable; however, they can act as competitors in the photostimulation pathway. These shallow traps can capture (retrap) charges that are photo-stimulated from the dosimetric traps. At low temperatures these recaptured electrons are not able to escape to the conduction band due to the lack of sufficient thermal energy and therefore do not contributing to the PSL. As a result, the overall PSL intensity is smaller than that would be expected. However, as the shallow traps become filled, the competition process becomes less important and consequently the PSL intensity increases.

In order to further understand the fading behavior of the KCl:Eu²⁺, PSL intensity vs. time post-irradiation at various irradiation temperatures was recorded (Figure 3). As the irradiation temperature decreased, the decay gradually slowed down. At 205 K irradiation, the PSL intensity remained almost constant vs. time. This suggests that there are certain types of charge-storage centers are not stable at temperatures above 200 K that contribute to the fast fading. It has been reported that V_k centers in BaFBr:Eu²⁺ are stable at low temperatures but migrate around at temperatures above 200 K [7, 8, 11]. Therefore, the hole-

storage V_k centers may be primarily responsible for the fast fading due to high mobility at relatively high temperatures (above 200 K).

3.3 Temperature dependence of PSL intensity

The temperature dependence of the PSL intensity is plotted in Figure 4. $KCl:Eu^{2+}$ were irradiated at prescribed temperature and remained at the same temperature for at least 20 hrs to avoid any confounding variable due to fading. PSL intensity vs. temperature was then recorded while the $KCl:Eu^{2+}$ samples were cooled down to 50 K except the 50 K sample. For the latter, the PSL was measured while the temperature was increasing. The samples were stimulated at various peak wavelengths ranging from 545 to 560 nm, as shown in Figure 1b. The intensity of the stimulation light was so low such that the whole temperature experiment could be performed without needing to correct for PSL loss due to repeated readings. As shown in Figure 4, at irradiation temperatures low than RT, a thermally-activated process was evident in the range of 50 K to 150 K.

For example, for irradiations at 50 K, a thermally activated increase in PSL vs. temperature was observed with an activation energy of about 20 meV until saturation occurred followed by a PSL decrease above 200 K. The increase in PSL with increasing temperature between 50 K and 150 K for each curve could be explained using von Seggern/Thoms model in term of spatially-correlated and uncorrelated storage centers [7, 12]. After photostimulation, F -center electrons require thermal energy to be released from the relaxed excited state (RES) of the F -center into the conduction band. When the temperature is too low an electron in the RES will not be able to thermally leave the F -center, and will either decay back into the ground state or tunnel to a neighboring V_k -center. In the case of tunneling, spatial proximity of the F -center and the V_k -center is required. Centers which are not spatially nearby require thermal energy to release the photostimulated electrons from the RES of the F -center into the conduction band and are called non-correlated. Thus, PSL yield at low temperatures corresponds to the concentration of spatially correlated traps. As shown in Figure 4, about 24% of the storage centers were spatially correlated for irradiation at 50 K. This number increased slightly when the samples were irradiated at higher temperatures up to 180 K (data not shown), and then reached 31% at 195 K, 39% at 205 K and 65% at 250 K. For irradiations at RT, almost all storage centers were correlated. These results provide strong evidence that charge-storage centers, at least the V_k centers, become noticeably mobile around 200 K and above, thus being able to form spatially-correlated photostimulable luminescence complex [8].

4. Conclusions

The PSL intensity of $KCl:Eu^{2+}$ stayed almost unchanged vs. time for irradiations at around 200 K, suggesting that charge-storage centers were relatively stable at temperatures below 200 K. They, probably V_k centers, became more mobile at temperatures at 200 K and above, as evidenced by an increased percentage of spatially-correlated photostimulable luminescence complexes. The observed recuperation effect at irradiation temperatures below 200 K was probably due to a re-trapping process by competing shallow traps.

Acknowledgments

This work was supported in part by NIH Grant No. R01CA148853.

References

1. Ezzell GA, Galvin JM, Low D, Palta JR, Rosen I, Sharpe MB, Xia P, Xiao Y, Xing L, Yu CX. Med Phys. 2003; 30:2089–2115. [PubMed: 12945975]
2. Galvin JM, Ezzell G, Eisbrauch A, Yu C, Butler B, Xiao Y, Rosen I, Rosenman J, Sharpe M, Xing L, Xia P, Lomax T, Low DA, Palta J. Int J Radiat Oncol Biol Phys. 2004; 58:1616–1634. [PubMed: 15050343]
3. Zheng Y, Han Z, Driewer JP, Low DA, Li H. Med Phys. 2010; 37:146–153. [PubMed: 20175476]
4. Han Z, Driewer JP, Zheng Y, Low DA, Li H. Med Phys. 2009; 36:3748–3757. [PubMed: 19746808]
5. Leblans P, Vandenbroucke D, Willems P. Materials. 2011; 4:1034–1086.
6. Hangleiter T, Koschnick FK, Spaeth J-M, Nuttall RHD, Eachus RS. J Phys: Condens Matter. 1990;6837–6846.
7. Thoms M, von Seggern H, Winnacker A. Phys Rev B. 1991; 44:9240–9247.
8. Harrison A, Harrison MT, Keogh GP, Templer RH, Wills AS. Physical review. B, Condensed matter. 1996; 53:5039–5042.
9. Konitzer JD, Markham JJ. J Chem Phys. 1960; 32:843–856.
10. McKeever SWS, Bøtter-Jensen L, Larsen NA, Duller GAT. Radiation Measurements. 1997; 27:161–170.
11. Hackenschmied P, Li H, Epelbaum E, Fasbender R, Batentschuk M, Winnacker A. Radiat Meas. 2001; 33:669–674.
12. von Seggern H, Voigt T, Knüpfer W, Lange G. J Appl Phys. 1988; 64:1405–1412.

Figure 1. PSL stimulation spectra measured at 10 K and RT after irradiations at 250 K. (a) BaFBr:Eu²⁺ (Agfa) and (b) KCl:Eu²⁺.

Figure 2.

PSL vs. time after irradiations at (a) RT and (b) 50 K for KCl:Eu^{2+} and BaFBr:Eu^{2+} (Agfa and Fuji). Measuring temperature was kept at the irradiation temperature. PSL intensity was normalized to that at the 13th hour.

Figure 3.

PSL vs. time after irradiations at various temperatures ranging from 50K to RT for KCl:Eu²⁺. Measuring temperature was kept at the corresponding irradiation temperature.

Figure 4.
Normalized PSL vs. temperature for KCl:Eu²⁺.