The role of activator concentration and precipitate formation on optical and dosimetric properties of KCl:Eu²⁺ storage phosphor detectors

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Purpose: The activator ion (Eu²⁺ in KCl:Eu²⁺) plays an important role in the photostimulated luminescence (PSL) mechanism of storage phosphor radiation detectors. In order to design an accurate, effective, and robust detector, it is important to understand how the activator ion concentration affects the structure and, consequently, radiation detection properties of KCl:Eu²⁺.

Methods: Potassium chloride pellets were fabricated with various amounts of europium dopant (0.01–5.0 mol.% Eu²⁺). Clinical radiation doses were given with a 6 MV linear accelerator. Radiation doses larger than 100 Gy were given with a ¹³⁷Cs irradiator. Dose response curves, radiation hardness, and temporal signal stability were measured using a laboratory PSL readout system. The crystal structure of the material was studied using x ray diffraction and luminescence spectroscopy.

Results: The most intense PSL signal was from samples with 1.0 mol.% Eu. However, samples with concentrations higher than 0.05 mol.% Eu exhibited significant degradation in PSL intensity for cumulated doses larger than 3000 Gy. Structural and luminescence spectroscopy showed clear evidence of precipitate phases within the KCl lattice, especially for high activator concentrations. Analysis of PL emission spectra showed that interactions between Eu-V_c dipoles and Eu-V_c trimers could explain trends in PSL sensitivity and radiation hardness observations.

Conclusions: The concentration of the activator ion (Eu²⁺) significantly affects radiation detection properties of the storage phosphor KCl:Eu²⁺. An activator concentration between 0.01 and 0.05 mol.% Eu in KCl:Eu²⁺ storage phosphor detectors is recommended for linear dose response, good PSL sensitivity, predictable temporal stability, and high reusability for megavoltage radiation detection. © 2013 American Association of Physicists in Medicine. [<http://dx.doi.org/10.1118/1.4817522>]

Key words: radiation detector, storage phosphor, radiation hardness

1. INTRODUCTION

BaFBr:Eu²⁺ storage phosphors have been the radiation detector of choice for decades.^{1–3} The recent development of needle-shape CsBr:Eu²⁺ has made this material an excellent addition to this class of detectors.^{4–6} These materials record ionizing radiation information via the photostimulated luminescence (PSL) mechanism (also known as optically stimulated luminescence or OSL). During irradiation, electron and hole traps become occupied with radiation-induced electrons or holes, respectively. Charge carriers can be released by stimulating the material with visible light. During the stimulation process, electrons are excited to the conduction band and then recombine with trapped holes. The energy released promotes an electron in the luminescent activator center to the excited state and results in blue photon emission. The PSL emission intensity is proportional to the absorbed x ray dose. Scanning a storage phosphor panel with a stimulating light source and recording the PSL emission signal creates a radiation deposition image. While these high Z materials exhibit excellent storage performance, they are less useful for radiation detection that requires water-equivalent measurements, for example, in radiation therapy dosimetry. Also, it has been reported that the PSL signal of CsBr:Eu²⁺ degrades by 20% with cumulated doses of 100 Gy.⁷ This may be sufficient for diagnos-

tic computed radiography but limits the number of times the detector can be reused for radiation therapy dosimetry with a typical 2 Gy per use.

Recent work has shown that KCl:Eu²⁺ has great potential for use in megavoltage radiation therapy dosimetry because this material exhibits excellent storage performance and is reusable due to strong radiation hardness.^{8,9} KCl:Eu²⁺ has a much lower Z-number which means that it is more conducive to clinical dosimetry. Furthermore, recent calculations¹⁰ have demonstrated that ultrathin KCl:Eu²⁺ panels (of the order of 1 μm) would exhibit nearly water-equivalent dose response.

The activator ion (Eu²⁺ of KCl:Eu²⁺) plays an important role in storage phosphors. Optical and, consequently, dosimetric properties can be affected by europium ion concentration due to the formation of various agglomerate or precipitate phases. For example, increasing the activator concentration could improve PSL sensitivity. The PSL sensitivity should be high enough to obtain a good signal-to-noise ratio to reduce measurement uncertainty, but should be below concentrations at which PSL quenching occurs. Also, minimizing the amount of rare-earth metals is desirable because recent geopolitical relationships may impact the supply and commercial manufacturing costs of detectors that contain europium.¹¹ Therefore, in order to design a robust, high-quality radiation detector, it is important to optimize the activator concentration in

terms of linear dose response, PSL sensitivity, signal temporal stability, and radiation hardness.

The goal of this work is to understand how the activator concentration affects precipitate formation and the radioluminescence properties in KCl:Eu²⁺. Specifically, we will (1) show the effects of activator concentration on PSL sensitivity, temporal stability, dose response, and radiation hardness, (2) observe precipitate formation in KCl:Eu²⁺ as a function of activator concentration, and (3) use the photostimulated luminescence (PL) emission spectra to explain trends in PSL properties of KCl:Eu²⁺.

2. MATERIALS AND METHODS

2.A. KCl:Eu²⁺ detector fabrication

High purity KCl (99.995%, Sigma Aldrich) powder with grain size of 45–63 μm was combined with EuCl₃·6H₂O powder using a mortar and pestle and a high frequency shaker. Nominal europium mole percent concentrations were: 0.01, 0.05, 0.1, 0.5, 1.0, 2.0, and 5.0. The KCl:Eu²⁺ powder was baked for 3 h at 310 °C to minimize the amount of water in the powder. After baking, the powders were pressed with 2200 lbs of force in a hydraulic press into a 1 mm thick, 6 mm diameter pellet. Pellets were then sintered at 710 °C for 3 h in air.

2.B. Dosimetric properties

2.B.1. Irradiations

A 6 MV Varian Trilogy (Varian Medical Systems, Palo Alto, CA) linear accelerator, calibrated according to the AAPM TG-51 protocol, was used for clinical irradiations. The nominal dose rate was 600 MU/min. The detector plane was perpendicular to the beam central axis for all irradiation and the source-to-surface distance was 100 cm. Thirty-by-thirty cm² water-equivalent sheets (SW-457, Gammex RMI, Middleton, WI) were arranged to provide 10 cm of backscatter and 1.5 cm of build-up. Detectors were placed in a 0.5 cm thick slab machined with a linear array of holes across the center. Any background signal created by environmental radiation was removed using a 500 W tungsten-halogen lamp prior to irradiation.

For doses larger than 100 Gy, a high dose rate ¹³⁷Cs irradiator (J.L. Shepherd and Associates, Mark I Model 25, San Fernando, CA) was used. Detectors were placed on a foam block and both items were placed near the center of the irradiation chamber. The block was rotated during irradiation to mitigate any inverse-square distance dependence of dose delivery to individual detectors. The dose rate to water was 10.7 Gy/min according to factory calibrations. The delivered dose was verified using a commercial radiochromic film (EBT2, International Specialty Products, Wayne, NJ).

2.B.2. Optical readout setup

The stimulating light was a 2 mW, 594 nm He-Ne laser (Melles Griot, Covina, CA). The stimulating light was

chopped with an optical chopper (Model SR540, Stanford Research System, Sunnyvale, CA) set to 150 Hz in order to provide a reference signal to a lock-in amplifier (Model SR830, Stanford Research Systems) for phase sensitive detection. A photomultiplier tube (R1924A, Hamamatsu, Bridgewater, NJ) and a narrow bandpass filter FB420-10 (420 nm wavelength with 10 nm full-width-half-maximum, FWHM, Thorlabs, Newton, NJ) were used to detect the PSL. A measurement involved opening the shutter, waiting 1 s for the signal to stabilize, and then integrating the luminescence over 1 s.

2.B.3. Dosimetric measurements

Dose response linearity for various activator concentrations: Detectors were irradiated with clinical doses (0.5–3 Gy) with a 6 MV Linac and were readout approximately 17 h postirradiation.

Temporal stability for various activator concentrations: Detectors were given 2 Gy from a 6 MV Linac. A single PSL measurement was recorded every hour for 17 h postirradiation. The readout power for the laser source was attenuated by neutral density filters to allow for repeated readings. The readout loss of approximately 0.1% per reading was corrected for.

PSL intensity with increasing activator concentration: Dosimeters were given 2 Gy with a 6 MV Linac and the PSL signal was readout approximately 17 h postirradiation. The PSL signal was plotted in comparison to the activator concentration.

PSL intensity with cumulated dose: KCl:Eu²⁺ detectors were irradiated with 2 Gy from a 6 MV Linac to determine the sensitivity of the detector with zero Gy history. Detectors were then bleached with a halogen lamp and given large radiation doses (0–7000 Gy) with a ¹³⁷Cs irradiator. After each large dose, detectors were optically bleached with a halogen lamp and then given 2 Gy with the Linac. The PSL sensitivity was recorded approximately 17 h postirradiation and the PSL intensity was normalized to the 0 Gy PSL signal.

2.C. Spectroscopic measurements

2.C.1. PSL stimulation spectra

The PSL stimulation spectra of KCl:Eu²⁺ measure the emission intensity at 420 nm for a range of stimulation wavelengths. The stimulating light was a 150 W, UV enhanced Xe arc lamp (Newport, Stratford, CT). A range of wavelengths was provided using a motorized monochromator (Cornerstone 130, Newport) with a grating of 1200 lines/mm. The slit width on the excitation monochromator was kept at 60 μm to minimize effects of bleaching storage traps. Light was passed to the sample through a series of optical filters and detected using a photomultiplier tube (R1924A, Hamamatsu, Bridgewater, NJ) and a narrow bandpass filter FB420-10 (420 nm wavelength with 10 nm full-width-half-maximum, FWHM, Thorlabs, Newton, NJ). A lock-in amplifier was used to increase the signal-to-noise ratio.

2.C.2. PSL and PL emission spectra

PSL and PL emission spectra were obtained using a Nanolog Spectrofluorometer (Horiba Jobin Yvon Kyoto, Japan). A 450 W Xe lamp was used for the excitation source and the excitation light passed through a 1200 lines/mm grating then through fiber optic cables and finally to the solid sample. Solid pellet samples were placed in a 6-in. diameter Quanta-phi integrating sphere. Emission light was detected using a Synapse Open-electrode CCD detector (Horiba, Kyoto, Japan) sensitive between 300 and 950 nm.

2.D. X-ray diffraction measurements

X-ray diffraction spectra were obtained using a Rigaku Giegerflex D-MAX/A Diffractometer using Cu-K α radiation. The step size for each of the following spectra was 0.01 and the dwell time was 1 s per step. The operating power used was 35 kV and 35 mA.

3. RESULTS

3.A. Dosimetric measurements

Dose response linearity for various activator concentrations: Figure 1 shows that the dose response of KCl:Eu²⁺ to ionizing radiation remains linear for x-ray doses, regardless of europium concentration.

Temporal stability for various activator concentrations: The PSL emission intensity in storage phosphors is known to exhibit temporal instability following irradiation. That is, the emission intensity is known to decrease by approximately 50% in the hours following irradiation and then stabilize. The PSL signal decay typically consists of a fast decay component immediately after irradiation and a subsequent slower component. Figure 2 compares the PSL fading behavior of samples with different europium concentrations. Despite additional activator ions, the fast fading component and the slow fading component remain constant, regardless of activator concentration.

FIG. 1. Dose response linearity for various activator concentrations. Dose response curves were normalized to the 2 Gy dose. The dose response curves show that the dose response remains linear, regardless of activator concentration.

FIG. 2. Temporal stability for various activator concentrations. The PSL sensitivity was monitored for 17 h after a 2 Gy irradiation from the Linac. Despite additional activator ions, the fast fading component remains constant which indicates that multiple mechanisms may be responsible for temporal instability of KCl:Eu²⁺.

PSL intensity with increasing activator concentration: The PSL sensitivity as a function of activator concentration is shown in Fig. 3. All samples were given a dose of 2 Gy from a 6 MV clinical linear accelerator. The PSL intensity was read 17 h postirradiation. The highest PSL sensitivity is obtained for samples with 1 mol.% Eu and declines with higher activator concentrations.

PSL intensity with cumulated dose: An ideal detector for clinical applications should exhibit a consistent optical response with repeated usage. One method to evaluate KCl:Eu²⁺ detectors for reusability is to expose the detectors to extremely high x ray doses and then re-evaluate the dosimetric properties (i.e., measuring the radiation hardness). Figure 4 shows the PSL sensitivity as a function of cumulated dose for various activator concentrations. Figure 4 shows the PSL sensitivity increases for samples with less than or equal to 0.05 mol.% Eu with 3500 Gy dose history. However, for higher Eu concentrations, no increase in PSL intensity was observed. In fact, activator concentrations greater than

FIG. 3. PSL intensity with increasing activator concentration. PSL intensity increases with activator concentration up to 1.0 mol.% Eu. The PSL intensity decreases with concentrations higher than 1.0 mol.% Eu, which is likely due to precipitate formation and luminescence quenching. The line is added to guide the eye.

FIG. 4. PSL intensity with cumulated dose. Samples were given large doses with a Cs-137 irradiator, optically bleached with a halogen lamp to remove storage information, then given 2 Gy with a 6 MV linear accelerator. The PSL was readout 17 h postirradiation. Samples with less than or equal to 0.05% Eu retained at least 90% of the initial signal with 7000 Gy history, while samples with higher activator concentrations exhibited dramatic reductions in PSL sensitivity with high cumulated doses.

0.05 mol.% result in drastic reductions in PSL intensity with cumulated dose. For example, for 3500 Gy cumulated dose, the PSL intensity for samples with 0.1 mol.% Eu decreased by 20%, while PSL intensity decreased by over 80% for 5.0 mol.% Eu samples.

3.B. Spectroscopic measurements

PSL stimulation spectra: Figure 5 shows the normalized PSL spectra as a function of Eu concentration. The spectra show that the overall shape remains constant, which indicates that no new electron storage-centers are created by the presence of additional activator ions.

PSL emission spectra: The PSL emission spectra, shown in Fig. 6, were obtained by stimulating samples with a 560 nm light. Figure 6 shows that the peak wavelength is redshifted with increasing concentration (421 nm for 0.01% Eu and 427 nm for 2.0% Eu).

FIG. 5. PSL stimulation spectra for various Eu-concentrations. The stimulation wavelength was varied as PSL emission was collected at 420 nm. The maximum stimulation efficiency for PSL remained constant at approximately 560 nm, regardless of activator concentration.

FIG. 6. PSL emission spectra. The stimulating wavelength was 560 nm. Although there is a shift in peak from 421 to 427 nm with increasing concentration, all detectors emit intense PSL emission around 420 nm.

PL emission spectra: The PL spectra (Fig. 7) show that the intensity correlates well with the PSL intensity measurements in Fig. 3, with the highest intensity for samples with 1.0 mol.% Eu and lowest intensity for samples with 5 mol.% Eu. The shape of the PL emission broadens and there is a red-shift of the peak wavelength with increasing concentration.

FIG. 7. Absolute (a) and normalized (b) PL emission spectra as a function of europium concentrations. The excitation wavelength was 340 nm. The PL peak redshifted and the emission band spectra broadened with increasing activator concentration. The PL emission spectra can be used to identify differences in local electronic environments of the Eu²⁺ ion, which may be due to precipitates phases or other aggregations.

FIG. 8. X-ray diffraction spectra for various europium concentrations. There is clear evidence for the presence of secondary phases, particularly at high activator concentration. These secondary phases likely affect optical and dosimetric properties.

3.C. Structural measurements

X-ray diffraction: The x-ray diffraction spectra (Fig. 8) show that solid pellet samples are composed of highly crystalline KCl. However, other phases are observed, particularly at high concentration. The peaks at 35° and 46° are tentatively assigned to K₂EuCl₅.¹² The XRD data also show evidence for EuCl₂, particularly at high activator concentrations. These EuCl₂ crystals could be associated with the metastable phases of EuCl₂ as reported by others.^{13–16}

Ratio of the area of the Eu-V_c trimer emission band to the area of the Eu-V_c dipole emission band as a function of activator concentration: Based on the XRD results presented in Fig. 8, there are precipitate formations that become significant with increasing activator concentrations. These precipitate phases have been associated with different PL emission peaks at room temperature.¹⁴ We have used a multi-peak Gaussian fitting process to identify the relative contribution of different precipitate phases for different activator concentrations. The inset of Fig. 9 shows a sample Gaussian fit of the PL emission spectra into different emission bands which represent metastable EuCl₂ phases, Eu-V_c dipoles, or Eu-V_c trimers (also known as the Suzuki phase¹⁶). Eu-V_c dipoles consist of an isolated divalent europium ion and a cation (potassium) vacancy. A potassium vacancy creates charge neutrality to compensate for the divalent Eu²⁺ ion in the monovalent potassium site of the KCl lattice. Eu-V_c trimers consist of three Eu-V_c dipoles aggregated together in the crystal structure.¹⁷ In the main plot of Fig. 9, we have compared the areas of the Eu-V_c trimer and Eu-V_c dipole emission bands to identify correlations between trimer emission and changes in dosimetric properties as a function of concentration. The data in Fig. 9 indicate that emission from Eu-V_c trimers becomes more significant with increasing activator concentration. The increase

in trimer emission correlates with a significant decrease in PSL sensitivity (Fig. 3) for samples with high concentrations. (Note that the emission band ratio of the 5 mol.% Eu sample is not analyzed because Gaussian fitting is difficult with low signal-to-noise data.)

4. DISCUSSION

The PSL process in KCl:Eu²⁺ is complex and can be affected by many factors, including activator concentration. The activator concentration can affect PSL sensitivity, manufacturing costs, dose linearity, and other dosimetric properties.

FIG. 9. The ratio of the area under the emission band for trimer to dipoles band emission as a function of activator concentration. The data indicate that emission from Eu-V_c trimers becomes more significant with increasing activator concentration. (Inset) Sample Gaussian fitting of PL emission spectra into different emission bands as described in Ref. 14. Each deconvoluted band represents emission from metastable EuCl₂ phases, Eu-V_c dipoles, or Eu-V_c trimers.

In order to design a high-quality radiation detector using the storage phosphor material, KCl:Eu²⁺, it is important to understand the implications of variations with the activator concentration. In the current work, we have systematically examined how the activator concentration influences the lattice structure of KCl:Eu²⁺ and ultimately how structural changes affect optical and dosimetric properties.

Additional activator centers could introduce lattice defects within the lattice. These lattice perturbations could act as new charge storage-centers which could introduce nonlinearity response with the dose.¹⁸ However, Fig. 1 shows that the PSL dose response remains linear between 0 and 3 Gy, regardless of europium concentration. The constant dose linearity correlates well with the PSL stimulation and emission spectra. Figures 5 and 6 show that increasing the activator concentration does not significantly change the stimulation or emission spectra. These results mean that there are no major changes in the types of both electron storage centers and recombination centers. The PSL emission spectra in Fig. 6 show that the peak wavelength is redshifted with increasing concentration (421 nm for 0.01% Eu and 427 nm for 2.0% Eu). This redshift is due to the increase in splitting between the 10Dq energy levels of the 5d electrons.^{13,19} The emission band begins to broaden with increasing activator concentration which has also been observed in BaFBr:Eu.²⁰ PSL emission band broadening is caused by perturbations within the lattice due to the size difference in activator ion and the host cation.²⁰ Also, the PSL emission spectra agrees with the PL spectra (Fig. 8) which shows that the emission is largely due to the promotion of a Eu²⁺ electron to the 4f⁶5d¹ excited state and then radiative decay to the 4f⁷ ground state. For dosimetric applications, the results of Figs. 5 and 6 show that optical components (filters, light excitation sources) do not need to be altered or changed for PSL readout because the stimulation and emission peak remain constant with increasing activator concentration.

The temporal stability of stored x ray information is another important property of KCl:Eu²⁺ detectors.²¹ Previous work on KCl:Eu²⁺ and other alkali halide phosphors has shown that the PSL readout intensity decreases with time after irradiation. During the first 5–7 h postirradiation, the rate of decrease in PSL is large (referred to as the fast fading component). After 12 h, the PSL intensity continues to decrease; however, the rate of decrease is much slower (referred to as the slow fading component). According to Xiao *et al.*,²² V_k centers (a dihalide ion with a trapped hole) are mobile and can become stabilized by forming a complex with an activator ion. These complexes will remain stable until photon stimulation. V_k centers that do not form complexes with activators can recombine with F centers, thereby contributing to the fast fading component. Therefore, the addition of more activator centers was thought to result in the reduction of the fast-fading component of the fading curve, because the mobile V_k centers are more likely to encounter and thus become stabilized by an activator center. However, the results in Fig. 2 show that the fast fading rate remained almost constant, regardless of europium concentration. The results in Fig. 2 indicate that there may be another mechanism or another center that is responsi-

ble for the fast component of the fading curve. For example, alkali halides are known to absorb water from the atmosphere and form aggregations within the lattice.²³ Oxygen from water molecules could stabilize the V_k centers. Thus, the fast fading component may be dependent on oxygen content, rather than the activator concentration.

Regardless of the physical mechanism, the data in Fig. 2 show that KCl:Eu²⁺ detectors can be available for readout within 24 h because the fading behavior is stable within several hours postirradiation. (Note: In previous work,²² we have shown that, for 0.05% Eu samples, a 15 min thermal treatment at 70 °C in air eliminates the fast fading component and renders the detector available for readout in less than 1 h.) Further, the results of Fig. 2 have important implications for future manufacturing challenges. Commercial manufacturing of KCl:Eu²⁺ panel detector may result in pixel-to-pixel variation of actual activator concentration. Because the slow fading component is the same after 12 h, regardless of activator concentration, dosimetric measurement uncertainty due to variations in fading behavior is negligible.

The PSL sensitivity (or PSL emission intensity) is another important property that must be optimized in order to achieve a good signal-to-noise ratio for readout and to reduce measurement uncertainty. The results in Fig. 3 show that the PSL intensity steadily increases for activator concentrations up to 1 mol.% Eu. This increase is due to the increasing number of luminescent-activator centers. For concentrations higher than 1 mol.%, the PSL intensity decreases dramatically. PSL quenching in europium-doped alkali halides is likely due to agglomeration of europium ions to form various precipitate formations. Savel'ev has shown that KCl is less susceptible to precipitate formation, compared to CsBr, because the size difference between the activator ion and the host cation introduces less elastic deformation into the lattice.¹⁷ This observation is demonstrated by the fact that the quenching concentrations for BaFBr:Eu²⁺ (Ref. 24) and CsBr:Eu²⁺ (Ref. 25) (0.1 and 0.05 mol.% Eu, respectively) are much lower than KCl:Eu²⁺. The results in Fig. 3 also show that detectors retain adequate sensitivity for very low concentrations. Minimizing the europium concentration is desirable for cost-effective manufacturing because geopolitical relationships have made the supply and price of many rare-earth metals, including europium, unstable. Therefore, the europium concentration must be optimized to provide excellent PSL sensitivity while simultaneously minimizing manufacturing costs and supply issues.

While the highest PSL sensitivity was obtained for samples with 1.0 mol.% Eu, the radiation hardness properties were optimal for samples with activator concentrations less than or equal to 0.05 mol.% Eu (Fig. 4). Observing changes in the PSL intensity with cumulated dose is important for determining the reusability of a radiation detector. A reusable radiation detector is desirable not only for lowering operation cost but also for ensuring measurement reliability. In previous work,⁹ we have shown that for cumulated dose of 3000 Gy, the PSL intensity increases to about 15% of the initial PSL for 0.05 mol.% Eu. Figure 4 shows that a similar trend in PSL intensity can be observed for 0.01 mol.% Eu. However, for higher Eu concentrations, no increase in PSL intensity

was observed. In fact, activator concentrations greater than 0.05 mol.% result in drastic reductions in PSL intensity with cumulated dose. For example, for 3500 Gy cumulated dose, the PSL intensity for samples with 0.1 mol.% Eu decreased by 20%, while PSL intensity decreased by over 80% for 5.0 mol.% Eu samples.

For comparison, Zimmerman *et al.*²⁶ have shown that the PSL intensity of CsBr:Eu²⁺ decreases to less than 20% of the initial PSL at a cumulated dose of just 100 Gy. Recently Barentschuk *et al.* reported that radiation hardness of CsBr:Eu²⁺ could be significantly improved by using an oxygen-free Eu²⁺-containing precursor with only a 20% decrease in sensitivity for a cumulated dose of 100 Gy.⁷ The degradation of PSL with cumulated dose was attributed to agglomerations of Eu²⁺ ions, which lead to PSL quenching. Agglomeration of activator ions into various precipitate formations affects the PSL properties in KCl:Eu²⁺; however, the degree and mechanism by which these precipitate formations affect the KCl:Eu²⁺ lattice are unclear. We have used XRD and PL spectroscopy to identify precipitate phases and to understand the effects of precipitate formation on PSL intensity in relation to structure and radiation damage.

The x ray diffraction spectra (Fig. 8) show that solid pellet samples are composed of highly crystalline KCl. However, other phases are observed, particularly at high concentration. The peaks at 35° and 46° are tentatively assigned to K₂EuCl₅, which means that europium is in the trivalent state. However, the PL emission from trivalent europium ions is very low, suggesting that the concentration of Eu³⁺ is very low. Therefore, the trivalent ions are not responsible for the decrease in PSL, which is consistent with Zimmerman's results.²⁶ The XRD data also show evidence of EuCl₂ phases, particularly at high activator concentrations. These EuCl₂ crystals could be associated with metastable phases of EuCl₂, as reported by others.^{13–16} The formation of additional crystal phases within the KCl lattice means that activator ions experience different local electronic environments. Variations in the local environment affect the 10Dq splitting energy levels of the divalent europium ion.¹⁹ These changes in the 10Dq splitting can be observed in the PL emission spectra. Therefore, the PL emission spectra can be used to identify various precipitate phases.¹³

In order to identify various precipitate phases, we have deconvoluted the PL emission spectra using a procedure similar to Ref. 14. Alvarez-Garcia *et al.* identified several different Gaussian bands and assigned them to metastable EuCl₂ phases, Eu-V_c trimers, and Eu-V_c dipoles. (Note that V_c denotes a cation vacancy. The cation for KCl is potassium.) Eu-V_c dipoles consist of the activator ion and a cation (potassium) vacancy. Upon thermal treatment, these dipoles have a tendency to aggregate and form trimers. Savel'ev and others have identified Eu-V_c trimers as consisting of three Eu-V_c dipoles that form a close-packed structure with minimal energy.¹⁷ Alvarez-Garcia *et al.* have attributed emission from other bands to various EuCl₂ phases. In this work, we compare the emission band area of the Eu-V_c trimers to Eu-V_c dipoles. Emission from isolated Eu-V_c dipoles can be thought of as Eu²⁺ emission that would result from lattices with min-

imal lattice perturbations. Emission from Eu-V_c trimers is representative of Eu²⁺ emission from lattices with significant lattice perturbations and distortions. By comparing emission from these formations, a better understanding of the effects of activator concentration on precipitate/aggregate formation and PSL properties can be obtained.

The Gaussian fitting results of the PL spectra are shown in Fig. 9. The ratio of the area under the emission band of Eu-V_c trimers to Eu-V_c dipoles increases with activator concentration. The initial formation of trimers could result in better separation of radiation-generated electron-hole pairs,²⁷ which would lead to an increase in emission intensity. However, as the activator concentration increases, formation of precipitates is more prevalent and the boundaries between the precipitate phases begin to overlap. Overlapping phase boundaries could result in quenching of PL emission because activator centers are close enough to transfer energy nonradiatively to other activator centers. The ratio of emission from the dipoles and trimers likely explains the trends in Fig. 3. The PSL intensity increases with europium concentration up to 1.0 mol.%. In this concentration range, trimer formation is likely well distributed and spatially isolated from other trimers. Thus, for low concentrations, the PSL intensity increases because of improved charge separation and no interference of nearby trimer formations. Further, as discussed above, the KCl lattice is resistant to precipitate formation, which means optical properties will remain unchanged, despite the presence of lattice perturbations. However, samples with activator concentrations higher than 1.0 mol.% exhibit a drastic reduction in PSL, which is likely caused by nonradiative energy transfer between nearby activator centers (the activators are close together because of precipitate formation).

Based on the results presented here, the relationship between activator concentration and cumulated dose shows that precipitate phases are detrimental to radiation hardness properties, particularly at high concentrations. As suggested by Zimmerman *et al.*, large doses of ionizing radiation increase the tendency of Eu²⁺ ions to form aggregates.²⁶ For CsBr, these aggregations cause degradation of PSL properties with radiation doses of less than 100 Gy. In contrast, because KCl is more resistant to precipitate formation, large cumulated doses of ionizing radiation have an insignificant effect on PSL properties for activator concentrations less than or equal to 0.05 mol.% Eu. However, for higher activator concentrations, large cumulated doses of ionizing radiation appear to render the KCl lattice susceptible to form precipitates. High cumulated doses accelerate the aggregation and formation of Eu²⁺ precipitates. This coupled effect of high activator concentration and high cumulated dose likely results in significant precipitate formation, which ultimately results in dramatic PSL quenching. In relation to the results in Fig. 9, trimer formation is significant for high activator concentration samples with no cumulated dose history. It is likely that the ratio of trimer emission to dipole emission is well above unity for samples with high activator and high cumulated dose. Further, the PL emission band may significantly redshift due to the coupled effects of high activator concentration and high cumulated

doses. The increase in trimer emission may also explain the redshift observed in Fig. 7 of Ref. 9.

5. CONCLUSIONS

A clinically viable radiation detector must exhibit high sensitivity, linear response to x ray dose, and have excellent radiation hardness properties. The results of this study show that the PSL response of KCl:Eu²⁺ remains linear, regardless of activator concentration. Further, PSL stimulation and emission wavelength remain constant, regardless of activator concentration, which means that inexpensive optical equipment can be used for PSL readout. The highest PSL sensitivity was obtained for samples with 1.0 mol.% Eu. However, samples with activator concentrations less than or equal to 0.05 mol.% Eu were optimal for radiation hardness properties. XRD and PL spectroscopy were used to identify precipitate phases for each concentration. For low to moderate activator concentrations, precipitate phases increase PSL sensitivity by improving charge separation. However, PSL quenching occurs for higher concentrations due to interactions between nearby activator centers. The results presented in this report show that precipitate phases significantly degrade radiation hardness properties for activator concentrations greater than 0.05 mol.% Eu, which is likely due to accelerated precipitate formation within the KCl lattice for high activator concentrations. In conclusion, for megavoltage radiation therapy dosimetry applications, an activator concentration between 0.01 and 0.05 mol.% Eu in KCl is recommended for linear dose response, good PSL sensitivity, predictable temporal stability, high reusability, and reducing manufacturing costs.

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