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The role of oxygen in the photostimulation luminescence process of europium doped potassium chloride

Zhiyan Xiao, Thomas R. Mazur, Joseph P. Driewer, and H. Harold Li^(a)

Medical Physics Division, Department of Radiation Oncology and Center for Materials Innovation, Washington University School of Medicine, MO, USA

Abstract

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. The purposes of this work are to investigate the role of oxygen in the photostimulation luminescence (PSL) process and to determine if both increased PSL yield and improved temporal stability could be realized in KCl:Eu²⁺ by incorporating oxygen in the material fabrication process. Regardless of synthesis atmosphere, air or pure nitrogen, PSL amplitude shows a maximum at 1.0 mol % Eu. Depending on europium concentration, dosimeters fabricated in air exhibit stronger PSL by a factor of 2 to 4 compared to those made in N₂. There is no change in PSL stimulation spectrum while noticeable shifts in both photoluminescence and PSL emission spectra are observed for air versus nitrogen. Almost all charge-storage centers are spatially correlated, suggesting oxygen's stabilization role in the PSL process. However, oxygen alone does not improve material's temporal stability in the first few hours post irradiation at room temperature, probably because a significant portion of radiation-induced holes are stored in the V_k centers which are mobile.

I. INTRODUCTION

About 60 percent of cancer patients are treated with radiation at some time during their course of treatment. Modern radiation therapy treatment modalities such as intensity modulated radiation therapy (IMRT) are able to deliver dose that exquisitely conforms to diseased tissue while sparing healthy tissue. Often these treatments deposit dose in a complicated manner to produce steep, three-dimensional dose gradients that conform to irregular anatomical surfaces. The potential benefits are greatly desirable, including the reduction of side effects in normal tissue and the possibility of dose-escalation to the tumor with associated higher probability of cure. Film, either radiographic (Pai et al., 2007) or radiochromic (Lynch et al., 2006), has been the detector of choice for high spatial-resolution IMRT dose distribution verification. Film can be inserted in any orientation in a physical

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^(a)hli@radonc.wustl.edu.

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phantom mimicking a patient's anatomy and has unparalleled high spatial-resolution that is essential for verification of steep dose gradients. While phantom integration and high spatial-resolution are clearly desirable characteristics, a dosimeter should also be reusable so that response variation from pixel to pixel can be quantified and therefore corrected. More importantly, reusability is central to building medical physicists' confidence in dosimetric measurements through the acquisition of benchmarking datasets and through long-term, repeated use and performance monitoring. The lack of reusability has contributed to the relegation of film to relative dosimeter. Quantitative measurements with film would require the acquisition of a sensitometric curve for each measurement; yet even this practice carries with it a questionable assumption that individual films from a single batch and individual pixels on the same sheet share a common response (Hartmann et al., 2010).

In 2005, Olch (Olch, 2005) showed that BaFBrI:Eu²⁺-based computed radiography (CR) storage phosphor panels have the potential to be used for two-dimensional megavoltage radiation therapy dosimetry. However, BaFBrI has a high Z number ($Z_{\text{eff}} = 49$) which leads to a strong photon energy dependence and consequently unacceptable measurement accuracy. Also, BaFBrI or CsBr-based panels were designed for diagnostic radiology where radiation doses are on the order of μGy or mGy (Batentschuk et al., 2009). For radiation therapy, a typical fractionated dose is 2 Gy. Therefore, a reusable dosimeter with tissue-like response, high spatial-resolution, and excellent radiation hardness properties is needed for quantitative radiation therapy dosimetry but is not currently available.

Recent work (Li et al., 2014) 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. Hansel *et al.* (Hansel et al., 2014) report that KCl:Eu²⁺ samples provide excellent signal even after they were given doses of up to 200 kGy at the Louisiana State University Synchrotron facility. Functionally, KCl:Eu²⁺ relies on a mechanism of photostimulated luminescence (PSL), similar to BaFBrI:Eu²⁺. Irradiation of the material produces electron-hole pairs that are stored in metastable energy traps. The spatial distribution of these trapped charge carriers forms a latent image whose information can be read out by stimulating the trapped charge carriers to recombine and release PSL photons proportional to the locally deposited dose. Charges remaining trapped after readout can be erased with a bright, broadband light and the material can be used again in the same manner.

Although KCl has a higher effective Z than water, i.e. $Z=18$ vs. 7, Monte-Carlo simulations demonstrate that reducing the dimensions of the KCl:Eu²⁺ dosimeter to a few microns would convert a Burlin-cavity dosimeter to a Bragg-Gray dosimeter (Li, 2012), thus providing minimal energy-dependence for megavoltage therapeutic beam dosimetry. Future development would involve the creation of a large-area KCl:Eu²⁺-based storage phosphor film using modern thin film techniques, for example, tape casting (Mistler and Twinn, 2001) or physical vapor deposition (Hell et al., 2008; Leblans et al., 2000; Schmitt et al., 2002).

High PSL sensitivity is paramount in achieving high signal-to-noise ratio and thus reducing dose measurement uncertainty as radiation therapy dosimetry requires an accuracy as low as

2–3%. Studies (Hackenschmied et al., 2003; Hackenschmied et al., 2002; Hesse et al., 2007; Hesse et al., 2006) have shown that material annealing atmosphere plays an important role in PSL enhancement. For example, an appropriate thermal annealing at 190 °C in oxygen-rich air, rather than nitrogen only, greatly increases the PSL efficiency of CsBr:Eu²⁺. The authors concluded that oxygen plays a decisive role in the PSL process, which has also been found to be the case for other storage phosphor materials such as BaFBr:Eu²⁺.

For radiation therapy dosimetry, another important property of a storage phosphor detector is the stability of the information stored in the detector after irradiation. Due to unstable charge storage centers, PSL intensity decreases with storage time between irradiation and PSL readout, typically consisting of a fast component right after irradiation and a slower component afterward. When evaluating BaFBr:Eu²⁺-based storage phosphor dosimeters for radiation therapy dosimetry, Olch (Olch, 2005) suggested that dosimeters should be readout the day after irradiation in order to minimize measurement uncertainty. Although irradiating the dosimeters in the evening and reading on the following day works well in the clinical schedule as medical linear accelerator treatment devices are typically only available to a clinical physicist after hours, improving temporal stability post irradiation is desirable, thereby being able to reduce the wait time to few hours or less.

Given the promising application of KCl:Eu²⁺, the purposes of this work are to investigate the role of oxygen in the PSL process and to determine if both increased PSL yield and improved temporal stability could be realized in KCl:Eu²⁺ by incorporating oxygen in the material fabrication process. The findings could be of importance in better understanding the PSL process in KCl:Eu²⁺, thereby stimulating new thoughts in improving the dosimeter's performance in radiation dose measurements.

II. MATERIALS AND METHODS

A. Dosimeters and irradiation

The prototype KCl:Eu²⁺ dosimeters used in this study had a physical makeup similar to thermoluminescent dosimeter chips. High purity KCl (99.995%, Sigma-Aldrich) particles sized between 45–63 µm and reagent grade EuCl₃·6H₂O particles (<25 µm) were baked for 3 hours at 375 °C to minimize the amount of residual water before they were mixed at a range of molar ratios (0.05%, 0.5%, 1% and 2%). The mixed powders were pressed with 2200 lbs force in a hydraulic press into 1 mm thick, 6 mm diameter dosimeters. Dosimeters were sintered at 710 °C for 3 hours either in air or nitrogen (N₂, 99.999%, Airgas, MO), and then allowed to cool naturally to 300 °C followed by a rapid cooling to room temperature (RT). Optical annealing with a 500-W tungsten-halogen lamp prior to irradiation removed background signal created through environmental irradiation. Dosimeters were irradiated to 2 Gy using a 6 MV beam from a Varian medical linear accelerator.

B. Dosimetric readout

The photostimulation light source consisted of either a 2 mW, 594 nm He-Ne laser (Melles Griot, Covina, CA) or a 150 W, UV enhanced Xe arc lamp (Newport, Stratford, CT) with wavelength selection provided by a motorized monochromator (Cornerstone 130, Newport) with a grating of 1200 lines/mm.. Readout light was directed to an integrating sphere

(LabSphere, North Sutton, NH) using either glass or UV silica lenses. A custom mount held dosimeters in place on the integrating sphere during measurement. PSL (420 nm, FWHM 10nm) was separated from readout light by means of optical filters and detected by a photomultiplier tube (PMT) (Hamamatsu, Bridgewater, NJ) connected to a lock-in amplifier (Model SR830, Stanford Research Systems). For the laser source, the readout power was attenuated by neutral density (ND) filters to minimize signal depletion to allow for repeated readings.

The signal temporal stability of dosimeters was monitored by probing the signal at various times post-irradiation at RT and 50 K in a cryostat (Model CCS-450, JANIS, Wilmington, MA). The temperature dependence of the PSL intensity was also measured down to 10 K.

C. Structure and luminescence characterization

X-ray diffraction (XRD) was obtained using a Rigaku Geigerflex D-MAX/A Diffractometer using Cu-K α radiation and was used to determine the phase composition of the dosimeters. The step size for each of the following spectra was 0.01 and the dwell time was 1s per step. The operating power used was 35 kV and 35 mA.

Photoluminescence (PL) and photostimulated luminescence (PSL) 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 was passed through a 1200 lines/mm grating then through fiber optic cables and finally to the solid sample. Solid dosimeter samples were placed in a 6-inch diameter Quanta-phi integrating sphere. Emission light was detected using a Synapse Open-electrode CCD detector (Horiba, Kyoto, Japan) sensitive between 300–950nm.

The PSL stimulation spectra of KCl: Eu²⁺ measures the emission intensity at 420 nm for a range of wavelengths. To measure the PSL stimulation spectra, 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. 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). 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.

III. RESULTS

PSL intensity vs europium concentration for two sets of KCl: Eu²⁺ dosimeter is shown in Figure 1. For both sets of dosimeters made in either air or oxygen, the PSL intensity increased with the increasing Eu concentration up to 1.0 mol %, and then declined with higher concentration. Higher PSL intensity was obtained for dosimeters made in oxygen-rich air than those fabricated in N₂ regardless of activator concentration. For example, at 1.0 mol % europium doping, the PSL intensity made in air was about 2 times stronger. The magnitude of increase is even greater at lower europium concentration.

Figure 2 shows the X-ray diffraction patterns for 1%-doping samples. Hansel *et al* (Hansel et al., 2013) reported that noticeable secondary phases were present at higher doping concentrations, for example, 5%. They assigned the secondary phase to K_2EuCl_5 . Similar results have been reported in the CsBr:Eu^{2+} studies (Hesse et al., 2007; Hesse et al., 2006).

As shown in Figure 3, all PL emission spectra showed a single blue emission peak from Eu^{2+} characteristic transition ($4f^65d^1 \rightarrow 4f^7$) centered at around 420 nm. The absolute PL emission intensities from the samples made either in air or N_2 showed a similar trend as shown in Figure 1, namely, the PL intensity increased with the increasing Eu percentage concentration and reached a maximum for 1% mol Eu samples before it went down. Furthermore, as shown in Figure 3, a shift to longer PL emission wavelength for air versus N_2 was obvious for the 1% Eu samples, which was less obvious for the lower doping samples. This suggests that different atmosphere may affect the electronic environment surrounding an europium activator, which may affect the intrinsic luminescence.

To investigate X-ray storage and the subsequent photostimulation, PSL stimulation spectra were recorded from both sets of samples. Figure 4 shows the normalized PSL stimulation spectra as a function of Eu concentration. The spectra were independent of the fabrication atmosphere. Besides the well-known F-center centered at 560 nm, no other stimulation peak was observed. There was no change in the spectral shape and their full-width-at-half-maximum (FWHM), suggesting that activator concentration and fabrication atmosphere were not perturbing the chloride based vacancies, which were filled by the X-ray generated free electrons to form F-centers.

As shown in Figure 5, a shift in PSL emission spectra was evident for all the samples, air versus nitrogen. A wider FWHM of the PSL emission was also observed.

Figure 6 compares the PSL fading behavior of samples irradiated and kept at RT and 50 K, respectively. While the samples showed similar fading behavior at RT, the stabilization process is quite different for the irradiation and subsequent measurement at 50 K. That is, the air sample showed an initial increase in PSL in the first 2 hrs post irradiation and then stabilized, while the nitrogen sample retained the RT behavior but showed less dramatic change in PSL vs. time post irradiation.

The temperature dependence of the PSL intensity post irradiation is plotted in Figure 7. KCl:Eu^{2+} were irradiated at RT and kept 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 10 K. The intensity of the stimulation light was low enough that the whole temperature experiment could be performed without needing to correct for PSL loss due to repeated readings. As shown in Figure 7, both samples showed the same PSL efficiency from 200 K down to 10 K, suggesting that for irradiations at RT, almost all storage centers were spatially correlated (cf. Discussion).

IV. DISCUSSION

Hackenschmied et al. (Hackenschmied et al., 2003) report that segregations of CsEuBr_3 and/or Cs_4EuBr_6 formed within CsBr:Eu^{2+} during annealing in oxygen-rich air are

responsible for an increase in the PSL yield. However, a later study by Hesse et al. (Hesse et al., 2006) reports that CsEuBr_3 degrades in normal atmosphere into $\text{Cs}_2\text{EuBr}_5 \cdot 10\text{H}_2\text{O}$. Consequently, the increased PSL yield after annealing in air may not be due to the segregations because the trivalent nature of the europium in the segregations renders them PSL inactive. Although no significant second phases were observed in KCl:Eu^{2+} samples (Figure 2), possible contributions of such phases cannot be completely excluded due to the detection limitation of the XRD technique. Alternatively, Hesse et al. (Hesse et al., 2007) propose that oxygen is crucial for the observed strong PSL. In fact, it had been previously reported that the charge storage centers in BaFBr:Eu^{2+} had to be related to oxygen content. In this study, the direct head-to-head comparison of KCl:Eu^{2+} samples made in oxygen-rich air versus nitrogen with a range of europium concentration appears to support these authors' findings, namely that oxygen can enhance PSL, probably in three ways: 1) stronger charge separation due to the $\text{Eu}^{2+}\text{-O}^{2-}$ -dipole, 2) increasing number of the preexisting chlorine vacancies, and 3) stabilization of the x-ray generated holes, which are explained as follows. The divalent nature of the Eu^{2+} -ion in the monovalent KCl lattice requires a charge-compensating mechanism. Probable mechanisms could be 1) potassium vacancy ($V_{\text{potassium}}$) forming a $\text{Eu}^{2+}\text{-}V_{\text{potassium}}$ -dipole, and 2) oxygen residing on a chlorine site, $\text{O}^{2-}_{\text{Cl}}$, in the vicinity of a divalent Eu^{2+} -ion forming an $\text{Eu}^{2+}\text{-O}^{2-}$ -dipole. The $\text{Eu}^{2+}\text{-O}^{2-}$ -dipole has a stronger dipole moment that may result in a better charge separation of the x-ray generated electron/hole pairs. Second, oxygen can also be charge compensated locally by a chlorine ion vacancy. The increased preexisting number of chlorine vacancies in oxygen-rich samples, in which x-ray generated electrons are stored, may contribute to the increased PSL. Third, a portion of the x-ray generated holes could be trapped as $\text{Cl}_2^- V_{\text{K}}$ centers at low temperatures, which are thought to be mobile on warming to RT. Some of the holes recombine with F centers to produce non-PSL related luminescence, while others encounter the $\text{O}^{2-}_{\text{Cl}}$ sites and are subsequently stabilized to form $\text{O}^{2-}_{\text{Cl}}$ storage centers at RT.

It should be noted that oxygen impurities could be present even in the samples which have been produced with great care to exclude oxygen or water, in our case using pure nitrogen. Therefore, the primary difference between air and nitrogen samples could be oxygen concentration in the resulting dosimeters. It is reasonable to assume that more oxygen has been incorporated into a dosimeter's lattice if it is fabricated in air, which may in turn explain the increased PSL as explained above. However, both intrinsic PL and PSL emissions show a single emission peak around 420 nm, which is the characteristic emission of the Eu^{2+} . We did not observe an emission peak related to the emission from oxygen, which may cast some doubt on whether oxygen has been incorporated into the KCl lattice even when made in oxygen-rich air. It was reported (Hesse et al., 2007) that in the CsBr matrix, the PSL emission from the luminescent oxygen ions can only be observed at low oxygen concentrations (<0.05 mol %), but not for higher oxygen concentrations (>0.1 mol %). The reason could be that energy transfer, as a result of photostimulated electron-hole recombination, to oxygen seems to be completely blocked due to the formation of oxygen agglomerates (Hesse et al., 2007). In the KCl:Eu^{2+} air samples, effective oxygen incorporation into the KCl matrix is likely since the mixed powders were fired at 710 °C, which was close to KCl's melting point. Although we were not able to identify oxygen luminescence in the current emission spectra, other experimental results may support the

incorporation of oxygen impurities in the lattice, for example, the shifts in emission peaks for both PL and PSL emission spectra for air versus nitrogen (Figure 3 and 5), which could be due to the increase in splitting between the $10Dq$ energy levels of the $5d$ electrons (Cordero-Borboa et al., 2012; Lopez et al., 1980).

It should also be noted that water could be present in the $KCl:Eu^{2+}$ samples as KCl is hygroscopic. Weidner (Weidner, 2009) reports that the presence of oxygen is not sufficient for strong PSL in $CsBr:Eu^{2+}$. Not only in moist air or O_2 but also in moist N_2 and $N_2 + H_2$, a PSL increase is achieved than in dry air. Appleby *et al.* (Appleby et al., 2011) confirmed the essential role of water by demonstrating that the PSL increases under high relative humidity conditions. Therefore, it is possible that oxygen in our air sample impacts the PSL with water together.

The several-fold increase in PSL for a sample fabricated in oxygen-rich air is clinically significant as high PSL sensitivity is important for improving a dose measurement's signal-to-noise ratio and thus lowering uncertainty, as discussed previously. Synthesis in a reduction atmosphere was thought to be mandatory in order to retain europium activator's divalent status to be PSL active. Fortunately, divalent europium can be well preserved in an oxygen-rich atmosphere.

A second clinically relevant issue is if oxygen incorporation can improve the dosimeter's temporal stability at RT. As shown in Figure 6 in which PSL vs. time post irradiation is normalized at that at 10 hr, PSL for dosimeters made in air decays in a similar manner at RT to that of dosimeters fabricated under nitrogen. Moreover, from Figure 1, it is evident that the presence of oxygen improves the x-ray storage by several folds immediately after x-ray irradiation. However, a significant portion of the x-ray induced free-holes are stored at the, for example, $Cl_2^- V_k$ centers, which are mobile at RT, thus resulting in the decay of PSL vs. time post irradiation, until they are stabilized by, for example, an oxygen impurity. Note that europium activator itself can also stabilize a PSL complex, which is well known for classic $BaFBr:Eu^{2+}$ storage phosphor. (Rüter et al., 1990) By contrast, at lower temperature, for example, 50 K, $Cl_2^- V_k$ storage centers are more stable, leading to less pronounced PSL change vs. time, even in the nitrogen samples. It is interesting to observe an increase in PSL vs. time for the first few hours post irradiation for an air sample. Similar initial increase in the PSL has been reported for $Al_2O_3:C$ materials (McKeever et al., 1997). Intrinsic traps, especially shallow traps, may exist in the polycrystalline $KCl:Eu^{2+}$ 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. If we account for this effect, the air sample seems to have an overall better stability in PSL vs. time at 50 K, probably due to oxygen's stabilization role as more PSL active centers are created and stored in the neighborhood of oxygen ions.

Data shown in Figure 7 provide additional support of oxygen's stabilization role in the PSL process. The Takahashi model assumes the existence of F^+ centers in the lattice prior to irradiation (Takahashi et al., 1984). On the other hand, according to Itoh (Itoh, 1982), the photostimulable centers in alkali halides can also be created by ionizing radiation by the process in which a self-trapped exciton undergoes an isomeric transformation to an F-H pair. Recently Weidner *et al.* (Weidner et al., 2009) report that the storage centers in CsBr:Eu^{2+} are formed via the nonradiative decay of the dihalide selflocalized excitons close to the Eu^{2+} -containing emission centers, providing the latest evidence in support of the Itoh mechanism. Itoh's model suggests that electron and hole storage centers created by ionizing radiation are spatially correlated, which has been confirmed by von Seggern et al. (von Seggern et al., 1988). 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, therefore, will either decay back into the F-center ground state or tunnel to a nearby V_k -center to recombine. However, in order for an electron to tunnel to a nearby V_k center, the F center must be physically close (spatially correlated) to the V_k center. Thus, PSL yield at low temperatures corresponds to the concentration of spatially correlated traps (Thoms et al., 1991; Zimmermann et al., 2007). As shown in Figure 7, for irradiations at RT, almost all storage centers were correlated for both air and nitrogen samples, suggesting both europium and oxygen can become part of a stable PSL complex.

V. CONCLUSIONS

Higher PSL intensity was obtained for dosimeters made in oxygen-rich air than those fabricated in pure N_2 for a range of activator concentration. Shifts in PL and PSL emission peaks were observed for air versus nitrogen. All charge-storage centers were spatially correlated, suggesting the stabilization role of oxygen with regard to a PSL complex. Although there was no improvement in temporal stability at RT for an oxygen sample, oxygen seemed to improve the overall stability at lower temperature, for example, 50 K.

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Higher PSL intensity is obtained for dosimeters made in air than in pure nitrogen.

Shifts in emission peaks are observed for air versus nitrogen.

All charge-storage centers are spatially correlated, suggesting the stabilization role of oxygen.

There is no improvement in temporal stability at RT for an air sample.

Oxygen improves the stability at lower temperature, for example, 50 K.

FIG. 1. PSL intensity as a function of europium concentration for two sets of samples made in either air (black square) or high purity N₂ (red circle). A significant increase in PSL (a factor of 2 to 4) was observed in air versus in nitrogen.

FIG. 2.

X-ray diffraction patterns of KCl: Eu²⁺ with 1% Eu doping concentrations made in air or in nitrogen. Reference data of pure KCl is shown at top. All XRD diffraction intensities are normalized to its (200) diffraction peaks.

FIG. 3.

PL emission spectra at an excitation wavelength of 340 nm. A shift to longer wavelength for air versus N₂ was evident for the 1% Eu samples, which was less obvious for the lower doping samples, for example, 0.05%.

FIG. 4. PSL stimulation spectra for various Eu concentrations. The PSL emission intensity at 420 nm was collected when the stimulation wavelength was varied. The maximum stimulation efficiency remained constant at approximately 560 nm regardless of Eu concentration and synthesis atmosphere.

FIG. 5.
PSL emission spectra post $\times$ ray irradiation. There is a red-shift in PSL emission peak for samples made in air versus in nitrogen.

FIG. 6.

Temporal stability for irradiation and following PSL measurement at RT (a) and 50K (b).

The samples, air vs. nitrogen showed similar fading behavior when they were irradiated and kept at RT. However, the air sample showed a distinctive stabilization behavior compared to the nitrogen sample when they were irradiated and kept at 50 K.

FIG. 7.

Normalized PSL vs. temperature post irradiation. Samples were irradiated at RT and kept at RT for at least 20 h to avoid any confounding variable due to fading. PSL intensity vs. temperature was then recorded while the KCl:Eu²⁺ samples were cooled down to 10 K. Both samples showed almost 100% PSL efficiency from 200 K down to 10 K, suggesting that for irradiations at RT, almost all storage centers were spatially correlated.