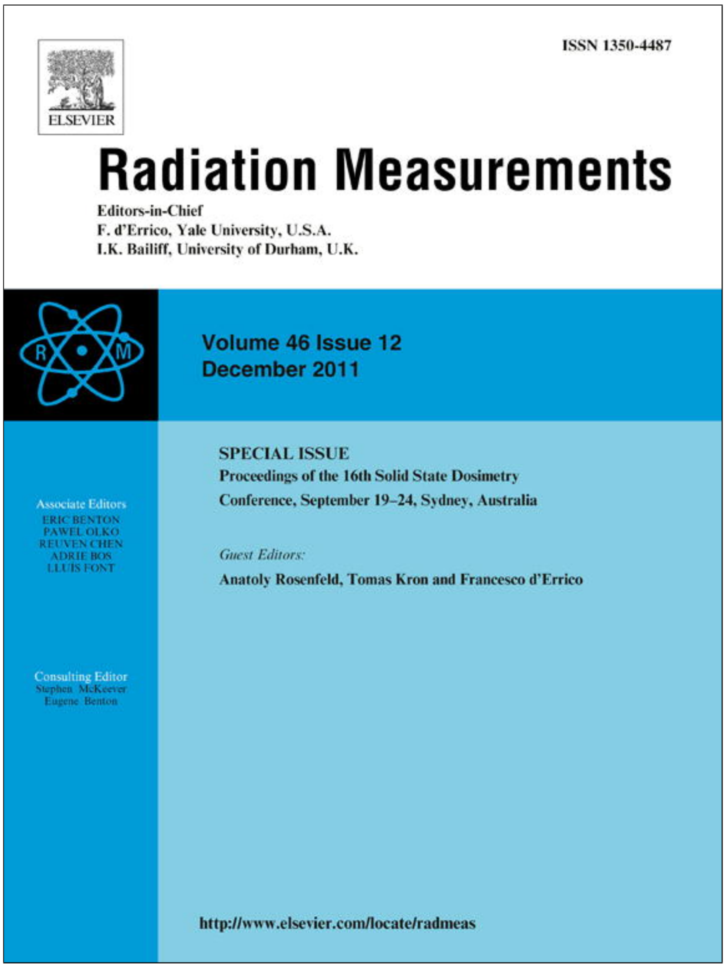
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Radioluminescence of rare-earth doped potassium yttrium fluorides crystals

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ABSTRACT

The radioluminescence (RL) properties of K_2YF_5 crystals doped with Ce^{3+}, Tb^{3+} and Dy^{3+} under ionizing irradiation excitation have been studied for the first time. The main objective of this work has been to assess the feasibility of using these crystals as detectors for fiberoptic radioluminescent dosimetry. In particular, it has been found that the RL intensity from both K_2YF_5:Tb (10%) and K_2TbF_5 is comparable to that from a commercial Al_2O_3:C crystal. Longer wavelength emission from these fluorides makes simple optical filtering technique possible to use in order to avoid the stem effect. Afterglow decay times for these fluorides have been found to be similar to that for Al_2O_3:C and, in particular, K_2TbF_5 does not show longer afterglow decay time compared to Al_2O_3:C.

1. Introduction

The development of new luminescent materials for radiation detection applied to industrial, environmental and medical dosimetry is a steadily growing research area (Dhoble et al., 2007; Sommer et al., 2008; Nagpure et al., 2009; Jahn et al., 2010). In this context double fluorides of rare-earth and alkali elements are promising detector materials by taking into account several reports confirming the feasibility of using this kind of crystals for thermoluminescence, optically stimulated luminescence and radioluminescence radiation detection (Caselli et al., 2005; Marcazzo et al., 2004; Kui et al., 2006; Marcazzó et al., 2007, 2008, 2009, 2010).

In recent years, highly accurate radiotherapy techniques require the development of high spatial resolution dosimetry systems for in-vivo, real-time dose assessment (Beddar, 2007). Among the different methods reported up to date to achieve this goal, the so-called fiberoptic dosimetry (FOD) technique has shown to meet most of the requirements presented by radiotherapy. This technique is based on the use of a tiny piece of a scintillation crystal, which is attached at the end of an optical fiber. The fiber collects the light emitted by the scintillation crystal during irradiation (RL) and a light detector placed at the other extreme of the fiber measures its intensity. So far plastic scintillators and C-doped aluminum oxide (Al_2O_3:C) are the most promising converters of the ionizing radiation to light from the viewpoint of application for this technique (Erfurt et al., 2000; Andersen et al., 2006; Archambault et al., 2006; Damkjaer et al., 2008; Molina et al., 2010).

One of the problems afflicting the FOD technique is the spurious luminescence produced in the optical fiber (stem effect), which adds to the RL emission from the scintillator. The main component of the stem effect is the Cerenkov radiation produced in the fiber, which dominates in the blue/green spectral region (De Boer et al., 1993). Since the spectrum of the RL emission of plastic scintillators and Al_2O_3:C partially overlaps with that of Cerenkov radiation, different methods have been implemented to suppress the stem effect. In the case of plastic scintillators two methods have been successfully employed to get rid of the Cerenkov radiation contribution: the two chromatic channels method and the temporal separation technique (Clift et al., 2002; Fontbonne et al., 2002). Both techniques have been also useful to reduce the contribution of the stem effect when using Al_2O_3:C-based FOD probes (Kertzscher et al. 2010).

Radioluminescence signal from Al_2O_3:C presents two main drawbacks from the viewpoint of its direct application in RL in-vivo real-time dosimetry, namely, the RL response is not constant and there is phosphorescence (i.e. afterglow) (Markey et al., 1995; Andersen et al., 2006; Damkjaer et al., 2008). Both effects are related to the existence of shallow traps. It should be mentioned that recently Damkjaer et al. (2008) developed an improved

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algorithm, previously presented by Andersen et al. (2006), which greatly reduces the influence of shallow traps on the shape of the RL signal from Al_2O_3:C. From a general point of view there is a permanent interest in developing new RL materials showing no shallow trap effects and emitting at wavelength regions longer than that where the stem effect is important (Marcazzó et al., 2007; Molina et al., 2010). In this case there would be no need of using correction algorithms and simple optical filtering could be used to get rid of the stem effect making the FOD technique cheaper and more robust to use in irradiation facilities.

In this work the RL-sensitivity, afterglow decay time and spectral emission of different potassium rare-earth fluoride crystals are investigated for the first time in order to assess their possible use in the framework of the FOD technique with simple optical filtering of the stem effect.

2. Materials and methods

K_2YF_5 single crystals doped with 1 and 10 at.% of Tb^{3+}, 1 and 2 at.% of Dy^{3+}, 5 at.% of Ce^{3+}; doubly doped with 10 at.% of Tb^{3+} and 5 at.% of Ce^{3+}; and 1 at.% of Tb^{3+} and 2 at.% of Dy^{3+}; as well as undoped K_2TbF_5 and doped with 10 at.% of Ce^{3+} were grown under hydrothermal conditions Kui et al. (2006). Crystals with dimensions of approximately 1 mm^3 were studied within this research. For comparison Al_2O_3:C pellets from Landauer Inc. were used. The samples were weighted and all data were normalized to the weight.

Radioluminescence was investigated under excitation by electron beams from a ^{90}Sr beta source rendering a dose rate of 0.024 Gy min^{-1} at the sample location, at room temperature. The measurements of the RL intensity as a function of time (RL curves) were performed with a lab-made RL reader. The light detection system was performed by means of an Electron Tubes P25PC-02 photon counting head having sensitivity between 180 and 630 nm. One meter of a standard PMMA optical cable with a core diameter of 980 μm was used to collect light from the sample to the photon counting head. Spectra of RL emission were measured by means of a Czerny-Turner monochromator SP-2155 (Acton Research) with a focal length of 0.15 m and a resolution of 10 nm and a 600 gmm^{-1} grating with the 500 nm blaze wavelength. An Electron Tubes P25PC-02 photon counting placed at the exit slit was employed to detect the scattered light from the sample. The samples were positioned in front of the entrance slit (1 mm width) perpendicular to the electron beam from the ^{90}Sr source, which was closely placed behind the sample.

In order to investigate the fast component of the afterglow decay time of the RL emission, the light emitted by the samples after a X-ray shot was measured. A X-ray machine was employed with the following set-up: output voltage 76 KVp, current 100 mA and pulse duration 0.1 s. A sample inserted into a light shielded plastic holder was placed at 1 m distance from the source in a 10 × 10 cm^2 field. A PMMA optical fiber was employed to collect light outgoing from the sample and an Electron Tube P25PC-02 PMT was utilized as light detector. All the measurements were performed at room temperature.

3. Results and discussion

The RL curves of the different crystals investigated in this work are presented in Fig. 1. As can be seen from Fig. 1 Al_2O_3:C shows the highest RL intensity (curve a) followed by K_2YF_5:Tb (10%) and K_2TbF_5 (curves b and c respectively). It is apparent from the figure that the higher the Tb content, the higher the RL efficiency. In fact, nominally pure Tb fluoride (K_2TbF_5) is almost as efficient as K_2YF_5:Tb (10%). In principle, this result implies that no optical quenching effects related to the increase of the dopant

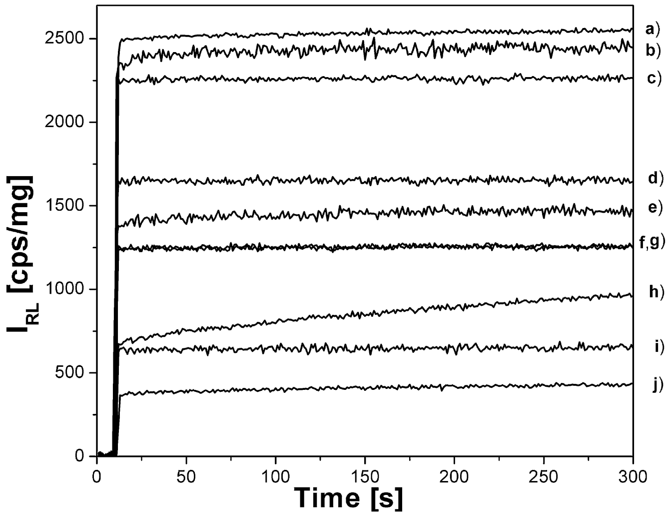

Fig. 1. RL intensity as function of time for: a) Al_2O_3:C; b) K_2YF_5:Tb (10%); c) K_2TbF_5; d) K_2YF_5:Tb, Ce (10%, 5%); e) K_2YF_5:Tb (1%); f) K_2TbF_5:Dy (1%); g) K_2TbF_5:Ce (10%); h) K_2YF_5:Tb, Dy (1%, 2%); i) K_2YF_5:Ce (5%); j) K_2YF_5:Dy (2%) under beta radiation.

concentration seem to be present in this fluoride. The reason for this observation could be related to the fact that Tb cations replace Y atoms with minimum lattice distortion (Zverev et al., 2011).

In order to investigate whether the RL efficiency changes as function of dose accumulation, long-term RL measurements were performed on the three samples showing the highest RL intensity, namely Al_2O_3:C, K_2YF_5:Tb (10%), and K_2TbF_5 (see Fig. 2). As expected from previous reports, the change in RL-sensitivity for Al_2O_3:C after 2 h of beta radiation excitation is significant (Fig. 2 curve a) but no changes in the RL-sensitivity are observable for K_2YF_5:Tb (10%) and K_2TbF_5 (Fig. 2 curves b and c respectively) (Andersen et al., 2006). In the inset of Fig. 2 the afterglow of the three samples is shown. As can be seen, the intensity of the afterglow of the Al_2O_3:C crystal is still important after 3 min after irradiation. This effect has been assigned in Al_2O_3:C to the presence of shallow traps (Damkjaer et al., 2008). On the other hand, no long decay time afterglow is observable for K_2TbF_5 (inset of Fig. 2, curve c). By following Damkjaer et al., (2008) this result could imply that

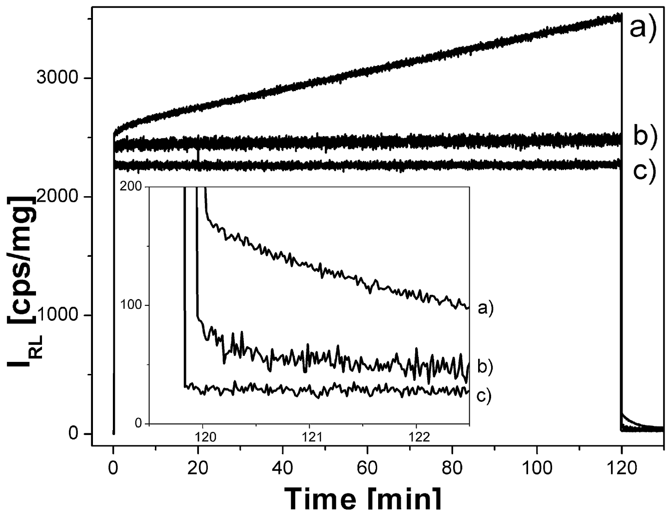

Fig. 2. Long-term RL measurements for a) Al_2O_3:C, b) K_2YF_5:Tb (10%), and c) K_2TbF_5 under beta radiation excitation. 2 h of irradiation followed by 10 min with no irradiation. Inset: afterglow from the samples.

shallow traps have no influence on the RL process in K_2TbF_5 or that the equilibrium between charge-trapping and detrapping rates is rapidly reached in this compound. In the case of the K_2YF_5:Tb (10%) sample there appears to be some small changes in RL response at the beginning of the irradiation and some afterglow is also observed which could be caused by the presence of a small shallow traps concentration.

Although no long lifetime decay is observable for the afterglow from the K_2TbF_5 sample (inset of Fig. 2, curve c), it cannot be assumed that there will be no short component in the afterglow decay time. For this reason, Al_2O_3:C, K_2YF_5:Tb (10%), and K_2TbF_5 samples have been excited with a short X-ray pulse. The decay curves of RL normalized to maximum value from these samples are shown in Fig. 3. It is apparent that excited state lifetimes for K_2YF_5:Tb (10%) and K_2TbF_5 are of the same order as that for Al_2O_3:C. In principle this result implies that the temporal separation technique could be used to suppress the stem effect if these fluorides are employed as FOD scintillators in LINACs, as it has been successfully employed when irradiating Al_2O_3:C-based FOD probes (Andersen et al., 2006; Damkjaer et al., 2008). This technique takes advantage of the pulse-shaped characteristic of the radiation delivered by LINAC. In fact, a single exponential decay fitting shows that the excited state lifetimes for Al_2O_3:C, K_2TbF_5 and K_2YF_5:Tb (10%) are 37, 48 and 73 ms, respectively. These luminescence lifetimes allows to synchronously measured RL emission only between LINAC pulses, and taking into account that Cerenkov emission has a lifetime of about some nanoseconds, its contribution could be suppressed.

According to Nowotny (2007) low intensity light generated in PMMA optical fiber during irradiation with low energy X-ray (<190 keV) is expected. In our case no signal was observed when exposing an optical fiber without a scintillating material to X-ray shots, even when exposed length of the optical fiber was significantly increased. This result ensures that no luminescence component from optical fiber is observed in measurements shown in Fig. 3.

In Fig. 4 the RL spectra of K_2YF_5:Tb (10%) and K_2TbF_5 are compared to that of Al_2O_3:C. Also the RL spectra from an optical fiber without a scintillator is shown for comparison. As can be seen, the RL spectrum from fluoride compounds show the characteristic luminescence bands between 470 and 750 nm, which can be assigned to the $^5D_3 \rightarrow ^7F_J$ ($J = 0$–6) transitions of the Tb^{3+} ion, indicating that Tb^{3+} sites act as luminescence centers under

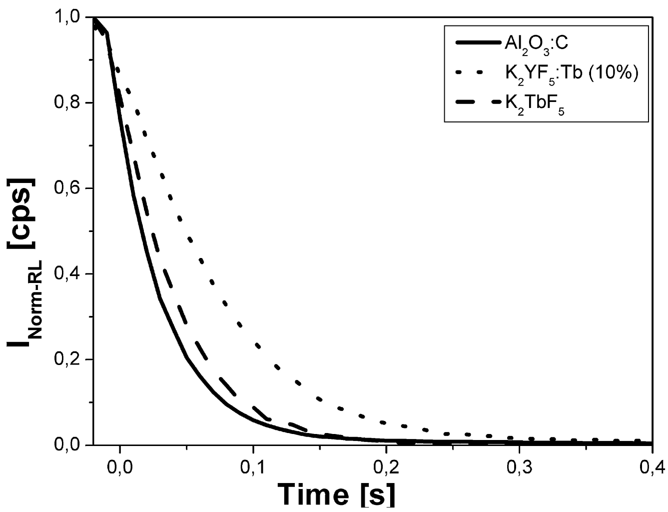

Fig. 3. Afterglow decays curve for Al_2O_3:C (solid line), K_2YF_5:Tb (10%) (dot line), K_2TbF_5 (dash line).

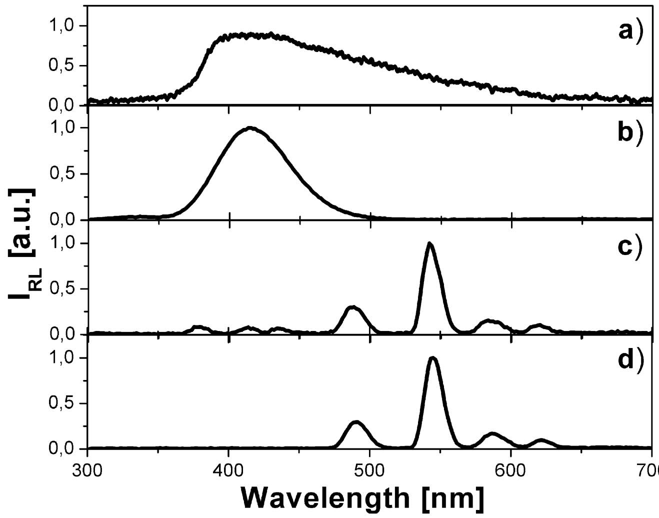

Fig. 4. RL spectra from a) optical fiber (stem effect), b) Al_2O_3:C, c) K_2YF_5:Tb (10%), and d) K_2TbF_5 under beta radiation excitation.

ionizing irradiation excitation, as observed in other radiation-induced phenomena in Tb-doped compounds Bos et al. (2006); Kui et al. (2006); Mittani et al. (2008). On the other hand, weak RL emission bands from the $^5D_4Tb^{3+}$ level in the range 360–470 nm are also detected only in the case of K_2YF_5:Tb (10%). The absence of these bands on the spectrum for K_2TbF_5 could be related to the concentration quenching associated with the cross-relaxation process $(D_3 \rightarrow ^5D_4) \leftrightarrow (J_0 \rightarrow ^5J_4)$ resulting in enhanced emission from the $^5D_4$ level at the expense of $^5D_3$ emission Marcazzó et al. (2007). As can be seen in Fig. 4, the emission bands of these fluoride compounds are located at wavelengths longer than the wavelength of the emission band from Al_2O_3:C. For this reason the light emitted by both K_2YF_5:Tb (10%) and K_2TbF_5 is expected to be less affected by the stem effect emission if these crystal are employed as FOD scintillators. Using a 530 nm long pass filter, reduction of the RL signal of 33% and 23% for K_2YF_5:Tb (10%) and K_2TbF_5, respectively is expected while a significant 80% reduction of the stem effect can be realized in this case.

4. Conclusions

The results of this work demonstrate the feasibility of using K_2YF_5:Tb (10%) and K_2TbF_5 crystals as scintillators in the FOD technique. Efficient RL from these crystals in the green spectral region would allow using simple optical filtering methods to get rid of the spurious luminescence caused by the stem effect. The short decay times of the afterglow emission from these crystals, which are similar to that from Al_2O_3:C, indicate that time removal technique could also be used provided that K_2YF_5:Tb (10%) and K_2TbF_5 are employed as FOD scintillators in LINACs. However, the more important features of K_2TbF_5 crystals have been found to be that no changes in RL response and no long afterglow decay are observed during beta irradiation. Summarizing, this work has demonstrated prospects for further research of potassium rare-earth fluoride crystals as FOD RL phosphors for dose assessment.

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