Radioluminescence of rare-earth doped aluminum oxide

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Abstract

Carbon-doped aluminum oxide (Al_2O_3:C) is one of the most used radioluminescence (RL) materials for fiberoptic dosimetry due to its high efficiency and comercial availability. However, this compound presents the drawback of emitting in the spectral region, where the spurious radioluminescence of fibers is also important. In this work, the radioluminescence response of rare-earth doped Al_2O_3 samples has been evaluated. The samples were prepared by mixing stoichiometric amounts of aluminum nitrate, urea and dopants with different amounts of terbium, samarium, cerium and thulium nitrates varying from 0 to 0.15 mol%. The influence of the different activators on the RL spectra has been investigated in order to determine the feasibility of using these compounds for RL fiberoptic dosimetry.

Keywords: Oxides, Radioluminescence, Dosimetry

PACS: 29.40.Mc, 87.53.Bn

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1 Introduction

State-of-the-art radiotherapy techniques for treating cancer such as intensity modulated radiation therapy (IMRT) and volumetric modulated arc therapy (VMAT) have posed new requirements to ensure that the dose delivered to the patient corresponds to the treatment planned dose. In spite of the complexities implied for the clinical routine, in-vivo real time patient-specific protocols for dose verification seems to be the most suitable way to achieve this goal. In vivo dosimetry offers the advantage of verifying the accuracy of every treatment fraction actually delivered to the patient, which is of the major concern to medical physicists and oncologists as the complexity of the treatment technologies increases (Asuni et al., 2011).

One of the most recent techniques for real time dosimetry is that known as fiberoptic dosimetry (FOD). This technique relies on the use of a small piece of a scintillating material, whose radioluminescence (RL) during irradiation is monitored by means of an optical fiber transporting the emitted light up to a light detector placed outside the treatment room. Dosimetry is possible because the RL yield is usually proportional to the absorbed dose rate. FOD has attractive characteristics: a) the small size of the scintillator (~1mm^3) provides the best spatial resolution with respect to other dosimetry techniques (Klein et al., 2011); b) no electrical bias is in contact with the patient; c) the optical fiber-based system shows mechanical strength for routine use; and, d) real time measurements are possible.

The main problem afflicting FOD has to do with the spurious light produced by radiation in the optical fiber, which adds to the RL emitted by the scintillator. Since spurious light, also dubbed stem effect, depends on the actual position of the fiber with respect to the radiation beam, its contribution is unpredictable. For this reason, the stem effect must be somehow removed in order to obtain reliable dose measurements by means of this technique. Several methods have been put forward for stem effect removal. Among them the cheapest one consists in filtering the stem effect contribution by means of optical filters. This approach takes advantage of the fact that the stem effect seems to be mainly composed of Cherenkov emission produced by ionizing radiation in the fiber (Santiago et al., 2009). The intensity of the Cherenkov emission is inversely proportional to the third power of the wavelength, namely, it is important in the blue-green region of the visible range. For this reason, the optical filtering technique is expected to be useful when red-emitting scintillators are employed, say, when the spectral overlap between the RL emission of the scintillator and the stem effect is minimal.

One of the most used materials so far in the framework of the FOD technique is carbon-doped alumina (Al_2O_3:C). Although Al_2O_3:C has the significant advantages of being highly efficient and commercially available, some shortcomings preclude its direct application in

the field. One of them is related to its RL spectrum. In particular, Al_2O_3:C emission features a broad band peaking at 430 nm, which strongly overlaps with the stem effect spectrum. For this reason it is not possible to efficiently remove the stem effect by optical filtering. In fact, more expensive, rather sophisticated methods have been necessary to overcome this shortcoming in particular applications of Al_2O_3:C in FOD (Andersen et al., 2011). Another problem of Al_2O_3:C is related to the fact that Al_2O_3:C shows an RL response, which depends on the accumulated dose. For this reason, computed algorithms have been necessary to be applied for read-out correction (Damkjær et al., 2008). The dependence of the RL response of Al_2O_3:C on accumulated dose has been assigned to the presence of crystal defects, which trap charges during irradiation. In particular, the existence of shallow traps in Al_2O_3:C is evidenced by the afterglow appearing once irradiation turns off (Damkjær et al., 2008). Finally, another point which could be of concern when mass application of Al_2O_3:C in the clinical field is envisaged, is the cost of crystal production. Commercial Al_2O_3:C dosimeters are fabricated by means for Czolchralsky, Vernuil or Stepanov crystal growth techniques, in furnaces at high temperature (2050ºC) and highly reducing atmospheres. In this context, alternative, low cost synthesis routes for fabricating Al_2O_3:C would be desirable (Barros et al., 2010).

In this work, rare-earth doped Al_2O_3 samples have been fabricated by means of the low cost Combustion Synthesis (CS) route and their RL properties have been investigated. In particular, the RL efficiency, the shape of the RL curve and the RL spectrum of the different compounds have been studied and compared with those of commercial Al_2O_3:C in order to assess their potential use as radiation detectors for FOD.

2 Experimental details

Aluminum oxide samples doped with different rare-earth (RE) cations, namely, Tm^{3+}, Ce^{3+} and co-doped with Tb^{3+}-Sm^{3+} and Ce^{3+}-Tm^{3+} were prepared by mixing stoichiometric amounts of aluminum nitrate, urea and the appropriate RE nitrate in order to attain nominal RE:Al relative concentrations of 0.1 mol%. The excess water from the reactants was evaporated in a glass beaker on a hot plate until a gelatinous pre-combustion mixture was obtained. The solution was then transferred to a muffle furnace and pre-heated up to 500°C to start the reaction. After a few minutes, the reactants ignited spontaneously resulting in a fluffy white powder. The product powders were hot pressed at 1300°C for 10 h to obtain 1.0 mm thick, 1.0 cm diameter opaque discs. X-ray diffraction measurements were performed with a RIGAKU model D/MAX 2200 diffractometer with a Cu K_α(λ = 0.1540 nm) radiation in order to confirm formation of α-Al_2O_3 phase (Barros et al., 2008, 2010).

Radioluminescence curves were obtained at room temperature by irradiating the samples by means of a 3.7×10^8 Bq ophthalmic ^{90}Sr beta-source rendering a dose rate of 0.02 Gy min^{-1} at the sample position and detecting the light emission with a Hamamatsu H9319 photon counting head (300 to 850 nm sensitivity range) (Molina et al., 2011). Emission spectra were recorded by resorting to an Acton Spectra-Pro SP-2155 0.150 m focal length monochromator featuring a 600 Gmm^{-1}, 500 nm blaze ruled grating. The Hamamatsu light detector mentioned above was employed to detect the scattered light. Slit widths were set to provide 10 nm overall resolution of the spectral system. The RL yield of a commercial Al_2O_3:C disc (translucid, 5 mm diameter, 1 mm thick) by Landauer Inc. was also recorded for comparison.

3 Results and discussion

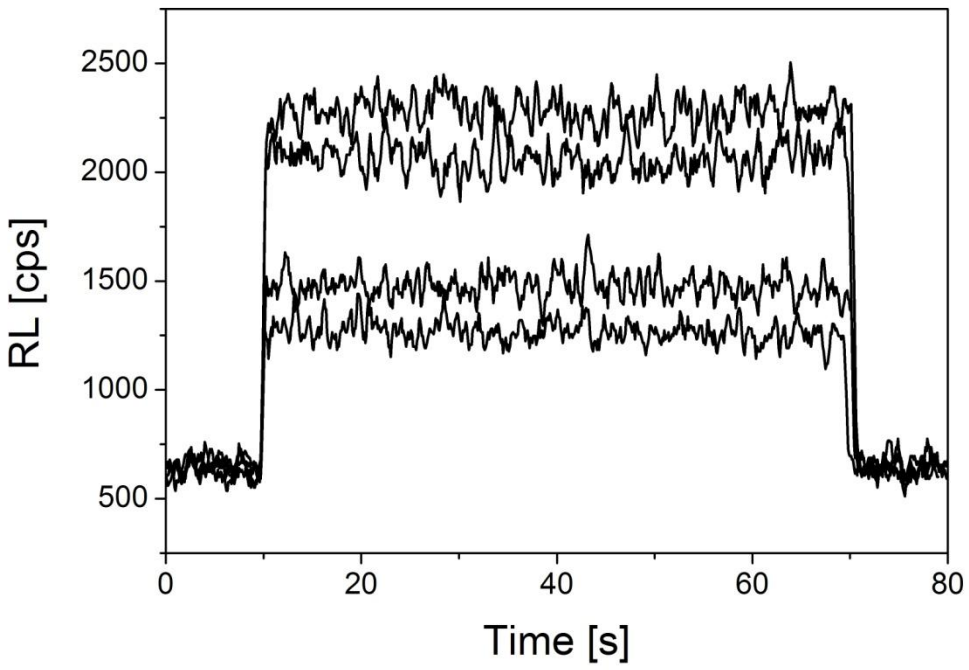

Figure 1: RL intensity as function of time of the studied compounds. From bottom to top the curves correspond to: a) Al_2O_3:Ce, b) Al_2O_3:Tm, c) Al_2O_3:Ce,Tm, and d) Al_2O_3:Tb,Sm. Dark counts appear as a background having an approximate value of 600 counts per second.

In figure 1 the RL intensity as function of time of the investigated compounds is shown. It is apparent from the figure that the RL efficiency of the co-doped samples almost doubles that of the single doped compounds. In all cases the RL signal of each sample is constant during the irradiation time, say, no effects related to dose accumulation are observed. On the other hand, no afterglow is appreciable in the RL curves once irradiation has switched off. The last two observations could be related to a low concentration of traps in these compounds, which results in a rapid equilibrium attainment between trapping and recombination processes during irradiation.

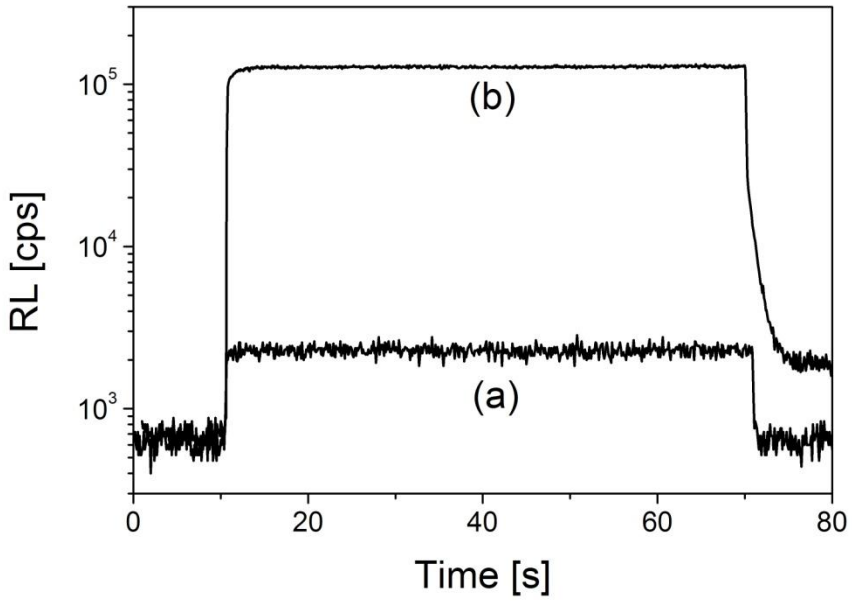

Figure 2: RL response of Al_2O_3:Tb,Sm (curve a) compared to that of commercial Al_2O_3:C (curve b).

In order to have a practical estimate of the RL efficiency of the investigated compounds the RL curve of a commercial Al_2O_3:C disc has been recorded and compared to that of the most efficient sample, namely, Al_2O_3:Tb,Sm (see figure 2). As can be see from the figure Al_2O_3 :C is more than 50 times more efficient than Al_2O_3:Tb,Sm. In any case, the previous result should be regarded as a rough estimate, since Al_2O_3:Tb,Sm and Al_2O_3:C discs are opaque and translucid respectively. The afterglow effect, say, the slow decay of the RL emission

after irradiation, is clearly observed in the RL curve of Al_2O_3:C in figure 2. As mentioned, this effect seems to be absent in the RL emission of the Al_2O_3:RE compounds, at least for the irradiation times employed in this work.

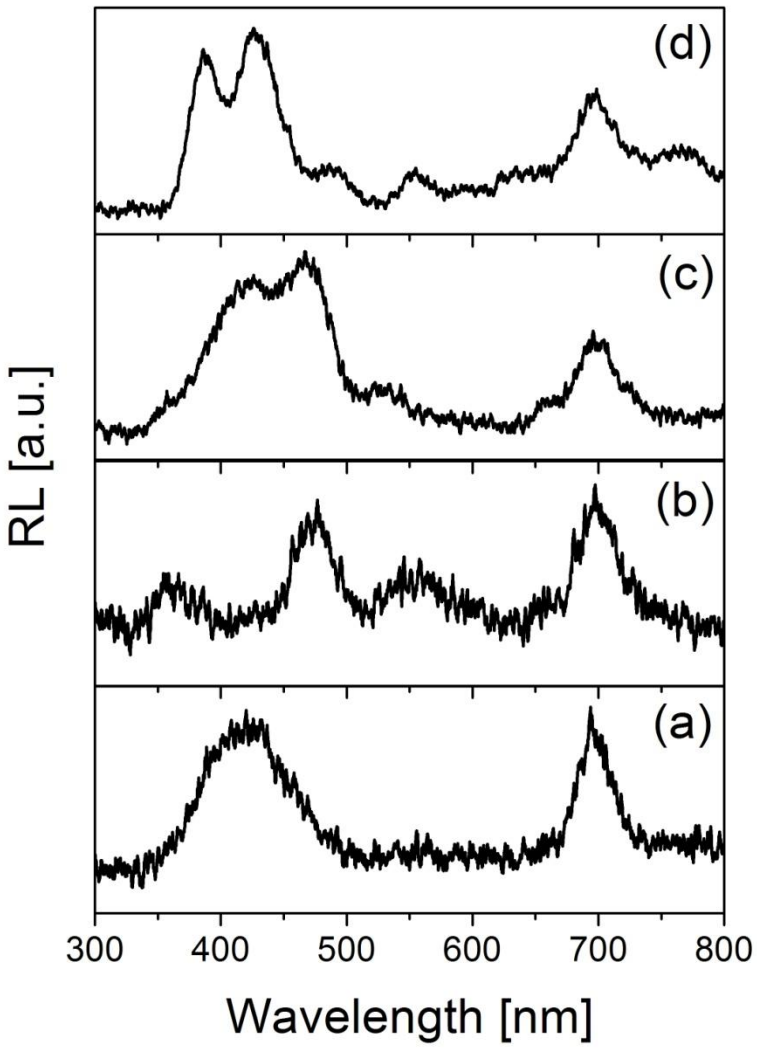

Figure 3: RL spectra of the investigated compounds: a) Al_2O_3:Ce, b) Al_2O_3:Tm, c) Al_2O_3 :Ce,Tm, and d) Al_2O_3:Tb,Sm.

In figure 3 the RL spectra of samples Al_2O_3:Ce (curve a), Al_2O_3:Tm (curve b), c) Al_2O_3 :Ce,Tm (curve c), and Al_2O_3:Tb,Sm (curve d) are depicted. In Al_2O_3:Ce, two broad bands are observed, centered at 415 and 700 nm approximately. The former could be assigned to transitions from 5d to 4f states of Ce^{3+}, as observed by Rakov et al. (2004) in Ce-doped Al_2O_3 crystalline ceramic powders prepared by low temperature direct combustion synthesis. However, intrinsic luminescence of F centers in the Al_2O_3 host could also be possible in the same spectral region (Ghamnia et al., 2003). The fact that this band is also present in the RL spectra of all samples supports this possibility. As to the emission band at 700 nm, which is also present in all the spectra, it could be related to impurity traces present in the reactants during fabrication (Ghamnia et al., 2003). In the case, of the RL spectrum of Al_2O_3:Tm, different bands corresponding to characteristic Tm^{3+} transitions can be identified. In particular, emission at 360, 470 nm can be attributed to $^1D_2$-$^3H_6$ and $^1G_4$-$^3H_6$ respectively (Piramidowicz et al., 2009; Xiao et al., 2010). On the other hand, the broad emission band centered at approximately 550 nm could be assigned to $^1D_2$-$^3H_5$ transition of Tm^{3+} as observed by Lozykowski et al. (1999) in cathodoluminescence experiments with GaN:Tb samples. As to the Ce-Tm co-doped Al_2O_3, it is apparent from figure 3, curve (c), that the spectrum corresponding to Al_2O_3:Ce,Tm is roughly the sum of Al_2O_3:Ce and Al_2O_3:Tm spectra. In principle, a more detailed spectroscopic analysis should be necessary to evaluate whether energy transfer processes occur between both cations during excitation. Finally, in the RL spectrum corresponding to Al_2O_3:Tb,Sm several overlapped broad bands are observed, which can be ascribed to Tb^{3+} f-f transitions. In particular, the band at 387 could be related to $^5D_3$-$^7F_6$ transition, while the band at 427 seems to comprise a group of Tb^{3+} transitions, namely, $^5D_3$-^7F_J with J = 5,4,3,2 (Hirrle et al., 1989). On the other hand, minor bands at 490, 556 595 and 641 nm could be assigned to $^5D_4$-^7F_J transitions of Tb^{3+} in this host (Rakov et al., 2004). In the case of Al_2O_3:Tb,Sm sample, emission at 700 nm could also contain the contribution of Sm^{3+} characteristic emission at this wavelength, as observed in other hosts doped with this trivalent RE (Lavat et al., 2004).

From the point of view of the application of the investigated materials as FOD detectors, none of them show particularly intense emission in the red region of the visible range to be directly employed in the framework of the FOD technique. However, the low cost CS has shown to be successful to incorporate the different dopants into the Al_2O_3 host as active emitters upon ionizing irradiation. As widely known, incorporating RE cations as dopants provides a very suitable route to tune up the spectroscopic characteristics of different host

in order to meet the requirements of specific applications. In this context, the results of this investigation can be regarded as a preliminary step demonstrating the feasibility of this approach to fabricate optimized FOD detectors, which deserves further investigations.

4 Conclusions

Different samples of Al_2O_3 single doped with Ce and Tm, and co-doped with Ce-Tm and Tb-Sm have been fabricated by the low cost combustion synthesis route in order to determine the feasibility of using them as FOD detectors. The RL signal of the investigated samples is stable upon irradiation with beta particles and no afterglow is observed. Among the compounds studied in this work Al_2O_3:Tb,Sm is the most efficient. However, its RL yield is almost 50 times lower than that of commercial Al_2O_3:C irradiated in the same conditions. The RL spectra of the RE doped Al_2O_3 compounds investigated in this work show characteristic emission of the respective rare-earth cations employed as dopant in each case. Although the RL emission of different RE-doped samples in the red region of the visible range is not intense, further developments should be of interest to optimize emission at long wavelengths.

Acknowledgments

This work was partially supported by grant PICT Red 1907 (Agencia Nacional de Promoción Científica y Tecnológica, Argentina) and PIP 241 (CONICET, Argentina).

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