

NIR Persistent Luminescence of Lanthanide Ion-Doped Rare-Earth Oxycarbonates: The Effect of Dopants

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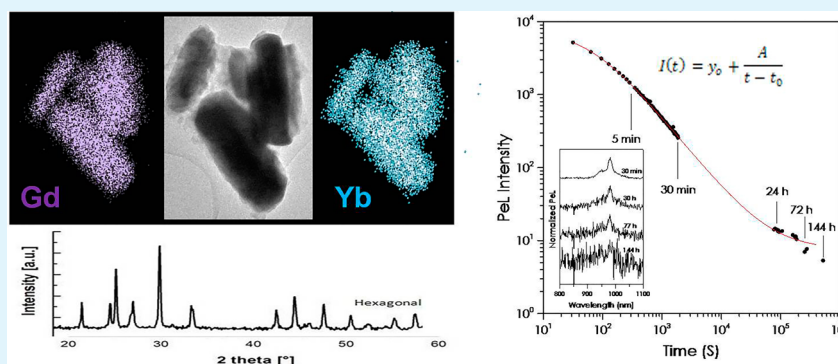
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Supporting Information



ABSTRACT: A series of luminescent rare-earth ion-doped hexagonal II-type Gd oxycarbonate phosphors $\text{Gd}_{2-x}\text{RE}_x\text{O}_2\text{CO}_3$ (RE = Eu^{3+} , Yb^{3+} , Dy^{3+}) have been successfully synthesized by thermal decomposition of the corresponding mixed oxalates. The Yb^{3+} doped Gd-oxycarbonate has evidenced a high persistent luminescence in the NIR region, that is independent from the temperature and makes this materials particular attractive as optical probes for bioimaging.

KEYWORDS: NIR luminescence, persistent luminescence, rare-earth ions luminescence, oxycarbonates, athermal tunneling luminescence

Persistent luminescence is an interesting phenomenon in which the long-lasting emission of the material persists for a long time after the removal of the excitation source.^{1–3} On the basis of this intrinsic property, great interest was focused on the development of various rare-earth ions doped crystals and glasses excited by UV or infrared laser for applications in luminous ceramic, emergency signs, graphic arts, etc.^{4–7} A great effort has been made to improve the persistence time from minutes to tens of hours. In the past decade, in fact, phosphors with persistent luminescence have been rapidly developed and one of the most efficient long-lasting phosphors is based on alkaline-earth aluminates, the green $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ discovered in 1996 and characterized by 30 h of afterglow.^{8,9} Since then, several studies indicate that long-lasting phosphorescence performances can be improved greatly using suitable auxiliary dopants such as lanthanide ions to create highly dense trap levels.^{10,11} Moreover, it would be very interesting to address the research in the development of persistent phosphors in the NIR region (700–2500 nm) due to the possible applications as optical probes in bioimaging.^{12–14} Recently, only a few NIR

persistent phosphors have been reported with the afterglow times ranging from several minutes to several hours after excitation by UV light.^{15–17} In this context, beside the huge variety of materials that can be explored, the rare-earth oxycarbonates doped with suitable optically active lanthanide ions are promising systems for application as optical probes because of the prolonged afterglow observed in the NIR region.¹⁵

Because of the high interest of the scientific community in this field, we have focused our research on the development of oxycarbonate systems doped with different lanthanide ions such as Eu^{3+} , Yb^{3+} , and Dy^{3+} , to explore the different performances of these ions in the persistent luminescence and their possible applications as bioimaging probes.

Rare-earth based oxycarbonates can exist in three different crystal structures: tetragonal (type I), monoclinic (type Ia) and

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hexagonal (type II).¹⁸ Among these three structures, the type II oxycarbonate possesses high thermal and chemical stability against water and carbon dioxide¹⁸ and, in addition, it is the most suitable structure to host dopant ions,^{18,20–22} nevertheless, it is difficult to obtain single-phase hexagonal type II oxycarbonates and the success of the synthesis is strongly correlated with the synthetic route adopted and is strongly dependent on the temperature, atmosphere and treatment time.²² To date, we successfully synthesized a series of rare-earth ion-doped gadolinium oxycarbonates $Gd_{2-x}RE_xO_2CO_3$ ($RE = Eu^{3+}, Yb^{3+}, Dy^{3+}$) with hexagonal structure. An undoped sample was also prepared as a reference. These phosphors have been synthesized by a thermal decomposition of the corresponding mixed oxalates which were obtained via a coprecipitation method²³ starting from commercial Gd_2O_3 , Dy_2O_3 , Yb_2O_3 , Eu_2O_3 powders. The mixed oxalates were calcined at 600 °C for 6 h in air and then treated at 600 °C in a fluent CO_2 atmosphere with a flux of molten salts (eutectic mixture $Li_2CO_3-Na_2CO_3-K_2CO_3$) for 12 h.^{24,25} The ion-doped oxycarbonates synthesized were then washed with deionized water and dried in air. The dopant lanthanide ions loading used was 4% mol for all samples; the 4% dopant concentration was selected being an intermediate value, high enough to produce luminescence and not too high to cause excessive distortion of the crystal structure and luminescence extinction, caused by the critical doping concentration.²⁶ In Table 1, the acronyms, formula and loading of dopant ions of the synthesized phosphors are listed.

Table 1. Acronyms and formula of the doped-oxycarbonates synthesized

acronyms	formula	dopant	mol %
Eu4%	$Gd_{1.92}Eu_{0.08}O_2CO_3$	Eu^{3+}	4
Dy4%	$Gd_{1.92}Dy_{0.08}O_2CO_3$	Dy^{3+}	4
Yb4%	$Gd_{1.92}Yb_{0.08}O_2CO_3$	Yb^{3+}	4

All the samples were characterized by X-ray powder diffraction (XRD) to confirm the presence of the hexagonal form. Morphology, size and dispersion were assessed through high-resolution transmission electron microscopy (HRTEM).

The XRD pattern of the Yb-doped gadolinium oxycarbonate is reported in Figure 1A; as it can be seen by the comparison with reference pattern of $Gd_2O_2CO_3$ compound (Pearson's Crystal Data; powder pattern of compound #1127181), it is in

good agreement with that of a single phase of the hexagonal rare-earth oxycarbonate (type II) and no impurity are observed.²⁷ This pattern should be considered representative for all of the investigated samples because the low doping rates performed induce only small variations in the elementary cell parameters that cannot be detected. HRTEM investigation combined with Energy Dispersive X-ray spectroscopy (EDX) revealed that all the samples are composed of sub micrometric particles characterized by regular and uniform rodlike morphology, homogeneous distribution of the rare-earth elements in the sample and organized crystalline structure. Furthermore, elemental analysis performed via the EDX microprobe confirmed the presence of the dopant lanthanide ions in the percentage expected on the basis of the synthetic ratio applied (see Figure S4–S6 in the Supporting Information). In Figure 1B and 1C HRTEM images, taken at different magnifications, of the sample Yb4% are reported as an example.

The luminescence efficiency of the synthesized oxycarbonates under X-ray irradiation was investigated by means of radioluminescence (RL) measurements. Figure 2A reports the normalized spectra together with the relative intensity integrated over the respective emission range. As expected, the emission spectra show the characteristic lines due to the $f-f$ transitions of the dopant rare-earth ions.^{28,29} In particular: the Yb4% sample emission spectrum is dominated by the $Yb^{3+}F_{7/2}-F_{5/2}$ transition at 970 nm;³⁰ the Eu4% spectrum shows a group of lines characteristic of the ${}^5D_0-{}^7F_J$ Eu^{3+} transitions with the most intense one emitting around 612 nm;³¹ finally, the Dy doped sample emission lines are ascribed to the ${}^4F_{9/2}-{}^6H_J$ transitions (the most intense line emitting around 575 nm) of Dy^{3+} ion.³² The undoped sample RL spectrum, shows a broad band in the 450–650 nm range possibly due to a defect emission. Moreover, the contamination with rare-earth elements (REE) other than Gd (Yb and Eu in particular) is evident. This is a common problem of materials containing REE as the main constituents of the host matrix, because of the difficulty in refining the lanthanide ions.³³ Trace REE contaminations can, in fact, be easily detected because of the high luminescence efficiency of these ions. Minor contribution due to Eu^{3+} can be detected also in the RL spectrum of the Yb4%. The RL intensity of the contaminant ions, however, is always negligible when compared to the one of the main dopants. The occurrence of persistent luminescence (PeL) due to delayed recombination of charges

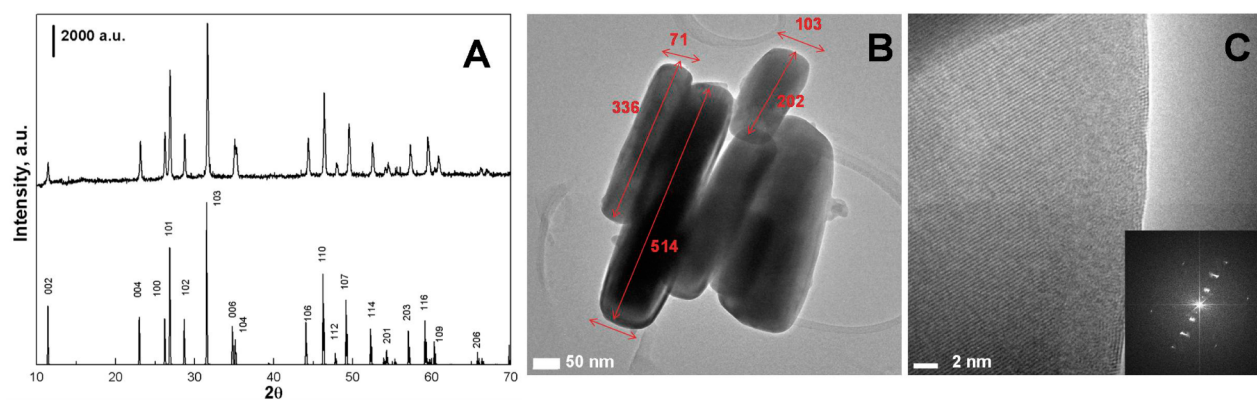


Figure 1. (A) XRD pattern of the Yb4% sample ($Gd_{1.92}Yb_{0.08}O_2CO_3$) (top) and reference pattern of $Gd_2O_2CO_3$ (bottom); (B, C) HRTEM images of the Yb4% sample.

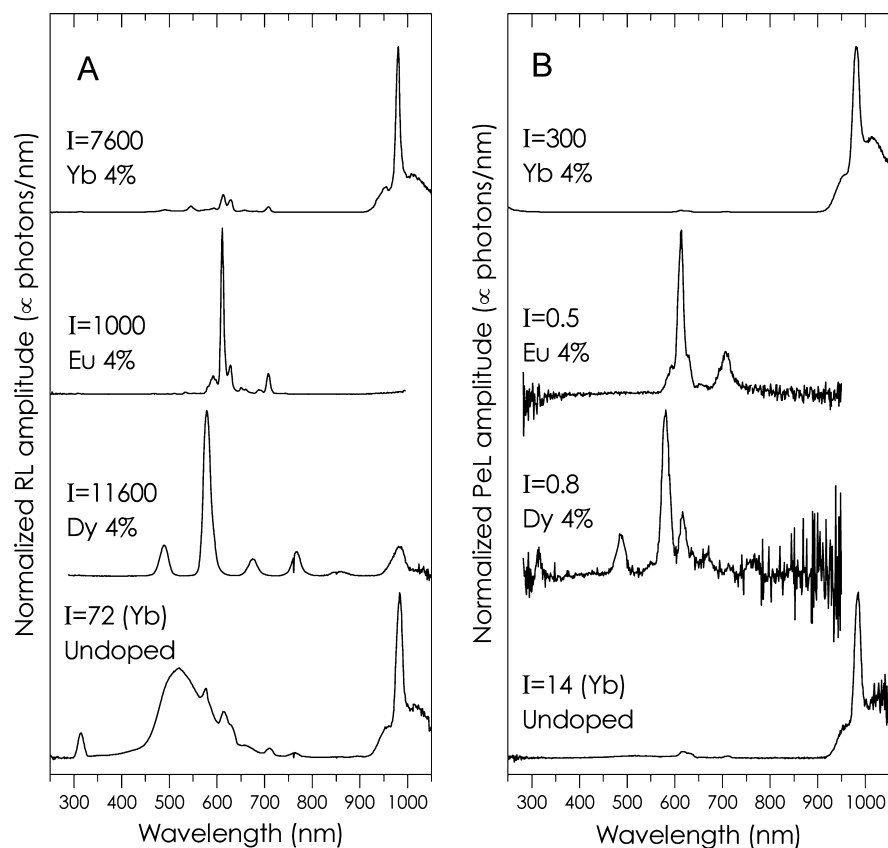


Figure 2. (A) RL and (B) PeL normalized emission spectra of $\text{Gd}_2\text{O}_2\text{CO}_3$ phosphors doped with different REE. The relative intensity (proportional to the number of photons) is also reported.

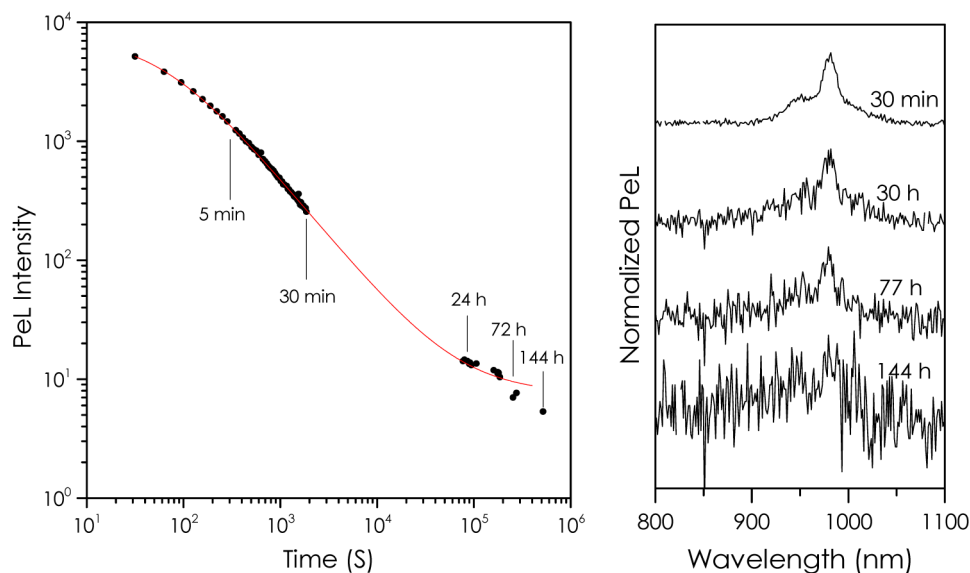


Figure 3. Time dependence of Yb4% sample PeL intensity. The experimental data are fitted using a hyperbolic decay (red curve). Some of the normalized PeL spectra at different times are shown.

temporarily trapped at localized defects was investigated by monitoring, on a long time scale, the luminescence intensity after the end of the excitation, performed employing X-ray irradiation (see the Supporting Information for further details). Figure 2B reports the normalized PeL spectra collected immediately after the end of the irradiation. The integrated intensity (proportional to the number of emitted photons) is also reported. The PeL intensity detected in the case of both

the Eu and Dy doped samples was extremely weak and short-lived. In particular, the PeL observed for Eu4% sample was due exclusively to Eu^{3+} emission whereas, in Dy4% system, beside Dy^{3+} emission, a contribution from Gd^{3+} (around 300 nm) and Eu^{3+} was also detected. Such emissions, rather than PeL, should be more properly named afterglow, a phenomenon due to the presence of shallow traps (unstable at room temperature) responsible for the delayed recombination of a fraction of the

electron–hole pairs.³⁴ At variance, the Yb4% PeL emission shows markedly different features, when compared to that of Eu³⁺ and Dy³⁺, being relatively more intense and detectable for a long time after the end of the excitation. Despite the Yb³⁺ NIR PeL emission being detected as well in the undoped samples, as expected, the most intense emission was observed for the Yb4% sample.

In fact, the emission around 970 nm could be monitored for 6 days, although after such time from the end of the irradiation, the signal-to-noise ratio was strongly reduced making the Yb³⁺ emission barely detectable. It is important to remind that the detectability of the PeL at a given time depends on several factors such as the amount of material considered, the sensitivity of the detection system, the light collection geometry, the width of the monochromator slit, etc. and is, thus, strictly dependent on the experimental conditions. The sensitivity in the NIR of our detection system is extremely low and the use of a more efficient detector in the Yb³⁺ emission region would further extend the detectability time for the PeL. The decay profile of the Yb4% PeL intensity was found to be not exponential but to follow a hyperbolic curve. Figure 3 shows the PeL intensity as a function of time and some of the PeL spectra (normalized, in order to better evaluate the signal-to-noise ratio) of the Yb4% sample. A numerical fit was performed by using the hyperbolic function

$$I(t) = y_0 + \frac{A}{t - t_0}$$

where y_0 is the background offset, A is a proportionality constant and t_0 is a constant introduced to account for the initial transient period. If we exclude the last three points, related to spectra with low intensity (making the integral evaluation less reliable), the theoretical curve (red line) is in perfect agreement with the experimental data.

This time decay profile is compatible either with the presence of a continuous distribution of trapping energy levels or with an athermal tunnelling luminescence mechanism.^{12,35} The former case is typical of matrices with an amorphous structure or with a similarly strongly distorted lattice (possibly only on a local scale). Despite both XRD and HRTEM measurements on the investigated samples revealed a high degree of crystallinity, it is nevertheless not possible to completely rule out the presence of a continuous distribution of trap energy levels. In fact, the defects involved in the PeL could be, for example, concentrated on the grain boundaries where the lattice is relatively disordered with no evidence in the XRD spectra.

As a second hypothesis, the same hyperbolic luminescence decay could be explained, even in a perfectly crystalline lattice, by considering a direct tunnelling recombination between the trapped charges and the luminescence centers residing at different distances between each other. Further detailed studies are, nevertheless, necessary in order to better understand the luminescence process and to discriminate between the two proposed hypotheses.

Regardless of the mechanism actually involved, from a practical point of view, it is important to evaluate the temperature dependence of the PeL intensity decay. We have investigated the effect of temperature on the PeL time decay in the range from 280 to 320 K and the experimental curves are reported in Figure 4. Both the decay profile and the absolute intensity of the PeL do not significantly depend on temperature.

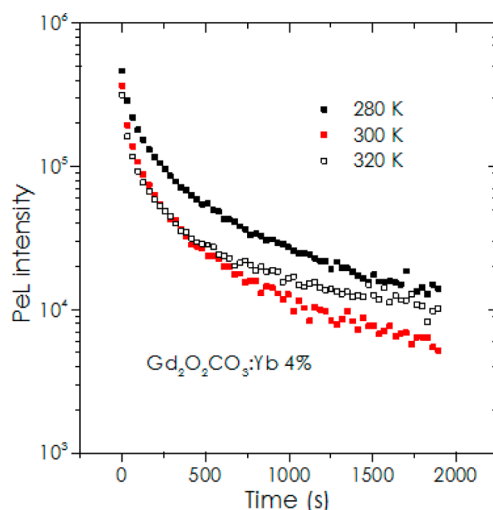


Figure 4. Temperature dependence of PeL emission of Gd_{1.92}Yb_{0.08}O₂CO₃ monitored for 30 min after X-ray irradiation.

Because of the luminescence in the NIR region and the long afterglow exhibited, the Yb4% phosphor looks particularly promising for applications in biomedicine (cell labeling, detection of biomolecules, drug delivery).³⁶ Although the optimal size for systems usually employed in biological applications ranges from few tenths to few hundreds of nanometers, micrometric or submicrometric particles can be successfully employed too.³⁷

To investigate the potential of the Yb4% sample as bioimaging agent some preliminary tests were carried out by incubating *E. coli* cells (strain ATCC11775) with suspensions of the material and evaluating then the antimicrobial effect and the persistent luminescence in the biological sample. Persistent luminescence was measured in the presence of the biological sample, thus confirming the promising features of this new material (see Figure S10 in the Supporting Information).³⁸

In summary, a series of luminescent rare-earth ion-doped hexagonal II-type Gd oxycarbonate phosphors Gd_{2-x}RE_xO₂CO₃ (RE = Eu³⁺, Yb³⁺, Dy³⁺) have been synthesized and the effect of the dopant ion on the luminescence performance of the Gd oxycarbonate have been investigated. In particular, Yb4% phosphor has showed a significant persistent NIR luminescence. Moreover, the decay profile was found to be compatible with either an athermal tunnelling luminescence mechanism or with the presence of a continuous distribution of trapping energy levels. Irrespective of the process involved, which is currently under investigation, it is interesting to underline that the persistent luminescence in the NIR region was found to be quite independent from the temperature. These interesting features make Yb4% phosphor an ideal optical probe for deep-tissue bioimaging.

■ ASSOCIATED CONTENT

Supporting Information

Materials and methods section, XRD patterns and HRTEM images for all the samples, preliminary biological tests. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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