1. Introduction

Persistent phosphors are uncommon luminescent materials that possess the unique ability to emit light long after being photoexcited.\[^1,2\] Key to this phenomenon is the temporary storage of energy and its subsequent gradual release, which relies on the presence of devised structural defects.\[^3,4\] These defects can be intrinsic (oxygen vacancies or antisites, for instance)\[^5,6\] or induced by dopants, such as rare earth or transition metal ions.\[^7,8\] Once persistent phosphors absorb light, in addition to conventional photoluminescence (PL) emission, a part of the absorbed energy can be transferred to such defects to form metastable states leading to the so-called energy storage, which typically takes place under the form of electron and/or hole trapping.\[^2\] Finally, external stimulation, provided by thermal energy at room temperature, triggers the return of trapped charges to the ground state, which eventually leads to the observed delayed and long-lasting emission commonly known as persistent luminescence (PersL).

Persistent phosphors find commercial interest for signaling, night vision displays, and ornamentation, among others.\[^9,10\] Also, these luminescent materials are relevant for new application niches that include nanomedicine,\[^11–15\] X-Ray imaging,\[^16\] night lighting,\[^17,18\] data storage,\[^19–21\] or anticounterfeiting.\[^22,23\] Although most widely studied persistent phosphors are strontium and calcium aluminates,\[^9,10,25\] complex garnet oxides have little to envy them in terms of PersL properties. In fact, \(\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}\) (YAGG) doped with \(\text{Ce}^{3+}\) and \(\text{Cr}^{3+}\) emits bright and long PersL in the green part of the electromagnetic spectrum, where maximum eye sensitivity under weak illumination conditions occurs.\[^26,27\] Furthermore, garnets are highly interesting because they allow emission color tuning through composition engineering\[^28–31\] and can be charged using visible light in contrast to most persistent phosphors.\[^22\] Nevertheless, significant challenges regarding the fabrication, processing, and properties of these materials need to be overcome to provide actual technological solutions and bridge the gap toward real-world applications.\[^32\] In this context, transparent persistent phosphors are highly demanded as light-emitting coatings that allow reading through, for security, labeling, or optical data storage applications. Also, limited fraction of the incident light scattered allows controlling the penetration depth of the excitation light in the material, providing effective charging throughout the film.\[^28,33\] So far, single crystals,\[^14,15\] ceramics,\[^28,36,37\] and glass-ceramic composites\[^38,39\] have been processed as transparent materials with PersL properties, but only a few papers have reported on the preparation of persistent transparent films.\[^22,40\] In particular, wet deposition techniques have been employed to process...
uniform nanoparticles that can be dispersed in solvents, to demonstrate PersL in transparent ZnGa$_2$O$_4$:Cr$^{3+}$ and NaYF$_4$:Ln$^{3+}$ films using high-energy light sources for charging. Prompted by the interest in developing nanoprobes for in vivo imaging during the past ten years,[41,42] colloidal stability is unlocking new possibilities for PersL material processing that are yet to be explored.[42] Nevertheless, developing alternative routes to obtain transparent coatings with tailored PersL properties remains a challenge.

Herein, we demonstrate a novel persistent phosphor elaboration strategy based on simple metal salt-based sol–gel route that leads to complex garnet thin films. Compared to methods based on the casting of colloids, this approach possesses the experimental advantages of being quick, “one-pot,” and easy to carry out, along with a large degree of control over material composition. Besides, in order to assess its potential for industrial production, the sol–gel approach features low amounts of solvent and chemical waste, which impacts on its environmental footprint. Viscous precursor solutions are spin coated on transparent quartz substrates and finally annealed at high temperature to ensure sufficient crystalline quality as to demonstrate PersL properties. We prove YAGG-based transparent persistent films that can be activated with blue light. The versatility of our method allows obtaining a wide range of persistent emission colors by engineering the composition of the complex garnet. Finally, due to the unique possibility of stacking transparent phosphors with different PersL characteristics, we demonstrate the first persistent phosphor with time-dependent persistent chromaticity. This novel characteristic might be a breakthrough for the development of multidimensional optical information storage materials and next-generation anticounterfeiting agents.

2. Results and Discussion

2.1. Transparent Y$_3$Al$_2$Ga$_3$O$_{12}$:Ce$^{3+}$,Cr$^{3+}$ Thin Films

The elaboration process of the films is outlined in Figure 1a. A precise control of the precipitation of the reactive species is central to attain precursor dispersions with rheological properties that allow depositing homogeneous films. For this reason, propylene oxide (PO) is employed as proton scavenger to ensure that hydrolysis and condensation occur uniformly.[43–49] With a similar aim, polyvinylpyrrolidone (PVP) is added to the mixture to adjust its viscosity before deposition. Thin layers, whose thickness can be tuned through the deposition conditions, are prepared by spin-coating the viscous concoction on quartz substrates and then annealed at 1100 °C. Figure 1b,c display scanning electron microscopy (SEM) images of the cross section and top view, respectively, of a representative 300 nm thick film, which presents some porosity due to PVP evaporation during thermal processing. As detailed in the Supporting Information, see Protocol S1 and Figure S1–S3, the determination of the effective refractive index of YAGG layers allows estimating the porosity of the films, which

![Figure 1.](image)

(a) Polyvinylpyrrolidone
Propylene oxide

(b) Solvent and polymer evaporation
Annealing
1100 °C

(c) Viscous solution
Spin coating

(d) Nitrate precursors in H$_2$O/EtOH

(e) X-Ray diffraction (XRD) pattern of a YAGG:Ce$^{3+}$,Cr$^{3+}$ film after thermal processing at 1100 °C. PDF 01-75-0555 reference pattern is plotted as green lines for comparison.[51]

(f) Experimental total transmittance spectrum of the same film.
is found to be 14%. Nevertheless, in-depth characterization of the morphology of Al₂O₃ and Y₃Al₂O₁₂ materials obtained by a similar approach can be found elsewhere. A characteristic X-ray diffractogram of a YAG film is shown in Figure 1d. YAG reflexion peaks are observed at the angular positions where they are expected. Besides, the broad contribution shown at ≈21° is associated to the quartz substrate. Both crystalline structure and stoichiometry determine the optical performance of complex garnet oxides, being the Al:Ga ratio a key parameter. In particular, our films feature a 2:3 ratio, which has been shown to provide the best persistent luminescent properties. Please note that this is possible because our “one-pot” sol-gel elaboration strategy enables a very precise control of the stoichiometry through reactants, see Figure S4 Supporting Information. Le Bail refinement of the XRD pattern shown in Supporting Information, allows estimation of crystallite size, which is found to be ≈44 nm. This value is in good agreement with results previously obtained on materials prepared in a similar manner. Remarkably, despite the high temperature processing, films are fairly transparent in the visible range. Figure 1e, as transmittance spectrum shows, Figure 1f. Our method, thus, appears suitable for the preparation of transparent thin layers made of complex garnet oxides.

2.2. Persistent Y₃Al₂Ga₃O₁₂:Ce³⁺,Cr³⁺ Thin Films

YAG:Ce³⁺ transparent thin films show a green emission band centered at ≈515 nm due to 5d → 4f Ce³⁺ transition, Figure 2a. Interestingly, films can be excited in the visible range via Ce³⁺. In fact, the PL excitation spectrum shown in Figure 2a reveals typical excitation bands of Ce³⁺, which appear at ≈345 and ≈430 nm and are associated to 4f→5d² and 4f→5d¹ transitions, respectively. In order to optimize Ce³⁺ content in YAGG, we measure the PL of films with similar thickness and different Ce³⁺ doping concentration. Inset of Figure 2a shows the integrated PL of films with 1% Ce³⁺ content. For low doping concentration, the emission intensity is roughly proportional to the number of emitting cations for λexc = 430 nm. Integrated emission increases with the concentration of dopants until it reaches a maximum at 1% doping. PL quantum yield (PLQY) of films with 1% Ce³⁺ is found to be as high as 70%. A further increase in concentration produces a reduction in PLQY, and consequently, in emission intensity, see the inset of Figure 2a, which is attributed to concentration quenching. In order to provide YAGG:Ce³⁺ films with afterglow properties, we introduced Cr³⁺ as a codoping agent in the preparation of precursors (see Experimental Section). Cr³⁺ endows complex garnet phosphors with an electron trapping mechanism (Cr³⁺ + e⁻ → Cr²⁺), which enables a delayed emission. We fabricated films with different [Cr³⁺] at a fixed 1% Ce³⁺ and similar thickness and measured their PL. The colormap obtained as a result is plotted in Figure 2b. A Cr³⁺ band emission emerges at ≈700 nm, associated to the 2E → 4A₂ transition, while the intensity of Ce³⁺ band decreases with Cr³⁺ content. The excitation spectra attained when monitoring Cr³⁺ emission (see Figure S6, Supporting Information) is composed of one weak band located at 610 nm related to the 4A₂ → 4T₂ absorption of Cr³⁺ and two intense bands peaking at ≈345 and 430 nm related to Ce³⁺ absorption. These features indicate an energy transfer from excited Ce³⁺ to Cr³⁺ with the addition of chromium.

Figure 2. a) Normalized photoluminescence (PL) spectrum attained exciting with λexc = 430 nm (solid curve) and PL excitation spectra monitoring Ce³⁺ emission, λem = 515 nm (dotted curve). The inset shows the normalized integrated intensity of YAGG films with different Ce³⁺ doping content. b) PL intensity spectra of YAGG:Ce³⁺,Cr³⁺ thin layers with different Cr³⁺ doping content. c) Picture taken with a digital camera of the PersL of YAGG:Ce³⁺,Cr³⁺ films after 30 s charging with UV light through letter masks. Scale bar is 1 cm.
Figure 2c shows the green PersL of YAGG:Ce\textsuperscript{3+},Cr\textsuperscript{3+} films after 30 s excitation through different letter masks to display YAGG.

To investigate the afterglow properties of the films, we perform time-dependent luminescent measurements using blue light (\(\lambda_{\text{exc}} = 430\) nm) for charging. Figure 3a shows the PersL decay of a YAGG film with 1\% Ce\textsuperscript{3+} and 0.1\% Cr\textsuperscript{3+}. Figure 3b displays PersL spectrum of a YAGG:Ce\textsuperscript{3+},Cr\textsuperscript{3+}, which is obtained, for each wavelength, integrating the light emitted for 5 min after the excitation with blue light ceases. Although the main emission band centered at \(\approx515\) nm corresponds to Ce\textsuperscript{3+}, a small feature associated to Cr\textsuperscript{3+} radiative transition can be also observed at \(\approx700\) nm in Figure 2c. The spectral content of PersL and PL is essentially the same since the emission is in both cases originated from the radiative transitions of Ce\textsuperscript{3+}. Color coordinates associated to PersL spectrum are in the green region of the color space, close to maximum sensitivity of human eye in low intensity conditions (see Figure S7, Supporting Information). As a matter of fact, PersL is observable by naked eye for few seconds in spite of the reduced thickness of the films, as shown in Figure 2c. In order to optimize Cr\textsuperscript{3+} content in persistent YAGG films, we measure PersL decays of films prepared with a fixed [Ce\textsuperscript{3+}], i.e., 1 at\% relative to [Y\textsuperscript{3+}], and different Cr\textsuperscript{3+} doping content. Figure 3c shows time-integrated PersL of YAGG:Ce\textsuperscript{3+}, Cr\textsuperscript{3+} films as a function of [Cr\textsuperscript{3+}]. Integrated PersL rises for low values of [Cr\textsuperscript{3+}] due to a gradual increase in the density of trap states of the films, key for electron storage. It reaches a maximum at [Cr\textsuperscript{3+}] = 0.1\%, followed by a decrease in the PersL intensity for higher [Cr\textsuperscript{3+}] values due to concentration quenching, as it has been already observed in similar systems. Our results indicate that different [Cr\textsuperscript{3+}] leads to a modification of the initial PersL intensity at \(t = 0\), but has no significant effect on the slope of the decay (see Figure S8, Supporting Information). In fact, Cr\textsuperscript{3+} content influences the density of the traps and, therefore, the storage capacity of the material, but this hardly affects the depth of the traps and the speed at which they are filled or emptied, so it does not impact the emission kinetics. Also, notice that YAGG films codoped with 1\% Ce\textsuperscript{3+} and 0.1\% Cr\textsuperscript{3+} feature PLQY values of 55\%, which are lower than that of films devoid Ce\textsuperscript{3+} doping. Such quantum efficiency decrease can partly be explained by the energy transfer from Ce\textsuperscript{3+} to Cr\textsuperscript{3+} that might not be 100\% efficient. Furthermore, the presence of traps is also known to reduce PLQY in phosphors. Indeed, in addition to direct photon emission, photon absorption can induce charge carrier trapping. Filled traps might then be able to absorb excitation light, leading to optically stimulated luminescence (OSL). Since a first photon is needed to trap charge carriers, OSL process requires the absorption of 2 photons to emit one, being its maximum efficiency 50\% and inevitably lowering the PLQY of the material. Moreover, it has been demonstrated that filled traps and active cations might have different absorption cross sections. This feature brings an excitation intensity dependence of the PLQY, in stark contrast with common downshifting phosphors, making challenging the precise assessment of PLQY in PersL materials. Finally, we record PersL excitation spectra for YAGG:Ce\textsuperscript{3+}, Cr\textsuperscript{3+} films to find out the spectral ranges able to trigger efficient charge storage and, therefore, lead to bright PersL. Results are shown in Figure 3d for a YAGG film codoped with 1\% Ce\textsuperscript{3+} and 0.1\% Cr\textsuperscript{3+}. Similarly to PL, see Figure 2b, PersL...
excitation spectra is composed by two Ce$^{3+}$ bands: 4f → 5d$^2$ and 4f → 5d$^1$, which appear at ≈345 and ≈430 nm, respectively. The later overlaps well with the blue emission of standard white LEDs (wLEDs), as shown in Figure 3d. Note that the intensity ratio between the two PersL excitation bands is significantly different compared with those of the PL excitation spectrum, with the high energy band having a higher relative intensity for PersL excitation. This contrast may originate from the distinct mechanisms responsible for PL and PersL. In fact, it has been demonstrated that to populate an electron trap, it is necessary to overcome an energy barrier when charging is carried out by the excitation of cations such as Ce$^{3+}$ or Eu$^{2+}$.[25,56] Such barrier is related to the energy required to delocalize an electron in the conduction band (CB). As the energy difference between the 5d$^2$ level and the CB is lower than that associated to the 5d$^1$ level, it is more efficient to excite the PersL of Ce$^{3+}$ through the high energy excitation band.

2.3. Alternative Complex Garnets: Gd$_3$Al$_2$Ga$_3$O$_{12}$:Ce$^{3+}$,Cr$^{3+}$ Persistent Thin Films

Our method can be extended to fabricate transparent persistent thin films with different complex garnet compositions. Gd$_3$Al$_2$Ga$_3$O$_{12}$:Ce$^{3+}$,Cr$^{3+}$ (GAGG:Ce$^{3+}$,Cr$^{3+}$) is another appealing persistent phosphor featuring yellow PersL, which can be activated eventually by the blue light provided by wLEDs. Herein, we demonstrate the elaboration and persistent properties of transparent thin layers of this composition. Sol–gel precursors were prepared, casted, and finally annealed using the same process we follow to fabricate YAGG films (see Methods section). GAGG:Ce$^{3+}$,Cr$^{3+}$ layers are highly transparent and feature gadolinium-based garnet crystalline phase (see Figure S9, Supporting Information). The excitation spectrum plotted in Figure 4a is composed of two intense bands related to Ce$^{3+}$ absorption. Interestingly, Ce$^{3+}$ bands in GAGG:Ce$^{3+}$,Cr$^{3+}$ appear shifted compared to YAGG:Ce$^{3+}$,Cr$^{3+}$. 4f → 5d$^1$ Ce$^{3+}$ excitation band peaks at ≈438 nm (compared to ≈430 nm in YAGG:Ce$^{3+}$,Cr$^{3+}$), whereas 4f → 5d$^2$ Ce$^{3+}$ band peaks at ≈340 nm (compared to ≈345 nm in YAGG:Ce$^{3+}$,Cr$^{3+}$). This originates from the substitution of Y$^{3+}$ cations in the dodecahedral [A] site by Gd$^{3+}$. Gd$^{3+}$ ions typically induce a stronger crystal field compared to Y$^{3+}$, which yields a red shift of the 4f → 5d$^1$ Ce$^{3+}$ band, along with a blue shift of the 4f → 5d$^2$ Ce$^{3+}$ band. The possibility to tune the spectral features of the material simply by cationic engineering makes Ce$^{3+}$-doped garnets particularly interesting phosphors.[28,50] Notice that the low energy band of the PersL excitation spectra (≈435 nm) is also redshifted with respect to YAGG:Ce$^{3+}$,Cr$^{3+}$ and overlaps fairly well with the blue band of standard wLEDs, which is key for sustainable PersL activation. Besides, main Ce$^{3+}$ emission band shifts to ≈545 nm (≈515 nm for YAGG:Ce$^{3+}$,Cr$^{3+}$), as it can be observed in Figure 4b. In contrast, Cr$^{3+}$ emission band is located at the same spectral position, i.e., at ≈700 nm, since $^2$E $→ ^4$A$_2$ transition is hardly affected by the crystal field. PLQY of GAGG:Ce$^{3+}$,Cr$^{3+}$ films is measured to be 15%, lower than that of transparent thin layers of YAGG:Ce$^{3+}$,Cr$^{3+}$.

**Figure 4.** a) Normalized photoluminescence (PL) excitation (dotted line) and PersL excitation (solid line with symbols) spectra of the GAGG: 1% Ce$^{3+}$, 0.1% Cr$^{3+}$ film ($\lambda_{em} = 545$ nm) along with the typical emission spectra of a smartphone wLED (blue). b) Normalized PL (solid line) and PersL (symbols) spectra of the films ($\lambda_{exc} = 438$ nm). c) Picture of GAGG:Ce$^{3+}$,Cr$^{3+}$ film after 30 s charging using typical w-LED through a letter mask. Scale bar is 0.5 cm. d) Normalized PersL decays of the same film.
of YAGG:Ce$^{3+}$, Cr$^{3+}$. This can be explained in part by higher thermal quenching. Indeed, the red shift of the 5d$^1$ Ce$^{3+}$ level brings a lower energy difference between the bottom of the 5d$^1$ excited state of Ce$^{3+}$ and its crossing point with the 4f ground state.[56] Figure 4c displays the PersL of the film when excited through a letter A mask. Compared to YAGG:Ce$^{3+}$, Cr$^{3+}$, GAGG:Ce$^{3+}$, Cr$^{3+}$ PersL appears shifted from green to yellow in the color space (see Figure S7, Supporting Information). PersL decay curve presented in Figure 4d shows that PersL kinetics of the GAGG:Ce$^{3+}$, Cr$^{3+}$ films is also altered. The substitution of Y$^{3+}$ ions by Gd$^{3+}$ ions leads to a diminution of the bandgap energy that yields shallower electron traps.[29] As a result, time-dependent PersL of GAGG:Ce$^{3+}$, Cr$^{3+}$ films feature higher intensity at t = 0, but steeper decay compared to that of YAGG:Ce$^{3+}$, Cr$^{3+}$. Our method opens the door to tune the PersL properties of transparent thin films by tuning the composition of the complex garnet, as it has been recently demonstrated for phosphor ceramics.[29]

2.4. Preparation of Persistent Stacks for Time-Dependent Chromaticity

The development of transparent layers with tuneable properties opens the path to engineer novel PersL properties and functionalities. We combine two persistent films with similar thickness ($\approx$200 nm each) but distinct chromaticity and afterglow dynamics in a layered stack. In particular, we prepare Gd$\text{Al}_2\text{Ga}_3\text{O}_{12}$: Ce$^{3+}$, Cr$^{3+}$ over Y$\text{Al}_2\text{Ga}_3\text{O}_{12}$: Ce$^{3+}$, Cr$^{3+}$ (GAGG o/YAGG) layered films in two steps, see Figure 5a. Results on Y$\text{Al}_2\text{Ga}_3\text{O}_{12}$: Ce$^{3+}$, Cr$^{3+}$ over Gd$\text{Al}_2\text{Ga}_3\text{O}_{12}$: Ce$^{3+}$, Cr$^{3+}$ (YAGG o/GAGG) layers are shown in the Supporting Information. First, the bottom layer was spin-casted and annealed at 1100 °C to ensure its mechanical and chemical stability. Then, a second phosphor layer was deposited atop the first one following the same procedure, without compromising the transparency of the stack (see Figure S10 and S11, Supporting Information). PL properties of the coatings were characterized prior to study their afterglow characteristics. Emission of stack results from the combination of the luminescence of each phosphor film. It features a broad emission band, due to 5d $\rightarrow$ 4f Ce$^{3+}$ emission, along with a lower intensity band centered at $\approx$700 nm associated to $^2E \rightarrow ^4A_2$ Cr$^{3+}$ transition (see Figure S12, Supporting Information). The thickness of each layer comprising the stack and its PLQY determine the chromaticity of the emission. Thus, the spectral position of the intense broad band can be tuned both through the bilayer configuration and the photoexcitation wavelength (see Figure S13, Supporting Information).[57] Emission of GAGG o/YAGG appears centered at $\approx$526 nm under 430 nm photoexcitation. Besides, as PersL kinetics of YAGG:Ce$^{3+}$, Cr$^{3+}$ and GAGG:Ce$^{3+}$, Cr$^{3+}$ phosphor layers are different, the configuration of the stack also sets the afterglow dynamics of the layered phosphor, which is unique. In fact, low energy components of the persistent emission decay faster than high energy ones in this particular case (see Figure S14, Supporting Information). As a result, the PersL spectrum of the stack varies with the time after excitation stops, as shown in Figure 5b. Specifically, PersL blue-shifts with time. This unconventional behavior yields a time-dependent chromaticity of the color coordinates associated to PersL, as displayed in Figure 5c. Persistent emission shifts from yellow to green with time. Right after the excitation is stopped, a more pronounced GAGG-like character of the layered phosphor is observed due to the high intensity of GAGG:Ce$^{3+}$, Cr$^{3+}$ films at t = 0. In turn, the stack veers to be YAGG-like, since PersL of YAGG:Ce$^{3+}$, Cr$^{3+}$ is initially weaker compared with that of GAGG:Ce$^{3+}$, Cr$^{3+}$ but with a longer decay. Indeed, color coordinates go with time toward that of YAGG:Ce$^{3+}$, Cr$^{3+}$, see

![Figure 5.](image-url)

Figure 5. a) Schematic of the GAGG o/YAGG-layered phosphor film. b) Normalized persistent luminescence (PersL) spectra of the layered phosphor recorded 3 s (green squares) and 60 s (blue circles) after charging ($\lambda_{\text{exc}} = 435$ nm during 1 min) stops. c) Color coordinates in a CIE 1931 chromacity diagram of PersL taken 3, 10, 20, and 60 s after charging stops. d) Zoom in of (c) in the green/yellow range.
Figure 5d. Layering renders phosphor films with unconventional time-dependent properties. An opportunity that can be exploited for different applications including multidimensional optical information storage and anticounterfeiting.

3. Conclusions

We have demonstrated a general procedure to develop transparent films with PersL properties using a simple and rapid sol–gel method based on metal salts. After sintering at high temperature, the films so obtained are around a few hundreds of nanometres thick, highly transparent in the visible range (average transparency above 80%), and possess a Y₃AₓGaxO₁₂ garnet crystalline phase. After doping content optimization, Ce³⁺, Cr³⁺, YAGG-based thin films show PersL in the green part of the electromagnetic spectrum. Activation is achieved through Ce³⁺ absorption bands, i.e., in the blue range, which permits the use of sunlight or white LEDs for charging. Another key advantage of the presented method is its versatility as it unlocks the design of transparent films with different PersL chromaticity simply by changing one of the metal salts employed in the synthesis. Indeed, replacing Y³⁺ by Gd³⁺ enables the preparation of yellow-emitting PersL transparent films. Due to different band structure, the energy depth of trapping centers in GAGG and YAGG phosphors is significantly different, leading to distinct PersL kinetics. Taking advantage from these intrinsic differences, we elaborate the first phosphor with time-dependent persistent chromaticity, with a layered material that shifts its emission from green to yellow after charging stops. Our transparent persistent luminescent layers with dynamic chromaticity promise great opportunities as multifunctional light-emitting coatings for anticounterfeiting agents and multidimensional optical information storage. However, further work to optimize the storage process at room temperature, and the number of emitted photons in the afterglow regime is needed to bridge the gap between PersL nanomaterials and real-world applications.

4. Experimental Section

**Chemicals:** Yttrium nitrate hexahydrate (Y(NO₃)₃·6H₂O, Sigma Aldrich, 99.8%), aluminum nonanitrate nonhydrate (Al(NO₃)₃·9H₂O, Sigma Aldrich, 98%), gallium nitrate hydrate (Ga(NO₃)₃·xH₂O, Sigma Aldrich, 99.9%), gadolinium nitrate hexahydrate (Gd(NO₃)₃·6H₂O, Sigma Aldrich, 99.9%), cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O, Sigma Aldrich, 99%), chromium nitrate nonhydrate Cr(NO₃)₃·9H₂O, Sigma Aldrich, 99%), PO (CH₃CHCH₂O, Sigma Aldrich, 99.5%), chromic acid (Cr₂O₃, Sigma Aldrich, 99%), PO (CH₃CHCH₂O, Sigma Aldrich, 99.5%), PO (CH₃CHCH₂O, Sigma Aldrich, 99.5%), PVP (C₆H₄(NO)₃, average mol wt 40 000 g mol⁻¹, Sigma Aldrich), ethanol absolute (C₂H₅OH, VWR Chemicals), and MilliQ water were used without further purification (or as received).

**Synthesis of Sol Precursors:** The precursors were obtained via a metal salt-based sol–gel route, described elsewhere for other compositions,[43–49] using the metal salts listed earlier. Briefly, an appropriate amount of the nitrate precursors was poured into a vial and stirred in a water/ethanol mixture (1.35 mL/1.07 mL) to form the reactive metal hydroxide species. Typically, for the elaboration of the undoped YAGG material, 1 mmol Y(NO₃)₃, 0.66 mmol Al(NO₃)₃, and 1 mmol Ga(NO₃)₃ were dissolved in the water/ethanol mixture under magnetic stirring for 30 min. About 50 mg of PVP was then added and dissolved under magnetic stirring for 15 min. Finally, 0.422 mL PO was poured in the vial and the agitation was kept for 2 min. After letting the mixture rest for at least 1 h under atmospheric conditions, the reactions took place, experimentally traduced by a noticeable viscosity increase. As highlighted in Figure 1a, the very same process was used for the elaboration of doped precursor solutions simply modifying the amount of chemicals. For instance, to prepare the 1% Ce³⁺, 0.1% Cr³⁺–codoped sample, 0.01 mmol Ce(NO₃)₃, 0.00066 mmol Cr(NO₃)₃, and 0.00066 mmol Al(NO₃)₃ were added, whereas the same amounts of Y(NO₃)₃, and Al(NO₃)₃ were removed as Ce³⁺ substitutes for Y³⁺ and Cr³⁺ substitutes for Al³⁺. Again, the very same process was used for the elaboration of the GAGG viscous precursor solution, simply replacing Y³⁺ metal salts by Gd³⁺ ones.

**Preparation of Transparent Films:** The complex garnet thin films were then deposited over the quartz substrates by spin coating 100 μL of the precursor solution, using a rotation speed of 2000 rpm for 10 s with a 15 500 rpm s⁻¹ acceleration ramp. The spin coating process was repeated 5 times for the YAGG and GAGG sol precursors. The films were then annealed on a hot plate for solvent and polymer removal to obtain mechanically stable films with the following program: 80°C in 30 min for 2 h, 200°C in 24 min for 30 min, and 300°C in 20 min for 30 min. Finally, the films were annealed at 1100°C for 2 h with a heating ramp of 5°C min⁻¹. For the preparation of the layered films, the same deposition process was repeated 3 times atop of the already crystallized layer changing the precursor solution.

**Structural Characterization of the Complex Garnet Thin Films:** The crystalline phase of the thin layers was characterized by X-Ray diffraction (XRD) using a Panalytical X’Pert Pro diffractometer (CuKa) with grazing incidence conditions. The X-Celerator detector was used over an angular range of 10° < 2θ < 80°, with a step width in 2θ of 0.05° and 1 s of integration time. The nature of the crystalline phase was confirmed by comparison with the Powder Diffraction File (PDF) database.

Scanning electron microscopy (SEM) images of the thin films deposited onto quartz substrates in the top view and cross section modes were taken using a Hitachi S4800 microscope.

**Optical Characterization of the Complex Garnet Thin Films:** Total transmittance was measured using a Cary 7000 series UV–vis–NIR spectrophotometer coupled to an integrating sphere. PL and PL excitation spectra of the films were recorded at room temperature using an Edinburgh FLS1000 spectrophotometer which enables to tune both emission and excitation wavelengths from UV to VIS. PersL decay curves, PersL excitation spectra and PersL spectra were recorded using the same equipment. Prior to PersL decay curves measurements, the films were annealed at 150°C for 5 min and then cooled down to RT. The samples were then excited for 5 min at RT with a fixed wavelength. To maximize the detected signal, the excitation and emission slits were opened at their maximum (13 nm), and an optical density filter (5%) was placed in the samples emission pathway to prevent from detector saturation during the charging stage. The filter is quickly removed when the charging period finishes to avoid attenuating the signal when we record the persistent emission. The PersL excitation spectra were obtained by integrating the PersL decay curves recorded for 10 min with λem = 515 and λem = 545 nm for YAGG and GAGG samples, respectively, using different excitation wavelengths for charging. The PersL spectra were obtained in a similar way but changing the emission wavelength with a fixed excitation wavelength at λem = 430, λem = 438, and λem = 435 nm for the YAGG, GAGG, and layered films, respectively.

Pictures of optically encoded PersL letters and signs were taken using a Canon EOS 700D digital camera with a 18/130 mm objective using 1600 ISO and 10 s exposure time in dark ambient conditions.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
anticounterfeiting, Ce$^{3+}$ and Cr$^{3+}$ doping, complex garnet oxides, persistent luminescence, time-dependent chromaticity, transparent thin films, visible light charging

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