Optical properties upon vacuum ultraviolet excitation of sol-gel based $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Tb}^{3+}$, Ce^{3+} powders

A. Potdevin, G. Chadeyron,^{a)} D. Boyer, and R. Mahiou

Laboratoire des Matériaux Inorganiques, Université Blaise Pascal and ENSCCF, 24 Avenue des Landais, 63177 Aubière Cedex, France

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Optical properties in the vacuum ultraviolet (VUV) region of cerium and terbium activated $\text{Y}_3\text{Al}_5\text{O}_{12}$ powders obtained by the sol-gel process were investigated at room and low temperatures. Both Tb^{3+} and Ce^{3+} doped samples exhibited a broad absorption band within the conventional Xe-Ne plasma emission range (140–190 nm). Optimal doping rates have been determined for both rare-earth ions. Emission spectra from cerium doped samples were recorded at 8.2 K and uncovered the splitting of the ground state of Ce^{3+} ions. Decay times of Ce^{3+} fluorescence can be fitted by double exponential curves, which can be ascribed to a re trapping phenomenon. Eventually, optical characteristics of codoped $\text{Y}_3\text{Al}_5\text{O}_{12}:(\text{Tb},\text{Ce})$ and $\text{Y}_3\text{Al}_5\text{O}_{12}:(\text{Tb},\text{Gd})$ were studied. © 2007 American Institute of Physics. [DOI: 10.1063/1.2784998]

I. INTRODUCTION

During the last decade, more and more attention has been paid to the research on phosphors excitable by vacuum ultraviolet (VUV) radiations because of the development of mercury-free lamps and plasma display panels (PDPs).^{1–5} In both devices, phosphor converts the VUV light (147 nm line and 172 nm band) from Xe/Ne gas discharge³ into visible light. Such devices require phosphors with high quantum efficiencies and long lifetime together with suitable fluorescence decay times (especially for PDPs).²

It is well known that luminescence efficiency widely depends on the particles morphology of phosphors, which relies on the synthesis route used.^{6,7} Furthermore, especially when excited by VUV radiations, the influence of the host lattice is significant.^{2,3,5} Consequently, research has been developed toward either original host materials or soft chemical methods for which particles morphology seems tunable.^{3,6,8–11}

Yttrium aluminum garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}=\text{YAG}$) shows a broad absorption band in the VUV region, associated with excellent chemical and mechanical stabilities under electronic bombardment.¹² As a result, when activated by rare-earth ions, it represents a very promising candidate as phosphor in plasma-based devices.^{13–19} Among the numerous synthesis routes developed to obtain luminescent YAG based materials (solid-state reaction, co-precipitation, spray pyrolysis, sol-gel,...),^{7,16–20} we have chosen to achieve them by the sol-gel process from alkoxide precursors.^{21,22} Indeed, materials resulting from this process exhibit better purity, high degree of homogeneity, and particles of narrow size distribution,^{6,23} which should enhance the absorption of VUV energy.⁶

In this article, $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Tb}^{3+}$ and $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ powders were synthesized by the sol-gel process. The purity of derived materials was investigated by means of x-ray diffraction (XRD). Since optical properties of phosphors are largely

influenced by their morphology, their crystallite sizes were determined from XRD analysis, and micrographs were carried out by means of scanning electron microscopy (SEM). To check the potentialities of these phosphors in mercury-free fluorescent tubes or PDPs,²⁴ excitation spectra were recorded in the VUV region for both Ce^{3+} and Tb^{3+} doped samples. Emission spectra under VUV radiations ($\lambda_{\text{exc}}=173$ or 180 nm) were also carried out at room temperature (RT) and at 8.2 K. Additionally, decay times of Ce^{3+} activated samples were measured. Finally, the influence of codoping (Tb^{3+} , Ce^{3+} and Tb^{3+} , Gd^{3+}) on optical properties of YAG:Tb(20 mol %) samples was evaluated.

II. EXPERIMENTAL PROCEDURE

A. Modus operandi

Undoped or terbium or cerium doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ powders were achieved via a synthesis procedure already described.^{21,22} The influence of codoping has been assessed by studying YAG:Tb(20%), Ce(1%) and (Y,Gd)AG:Tb(20%) (with $n_{\text{Y}}/n_{\text{Gd}}=7/3$). These doping rates in cerium and terbium have been chosen since they have been determined to be the optimal concentrations of lanthanide ions under blue excitation.²²

The synthesis was carried out under anhydrous conditions in a dry argon atmosphere since moisture significantly affects alkoxide stability. Experimentally, two solutions were prepared: solution A consisting of anhydrous yttrium chloride [(3– x) molar equivalent, 99.99% pure, Aldrich] and terbium anhydrous chloride (x eq., 99.99% pure, Aldrich) dissolved in anhydrous isopropanol ($i\text{PrOH}$, 99.8+ % pure, Aldrich), and solution B of potassium isopropoxide (metallic potassium, 9 eq., 98% pure, Aldrich, $i\text{PrOH}$). Chunks of potassium need to be carefully cleaned by removing a superficial crust prior to the addition of isopropanol.

Solution B is slowly added to solution A with vigorous stirring, the reaction is highly exothermic, and KCl is immediately formed. After a 1 h reflux of the mixed solutions

^{a)}Electronic mail: genevieve.chadeyron@univ-bpclermont.fr

at 85 °C, a powder of aluminum isopropoxide (5 eq., 99.99+ % pure, Aldrich) was added directly to the solution. A homogeneous solution was obtained after further refluxing (85 °C) and vigorously stirring for 4 h. After cooling, KCl was separated by centrifuging and a clear sol was collected. Afterwards the sol was hydrolyzed by introducing an excess of water, resulting in a transparent gel that was further dried at 80 °C to yield a white xerogel. The latter was annealed in a muffle furnace for 4 h at 800 °C or 1100 °C.

For samples containing Gd^{3+} and Ce^{3+} ions, the precursors used were gadolinium and cerium chlorides (Aldrich, GdCl_3 99.99% and CeCl_3 99.99+ %, respectively).

B. Characterization techniques

XRD measurements were performed on a Siemens D500 operating with the Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å). SEM micrographs were recorded by means of a ZEISS Supra 55VP operating in high vacuum at 4 kV, using a secondary electron detector (Everhart-Thornley detector). Specimens were powdered onto the surface of an adhesive carbon film.

Measurements of excitation and emission spectra as well as decay times in the VUV range were performed at the Deutsches Elektronen Synchrotron (DESY, Hamburg) using the facility of SUPERLUMI station²⁵ at HASYLAB. The experiments were carried out at room temperature (RT) or at 8.2 K.

Emission spectra were recorded within 300–900 nm range using a 0.3 m Czerny-Turner-type secondary monochromator-spectrograph SpectraPro-308 (Acton Research Corporation) equipped with a liquid nitrogen cooled CCD detector (Princeton Instruments). For excitation spectra and time-resolved measurements, the luminescence was detected by a HAMAMATSU R6358P PMT photomultiplier (200–800 nm range). Luminescence excitation spectra were scanned with the primary 2 m monochromator in 15° McPherson mounting (resolution of 3.2 Å). A single photon counting method provided the possibility to accumulate the luminescence decay curve within 0–200 ns range (period of the excitation pulse repetition in five bunch mode of DORIS storage ring operation) and use the time-resolved luminescence technique. Integrated spectra correspond to the total signal formed by the photomultiplier. Luminescence excitation spectra have been corrected on the incident photon flux.

III. RESULTS AND DISCUSSION

A. Powder x-ray diffraction

The XRD patterns of the sol-gel derived undoped YAG, YAG:Tb(20 mol %), and YAG:Ce(1 mol %) powders are gathered in Fig. 1. An 800 °C heating treatment [Fig. 1(a)] leads to a single crystallized phase consistent with YAG structure (JCPDS file 33-0040). This crystallization temperature is much lower than that required in solid-state reaction^{14,17,26} and close to the temperatures needed for recent soft chemical routes.^{18,19,27} However, a weak and broad band centered around 32° (2 θ) is also observed. It may correspond to an amorphous phase or to an unachieved crystallization of the YAG phase. This latter assumption is con-

FIG. 1. XRD patterns of undoped YAG powders sintered at (a) 800 °C and (b) 1100 °C for 4 h, (c) YAG:Tb(20 mol %), and (d) YAG:Ce(1 mol %) powders heated at 1100 °C for 4 h. Patterns are compared with the YAG ASTM file 33-0040 represented in dotted lines.

firmed by the disappearance of this band after a sintering at 1100 °C [Fig. 1(b)]. Indeed, such a sintering treatment entails a better crystallization state characterized by sharper and more well-defined diffraction peaks [Fig. 1(b)]. XRD patterns are not strongly affected when the YAG host is activated by either 20 mol % Tb^{3+} [Fig. 1(c)] or 1 mol % Ce^{3+} [Fig. 1(d)] since Y^{3+} and Tb^{3+} have roughly the same ionic radii.

As detailed in a previous paper,²¹ a 4 h sintering-treatment at 1100 °C was chosen to anneal all the samples since it corresponds to the best conditions so as to provide suitable crystallized YAG to perform optical analyses. As a matter of fact, such a heating treatment leads to the pyrolysis of all organic residues as it was revealed²⁸ by infrared and Raman spectroscopies.

B. Samples morphology

From XRD study, crystallite average sizes of undoped and YAG:Tb(20%) sintered powders have been assessed, applying Scherrer's formula:²⁹

$$\langle D \rangle = \frac{0.9\lambda}{\beta \times \cos \theta},$$

where $\langle D \rangle$ is the crystallite average size (Å), λ is the X-ray wavelength ($\lambda = 1.5406$ Å here, Cu $K\alpha$), θ is the Bragg diffraction angle, and β is the full width at half maximum (FWHM).

Figure 2(a) shows the temperature dependence of the mean crystallite size, evaluated from the FWHM of the (420) XRD peak ($2\theta \sim 32^\circ$). An increase of the average crystallite size with the heating temperature is observed. The undoped sample calcined at 800 °C is constituted of 25 nm particle grains whereas the powder sintered at 1200 °C is characterized by crystallites for which the diameter is greater than 50 nm. It can be also noticed that the incorporation of rare earth ions (Tb^{3+}) entails a grain's enlargement only for the samples

FIG. 2. (a) Temperature dependence of mean crystallite diameters for YAG:Tb(20%) powders; (b) SEM micrograph recorded at 125 000 $\times$ magnification from YAG:Tb(20%) annealed at 1100 $^{\circ}$ C for 4h.

heated at 1200 $^{\circ}$ C: terbium-doped powder exhibits a mean crystallite size near 75 nm versus 55 nm for the undoped specimen.

Figure 2(b) represents a SEM micrograph recorded from the YAG:Tb(20%) powder calcined at 1100 $^{\circ}$ C. It can be seen as a regular nanostructured network that can be qualified as “sponge-like.” Primary particles are not easily distinguishable and the network is characterized by a nanoporosity.

C. Optical properties of YAG:Tb³⁺ samples

In order to assess their application potentialities in devices based on the plasma technology, excitation spectra of YAG:Tb samples in the VUV range have been recorded at room temperature, monitoring the $^5D_4 \rightarrow ^7F_5$ transition located at 544 nm.

Excitation spectra obtained from YAG crystallized powders containing 1 and 20 mol % of terbium are shown in Fig. 3. These samples exhibit a broad band centered around 170 nm, overlapping the Xe-Ne plasma emission. This corresponds to the band absorption of the host lattice^{3,16,17,19,30} since the band gap energy of YAG is approximately 7.0 eV. This band originates from a partial transfer of the energy absorbed by the host to the luminescent center.¹⁶ A slight shift toward the UV range is observed when increasing the

FIG. 3. Room temperature excitation spectra of crystallized YAG:Tb(*x* mol %) powders [(a) *x*=1 and (b) *x*=20] in VUV range monitored at 544 nm.

terbium concentration, corresponding to the substitution of yttrium by a slightly larger ion ($r_Y^{3+}=1.02$ Å and $r_{Tb}^{3+}=1.04$ Å in coordination VIII).³¹ This trend has already been observed for Eu³⁺ ($r_{Eu}^{3+}=1.066$ Å in coordination VIII)³¹ doped YAG phosphors.¹⁹ It suggests that tuning the absorption band relative to the host is possible by varying the rare-earth ion concentration.

Besides, three other absorption bands are observed: a very weak signal around 200 nm and two relatively broad bands located at 228 and 273 nm. Whereas the host sensitization band is more intense when YAG contains 1 mol % Tb³⁺, these bands are stronger and broader when YAG is doped with 20 mol % of Tb³⁺. These bands can be attributed to the excitation of the electron ground state to the split 5*d* energy levels.^{10,13,16,18} Indeed, Tb³⁺ ions exhibit a 4*f*⁸ electron configuration for which the ground state is 7F_6 . The 4*f*⁷ 5*d* excitation levels present two spin states: the high spin 9D_I (or 9E) and the low spin 7D_I (or 7E)¹⁸ ($I=0, \dots, 5$). Regarding Hund's rule,³² the 7E levels are higher than the 9E ones. As a consequence, excitation spectra of a Tb³⁺ doped host generally present two groups of absorption bands: the first, corresponding to spin-allowed *f*–*d* transitions, is located at high energy (low wavelength) and the second, related to spin-forbidden transitions, is situated at low energy (high wavelength). The bands centered at 228 and 273 nm present a relatively strong intensity and thus seem to be related to the allowed transitions $^7F_6 \rightarrow ^7D_I$. In agreement with the recent work of Dorenbos,³³ these bands can be ascribed to $^7F_6 \rightarrow ^7D_5$ and $^7F_6 \rightarrow ^7D_4$ transitions, respectively. The weak signal distinguished around 200 nm is also attributed to the 4*f*→5*d* transitions of Tb³⁺ ion, more precisely to the prohibited transition $^7F_6 \rightarrow ^9D_3$. The intensity of this transition increases with terbium concentration but remains weak in comparison with the two other excitation bands observed at lower energy.^{13,16}

Emission spectra recorded for the same samples under 180 nm excitation are gathered in Fig. 4. For the lowest concentration of Tb³⁺ [Fig. 4(a)], the spectrum can readily be divided into two groups of lines: the blue emission below 480 nm is related to $^5D_3 \rightarrow ^7F_J$ transitions whereas the green emission arises from $^5D_4 \rightarrow ^7F_J$ ($J=6$ to 0) transitions.^{34–37} When the terbium concentration reaches 20 mol % [Fig.

FIG. 4. Room temperature emission spectra of crystallized YAG:Tb(x mol %) powders [(a) $x=1$ and (b) $x=20$] and (c) concentration dependence of Tb^{3+} emission intensity of $^5D_4 \rightarrow ^7F_5$ transition upon 180 nm excitation.

4(b)], the blue emission disappears: only $^5D_4 \rightarrow ^7F_J$ transitions are recorded. Such observation corresponds to the well-known cross relaxation phenomenon^{34,35} observed under UV or blue excitation.^{22,34,37} It can be summarized by the following equation:^{2,37}

Besides, the most efficient doping rate has been determined by integrating the area of the $^5D_4 \rightarrow ^7F_5$ transition located at 544 nm. Results are shown in Fig. 4(c). On this basis, the higher luminescence yield upon VUV excitation is obtained for 10 mol % of Tb^{3+} . Above it, concentration quenching occurs. Interestingly, this optimal doping rate is different from that determined under blue excitation, which was 20 mol %.²²

These results, combined with a decay time lying between 3 and 10 ms,²¹ make YAG:Tb³⁺ samples suitable phosphors for application in devices based on plasma excitation.²

FIG. 5. Room temperature excitation spectra of crystallized YAG:Ce(x mol %) powders [(a) $x=0.5$ and (b) $x=2$] in VUV range monitored at 559.5 nm.

D. Optical properties of YAG:Ce³⁺ samples

Excitation spectra recorded at room temperature monitoring the broad emission band centered at about 560 nm (Ref. 37) are presented in Fig. 5. As in the case of terbium doped samples, a broad band corresponding to the matrix absorption is observed within the Xe-Ne plasma emission range. Furthermore, another weak absorption signal situated at about 229 nm (see the inset) is observed, corresponding to $4f^1 \rightarrow 5d^1$ electron transitions.³⁸

When excited by a VUV source, samples exhibit the characteristic yellowish green emission of Ce³⁺ in a YAG host,³⁷ as one can see in Fig. 6. At room temperature, only a broad band lying between 470 and 710 nm is observed [Fig. 6(a)] while at 8.2 K two signals are well distinguished [Fig. 6(b)], originating from the transition of $5d$ levels to the ground state consisting of a doublet ($^2F_{5/2}$ and $^2F_{7/2}$).^{37,38} Results of the Gaussian fit applied to the emission spectrum recorded at low temperature are gathered in Table I. The energy difference between these two signals (1897 cm⁻¹) is concordant with the ground state configuration of Ce³⁺, for which the two levels are separated by almost 2000 cm⁻¹ due to spin-orbit coupling.^{36–38}

FIG. 6. Emission spectra of crystallized YAG:Ce(0.5 mol %) powders recorded upon 173 nm excitation at (a) room temperature and (b) 8.2 K (solid line) associated with corresponding fitted Gaussian curves (dot lines).

TABLE I. Parameters describing the Gaussian fit of the $5d \rightarrow 4f$ emissions of Ce^{3+} in $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (0.5 mol %) recorded at 8.2 K.

Transition	$5d \rightarrow {}^2F_{5/2}$	$5d \rightarrow {}^2F_{7/2}$
X (cm^{-1})	19 327	17 430
Intensity (a.u.)	3665	2813
Width (cm^{-1})	2355	1187
$\Delta E = 1897 \text{ cm}^{-1}$ $R^2 = 0.999\ 12$		

Moreover, the most efficient doping rate has been determined by integrating the area of the broad band observed at RT [Fig. 6(a)]. Results are gathered in Fig. 7. On this basis, the most efficient phosphor corresponds to 1 mol % of Ce^{3+} . This value is similar to that determined under blue excitation.³⁹

Finally, the decay curves of the sample doped with 0.5 mol % of Ce recorded at RT and at 8.2 K (monitoring $5d \rightarrow {}^2F_{5/2}$ and $5d \rightarrow {}^2F_{7/2}$ transitions) are presented in Figs. 8(a)–8(c). They can be well fitted by a double exponential decay, which is composed of a short component and a longer one. The latter is related to a re trapping phenomenon of migrating electrons and holes, which entails a delayed recombination at Ce^{3+} centers.⁴⁰ It is a commonly encountered phenomenon in Ce^{3+} -doped crystals under gamma excitation⁴¹ and has already been observed in $\text{YAG}:\text{Ce}^{3+}$ crystals⁴² and ceramics.⁴⁰ Time constants of decays are collected in Table II. Interestingly, for the measurements carried out at RT, the values of the two components are in agreement with that determined by Zych *et al.*⁴² at RT under 178 nm excitation in crystals (68 versus 85 ns and 354 versus 320 ns for the shorter and longer components, respectively).

E. Influence of codoping

Since it is known that Ce^{3+} or Gd^{3+} can be used as sensitizers for Tb^{3+} ions,^{10,12,17,38,43} the influence of Y^{3+} substitution by these ions, keeping the terbium concentration at 20 mol %, has been investigated.

Figure 9 shows the excitation spectra of $\text{YAG}:\text{Tb}$ (20 mol %), $(\text{Y}, \text{Gd})\text{AG}:\text{Tb}$ (20 mol %) and $\text{YAG}:\text{Tb}$ (20 mol %), Ce (1 mol %) in the VUV range. Gadolinium allows shifting the host band at lower energy, re-

FIG. 7. Concentration dependence of Ce^{3+} emission intensity of $5d \rightarrow 4f$ transitions upon 173 nm excitation.

FIG. 8. (Color online) Luminescence decay traces of the $5d \rightarrow 4f$ emissions of Ce^{3+} in $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (0.5 mol %) at (a) RT and (b), (c) 8.2 K upon 173 nm excitation associated with corresponding fitted double exponential curves (dashed lines).

sulting in a better overlapping with the Ne-Xe plasma emission [Fig. 9(b)]. This trend has already been observed in borates³ and may be due to the increase of Ln^{3+} radius when Y is substituted by Gd ($r_Y^{3+} = 1.02 \text{ \AA}$ and $r_{\text{Gd}}^{3+} = 1.053 \text{ \AA}$ in coordination VIII).³¹ Moreover, the powder codoped with cerium and terbium leads to a weak absorption in the VUV range [Fig. 9(c)]. It is also noteworthy that Gd^{3+} enhances the intensity of excitation bands whereas Ce^{3+} makes it decrease significantly.

On the other hand, emission spectra of the same samples excited at 180 nm are also gathered in Fig. 9: the presence of gadolinium increases significantly the emission intensity [Fig. 9(b)], indicating an efficient energy transfer from host lattice to Tb^{3+} with Gd^{3+} as an intermediate. In the case of cerium [Fig. 9(c)], the emission spectrum exhibits typical transitions of both Ce^{3+} and Tb^{3+} ions, indicating a weak energy transfer from Ce^{3+} to Tb^{3+} . Meanwhile, when adding 1 mol % of Ce, the emission intensity drops drastically. Such behaviors have already been brought out in YAG^{17} and in other matrices.^{10,43}

IV. CONCLUSION

To conclude, we have shown that the sol-gel process is a convenient route to synthesize monophased YAG powders from 800 °C, which represents a much lower crystallization temperature compared to the solid state synthesis. Furthermore, optical study has revealed wide absorption bands located in the VUV range, which entails the potential utilization of YAG based materials in applications using VUV

TABLE II. Parameters describing shape of decay traces of the $5d \rightarrow 4f$ emissions of Ce^{3+} in $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (0.5 mol %) fitting by a double exponential curve.

	$T=300\text{ K}$	$T=8.2\text{ K}$	
	$\lambda_{exc}=173\text{ nm}$		
	$\lambda_{em}=559.5\text{ nm}$	$\lambda_{em}=525\text{ nm}$	$\lambda_{em}=575\text{ nm}$
$\tau_1\text{ (ns)}$	68	103	94
$\tau_2\text{ (ns)}$	354	909	847

FIG. 9. Room temperature excitation ($\lambda_{em}=544$ nm) and emission ($\lambda_{exc}=180$ nm) spectra of crystallized (a) YAG:Tb(20 mol %), (b) (Y, Gd)AG:Tb(20 mol %), and (c) YAG:Tb(20 mol %), Ce(1 mol %) powders.

excitations such as PDPs or free Hg lamps. The optimal doping rates of Tb^{3+} and Ce^{3+} ions in YAG have been determined to be 10 and 1 mol %, respectively. As it has been noticed, these results are not the same as those obtained under blue excitation. This points out the relevance of adjusting the rare-earth concentration according to the excitation source used.

On the basis of this work undertaken on rare-earth activated YAG matrices, it appeared that Ce^{3+} ions quenched Tb^{3+} luminescence whereas the presence of Gd^{3+} entailed a sensitive enhancement of emission intensity under VUV radiation. Further investigations on codoping effects have to be carried out to obtain enough efficient phosphors for use in devices.

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