



Tunable light emission and similarities with garnet structure of Ce-doped LSCAS glass for white-light devices

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ABSTRACT

In this paper, we report results concerning tunable light emission and color temperature in cerium-doped low-silica-calcium-alumino-silicate (LSCAS) glass for smart white-light devices. Spectroscopic results, analyzed using the CIE 1931 *x*-*y* chromatic diagram, show that this glass presents two broad emission bands centered at 475 and 540 nm, whose intensities can be tuned by the excitation wavelength. Moreover, the same emission can be achieved from a color temperature range from 3200 to 10,000 K, with a color-rendering index (CRI) of around 75% obtained by changing the optical path length of the sample. Our new phosphor LSCAS glass, which is a unique system that exhibits tunable yellow emission, combines all qualities for white-light devices.

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1. Introduction

Recently, much effort has been dedicated to develop luminescent materials able to produce a new generation of white light (WL) for light sources and components used in electronic display devices [1]. White-light-emitting diodes (WLEDs) and many materials doped with luminescent ions have been studied as potential WL generators. Among those materials with luminescent ions, the most used are oxides doped with rare-earth ions like Sm³⁺, Pr³⁺, Tb³⁺, Dy³⁺, Eu³⁺ and Eu²⁺ and co-doped with Ce³⁺ ions as activators [2–7]. In particular, the Ce³⁺ ion is interesting for phosphors due to both short lifetime (about 50 ns) and a broad emission band centered between 350 and 550 nm that is associated to the allowed 5d → 4f electronic transition [8]. One material that has been extensively studied is the phosphor Ce³⁺:YAG, which presents a broad yellow luminescence when excited with sources emitting in the range between 410 and 480 nm. This system is very interesting because the radiation of the GaN-based UV-blue LED can be used simultaneously for excitation and to be added to the yellow emission of the Ce³⁺:YAG, with an appropriate intensity, yielding WL [9–11]. Although crystals are interesting for WL generation, they have some disadvantages: their production is expensive, difficult

to grow and demand high Ce³⁺ concentrations (~2 at.%), leading to fast luminescence quenching. Another drawback of Ce³⁺-doped crystals is the low color-rendering index (CRI), which is due to its very weak emission intensities in the red region [10]. There are few Ce³⁺-doped crystals emitting in the yellow region, and, until recently, those reported in the literature exhibit a garnet structure [10–13]. For other Ce³⁺-doped materials, the emissions are located in the UV or blue spectral regions.

In the last few years, we have focused our attention on the study of the optical properties of OH⁻ free rare-earth and metal-transition-doped low-silica-calcium-aluminosilicate (LSCAS) glass. This glass exhibits phonon energy of approximately 800 cm⁻¹, lower than those of silicate glasses [14]. When co-doped with Er³⁺/Yb³⁺, it presents high emission rates in the mid infrared, near 2.8 μm [15]. Additionally, laser emission at 1.07 and 1.37 μm were observed when this glass was doped with Nd³⁺ [16] and Yb³⁺ [17]. More recently, a long lifetime (~2.0 ms at 77 K and 170 μs at room temperature) and a broad emission band of 190 nm (4237 cm⁻¹) centered at 637 nm (15698 cm⁻¹) were found in a Ti³⁺-doped LSCAS glass [18], which also shows high values of both gain cross section (~4.7 × 10⁻¹⁹ cm²) and luminescence quantum efficiency (~70%) [19] comparable to the values for Ti³⁺:sapphire crystals. Our most recent achievement in this host glass was to show that, when doped with cerium, it can produce smart WL combining a glass phosphor with light-emitting diodes (LEDs) at 405 nm, resulting in an emission close to ideal WL [20].

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In this work, we deal with results concerning the possibility of tunable emission in Ce^{3+} :LSCAS glass in two ways: by changing the excitation wavelength within the violet and blue regions or by changing the re-absorption by varying the sample thickness. A structural interpretation was proposed to explain this glass particularity, which indicates that the LSCAS glass system is able to change its color temperature in accordance to the occasion. This is very interesting for the regulation of the circadian rhythms of humans, which is a great advantage for this material when compared with crystals. This matter of circadian rhythms will be a new direction of research for commercial luminophosphors of interest for artificial lights.

2. Experimental details

2.1. Sample preparation

The glass, in wt.%, were prepared with high-purity oxides having 41.5% of Al_2O_3 (5N), 47.4% of CaO (5N), 7% of SiO_2 (5N), 2.1% of MgO (5N) and 2.0% of CeO_2 (4N). The mixture was melted under vacuum atmosphere at 1600 °C for 2 h, condition used to remove the OH^- molecules from the glass structure. This procedure revealed to be a successful route to obtain a high ratio of Ce^{3+} oxidation state in the glass. The glasses presented excellent yellow-coloration homogeneity and transparency. It is important to mention that this glass presents excellent thermomechanical properties as shown before for the undoped and rare earth doped samples [21,22]. For the measurements, the sample was optically polished until reaching a thickness around 1.5 mm.

2.2. Spectroscopic characterization

Experiments were performed through optical absorption (OA), UV-Vis optical excitation (OEx) and emission (OEm), and micro Raman spectroscopy. The emission spectra were analyzed in a CIE 1931 color diagram.

The OEx experiments were carried out using a 450 W Xe^+ lamp and a H10D Horiba-Jobin Yvon monochromator. The OEm was collected by an optical fiber and analyzed by a Triax 320 Jobin Yvon monochromator with a 600-grooves/mm grating, a 0.05 nm resolution and a Peltier cooled charge-coupled-device detector (CCD). The dependence of the emission spectra as a function of the excitation was obtained by scanning the excitation wavelengths from 200 to 450 nm with 5 nm steps and recording the optical emission for each excitation.

The Raman spectra obtained with an excitation wavelength at 632 nm (supplied by a He-Ne laser) were recorded by a LabRAM ARAMIS (Horiba-Jobin-Yvon) spectrometer with a 1800-grooves-per-mm grating with a microscopic attachment (objective X50), associated with an Edge filter to reject the Rayleigh line. The signal was collected with a cooled Andor CCD. The acquisition time integration was 60 s.

3. Results and discussion

3.1. Tunable light emission spectroscopy

Fig. 1(a) shows the optical excitation and emission spectra for the 2 wt.% CeO_2 -doped LSCAS glass. The excitation spectra were developed by observing the emission at 410 and 550 nm. Two main excitation bands centered at 325 (UV) and 405 nm (violet) are observed, which are responsible for two broad emission bands centered at 475 (blue) and 540 nm (yellow), respectively. The blue emission observed under UV excitation is commonly found in many Ce^{3+} -doped materials reported in the literature, except in Ce^{3+} -doped non-garnet materials [10]. The intense and broad yellow emission is characteristic of Ce^{3+} -doped garnets crystals [10–13]. Fig. 1(b) shows the optical absorption cross section with the excitation spectra for the 570 nm emission. It can be observed that this excitation band, responsible for the broad yellow emission, fitted inside the absorption cross section spectra, does not match with the maximum of the absorption band. The maximum cross section for this band, obtained from graph is $1.44 \times 10^{-20} \text{ cm}^{-2}$ at 409 nm. As already presented in Fig. 1(b) of Ref. [18], despite this excitation band (absorption) be much less intense than that of the UV one, the emission in the yellow region is more intense than that in the blue, which means that its quantum efficiency is higher. The origin of these two emission bands is related to two main sites of the Ce^{3+} ion in the glass, which will be discussed later.

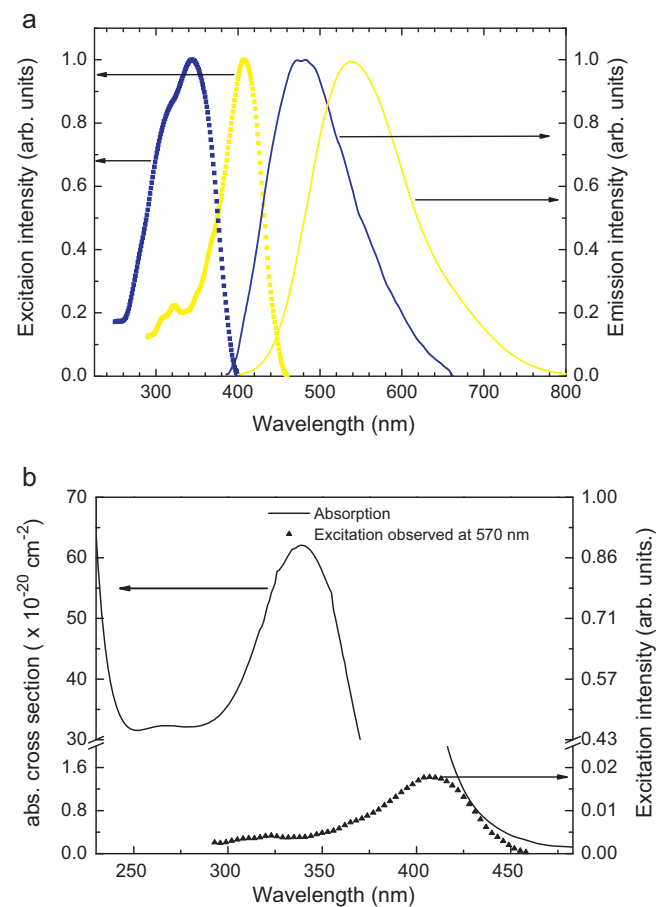


Fig. 1. (a) Optical excitation and emission of 2 wt.% CeO_2 -doped LSCAS glass, monitoring the emission at 410 and 550 nm. The blue line is the emission obtained under 320-nm excitation, and the yellow line represents the emission under 405 nm excitation. (b) Absorption cross section spectra of the same glass with the excitation spectra for 570 nm emission.

It is important to note that there is a superposition of two broad excitation bands. In this case, it is possible to obtain continuously different emission bands by changing the excitation wavelength. Fig. 2 shows the CIE 1931 color diagram for different excitation wavelengths from 305 to 425 nm. The maximum peaks of the emission wavelength from 305 to 365 nm do not change significantly. From 365 to 425 nm, a 10-nm change in the excitation wavelength leads to a significant change in the CIE color coordinate, and the emission shifts from the blue to the yellow region. In addition, correlated color temperature CCT decreases from about 10,000 to 3200 K, when the excitation wavelength is increased. This displacement is also followed by a broadening of the emission band. The CIE 1976 uniform color diagram indicate that (u', v') color coordinates for 365 nm and 425 nm excitation wavelength, mentioned before, change from (0.15, 0.46) to (0.19, 0.48). The spectra shown in Fig. 1(a), obtained under 410 nm excitation (the wavelength of the maxima emission intensity), indicate a CCT of 4450 K and a (u', v') color coordinates of (0.19, 0.54). Then, the nearest distance from the Planck locus (D_{uv}) in (u', v') color diagram is 0.058. Table 1 summarizes the emission properties of some garnet crystals that can be compared with the Ce^{3+} :LSCAS glass. As observed, the emission spectra of this glass have a similar peak position compared with those of Ce^{3+} -doped garnet structure, but shows a broader band. Moreover, the other Ce^{3+} -doped materials present their emission band in just one fixed spectral position in the UV and blue or, in the case of materials with garnet structure, in the green or yellow regions [12,23]. Taking account the emission of a LED emitting at

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