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Emission tunability and local environment in europium-doped OH^--free calcium aluminosilicate glasses for artificial lighting applications

Aline M. Farias [a], Marcelo Sandrini [a], José Renato M. Viana [a], Mauro L. Baesso [a], Antônio C. Bento [a], Jurandir H. Rohling [a], Yannick Guyot [b], Dominique De Ligny [c], Luiz Antônio O. Nunes [d], Flávio G. Gandra [e], Juraci A. Sampaio [f], Sandro M. Lima [g], Luis Humberto C. Andrade [g], Antônio N. Medina [a, *]

[a] Departamento de Física, Universidade Estadual de Maringá, Av Colombo, 5790, 87020-900, Maringá, PR, Brazil
[b] Laboratoire de Physico–Chimie des Matériaux Luminescents, Université de Lyon, Université Claude Bernard Lyon 1, Villeurbanne, UMR 5620 CNRS 69622, France
[c] Department of Materials Science and Engineering, University of Erlangen Nürnberg, Martens str. 5, 91058, Erlangen, Germany
[d] Instituto de Física de São Carlos, Universidade de São Paulo, Av. Trabalhador São-Carlense400, 13566-590, São Carlos, SP, Brazil
[e] Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, 13083-859, Campinas, SP, Brazil
[f] Lab Ciências Físicas, Universidade Estadual Norte Fluminense, 28013-602, Campos Dos Goytacazes, RJ, Brazil
[g] Grupo de Espectroscopia Óptica e Fototérmica, Universidade Estadual de Mato Grosso do Sul-UEMS, Dourados, MS, C. P. 351, CEP 79804-970, Brazil

HIGHLIGHTS

- Eu^{2+}-doped OH^- free calcium aluminosilicate glass as a new source for white lighting.
- Correlation between emission tunability and local environment of europium ions.
- Significant reduction of Eu^{3+} to Eu^{2+} by melting the glasses under vacuum atmosphere.
- Broad, intense and tunable luminescence ranging from blue to red.

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ABSTRACT

The relationship between emission tunability and the local environment of europium ions in OH^--free calcium aluminosilicate glasses was investigated, focusing on the development of devices for artificial lighting. Significant conversion of Eu^{3+} to Eu^{2+} was obtained by means of melting the glasses under a vacuum atmosphere and controlling the silica content, resulting in broad, intense, and tunable luminescence ranging from blue to red. Electron spin resonance and X-ray absorption near edge structure measurements enabled correlation of the luminescence behavior of the material with the Eu^{2+}/Eu^{3+} concentration ratio and changes in the surrounding ions' crystal field. The coordinates of the CIE 1931 chromaticity diagram were calculated from the spectra, and the contour maps showed that the light emitted from Eu^{2+} presented broad bands and enhanced color tuning, ranging from reddish-orange to blue. The results showed that these Eu doped glasses can be used for tunable white lighting by combining matrix composition and the adjustment of the pumping wavelength.

1. Introduction

A major challenge in the development of a new generation of artificial lighting is the tailoring of phosphor materials that possess efficient and tunable emissions across the whole range of the visible spectrum [1–7]. Europium and cerium are currently the most widely used phosphors in devices for lighting and displays, and both can coexist in several oxidation states in the host matrices. In addition, their emissions are known to be strongly dependent on the surrounding ions' crystal field [2].

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[*] Corresponding author.
E-mail address: medina@dfi.uem.br (A.N. Medina).

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There are several factors that determine the luminescence properties of a material, such as the phonon energy, the presence of impurities, the nature and intensity of the surrounding crystal field, the oxidation states of the sensitizer ions, the synthesis procedure, and the morphology and geometry of the final material. From the point of view of materials science, tailoring of the surrounding ions' crystal field is essential in order to control the luminescence behavior. Consequently, many different materials have been developed for solid-state lighting, including crystals [2], ceramics [8], polymers [3,9], and glasses [1,7,10–12]. Specifically, the amorphous nature of glasses means that their broad luminescence properties are influenced by the average local crystal field surrounding the dopant ions. Selection of the matrix composition, the phosphor doping level, and the melting procedure are important ways of obtaining the desired emission characteristics.

We recently proposed the use of OH^--free low-silica calcium aluminosilicate (LSCAS) glass as an alternative luminescent material for tunable white lighting, due to its intense and broad emission spectrum in the visible region. These studies employed systems doped with Ce [7,12], Eu [10], and Ce–Eu [11]. The results revealed a significant influence of melting under a vacuum atmosphere on the production of glasses with ions in reduced oxidation states and with minimal presence of OH^- in their structures. This LSCAS glass is known to have superior thermo-mechanical properties, good chemical resistance, transparency from the UV–visible to the near infrared (up to 5 μm), reduced oxidation states for some dopant ions, and efficient laser emissions [13–18].

The certification of visible light sources for artificial lighting can employ parameters such as the correlated color temperature (CCT), the color rendering index (CRI), and the distance from the Planckian locus to the (u', v') color coordinates. The latter is known as Du'v' and describes how close the tested light source is in relation to the ideal lighting. These parameters, which characterize the emission, can be used to evaluate the melting procedure and the changes in composition, in order to optimize the glass luminescence. To this end, knowledge of the oxidation states of the sensitizer ions and the nature of the surrounding crystal field are important for tailoring the intended luminescent source.

Given the above considerations, this work therefore involved the development of a set of OH^--free Eu-doped aluminosilicate glasses with different silica contents. Investigation was made of the influence of the surrounding ions' crystal field and their oxidation states on the luminescence properties. The techniques used for characterization of the samples were electron spin resonance (ESR), X-ray absorption near edge structure (XANES), and photoluminescence (PL).

Table 1
Compositions (wt%), theoretical % of non-bridging oxygen (NBO), and optical basicity (Λ_{th}) of the glasses.

Samples	CaO	Al_2O_3	SiO_2	MgO	Eu_2O_3	NBO (%)	Λ_{th}
LSCAS	47.4	39.0	7.0	4.1	2.5	48.07	0.74
CAS 10	45.9	37.5	10.0	4.1	2.5	46.47	0.73
CAS 15	43.4	35.0	15.0	4.1	2.5	43.89	0.71
CAS 20	40.9	32.5	20.0	4.1	2.5	41.41	0.69
CAS 30	35.9	27.5	30.0	4.1	2.5	36.73	0.66
CAS 34	33.9	25.5	34.0	4.1	2.5	34.96	0.65
CAS 40	30.9	22.5	40.0	4.1	2.5	32.40	0.63
CAS 45	28.4	20.0	45.0	4.1	2.5	30.34	0.62
CAS 50	25.9	17.5	50.0	4.1	2.5	28.36	0.60
CAS 55	23.4	15.0	55.0	4.1	2.5	26.45	0.59
CAS 60	20.9	12.5	60.0	4.1	2.5	24.60	0.57
CAS 65	18.4	10.5	65.0	4.1	2.5	22.81	0.56

2. Experimental

High purity reagents (>99.995%) were used to prepare the glass samples. Table 1 shows the compositions (in wt%) required in order to obtain 6 g of the glasses. The reagents were mixed in a ball mill for 12 h, after which the mixtures were melted in graphite crucibles for 2 h under a vacuum atmosphere (10^{-3} mbar), at temperatures between 1400 °C and 1600 °C, according to the specific composition. Quenching was achieved by switching off the heater and moving the crucible up to a cooled vacuum chamber. Annealing was then performed by returning the crucible to the melting position, where the temperature was around 800 °C, and allowing it cool to room temperature, while maintaining the vacuum. This procedure took about 5 h. Further details of the preparation process can be found elsewhere [15,18]. The glass samples presented good optical quality, with no evidence of crystallization. They were cut and optically polished for the luminescence and XANES measurements, while for ESR the samples were in the form of powders.

ESR measurements were performed at room temperature using the microwave in the X-band spectral region ($\nu = 9.52$ GHz), with a power of 5 mW and a 10 Gauss amplitude modulated field at 100 kHz.

X-ray LIII edge (6977 eV) absorption spectra were measured using the D04B-XAFS2 beamline of the Brazilian National Synchrotron Light Laboratory (Laboratório Nacional de Luz Sincroton, LNLS) in Campinas, Brazil). The XANES spectra were collected in fluorescence mode using a Canberra GL0055S LEGe detector with an array of 15 elements [19]. The data were acquired as the averages of three scans for each sample. Excitation/emission contour maps were obtained using a Xe^+ lamp as the excitation source, with the wavelengths selected by a JobinYvon H10D monochromator. The excitation beam was focused on the sample and the emission was collected by means of an optical fiber and detected by a CCD array connected to a microcomputer. Luminescence measurements were also carried out using an Ar^+ ion laser at 355 nm - 365 nm and a diode laser at 532 nm as excitation sources, with detection by a silicon photodiode. The detection system was calibrated by using an irradiance and illuminance standard source (from the National Institute of Standards and Technology, NIST) from Gooch & Housego, model 752-10 E.

3. Results and discussion

Fig. 1 shows the ESR spectra as a function of the silica content. The data were normalized in terms of the Eu_2O_3 weight. Eu^{3+} ions

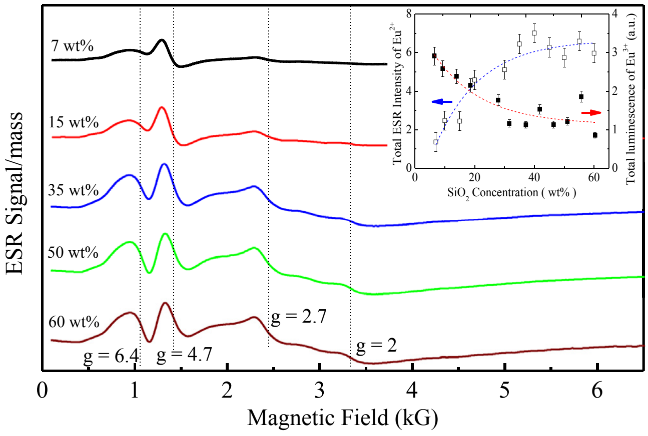

Fig. 1. Normalized ESR spectra for the samples with 7, 15, 34, 50, and 60 wt% of silica. The inset shows the integrated areas of the ESR absorption spectra and the selective Eu^{3+} total luminescence obtained by pumping the samples at 532 nm.