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# Luminescent properties of Eu-doped calcium aluminosilicate glass-ceramics: A potential tunable luminophore

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ABSTRACT

Eu-doped calcium aluminosilicate glass-ceramics have been successfully prepared from the initial calcium aluminosilicate glass, containing 50 wt% of silica, under heat-treatment. Structural and optical properties of glass and obtained glass-ceramics were investigated. Control of crystallization using X-ray diffraction and Raman spectroscopy allowed to identify two main crystalline phases: anorthite [$CaAl_2Si_2O_8$] as the major phase and melilite [$Ca_2Mg_{0.75}Al_{0.5}Si_{1.75}O_7$] as the minor phase. Luminescent properties were investigated by emission spectra, lifetime measurements and color point analysis. The $Eu^{3+}$ ion emission was used as an environment probe in the initial glass and glass-ceramics. Additionally, the broad band emission due to $4f^6 5d^1 \rightarrow 4f^7$ showed that $Eu^{2+}$ is incorporated into the crystalline phases after reduction of $Eu^{3+}$ during annealing. This incorporation, increasing with time of heat-treatment, enhanced $Eu^{2+}$ luminescence.

## 1. Introduction

White light emitting diodes (W-LEDs) are considered as a new generation of phosphor materials for many reasons such as long lifetime, environmental benefits, low energy consumption and flexibility to many applications as displays or lighting [1–5]. One method to make W-LEDs is the combination of UV or blue LED chips with actually one, two or three phosphors materials. The first commercial W-LEDs consist of GaN-based blue chips and YAG: $Ce^{3+}$ yellow phosphor [6]. Therefore, it is interesting to develop suitable rare-earth elements (REE) ion doped material capable of generating white light under blue LED chips.

REE ions have versatile applications and their properties are strongly host dependent [7–9]. $Eu^{3+}$ and $Eu^{2+}$ have found important applications. The $Eu^{3+}$ doped phosphors show orange-red emission by 4f→4f transitions whose positions are practically independent of ligands. However, the relative intensity between those transitions is correlated with the local environment symmetry. While, the $Eu^{2+}$ doped phosphors show broad emission band with large cross sections by $4f^6 5d^1 \rightarrow 4f^7$ transition depending on the ligands field. Because their typical emission spectra cover wide wavelength range from violet to yellow, the $Eu^{2+}$ doped phosphors become one of the most important components in the phosphors converting W-LEDs.

For many years, REE ions doped calcium aluminosilicate (CAS) glass have been synthesized for different optical purposes. These $OH^-$ free glass prepared under vacuum atmosphere, present potential applications as white light generation devices when particularly doped with $Eu^{2+}$ [10] and $Eu^{2+}/Eu^{3+}$ [11] ions.

Over these years, in order to increase luminescence efficiency, glass-ceramic may be used. These systems doped with REE ions possess excellent characteristics from both glasses and crystals such, better thermal stability, lower production cost, low phonon energy and good crystal environment for REE ions [12–14]. Furthermore, it is desirable to combine advantages of glasses and crystal materials via developing glass-ceramics for W-LEDs with better luminescence intensity.

In recent years, it was observed that devitrification in aluminosilicate glass systems containing CaO, $Al_2O_3$ and $SiO_2$ as the major components showed that crystallization occurs via surface [15]. Also, it was reported that addition of nucleating agent like $TiO_2$ and $Fe_2O_3$ was effective to generate bulk crystallization [16]. In our $SiO_2{-}Al_2O_3{-}CaO{-}MgO$ glass system, without nucleating agents, crystallization achieved by simple heat treatment showed that crystallization is quite heterogeneous over surface sample [17], but only in

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recent years, a simultaneous high pressure and temperature was applied in the same CAS glass in attempt to obtain glass ceramics having homogeneous crystallization over the bulk sample [18,19].

In the present work, we report the synthesis of Eu-doped novel calcium aluminosilicate glass-ceramics with higher silica content CAS50 (50% of $SiO_2$, in Wt %) using heat treatment and controlled crystallization of initial glass. The crystallization behaviors of glass-ceramics were characterized by X-ray diffraction and Raman spectroscopy. Luminescence properties of these materials using emission spectra, lifetime measurements and color coordinates of these materials were investigated. The present results are compared with our previous study realized with a lower silica content CAS34 (34% of $SiO_2$, in Wt %) [17] as to deduce new direction to further tune the Eu emission with both chemical compositions and crystallization.

## 2. Experimental

Eu-doped calcium aluminosilicate glass with the composition (in Wt %): 25.57 CaO-19.67 $Al_2O_3$-49.67 $SiO_2$-4.1 MgO-1 $Eu_2O_3$ was prepared with high purity reagents by conventional melt-quenching method. This composition is often called CAS50 in our previous publications [11]. The process was made at 1600 °C for 2 h under vacuum atmosphere promoting the absence of $OH^-$ from the glass structure. The detail about glass preparation was described elsewhere [20]. The as-prepared glass was cut into desired dimensions and optically polished for crystallization and subsequent characterization. Thermal properties of fine powder of undoped calcium aluminosilicate with 50% of $SiO_2$ (in Wt %) glass measured by differential thermal analysis (DTA) at rate of 10 °C.min$^{-1}$ from room temperature to 1200 °C [21] showed that, the onset glass transition temperature (Tg) was 771 °C and crystallization peak temperature (Tc) was 993 °C. Since in most the cases, the nucleation temperature is 50–100 °C above the Tg temperature [22]. Therefore, the selected temperature for heat treatment in this study was chosen to be 900 °C. The initial glass samples labeled CAS50 were thermally treated by an isotherm step at 900 °C for 0.5, 1.5, 2, 2.5, 3, 4 and 8 h. These samples were labeled as xxGCyy, where xx is the wt% of $SiO_2$ and yy is the heat treatment time (hours). Temperature in the furnace was controlled with a Pt thermocouple in contact with the glass simple holder. The absolute error in time is estimated to be less than 2 min.

A Brucker D8 X-ray diffraction using the CuKα radiation ($\lambda = 0.154$ nm) was used to identify the crystalline phases formed after heat treatment process. Raman spectra were recorded using an ARAMIS (Horiba Jobin-Yvon) spectrometer with laser excitation line at 633 nm. In order to estimate the homogeneity of the crystallization, a coupled microscopic (objective ×50) with a numerical aperture of 0.5 which allows a lateral resolution $< 1.5$ µm and an axial resolution $< 10$ µm, was used to focus the laser on the surface ($z = 0$ µm) and below ($z = -80$ µm) the sample. Luminescence spectra of the glass and glass-ceramics were also recorded under microscopic objective, but using 3 different continuous excitations: an RM 1000 Renishaw spectrometer using excitation at 532 nm (60 s of acquisition), an ARAMIS spectrometer using excitation at 473 nm supplied by diode-pumped solid state laser (5s of acquisition) and blue LED ($\lambda_{ex.} = 405$ nm). Global luminescence decay curves were recorded using an optical parametric oscillator pulsed laser (OPO, EXSPLA NT342B, 10 Hz, 7 ns). The signal was analyzed by a Jobin-Yvon HRS1 monochromator intensified by a Hamamatzu photomultiplier (PM) and the data were recorded with a digital Lecroy oscilloscope. All the measurements were performed at room temperature.

## 3. Results and discussion

### 3.1. Structural characterization

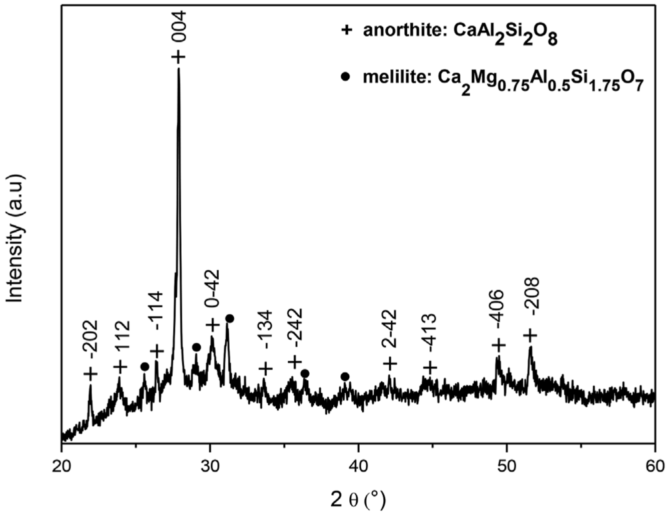

**Fig. 1.** XRD patterns of the glass-ceramics 50GC8 obtained after heat treating the CAS50 initial glass at 900 °C for 8 h duration.

The XRD patterns of 50GC8 is shown in Fig. 1. Intense diffraction peaks correspond to the anorthite [$CaAl_2Si_2O_8$] (JCPDS 00-041-1486), as the major crystalline phase with triclinical symmetry of the P-1 space group [23]. In addition, melilite [$Ca_2Mg_{0.75}Al_{0.5}Si_{1.75}O_7$] is as well identified in the glass as a minor crystalline phase (JCPDS 00-014-4687) with a tetragonal symmetry of the P-$42_1$m space group [24]. The melilite phase, solid solution between akermanite $Ca_2Mg$ [$Si_2$]$O_7$ and gehlenite $Ca_2Al$ [AlSi]$O_7$, is an Mg-rich akermanite with relation akermanite/gehlenite = 75/25 (mol %). Recently, the devitrification of calcium aluminosilicate glass with 34% (in Wt) of silica content, also called CAS34, was investigated and showed that a melilite, [$Ca_2Mg_{0.25}Al_{1.5}Si_{1.25}O_7$], an Mg-rich gehlenite with a ratio akermanite/gehlenite = 25/75 is the major phase and anorthite as the minor one [17]. More recently, the crystallization in calcium aluminosilicate system $CaO{-}MgO{-}Al_2O_3{-}SiO_2$ was reported and the result showed the formation of three crystalline phases: diopside ($CaMgSi_2O_5$), gehlenite and anorthite [25]. Generally crystalline phases obtained after devitrification of the initial glass are largely dependent of the composition in the initial system. Indeed, our glass composition 25.57 CaO-19.67 $Al_2O_3$-49.67 $SiO_2$-4.1 MgO-1 $Eu_2O_3$ reported in the quaternary $MgO{-}CaO{-}Al_2O_3{-}SiO_2$ system [26], is well within the range of the formation of anorthite phase. Moreover, its chemical composition can be decomposed completely in the following way 33.8% anorthite, 15.2% gehlenite, 32.2% akermanite and 18.8% quartz ($SiO_2$). Which leads to a theoretical melilite with a ratio akermanite/gehlenite = 68/32. In the same manner the CAS34 decomposes as: 22.4% anorthite, 48.2% gehlenite, 14.0% akermanite and 15.4% diopside. For this later case the theoretical melilite is with a relation akermanite/gehlenite = 23/77. Therefore, this composition mainly promotes the precipitation of anorthite as the major one which is in agreement with the XRD results.

In order to investigate the type of crystallization taking place, a Raman scanning was carried on (0 µm) and below (−80 µm stage displacement) the surface of the glass and glass-ceramics. Fig. 2 shows the Raman spectra of the samples in the range 200–1200 cm$^{-1}$. The spectra of CAS50 glass (Fig. 2 a and b), are mainly characterized by two broad bands centered at 520 and 980 cm$^{-1}$. In calcium aluminosilicate glass, rich-silica, the band in the low frequency is generally assigned to the motions of brindging oxygen in T-*O*-T linkages (T ≡ Si, Al) of $SiO_4$ and $AlO_4$ tetrahedra [27]. The band in the high frequency region is typically assigned to the T-O (T ≡ Si, Al) symmetric bond stretching motions of $Q^n$ species, corresponding to the $TO_4$ units with n bridging oxygen [19,28]. From the glass composition, it can be evaluated that CAS50 has a theoretical ratio of non-bridging oxygen per tetrahedrals of 0.6. Assuming an equal repartition of non-bridging oxygen on the tetrahedrals,