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# Reduction of $Eu^{3+}$ to $Eu^{2+}$ in $\alpha$-$Y_2Si_2O_7$ and X1-$Y_2SiO_5$ and their luminescent properties

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## Abstract

Due to its bright tunable emission, Eu-doped yttrium silicates are very interesting materials for LED applications. The microparticles of $\alpha$-$Y_{1.98}$ $Eu_{0.02}$ $Si_2O_7$ and the low-temperature phase of $Y_{1.98}$ $Eu_{0.02}$ $SiO_5$ (*X*1) were prepared by sol gel technique. Then, the samples were reduced at high temperatures using pure hydrogen as reduction agent. The materials obtained were characterized by X-Ray diffraction, Scanning Electron Microscopy, Energy Dispersive X-Ray and Photoluminescence spectroscopy. The presence of $Eu^{2+}$ in the materials after the reduction was confirmed by the blue-green band emission and the wide absorption band, observed only in the excitation spectra of the reduced samples. These bands are congruent with the information previously reported in the literature. A red shift of the broadband emission of $Eu^{2+}$ doped α-$Y_2Si_2O_7$ system was observed compared to previously reported results. Also, the luminescent properties of $Eu^{2+}$ host in X1-$Y_2SiO_5$ are presented for first time. The relative contribution of $Eu^{2+}$ and $Eu^{3+}$ depends on the excitation wavelength leading to a tunable emission phosphor with potential application in white LEDs. Summarizing, the reduction of Eu ions in yttrium silicates is presented in this work, leading to a tunable emission phosphor with potential application in white LEDs.

**Keywords:** Inorganic materials; Phosphors; Optical properties; Rare earth; Sol-gel processes; Optical spectroscopy.

## 1. Introduction

In recent years, the interest in single compound phosphors has increased since they simplify the LED production process, overcome the drawbacks of self-absorption and facilitate the adjustment of the color [1–3]. Usually, white-light emission from a single host can be obtained by codoping with multiple activators or using different luminescent centers from the same ion [3–8]. Recently, mixing valences of Eu ions in inorganic compounds have been studied as an interesting alternative. The spectra of $Eu^{2+}$ and $Eu^{3+}$ codoped phosphors have been explored in host lattices like $Ba_{1-x}Sr_xGd_{1-y}Y_yB_9O_{16}$, $Ca_2NaSiO_4F$, $Ca_2Tb_8(SiO_4)_6O_2$, $LaF_3$, $BaZnSiO_4$, $Na_5Al(PO_4)_2F_2$ [9–14]. These compound have the presence of alkali or alkaline earth metals in common, whit the purpose to successfully reduce $Eu^{3+}$ ions to $Eu^{2+}$.

Among the silicate compounds, the different compositions of yttrium silicates have been highlighted due to their excellent properties as host lattice for rare earth elements [15–20].

While $Y_2Si_2O_7:Ce^{3+}$ has potential as scintillation material and $Y_2Si_2O_7:Eu^{3+}$ as red phosphor [21,22]; $Y_2SiO_5$ is widely used as cathodoluminescent material and, doped with $Eu^{3+}$, is a promising candidate for coherent time-domain optical memory and red phosphor for lamps and display applications [23–27]. Although yttrium silicates are not considered suitable for $Eu^{2+}$ ions, they are an interesting option to study.

Only one investigation has reported the reduction of $Eu^{3+}$ in this kind of materials [28]. Sokolnicki prepared $Eu^{3+}$ doped α-$Y_2Si_2O_7$ by reaction of nanostructured $Y_2O_3:Ln^{3+}$ ($Ln^{3+}$ = $Eu^{3+}$, $Tb^{3+}$ and $Ce^{3+}$) and colloidal $SiO_2$ at high temperatures for later treatment of the samples at different temperatures applying a reducing atmosphere ($75\%N_2+25\%H_2$). The presence of $Eu^{2+}$ was confirmed by electron paramagnetic resonance (EPR) and it was shown that synthesis conditions influenced the spectroscopic properties.

In this work α-$Y_{1.98}Eu_{0.02}Si_2O_7$ and the low-temperature phase of $Y_{1.98}Eu_{0.02}SiO_5$ (X1 type) were synthesized by sol-gel technique and then $Eu^{3+}$ ions were partially reduced to $Eu^{2+}$ using pure hydrogen as reduction agent, as confirmed by photoluminescence measurements.

## 2. Experimental

### *2.1 Synthesis*

Samples $Y_{2(1-x)}Eu_{2x}Si_2O_7$ and $Y_{2(1-x)}Eu_{2x}SiO_5$ (x = 0.01) were prepared by the sol gel technique using $Na_2SiO_3$ (J. T. Baker Reagent), $Y_2O_3$ (Sigma Aldrich Reagent) and Eu $(NO_3)_3$ (Sigma Aldrich Reagent) as precursors. First, a mixture of $Y_2O_3$ and 25 mL of water was heated with constant stirring until reaching 92°C. Then, concentrated nitric acid (J. T. Baker, 65.9%) was added drop by drop until the solution was observed transparent. The heating was stopped and europium nitrate was added. Finally, the solution was cooled to room temperature. Meanwhile, a stoichiometric amount of $Na_2SiO_3$ was dissolved in 50 mL of water. The acidic solution was incorporated in the basic one and the pH was adjusted to 9 using a 1M solution of sodium hydroxide (Riedel-de Haën, 99%). The formed precipitate was recovered by vacuum filtration and it was washed ten times with warm water. The wet samples $Y_{1.98} Eu_{0.02} Si_2O_7$ and $Y_{1.98} Eu_{0.02} SiO_5$ were dried at 120°C for 4h, ground in an agate mortar and thermally treated in air at 950°C and 1100°C respectively for 24h using a heating rate of 10°C/min. The powders recovered were ground in an agate mortar for their use in the reduction process.

### *2.2 Reduction process*

Approximately 200 mg of each sample, $Y_{1.98} Eu_{0.02} Si_2O_7$ and $Y_{1.98} Eu_{0.02} SiO_5$, was annealed under a reducing atmosphere at 850°C for 36h and 900°C for 78h respectively. At longer periods no significant changes in the emission spectra were observed. A flow of pure hydrogen was used as reduction agent (~ 0.001L/s).

### *2.3 Structural and optical analysis*

Crystal structure of the recovered powders was determined using X-ray diffraction technique with Cu Kα radiation (λ = 1.5045 Å) on a Siemens D5000 X-ray diffractometer (40kV, 40mA). SEM images and EDX analysis were obtained using a FEI Quanta-FEG 200 microscope at 25.0 kV. Photoluminescence excitation and emission spectra were measured at room temperature using an Edinburgh Instruments FS920 spectrometer, equipped with a monochromated 450 W Xe-arc lamp as the excitation source. Finally the quantum efficiency (QE) was measured with an integrating sphere [29].

## 3. Results and discussion

### 3.1 Structural characterization

Fig.1 shows the XRD patterns of the samples before and after the reduction process, it is observed that there were no significant differences between them. The patterns obtained for $Y_{1.98}$ $Eu_{0.02}$ $Si_2O_7$ are displayed on Fig. 1(a). The principal diffraction peaks are indexed with the standard card JCPDS (38-0223) indicating the majority phase is $\alpha$-$Y_2Si_2O_7$. Some extra peaks (*) were identified as the monoclinic *X*1-$Y_2SiO_5$. In Fig. 1(b) the diffractograms of $Y_{1.98}$ $Eu_{0.02}$ $SiO_5$ system are presented. According to the standard card JCPDS (41-0004) the principal phase is X1- $Y_2SiO_5$. Peaks not related (°) are observed owing to the presence of a second phase, which is identified with the standard pattern JCPDS (30-1457) as $Y_{4.67}$ $(SiO_4)_3O$. The peaks between 27-29° in the first diffractogram and those three that protrude between 35-39° in the second one could not be identified due to the lack of information.

***FIGURE 1 ABOUT HERE***

The morphology of the reduced samples was studied using SEM. The micrographs (Fig. 2 (a) and (b)) display microparticles with irregular shape and different sizes, the bigger ones with a magnitude of approximately 50µm. Furthermore, EDX elemental color mapping measurements were performed to explore the element composition and distribution. For both reduced samples, yttrium, silicon and europium are homogenously distributed in the host lattice. Table 1 shows the average valued of the atomic percentage of each element over the area shows in Fig. 2, excluding the contribution of oxygen, which is difficult to quantify using EDX. They provide an overview of the proportions of the elements in the lattice. The values are congruent with the stoichiometric ratio for both systems.

***FIGURE 2 ABOUT HERE***

***TABLE 1 ABOUT HERE***

### *3.2 Luminescence properties*

Fig. 3 shows the emission and excitation spectra of the samples before and after the reduction process at different excitation and monitoring wavelengths. Emission spectra of the non-reduced samples (Fig.3 (a) and (c)) exhibit spectral lines corresponding to the transitions $^5D_0$-$^7F_J$ ($J$ = 0, 1, 2, 3, 4) of the typical red-orange emission of $Eu^{3+}$[30,31]. While for $Y_{1.98}Eu_{0.02}Si_2O_7$ and $Y_{1.98}Eu_{0.02}SiO_5$ reduced (Fig.3 (b) and (d)), it is possible to observe a broad band emission in addition to the spectral lines related with $Eu^{3+}$ ions, located between 400-560 nm and 475-600 nm respectively. It is unlikely that these bands are related with transitions from higher energy levels of $Eu^{3+}$ ($^5D_1$, $^5D_2$) because the multiphonon relaxation due to the vibration of silicate groups [32]. Since the bands are not observed in the non-reduced sample it is safe to associate these bands with the presence of $Eu^{2+}$ ions. Therefore, the partial reduction of $Eu^{3+}$ ions to $Eu^{2+}$ was carried out despite the difference in the charge between $Y^{3+}$ and $Eu^{2+}$. The charge compensation is expected to occur through the formation of oxygen vacancies, which are common in a reducing atmosphere[14,28].In addition, it has been widely reported that this band is related with the $5d \rightarrow 4f$ allowed transition of $Eu^{2+}$ ions. The reduction of europium in matrixes formed by trivalent cations and even the presence of a similar band due to $Eu^{2+}$ in the $Y_2Si_2O_7$ lattice is found in literature [14,28,33].

Excited at 362 nm, the band emission observed for $Y_{1.98}Eu_{0.02}Si_2O_7$ system presents a maximum peak at 509 nm. The band is wider and exhibit a red shift compared with the band reported by Sokolnicky, which shows a maximum value of intensity at 480 nm [28].

The presence of $Eu^{2+}$ ions with different environment due to the presence of more than one phase in the samples and the possible deformation of the local structure for the differences in size between $Eu^{3+}$ and $Eu^{2+}$, could lead a combination of different emission spectra.

The relative contribution of $Eu^{2+}$ and $Eu^{3+}$ in the total emission of reduced samples depends on the excitation wavelength. Upon excitation at 254 nm, only the $Eu^{3+}$ red emission is significantly visible, while at 325 nm ($Y_{1.98}$ $Eu_{0.02}$ $Si_2O_7$) and 330 nm ($Y_{1.98}$ $Eu_{0.02}$ $SiO_5$) the $Eu^{2+}$ related blue-green emission is predominant. The large width of the excitation bands of the blue-green emission is a confirmation of the assignment to $Eu^{2+}$, since in this case; both excitation and emission spectra are expected to be broad.

The excitation spectra of all samples monitored for the red $Eu^{3+}$ related emission exhibit a wide band between 225-300 nm. This band is characteristic of the charge transfer (CT) transition of $O^{2-} - Eu^{3+}$[30,34–37]. Also, sharp weak peaks at longer wavelength are observed, corresponding to the $4f \rightarrow 4f$ absorption transitions in $Eu^{3+}$. Monitored at 530 nm, only the reduced materials display a wide excitation band between 225-450 nm for $Y_{1.98}$ $Eu_{0.02}$ $Si_2O_7$ and 225-500 nm for $Y_{1.98}$ $Eu_{0.02}$ $SiO_5$, both bands with two centers. These bands are congruent with the pattern observed for 4f – 5d transition absorption of $Eu^{2+}$ hosted in matrixes based on silicates and others compounds like aluminates[9,38–41].

***FIGURE 3 ABOUT HERE***

In order to characterize the color of the total emission for each material, the corresponding chromaticity coordinates was obtained at different excitation wavelengths. The coordinates were calculated from the luminescence spectral data for reduced samples and plotted in the 1931chromaticity diagram in Fig. 4. The respective values for the coordinates, CCT (correlated color temperature), CRI (color rendering index $R_a$) and deviation from the planckian locus (Du'v') are shown in Table 2. It is observed that coordinate values strongly depend on the excitation wavelength. For reduced $Y_{1.98}Eu_{0.02}Si_2O_7$, the coordinates lie in a wide range of the white region near the blackbody locus, and for some excitation wavelength, their values are close to the standard white light ( x = 0.33 and y = 0.33)[42,43]. The CCT values for each pair of coordinates range from 2584 K to 9202 K. Most of the values of Du'v' are above of the blackbody locus indicating that the white emission has a greenish tint. The coordinates of $Y_{1.98}Eu_{0.02}SiO_5$ after the reduction process are located in the green-yellow region and their CCT values are between 1900 K and 4500 K. According with these values the total emission of the sample has a lack of blue light. Finally, the internal quantum efficiency of both materials was measured. The values obtained were 20.8% for $Y_{1.98}Eu_{0.02}Si_2O_7$ and 5.06% for $Y_{1.98}Eu_{0.02}SiO_5$.

***FIGURE 4 ABOUT HERE***

***TABLE 2 ABOUT HERE***

## 4. Conclusions

Microparticles of different sizes of α-$Y_{1.98}Eu_{0.02}Si_2O_7$ and the low-temperature phase of $Y_{1.98}Eu_{0.02}SiO_5$ were prepared by sol gel technique, and then, reduced at high temperatures using pure hydrogen as reduction agent. With the synthesis method used, single phase Y-Si-O compounds were not obtained, but depending on the conditions, $Y_2Si_2O_7$ or $Y_2SiO_5$ could be synthesized as a majority phase, with a small contribution from a minority phase. After synthesis, all Eu was found in a 3+ oxidation state.

The presence of $Eu^{2+}$ in the materials after the reduction process was confirmed by the blue-green band emission and the wide absorption band, observed only in the excitation spectra of the reduced samples. These bands are congruent with the information previously report in the literature and their large width is the expected for the characteristic bands of $Eu^{2+}$ ions. There was no significant change in their excitation and emission spectra after treatment of the powders at high temperature under reducing atmosphere during times longer than 36h for $\alpha$-$Y_{1.98}$ $Eu_{0.02}$ $Si_2O_7$ and 78h for X1- $Y_{1.98}$ $Eu_{0.02}$ $SiO_5$, indicating that $Eu^{3+}$ ions only can be partially reduced in these matrixes even when pure hydrogen is used. The relative contribution of $Eu^{2+}$ and $Eu^{3+}$ in the total emission of both materials depends on the excitation wavelength, leading to a tunable emission phosphor with potential application in white LEDs.

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## Figure captions

**Fig. 1** Diffractograms of (a) $Y_{1.98}$ $Eu_{0.02}$ $Si_2$ $O_7$ and (b) $Y_{1.98}$ $Eu_{0.02}$ Si $O_5$ before and after the reduction process with the respective reference patterns (red lines). The additional marks point the presence of a second phase (*) *X*1-$Y_2SiO_5$ and (°) $Y_{4.67}(SiO_4)_3O$.

**Fig. 2** SEM (a, b) and EDX elemental color mapping of (c) $Y_{1.98}$ $Eu_{0.02}$ $Si_2$ $O_7$ and (d) $Y_{1.98}$ $Eu_{0.02}$ Si $O_5$.

**Fig. 3** Emission and excitation spectra of $Y_{1.98}$ $Eu_{0.02}$ $Si_2$ $O_7$ (upper) and $Y_{1.98}$ $Eu_{0.02}$ Si $O_5$ (down), before (a, c) and after (b, d) the reduction process. Excitation wavelengths for the emission spectra and monitoring wavelengths for the excitation spectra are indicated in the graphs.

**Fig. 4** CIE diagram (1931) of (a) $Y_{1.98}$ $Eu_{0.02}$ $Si_2$ $O_7$ and (b) $Y_{1.98}$ $Eu_{0.02}$ Si $O_5$, reduced for 36h and 78h respectively, excited at different wavelengths.

## Table 1

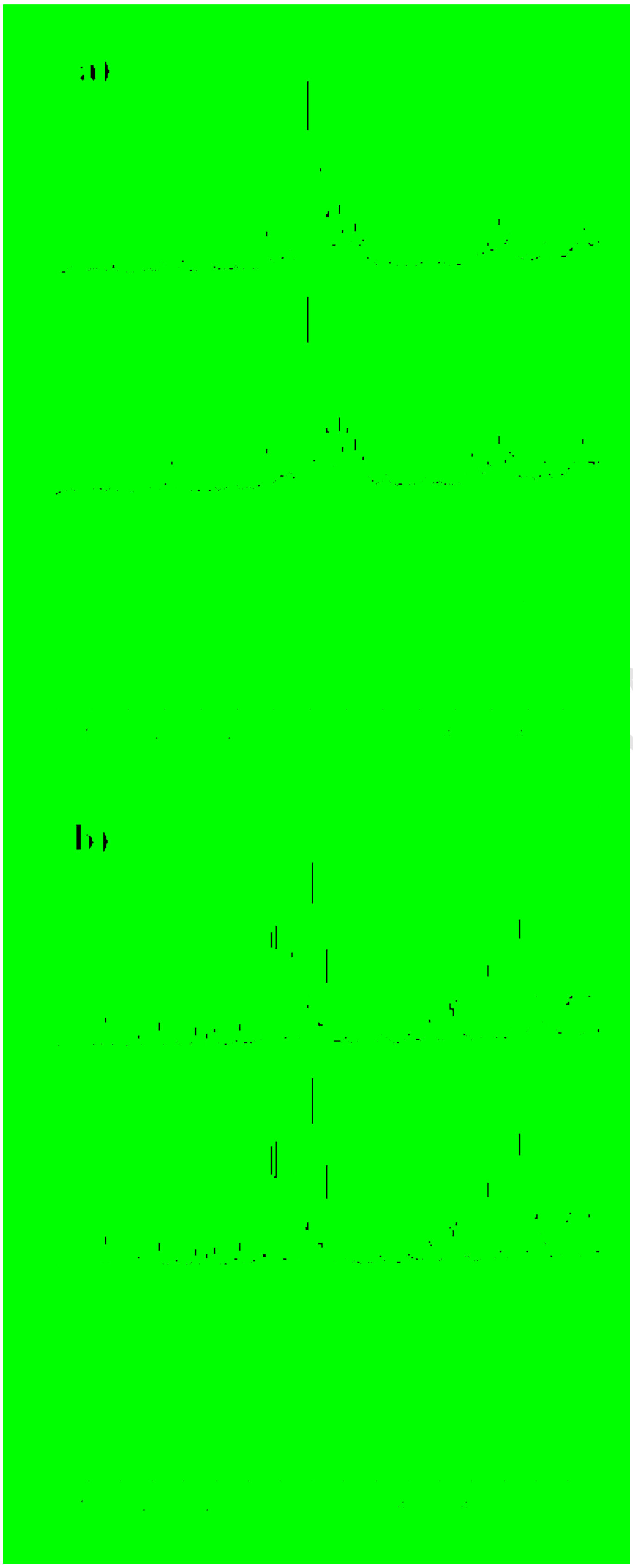
Atomic percentage (excluding oxygen) of the different metals in the reduced samples. The expected values are presented in brackets.

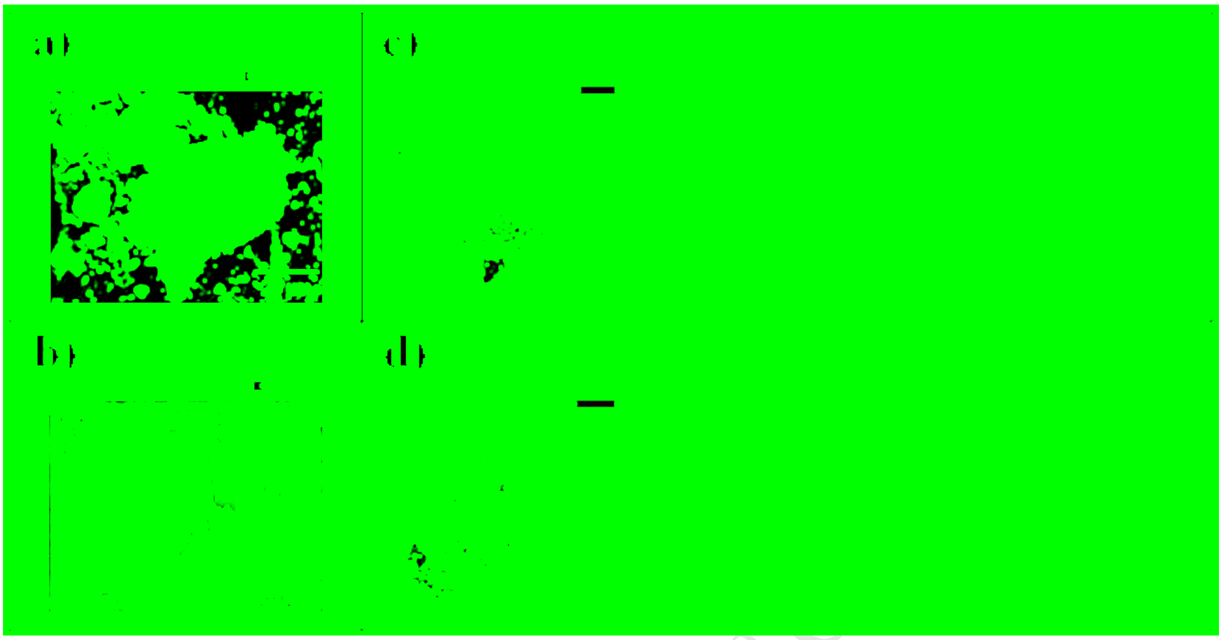
| | $Y_{1.98}$ $Eu_{0.02}$ $Si_2O_7$ | $Y_{1.98}$ $Eu_{0.02}$ $SiO_5$ |
|---|---|---|
| **Element** | **Atom %** | |
| **Y** | 47.2 [49.5] | 64.2 [66.2] |
| **Si** | 52.2 [50.0] | 34.8 [33.3] |
| **Eu** | 0.64 [0.50] | 0.96 [0.67] |

## Table 2

CIE coordinates, CCT (in kelvin), CRI ($R_a$) and deviation from planckian locus Du’v’ of emission spectra of the reduced samples excited at different wavelengths. For very large values of Du’v’, CCT was not calculated since this becomes meaningless in this case.

| **Excitation Wavelength (nm)** | $Y_{1.98}Eu_{0.02}Si_2O_7$ | | | | | $Y_{1.98}Eu_{0.02}SiO_5$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | CIE coordinates | | CCT | CRI | Deviation from planckian locus (Du’v’) | CIE coordinates | | CCT | CRI | Deviation from planckian locus (Du’v’) |
| | x | y | | | | x | y | | | |
| **319** | 0.2737 | 0.3204 | 9202 | 87 | 0.0226 | 0.4371 | 0.4703 | 3466 | 83 | 0.0348 |
| **350** | 0.2785 | 0.3439 | 8239 | 81 | 0.0320 | 0.3620 | 0.4943 | - | 68 | 0.0666 |
| **362** | 0.3100 | 0.3568 | 6453 | 89 | 0.0216 | | | | | |
| **366** | 0.3073 | 0.3838 | 6417 | 80 | 0.0373 | 0.3692 | 0.5078 | - | 65 | 0.0698 |
| **373** | | | | | | 0.3888 | 0.5007 | 4434 | 70 | 0.0611 |
| **383** | 0.3614 | 0.3897 | 4616 | 89 | 0.0158 | 0.4245 | 0.4806 | 3729 | 80 | 0.0426 |
| **393** | 0.4543 | 0.3863 | 2584 | 80 | -0.0129 | 0.5369 | 0.4195 | 1956 | 75 | 0.0034 |
| **402** | 0.3969 | 0.4453 | 4043 | 80 | 0.0332 | 0.4251 | 0.4864 | 3751 | 77 | 0.0452 |


a)
b)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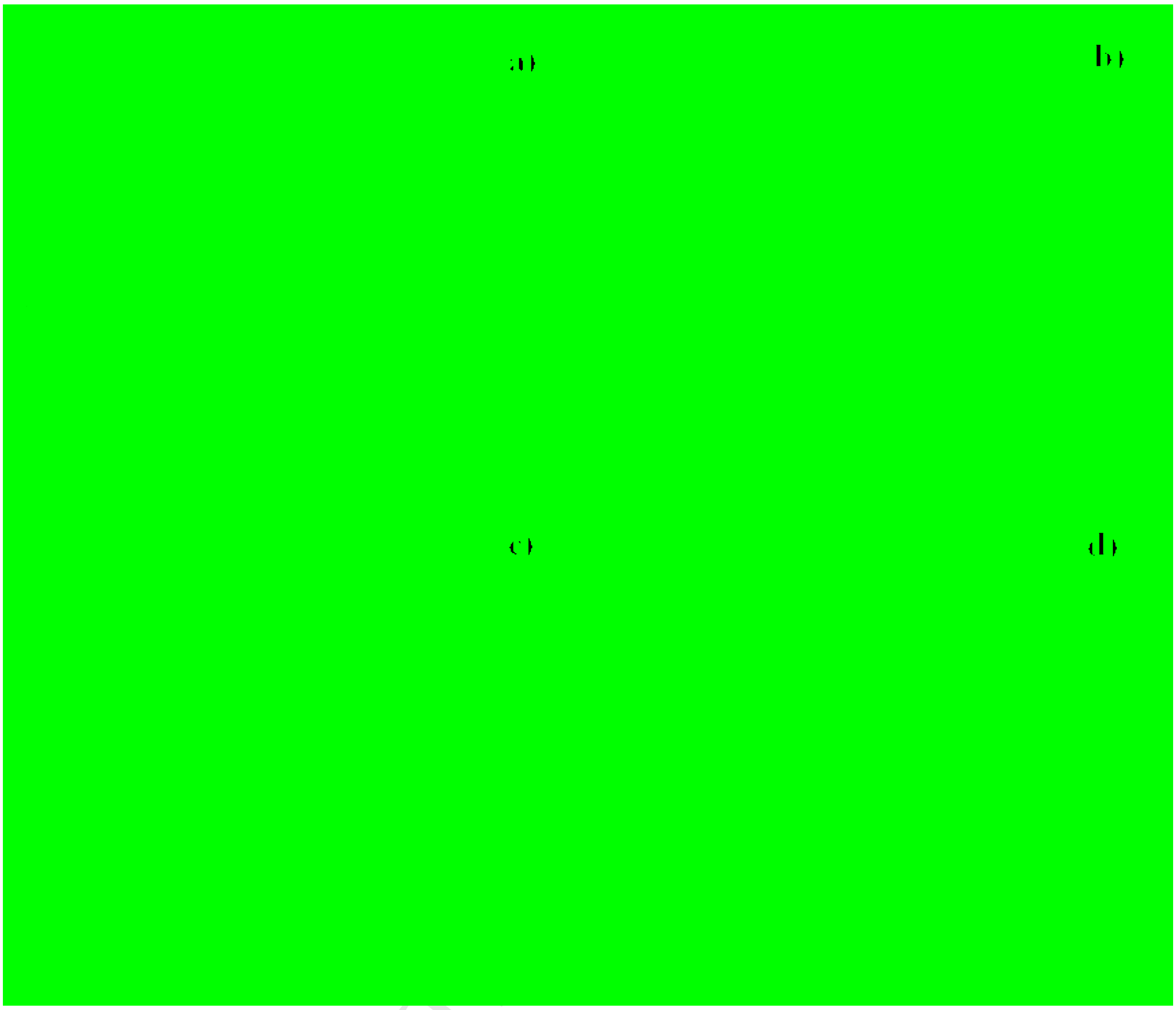
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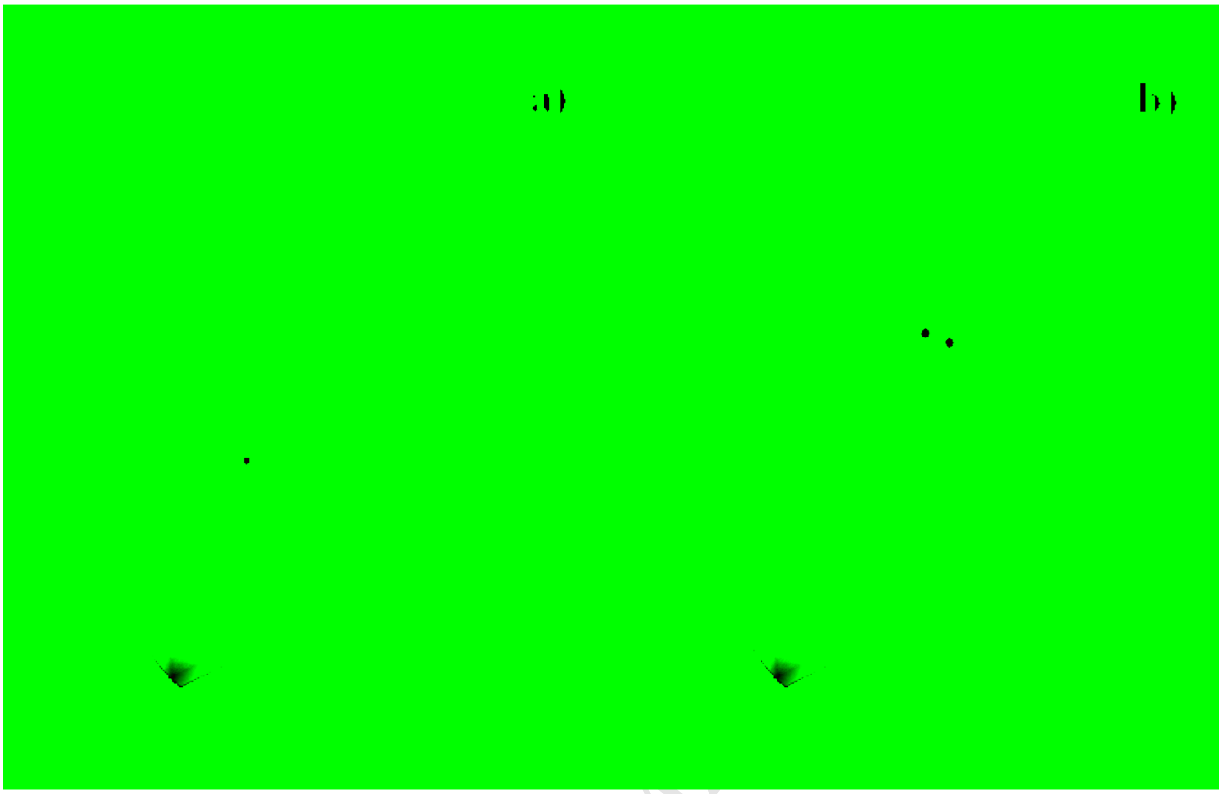
a)
b)

## Highlights

- $Eu^{3+}$ doped yttrium silicate powders were annealed under pure hydrogen atmosphere.
- A blue-green band emission was observed only in the spectra of reduced samples.
- $Eu^{3+}$ ions only can be partially reduced.
- The relative contribution of $Eu^{2+}$ and $Eu^{3+}$ depends on the excitation wavelength.
- Tunable emission phosphors were obtained.