

# **Synthesis, vacuum ultraviolet and near ultraviolet excited luminescent properties of $\text{GdCaAl}_3\text{O}_7:\text{RE}^{3+}$ (RE = Eu, Tb)**

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## Abstract

Vacuum ultraviolet (VUV) excitation and photoluminescent (PL) properties of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ion doped aluminate phosphors,  $\text{GdCaAl}_3\text{O}_7:\text{Eu}^{3+}$  and  $\text{GdCaAl}_3\text{O}_7:\text{Tb}^{3+}$  have been investigated. X-ray diffraction (XRD) patterns indicate that the phosphor  $\text{GdCaAl}_3\text{O}_7$  forms without impurity phase at  $900^\circ\text{C}$ . Field emission scanning electron microscopy (FE-SEM) images show that the particle size of the phosphor is less than  $3\mu\text{m}$ . Upon excitation with vacuum ultraviolet (VUV) irradiation, the phosphors show a strong emission at around 619 nm corresponding to the forced electric dipole  ${}^5D_0 \rightarrow {}^7F_2$  transition of  $\text{Eu}^{3+}$ , and at around 545 nm corresponding to the  ${}^5D_4 \rightarrow {}^7F_5$  transition of  $\text{Tb}^{3+}$ . The results reveal that both  $\text{GdCaAl}_3\text{O}_7:\text{RE}^{3+}$  (RE = Eu, Tb) are potential candidates as red and green phosphors, respectively, for use in Plasma Display Panel (PDP).

**Keywords:**  $\text{GdCaAl}_3\text{O}_7:\text{RE}^{3+}$  (RE = Eu, Tb); Citrate sol-gel; Luminescence, PDP green phosphors.

## 1. Introduction

Plasma display panel (PDP) is the most promising technique for the large sized flat panel display [1, 2, 3]. Phosphors used in PDP are required to have good quantum efficiency under the vacuum ultraviolet (VUV) excitation. Some oxide compounds with aluminate, borate and silicate groups have a strong absorption in the VUV region [4]. Therefore, aluminate is a good candidate for PDP phosphors.  $\text{GdCaAl}_3\text{O}_7$  is one of complex oxides in the rare earth calcium aluminate family with a general composition of  $\text{ABC}_3\text{O}_7$ , where A is an alkaline earth cation, B is yttrium (Y), scandium (Sc) or a trivalent rare earth element and C is aluminum (Al), gallium (Ga) or a transition metal ion. The compound forms tetragonal crystals belonging to the space group  $P4_2/m$ , in which the distribution of the rare earth ions and  $\text{Ca}^{2+}$  ions is considered to be close to disordered [5]. The compound structures are formed by five-membered rings constructed from  $\text{AlO}_4^{5-}$  tetrahedral linked at each corner. The rare earth ions and  $\text{Ca}^{2+}$  ions are located at the centers of these rings [6]. Recently, long-lasting phosphorescence has been reported in  $\text{Ce}^{3+}$ -doped  $\text{YCaAl}_3\text{O}_7$  crystals at room temperature [7]. The luminescence properties of  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Tm}^{3+}$  in strontium-lanthanum gallate  $\text{SrLaGa}_3\text{O}_7$ , prepared using the solid state method, have been systematically examined [6]. Compared with the conventional ways of solid-state sintering, the soft chemical method has the advantages of short heating time, small particle size and narrow particle size distribution. The sol-gel method has the merits of easy stoichiometric control, lower calcination temperature and shorter heating time, good homogeneity through mixing the starting materials at the molecular level in solution. Citrate sol-gel method is a particularly attractive method for the synthesis of the superfine powders [8,9,10].

In this paper, we report the preparation of  $\text{GdCaAl}_3\text{O}_7:\text{RE}^{3+}$  phosphors using citrate sol-gel (CSG) and solid state (SS) methods respectively. To the best of our knowledge, this is the first report to use the approaches for successfully synthesizing  $\text{GdCaAl}_3\text{O}_7:\text{RE}^{3+}$  (RE = Eu, Tb). The results of X-ray diffraction, field emission scan electron microscopy (FE-SEM) and photoluminescence (PL) of  $\text{GdCaAl}_3\text{O}_7:\text{RE}^{3+}$  phosphors will be discussed. Finally, conclusion will be drawn.

## 2. Experiments

### (a) Preparation of $\text{GdCaAl}_3\text{O}_7:\text{RE}^{3+}$ (RE = Eu, Tb) phosphor

In the citrate sol-gel (CSG) method,  $\text{Eu}_2\text{O}_3$  (99.99%),  $\text{Tb}_4\text{O}_7$  (99.99%) and  $\text{Gd}_2\text{O}_3$  (99.99%) were dissolved in concentrated nitric acid (70%, G.R.) to form  $0.5 \text{ mol} \cdot \text{L}^{-1}$  solution with pH of 3 ~ 4. Calcium, gadolinium, aluminum, europium or terbium citrates were prepared from the appropriate mixtures of nitrates (Ca/Gd/Al/Eu or Ca/Gd/Al/Tb) with citric acid in aqueous media. Ammonium hydroxide (25 ~ 28 %, A.R.) was used to keep the pH of the resulting solution at about 3.0. When a transparent solution was obtained, a certain amount of polyethylene glycol (PEG) was added. During the process, the molar ratio of the citric acid to total metal cation ( $[\text{citric acid}] / [\text{M}]$ ) and citric acid to PEG ( $[\text{citric acid}] / [\text{PEG}]$ ) was 3:1 and 1:1 respectively. After being evaporated for several hours in a  $65 \text{ }^\circ\text{C}$  water-bath, the solution became a yellowish polymeric gel, and the gel was dried at  $120 \text{ }^\circ\text{C}$  for 24 h to obtain the precursor particles. The precursor particles were put into a furnace for pre-calcination at  $500 \text{ }^\circ\text{C}$  for 3 h, and then calcined at the required temperatures ( $800 \text{ }^\circ\text{C} \sim 1400 \text{ }^\circ\text{C}$ ) for 5 h to obtain the phosphor samples.

In the solid state (SS) method, stoichiometric amount of  $\text{CaCO}_3$  (A.R.),  $\text{Al}_2\text{O}_3$  (A.R.),  $\text{Gd}_2\text{O}_3$  and  $\text{Eu}_2\text{O}_3$  were mixed in an agate mortar and then were trituated for a thorough

mixing. The mixtures were put into a furnace for pre-calcination at 500 °C for 3 h, and then calcined at 1400 °C for 5 h to obtain the phosphor samples.

### **(b) Characterization of GdCaAl<sub>3</sub>O<sub>7</sub>:RE<sup>3+</sup> (RE = Eu, Tb) phosphor**

Powder X-ray diffraction (XRD, 40 kV and 35 mA, Cu  $K\alpha$  = 1.5406 Å Rigaku/Dmax - 2200) was used for crystal phase identification. FE-SEM (LEO-1530) was used to study the morphology and size of the calcined particles. UV excitation spectra and UV excited emission spectra were measured in a fluorescence spectrophotometer, which is composed of a 1000 W xenon lamp integrated with Acton Spectra pro 2150i monochromator as the excitation source, Acton Spectra pro 275 monochromator and a photomultiplier tube (PMT Hamamatsu R636-10). The VUV excitation spectra and VUV excited emission spectra were measured at a VUV spectroscopic station using beam line 3B1B in the Beijing Synchrotron Radiation Facilities (BSRF), under high energy physics mode (1.8 GeV, 30–40 mA). A Seya type VUV monochromator (1200 g/mm) was used to provide the excitation VUV light, while an ARC SP-308 monochromator was used for the emission spectra. The optical signal was detected by a Hamamatsu H6240 photomultiplier. The relative VUV excitation intensity of the samples was corrected by dividing the measured excitation spectrum of the samples with that of sodium salicylate measured under the same conditions. The vacuum level in the sample chamber was kept at around  $2 \times 10^{-5}$  mbar. All luminescence spectrum were taken at room temperature.

### **3. Results and discussion**

The XRD patterns for the particles prepared by the sol-del and solid state methods are shown in Fig. 1. Spectra (a), (b), and (c) are the samples synthesized from a sol-gel

precursor heated for 5 h in air at 800 °C, 900 °C and 1000 °C, respectively. Spectrum (d) is a reference sample calcined at 1400 °C for 5 h by solid-state method. When the precursor is heated at 800 °C, the characteristic peaks of GdCaAl<sub>3</sub>O<sub>7</sub> (JCPDS 50-1808) appear with the existing peaks of Gd<sub>2</sub>O<sub>3</sub> (JCPDS 12-797). At 900 °C, however, GdCaAl<sub>3</sub>O<sub>7</sub> form without impurity phase. When the temperature is increased to 1000 °C, the intensity of the peaks does not change significantly, and no new peaks are observed. Compared with sample (b), the XRD pattern of the sample calcined at 1400 °C for 5 h by solid-state method still exhibits the characteristic peaks of Gd<sub>2</sub>O<sub>3</sub>.

Fig. 2 shows the FE-SEM images of GdCaAl<sub>3</sub>O<sub>7</sub> particles calcined at 900 °C (a), 1200 °C (b) and 1400 °C (c) for 5 h by citrate sol-gel method, and 1400 °C (d) for 5 h by solid state method respectively. The particles prepared through the citrate sol-gel method calcined at 900 °C have a narrow size distribution. By increasing the calcination temperature, the size of the particles enlarges. For GdCaAl<sub>3</sub>O<sub>7</sub>:Eu powders, the size increased and the particle morphology becomes irregular when the temperature increases from 1200 °C to 1400 °C. The particles prepared by the solid state method calcined at 1400 °C show a wide particle size distribution with irregular morphology.

Fig. 3(a) shows the room temperature UV excitation and emission spectra of the GdCaAl<sub>3</sub>O<sub>7</sub>:Eu<sup>3+</sup> samples prepared by the citrate sol-gel method. Upon excitation with 264 nm UV irradiation, all GdCaAl<sub>3</sub>O<sub>7</sub>:Eu<sup>3+</sup> particles emit intensely the red light corresponding to the Eu<sup>3+</sup> *f*–*f* transitions. As the calcination temperature is raised from 900 °C to 1400 °C, the emission intensity increases due to the improvement of crystallinity. When the detection wavelength is monitored at 619 nm, the excitation spectrum has a broad band with a maximum at about 264 nm. This result coincides with

the absorption band of  $\text{GdCaAl}_3\text{O}_7$  doped with  $\text{Eu}^{3+}$  ions, whereas this band is not found in the undoped  $\text{GdCaAl}_3\text{O}_7$  sample. The  $4f^6$  excitation peaks of  $\text{Eu}^{3+}$  around 400 nm are very weak, which suggests that the high quantum efficiency of the  $\text{Eu}^{3+}$  luminescence excitation originates from the charge transfer transition (CTS) of an electron from the oxygen  $2p$  state to a  $\text{Eu}^{3+}$   $4f$  state [11, 12]. Upon the UV excitation at the wavelength of 264 nm, the spectra are described by the well-known  ${}^5D_0 \rightarrow {}^7F_J$  ( $J = 0, 1, 2, \dots$ ) line emissions of the  $\text{Eu}^{3+}$  ions with the strong emission for  $J = 2$  at 619 nm. Among all cases studied, the phosphors prepared by citrate sol-gel method present the lowest emission intensity in spite of its lower starting crystalline temperature (900 °C), which is caused by the quenching effect from the remnant organic compounds used in this method. With the increase of calcination temperature (1200 °C), the amount of the organic impurities decreases significantly, hence resulting in the enhanced emissions. If a rare earth ion in the crystal lattice occupies a site with inversion symmetry, the optical transitions between the  $4f^n$  configurations are strictly forbidden as the electric dipole transition. They can only occur as magnetic-dipole transitions. If there is no inversion symmetry at the site of the rare earth ion, the electric dipole transitions exist, and the  ${}^5D_0 \rightarrow {}^7F_2$  transition can be observed, which is sensitive to the ligand environment [13]. In the emission spectra of  $\text{GdCaAl}_3\text{O}_7:\text{Eu}^{3+}$ , the electric dipole  ${}^5D_0 \rightarrow {}^7F_2$  transition around 619 nm is stronger than that of the magnetic dipole  ${}^5D_0 \rightarrow {}^7F_1$  transition around 590 nm. This indicates that  $\text{Eu}^{3+}$  ions occupy the non-inversion symmetric sites. Due to the differences in valence states and ion sizes between  $\text{Ca}^{2+}$  (99 pm) and  $\text{Eu}^{3+}$  (95 pm),  $\text{Eu}^{3+}$  ions substitute the  $\text{Gd}^{3+}$  (94 pm) site with the distorted  $C_s$  point symmetry [14]. The weak absorption peak at 313 nm is related to the  ${}^8S \rightarrow {}^6P$  transitions of  $\text{Gd}^{3+}$ , which are

possible to be detected due to the  $\text{Gd}^{3+} \rightarrow \text{Eu}^{3+}$  energy transfer.

The VUV excitation and emission spectra are shown in Fig. 3 (b). The excitation spectrum consists of two broad bands with maxima at about 184 nm and 250 nm respectively. The VUV band from 168 nm to 200 nm is the bandgap absorption region of the host lattice (aluminate) [4, 15, 16]. The broad band at 250 nm is attributed to the charge transfer band (CT band) resulting from an electron transfer between the ligand  $\text{O}^{2-}$  orbit and the empty states of the  $4f^6$  configuration of  $\text{Eu}^{3+}$  [11]. The emission spectrum of  $\text{GdCaAl}_3\text{O}_7:\text{Eu}^{3+}$  excited by VUV source at the wavelength of 172 nm is consistent with that excited by UV light. The emission lines of  $\text{Eu}^{3+}$  correspond to a group of typical  ${}^5D_0 \rightarrow {}^7F_J (J = 1, 2)$  transitions and the main line is the  ${}^5D_0 \rightarrow {}^7F_2$  transition at 619 nm, which is the typical transition of  $\text{Eu}^{3+}$  ions occupying the non-centrosymmetric sites.

Fig. 4(a) shows the room temperature UV excitation and emission spectra of the  $\text{GdCaAl}_3\text{O}_7:\text{Tb}^{3+}$  samples prepared by the citrate sol-gel method. Under the excitation of UV light at 249 nm, all the  $\text{GdCaAl}_3\text{O}_7:\text{Tb}^{3+}$  particles emit intense green light due to the  $\text{Tb}^{3+} f-f$  transitions. As the calcination temperature is risen from 900 °C to 1400 °C, the emission intensity increases with the calcination temperature which is similar to the case of  $\text{GdCaAl}_3\text{O}_7:\text{Eu}^{3+}$ . When the detection wavelength is monitored at 545 nm, the excitation spectrum is contributed by the  $4f^8 - 4f^75d$  transition which includes two bands, the spin-allowed transition at the shorter wavelength with a higher intensity and the spin-forbidden transition at the longer wavelength with weaker intensity, as well as the  $f-f$  transition lines at the longer wavelength. Under the excitation of UV light at 249 nm, the characteristic luminescence is obtained which corresponds to  ${}^5D_4 \rightarrow {}^7F_J (J = 6, 5, 4, 3)$



line emissions of the  $\text{Tb}^{3+}$  ions with the strongest emission for  $J = 5$  at 545 nm, while the  $f - f$  transition lines from the higher level  $^5D_3$  are not observed due to the increased concentration of  $\text{Tb}^{3+}$  [17].

The VUV excitation and emission spectra are shown in Fig. 4 (b). The excitation spectrum consists of two broad bands with maxima at 186 nm and 240 nm respectively. The band in the VUV region around 186 nm is the band-gap absorption region of the aluminate in the  $\text{GdCaAl}_3\text{O}_7:\text{Tb}^{3+}$ . The broad band at 240 nm is attributed to the transitions between the lower energy level of  $4f^8$  configuration and the higher energy levels of  $4f^75d$  configuration of  $\text{Tb}^{3+}$  ion [16]. There is an energy transfer from host to the  $\text{Tb}^{3+}$  ion because the  $4f - 5d$  transition absorption of  $\text{Tb}^{3+}$  is in the range of 150 ~ 260 nm[18], which is partially overlapped with the host absorption. The weak absorption peak at 274 nm is related to the  $^8S \rightarrow ^6I$  transitions of  $\text{Gd}^{3+}$ , which are possible to be detected due to the  $\text{Gd}^{3+} \rightarrow \text{Tb}^{3+}$  energy transfer. The emission spectrum of  $\text{GdCaAl}_3\text{O}_7:\text{Tb}^{3+}$  excited under VUV excitation (172 nm) is also consistent with that excited under UV light. The emission lines of  $\text{Tb}^{3+}$  are contributed by a group of  $^5D_4 \rightarrow ^7F_J (J = 6, 5, 4, 3)$  transitions and the main line is the  $^5D_4 \rightarrow ^7F_5$  transition at 547 nm as shown in Fig. 4 (b).

### 3 Conclusion

$\text{GdCaAl}_3\text{O}_7:\text{RE}^{3+}$  (RE = Eu, Tb) phosphors have been synthesized using citrate sol-gel and solid state methods. Upon the excitation with vacuum ultraviolet (VUV) irradiation, the phosphors show a strong emission at around 619 nm corresponding to the forced electric dipole  $^5D_0 \rightarrow ^7F_2$  transition of  $\text{Eu}^{3+}$ , and at around 545 nm corresponding

to the  ${}^5D_4 \rightarrow {}^7F_5$  transition of  $Tb^{3+}$ . The results reveal that both  $GdCaAl_3O_7:RE^{3+}$  (RE = Eu, Tb) are potentially candidates as PDP red and green phosphors.

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### Figure Captions:

Fig.1 XRD patterns of the  $\text{GdCaAl}_3\text{O}_7$  prepared by the sol-gel method calcined at (a): 800 °C, (b): 900 °C and (c): 1000 °C for 5 h, by the solid state method calcined at (d) 1400 °C for 5 h

Fig.2 FE-SEM images of  $\text{GdCaAl}_3\text{O}_7$  prepared by the sol-gel method calcined (a) at 900 °C, (b) at 1200 °C, (c) at 1400 °C for 5 h, by the solid state method calcined at (d) 1400 °C for 5 h

Fig.3 (a) Room-temperature UV excitation ( $\lambda_{\text{em}} = 619$  nm) and emission ( $\lambda_{\text{ex}} = 264$  nm) spectra of  $\text{GdCaAl}_3\text{O}_7$ : 16 mol % $\text{Eu}^{3+}$  samples prepared by the sol-gel method calcined (a) at 900 °C, (b) at 1200 °C, (c) at 1400 °C for 5 h, (b) room-temperature VUV excitation ( $\lambda_{\text{em}} = 619$  nm) and emission ( $\lambda_{\text{ex}} = 172$  nm) spectra of  $\text{GdCaAl}_3\text{O}_7$ : 16 mol % $\text{Eu}^{3+}$  samples prepared by the sol-gel method calcined at 1400 °C for 5 h

Fig.4 (a) Room-temperature UV excitation ( $\lambda_{\text{em}} = 545$  nm) and emission ( $\lambda_{\text{ex}} = 249$  nm) spectra of  $\text{GdCaAl}_3\text{O}_7$ : 14 mol % $\text{Tb}^{3+}$  samples prepared by the sol-gel method calcined (a): at 900 °C, (b): at 1200 °C, (c): at 1400 °C for 5 h, (b) room-temperature VUV excitation ( $\lambda_{\text{em}} = 547$  nm) and emission ( $\lambda_{\text{ex}} = 172$  nm) spectra of  $\text{GdCaAl}_3\text{O}_7$ : 14 mol % $\text{Tb}^{3+}$  samples prepared by the sol-gel method calcined at 1400 °C for 5 h

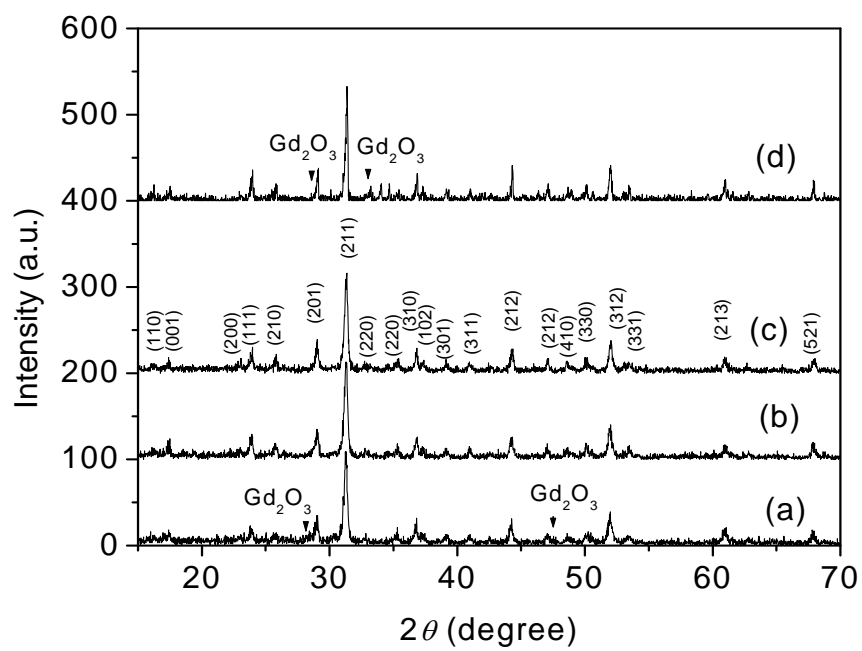


Fig. 1

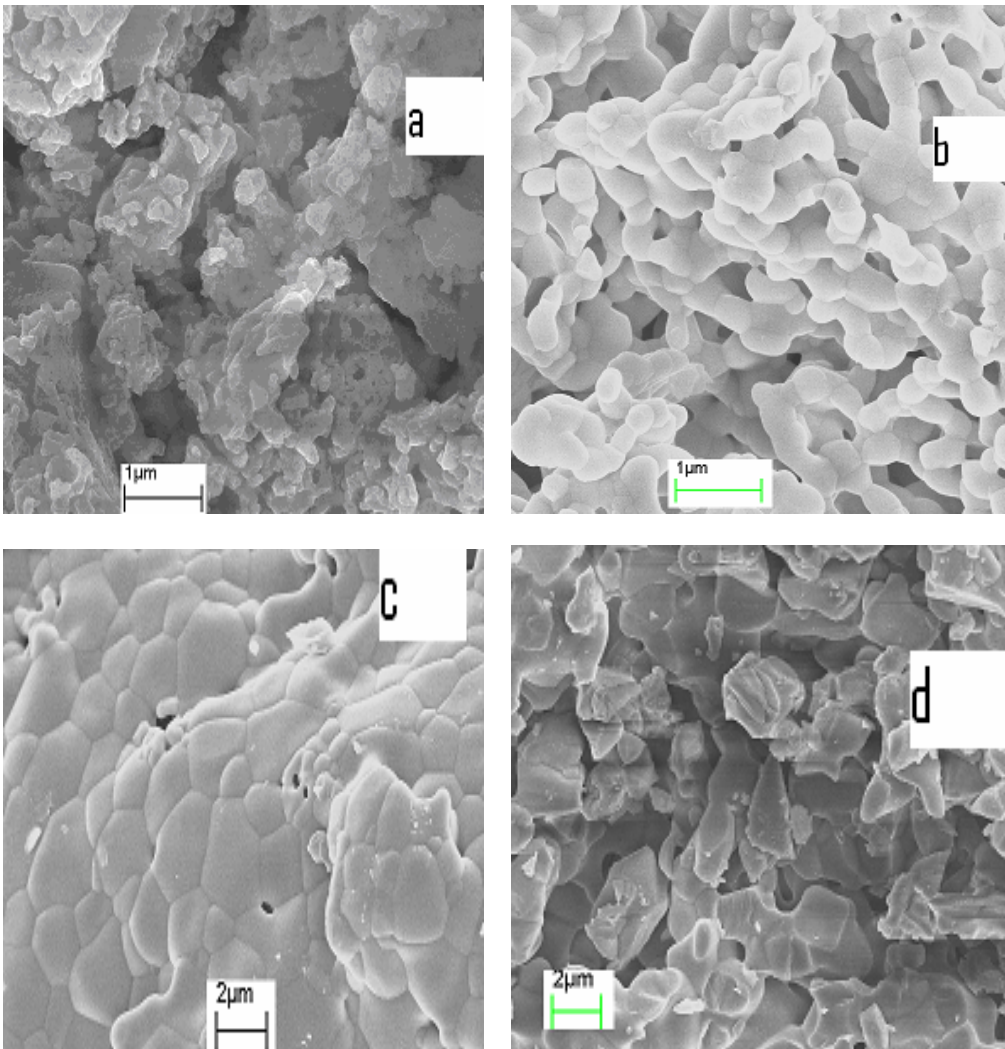


Fig. 2

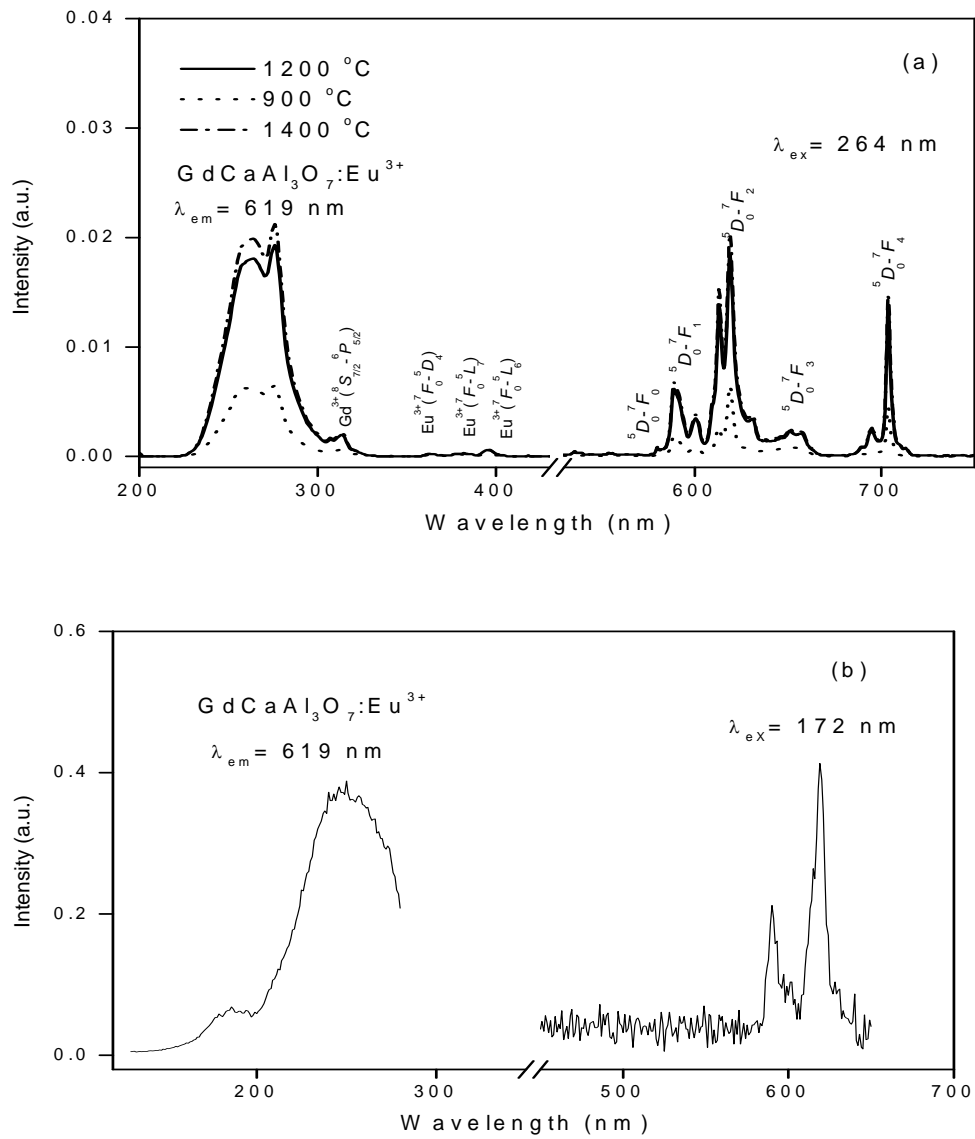


Fig. 3



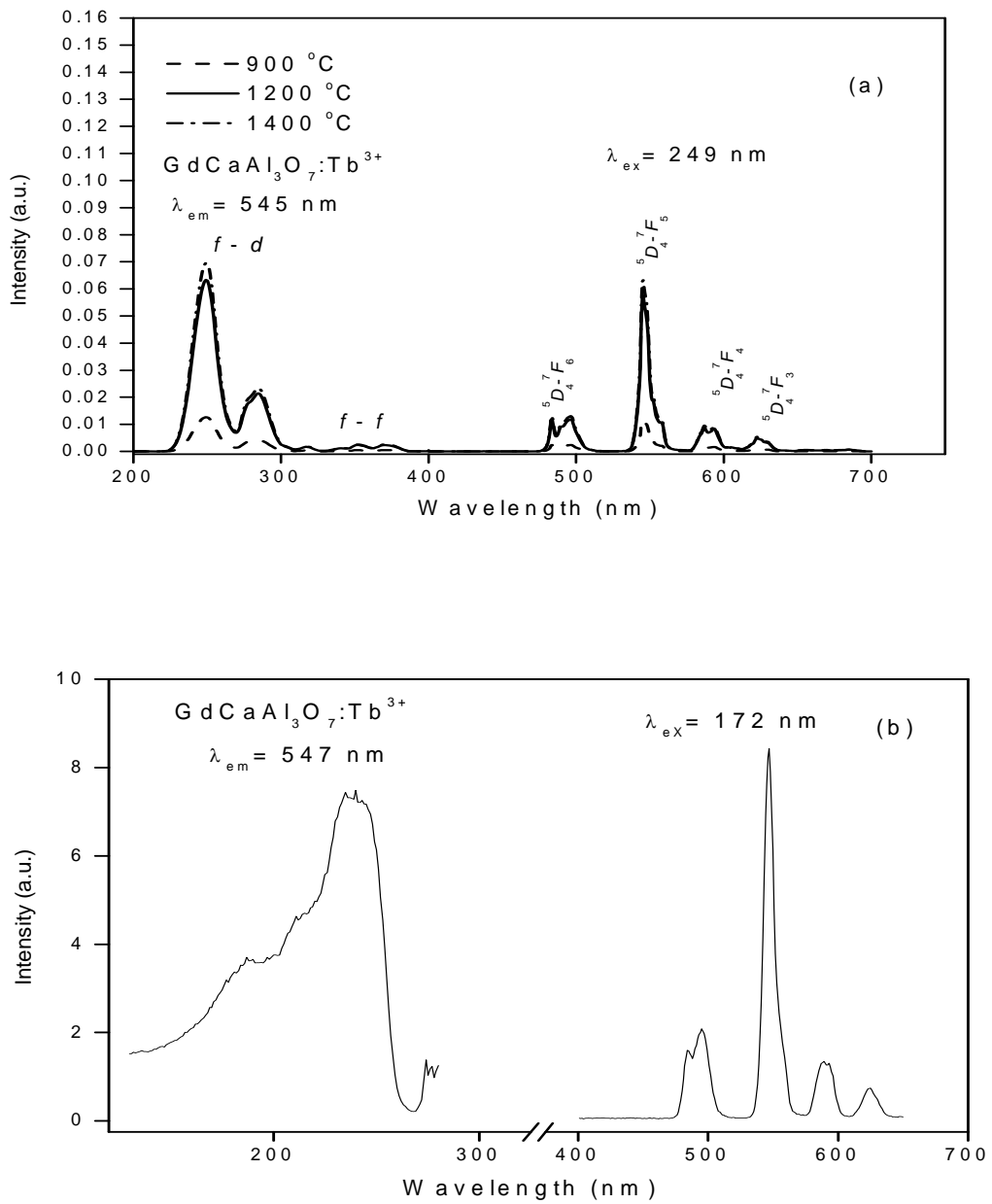


Fig. 4