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Synthesis, vacuum ultraviolet and near ultraviolet-excited luminescent properties of $GdCaAl_3O_7$: RE^{3+} (RE = Eu, Tb)

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Abstract

Vacuum ultraviolet (VUV) excitation and photoluminescent (PL) properties of Eu^{3+} and Tb^{3+} ion-doped aluminate phosphors, $GdCaAl_3O_7$:Eu^{3+} and $GdCaAl_3O_7$:Tb^{3+} have been investigated. X-ray diffraction (XRD) patterns indicate that the phosphor $GdCaAl_3O_7$ forms without impurity phase at 900 °C. Field emission scanning electron microscopy (FE-SEM) images show that the particle size of the phosphor is less than 3 μm. Upon excitation with 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 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 potential candidates as red and green phosphors, respectively, for use in plasma display panel (PDP).

Keywords: $GdCaAl_3O_7$: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 [1–3]. 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. $GdCaAl_3O_7$ is one of complex oxides in the rare earth calcium aluminate family with a general composition of ABC_3O_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 $P42_1m$, in which the distribution of the rare earth ions and Ca^{2+} ions is considered to be close to disordered [5]. The compound structures are formed by five-membered rings constructed from AlO_4^{5-} tetrahedral linked at each corner. The rare earth ions and Ca^{2+} ions are located at the centers of these rings [6]. Recently, long-lasting phosphorescence has been reported in Ce^{3+}-doped $YCaAl_3O_7$ crystals at room temperature [7]. The luminescence properties of Eu^{3+}, Tb^{3+} and Tm^{3+} in strontium–lanthanum gallate $SrLaGa_3O_7$, prepared using the solid-state method, have been systematically examined [6]. Compared to 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

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solution. Citrate sol–gel (CSG) method is a particularly attractive method for the synthesis of the superfine powders [8–10].

In this paper, we report the preparation of $GdCaAl_3O_7$:RE^{3+} phosphors using 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 $GdCaAl_3O_7$:RE^{3+} (RE = Eu, Tb). The results of X-ray diffraction (XRD), field emission scan electron microscopy (FE-SEM) and photoluminescence (PL) of $GdCaAl_3O_7$:RE^{3+} phosphors will be discussed. Finally, conclusion will be drawn.

2. Experiments

2.1. Preparation of $GdCaAl_3O_7$:RE^{3+} (RE = Eu, Tb) phosphor

In the CSG method, Eu_2O_3 (99.99%), Tb_4O_7 (99.99%) and Gd_2O_3 (99.99%) were dissolved in concentrated nitric acid (70%, G.R.) to form 0.5 mol 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. grade) was used to keep the pH of the resulting solution at about 3.0. When a transparent solution was obtained, polyethylene glycol (PEG) was added. The molar ratio of the citric acid to total metal cation ([citric acid]/[M]) and citric acid to PEG ([citric acid]/[PEG]) was 3:1 and 1:1, respectively. After being evaporated for several hours in a 65 °C water-bath, the solution became a yellowish polymeric gel, and the gel was dried at 120 °C for 24 h to obtain the precursor particles. The precursor particles were put into a furnace for pre-calcination at 500 °C for 3 h, and then calcined at the required temperatures from 800 to 1400 °C for 5 h to obtain the phosphor samples.

In the SS method, stoichiometric amount of $CaCO_3$ (A.R. grade), Al_2O_3 (A.R. grade), Gd_2O_3 and Eu_2O_3 were mixed in an agate mortar and then were triturated 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.

2.1.1. Characterization of $GdCaAl_3O_7$:RE^{3+} (RE = Eu, Tb) phosphor

Powder 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 photomulitiplier 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, under high energy physics mode (1.8 GeV, 30–40 mA). A Seya type VUV monochromator (1200 g mm^{-1}) 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 2×10^{-5} mbar. All luminescence spectra were taken at room temperature.

3. Results and discussion

The XRD patterns for the particles prepared by the sol–gel and SS 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, 900 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 $GdCaAl_3O_7$ (JCPDS 50-1808) appear with the existing peaks of Gd_2O_3 (JCPDS 12-797). At 900 °C, however, $GdCaAl_3O_7$ form without impurity phase. When the temperature is increased to 1000 °C, the intensity of the

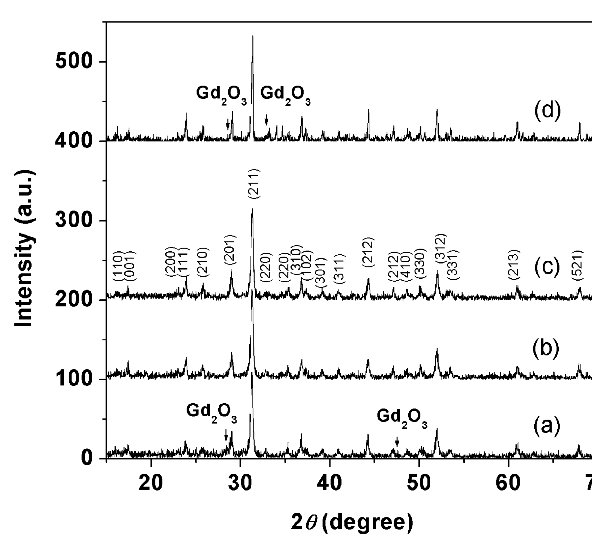

Fig. 1. XRD patterns of the $GdCaAl_3O_7$ prepared by the sol–gel method calcined at (a) 800, (b) 900 and (c) 1000 °C for 5 h, by the solid state method calcined at (d) 1400 °C for 5 h.

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_2O_3.

Fig. 2 shows the FE-SEM images of $GdCaAl_3O_7$ particles calcined at (a) 900 °C, (b) 1200 °C and (c) 1400 °C for 5 h by CSG method, and (d) 1400 °C for 5 h by SS method, respectively. The sample prepared through the CSG method calcined at 900 °C the morphology likes coalesced grains with irregular shape. When temperature increases to 1200 °C, some irregular fringes form and less disordered as compared to Fig. 2(a). When the temperature reaches 1400 °C, a smooth morphology is obtained. There are some holes on the samples although the reasons of the holes are still unclear. As compared with the sol–gel method calcined at 900 °C, clear grains form in the solid-state method with well-defined boundaries.

Fig. 3(a) shows the room temperature UV excitation and emission spectra of the $GdCaAl_3O_7$:Eu^{3+} samples prepared by the CSG method. Upon excitation with 264 nm UV irradiation, all $GdCaAl_3O_7$:Eu^{3+} particles emit intensely the red light corresponding to the Eu^{3+} *f–f* transitions. As the calcination temperature is raised from 900 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 $GdCaAl_3O_7$ doped with Eu^{3+} ions, whereas this band is not found in the undoped $GdCaAl_3O_7$ sample. The $4f^6$ excitation peaks of Eu^{3+} around 400 nm are very weak, which suggests that the high quantum efficiency of the Eu^{3+} luminescence excitation originates from the charge transfer transition of an electron from the oxygen $2p$ state to a Eu^{3+} $4f$ state [11,12]. Upon the UV excitation at the wavelength of 264 nm, the spectra are described

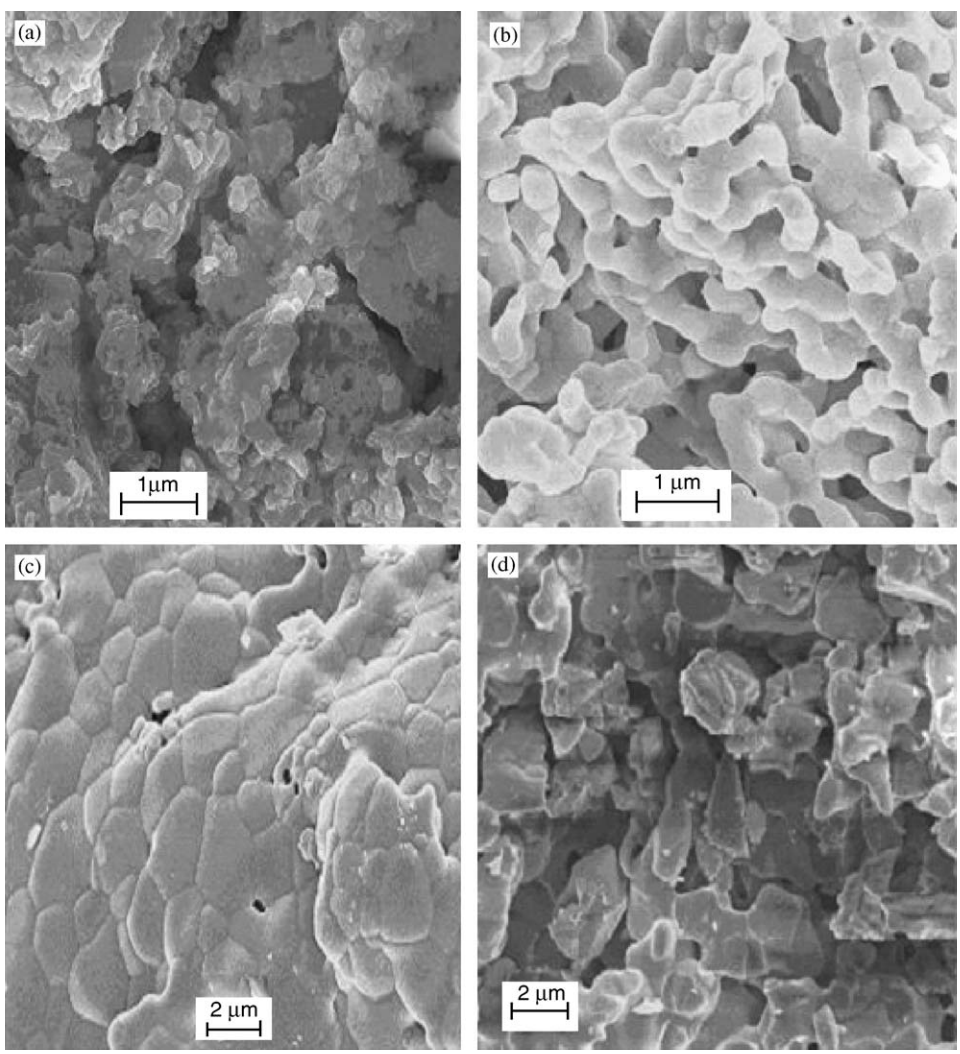

Fig. 2. FE-SEM images of $GdCaAl_3O_7$ prepared by the sol–gel method calcined (a) at 900, (b) at 1200, (c) at 1400 °C for 5 h, by the solid state method calcined at (d) 1400 °C for 5 h.

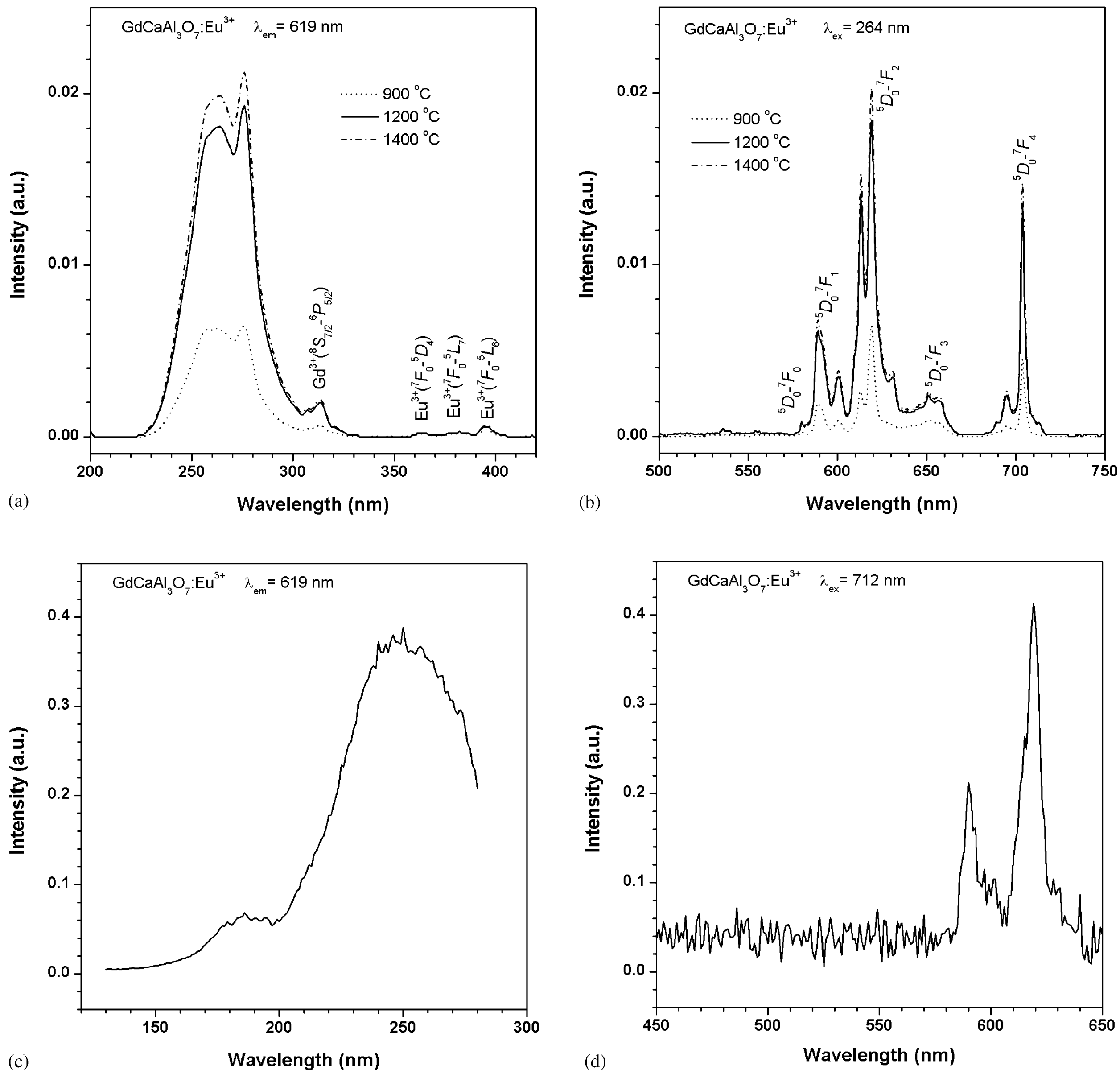

Fig. 3. (a) Room-temperature UV excitation ($\lambda_{em} = 619$ nm) and (b) emission ($\lambda_{ex} = 264$ nm) spectra of GdCaAl$_3$O$_7$: 16 mol %Eu^{3+} samples prepared by the sol–gel method calcined at 900 °C (short dash line), at 1200 °C (solid line), and at 1400 °C (dashed-dot line) for 5 h, (c)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

by the well-known $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, \ldots$) line emissions of the Eu^{3+} ions with the strong emission $J = 2$ at 619 nm (i.e. $^5D_0 \rightarrow {}^7F_2$). Among all cases studied, the phosphors prepared by CSG 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 GdCaAl$_3$O$_7$: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 Eu^{3+} ions occupy the non-inversion symmetric sites. Due to the differences in valence states and ion sizes between Ca^{2+} (99 pm) and Eu^{3+} (95 pm), Eu^{3+} ions substitute the 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 Gd^{3+}, which are possible to be detected due to the $Gd^{3+} \rightarrow Eu^{3+}$ 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 and 250 nm, respectively. The VUV band from 168 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 O^{2-} orbit and the empty states of the $4f^6$ configuration of Eu^{3+} [11]. The emission spectrum of $GdCaAl_3O_7$:Eu^{3+} excited by VUV source at the wavelength of 172 nm is consistent with that excited by UV light. The emission lines of 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 Eu^{3+} ions occupying the non-centrosymmetric sites.

Fig. 4(a) shows the room temperature UV excitation and emission spectra of the $GdCaAl_3O_7$:Tb^{3+} samples

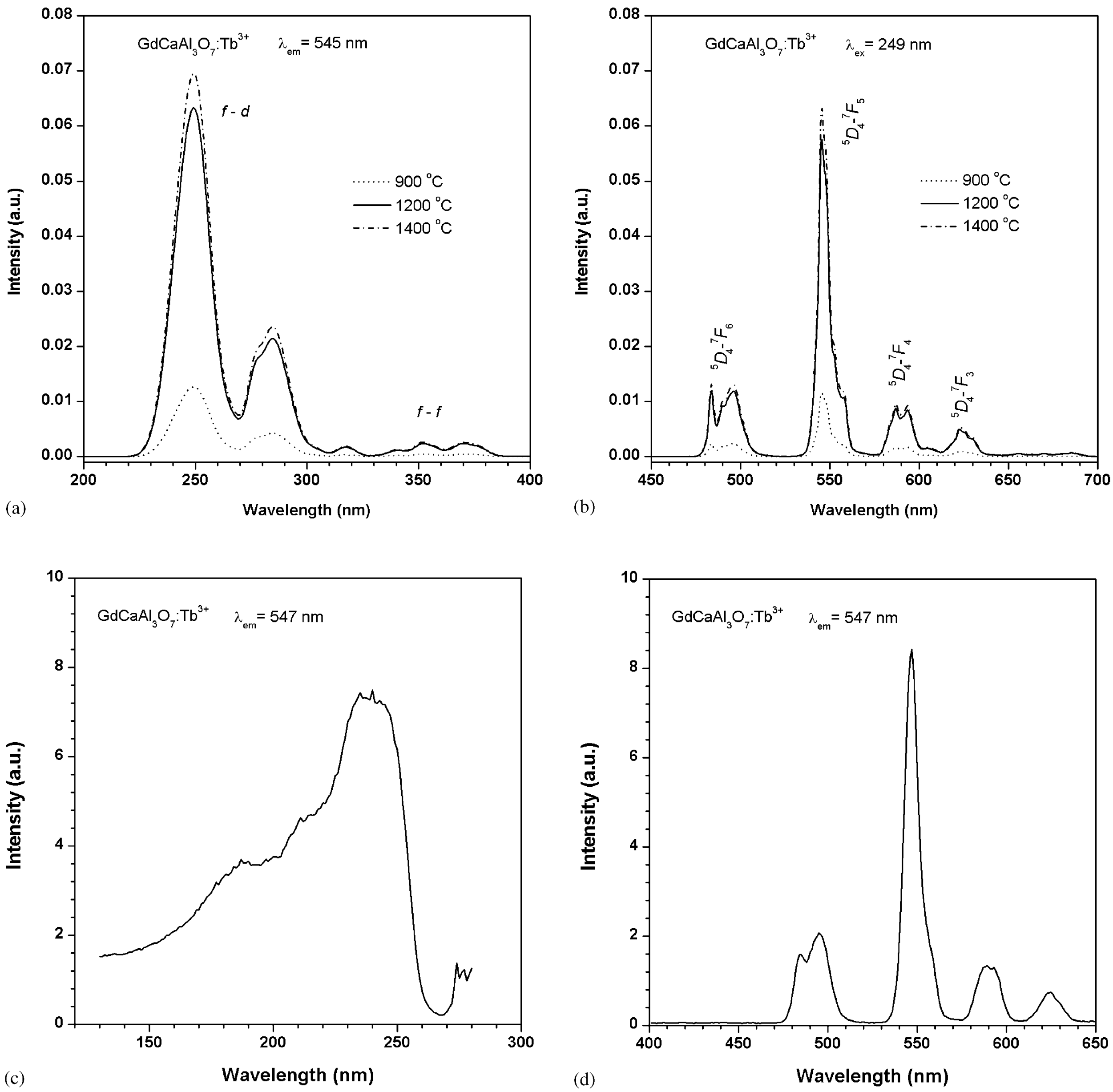

Fig. 4. (a) Room-temperature UV excitation ($\lambda_{em} = 545$ nm) and (b) emission ($\lambda_{ex} = 249$ nm) spectra of $GdCaAl_3O_7$: 14 mol %Tb^{3+} samples prepared by the sol–gel method calcined at 900 °C (short dash line), at 1200 °C (solid line), and at 1400 °C (dashed-dot line) for 5 h, (c) room-temperature VUV excitation ($\lambda_{em} = 547$ nm) and (d) emission ($\lambda_{ex} = 172$ nm) spectra of $GdCaAl_3O_7$: 14 mol %Tb^{3+} samples prepared by the sol–gel method calcined at 1400 °C for 5 h.

prepared by the CSG method. Under the excitation of UV light at 249 nm, all the $GdCaAl_3O_7:Tb^{3+}$ particles emit intense green light due to the Tb^{3+} *f–f* transitions. As the calcination temperature is risen from 900 to 1400 °C, the emission intensity increases with the calcination temperature which is similar to the case of $GdCaAl_3O_7:Eu^{3+}$. 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 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 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 and 240 nm, respectively. The band in the VUV region around 186 nm is the band-gap absorption region of the aluminate in the $GdCaAl_3O_7:Tb^{3+}$. 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 Tb^{3+} ion [16]. There is an energy transfer from host to the Tb^{3+} ion because the 4*f*–5*d* transition absorption of 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 Gd^{3+}, which are possible to be detected due to the $Gd^{3+}\rightarrow Tb^{3+}$ energy transfer. The emission spectrum of $GdCaAl_3O_7:Tb^{3+}$ excited under VUV excitation (172 nm) is also consistent with that excited under UV light. The emission lines of 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).

4. Conclusion

$GdCaAl_3O_7:RE^{3+}$ (RE = Eu, Tb) phosphors have been synthesized using citrate sol–gel and SS 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 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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