

Synthesis and luminescence properties of composite $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7 : \text{Re}^{3+}$ ($\text{Re}^{3+} = \text{Tb}^{3+}, \text{Sm}^{3+}$) phosphors for application white LEDs

Hongjun Dong*

Department of Chemistry, Bai Cheng Normal College, Bai Cheng, 137000, China

Composite $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7 : \text{Re}^{3+}$ ($\text{Re}^{3+} = \text{Tb}^{3+}, \text{Sm}^{3+}$) phosphors were prepared by the SPCS technique, which were studied via XRD, SEM, FT-IR spectra and luminescent spectra. The results show that the crystal lattice structure of them needs slight distortion to improve luminescence properties. They exhibit wider near-UV excitation band around 380 nm. Upon exciting with 380 nm, $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7 : \text{Tb}^{3+}$ shows a strong green-light at 548 nm corresponding to a $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of Tb^{3+} ions, and $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7 : \text{Sm}^{3+}$ presents strong red-light at 604 nm corresponding to a $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ transition of Sm^{3+} ions. The product fired at 900 °C exhibit high quality crystallinity and with a size of that is approximately 1-3 μm . All the above characteristics of the products are beneficial for phosphors for white LEDs.

Key words: SPCS, $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7 : \text{Re}^{3+}$ ($\text{Re}^{3+} = \text{Tb}^{3+}, \text{Sm}^{3+}$), luminescence properties, white LEDs.

Introduction

Electric lamps, color TVs and medical imaging etc have been widely used from the mid-20th century. Since high power output blue indium gallium nitride (GaInN) light-emitting diodes (LEDs) were reported by Nakamura and co-workers [1-2], white LEDs have been developed rapidly. After nitride and phosphide LEDs gave line three primary colors of light, the study of white LEDs has surpassed that of incandescent and fluorescent lamps, due to the advantages of high brightness, high reliability, low electric consumption, long lifetime and environmentally friendly characteristics [3-6]. For these reasons, a focus of investigation has become exploring the preparation of superior phosphors meeting the requirements for wide application of white LEDs. The appropriate phosphors for near-UV white LEDs must show a stronger and broader absorption band around 400 nm. It is well known that Tb^{3+} and Sm^{3+} ions present stronger absorption around 380 nm. When the host compound is doped by rare earth ions, the sublattice structure around luminescent center ions will be somewhat distorted. Consequently, the spectral lines of rare earth ions are expected to be broadened. Recently, most attention mainly concentrates on red $\text{Y}_2\text{O}_3 : \text{Eu}^{3+}$ and green $\text{ZnS} : \text{Cu}^+/\text{Al}^{3+}$ phosphors etc. However, the efficiency and lifetime of the traditionally applied $\text{Y}_2\text{O}_3 : \text{Eu}^{3+}$ phosphor is much lower compared to that of the green and blue phosphors. In addition, sulfide phosphors are unstable and are accompanied with the released of harmful sulfide gas [7-8].

Aluminates are good candidate as phosphor host materials

and are widely applied because of their high quantum efficiency, good stability, high quenching temperature, anti-radiation, being of low cost, pollution-free, nontoxic etc. [9]. Tb^{3+} or Sm^{3+} doped composite calcium aluminate phosphors have rarely been investigated, are usually prepared by a traditional solid-state reactive method, whose synthesis temperature is high. Additionally, the products display larger particle sizes and more serious agglomeration, and require taking a long time to crush in order to adapt to the requirements applying to white LEDs. On the other hand, the crystal shapes of the phosphor particles are seriously damaged and the luminescent intensity obviously reduced. Whereas, the self-propagating combustion synthesis (SPCS) technique possesses a fast reaction, at a low temperature, saving energy etc. giving evident advantages [10-12]. In particular, the products present loose powders, with small particle sizes, large specific surface areas, effective crystallization and easy crushings. It has been proved that the SPCS technique is regarded as one of the most promising synthesis methods. In this paper, we report the luminescence properties of Tb^{3+} or Sm^{3+} doped composite $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7$ prepared by the SPCS technique.

Experimental

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (15.0054g, A.R.), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (2.7771g, A.R.), Tb_4O_7 (0.0299g, 99.9%) and Sm_2O_3 (0.0279g, 99.9%) were exactly weighted. Tb_4O_7 or Sm_2O_3 was put in 250 ml beaker and dissolved using a little concentrated HNO_3 (A.R.), then adding $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{CO}(\text{NH}_2)_2$ (A.R.) were added and the appropriate amount of distilled water. The solution was stirred and heated until the solution was evaporated to become viscous. Subsequently, the beaker was put in a muffle furnace at 500 °C. After a few

*Corresponding author:
Tel : +86-436-3273060
Fax: +86-436-3237942
E-mail: donghongjun6698@yahoo.com.cn

minutes, the solution boiled and underwent dehydration, decomposition, with swelling and frothing, following combustion. This combustion process resulted in ruptured foams with a flame and glowed to incandescence. A foamy, voluminous and amorphous precursor was obtained after five minutes. The precursor was later transferred into a corundum crucible and calcined in a muffle furnace at 900 for 6h. A white product was obtained.

The X-ray powder diffraction (XRD) patterns of the products were carried out with a Rigaku Dmax-2200 powder diffractometer ($\text{Cu K}\alpha_1 = 1.54056 \times 10^{-10} \text{ m}$, scanning speed $6^\circ/\text{minute}$, scanning 2θ range $3\text{-}80^\circ$ with steps of 0.02°). Fourier transform infrared (FT-IR) absorption spectra were recorded on a Nicolet 360 FT-IR spectrometer using KBr pellets in the range of $4000\text{-}400 \text{ cm}^{-1}$. The scanning electron microscopy (SEM) was performed on a Hitachi S-3000N. Excitation and emission spectra were measured by a Hitachi F4500 fluorospectrophotometer (EX slit 2.5 nm /EM slit 2.5 nm , scanning speed $12000 \text{ nm}/\text{minute}$). All the measurements were performed at room temperature.

Results and Discussion

Fig. 1 shows the XRD pattern of the $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7 : \text{Tb}^{3+}$ phosphor, which presents that two types X-ray diffraction peaks of aluminate crystal phases that are CaAl_2O_4 and CaAl_4O_7 . the diffraction intensities of CaAl_4O_7 peaks (the peaks are marked using the symbol $\blacktriangledown$) are stronger than from CaAl_2O_4 (the peaks marked using the symbol $\blacklozenge$), which indicates that raw material produced were CaAl_4O_7 with a quantity of CaAl_2O_4 . However, the relative intensity of the main diffraction peaks from them show on evident change, which indicates that crystal lattice becomes distorted when Ca^{2+} ions are non-equivalently replaced by Tb^{3+} doped into $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7$. This will affect the crystal field at the Ca^{2+} sites, consequently, cause a change of luminescent properties. FT-IR spectra of $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7 : \text{Tb}^{3+}$ and $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7 : \text{Sm}^{3+}$ phosphors are displayed in Fig. 2. We believe that the structure of $\text{CaAl}_2\text{O}_4\text{-}$

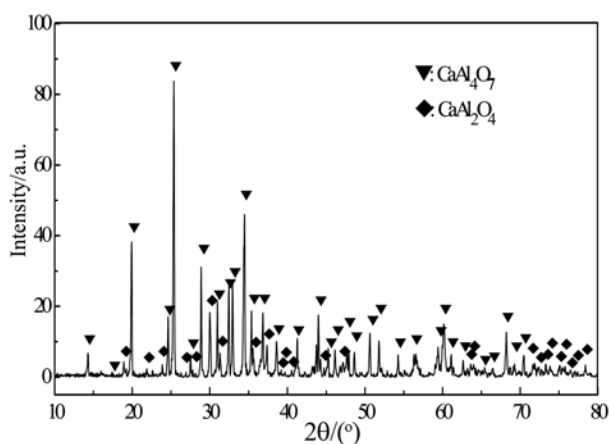


Fig. 1. XRD pattern of the $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7 : \text{Tb}^{3+}$ phosphor.

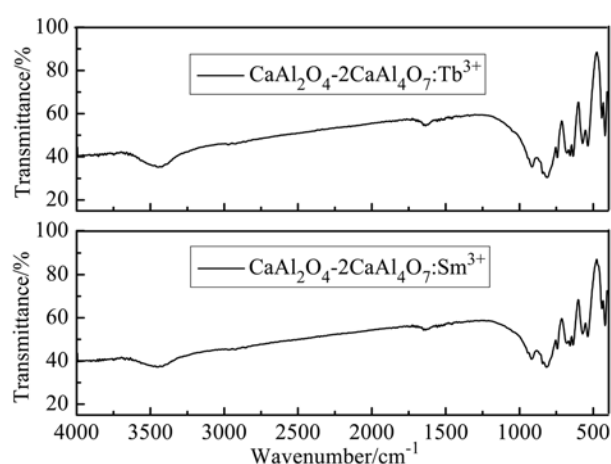


Fig. 2. FT-IR spectra of the $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7 : \text{Tb}^{3+}$ and the $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7 : \text{Sm}^{3+}$ phosphors.

$2\text{CaAl}_4\text{O}_7 : \text{Sm}^{3+}$ is similar to $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7 : \text{Tb}^{3+}$ due to the similar FT-IR spectra of them, although a XRD of $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7 : \text{Sm}^{3+}$ is not measured. The absorption bands around 1550 cm^{-1} and 3450 cm^{-1} belong to vibration absorption from CO_3^{2-} and OH^- groups, respectively, because of the CO_2 and H_2O existing in the air.

Fig. 3 shows the excitation and emission spectra of the $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7 : \text{Tb}^{3+}$ phosphor. The excitation spectrum was obtained by monitoring the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of Tb^{3+} ions (scanning wavelength 548 nm), whose excitation peaks that are located in the $200\text{-}300 \text{ nm}$ result from the well-known $4\text{f}^8\text{-}4\text{f}^75\text{d}^1$ transition absorption of Tb^{3+} ions. This is easily excited by a lower energy because 4f^7 possesses a stable half-filled electronic configuration. According to the Reisfeld and Jørgensen investigation, The ^7D energy level of $4\text{f}^7 \rightarrow 5\text{d}^1$ configuration displays more obvious coulomb exchange interaction than the ^9D of that. Thereby, the transition absorption of $^7\text{F}_6(4\text{f}^8) \rightarrow ^7\text{D}(4\text{f}^75\text{d}^1)$ is relatively located in the higher energy region by contrast with $^7\text{F}_6(4\text{f}^8) \rightarrow ^9\text{D}(4\text{f}^75\text{d}^1)$ [13]. The excitation peak at 250 nm maybe comes from $^7\text{F}_6 \rightarrow ^7\text{D}$, correspondingly, that at

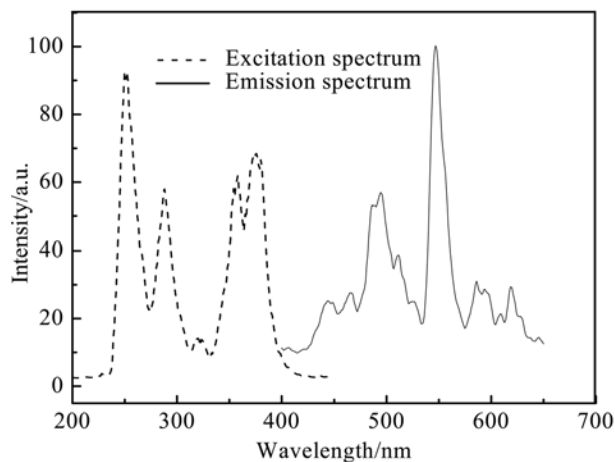


Fig. 3. Excitation and emission spectrum of the $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7 : \text{Tb}^{3+}$ phosphor.

288 nm maybe comes from ${}^7F_6 \rightarrow {}^9D$. This phenomenon is similar to the excitation characteristics of Tb^{3+} ions in the zeolite. Another three excitation peaks in the 300–400 nm near-UV excitation region relate to the 4f–4f transition absorption of Tb^{3+} ions, which respectively are attributed to ${}^7F_6 \rightarrow {}^5D_0$, ${}^7F_6 \rightarrow {}^5L_{10}$ and ${}^7F_6 \rightarrow {}^5L_9$ at 320 nm, 358 nm and 376 nm. The emission spectrum of $CaAl_2O_4-2CaAl_4O_7 : Tb^{3+}$ is excited by 380 nm wavelength irradiation. In general, the common linearly characteristic spectra of the Tb^{3+} doped phosphors are only displayed [14–15], while the emission spectrum of Tb^{3+} ions is broadened in Fig. 3. The emission peaks are attributed to 4f–4f transition of Tb^{3+} ions, which respectively correspond to ${}^5D_3 \rightarrow {}^7F_4$, ${}^5D_3 \rightarrow {}^7F_3$, ${}^5D_4 \rightarrow {}^7F_6$, ${}^5D_4 \rightarrow {}^7F_5$, ${}^5D_4 \rightarrow {}^7F_4$ and ${}^5D_4 \rightarrow {}^7F_3$ at 445 nm, 466 nm, (496 nm, 511 nm), 548 nm, (586, 594 nm) and (618, 624 nm). It is well known that the luminescent spectra of trivalent lanthanide ions in crystals mainly come from two types of electronic transitions that are the 4f–4f and 5d–4f transitions. The former generally shows sharp emission lines, while the latter have a broad band character. In order to eliminate forbidden parity, electronic configurations that are mixed with the opposite parity energy levels are not a charge transfer state (CTS) but the lower self-energy $4f^7 \rightarrow 5d^1$ levels, so the 4f–4f transition are broadened. In addition, the ${}^5D_4 \rightarrow {}^7F_6$ electric dipole transition of Tb^{3+} ions is less sensitively affected by ligand environments than the ${}^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} [16]. Therefore, a magnetic dipole transition ${}^5D_4 \rightarrow {}^7F_5$ of Tb^{3+} is strongest at 548 nm. The $CaAl_2O_4-2CaAl_4O_7 : Tb^{3+}$ phosphor emits green-light under 380 nm near-UV irradiation. The ${}^5D_3 \rightarrow {}^7F_4$ and ${}^5D_3 \rightarrow {}^7F_4$ transition emissions originating from higher excited states are observed, which indicates that the usual cross relaxation effect (${}^5D_3 + {}^7F_6 \rightarrow {}^5D_4 + {}^7F_5$) is not complete.

As can be seen from the emission spectrum of the $CaAl_2O_4-2CaAl_4O_7 : Sm^{3+}$ phosphor that is excited by 380 nm irradiation in Fig. 4, there is a broad band emission at 493 nm, besides the four emission peaks arising from the 4f–4f transition of Sm^{3+} ions that respectively are attributed to ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$, ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$, ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ and ${}^4G_{5/2} \rightarrow {}^6H_{11/2}$ at 568 nm, 604 nm, 654 nm and 713 nm. The emission intensity of the ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition is strongest, so the $CaAl_2O_4-2CaAl_4O_7 : Sm^{3+}$ phosphor emits red-light under near-UV irradiation. In general, the symmetry of luminescent centers in a crystal lattice is determined by the relative strength of the electric dipole transition and magnetic dipole transition. May and co-workers believe that the ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$ transition is due to its predominant magnetic dipole character. On the other hand, the ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition principally presents an electric dipole character, although a magnetic dipole transition is allowed. However, the hypersensitive ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition is forbidden by the magnetic dipole, in contrast, allowed by a forced electric dipole [17]. The ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition occurring in the emission peaks indicates that the symmetry of the $CaAl_2O_4-2CaAl_4O_7 : Sm^{3+}$ structure is lower. Namely, a portion of the Sm^{3+} ions are located at a non-symmetric

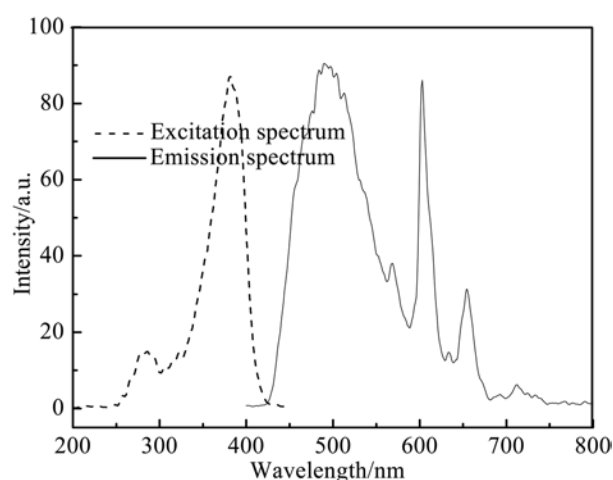


Fig. 4. Excitation and emission spectrum of the $CaAl_2O_4-2CaAl_4O_7 : Sm^{3+}$ phosphor.

centered lattice. Tamura reports that Sm^{3+} ions, if mainly occupy a non-symmetric centered lattice, produce a typical emission around 650 nm, by contrast, if they mainly occupy a symmetric centered lattice, produce a typical emission around 602 nm [18]. The ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition is stronger than the ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$, which indicates that Sm^{3+} ions mainly occupy a symmetric centered lattice in $CaAl_2O_4-2CaAl_4O_7 : Sm^{3+}$. The excitation spectra of $CaAl_2O_4-2CaAl_4O_7 : Sm^{3+}$ which is measured by monitoring the ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition of Tb^{3+} ions (wavelength of irradiation 604 nm), whose strongest excitation peak at 380 nm originates from the 4f–4f (${}^6H_{5/2} \rightarrow {}^4D_{1/2}$ or ${}^6H_{5/2} \rightarrow {}^6P_{7/2}$) transition absorption of Sm^{3+} ions. The relatively weaker excitation peak at 285 nm maybe results from the charge transfer state (CTS) of $Sm^{3+}-O^{2-}$.

In the application of phosphors for white LEDs, the size distribution and shape of the particles are very important. Fig. 5 presents the size and morphology of the green $CaAl_2O_4-2CaAl_4O_7 : Tb^{3+}$ and the red $CaAl_2O_4-2CaAl_4O_7 :$

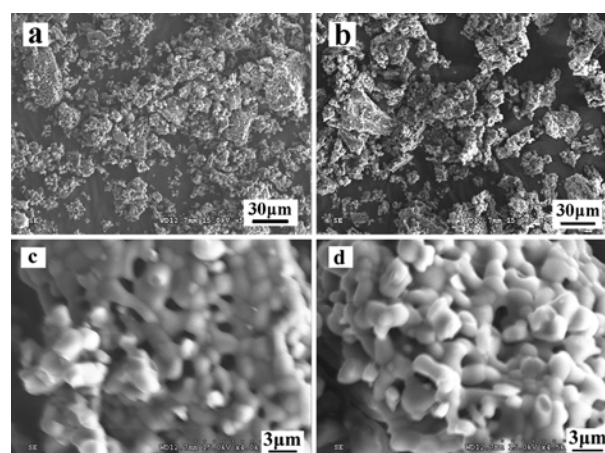


Fig. 5. SEM micrographs of $CaAl_2O_4-2CaAl_4O_7 : Re^{3+}$ (Re = Tb, Sm), a : $CaAl_2O_4-2CaAl_4O_7 : Tb^{3+}$, b : $CaAl_2O_4-2CaAl_4O_7 : Sm^{3+}$, c : $CaAl_2O_4-2CaAl_4O_7 : Tb^{3+}$ (higher magnification), d : $CaAl_2O_4-2CaAl_4O_7 : Sm^{3+}$ (higher magnification).

Sm^{3+} phosphors. Both $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7\text{: Tb}^{3+}$ Fig. 5(a) and $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7\text{: Sm}^{3+}$ Fig. 5(b) show that the products present have an irregular bulky shape distribution and are slightly agglomerated, which are due to calcination of the precursors at 900 °C. Correspondingly, both $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7\text{: Tb}^{3+}$ Fig. 5(c) and $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7\text{: Sm}^{3+}$ Fig. 5(d) show the product surfaces are smooth, dense, with high crystallinity and present a honeycomb shape. The particles adhere to each other to give approximate ellipsoidal particles. A lot of gases are released in the SPCS process due to the burning of urea, which holds back formation of the massive products. So crystal nuclei grow along the directions for the formation of the smooth spherical shape containing low surface energies [19]. This investigation indicates that spherical surfaces contribute to enhancing the luminescent intensity. The products fired at 900 °C exhibit high quality crystallinity and a size approximately is 1-3 μm , which are suitable for the requirements of phosphors for white LEDs.

Conclusions

Composite $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7\text{: Re}^{3+}$ ($\text{Re}^{3+} = \text{Tb}^{3+}, \text{Sm}^{3+}$) phosphors were prepared for the first time by the SPCS technique. The synthesis temperature was decreased significantly compared to the conventional solid-state reactive method (starting oxides CaO and Al_2O_3). A small quantity of dopant Tb^{3+} or Sm^{3+} ions give a slight distortion to the crystal lattice structure of $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7$. The products show the particle sizes of approximately 1-3 μm dimension and high quality crystallinity. The composite $\text{CaAl}_2\text{O}_4\text{-}2\text{CaAl}_4\text{O}_7$ is a good type of candidate as a host material. The luminescence properties of them indicate that they possess a wider near-UV excitation band around 380 nm and emit green-light and red-light under near-UV irradiation. All the above mentioned results are beneficial to the requirements of the phosphors for white LEDs.

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