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Synthesis and luminescence of sub-micron sized $Ca_3Sc_2Si_3O_{12}$:Ce green phosphors for white light-emitting diode and field-emission display applications

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ABSTRACT

$Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ phosphors with sub-micron size were successfully synthesized by a gel-combustion method. The crystal structure and morphology of the phosphors and their photoluminescence were investigated. The results indicate that the pure phase of $Ca_3Sc_2Si_3O_{12}$ can be obtained at 1100 °C of firing temperature. The particles of phosphor are basically spherical in shape with the mean size less than 1 μm. The grain of the phosphor grows up gradually with the increasing of the firing temperature. The excitation spectrum shows a broad and strong absorption band centered around 450 nm, compatible with the excited wavelength of commercial blue light-emitting diode (LED) for white LED lighting. Bright green-emission located at 505 nm is observed and the intensity of the green-emission increases with the increase of firing temperature. Additionally, under low-voltage (2.5 kV) excitation of electron beam, bright green cathodoluminescence (CL) is also observed, which is attributed to the characteristic emission from Ce^{3+}. Our work suggests that $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ phosphors are promising for both white LED and field-emission display applications.

1. Introduction

White light-emitting diodes (LEDs) are expected to be useful as environmentally friendly lighting systems for energy saving, long lifetime and safety [1–3]. Recently, white LEDs have also been applied as back-light units in liquid crystal displays and other types of displays. The most widely used white LED consists of a high performance InGaN LED and YAG:Ce yellow phosphor [4–5]. However, this type of white LED lacks red and green light, which causes high color temperature and low color rendering index. These problems could be solved by mixing green and red phosphors instead of single $YAG:Ce^{3+}$ phosphor.

Shimomura and Kijima [6] reported to synthesize a novel green phosphor of $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ with high quantum efficiency and thermal stability by solid-state reaction method [7,8]. A single phase of $Ca_3Sc_2Si_3O_{12}$ phosphor has been synthesized by gel-combustion method in our previous work [9]. The gel-combustion method has lots of advantages such as a usage of inexpensive precursors, facile operation, low firing temperature, energy efficiency and small particles with narrow size distribution in the obtained product. In addition to the photoluminescence (PL), in our earlier reports the cathodoluminescence (CL) and electroluminescence (EL) properties of materials were found to be essential for field-emission displays (FEDs) and EL displays, respectively, [10–12] which are promising emissive displays realizing high resolution and low consumption of electric power. Low-voltage CL properties of $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ have not been reported so far. Phosphors used in FEDs require several new properties, such as high CL efficiency under low excitation voltage (≤5 kV) and specific morphology and surface conditions [13]. In this work, $Ca_3Sc_2Si_3O_{12}$:Ce green phosphor with sub-micron size and basically spherical grain was successfully synthesized by adjusting the firing temperature and using H_3BO_3 flux in gel-combustion method. The phase structure and morphology of the phosphors at different firing temperatures were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The PL, lifetime and CL characteristics of the phosphors were also investigated.

2. Experimental

2.1. Raw materials

Tetraethoxysilane (TEOS 98.5%, International Laboratory, USA), H_3BO_3 (98.5%, Advanced Technology Co., Ltd.), $Ca(NO_3)_2{\cdot}4H_2O$ (98.5%, Advanced Technology Co., Ltd.), $Ce(NO_3)_2{\cdot}6H_2O$ (99.9%, International Laboratory, USA), anhydrous ethanol (99.8%, Advanced Technology Co., Ltd.), Sc_2O_3 (99.99%, Shanghai Yuelong New Materials Co., Ltd.) and urea (99.0%, Farco Chemical) were used as starting materials.

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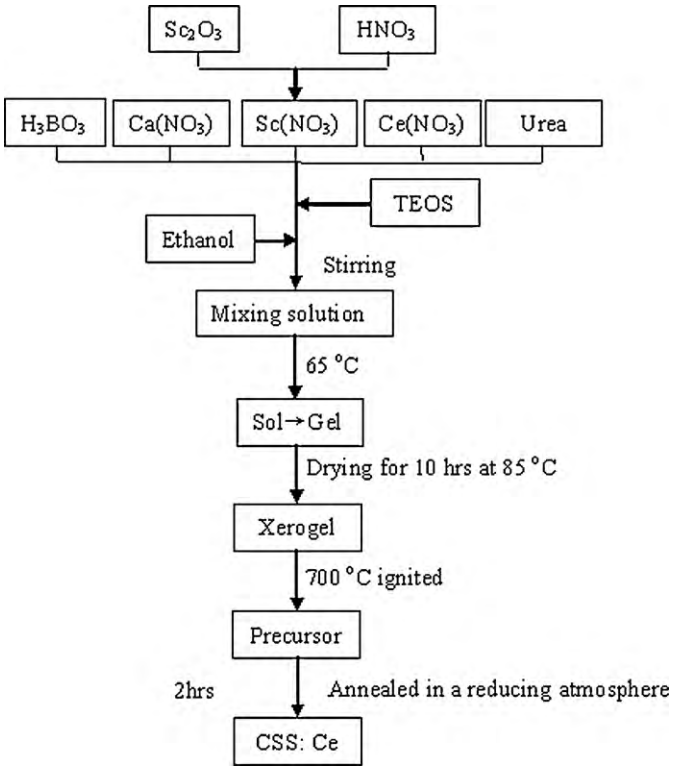

Fig. 1. The synthetic procedure of $Ca_3Sc_2Si_3O_{12}$:Ce green phosphor.

2.2. Preparation of phosphor powder

The synthetic procedure of $Ca_3Sc_2Si_3O_{12}$:Ce green phosphor by a gel-combustion method is presented in Fig. 1. Firstly, Sc_2O_3 was dissolved in an appropriate nitric acid to form nitrate solution. Then, stoichiometric $Ca(NO_3)_2{\cdot}4H_2O$, $Ce(NO_3)_2{\cdot}6H_2O$, and $Sc(NO_3)_3$ solutions were mixed in a crucible. Appropriate amounts of TEOS, anhydrous ethanol and H_3BO_3 were added into the crucible and continuously stirred for half an hour. The resulted solution was heated at 65 °C for 10 h in a dry oven so that superfluous water was evaporated, gradually polymerized into a transparent gel, and dried at 85 °C to obtain xerogel. The xerogel was ignited at 700 °C in a muffle furnace. The xerogel was simultaneously burnt in a self-propagating combustion manner until the dry sponge sample so-called precursor was formed. Finally, the precursor was fired in a muffle furnace in carbon monoxide mixing gas produced by active carbon at high temperature at different temperature for 2 h to obtain green-emitting phosphor of $Ca_3Sc_2Si_3O_{12}$:Ce^{3+}.

2.3. Characterization of phosphor powders

The crystal structure determination of the powder was carried out using a Bruker D8 X-ray diffractometer operating at 40 kV and 40 mA with CuKα radiation. The PL lifetime, excitation, and emission spectra were obtained with a FLS920P Edinburgh Instruments apparatus.

3. Results and discussion

3.1. X-ray diffraction analysis

XRD analysis was used to determine the crystal structure and morphology of the phosphors. As shown in Fig. 2, obvious diffraction peaks corresponding to $Ca_3Sc_2Si_3O_{12}$ phase were observed in the samples fired at 900 °C. The impurity phase in the XRD patterns of the phosphor could be SiO_2. The existence of the impurity in Fig. 2 is due to the use of low processing temperature at which the pure phase of $Ca_3Sc_2Si_3O_{12}$ crystal cannot be formed completely. As the firing temperature increases, the intensity of diffraction peak increases, suggesting the improved crystallization of the material. An improvement in crystallinity is in favor of an enhancement of PL intensity from the phosphor as shown in later section. The XRD pattern of the sample fired at 1100 °C agrees with the powder data of $Ca_3Sc_2Si_3O_{12}$ with a garnet-type structure (space group *Ia3d*, cubic system) in PDF card (No. 72-1969) [14]. Compared with other synthesis methods, pure $Ca_3Sc_2Si_3O_{12}$ phase can be obtained at a relatively low temperature of 1100 °C by gel-combustion method. Possible mechanism behind the process at low temperature is related to the use of metal nitrates and TEOS rather than oxides of the raw materials in our gel-combustion method.

In the gel-combustion method, a gel network can be formed during the hydrolysis of TEOS as below.

$$n\mathrm{Si(OC_2H_5)_4} + 2n\mathrm{H_2O} \rightarrow (\mathrm{-O-Si-O-})_n + 4n\mathrm{C_2H_5OH} \quad (1)$$

The metal ions in the solution could also be involved in this Si–O gel network, and consequently an atomic-scale mixing is preserved. Therefore, the $Ca_3Sc_2Si_3O_{12}$ compound obtained by gel-combustion method is single phase and no impurity phase such as Sc_2O_3 was observed as shown in Fig. 2.

The SEM images as shown in Fig. 3 illustrate morphology of the samples fired at different temperatures. It can be seen from Fig. 3(a) that the particles of the sample fired at 900 °C are fine and uniform, with an average grain size of 200 nm. It can be seen that grains tend to agglomerate at 1000 °C. With further increase in firing temperature, the grains of the sample grow gradually. The particles of the sample fired at 1100 °C are dispersing well. The average size of grains is less than 1 μm. Phosphors with narrow size distribution and non-agglomeration can make better slurry property and more uniform distribution of light intensity. Furthermore, phosphor particles with spherical shape can decrease the scattering of light and make high packing densities [15,16]. With further increasing of firing temperature or keeping more hours at high temperature, the product becomes hard and needs further grinding, which can make much deficiencies. Accordingly, the luminescence intensity of the phosphor becomes weaker.

The possible mechanism to obtain sub-micron sized phosphor here may be due to a large volume of decomposed gasses during the exothermic redox reaction between metal nitrate and urea as an oxidizing agent and reducing agent, respectively. In addition, the interconnected particles could be broken with the decomposed gasses. On the other hand, low temperature process in gel-combustion method would be helpful to restrain the aggregation of the particles in the phosphors.

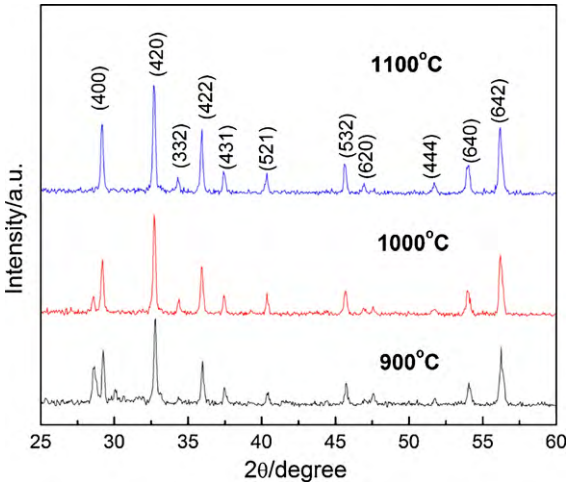

Fig. 2. X-ray diffraction patterns of the samples fired at different temperatures.