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Facile synthesis of Ca-α-SiAlON:Eu^{2+} phosphor by the microwave sintering method and its photoluminescence properties

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Pure Ca-α-SiAlON:Eu^{2+} was synthesized by microwave sintering method at a relatively low temperature of 1550°C. Photoluminescence intensity of the resultant phosphor was higher than those of the samples synthesized by conventional gas-pressure sintering technique at 1750°C. When it was excited at 450 nm, the as-prepared yellow Ca-α-SiAlON:Eu^{2+} sample had an external quantum efficiency of 42%, comparable to the sample synthesized at 1750°C under 0.5 MPa N_2 gas pressure by the GPS method reported in reference. The experimental results demonstrated that the microwave sintering method was also an interesting approach for synthesizing nitride phosphors, which promises lower firing temperature than those by carbothermal reduction and nitridation (CRN) methods, higher heating rate and shorter duration time compared with those by gas-pressure sintering.

nitride, phosphor, microwave sintering, SiAlON, solid-state reaction

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α-SiAlONs are solid solution compounds derived from α-Si_3N_4 with partial replacement of Si^{4+} by Al^{3+} and N^{3-} by O^{2-}, having an overall composition in the formula $M_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ ($x=m/v$, v is the valence of metal M) with M=Li, Ca, Mg, Y, and rare earth [1–3]. The valence balance is achieved by introducing cations M into large interstices available in the network of (Si, Al)–(O, N). As the rare earths can be accommodated in the α-SiAlON lattice, it is a high possibility that they can also act as luminescent centers if the host composition and rare earth concentration are carefully controlled. Ca-α-SiAlON:Eu^{2+} phosphor shows a strong absorption in the UV-visible spectral region and exhibits intense yellow emission in range of 570–600 nm, making it an attractive wavelength-conversion phosphor for white light-emitting diodes (LEDs) when coupled with a blue GaN-based chip [4,5]. Thus, in recent years α-SiAlON has been investigated extensively as a host material for phosphors [4–11].

Generally, Ca-α-SiAlON:Eu^{2+} phosphors are synthesized at some unusual conditions, such as high firing temperature and high nitrogen gas pressure (1750°C, 0.5 MPa). Up to date, three major synthetic methods have been used to synthesize Ca-α-SiAlON:Eu^{2+} phosphors: solid-state reaction [6], gas-reduction nitridation (GRN) [7], and carbothermal reduction and nitridation (CRN) [8]. The gas-pressure sintering (GPS) method is a prevailing method for synthesizing Ca-α-SiAlON:Eu^{2+}, which requires elevated temperature and high nitrogen gas protection, as well as high-purity nitrides as starting materials. GRN and CRN [7,8] methods have been recently attempted to produce the fine or nano-scale phosphor particles at low temperatures. However, both methods are not energy-saving, and have disadvantages of long heating time as well as duration time. Therefore, it is crucial to develop a green and cost-effective method for synthesizing oxynitride/nitride phosphors with controlled particles morphology and outstanding optical features.

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The microwave sintering method is a promising technique in powder manufacture industries, since it offers several advantages to the resultant products over conventional heating methods, including production reliability, energy saving, and low manufacturing cost. During the heating process, the electromagnetic wave can penetrate into materials and heat them owing to the interaction between polarized molecular (or ions) and electromagnetic field, finally resulting in volumetric heating to make it possible to achieve a rapid and uniform heating. In the past decades, the microwave heating method has been widely used for processing and drying solutions [12], sintering ceramics [13], fabricating functional materials [14]. However, to our best knowledge, there are rare reports that conduct researches on microwave sintering of nitride phosphors. In this article, microwave sintering of Eu^{2+}-doped Ca-α-SiAlON phosphor was attempted, and the PL properties of the phosphor were investigated and discussed.

1 Experimental procedure

Eu^{2+}-doped $Ca_{0.3}Eu_{0.7}Si_9Al_3O_1N_{15}$ ($Ca_{(m/2)}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$, $m = 2$, $n = 1$, Eu = 7 mol%) was prepared at 1550°C for 2 h with a constant heating rate of 15°C/min from the starting powders of Si_3N_4 (SN-E10, Ube Industries, Tokyo, Japan), AlN (Type F, Tokuyama Corp., Tokyo, Japan), $CaCO_3$ (99.99%, Aladdin Chemistry Co. Ltd., Shanghai, China) and Eu_2O_3 (99.999%, Aladdin Chemistry Co. Ltd., Shanghai, China) by using the microwave sintering technique (MWS) under an ambient pressure of N_2/H_2 (5%). For comparison, the sample was also prepared by the gas-pressure sintering method (GPS, 1750°C×2 h, 0.5 MPa N_2). For the microwave sintering technique, firstly, we put the mixture powders into BN crucible; and then, put the BN crucible into an attemperator with heating assistant materials; finally, put the attemperator into microwave reaction furnace and sintered it. During the heating process, the electromagnetic wave can penetrate into the mixture raw materials and heat them owing to the interaction between polarized molecular (or ions) and electromagnetic field, resulting in volumetric heating to make it possible to achieve a rapid and uniform heating. This heating mechanism is advantageous due to the following facts: enhanced diffusion process, reduced energy consumption, very rapid heating rates, considerably reduced processing times, decreased sintering temperature, improved physical and mechanical properties, with simplicity and lower environmental hazards.

Phase purity of the resultant samples was analyzed by X-ray powder diffraction (Bruker AXS, D8 Advance) with Cu-Kα radiation. Photoluminescence spectra were recorded at room temperature using a fluorescent spectrophotometer (F-4500, Hitachi Ltd., Tokyo, Japan) with a 150 W Xe-lamp as an excitation source. Particle size distribution was measured by microtrac particle size analyzer (S3500-special, Microtrac Ltd., New York, USA). Powder morphology was observed by field-emission scanning electron microscopy (FESEM, JEOL-840A). Temperature dependent luminescence and the quantum efficiency of the phosphors were measured using a Hamamatsu MPCD-7000 multichannel photo detector with a 200 W Xe-lamp as an excitation source.

2 Results and discussion

Figure 1 presents the XRD patterns of Ca-α-SiAlON:Eu^{2+} synthesized by MWS and GPS techniques. It can be seen that the pure Ca-α-SiAlON phase was obtained for the samples synthesized by MWS at 1550°C and by GPS at 1750°C (see JCPDS card No. 42-0252), whereas unreacted Si_3N_4 was still remained in the sample prepared by the GPS method at 1550°C. It indicates that the microwave heating enables to reduce the synthesis temperature, avoiding the sintering-like glomeration phenomenon that is usually observed in GPS samples. The much lower synthesis temperature applied in the microwave heating method may be due to the fact that the microwave-irradiated processing gives rise to an additional driving force (named ponderomotive force) for mass transport beside driving forces provided by the matter concentration gradient and temperature gradient, which has been identified by Booske et al. [15], Freeman et al. [16] and Rybakov et al. [17] through experimental evidence and numerical simulation in the study of ionic system under microwave radiation. They claimed that the ponderomotive force could pump defects to the crystal boundary and promote mass transport in a long-distance into the crystal interior through enhanced diffusion kinetics. It is believed that, although the ponderomotive force (less than 0.1 Pa) is not comparable to macroscale mechanical stresses always applied during ceramics sintering, it is directly applied to the dangling bonds and mobile atoms/molecules in

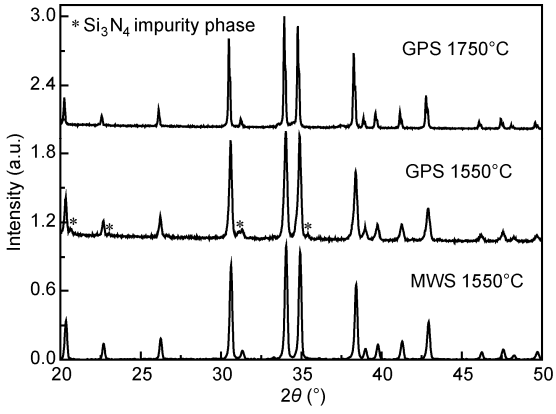

Figure 1 X-ray diffraction (XRD) patterns of Ca-α-SiAlON:Eu^{2+} fired at 1550°C by microwave method and gas-pressure sintering technique at 1550°C and 1750°C, respectively.

between interfaces or on the surfaces of reactants. Therefore, the ponderomotive force during the process of synthesizing Ca-α-SiAlON:Eu^{2+} by microwave sintering method may enhance the mobility of lattice defects (vacancies and substitution defects) that are inherent in the raw materials or are originated from the substitution of Ca^{2+} by Eu^{2+} in the crystal structure. The lattice defects then move to the grain boundary, which accelerate the mass transport. This can be further explained from a kinetic point of view for accelerated formation of critical nuclei during solid state reaction according to classical homogeneous nucleation theory [18]. The phase and microstructural evolutions of nitride materials under microwave radiations are under investigation and will be discussed elsewhere.

Photoluminescence properties of both Ca-α-SiAlON:Eu^{2+} phosphors synthesized by the MWS method (MW-sample, 1550°C) and the GPS method (GPS-sample, 1750°C) were measured, as shown in Figure 2. Note that, the MWS-sample has stronger excitation and emission intensities than those of the GPS-sample. The higher emission intensity may be attributable to the fine particle size and small particle size distribution of the product prepared by the MWS method. The existence of the unique athermal effect under the ponderomotive force during the microwave radiation can enhance the solid-state ionic mass transport, increase the kinetic rate in this solid-state reaction, and finally promote the new phase formation as well as the following Ostwald ripening process [19]. These contribute to a low firing temperature of 1550°C of the MW-sample which was prepared under the reducing atmosphere of 5%H_2/95%N_2. This lower sintering temperature and special microwave heating mechanism are advantage to obtain fine particle size and small particle size distribution (Figure 3). It can be seen that the particle sizes (d_{50}) of the sample prepared using MWS (Figure 3(a)) and GPS (Figure 3(b)) are about 2.8 and 3.3 μm, respectively. Moreover, the particle size distribution in the powder synthesized via MWS meth

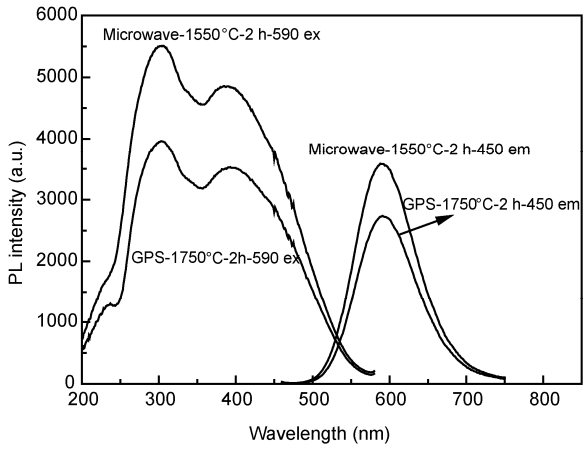

Figure 2 Photoluminescence spectra of Ca-α-SiAlON:Eu^{2+} samples synthesized by the microwave sintering method (1550°C×2 h) and the gas-pressure sintering technique (1750°C×2 h).

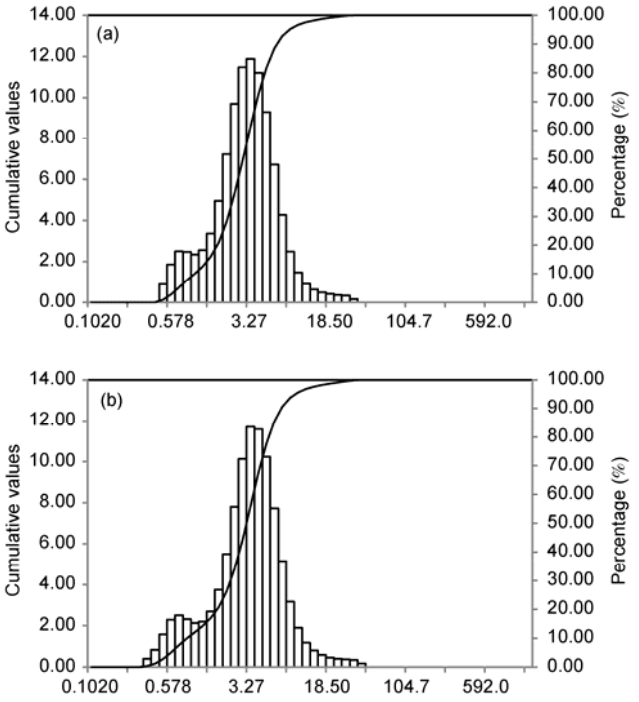

Figure 3 Particle size distributions of the samples prepared by MWS (a) and GPS (b).

od is relatively narrower than that via GPS technique. This would enhance the packing density of the powders and reduce the light scattering, finally causing the increase of the luminescence intensity, by comparing with the phosphor with large particle size synthesized by GPS method. This phenomenon has been proved by Xie et al. [6]. In their study, they synthesized a series of beta-SiAlON:Eu^{2+} phosphors with various z values. They found that beta-SiAlON:Eu^{2+} with higher z values has the particle coarsening and a broad particle-size distribution exhibit lower emission intensity, due to relatively low packing density. Furthermore, for the sample synthesized by GPS method, the resultant powders have hard agglomeration due to high temperature sintering. To make fine powders, it is essential to pulverize the as-synthesized powders, which can easily damage the particle surfaces and reduce the emission intensity.

We have also presented the morphology comparison of the Ca-α-SiAlON sample prepared by MWS and GPS methods in Figure 4. It can be observed that the particles of the sample prepared by MWS (Figure 4(a)) show nearly spherical shape, relatively small size, uniform morphology and good dispersion; whereas the appearance of the sample prepared by GPS exhibits spherical and rodlike morphology, large size, and hard aggregation (Figure 4(b)). These uniform morphology and good dispersion may be the another reason for higher emission intensity of the sample synthesized by MWS.

Figure 5 shows the quantum efficiencies and the temperature-dependent emission intensity of the MW-sample.

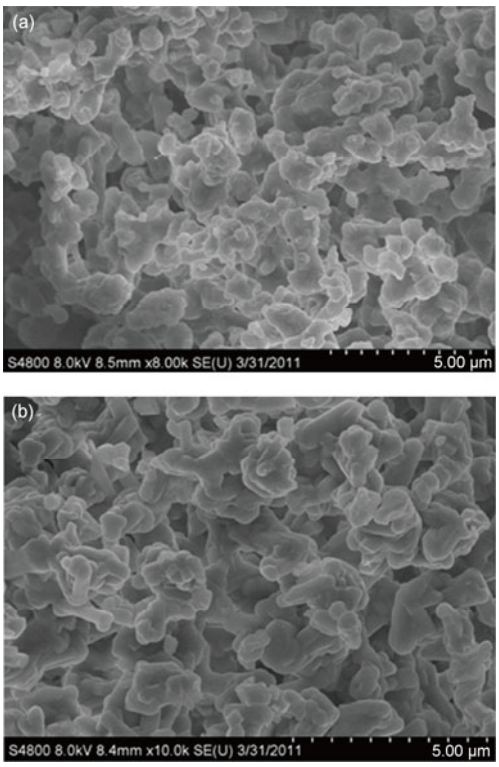

Figure 4 Morphology of the samples prepared by MWS (a) and GPS (b).

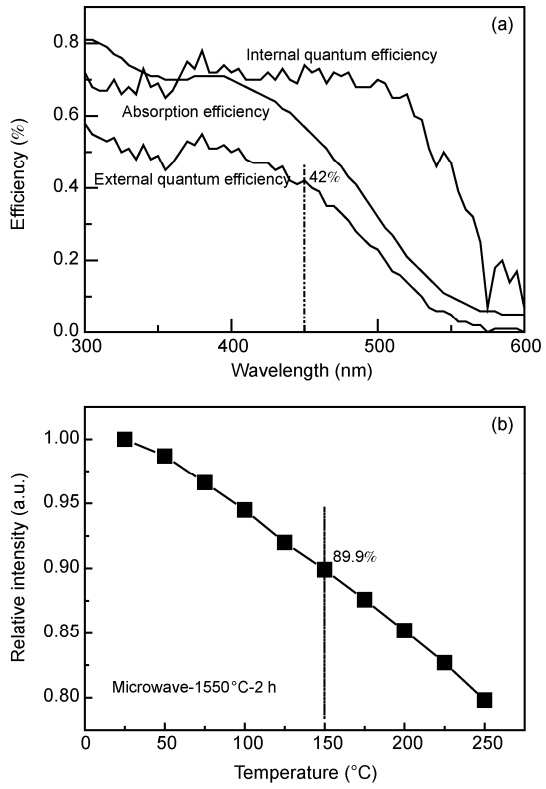

Figure 5 (a) Absorption and quantum efficiencies of Ca-α-SiAlON:Eu^{2+} synthesized by the microwave sintering method; (b) the temperature dependence of the emission intensity of Ca-α-SiAlON:Eu^{2+} synthesized by the microwave sintering method.

Obviously, the external quantum efficiency of the as-synthesized MW-sample (42%) is comparable to that reported in literature (40%) [20]. Meanwhile, the MW-sample has a comparatively small thermal quenching. At 150°C, the emission intensity remains about 90% of its initial one at room temperature. This value is similar to that reported in literature (87.6%) [21]. This small temperature-dependent fluorescence of the phosphor is one of key factors determining the quality of high power LED devices. The results mentioned above reveal that the microwave sintering approach is a very promising technique for obtaining high-performance Ca-α-SiAlON:Eu^{2+} phosphors at temperature as low as 1550°C and under ambient pressure. In comparison with the GPS and GRN/CRN methods, the microwave sintering method promises lower firing temperature, faster heating rate as well as shorter duration time. It is thus considered as a green and cost-effective method for producing nitride phosphors.

3 Conclusions

The yellow Ca-α-SiAlON:Eu^{2+} phosphor has been synthesized successfully by a green and cost-effective microwave heating method. The microwave sintering method could significantly lower the firing temperature of Ca-α-SiAlON:Eu^{2+}. The emission intensity and external quantum efficiency of the samples synthesized by the MWS method were comparable to those synthesized by the gas-pressure sintering method. The experimental results indicated that the microwave sintering technique could be an attractive synthesizing method for nitride phosphors.

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