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LETTER

Nano-sized PDP phosphors prepared by solution combustion method

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Recently, color plasma display panels (PDPs) have attracted considerable interest as a high-definition wall-attached TVs due to its obvious merits, such as a fast response, a wide viewing angle, large screen, low energy consumption, and high scalability [1–4]. However, much improvement is needed concerning luminous efficiency, lifetime and color purity. In particular, superior display performance requires improvement in phosphors particle characteristics such as morphology and particle size on the luminescent intensity, efficiency, and resolution. $BaMgAl_{10}O_{17}$**:**Eu^{2+} (BAM) as a component of the blue-emitting phosphor used in the PDPs, shows a high emission efficiency and ideal chromaticity under vacuum ultraviolet (VUV) irradiation [5–8].Thus far, commercialized BAM phosphors have been prepared by conventional solid-state synthesis route. However, the solid-state method has some disadvantages, such as (1) process complexity and energy-consuming (firing at high temperature, repetitive heat treatment, milling, and sieving), (2) inhomogeneous mixing and contamination by impurities, (3) product with irregularly shaped and aggregated particles unsuitable for screen brightness and high resolution. As a result, many attempts have been carried out to find alternative methods for the preparation of phosphors.

Solution combustion synthesis (SCS) is a promising method to prepare high-purity, small-sized and spherical particle phosphors because the starting raw materials are homogeneously mixed in liquid phases, and the high temperature generated instantly by exothermic reaction can volatilize low boiling point impurities leading to purer products. In addition, SCS results in products with narrow particle distribution because of the decreasing of reaction time (a few seconds during the combustion reaction) [9–11]. Therefore, SCS is obviously favorable to luminescent materials.

As to our best knowledge, the preparation of nanocrystalline of BAM has not been reported. In this letter, by adopting an improving facile combustion method, we successfully prepared the nanoscale Eu-doped BAM phosphors. Compared with the product fabricated by conventional solid-state synthesis, the phosphors resulted from combustion method possesses perfect spherical shape, fine size and high crystallinity.

The starting reagents were high-purity $Ba(NO_3)_2$ (99.9%), $Mg(NO_3)_2{\cdot}6H_2O$(99.9%), $Al(NO_3)_3{\cdot}9H_2O$ (99.9%), and $Eu(NO_3)_3$ (99.99%). According to the nominal composition of $Ba_{0.9}Eu_{0.1}$ $MgAl_{10}O_{17}$, a stoichiometric amount of metal nitrates were dissolved in a minimum quantity of deioned water in a cylindrical Pyrex dish, then a weighed quantity of urea was added and stirred well to obtain homogeneously mixing solution. The dish containing the solution was introduced into a muffle furnace maintained at 550±5 °C. After a while, the solution boils and undergoes dehydration followed by decomposition with liberating a large amount of gases such as H_2O, CO_2, NO_x, and NH_3, then, the mixture swells and burning instantaneously with bright flame. As the ignition occurred, the reaction went on vigorously for a few seconds. Finally, a fluffy white product was obtained after the combustion reaction. The whole process occurred within a few minutes.

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The crystal phase of the BAM phosphors prepared in the process was characterized by X-ray powder diffraction using a X'Pert PRO X-ray diffractometer having a Cu Kα radiation (λ = 1.5406 Å) at 40 kV tube voltage and 40 mA tube current. The particle size, morphology, and electron diffraction (ED) patterns were evaluated using Tecnai G2 20 transmission electron microscope (TEM).

Figure 1 shows the XRD pattern of the BAM particles obtained by the solution combustion method. It is clear that the XRD pattern is in excellent agreement with the pattern of barium magnesium aluminate (BAM) registered in the Joint Committee on Powder Diffraction Strands card (JCPDS 26-0163). All the diffraction lines are assigned well to BAM crystalline phase with the β-alumina structure corresponding to the space group $P6_3$ = mmc. No extraneous diffraction peaks are found in the pattern. The result indicates the phosphor obtained by the combustion process is monophasic BAM. On the contrary to this technique, in the conventional solid-state reaction, it was identified the presence of intermediates through the chemical reaction of each ingredient, which brought on impurities in the product [7]. Therefore, combustion synthesis can provide single BAM phosphors due to fast combustion reaction without the formation process of intermediate produces.

Also, it can be seen from the XRD pattern that the diffraction peaks are broadened, which indicates the fine nature of the product. The average crystallite size can be determined from the full width at half maximum (FWHM) of the diffraction peaks using Scherrer's equation $D = k\lambda/\beta\cos\theta$, where D is the mean particle size, k is a geometric factor, λ is the X-ray wavelength, and β is the half-width of diffraction peak. Estimated from the formula, the average crystallite sizes of the BAM nano particles prepared are about 24 nm.

Figure 2 shows the micrographs of the as-prepared material. In Fig. 2a, an overview of the particle morphology is given, while, Fig. 2b shows higher magnifications of the particle characteristics. The TEM images reveal the BAM nanocrystals exhibit an ideal spherical morphology. In general, spherical particles are more beneficial at increasing packing densities and brightness than irregularly shaped particles [12]. In addition, it can be seen from Fig. 2 that the synthesized grain size is distributed in the range of 20–25 nm. This is in good agreement with the X-ray results as well as the results calculated using Scherrer's formula. Figure 3 is the high-resolution TEM image of the BAM nanoparticle in Fig. 2b, which indicates the particle is

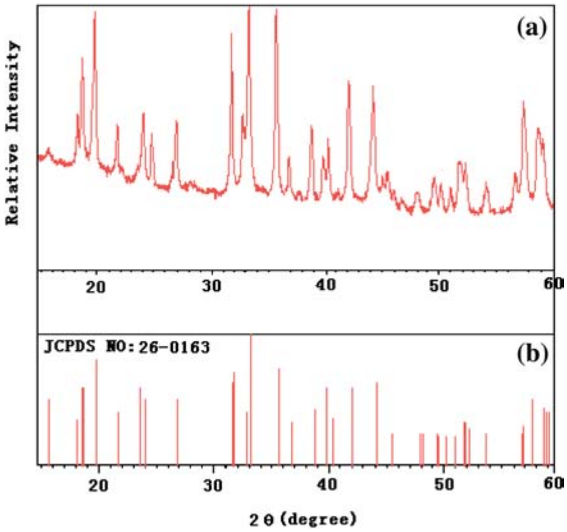

Fig. 1 XRD pattern of the as-prepared BAM phosphor (**a**) and the JCPDS card 26-0163 for BAM (**b**)

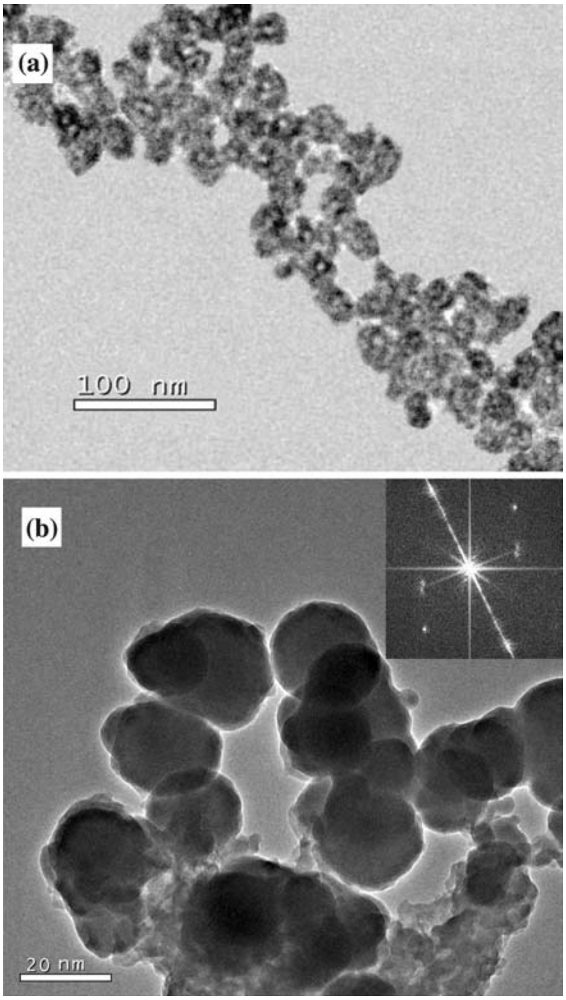

Fig. 2 TEM micrograph of the resulting BAM nanoparticles: (**a**) lower magnification and (**b**) higher magnification (scale bar: 100 nm for (**a**), 20 nm for (**b**))

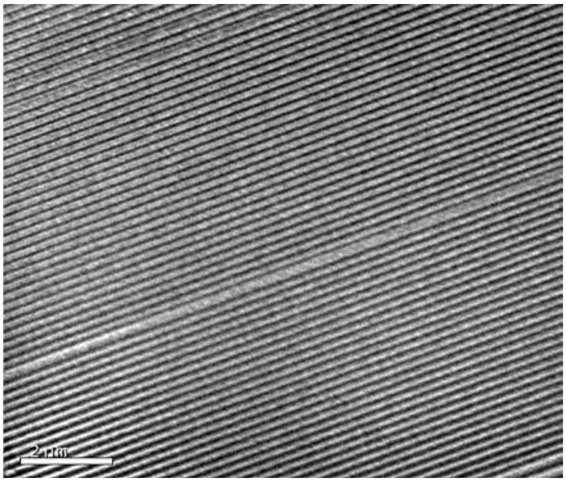

Fig. 3 High-resolution TEM image of the BAM nanoparticle in Fig. 2(b) (scale bar: 2 nm)

well-crystallized and not exist any displaces as well as twin crystals.

The mechanism of nanoparticle forming is as below. When heated rapidly at 550 °C, the solution containing stoichiometric amount of redox mixture boils, dehydrate, followed by decomposition generating combustible gases. The volatile combustible gases ignite and burn with a flame. The large amount of escaping gases dissipates heat and thereby prevents the material from sintering and thus provides conditions for formation of nanocrystalline phase. Also, as the gases escape they leave voluminous, foaming and crystalline fine powder occupying the entire volume of the container and have no chance of forming agglomerations unlike in the other conventional processes. Therefore, In case of combustion synthesis, instantaneous and in situ very high temperature, combined with release of large volume of volatiles from liquid mixture results in production of nanoparticles.

The luminescent property of BAM phosphor obtained is eminent and its excitation and emission spectra is given in Fig. 4. It can be seen that the excitation spectrum of the BAM phosphor shows a wide band peaking at 334 nm due to the direct excitation bands of Eu^{2+} centers, and the emission spectrum consists of a wide band with the peak at 450 nm, which corresponds to the transition from the $4f^65d$ excited state to the $4f^7$ ground state of a Eu^{2+} ion. The blue emission is excellently consistent with CIE chromaticity and quite suitable for Plasma display panels.

In general, Sol–Gel is also an important method to prepare submicroscopic scale BAM phosphors [13]. For comparison, Sol–Gel method was employed to prepare BAM phosphors at our laboratory. As seen in Fig. 5, the phosphors synthesized via combustion method exhibit higher emission intensity than those prepared by Sol–Gel. This is mainly because high purity and good crystallinity of the phosphors synthesized via a combustion process cause an increase in luminescence efficiency.

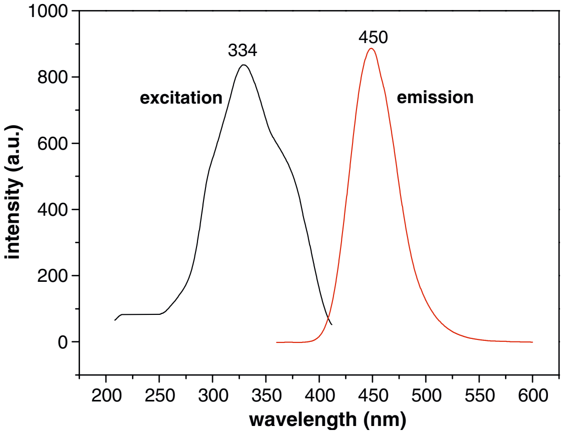

Fig. 4 Excitation and emission spectra of $BaMgAl_{10}O_{17}$:Eu blue phosphor

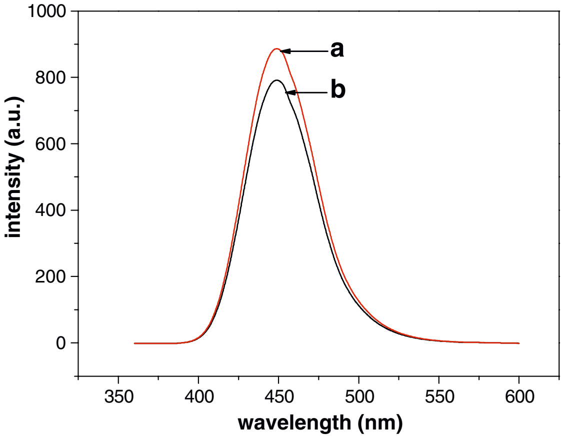

Fig. 5 Comparison of emission spectra of $BaMgAl_{10}O_{17}$:Eu obtained from solution combustion method (**a**) and Sol-Gel method (**b**)

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