Synthesis and Vacuum Ultraviolet Spectral Properties of Nano-scaled Phosphors

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The nano-scaled red phosphor $\text{YBO}_3: \text{Eu}^{3+}$, green phosphor $\text{ZnSiO}_4: \text{Mn}^{2+}$ and blue phosphor $\text{BaMgAl}_{10}\text{O}_{17}: \text{Eu}^{2+}$ were synthesized by wet-chemical techniques. The morphologies and spectral properties of the three nano-phosphors under 147 nm excitation were investigated. For $\text{YBO}_3: \text{Eu}^{3+}$, nano-sheets were obtained by solvent-thermal process, which reached 78.8% of the commercial red phosphor on emission intensity and exhibited better color purity than the latter. For $\text{ZnSiO}_4: \text{Mn}^{2+}$, different morphologies were obtained by hydrothermal method with varying ratio of CTAB to TEOS, among which the nano-spheres presented the strongest emission intensity and reached 86% of that of the commercial green phosphor. For $\text{BaMgAl}_{10}\text{O}_{17}: \text{Eu}^{2+}$, nano-rods were acquired using sol-gel process, which exhibited 78.15% of the commercial blue phosphor on emission intensity and the low γ value of color coordinates, which indicated that the nano-rods were efficient for restricting the deterioration during application.

Key Words : Synthesis, nano-phosphor, VUV

1. Introduction

The plasma display panel (PDP) was known as one of the promising flat panel display devices which utilized vacuum ultraviolet (VUV) exciting the phosphors, and a visible emission was generated^[1]. The representative tricolor commercial phosphors for PDP were $(\text{Y, Gd})\text{BO}_3: \text{Eu}^{3+}$, $\text{ZnSiO}_4: \text{Mn}^{2+}$ and $\text{BaMgAl}_{10}\text{O}_{17}: \text{Eu}^{2+}$ (BAM) due to their strong emission intensity and good color purity. However, there are still some deficiencies in these phosphors: The color purity of $(\text{Y, Gd})\text{BO}_3: \text{Eu}^{3+}$ was poor and the decay time of $\text{ZnSiO}_4: \text{Mn}^{2+}$ was too long for the application, while the degradation of $\text{BaMgAl}_{10}\text{O}_{17}: \text{Eu}^{2+}$ was an outstanding problem during panel manufacture^[2].

Recently, many researchers have focused on the preparation and luminescent properties of nano-phosphors because of their small size effect, surface effect, and the quantum size effect, which made them promising to present different optical and electrical properties compared with bulk phosphors^[3]. Besides, to meet the requirement of the PDP manufacture procedure, nano-phosphors were convenient to brush the panel and they could get higher resolution to make the pictures more vivid.

With the expectation of improving the physical, chemical and luminescent properties of ordinary particles, many soft-chemical techniques have been adopted to synthesize nano-particles on the account of their good mixing of starting materials and relatively low reaction temperature^[4]. In this work, the nano-scaled $\text{YBO}_3: \text{Eu}^{3+}$, $\text{ZnSiO}_4: \text{Mn}^{2+}$ and $\text{BaMgAl}_{10}\text{O}_{17}: \text{Eu}^{2+}$ were respectively prepared by different soft-chemical methods, which were solvent-thermal, hydrothermal method and sol-gel process. Their morphologies and spectral properties under VUV excitation were

investigated and discussed.

2. Experiments

2.1 $\text{YBO}_3: \text{Eu}^{3+}$ nano-phosphor

$\text{YBO}_3: \text{Eu}^{3+}$ nano-phosphor was synthesized by solvent-thermal method. The starting materials were Y_2O_3 (99.99%), Eu_2O_3 (99.99%) and H_3BO_3 (99.5%). Stoichiometric amounts of Y_2O_3 (95 wt %) and Eu_2O_3 (5 wt %) were dissolved in diluted nitric acid by heating, and drying to get a mixture of $\text{Y}(\text{NO}_3)_3$ and $\text{Eu}(\text{NO}_3)_3$. Stoichiometric amount of H_3BO_3 was added in the mixture. The mixture was dissolved in 50 mL of mixed water and ethanol hybrid solution (the relative volume ratio of water to ethanol are adjusted to 1:0, 1:1, 1:2 and 1:3, respectively) under ultrasonic mixing for 1 h. The initial pH value was adjusted to 8 with ammonia, since the reaction was a process of producing H^+ and weak alkaline conditions were propitious to reaction production. The solution was transferred into a 100 mL Teflon-lined, stainless steel autoclave. The solution was heated at 230°C and the reaction time was 3 h. White precipitates were collected, filtered and washed with distilled water and ethanol several times, and dried in an oven at 80°C to get the final product.

2.2 $\text{ZnSiO}_4: \text{Mn}^{2+}$ nano-phosphor

$\text{Zn}_2\text{SiO}_4: \text{Mn}^{2+}$ nano-phosphor was synthesized in an autoclave equipped with a Teflon reaction vessel by hydrothermal method. All the reagents are of analytical grade. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (99.0%), $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (99.0%) and $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$ (SiO_2 , 28.4%) (TEOS) were used as sources of zinc, manganese, and silicon, respectively. In a typical procedure, firstly, TEOS was dissolved in a mixed solution of distilled water and ethanol,

ammonium hydroxide was added as a catalyst for the hydrolysis of TEOS with vigorous stirring for an hour. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was dissolved in the distilled water and stirred continuously until complete dissolution occurred. Then the TEOS solution was slowly added to the aqueous solution of $\text{Zn}(\text{CH}_3\text{COO})_2$ and $\text{Mn}(\text{CH}_3\text{COO})_2$. After being stirred for half an hour, the mixed solution was transferred into the Teflon reaction vessel in the autoclave and heated at different temperature for 2 h. After cooling down to room temperature naturally, the resultant products were collected by filtration, followed by washing and drying. To control the morphology and the particle sizes of the phosphor, cetyl-tri-methyl-ammonium bromide (CTAB) as the surfactant was added to the solution of $\text{Zn}(\text{CH}_3\text{COO})_2$ and $\text{Mn}(\text{CH}_3\text{COO})_2$. The final phosphor obtained through the same procedure of hydrothermal method mentioned above.

2.3 $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ nano-phosphor

$\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ was synthesized by sol-gel process. The starting materials Eu_2O_3 (99.99%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.0%), $\text{Ba}(\text{NO}_3)_2$ (99.5%) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.0%) were weighted as the nominal composition of $\text{Ba}_{0.9}\text{MgAl}_{10}\text{O}_{17} \cdot 0.1 \text{Eu}^{2+}$. Then, citric acid were dissolved in deionized water and adjusted pH value to 3 by $\text{NH}_3 \cdot \text{H}_2\text{O}$. And then a stoichiometric amount of starting materials was dissolved in the citric solution. After all of the materials were dissolved, they were adjusted the pH value to 5 and heated to 60°C with ceaselessly stirring about half an hour to gain the sol. The sol was placed in room temperature for about 40 min in succession. Then it was dried in a muffle oven at 120°C and the volume of the gel expanded greatly and the puffy and porous dried gel was obtained. Finally the gel was grinded in an agate mortar and sintered at the temperature range of 850°C to 1300°C for 4 h under a reducing atmosphere (5% H_2/N_2 mixture gas) to obtain the product.

2.4 Characterizations

The X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max-2400 X Ray diffractometer. The morphology of the powders was examined by Transmission Electron Microscopy (TEM) performed with a Hitachi H-800 transmission electron microscope using an accelerating voltage of 200 kV and JEOL-5600 Scanning Electron Microscope (SEM). The emission spectra were measured at room temperature by FLS-920T fluorescence spectrophotometer with a VM-504-type vacuum monochromator. A deuterium lamp was used as the lighting source.

3. Results and discussions

3.1 $\text{YBO}_3:\text{Eu}^{3+}$ red nano-phosphor

Figure 1 shows XRD patterns of the $\text{YBO}_3:\text{Eu}^{3+}$ samples synthesized with different ratios of water to solvent. All the diffraction peaks could be indexed to the JCPDF card (No. 83-1205), and there is no second phase observed. As shown in the Figure 1, the relative intensity of the diffraction peaks for the solvent-thermal (SO) samples are different from the sample prepared by hydrothermal reaction (HR, the 1:0 samples). The (002) peak is the strongest for the HR samples but the (100) peak becomes strongest when the solvent was introduced in the reaction systems, indicating the appearance of a preferred orientation. Moreover, the broadening of the diffraction peaks in Figure 1 indicates that the crystallite size of sample is small. By Scherrer formula, the average crystallite sizes of the samples are 25.8 nm, 17.6 nm, 17.7 nm and 23 nm, corresponding to the different synthesis conditions (the ratio of water to ethanol hybrid) as 1:0,

1:1, 1:2 and 1:3, respectively. This result suggests that the addition of ethanol hybrid in the synthesis will restrict the growth of the grains.

The TEM photographs of the SO and HR samples are shown in Figure 2. In Figure 2(a), we could find that the HR particles are

Figure 1 XRD patterns of the $\text{YBO}_3:\text{Eu}^{3+}$ samples prepared with different ratios of water to solvent.

Figure 2 TEM images of $\text{YBO}_3:\text{Eu}^{3+}$ phosphors prepared by different reation (a) HR Samples; (b) SO samples.

rod-like with the average size of 150 nm in diameter and 300 nm in length. This differs from calculated results from XRD, indicating that a particle in this sample is polycrystalline and consists of several monocrystalline particles. By the addition of solvent, the morphology changes into nano-sheets with the size about 50 nm, which is consistent with the results of the XRD patterns. The particles in SO sample also represent better dispersion than that of HR samples. This result indicates that adding solvent will be conducive to decrease grain size and improve dispersion of the sample particle. The possible reason may be the alternation of the dielectric constant of the solution. With the addition of solvent to the aqueous solution, the dielectric constant of the mixed solvent decreased, which led to the decrease in solubility of the reaction materials during the crystallization process. As a result, it would lead to the formation of smaller particles.^[5-6]

Under 147 nm excitation, the emission spectra of the SO samples with different ratios of water to solvent are shown in Figure 3. All spectra consist of sharp lines ranging from 580 to 700 nm, which are associated with the transitions from the excited 5D_0 level to 7F_J ($J=1, 2, 3, 4$) levels of Eu^{3+} activators^[7]. The major emissions of $\text{YBO}_3: \text{Eu}^{3+}$ is at 592 nm ($^5D_0 \rightarrow ^7F_1$) and 611 and 627 nm ($^5D_0 \rightarrow ^7F_2$). It is observed that the strongest red emission is observed for the sample prepared at the water to solvent ratio of 1:2, and the PL intensity of sample d is obviously lower than the others. It can be due to the existence of a small amount of OH^- coordinated to lanthanide ions at the surface of phosphors prepared by the wet chemical method. Adding excessive amount organic solvent (over 1:3) lead to large amount of OH^- adhering on the surface of phosphor, which results in the poor PL intensity^[8]. As can be seen in the figure, the $^5D_0 \rightarrow ^7F_2$ emission increased and $^5D_0 \rightarrow ^7F_1$ emission decreased with solvent added. This must be associated with particle size of samples (observed before). It is well known that the relative intensity of $^5D_0 \rightarrow ^7F_1$ transition or $^5D_0 \rightarrow ^7F_2$ transition depends strongly on the local symmetry of Eu^{3+} . When the particle size decreases, smaller particles have higher effective surface area and larger lattice distortion, leading to the formation of Eu^{3+} ions occupying lower symmetry sites. This will increase the transition probability of $^5D_0 \rightarrow ^7F_2$ and thus improve color purity^[9]. It was found that the ratio of red emission (611 nm) intensity to

orange emission (592 nm) intensity (R/O) is 1.11, which predicts that the SO sample (solvent at 1:2) has the highest color purity.

3.2 $\text{ZnSiO}_4: \text{Mn}^{2+}$ green nano-phosphor

Figure 4 shows the XRD patterns of the $\text{Zn}_2\text{SiO}_4: 0.06\text{Mn}^{2+}$ phosphors prepared at different reaction temperatures. All the diffraction peaks can be indexed to pure hexagonal structured Zn_2SiO_4 (JCPDF card, No. 37-1485). The $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\text{H}_2\text{O}$ is not detected as that reported by Ref.^[10] in the hydrothermal procedure below 280°C, which means that there is no intermediate phase in our samples prepared by hydrothermal procedure even at a low reaction temperature. Furthermore, the XRD result shows that pure hexagonal-structured Zn_2SiO_4 can be obtained at the low temperature of 140°C, which is lower than the temperature of 220°C reported by Wan *et al.*^[11] and much lower than that using the conventional solid-state reaction method. The average crystallite sizes estimated from the Scherrer equation indicated all the samples were in nanoscaled, and $\text{Zn}_2\text{SiO}_4: \text{Mn}^{2+}$ sample prepared at 220°C represents the best crystallinity.

When CTAB was used in the hydrothermal procedure as the surfactant molecules, it was found that the size and the morphology of the $\text{Zn}_2\text{SiO}_4: \text{Mn}^{2+}$ phosphors could be controlled as shown in Figure 5(a)-(d). When the CTAB/TEOS=0.01 was adopted, the rod-like particles show the trends to the sphere-like shaped (Figure 5(b)). This is an interim morphology from rod-like to spheres. When the concentration of CTAB increased to CTAB/TEOS=0.05, TEM micrograph (Figure 5(c)) shows that the willemite phosphors are nano-spheres with the diameter about 60 nm. The nanoparticles dispersed well without agglomeration. When larger amount of CTAB are introduced, aggregation of the nanoparticles can be observed in the final products. It was known that the surfactant molecules could adsorb on the surface of particles and stabilize the particle by either electrostatic repulsion or steric force.^[12] Therefore, the particle size and shape of $\text{Zn}_2\text{SiO}_4: \text{Mn}^{2+}$ nanoparticles would be limited and controlled by the presence of CTAB in the hydrothermal procedure as shown in Figure 5.

The relative intensities of $\text{Zn}_2\text{SiO}_4: 0.06\text{Mn}^{2+}$ samples at different reaction temperatures under the 147 nm excitation are given in Figure 6(a). The strongest broad band emission at about 523 nm was observed, which is attributed to the $^4T_1 \rightarrow ^6A_1$ transition of Mn^{2+} . It shows that the luminescence intensity increases when

Figure 3 Emission spectra of $\text{YBO}_3: \text{Eu}^{3+}$ nano-phosphors prepared at different ratios of water to solvent.
 (a) 1:0; (b) 1:1; (c) 1:2; (d) 1:3 ($\lambda_{\text{ex}}=147$ nm).

Figure 4 XRD patterns of the $\text{Zn}_2\text{SiO}_4: 0.06\text{Mn}^{2+}$ samples prepared at different reaction temperatures.

Figure 5 TEM micrographs of the $\text{Zn}_2\text{SiO}_4: 0.06\text{Mn}^{2+}$ samples synthesized at different conditions. (a) Without CTAB, (b) CTAB/TEOS=0.01, (c) CTAB/TEOS=0.05, (d) CTAB/TEOS=0.20.

Figure 6 Emission spectra of $\text{Zn}_2\text{SiO}_4: 0.06\text{Mn}^{2+}$ phosphors (a) synthesized at different reaction temperature, (b) different ratio of CTAB to TEOS of samples a-d.

the temperature increases. This phenomenon would be ascribed to the higher crystallinity according to the XRD results as discussed previously.

The PL intensity among different morphology of the phosphors was also investigated. Figure 6(b) presents emission spectra for the samples with different morphology under VUV excitation. The green luminescence is the conventional green of $\text{Zn}_2\text{SiO}_4: \text{Mn}^{2+}$ phosphor, occurring at about 523 nm. As can be seen in Figure 6(b), change in morphology of phosphors has a certain extent influence on their luminescent intensity. It can be seen that the highest PL intensity was obtained when the $\text{Zn}_2\text{SiO}_4: \text{Mn}^{2+}$ phosphor has uniform spherical morphology (sample c) due to the unique properties of sphere morphology.

It is well known that particles in nanoscaled have large surface area. The large surface area has serious drawbacks in PL intensity due to the introduction of a large number of defects into the phosphor crystal. Defects have serious implications for luminescent materials as they provide non-radiative recombination routes for electrons and holes.[13] As the surfactant was adopted in the hydrothermal procedure, the defects of the phosphor decreased, which induced the increase in the PL intensity. Additionally, the spherical shape diminished light scattering as mentioned above, which resulted in the PL intensity of nanospherical $\text{Zn}_2\text{SiO}_4: \text{Mn}^{2+}$ phosphor being maximized. When excessive surfactant was adopted, the particles smaller than several nanometers agglomerated, and the PL intensity decreased for the increased surface defects as non-radiative recombination routes. This is the reason that PL intensity changed with different morphology.

3.3 $\text{BaMgAl}_{10}\text{O}_{17}: \text{Eu}^{2+}$ blue nano-phosphor

Figure 7 shows the typical XRD patterns of the sol-gel derived $\text{BaMgAl}_{10}\text{O}_{17}: \text{Eu}^{2+}$ samples prepared at different reaction temperatures for 4 h. At 850°C, the sample is amorphous. When the temperature rises to 1200°C, the BAM phase begins to form but still has an impurity peak (BaAl_2O_4). Farther rising to 1250°C, the impurity peak disappeared and forms a well BAM phase. It matches well with JCPDS card (No. 26-0163) of BAM with β -alumina structure corresponding to the space group $\text{P}6_3/\text{mmc}$. When the temperature rises to 1300°C, it is also single-phase with the crystallinity much improved. On the contrary to this technique,

Figure 7 XRD patterns for $\text{BaMgAl}_{10}\text{O}_{17}: \text{Eu}^{2+}$ prepared at different reaction temperatures.

in conventional solid-state reaction, the presence of intermediates was identified which brought on impurities in the product even at the temperature of 1600°C.

As shown in Figure 8, the images exhibit the SEM micrographs of the BAM samples under 1250°C (a) and 1300°C (b). As $\text{BaMgAl}_{10}\text{O}_{17}$ has the crystal structure of β -alumina, the particle takes the form of hexagonal platelets when the crystal freely grows^[14]. In the images of (a) and (b), the nanorods could be

Figure 8 SEM images of BAM phosphors synthesized at (a) 1250°C, (b) 1300°C.

Figure 9 Emission spectra of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ blue nano-phosphors synthesized by sol-gel method under 1250°C and 1300°C ($\lambda_{\text{ex}} = 147 \text{ nm}$); the inset is Gaussian fitted emission spectrum of BAM.

Table 1 The ratio of emission intensity and color coordinates of the tri-color nano-phosphor compared with commercial phosphor

Nano-scaled phosphor	$\text{YBO}_3:\text{Eu}^{3+}$	$\text{ZnSiO}_4:\text{Mn}^{2+}$	$\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$
Ratio (compared with commercial phosphor)	78.8%	86%	78.15%
Color coordinates of nano-scaled phosphor	(0.644,0.356)	(0.219,0.646)	(0.143,0.068)
Color coordinates of commercial phosphor	(0.645,0.355)	(0.248,0.649)	(0.144,0.069)
Color coordinates of NTSC	(0.67,0.33)	(0.21,0.71)	(0.147,0.08)

obviously seen and has a homogeneous grain size at 80-100 nm in diameter and 0.8-1 μm in length. In addition, we can also observe that the nano-rods are of well dispersion and maintain the morphology when the temperature rises from 1250°C to 1300°C. These results indicate that citric sol-gel process is an effective method for the preparation of nano-scaled phosphor with high dispersion which needs complicated synthesis conditions.

Figure 9. illustrates the comparison of the emission spectra of BAM nano-phosphors synthesized by sol-gel method under 1250°C and 1300°C by 147 nm excitation. On account of the 5d orbital of Eu^{2+} is easily split inasmuch the influence of the crystal field^[15], the emission spectrum of BAM nano-phosphor in Figure 9 presents a broad band locating at about 452 nm, and it could be attributed to the $4f^65d \rightarrow 4f^7(^8S_{7/2})$ transition of Eu^{2+} ^[16]. Moreover, the emission band is of asymmetrical distribution. This relates to the different sites of Eu^{2+} occupied in BAM. By Gaussian fitting the VUV emission spectrum (as shown in the inset of Figure 9), three peaks were found and these peaks located at 446 nm, 477 nm and 517 nm, corresponding to the emission of Eu^{2+} in the sites of BR, a-BR and spinel layer^[17-18]. With the temperature increasing from 1250°C to 1300°C, the emission intensity of these nano-phosphors by 147 nm excitation enhanced about 22%. The improvement of the emission could be ascribed to the improvement of the crystallinity as discussed in Figure 7.

3.4 Comparison to commercial phosphor

Table 1 shows the ratio of emission intensity and the color coordinates of the tri-color nano-phosphor compared with commercial phosphor. The emission intensity of nano-scaled $\text{YBO}_3:\text{Eu}^{3+}$, $\text{ZnSiO}_4:\text{Mn}^{2+}$ and $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ reaches 78.8%, 86%, 78.15% respectively compared with the commercial phosphor. The color coordinates of nano-scaled $\text{YBO}_3:\text{Eu}^{3+}$ and $\text{ZnSiO}_4:\text{Mn}^{2+}$ is superior to commercial bulk phosphor and more close to the National Television Systems Committee (NTSC). For nano-scaled $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$, the y value of the coordinates is lower than the value of both commercial phosphor and NTSC which means that it is useful for restricting the decrease of BAM efficiency during application.

4. Conclusion

$\text{YBO}_3:\text{Eu}^{3+}$ nano-sheets, $\text{ZnSiO}_4:\text{Mn}^{2+}$ nano-spheres and $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ nano-rods were synthesized by solvent-thermal, hydrothermal and sol-gel processes respectively. By 147 nm excitation, the $\text{YBO}_3:\text{Eu}^{3+}$ nano-sheets exhibit 78.8% on emission intensity of that of commercial phosphor and better color purity than the latter; The $\text{ZnSiO}_4:\text{Mn}^{2+}$ nano-spheres show the strongest

emission intensity than $\text{ZnSiO}_4: \text{Mn}^{2+}$ of other morphologies and reaches 86% of that of the commercial phosphor; The $\text{BaMgAl}_{10}\text{O}_{17}: \text{Eu}^{2+}$ nano-rods represent 78.15% of the emission intensity of commercial phosphor, and obtained low γ value of the BAM nano-rods suggesting that it was helpful for enhancing the thermal stability. All of the results indicated that the tricolor nano-scaled phosphors had an optimistic application prospect in PDPs.

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Note: In this paper, the data of $\text{YBO}_3: \text{Eu}^{3+}$ nano-phosphor is provided by Qizheng Dong, the data of $\text{ZnSiO}_4: \text{Mn}^{2+}$ nano-phosphor is provided by Xue Yu, and the data of $\text{BaMgAl}_{10}\text{O}_{17}: \text{Eu}^{2+}$ nano-phosphor is provided by Zhaofeng Wang.

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