

Comparative study on the synthesis, photoluminescence and application in InGaN-based light-emitting diodes of TAG:Ce³⁺ phosphors

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Abstract

Cerium-doped terbium aluminum garnet phosphors, Tb₃Al₅O₁₂:Ce³⁺ (TAG:Ce³⁺), were prepared with different methods: co-precipitation (CP), half dry–half wet (HDHW), sol-combustion (SC) and Pechini method plus conventional solid state reaction (SS) method. Comparative study on the phase-formation, particle size, morphologies and luminescent characteristics of the phosphors synthesized with different methods was carried out by means of XRD, FE-SEM and photoluminescence (PL) analysis and SC method was confirmed by the comparison of the results to be an easy and an effective process for preparing efficient and nano-sized Tb₃Al₅O₁₂:Ce³⁺ phosphors. Various factors influencing particle size, morphology and PL of the phosphors, such as precursor preparation, reaction temperature and heating time, were also investigated. Light-emitting diodes (LEDs) were fabricated with each phosphor and a ~460 nm emitting InGaN chip. The LEDs from SS, HDHW and CP exhibit strong white emission while those from SC and Pechini emit yellow, revealing that the emission characteristics of LEDs are influenced not only by the morphology and the particle size of the phosphors, but also by the preparing process of the phosphors.

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1. Introduction

Recently semiconductive white light-emitting diodes (WLEDs) has emerged as a novel generation of illumination technology [1–4]. As a conventional optical-magnetism material, Tb₃Al₅O₁₂ (TAG) host material has shown its wonderful optical character as a green–yellow component in WLEDs [5–9]. When doped with Ce³⁺, it has been found to be an efficient phosphor for converting the blue light-emitting diode (LED) radiation into a broad yellow emission band. White light can be produced by a combination of the yellow emission from the phosphors and the residual blue light which escapes through the phosphor.

Recently, nano-scaled particles are under extensive study and have become a hot topic in terms of both their fundamental and technological importance. As long as we

know, wet chemical methods such as co-precipitation (CP) [10,11], sol–gel (SG) [12,13], combustion (CB) [20,21] and hydrothermal and solvothermal synthesis [14,15] all can be used to prepare nano-scaled particles, since the starting materials can be mixed at molecular level through these processes.

Until now, although there are many reports about the preparation of nano-sized YAG (Y₃Al₅O₁₂):Ce³⁺ [11,15], YAG:Eu³⁺ [12] or YAG:Tb³⁺ [13,14] phosphor with all the above-mentioned methods, there is little information available in literature about the preparation of nano-sized TAG phosphor and its application in WLED, to our best knowledge, especially no comparative study on the TAG:Ce³⁺ phosphor syntheses was reported. In this article, we synthesized single phase of TAG phosphors with four different methods: CP with ammonium bicarbonate, half dry–half wet (HDHW), SC with citric acid and Pechini method [16,17] with citric acid and ethylene-glycol as well as bulk phosphors with solid state reaction (SS) technology as a control. A comparative study on the

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phase-formation, particle size, morphologies and photoluminescence (PL) of the TAG:3%Ce³⁺ phosphors obtained with different methods was carried out. White LEDs were also fabricated by combination of the phosphor with a ~460 nm emitting InGaN chip.

2. Experimental

2.1. Chemical reagents

Tb₄O₇ (99.99%), CeO₂ (99.99%) and Ce(NO₃)₃ (analytical grade) were used as rare earth sources of TAG:Ce³⁺. Al(OH)₃ (analytical grade) and Al(NO₃)₃·9H₂O (99.9%) were used as the sources of aluminum.

2.2. Co-precipitation method with ammonium bicarbonate (NH₄HCO₃)

For the wet chemical preparation, Tb(NO₃)₃ solution was formed by dissolving Tb₄O₇ in boiling nitric acid (HNO₃), and Al(NO₃)₃, Ce(NO₃)₃ solution was prepared by dissolving Al(NO₃)₃·9H₂O and Ce(NO₃)₃ in distilled water, respectively. All of the reagents were calculated and weighed exactly as the stoichiometric concentration.

The respective nitrate solutions with a cationic molar ratio of 2.91:5.00:0.09 for Tb: Al: Ce were mixed in a container. Then the mixture was added drop-wise into the precipitant solution (NH₄HCO₃) by magnetic stirring at room temperature, and the molar ratio of NH₄HCO₃ to rare-earth cations was 10:1. For multi-cations materials, the reverse strike technique has the advantage of higher cation homogeneity in the precursor. After aging for 30 min with a cap, the precipitated slurry was centrifugally filtered and dried at 100 °C for 12 h plus pre-heating at 500 °C for 2 h. Triturated in an agate mortar, the powder was transferred into a corundum crucible and calcined at 950–1200 °C for 4 h in an electric furnace in a reducing atmosphere created by burning activated carbon.

2.3. Half dry–half wet method

Stoichiometric amount of Tb₄O₇ and CeO₂ was triturated and mixed in an agate mortar, and then blended with certain amount of Al(NO₃)₃ solution to obtain a mixture with molar ratio of 2.91:5.00:0.09 for Tb: Al: Ce. The mixture was stirred magnetically for 30 min for a good mixing and then dried at 100 °C for 5 h plus pre-heating at 500 °C for 2 h. Triturated in an agate mortar, the powder was transferred in a corundum crucible and calcined at 950–1200 °C for 4 h in an electric furnace in a reducing atmosphere created by burning activated carbon.

2.4. Sol-combustion method with citric acid (C₆H₈O₇·H₂O)

With a final molar ratio of 2.91:5.00:0.09 for Tb: Al: Ce, the respective nitrate solutions were mixed with appro-

priate amount of citric acid under magnetic stirring and the molar ratio of total metal ions to citric acid was 1:2. After the citric acid was dissolved in the above solution, the resultant mixture was stirred at 70–80 °C for 4–5 h until a transparent sol was obtained. The sol was dried in oven at 180–200 °C and a few minutes later, the sol expanded and combust slowly accompanied by the evolution of brown foam. Finally, a yellowish and fluffy precursor remained [18]. The precursor was finely ground in an agate mortar, and then pre-heated at 900 °C for 3 h in air. After an intermediate grinding, the powder was sintered at various temperatures from 950 to 1200 °C for 4 h in an electric furnace in a reducing atmosphere created by burning activated carbon.

2.5. Pechini method with citric acid (C₆H₈O₇·H₂O) and ethylene-glycol (EG)

With a final molar ratio of 2.91:5.00:0.09 for Tb:Al:Ce, the respective nitrate solution was mixed with a certain amount of citric acid. After the citric acid was dissolved under magnetic stirring, an appropriate dosage of ethylene-glycol was added and go on stirring at 60–70 °C for 5–6 h, the appropriate ratio of total metal ions: citric acid: ethylene-glycol was defined to be 1:3:4.5 after several experiments. A transparent sol was obtained by slow evaporation of the concentrated solutions. The sol was dried in oven at 180–200 °C overnight to obtain a flexible and black colloidal material. The samples of crushed colloidal material were pre-heated at 900 °C for 3 h in air and then after an intermediate grinding, the powder was fired at various temperatures from 950 to 1200 °C for 4 h in an electric furnace in a reducing atmosphere created by burning activated carbon.

2.6. Solid-state reaction method

With a molar ratio of 2.91:5:0.09 (Tb: Al: Ce), stoichiometric amount of the starting materials, Al(OH)₃, Tb₄O₇ and CeO₂ were mixed in an agate mortar and then triturated for a good mixing, then transferred into a corundum crucible and calcined at 1500 °C for 4 h in an electric furnace under a reducing atmosphere created by burning activated carbon.

2.7. Measurements

X-ray powder diffraction (XRD) patterns of the products were recorded on a Rigaku D/max—IIIA diffractometer with CuK_α radiation. The morphology and particle size of the samples was inspected using a JEOL JSM-6330F field emission scanning electron microscope (FESEM), and the samples were gold-coated before the inspection. The PL excitation and emission spectra of all the phosphors were recorded on a JOBIN YVON FL3-21 spectrofluorometer at room temperature and a 450 W xenon lamp was used as excitation source.

2.8. Fabrication of LEDs

Five LEDs were fabricated by combining phosphors prepared by SS method at 1500 °C, CP, HDHW, SC, Pechini method at 1200 °C with ~460 nm emitting InGaN chips. The emission spectra of the LEDs were recorded on Labsphere Inc. LED-1100.

3. Results and discussion

3.1. X-ray powder diffraction

XRD patterns of the TAG phosphors synthesized by the CP, SC, Pechini, HDHW and SS methods and sintered at various temperatures, are shown in Fig. 1. It can be observed that single phase of TAG by SS method, which is in good agreement with JCPDS 17-35 ($\text{Tb}_3\text{Al}_5\text{O}_{12}$, body-center cubic), appeared only after sintering at 1500 °C. Compared with SS, the single TAG phase formation temperature by the four wet chemical methods was evidently lowered because the metal centers were homogeneously cross-linked and distributed in the precursor [19]. No more than 1000 °C was required to obtain pure TAG phase by CP, SC and Pechini methods, and the formation temperature of TAG single phase for the SC and Pechini methods is 50–100 °C higher than that for the CP method. In the HDHW process the single phase formation temperature was about 1200 °C, higher than that in the wet chemical methods but lower than that in the SS method, and the result is consistent with the reactant mixing levels.

3.2. Morphology

Fig. 2 shows the FE-SEM images of the TAG:Ce³⁺ phosphors. The samples prepared by the SC (Fig. 2a) and

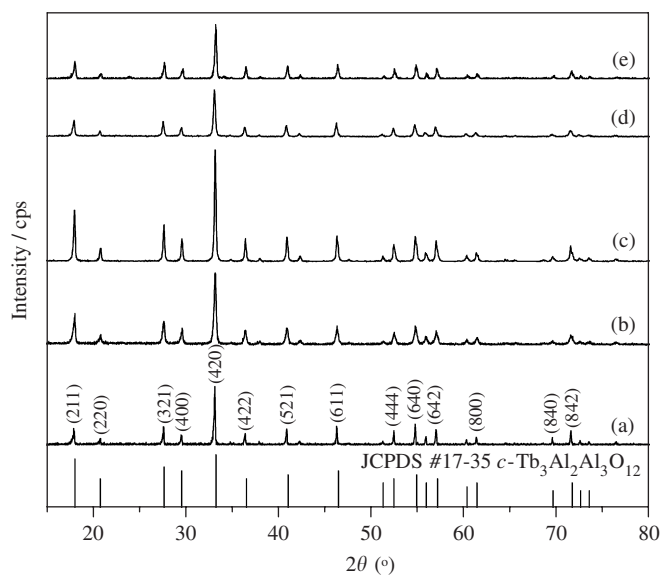


Fig. 1. XRD patterns of TAG:0.03Ce³⁺ prepared by different methods: (a) by SS fired at 1500 °C; (b) by CP fired at 900 °C; (c) by SC fired at 1000 °C; (d) by Pechini fired at 1000 °C; (e) by HDHW fired at 1200 °C.

CP (Fig. 2c) method sintered at 1100 °C for 4 h exhibit uniform and ellipse-spherical-like morphology with a particle size of about 150–200 nm. Our SC method is an integrated method combining both CB and Pechini method. In the SC process the citric acid not only acts as a chelate ligand, providing an environment inhibiting the hydrolysis of the metal cations, but also acts as a gentle fuel, so the reaction process goes mildly, smooth and homogeneously, in contrast to an ordinary CB method, in which urea always acts as fuel, and the reaction process usually is so violent that a large quantity of gases is released, and many pores are produced in the products [20,21]. Phosphors made with Pechini method (Fig. 2b) also shows a particle size of 150–200 nm, but it seems to be some aggregated. This phenomenon could be due to the bridging of adjacent particles through the hydrogen bonding of water and the significant capillary action generated during the drying process in the precursors [19]. Compared to the wet chemical methods, phosphors prepared by the HDHW method (Fig. 2d) show much more irregular morphology and larger particles, however, the particle size is still much smaller than that by the SS method (Fig. 2e). It looks that the HDHW method stands between the SS and the wet chemical methods, so the surface properties of its products also manifest the counteract of the two kinds of methods. Anyway, the morphological homogeneity of the wet chemical methods-derived products is much better than that of the SS method and the particle size was much smaller.

3.3. Excitation and emission spectra

Independent of the synthesis methods, the difference in the shape and wavelength of the peaks for the excitation and emission spectra of TAG:Ce³⁺ phosphors prepared by different methods is very small. Thus, the excitation ($\lambda_{\text{em}} = 550 \text{ nm}$) and emission ($\lambda_{\text{ex}} = 463 \text{ nm}$) spectra of the TAG:Ce³⁺ phosphors prepared by SC method fired at 1100 °C is presented as a representative (see Fig. 3). The excitation spectrum of the SC sample contains $4f^8-4f^75d$ transition bands at around 276 nm (spin-allowed, $\Delta S = 0$) and 325 nm (spin-forbidden, $\Delta S = 1$), as well as the $f-f$ transition lines of Tb³⁺ at longer wavelength (377 nm for $^7F_6-^5D_3$, etc.). The lowest-energy excitation band of Ce³⁺ originated by $f-d$ electron transition lies at about 463 nm, and the higher energy $f-d$ band of the Ce³⁺ ions overlaps with the Tb³⁺ $4f-5d$ transition related bands at 310–360 nm. Excited by the characteristic absorption wavelength of Tb³⁺ in 276 or 325 nm, the Ce³⁺ characteristic $5d(^2D)-4f(^2F_{5/2}, ^2F_{7/2})$ luminescence band centered at about 530–550 nm appeared in the emission spectrum, which confirms the energy transfer from Tb³⁺ to Ce³⁺, and the energy transfer process is proposed as follows: after Tb³⁺ is excited into its 2D state, it transfers the exciting energy to the adjacent Ce³⁺ ion and then the electron transition occurs from the excited state of Ce³⁺ to the ground state [22–24]. This is favorable to enhance the

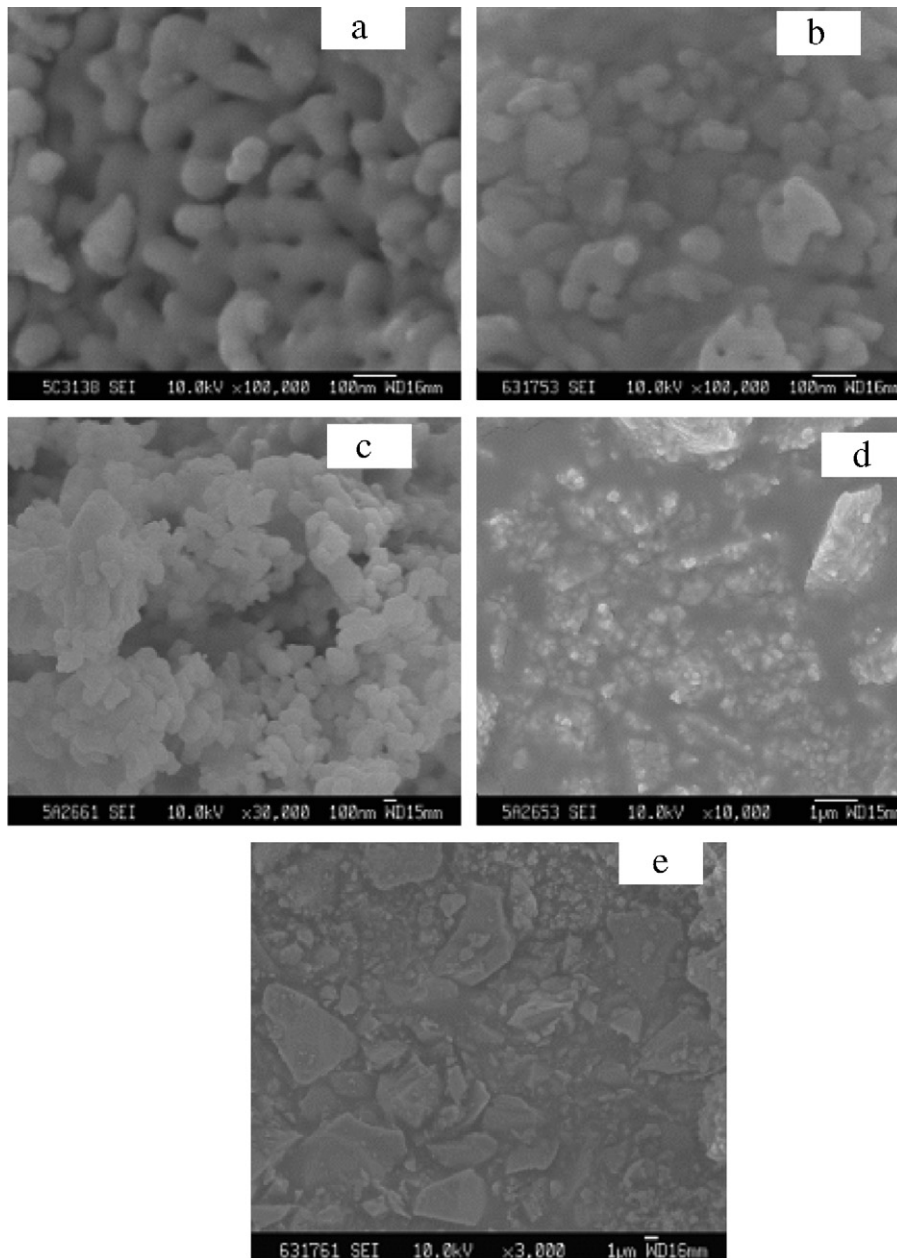


Fig. 2. FESEM images of crystalline TAG:0.03Ce³⁺ phosphors prepared by SC (a), Pechini (b), CP (c) methods sintered at 1100 °C for 4 h, HDHW (d) sintered at 1200 °C and SS (e) method sintered at 1500 °C for 4 h.

Ce³⁺ emission. Strong and broad green–yellow emission is found under 463 nm light excitation (Fig. 3), which is accord with the emission wavelength of a blue-emitting InGaN chip, revealing that the phosphor is a green–yellow phosphor candidate for fabrication of InGaN LEDs.

Fig. 4 is the emission spectra of TAG:Ce³⁺ phosphors prepared by the HDHW (b); SC (c); Pechini (d); CP (e) methods fired at 1200 °C for 4 h and the SS method (a) fired at 1500 °C for 4 h under 463 nm blue light excitation. All the broad green–yellow bands show similar shape and are originated from the Ce³⁺ 5d (²D)–4f (²F_{5/2}, ²F_{7/2}) transitions. However, the integrated emission intensities are different, depending on the synthesis

methods. The emission intensity order is as follows: SS > HDHW > SC > Pechini > CP.

The sample with the SC method shows highest intensity among the wet chemical methods. As mentioned in Section 3.2, SC method is an integrated method combining both CB and Pechini method. Compared with the Pechini and the CP samples, the higher emission intensity of the SC sample is in accord with its relatively uniform morphology from the CB process and the citric acid-sol process. So the SC method was confirmed to be an easy and an effective process for preparing highly efficient and nano-sized Tb₃Al₅O₁₂:Ce³⁺ phosphors. Weaker intensity of the phosphor made with Pechini method may be due to the

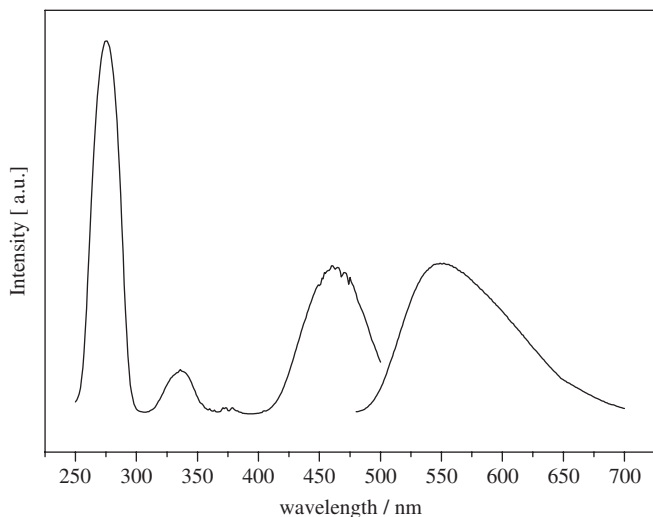


Fig. 3. The excitation ($\lambda_{em} = 550$ nm) and emission ($\lambda_{ex} = 463$ nm) spectra of the TAG:0.03Ce³⁺ phosphors prepared by the SC method at 1100 °C.

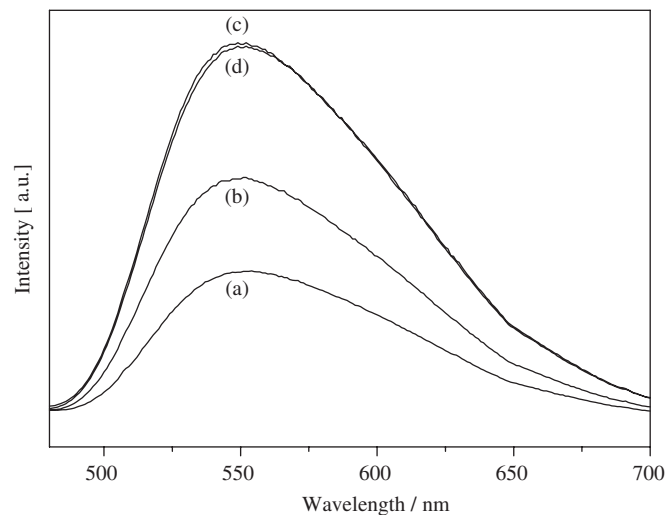


Fig. 5. Emission spectrum ($\lambda_{ex} = 463$ nm) of TAG:0.03Ce³⁺ phosphors prepared by the SC process and calcined at various temperatures.

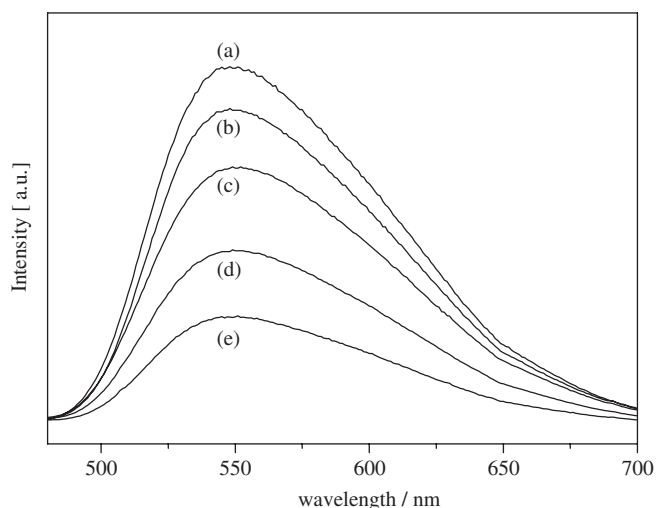


Fig. 4. Emission spectra ($\lambda_{ex} = 463$ nm) of TAG:0.03Ce³⁺ phosphors prepared by the HDHW (b); SC (c); Pechini (d); CP (e) methods at 1200 °C for 4 h and the SS method (a) at 1500 °C for 4 h.

carbon impurity introduced by the remains of organic compounds while the aggregation of the CP sample particles decreases its luminescence. The luminescent intensity of the bulk samples derived by the SS method was higher than the nano-sized TAG:Ce³⁺ samples prepared by the wet chemical methods. The fact indicates that as the particle size of the phosphor becomes smaller, the luminescence efficiency decreases. As have mentioned, the surface properties of the phosphor derived by the HDHW method stands between the SS and the wet chemical methods, so the emission intensity of the samples was weaker than that of the SS method and stronger than the wet chemical methods. It can be confirmed that as for nano-sized phosphors, the more homogeneous the morphology is, the more stronger the emission intensity of the products is. However, as the particle size increases to

micrometer scale, the size will become the most important factor influencing the emission intensity.

The relationship between luminescent intensity and calcination temperature is shown in Fig. 5, using the samples prepared by the SC method as representative. As for the phosphors prepared at different temperatures, the emission intensity of the obtained phosphors increased with a rise in the calcination temperature because of the enhanced crystallinity. However, the intensity remains almost constant when the sintering temperature reached above 1100 °C.

3.4. Comparison of LEDs with the phosphors

Fig. 6 shows the emission spectra of the LEDs with TAG:Ce³⁺ phosphors synthesized by different methods under 20 mA forward bias. The LEDs with the TAG:Ce³⁺ phosphors synthesized by HDHW, SS and CP methods emit strong white light. The corresponding Commission Internationale de l'Éclairage (CIE) chromaticity coordinates are calculated to be (0.338, 0.300) for HDHW, (0.309, 0.282) for SS and (0.288, 0.242) for CP, respectively, based on the emission spectra. Although the emission intensity of LED from SS is stronger, the CIE values of the LED from HDHW are more close to the NTSC standard values for white (0.333, 0.333), which may be attributed to the stronger absorption of the smaller and more regular particles from HDHW synthesis than that of the LED from SS, thus the surplus of the blue emission from the InGAN chip was reduced, and standard white light was emitted. However, the LEDs made with phosphors synthesized by SC and Pechini methods show yellow emission with chromaticity coordinates of (0.462, 0.470) and (0.491, 0.483). The reason may be due to the organic remains during the phosphor preparation process, which reacts with the epoxy resin used in the LED fabrication and

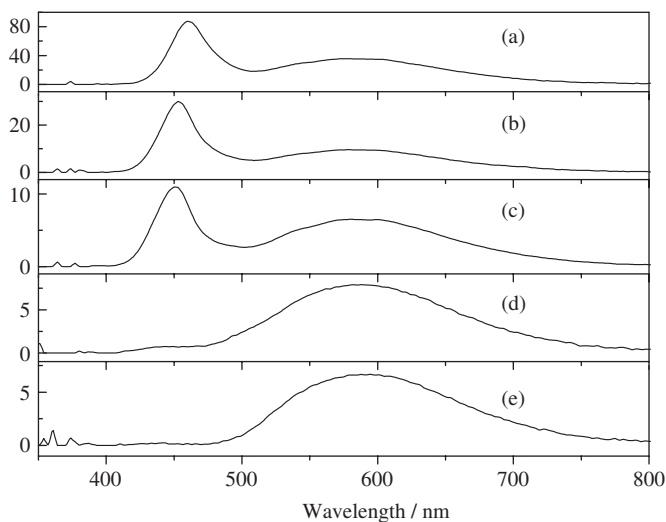


Fig. 6. Emission spectra of the LEDs with TAG:0.03Ce³⁺ phosphors synthesized by different methods (SS (a); CP (b); HDHW (c); SC (d); Pechini (e)) under 20 mA forward bias.

thus change the emission characteristics of the LEDs while different non-radiative mechanisms involved in the LED or physicochemical degradation during its fabrication are also not eliminated.

4. Conclusions

TAG:Ce³⁺ phosphors were prepared by different methods, CP, HDHW methods, SC and Pechini method plus conventional SS method and comparative investigations on the morphologies and the PL were completed. Among the wet chemical methods, SC method is an easy and effective method for preparing superfine phosphors. All the TAG:Ce³⁺ phosphors exhibit strong and broad green–yellow emission under ~460 nm blue light excitation, which is just accord with the blue emission from an InGaN chip. LEDs were fabricated with each phosphor and a ~460 nm emitting InGaN chip. The LEDs from HDHW, SS and CP exhibit strong white emission while those from SC and Pechini emit yellow, revealing that the emission characteristics of LEDs are influenced not only by the morphology and the particle size of the phosphors, but also by the preparing process of the phosphors.

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References

- [1] R. Mueller-Mach, G.O. Mueller, M.R. Krames, T. Trottier, IEEE J. Select. Top. Quant. Electron. 8 (2002) 339–345.
- [2] J.-H. Yum, S.-Y. Seo, S. Lee, Y.-E. Sung, J. Electron. Soc. 150 (2003) H47–H52.
- [3] J.S. Kim, P.E. Jeon, Y.H. Park, J.C. Chol, H.L. Park, G.C. Kim, T.W. Kim, Appl. Phys. Lett. 85 (2004) 3696–3698.
- [4] J.K. Park, C.H. Kim, S.H. Park, H.D. Park, S.Y. Chol, Appl. Phys. Lett. 84 (2004) 1647–1649.
- [5] Using multiple types of phosphor in combination with a light emitting device. Oon, Su Lin US 20050224828 A1
- [6] Manufacturing method and device for white light emission. Lai, Mu-jen US 20050161690 A1
- [7] LED-based white-light emitting lighting unit. Ellens, Andries WO 2001093342 A1
- [8] Luminescent materials for light sources and light sources using the materials. Kummer, Franz WO 2001008452 A1
- [9] M. Batentschuka, A. Osveta, G. Schierninga, A. Klier, J. Schneiderb, A. Winnackera, Radiat. Meas. 38 (2004) 539–543.
- [10] J. Su, Q.L. Zhang, C.J. Gu, D.L. Sun, Z.B. Wang, H.L. Qiu, A.H. Wang, S.T. Yin, Mater. Res. Bull. 1280 (40) (2005) 1279–1285.
- [11] Y.T. Nien, Y. Lin. Chen, I.G. Chen, C.S. Hwang, Y.K. Su, S.J. Chang, F.S. Juang, Mater. Chem. Phys. 93 (2005) 79–83.
- [12] W.T. Hsu, W.H. Wu, C.H. Lu, Mater. Sci. Eng. B 104 (2003) 40–44.
- [13] D. Hreniak, W. Strezk, P. Mazur, R. Pazik, M. Zazbkowska-Waclawek, Opt. Mater. 26 (2004) 117–121.
- [14] X. Li, H. Liu, J.Y. Wang, H.M. Cui, S.L. Yang, I.R. Boughton, J. Phys. Chem. Solids 66 (2005) 201–205.
- [15] X. Li, H. Liu, J.Y. Wang, H.M. Cui, F. Han, Mater. Res. Bull. 39 (2004) 1923–1930.
- [16] M. P. Pechini, US Patent No. 3330697, 1967.
- [17] C.A. Kodaira, H.F. Brito, M.C. Felinto, J. Solid State Chem. 171 (2003) 401–407.
- [18] G.D. Xia, S.M. Zhou, J.J. Zhang, L.H. Zhang, G.Q. Jia, J. Xu, Chin. J. Inorg. Chem. 21 (2005) 1203–1207.
- [19] Y.X. Pan, M. Wu, Q. Su, Mater. Sci. Eng. B 106 (2004) 251–256.
- [20] S.K. Shi, J.Y. Wang, J. Alloys Compd. 327 (2001) 82–86.
- [21] J.J. Zhang, J.W. Ning, X.J. Liu, Y.B. Pan, L.P. Huang, Mater. Res. Bull. 38 (2003) 1249–1256.
- [22] M.T. Jose, A.R. Lakshmanan, Opt. Mater. 24 (2004) 651–659.
- [23] B.Y. Zhang, T.M. Chen, C.R. Chen, G.Y. Hong, Y.M. Li, Chin. J. Lumin. 16 (1995) 139–144.
- [24] H.P. You, G.Y. Hong, Chin. J. Lumin. 18 (1997) 191–194.