

Synthesis and luminescence property of $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ red phosphor prepared by co-precipitation technique for white light emitting diodes

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$(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ red phosphor was synthesized by co-precipitation with ammonium bicarbonate as precipitant. X-ray diffraction result indicated the prepared samples have standard crystal structure of $\text{Sr}_3\text{Al}_2\text{O}_6$, and co-precipitation has lower crystallization temperature than solid state reaction. Scanning electron microscope image revealed the real morphology and particle size of obtained phosphors with weak agglomeration. Red emission of Eu^{2+} centers was shown at peak of 620nm under excitation with wavelength of 440~480 nm, which fitted well with GaN blue chip of white LEDs. As result, the luminescence property of obtained $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ phosphor was improved obviously prepared by co-precipitation comparing with solid-state reaction.

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1. Introduction

As yellow phosphor, $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ [1,2] with blue chip has already been used for white light emitting diode (W-LED). However, without containing red light component, the output “white” light cannot realize the desirable color balance for a true color rendition, which has limited the wide applications of W-LED, so red phosphor play an important role in the realization process of W-LEDs. However, commercial red phosphors for W-LEDs are still limited in sulfide-based materials like $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ and $\text{SrS}:\text{Eu}^{2+}$ [3,4], which have low light-emitting efficiency, large light decay and unstable chemical property. Recently, nitride phosphors with red-emission were reported by Xie and Li [5,6], these red phosphors have strong luminescence and chemical stability, but the raw materials for synthesis are very high cost and unstable, and the process condition is rigorous. Therefore, it is crucial to search for a stable and suitable red phosphor with high quantum efficiency and low cost.

Strontium aluminates with stable structure always used as phosphors by rare earth metal ions doping and they have showed excellent properties [7-12]. Some researchers have reported red luminescent behavior of Eu^{2+} ions in pure $\text{Sr}_3\text{Al}_2\text{O}_6$ phase [13-18], which is suitable for blue excitation chip of W-LED. Until now, all $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ phosphors have been prepared by solid-state reaction and sol-gel method. Always, in sol-gel process, citric acid acts as chelating agent to metal ions to yield a rigid polyester network in which metal atoms are distributed homogeneously [19]. However, aggregation of the uniform particles is appeared to be more serious in sol-gel [20]. The aggregated and sticky sample will have trouble in practical application in LEDs because the particles would

clog the injector during fabrication. Very high temperature heating is required for synthesis by solid-state reaction and the phosphor particles obtained with large size, or some additives as flux, to get a single phase and which often results in inhomogeneous products [21]. As well as known, co-precipitation method has the characteristic of the particle with good chemical uniformity and morphology, which is favorable to luminescent property for less contamination on the phosphor surface. Therefore, it is necessary to prepare $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ with small size and good morphology by co-precipitation method for excellent luminescence property.

In this work, we prepared ultrafine $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ powders at low temperature by co-precipitation. Effects of co-precipitation, wet reaction time and heating temperature on luminescence intensity were discussed. The $5d \rightarrow 4f$ transition of Eu^{2+} with red emission was checked in spectrum. The difference between phosphors prepared by co-precipitation and solid-state reaction were also investigated, such as crystallization temperature, particle size and luminescence intensity.

2. Experimental

With co-precipitation and solid-state reaction methods, $\text{Eu}(\text{NO}_3)_3$ and Eu_2O_3 (99.99%) were used as rare earth sources, $\text{Sr}(\text{NO}_3)_2$ and SrCO_3 were used as the sources of Sr. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and Al_2O_3 (99.99%) were used as the sources of Al, respectively.

2.1 Synthesis of $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ by co-precipitation method

Firstly, the homogeneous solution was prepared with a final molar ratio of 2.88Sr : 2Al : 0.12Eu, where 0.015 mol of Sr^{2+} was used. The solution was added dropwise to 100 ml of ammonium bicarbonate NH_4HCO_3 (0.1 mol) precipitant solution with magnetic stirring at room temperature. After addition finished, the solution was still kept strongly stirring for 2 h and aging for 1 h, and then the resultant suspension was filtered and washed with distilled water. Dried at 100 °C for 2 h and grinded uniformly, the powder was then transferred into a furnace and calcined at high temperature above 1100 °C for 4 h under N_2/H_2 (95/5) mixture atmosphere.

2.2 Synthesis of $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ by solid-state reaction method for contrast

The starting materials were mixed with a final molar ratio of 2.88Sr:2Al:0.12Eu. The mixture was milled thoroughly and transferred into a furnace for complete decomposition of carbonate and formation of new phase at a series of temperature above 1100 °C for 2 h under N_2/H_2 (95/5) mixture atmosphere.

2.3 Characterizations of $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$

The products were characterized by X-ray powder diffraction (XRD) collected on a SIEMENS X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Scanning electron microscopy (SEM) images were taken on a JEOL JSM-6330F field emission scanning electron microscope. Samples were gold coated prior to SEM analysis. The luminescence properties of all phosphors were studied on an Aminco Bowman Series 2 fluorescence spectrophotometer at room temperature.

3. Results and discussion

3.1 Structure

The structure of $\text{Sr}_3\text{Al}_2\text{O}_6:\text{Eu}^{2+}$ samples prepared by co-precipitation and solid-state reaction were investigated by XRD, and results were shown in Fig. 1. XRD pattern of the pure cubic structure for $\text{Sr}_3\text{Al}_2\text{O}_6$ (Fig. 1(a)) is essentially the same as that of the literature (PDF No. 24-1187). All diffraction peaks of samples could be indexed to the cubic system (Space Group: Pa3) of $\text{Sr}_3\text{Al}_2\text{O}_6$, which were matched up to the standard pattern without other phase. According to XRD phase analysis, a little amount of rare earth ions (Eu^{2+}) doping almost has not effect on the $\text{Sr}_3\text{Al}_2\text{O}_6$ phase, because of close ionic radii of Sr^{2+} and Eu^{2+} . In Fig. 1, it was seen that only as low as 1100 °C was necessary to obtain pure $\text{Sr}_3\text{Al}_2\text{O}_6$ phase by co-precipitation. The sample heated at 1200°C by co-precipitation (Fig. 1(c)) showed diffraction peaks become sharper and stronger with increasing heating temperature, which indicated the crystallization of $\text{Sr}_3\text{Al}_2\text{O}_6$ powders

enhanced. A mixture of $\text{Sr}_3\text{Al}_2\text{O}_6$, SrCO_3 , and other phases were observed by solid-state reaction at 1100 °C (Fig. 1(d)), which indicated that SrCO_3 could not be decomposed completely and still exist as residual state. This temperature was too low to obtain pure $\text{Sr}_3\text{Al}_2\text{O}_6$ phase by solid-state reaction. Pure $\text{Sr}_3\text{Al}_2\text{O}_6$ phase appeared when heating above 1300 °C by solid-state reaction (Fig. 1(e)). Compared with solid-state reaction, co-precipitation lowered the crystallization temperature evidently because metal ions were homogeneously cross-linked and distributed in the precursor at the molecular level.

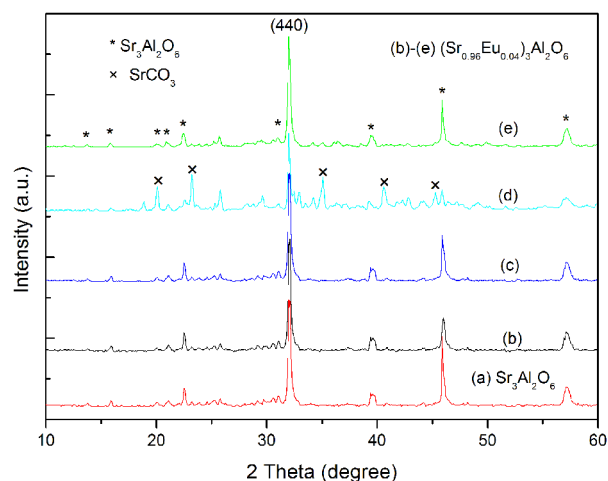


Fig. 1. XRD patterns of standard $\text{Sr}_3\text{Al}_2\text{O}_6$ (a) and $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ phosphors prepared by co-precipitation method: (b) 1100 °C heating, (c) 1200 °C heating; and by solid-state reaction: (d) 1100 °C heating, (e) 1300 °C heating.

3.2 Morphology of $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ phosphors

SEM micrographs were put in Fig. 2, to characterize and compare the microstructure of $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ phosphors prepared by different methods. Comparing with solid-state reaction (Fig. 2(a)), uniform and spherical $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ particles obtained by co-precipitation with homogeneous microstructure at 1100 °C (Fig. 2(b)). It is observed that the diameter of uniform spherical particles is smaller than 50 nm, this is because the reaction of NH_4HCO_3 and metal ions produces a carbonate precursor with an approximate composition of $\text{NH}_4\text{AlSr}(\text{CO}_3)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ [22]. Agglomeration is less serious maybe due to weaker hydrogen bonding in co-precipitation through the heating process [23]. After heating at high temperature, large and irregular particles of $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ with extensive aggregations were obtained by solid-state reaction. For large-scale application of the phosphor, besides of the particle size and morphology, the luminescence intensity should also be seriously considered. Strontium aluminates powders with large size are usually prepared by a solid-state reaction, and smaller particles are always obtained by grinding the

larger phosphor particles, which can easily induce additional defects and greatly reduce the luminescence efficiency.

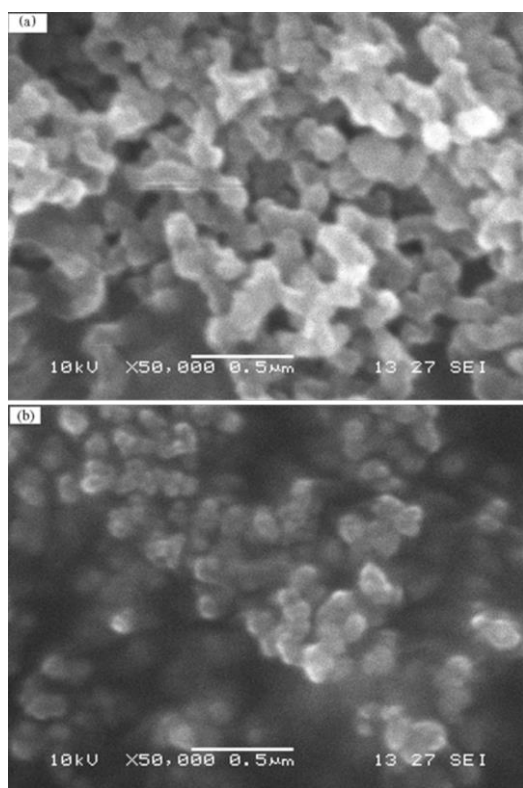


Fig. 2. SEM images of $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ phosphors prepared by (a) solid-state reaction and (b) co-precipitation method.

3.3 Photoluminescence property of $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$

Effect of Eu^{2+} doped-concentration in $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ on luminescent intensity at 620 nm was shown in Fig. 3. With excited at 460 nm, the phosphor powders exhibited a red light emission spectra within the range of 550–700 nm accompanying the main emission speak at 620 nm. This red emission has a broad-band feature, belonging to the emission of $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ions in $\text{Sr}_3\text{Al}_2\text{O}_6$ lattice [24]. With an increase of dopant concentration in the host lattice, the emission intensity of phosphor also can be increased. The optimal intensity was discovered at a Eu^{2+} concentration of about 4% (in mole fraction), and higher Eu^{2+} concentration in host would result in the reduction of luminescent intensity with concentration quenching. For luminescence contrast, other prepared phosphors, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ was used and its spectrum was characterized under the same conditions. Due to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} in 4f configuration, a narrow red emission was obtained from $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor. Under suitable excitation, with Eu^{2+} concentration increasing, the luminescence intensity of $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ is toward to that of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. When Eu^{2+} reaches 2%, $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ has a stronger intensity than $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. It is 2 times more in intensity than $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ when

$(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ with 4% Eu^{2+} , namely, $(\text{Sr}_{0.96}\text{Eu}_{0.04})_3\text{Al}_2\text{O}_6$.

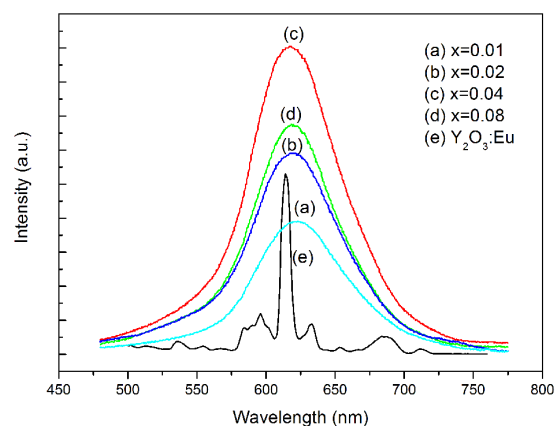


Fig. 3. Emission spectra of $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ phosphors with different Eu^{2+} concentration x under 460 nm excitation: (a) 1%, (b) 2%, (c) 4%, and (d) 8%, emission of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (e) was shown in Fig. as reference.

Generally, heating temperature and wet reaction time are both important factors which affect the crystallization and luminescence intensity. For co-precipitation method, with the increase of reaction time (stirring time), the luminescence intensity is improved significantly as indicated in Fig. 4. That's because longer stirring time can get more homogeneous solution, which improve crystallization of sample. However, the intensity almost remains constant when the reaction time exceeded 8 h regardless of the heating temperature. Both the shape and the position of the spectra show little change with the increase of reaction time, this indicates that the product obtained by the co-precipitation method is more homogeneous comparing with solid-state reaction due to the mixing of starting materials at molecular level [25].

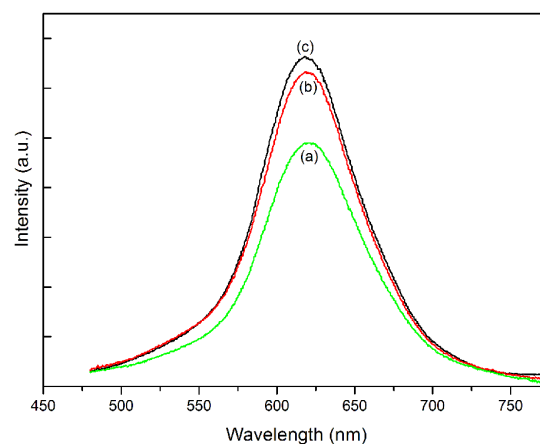


Fig. 4. Emission spectra ($\lambda_{\text{ex}} = 460 \text{ nm}$) of $(\text{Sr}_{0.96}\text{Eu}_{0.04})_3\text{Al}_2\text{O}_6$ prepared by co-precipitation method with different reaction (stirring) time: (a) 4 h, (b) 6 h, and (c) 8 h.

Fig. 5 shows emission spectra of the $(\text{Sr}_{0.96}\text{Eu}_{0.04})_3\text{Al}_2\text{O}_6$ powders by co-precipitation heat-treated at: (a) 1100 °C, (b) 1200 °C, (c) 1300 °C and (d) 1400 °C, respectively. With the excited wavelength at 460 nm, the powders exhibited the red light emission spectra within the range of 550–700 nm with the main emission speak at 620 nm. However, the emission intensity of sample in Fig. 5 ((b), (c) and (d)) was much stronger than that of sample in Fig. 5(a), that is, the emission intensity at 620 nm significantly increased with the increasing heat-treated temperature. The highest emission intensity was observed with the sample heat-treated at 1400 °C, that's because high temperature favors the doping Eu^{2+} ions into $\text{Sr}_3\text{Al}_2\text{O}_6$ lattice [17]. But if increase temperature unceasingly, the intensity would decrease because too large particle size prevent the emission from Eu^{2+} centers. These results indicate that the great dependence of the luminescent intensity on the crystallization of the prepared $(\text{Sr}_{0.96}\text{Eu}_{0.04})_3\text{Al}_2\text{O}_6$ powders. Generally, it is noted that synthesizing process for obtaining particles with the shape of a non-agglomerate as well as high crystallization plays an important role in the improvement of luminescent efficiency [26]. The difference in XRD intensities due to crystallization of powders causes variations in luminescence efficiency.

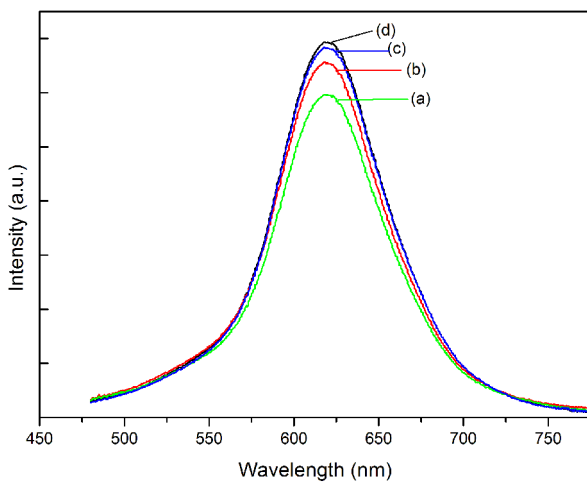


Fig. 5. Emission spectra ($\lambda_{ex} = 460$ nm) of $(\text{Sr}_{0.96}\text{Eu}_{0.04})_3\text{Al}_2\text{O}_6$ prepared by co-precipitation under N_2/H_2 flow for different heating temperature: (a) 1100 °C (b) 1200 °C (c) 1300 °C and (d) 1400 °C

3.4 Effect of preparation method on luminescence property

Heat treatment was carried at a temperature of 1100 °C and 1400 °C for co-precipitation and solid-state reaction methods. The excitation spectrum and comparative investigation on emission spectra were shown in Fig. 6. From 400 nm to 535 nm, the excitation spectrum of the phosphors shows a wide band in the visible light range from 440 nm to 480 nm with peak at about 460 nm. These can be attributed to crystal field splitting of Eu^{2+} d-orbital with $4f^7 \rightarrow 4f^65d$ transition. Luminescence intensity of the

products obtained through co-precipitation sintered at 1100 °C was much higher than that of the product through solid-state reaction sintered at same temperature. This is due to a molecular-level mixing of raw materials and the decrease of crystallization temperature through the combustion of organic reagents in wet chemical methods. The lower emission intensity of the phosphor obtained by solid-state reaction at 1100 °C is mainly attributed to an incomplete crystallization of $\text{Sr}_3\text{Al}_2\text{O}_6$ according to XRD (Fig. 1). However, with the higher heating temperature at 1400 °C under N_2/H_2 flow, both the phosphors obtained the stronger luminescence intensity, especially sample prepared by co-precipitation method, this maybe due to that the higher heating temperature can help Eu^{2+} ions doping into Sr^{2+} sites of $\text{Sr}_3\text{Al}_2\text{O}_6$ crystal lattice. But co-precipitation method is a better chose to improve luminescence intensity with good morphology and simple operation.

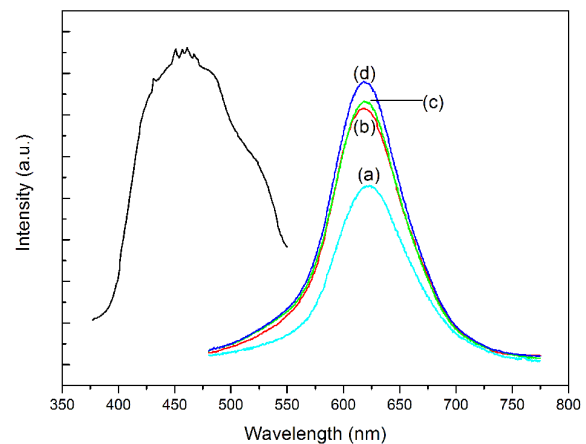


Fig. 6. Excitation and emission spectra ($\lambda_{ex} = 460$ nm & $\lambda_e = 620$ nm) of $(\text{Sr}_{0.96}\text{Eu}_{0.04})_3\text{Al}_2\text{O}_6$ prepared by different method heating under N_2/H_2 flow: (a) solid-state reaction at 1100 °C (b) co-precipitation method at 1100 °C (c) solid-state reaction at 1400 °C and (d) co-precipitation method at 1400 °C respectively.

4. Conclusions

In this paper, red-emitting phosphor, $(\text{Sr}_{1-x}\text{Eu}_x)_3\text{Al}_2\text{O}_6$ has been prepared successfully by co-precipitation and solid-state reaction, respectively. At same temperature, for example 1100 °C, the luminescence intensity of phosphor can be improved by co-precipitation comparing with solid-state reaction method. It's also indicated that co-precipitation always gives rise to spherical particles with small size and the crystallization temperature is much lower than solid-state reaction. Both using co-precipitation and increasing heating temperature affect the crystallization and luminescence intensity of aluminate phosphors, especially, co-precipitation method is a more effective way to improve luminescence property of phosphors. That's because it improves the crystallization and morphology of $\text{Sr}_3\text{Al}_2\text{O}_6$ particles and favors the doping Eu^{2+} ions into $\text{Sr}_3\text{Al}_2\text{O}_6$ lattice.

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References

- [1] V. Bachmann, C. Ronda, A. Meijerink, *Chem. Mater.* **21**, 2077 (2009).
- [2] Y.-T. Nien, K.-M. Chen, I.-G. Chen, *J. Am. Ceram. Soc.* **93**, 1688 (2010).
- [3] C. Guo, L. Luan, C. Chen, D. Huang, Q. Su, *Mater. Lett.* **62**, 600 (2008).
- [4] H.-S. Do, E.-J. Kim, S.-H. Hong, *J. Lumin.* **130**, 1400 (2010).
- [5] Z. Xu, C. Li, G. Li, R. Chai, C. Peng, D. Yang, J. Lin, *J. Phys. Chem. C* **114**, 2573 (2010).
- [6] L.-Y. Zhou, J.-S. Wei, F.-Z. Gong, J.-L. Huang, L.-H. Yi, *J. Solid State Chem.* **181**, 1337 (2008).
- [7] D. B. Bem, A. S. Luyt, F. B. Dejene, J. R. Botha, H. C. Swart, *Physica B* **404**, 4504 (2009).
- [8] S. Sakirzanovas, A. Katelnikovas, D. Dutczak, A. Kareiva, T. Jüstel, *J. Lumin.* **131**, 2255 (2011).
- [9] M. Ayvacıkl, A. Ege, S. Yerci, N. Can, *J. Lumin.* **131**, 2432 (2011).
- [10] X. Y. Chen, C. Ma, S. P. Bao, *Solid State Sci.* **12**, 857 (2010).
- [11] F. Clabau, X. Rocquefelte, S. Jobic, P. Deniard, M. Whangbo, A. Garcia, T. Le Mercier, *Solid State Sci.* **9**, 608 (2007).
- [12] M. Fechner, F. Reichert, N.-O. Hansen, K. Petermann, G. Huber, *Appl. Phys. B* **102**, 731 (2011).
- [13] Y. Xu, Y. He, X. Yuan, *Powder Technol.* **172**, 99 (2007).
- [14] M. Akiyama, C. Xu, K. Nonaka, T. Watanabe, *Appl. Phys. Lett.* **73**, 3046 (1998).
- [15] P. Huang, C. Cui, S. Wang, *Opt. Mater.* **32**, 184 (2009).
- [16] C. Chang, W. Li, X. Huang, Z. Wang, X. Chen, X. Qian, R. Guo, Y. Ding, D. Mao, *J. Lumin.* **130**, 347 (2010).
- [17] P. Zhang, M. Xu, Z. Zheng, L. Liu, L. Li, *J. Sol-Gel Sci. Technol.* **43**, 59 (2007).
- [18] M. Peng, N. Da, Y. Qiao, B. Wu, C. Wang, D. Chen, J. Qiu, *J. Rare Earth* **24**, 749 (2006).
- [19] P. Zhang, L. Li, M. Xu, L. Liu, *J. Alloys Compd.* **456**, 216 (2008).
- [20] S. Wu, S. Zhang, J. Yang, *Mater. Chem. Phys.* **102**, 80 (2007).
- [21] Y. Tian, P. Zhang, Z. Zheng, Y. Chai, *Mater. Lett.* **73**, 157 (2012).
- [22] C. Chang, Z. Yuan, D. Mao, *J. Alloys Compd.* **415**, 220 (2006).
- [23] Y. Pan, M. Wu, Q. Su, *Mater. Sci. Eng. B* **106**, 251 (2004).
- [24] S. K. Sharma, S. S. Pitale, M. Manzar Malik, M. S. Qureshi, R. N. Dubey, *J. Alloys Compd.* **482**, 468 (2009).
- [25] X. Y. Chen, S. P. Bao, Y. C. Wu, *J. Solid State Chem.* **183**, 2004 (2010).
- [26] G. Y. Hong, B. S. Jeon, Y. K. Yoo, J. S. Yoo, *J. Electrochem. Soc.* **148**, H161 (2001).

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