

Synthesis of cerium-doped yttrium aluminum garnet nanopowder low-temperature reaction combustion method

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Abstract. Nanopowders of cerium doped yttrium aluminum garnet ($Y_3Al_5O_{12}:Ce^{3+}$) - YAG:Ce were prepared by low-temperature sol-gel method. High-purity Y_2O_3 , $Al(NO_3)_3 \cdot 9H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$ in the presence of citric acid as complexing agent were used as initial materials. The YAG:Ce nanopowders were characterized using X-ray diffraction, SEM, dynamic light scattering particle size analyzer and a high resolution spectrometer-Microspec-235b. The particle sizes of the YAG:Ce powder were estimated from SEM image and dynamic light scattering particle size analyzer to be 4 – 80 nm. The annealing effect on the crystalline structure of the samples was reported.

Keywords: YAG:Ce nanopowder; Sol-Gel method; Photoluminescence (PL).

1. Introduction

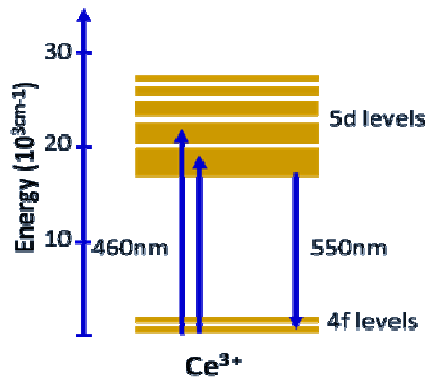
Yttrium aluminium garnet, $Y_3Al_5O_{12}$ (YAG) is a synthetic crystalline material of the garnet group. It is also one of three phases of the yttria-aluminium composite, the other two being yttrium aluminium monoclinic (YAM) and yttrium aluminium perovskite (YAP). Yttrium aluminium garnet (YAG) possesses many interesting properties such as excellent thermal conductivity, high mechanical strength, high temperature resistance and radiation resistance. Therefore, it has been widely used for lasers and luminescent materials [1-2]. YAG is commonly used as a host material in various solid-state lasers. Rare earth elements such as neodymium and erbium can be doped into YAG as active laser ions, yielding YAG:Nd and YAG:Er lasers, respectively. Cerium-doped YAG (YAG:Ce) is used as a phosphor in cathode ray tubes and white light-emitting diodes, and as a scintillator.

Cerium is a silvery metal, belonging to the lanthanide group. It is the most abundant of the rare earth elements having numerous commercial applications like catalysts, additives to fuel to reduce emissions and to glass and enamels to change their color. Cerium is especially interesting because of

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its variable electronic structure. The energy of the inner 4f level is nearly the same as that of the outer or valence electrons, and only small energy is required to change the relative occupancy of these electronic levels.

It is known that the YAG-based material, which developed by Nichia, has the best performance in terms of efficiency [3]. Under a blue light excitation, the luminescence spectrum of cerium doped yttrium aluminum garnet $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG:Ce) phosphor is broad from 500 to 650 nm, that is explained due to the 5d-4f transition of Ce^{3+} ion (Fig.1). This is why the YAG:Ce phosphor has extensive application in white light emitting diodes (WLED) by covering the YAG:Ce phosphor onto a chip of the blue InGaN diode. The white light appears in such WLEDs because of the converting part of the blue light of InGaN diode into yellow light emitted from YAG:Ce. However, such an arrangement gives less than ideal color rendering index. The output brightness decreases with increasing temperature, and thus further altering device color output. To obtain properties of higher power and brightness, there are many technologies used for preparation of YAG powder with high crystallinity, small particle size and regular morphology as solid-state reaction [4–7], co-precipitation [8–9], polymer network [10] and sol-gel process [11], etc. In this work, we used a sol-gel low temperature combustion method to prepare YAG:Ce phosphor. The aim of the research is to get the YAG:Ce phosphor with a high crystallinity, a small grain size and a uniform morphology at low preparation temperatures. Sol-gel was firstly prepared by the complex method using rare earth oxides, inorganic nitrate and citric acid as raw materials, and then YAG:Ce phosphor by low-temperature reaction combustion process was obtained.



2. Experimental

2.1 Raw materials

Nanocrystalline YAG and YAG:Ce (with a Ce concentration of 0.7 mol %) powders were prepared by low-temperature reaction combustion process. In order to get the YAG:Ce nanopowder at low temperature, the kind of raw materials for the precursor materials was chosen carefully. The following chemically pure reagents were used: Y_2O_3 , HNO_3 , $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ and ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$).

2.2 Preparation of phosphor powder

The experimental setting of a sol-gel low temperature combustion method is shown in Fig.2. The YAG:Ce powders with composition corresponding to the formula $Y_3Al_5O_{12}:Ce$ were synthesized from above mentioned precursor materials. The yttrium oxide Y_2O_3 was dissolved in a hot nitric acid in flask three necks to obtain solution. The solution was agitated for 2 hours at temperature of $60\text{ }^\circ\text{C} - 65\text{ }^\circ\text{C}$. Then the solution was added by the aluminum nitrate and cerium nitrate to get the bright yellow solution. In the next step, citric acid ($C_6H_8O_7 \cdot H_2O$) was added in the bright yellow solution. Citric acid was dissolved in this solution by half the mole of the total metal ions. The pH value of the solution was modulated to 4, and a gel was obtained after immersing the solution in a water bath at $80\text{ }^\circ\text{C}$ for 1 hour. Then the gels were dried to obtain canary xerogel. The xerogel was put into a muffle stove and a combustion reaction occurred at $245\text{ }^\circ\text{C}$ for 20 minutes, the spumous powder was obtained. The calcination was conducted at $700\text{ }^\circ\text{C}$ with a heating rate of $2\text{ }^\circ\text{C}/\text{min}$ and kept for 120 min, and then the temperature was increased up to different holding temperatures ($800-1300\text{ }^\circ\text{C}$) at a rate of $10\text{ }^\circ\text{C}/\text{min}$ for a fixed holding time of 120 minutes in air.

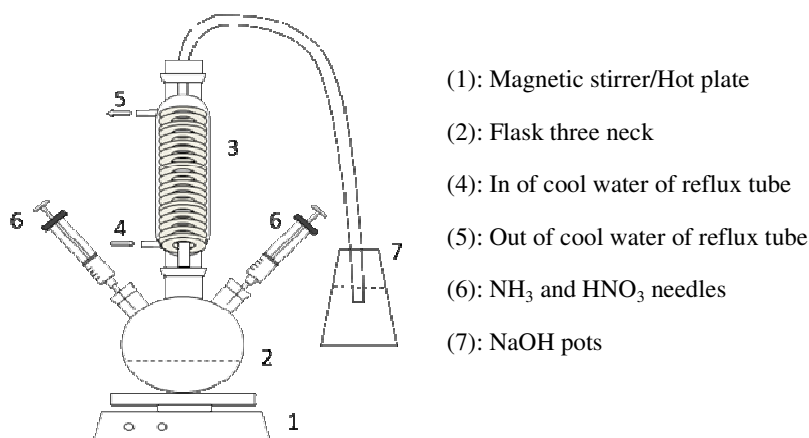


Fig. 2. Schematic diagram of synthesis of the YAG:Ce nanopowder by low temperature combustion method.

2.3 Characterization of phosphor powders

Crystalline phase analysis was accomplished with a "D8 Advance" – Bruker X-ray diffractometer. Particle sizes were evaluated using scanning electron microscopy (SEM) Hitachi S4800. The distribution of size of YAG:Ce particles was analyzed by using a "LB-550" dynamic light scattering particle size analyzer. The luminescence spectra were taken on a high resolution spectrometer with Acton SpectraPro-2300i.

3. Results and discussion

3.1. Annealing effects on crystallization

The XRD patterns shown in Fig. 3 indicate that the YAG powder was well crystallized above 1000 °C annealing temperature. The crystalline phase of CeO₂ was appeared in the XRD patterns revealing that there is still residual CeO₂ in the sample. The obtained results showed that the crystalline size of the YAG powders was strongly dependent on the annealing temperature. The crystallite phase of YAG did not appear for the sample annealed at 240 °C, and can only be seen in the samples annealing at 700 °C (curve b). Highly crystalline YAG was obtained after annealing the sample at 1200 °C (curve g).

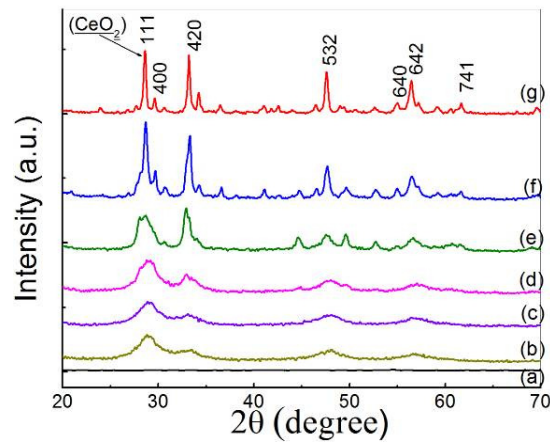
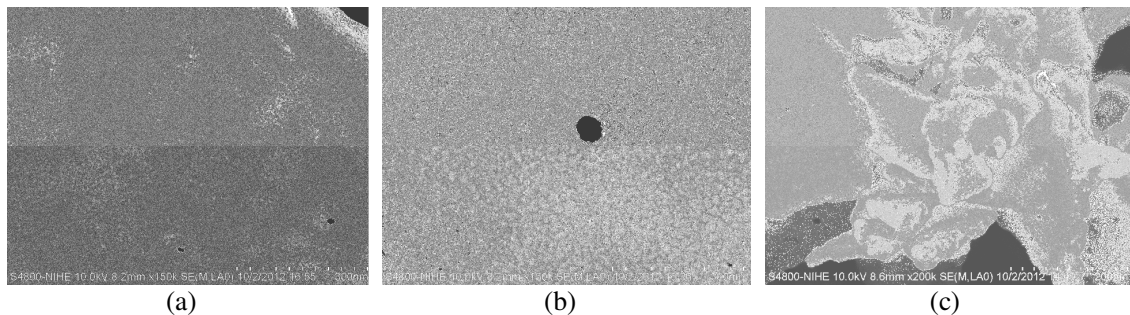


Fig. 3. XRD patterns of samples at different annealing temperatures: 240 °C (a), 700 °C (b), 800 °C (c), 900 °C (d), 1000 °C (e), 1100 °C (f), 1200 °C (g).

Fig. 4 shows the SEM images of YAG:Ce powders at different annealing temperature. The samples were calcined at different temperatures (700–1200 °C) for 120 minutes. It is not clear that the YAG:Ce are uniform and spherical particles.



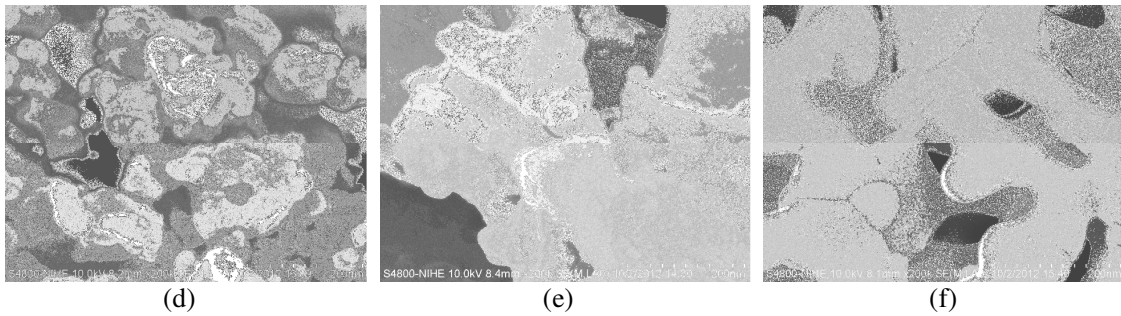
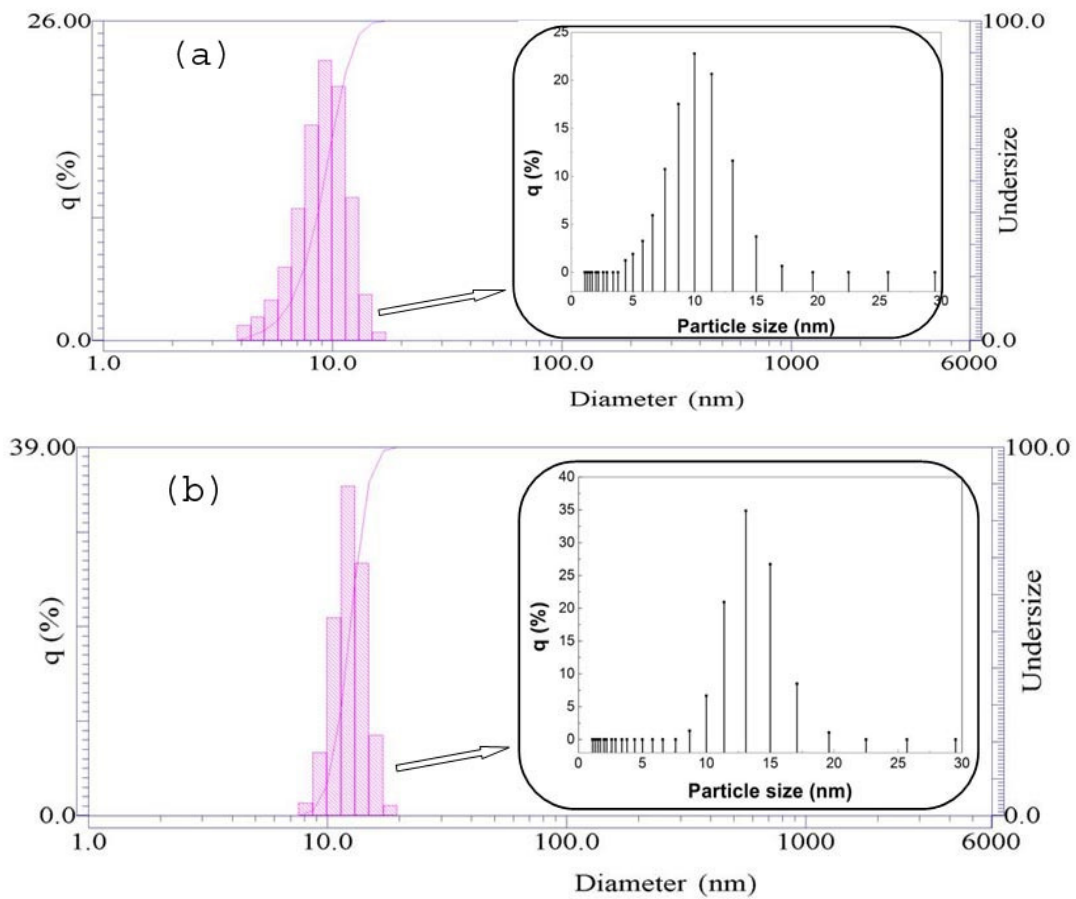


Fig. 4. SEM images of the YAG:Ce powders at difference annealing temperatures: 700 °C (a), 800 °C (b), 900 °C (c), 1000 °C (d), 1100 °C (e), 1200 °C (f).

To evaluate the uniform, spherical properties and size distribution of the YAG:Ce powder, we have investigated the samples on a LB-550 dynamic light scattering particle size analyzer. Figures 5 shows the size distribution of the YAG:Ce particles for the sample annealed at temperature of 700 °C, 1000 °C and 1200 °C.



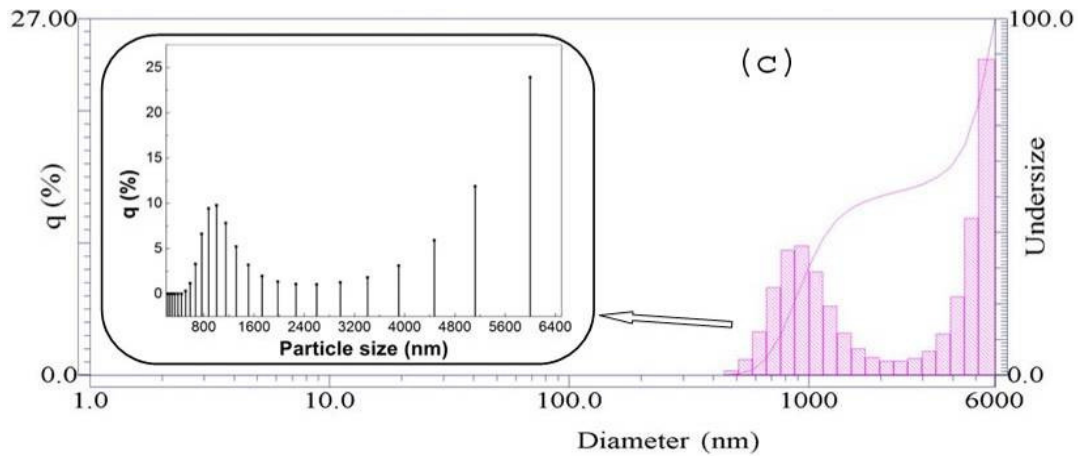


Fig. 5. Distribution of the particle size of the YAG:Ce powder annealed at difference temperatures: 700 °C (a), 1000 °C (b), 1200 °C (c)

From the Fig. 5 one can see that almost particles in the sample annealed at 700 °C are nanosize. Their size consists of from 4 to 17 nm. Whereas for the sample annealed at 1000 °C the dispersed particles have a size ranging from 8.7 nm to 20 nm, and for the sample annealed at 1200 °C there are no observed nanoparticles. Therefore, with the calcining temperature increasing to 1200 °C, the grain size grew gradually and having particle distribution from 500 nm to 6000 nm.

From our investigation it has been seen that the annealing temperature strongly affected to the growth of the particle size in the YAG:Ce powder. The particles size of the YAG:Ce powder annealed at 1200 °C is much larger in comparison with samples annealed at 700 and 1000 °C.

In terms of the luminescence, the small size of the YAG powder is not necessary. The bigger particle size is, the higher PL intensity is [11]. However, the formation of nano-sized YAG:Ce particles are also interesting result. With few nano-sized particles, YAG can be used for biomarker, pigments in printing, organic and inorganic hybrid solar cell, etc.

3.2 Photoluminescence spectra

Emission intensity is one of the key parameters for the application of the YAG:Ce powder. Fig. 6 is the emission spectra of the YAG:Ce powder prepared by low-temperature reaction combustion at an annealing temperature of 1200 °C and 0.5 mol% cerium doping concentration. Fig. 6 shows the characteristic 4f→5d transitions of Ce³⁺ of YAG:Ce powder under excitation wavelengths of 442 nm and 325 nm. The PL spectrum consists of a broadband emission in the green region centered at around 520 nm. Moreover, the Fig. 6 also indicates that the PL intensity was strongly depended on annealing temperature and the peak wavelength is not shift when increase temperature. The higher annealing temperature is, the stronger PL intensity is.

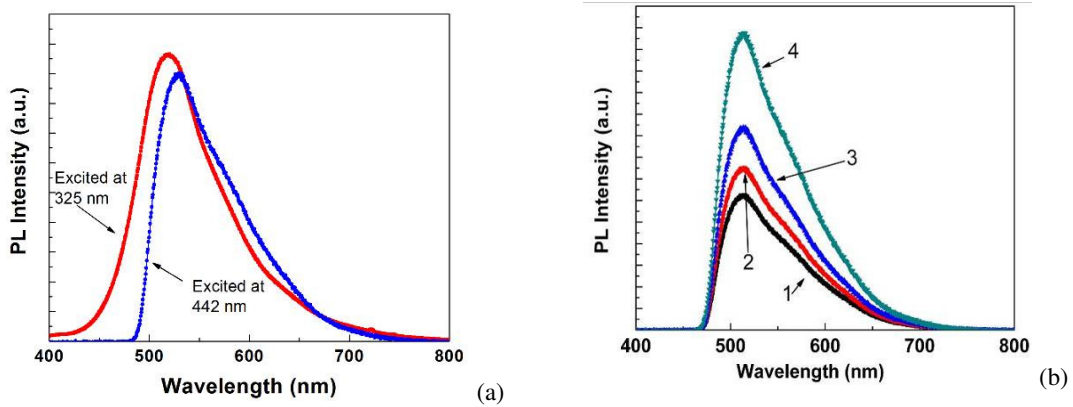


Fig. 6. PL of YAG:Ce: Excited by He-Cd laser at 325 nm and 442 nm (a); Excited by 442 nm at difference annealing temperature (b): (1) 700°C, (2) 900°C, (3) 1100°C, (4) 1200°C.

It is known that the YAG:Ce phosphor has extensive application in white light emitting diode (WLED). Figure 7 is the electroluminescence spectrum and CIE-1931 coordinate of WLED made by coating a nanocomposite with a weight ratio of 3/1 of YAG:Ce / MEH-PPV (Poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene]) composite on a blue LED chip. The emission spectrum of the WLED recorded under a supply voltage of 3.5 V and current of 200 mA by LED characterization system CCD array spectrometer (LCS-100). The peak of electroluminescence spectrum at 455 nm, 520 nm and 590 nm are contributed by blue LED chip, YAG:Ce and MEH-PPV, respectively. WLED has colour coordinates at $x = 0.2596$ and $y = 0.2674$. One can notice that the white light region is located inside the ellipse with the centre at E ($x = 0.33$ and $y = 0.33$). It is seen that for the WLED and the CRI was found to be as high as $R_a = 81.14$.

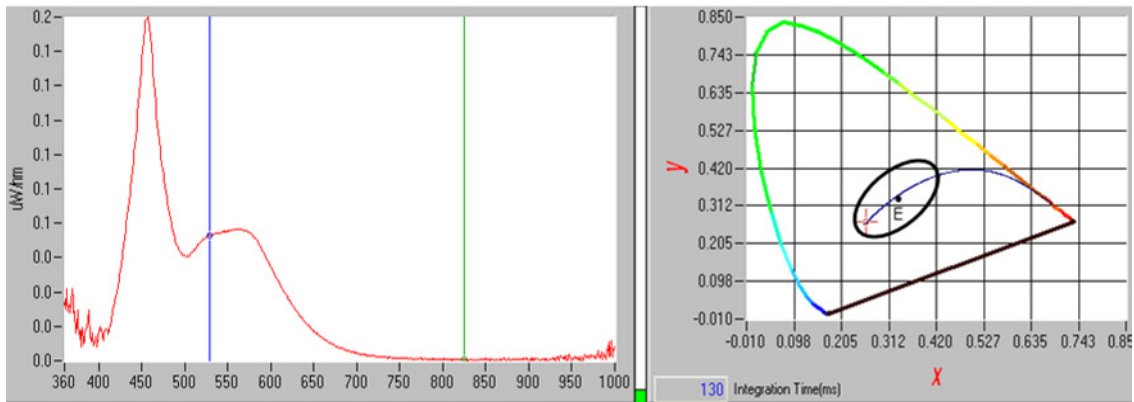


Fig. 7. Electroluminescence spectrum of WLED made by coating YAG:Ce and MEH-PPV hybrid composite onto InGaN blue chip.

4. Conclusion

The YAG:Ce powders of nanosized particles were prepared by a low-temperature reaction combustion method. The crystallization process and photoluminescent intensity of YAG:Ce powders was found to be strongly dependent on annealing temperature. The YAG:Ce powders exhibit a broad luminous emission with the peak at 520 nm. It is useful for fabrication WLED to get high colour rendering index.

Acknowledgments

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References

- [1] G. J. Li, H. J. Lee, T. Mori, Crystal phase and sinter-ability of wet-chemically derived YAG powders, *J. Ceram. Soc. JPN.* 108(5) (2000) 439.
- [2] C. Y. Miao, D. P. Li, L. F. Liu, X. X. Luo, K. Wei, Synthesis and luminescence properties of YAG:Ce³⁺, *Chin. J. Spec. Lab.* 3 (2004) 563.
- [3] Y. Shimizu, Development of White LED light source, *The Rare Earth Soc. JNP.* 40 (2002) 150.
- [4] Y. X. Pan, M. M. Wu, Q. Su. Tailored photoluminescence of YAG:Ce phosphor through various methods, *J. Phys. Chem. Sol.* 65 (2004) 845.
- [5] J. G. Li, T. Ikegami, J. H. Lee, T. Mori, Y. Yajima, Co-precipitation synthesis and sintering of yttrium aluminum garnet (YAG) powders: The effect of precipitant, *Journal of the European Ceramic Society*, 20 (2000) 2395.
- [6] S. J. Abell, R. I. Harris, B. Cockayne, B. Lent, An investigation of phase stability in the Y₂O₃-Al₂O₃ system, *J. Mater. Sci.* 9(4) (1974) 527.
- [7] Q. U. Zhang, F. Saito, Mechanochemical solid reaction of yttrium oxide with alumina leading to the synthesis of yttrium aluminum garnet, *Powder Technol.* 129 (2003) 86.
- [8] J. Su, Q. L. Zhang, C. J. Gu, D. L. Sung, B. Z. Wang, L. H. Qiu, H. A. Wang, T. S. Yin, Preparation and characterization of Y₃Al₅O₁₂(YAG) nano-powder by co-precipitation method, *Mater. Research Bulletin*, 40(8) (2005) 1279.
- [9] Z. H. Wan, L. Gao, K. Niihara, Synthesis of nanoscaled yttrium aluminum garnet powder by the co-precipitation method, *Mater. Sci. Eng.* A288 (2000) 1.
- [10] C. J. Liu, R. M. Yu, Z. W. Xu, J. Cai, X. H. Yan, X. T. Luo, Crystallization, morphology and luminescent properties of YAG:Ce³⁺ phosphor powder prepared by polyacrylamide gel method, *Tran. Nonferrous Met. Soc. China* 17(5) (2007) 1093.
- [11] V. Michael, M. Sanjay, K. Aivaras, J. Mohammad, Z. Michael, H. Volker, Low temperature synthesis of nanocrystalline Y₃Al₅O₁₂ and Ce-doped Y₃Al₅O₁₂ via different sol-gel methods, *J. Mate. Chem.* 9 (1999) 3069.