Journal of Alloys and Compounds 509 (2011) 4331–4335

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Luminescent properties of $Y(P,V)O_4:Eu^{3+}$ phosphors prepared by combining liquid phase precursor method and planetary ball milling

Jung-Hoo Shin[a], Sung-Woo Choi[a], Seong-Hyeon Hong[a,*], Soon-Jae Kwon[b], Soo-Yeon Seo[b], Hyun-Sik Kim[b], Young-Hyun Song[c], Dae-Ho Yoon[c]

[a] Department of Materials Science and Engineering and Research Institute of Advanced Materials, Seoul National University, Seoul 151-744, Republic of Korea
[b] Materials Research Lab, Samsung Advanced Institute of Technology, Yongin 446-712, Republic of Korea
[c] School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea

ARTICLE INFO

Article history:
Received 20 September 2010
Received in revised form 5 January 2011
Accepted 7 January 2011
Available online 14 January 2011

Keywords:
Phosphors
Optical properties
Luminescence
Planetary ball milling
$Y(P,V)O_4:Eu^{3+}$

ABSTRACT

Red emitting nano-sized $Y(P,V)O_4:Eu^{3+}$ phosphors were prepared by liquid phase precursor (LPP) method followed by grinding in planetary ball mill, and their photoluminescence (PL) properties were investigated. A single phase $Y(P,V)O_4:Eu^{3+}$ phosphor was successfully synthesized by LPP process, and as-synthesized phosphor exhibited an elongated morphology of ~2 μm long and ~400 nm wide. The planetary ball milling yielded a spherical nano-powder of ~100 nm size and its PL intensity decreased to 17% of as-synthesized phosphor due to some degree of amorphization. The subsequent annealing at 1100 °C produced a well-crystallized, polygonal shaped $Y(P,V)O_4:Eu^{3+}$ nano phosphor of ~300 nm size and its PL intensity increased to 120% compared to both as-synthesized and commercial $Y(P,V)O_4:Eu^{3+}$ phosphors.

1. Introduction

Eu^{3+}-doped yttrium orthovanadate ($YVO_4:Eu^{3+}$) has been used as a red phosphor in color television and cathode ray tubes, owing to its high luminescence efficiency upon electron-beam excitation [1]. Recently, it has been considered as an alternative red phosphor for a plasma display panel (PDP) application because it exhibits a great color saturation in the red compared to the commercial $(Y,Gd)BO_3:Eu^{3+}$ phosphor [2]. For the improved performance, the researches were focused on the effects of host matrix composition, particle size, and morphology on the luminescence properties. A complete solid solution has been reported in $Y(P_{1-x}V_x)O_4:Eu^{3+}$ thin films from $x=0$ to $x=1$ with xenotime structure [3], and the partial substitution of P for V and Gd for Y exhibited the better luminescent properties [4,5]. An extensive research work has been performed on the nanosized $YVO_4:Eu^{3+}$ [6,7], but nanoparticle phosphors (≪100 nm) usually showed low quantum yields and consequently low emission intensities compared to bulk counterparts [8–11]. The highest emission intensity in $YBO_3:Eu^{3+}$ phosphors was observed at ~500 nm size when examined in the range of 17–3000 nm-sized phosphors [12]. However, the nanocrystalline Y_2O_3:Eu phosphor (~100 nm) without any surface defect layer showed a 10–20% higher photoluminescence efficiency compared to the commercial bulk material [13], and similar improvement was observed in the microwave-induced solution combustion synthesized nanocrystalline $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) phosphor [14]. The spray pyrolysis-derived spherical $YVO_4:Eu^{3+}$ phosphors have a higher emission intensity than that of citrate gel-derived non-spherical phosphors due to high packing density and low scattering of light [15]. The hydrothermally synthesized $YVO_4:Eu^{3+}$ phosphors exhibited the different morphologies depending on the pH values, and the soybean-like nanopowders showed a higher intensity than those with other shapes [16]. The different host morphology in nanocrystalline $YVO_4:Eu^{3+}$ phosphor changes the site symmetry around Eu^{3+} ions, which influences the chromaticity (color purity) of phosphors [17]. In addition, the optimization of other extrinsic properties such as particle agglomeration, dispersion, surface passivation, and core-shell structure is also known to have a great impact on the luminescence efficiency [18–21].

In this study, a single phase $Y(P,V)O_4:Eu^{3+}$ red phosphor was synthesized by liquid phase precursor (LPP) method using cellulose pulp as a template, which yielded the elongated micron-sized powder. To produce nano-sized phosphor with spherical shape, as-synthesized powder was treated by a planetary ball milling and post-annealed at various temperatures. The photoluminescence (PL) properties of the obtained nano-sized $Y(P,V)O_4:Eu^{3+}$ phosphors were investigated and the comparison has been made

* Corresponding author. Tel.: +82 2 880 6273; fax: +82 2 884 1413.
E-mail address: shhong@snu.ac.kr (S.-H. Hong).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.01.060

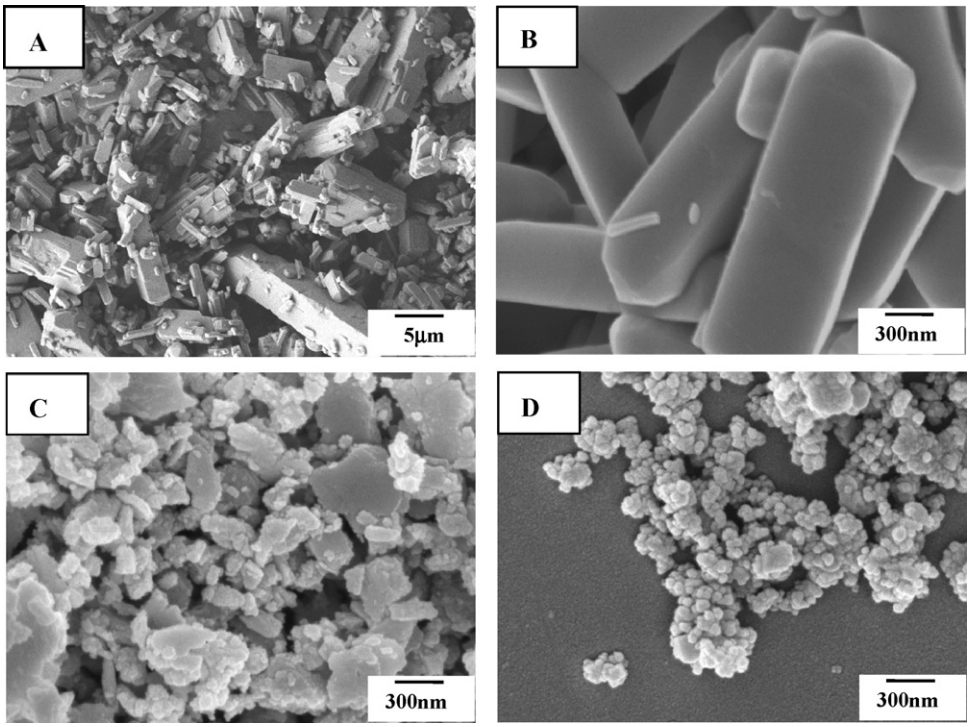

Fig. 1. FESEM micrographs of (A) commercial, (B) as-synthesized, and milled $Y(P,V)O_4$:Eu phosphors for (C) 12 h and (D) 48 h.

with both as-synthesized and commercially available micron-sized $Y(P,V)O_4:Eu^{3+}$ phosphors.

2. Experimental

$Y_{0.97}(P_{0.845}V_{0.455})O_4:Eu_{0.03}{}^{3+}$ phosphor was prepared by LPP technique using $V(SO_4)_2{\cdot}xH_2O$, $YCl_3{\cdot}6H_2O$, $Eu(NO_3)_3{\cdot}6H_2O$, and P_2O_5 as starting materials. The lint-free cellulose pulp ($C_6H_{10}O_6$) was used as a template and it was impregnated in the mixed aqueous solution of the stoichiometric metal salts at a ratio of 1.1–1.3 in weight. The impregnated pulp was calcined at 1150 °C for 1 h in air to obtain a single phase $Y(P,V)O_4$:Eu phosphor. Further details of material preparation are illustrated elsewhere [11]. A planetary ball milling was employed, which is known to be a very effective method to produce nano-sized powder [22]. Ball milling was conducted in planetary ball mill (Pulverisette 5, FRITSCH, Germany) with zirconia balls and zirconia jar in absolute ethanol medium. The rotation speed was 250 rpm and milling time was varied from 12 to 48 h. The milled powders were dried at 80 °C for 24 h and then post-annealed between 900 and 1200 °C for 1 h in air to eliminate the defects introduced by planetary ball milling and recover the crystallinity.

The phases of the obtained powders were examined by X-ray diffraction (XRD, M18XHF-SRA, MAC Science Co.). The powder morphology was observed by field emission scanning electron microscopy (FE-SEM, JSM-6330F, JEOL), after Pt coating on carbon tape. The specific surface area of the powders was determined using nitrogen absorption (BET) (Model ASAP 2010, Micromeritics, Norcross, GA). The particle size distribution was measured by dynamic light scattering spectrophotometer (DLS-700, Otsuka Electronics Co. Inc., Osaka, Japan). Photoluminescence spectra were measured at room temperature using a fluorescence spectrometer (FP-6500, JASCO) equipped with a 150 W Xenon lamp at a scanning speed of 500 nm/min and sampling interval of 0.1 nm.

3. Results and discussion

The morphology of as-synthesized and milled powders is shown in Fig. 1 along with the commercial $Y(P,V)O_4$:Eu phosphor (KASEI OPTONIX, LTD). The commercial phosphor exhibited a rod-like shape with a wide range of size distribution from 1 to 15 μm (Fig. 1(A)). The as-synthesized phosphor showed a similar elongated morphology, but the particle size was rather smaller, ~2 μm long and ~400 nm wide, with a narrow distribution (Fig. 1(B)). The as-synthesized powder exhibited a very smooth surface, but it was agglomerated. During the planetary ball milling, the particle fracture occurred and the size was significantly reduced. After milling for 12 h, the milled powder exhibited the irregularly fractured morphology and some of them still remained sub-micron size (Fig. 1(C)). The particle size was continuously reduced and the size distribution was narrowed with increasing the milling time. After 48 h milling, the powder was uniformly reduced to nano particle of ≤ 100 nm size and exhibited a rather spherical morphology (Fig. 1(D)). No noticeable change has been observed with further increase of milling time and thus, 48 h milling was chosen as an optimal milling time. Consistent with SEM observation, the specific surface area increased from 1.8 to 27 m^2/g after milling and the estimated equivalent particle size of milled phosphor was 52 nm assuming that the density of $Y(P,V)O_4$ is 4.3 g/cm^3 with a spherical morphology.

The XRD patterns of as-synthesized and milled $Y(P,V)O_4$:Eu phosphors are shown in Fig. 2. Both YPO_4 and YVO_4 are isomorphous (xenotime structure) with a space group of $I4_1/amd$ (141) [2]. The pattern for as-synthesized phosphor was completely indexed based on the xenotime structure and all the diffraction

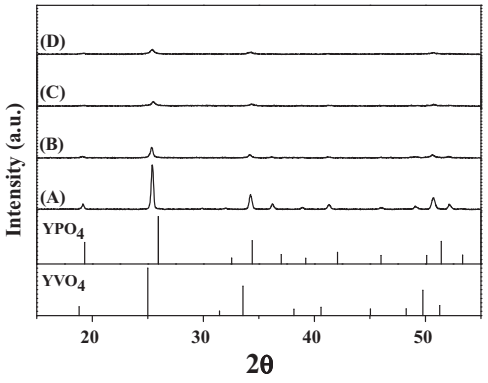

Fig. 2. XRD patterns of (A) as-synthesized, and milled $Y(P,V)O_4$:Eu phosphors for (B) 12 h, (C) 24 h, and (D) 48 h. The reference diffraction patterns of YPO_4 (JCPDS No. 73-1980) and YVO_4 (JCPDS No. 70-0194) are included.

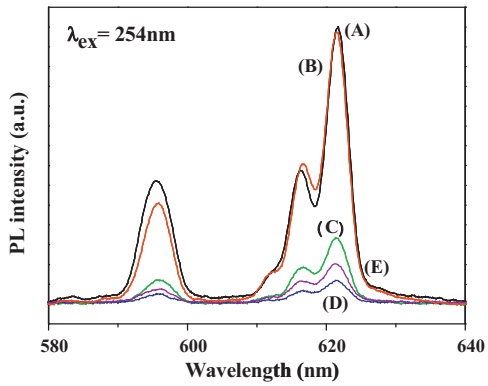

Fig. 3. Emission spectra of (A) as-synthesized, (B) commercial, and milled $Y(P,V)O_4$:Eu phosphors for (C) 12 h, (D) 24 h, and (E) 48 h.

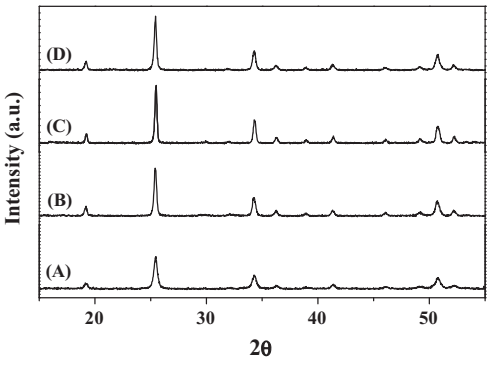

Fig. 5. XRD patterns of annealed $Y(P,V)O_4$:Eu phosphors at (A) 900, (B) 1000, (C) 1100, and (D) 1200 °C for 1 h.

peaks were located between the corresponding peaks for YPO_4 and YVO_4 (Fig. 2(A)). No phase change was found after planetary ball milling, but the diffraction peaks were broadened and their intensity was significantly reduced. After 24 h milling, no further decrease of intensity was observed and the diffraction patterns remained almost same (Fig. 2(C) and (D)). The decrease of peak intensity is associated with the surface defects and amorphization generated during the ball milling process. The formation of amorphous phase through high energy ball milling was already reported in other systems [23].

The PL spectra of as-synthesized and milled $Y(P,V)O_4$:Eu phosphors are shown in Fig. 3. The emission spectrum of as-synthesized phosphor exhibited one peak in the range of 590–600 and three peaks in the range of 610–630 nm under the excitation of $\lambda_{exc} = 254$ nm, which are attributed to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+} ion, respectively. The intensity of as-synthesized phosphor was comparable to that of commercial $Y(P,V)O_4$:Eu phosphor even though they are slightly different in particle size and morphology. Consistent with XRD results, the emission intensity dramatically decreased with milling time and it reached 17% of the original value after 24 h milling (Fig. 3(D)). There was no noticeable shift of peak position in the spectra of the milled phosphor. One thing to note in the spectra is that the PL intensity of 48 h milled powder was slightly higher than that of 24 h milled phosphor (Fig. 3(D) and (E)). It was reported that at the first stage of high energy milling, a dramatic refinement of particle size occurred and structural defects and disorder were induced, which lead to some degree of amorphization [24]. In the second stage, new (or desired) phases nucleated and grew from the activated amorphous matrix. Based on these observation, it is speculated that defect-free nuclei are nucleated in activated amorphous matrix and subsequently crystallized into nanometer scale $Y(P,V)O_4$:Eu particles after 24 h milling, which resulted in the increase of PL intensity without further decrease of XRD intensity as shown in Fig. 2. Further work such as TEM is required to confirm this hypothesis.

The morphology and XRD patterns of annealed $Y(P,V)O_4$:Eu phosphors after planetary ball milling are shown in Figs. 4 and 5, respectively as a function of annealing temperature. After annealing at 900 °C for 1 h, no particle coarsening occurred and the

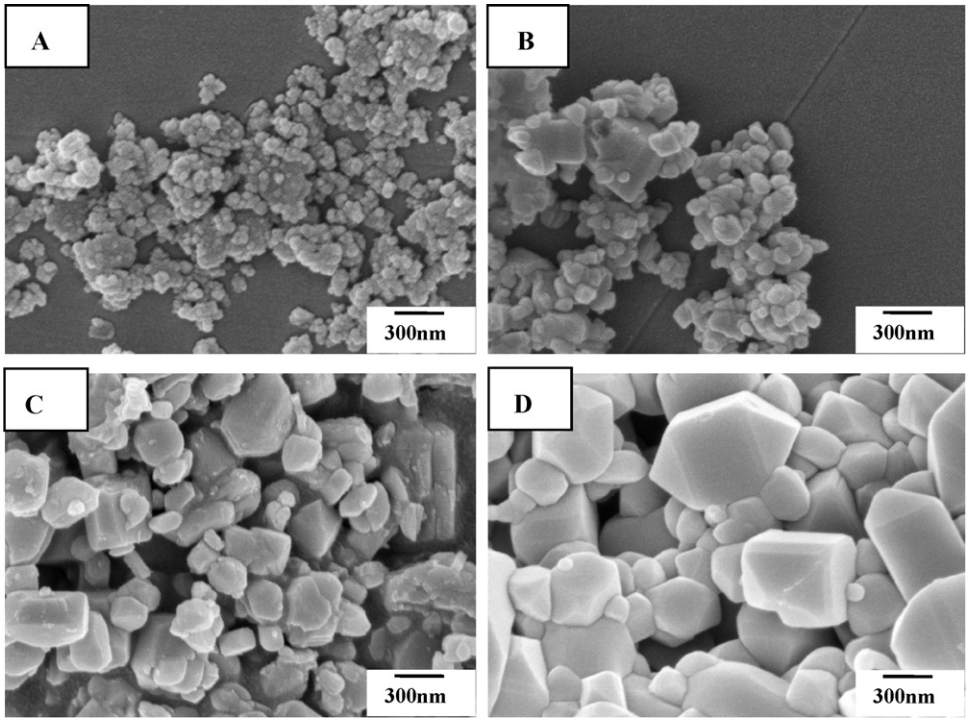

Fig. 4. FESEM micrographs of annealed $Y(P,V)O_4$:Eu phosphors at (A) 900, (B) 1000, (C) 1100, and (D) 1200 °C for 1 h.

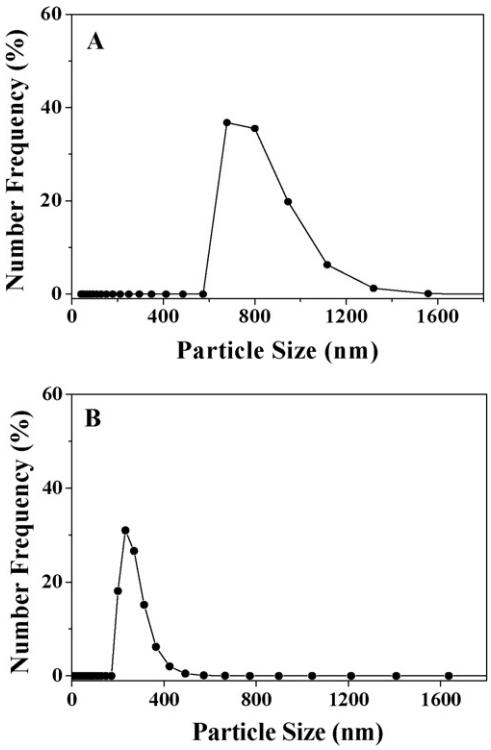

Fig. 6. Particle size distribution of (A) as-synthesized and (B) annealed $Y(P,V)O_4$:Eu phosphors at 1100 °C for 1 h.

shape and size remained almost same as those of milled powder (Fig. 4(A)). The diffraction peaks were still broad and their intensity was relatively low, indicating that the amorphous nature and the damages introduced during milling were not fully recovered (Fig. 5(A)). With increasing the annealing temperature, the particles were coarsened and polygonal shaped particles appeared, which are believed to be newly recrystallized, defect-free $Y(P,V)O_4$:Eu particles. At 1100 °C, the particles were grown up to ~300 nm with a polygonal shape (Fig. 4(C)). The specific surface area and equivalent particle size were 4.8 m^2/g and 280 nm, respectively. The obtained powder had a narrow size distribution (Fig. 6(B)) and was well dispersed in the absolute alcohol solution without a severe agglomeration compared to as-synthesized powder (Fig. 6(A)). It is believed that the present method yields more uniform-sized phosphors than the other methods such as solid state reaction, precipitation [25], and combustion [26]. The XRD intensity was almost recovered (Fig. 5(C)). Further increase of annealing temperature resulted in the well-faceted, polygon-shaped $Y(P,V)O_4$:Eu particles of 500–600 nm (Fig. 4(D)). No composition change has been found by the preliminary EDS analysis during milling and annealing processes.

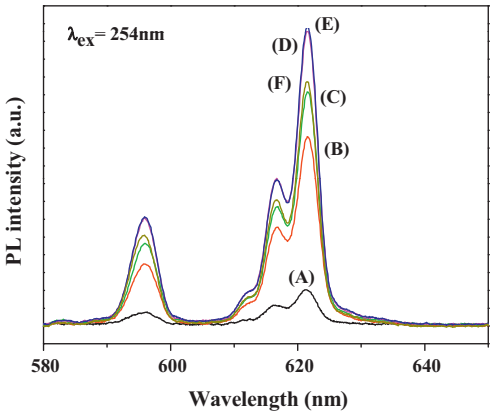

Fig. 7. Emission spectra of (A) as-milled, and annealed $Y(P,V)O_4$:Eu phosphors at (B) 900, (C) 1000, (D) 1100, and (E) 1200 °C for 1 h. The emission spectrum of commercial phosphor was included for reference (F).

The PL spectra of annealed $Y(P,V)O_4$:Eu phosphors after planetary ball milling are shown in Fig. 7. The shape and position of the emission peaks are unchanged revealing that the composition of $Y(P,V)O_4$:Eu phosphors is conserved during milling and annealing processes. The PL intensity increased with annealing temperature and it became comparable to that of as-synthesized phosphor at 1000 °C (Fig. 7(C) and (F)). The phosphor annealed at 1100 °C exhibited the enhanced PL properties and its intensity reached 120% compared to the original value (Fig. 7(D)), which can be attributed to the well-crystallized, uniform-sized particle with a smooth surface. Thus, the roundish shaped phosphor exhibited more improved luminescence properties than elongated or plate shaped phosphor. The annealing at 1200 °C increased the particle size approximately twice, but the improvement of PL intensity was insignificant (Fig. 7(D) and (E)), possibly due to the irregular shape and wide size distribution originating from particle coarsening [27].

4. Conclusions

The combined process, planetary ball milling and post-annealing, was employed to fabricate the nano-sized phosphor of spherical morphology and to improve the emission property of the phosphor. This approach was applied to the elongated micron-sized, red-emitting $Y(P,V)O_4$:Eu phosphor, prepared by the liquid phase precursor method. The planetary ball milling effectively reduced the particle size resulting in the ~100 nm sized, amorphous powder. The subsequent post-annealing at 1100 °C yielded the well crystallized, polygonal shaped $Y(P,V)O_4:Eu^{3+}$ phosphor. The obtained nano-phosphor was well dispersed in absolute alcohol and its PL intensity increased to 120% compared to both as-synthesized and commercial phosphors. It is expected that such a surface and shape modification process can improve the luminescence properties of $Y(P,V)O_4:Eu^{3+}$ and be applied to the other phosphor materials.

Acknowledgements

This research was supported by WCU (World Class University) program through National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (R31-2008-000-10075-0).

References

[1] A.K. Levine, F.C. Palilla, Appl. Phys. Lett. 5 (6) (1964) 118–120.
[2] K.S. Sohn, I.W. Zeon, H. Chang, S.K. Lee, H.D. Park, Chem. Mater. 14 (2002) 2140–2148.
[3] M. Yu, J. Lin, S.B. Wang, Appl. Phys. A 80 (2005) 353–360.
[4] B. Yan, X.Q. Su, Mater. Sci. Eng. B 116 (2005) 196–201.
[5] C.C. Wu, K.B. Chen, C.S. Lee, T.M. Chen, B.M. Cheng, Chem. Mater. 19 (2007) 3278–3285.
[6] H. Zhang, M. Lu, Z. Xiu, G. Zhou, S. Wang, Y. Zhou, S. Wang, Mater. Sci. Eng. B 130 (2006) 151–157.
[7] J. Wang, Y. Xu, M. Hojamberdiev, J. Peng, G. Zhu, Mater. Sci. Eng. B 156 (2009) 42–47.
[8] A. Huignard, T. Gacoin, J.P. Boilot, Chem. Mater. 12 (2000) 1090–1094.
[9] K. Riwotzki, M. Hasse, J. Phys. Chem. B 105 (2001) 12709–12713.
[10] H.D. Nguyen, S.I. Mho, I.H. Yeo, J. Lumin. 129 (12) (2009) 1754–1758.
[11] W.J. Park, M.K. Jung, J.W. Moon, T. Masaki, S.J. Im, D.H. Yoon, J. Nanosci. Nanotechnol. 7 (2009) 4371–4375.
[12] Z.G. Wei, L.D. Sun, C.S. Liao, X.C. Jiang, C.H. Yan, Y. Tao, X.Y. Hou, X. Ju, J. Appl. Phys. 93 (2003) 9783–9788.
[13] G. Wakefield, E. Holland, P.J. Dobson, J.L. Hutchison, Adv. Mater. 13 (2001) 1557–1560.
[14] Z. Chen, Y. Yan, J. Liu, Y. Yin, H. Wen, J. Zao, D. Liu, H. Tian, C. Zhang, S. Li, J. Alloys Compd. 473 (2009) L13–L16.

[15] S. Ray, A. Banerjee, P. Pramanik, Mater. Sci. Eng. B 156 (2009) 10–17.
[16] J. Wang, Y. Xu, M. Hojamberdiev, G. Zhu, J. Alloys compd. 487 (2009) 358–362.
[17] M. Bredol, U. Kynast, C. Ronda, Adv. Mater. 3 (1991) 361–367.
[18] A. Vecht, C. Gibbons, D. Davies, X. Jing, P. Marsh, T. Ireland, J. Silver, A. Newport, D. Barber, J. Vac. Sci. Technol. B 17 (1999) 750–757.
[19] J. Wang, Y. Xu, M. Hojamberdiev, J. Alloys Compd. 481 (2009) 896–902.
[20] R.S. Ningthoujam, L. Robindro Singh, V. Sudarsan, S. Dorendrajit Singh, J. Alloys Compd. 484 (2009) 782–789.
[21] J.M. Wu, Mater. Lett. 48 (2001) 324–330.
[22] M.A. Morris, D.G. Morris, J. Mater. Sci. 26 (1991) 4687–4696.
[23] J. Xue, D. Wan, S.E. Lee, J. Wang, J. Am. Ceram. Soc. 82 (7) (1999) 1687–1692.
[24] A. Newport, J. Silver, A. Vecht, J. Electrochem. Soc. 147 (10) (2000) 3944–3947.
[25] Ekambaram., K.C. Patil, J. Alloys Compd. 217 (1995) 104–107.
[26] C. Guo, W. Zhang, L. Luan, T. Chen, H. Cheng, D. Huang, Sens. Actuators B 133 (2008) 33–39.
[27] Y.C. Kang, S.B. Park, I.W. Lenggoro, K. Okuyama, J. Electrochem. Soc. 146 (1999) 2744–2747.