Journal of Alloys and Compounds 509 (2011) 4824–4827

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Preparation and luminescent properties of Eu^{2+} doped $Sr_3La(PO_4)_3$ phosphor

Fenghe Wang[a,*], Dongzhan Zhou[a], Shuyuan Ma[a], Hongwei Yu[b], Panlai Li[a], Zhiping Yang[a]

[a] College of Physics Science and Technology, Hebei University, Hebei, Baoding 071002, People's Republic of China
[b] College of Electronic and Informational Engineering, Hebei University, Hebei, Baoding 071002, People's Republic of China

ARTICLE INFO

Article history:
Received 13 January 2011
Received in revised form 26 January 2011
Accepted 28 January 2011
Available online 22 February 2011

Keywords:
Phosphor
Luminescence
$Sr_3La(PO_4)_3:Eu^{2+}$

ABSTRACT

Eu^{2+}-doped $Sr_3La(PO_4)_3$ phosphors were synthesized by solid-state reaction method. Their luminescent properties were investigated. The phosphor could be excited by ultraviolet light effectively. The emission spectra exhibit two emission peaks located at 418 nm and 500 nm, respectively. These two peaks originated from two different luminescent centers, respectively. One is nine-coordinated Eu(I) center, other is six-coordinated Eu(II) center. It was found that the doping concentration of Eu^{2+} ions affected the shape of emission spectra. As the doping concentration increasing, Eu^{2+} ions are more likely to form Eu(I) luminescent centers and emit purple light.

1. Introduction

As is well known eulytite-like compounds are potential and effective host materials used for phosphor, laser and plasma display panels [1–5]. Among the complex phosphates, eulytite-like $M_3Ln(PO_4)_3$ (M = alkali-earth element or Pb; Ln = rare earth, Bi or transition metal) compounds form a quite numerous family. In the past decades, there has been attracting more and more attends on luminescent materials with the structure above [6–9]. For example, Znamierowska et al. [10] synthesized $Ba_3Y(PO_4)_3:Nd^{3+}$ as a possible powder laser material; Zhang and Wang [11] reported that integral intensity of $Ba_3Bi(PO_4)_3:Eu^{3+}$ emission spectrum excited at 391 nm was about twice as strong as commercial red phosphor $Y_2O_3:Eu^{3+}$; Xu et al. [12] prepared Ce^{3+}, Tb^{3+} co-doped $Sr_3Y(PO_4)_3$ green emitting phosphor for fluorescent lamp; and Han et al. [13] analyzed that Gd^{3+} could enhance Dy^{3+} emission intensity in $Ba_3La(PO_4)_3$ effectively. To the best of our knowledge, rare earth doped $M_3Ln(PO_4)_3$ materials usually choose trivalent cations as activators, however for divalent rare earth ions, the luminescent properties in this structure has not been reported.

Eu^{2+} is a well-known activator with an electron configuration of $4f^65d^1$. The emission of Eu^{2+} is strongly dependent on the host lattice and can be shifted from the UV to the red region of the electromagnetic spectrum [14–23]. The absorption and emission of Eu^{2+} are characterized as efficient broad bands in many hosts, which makes Eu^{2+}-activated phosphors good candidates for photonic sources.

In order to study the luminescent properties of divalent rare earth ions in $M_3Ln(PO_4)_3$ materials, we synthesized Eu^{2+} doped $Sr_3La(PO_4)_3$ material by solid-state reaction. In the present paper, sample luminescent properties under ultraviolet light were investigated. The existence of two different luminescent centers was proved.

2. Experimental

2.1. Synthesis of $Sr_3La(PO_4)_3:Eu^{2+}$ phosphor

The phosphors $Sr_{3(1-x)}La(PO_4)_3:3xEu^{2+}$ (x = 0.002, 0.005, 0.01, 0.015, 0.02, 0.03) were synthesized by solid-state reaction technique. The starting materials, including $SrCO_3$, La_2O_3, $NH_4H_2PO_4$ and Eu_2O_3 of purity higher than 99.9%, were weighted in stoichiometric proportions, thoroughly mixed and ground by an agate mortar and pestle for 30 min till they were distributed. Then the grinded powder was heated at 1300 °C for 3 h in crucibles along with the reducing agent (active carbon). Finally, the samples were cooled to room temperature and grind them into power for measure.

2.2. Physical measurements

The phase identification of the as-prepared powder samples was performed using an X-ray diffraction spectroscopy (XRD6000 Shimadzu) with Cu Kα (λ = 0.15406 nm) radiation operating at 40 kV and 40 mA. The XRD profiles were collected in the range of 20–60°. The emission and excitation spectra were measured using Hitachi F-4600 fluorescence spectrophotometer equipped with a 450 W xenon lamp. The scan speed was 240 nm/min with a step of 0.2 nm and the response time was 0.05 s. For comparison, all measurements were performed at room temperature with the identical instrumental parameters.

---

* Corresponding author. Tel.: +86 312 5079423; fax: +86 312 5079423.
E-mail address: fenghe1206@sohu.com (F. Wang).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.01.178

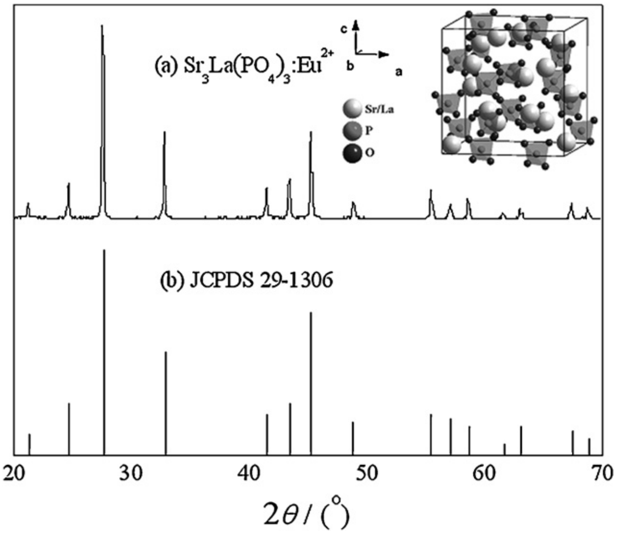

Fig. 1. XRD pattern of $Sr_3La(PO_4)_3:Eu^{2+}$ phosphor.

3. Results and discussion

3.1. XRD pattern of $Sr_3La(PO_4)_3:Eu^{2+}$ phosphor

The phase purity of $Sr_3La(PO_4)_3:Eu^{2+}$ sample was confirmed by XRD measurements (Fig. 1). As can be seen in the figure, the XRD pattern of $Sr_3La(PO_4)_3:Eu^{2+}$ matches well with the Joint Committee on Powder Diffraction Standards (JCPDS No. 29-1306). It is evident that the Eu^{2+} doped $Sr_3La(PO_4)_3$ sample is shown to be pure phase. $Sr_3La(PO_4)_3$ has a cubic crystal structure, with a space group $I\bar{4}3d$ (2 2 0) and its lattice constant is $a = 1.0192$ nm. Because ionic radii of Eu^{2+} ($r = 0.117$ nm with CN = 6 and $r = 0.120$ nm with CN = 9) [24,25] and Sr^{2+} ($r = 0.118$ nm with CN = 6; $r = 0.131$ nm with CN = 9) [26,27] are very close, it is concluded that Eu^{2+} ions probably occupy the Sr^{2+} sites in the $Sr_3La(PO_4)_3$ lattice.

3.2. Emission and excitation spectra of $Sr_3La(PO_4)_3:Eu^{2+}$

The typical emission spectra of $Sr_3La(PO_4)_3:Eu^{2+}$ are shown in Fig. 2a. The curves exhibit two broad bands, one dominating at 418 nm and another shoulder centering at 500 nm. Both the intense broad peaks are originated from 5d → 4f transition of Eu^{2+} ions. When excited at 320 nm, the phosphor shows a strong purple emission around 418 nm and a relatively minor cyan emission centered at 500 nm. However, we get an opposite result when 367 nm ultraviolet light used as exciting source. The obvious difference of emission curves shape under different excitation source implies that Eu^{2+} ions probably occupy two kinds of Sr^{2+} sites in $Sr_3La(PO_4)_3$ lattice and form two different luminescent centers, Eu(I) centers for purple emission peaks and Eu(II) centers for cyan. The Eu^{2+} shows broad emission bands which strongly depends on the chemical nature of the host lattice surrounding the Eu^{2+} ions present in host lattice [28]. The 5d orbital of Eu^{2+} strongly interacts with neighborhood ligand ions, and the position of the degenerate 5d band depends on the crystal field strength [29]. In some compounds, Eu^{2+} ions were reported to occupy two different cation sites and form two luminescent centers [30].

Fig. 2b represents the excitation spectra of the obtained $Sr_{2.97}La(PO_4)_3:0.03Eu^{2+}$ phosphor monitored at 418 nm and 500 nm, respectively. As can be seen in the figure, $Sr_3La(PO_4)_3:Eu^{2+}$ phosphor can be excited by ultraviolet rays ranged from 300 nm to 375 nm effectively, which means this phosphor may suitable for white LEDs application excited by NUV light. Excitation spectra monitored at 418 nm shows a maximum value at 320 nm. Excitation spectra monitored at 500 nm shows better excitation in longer wavelength. The same phenomenon was observed and discussed in our previous work [31]. The shapes of two excitation spectra curves are different which support our conjecture of two Eu^{2+} centers.

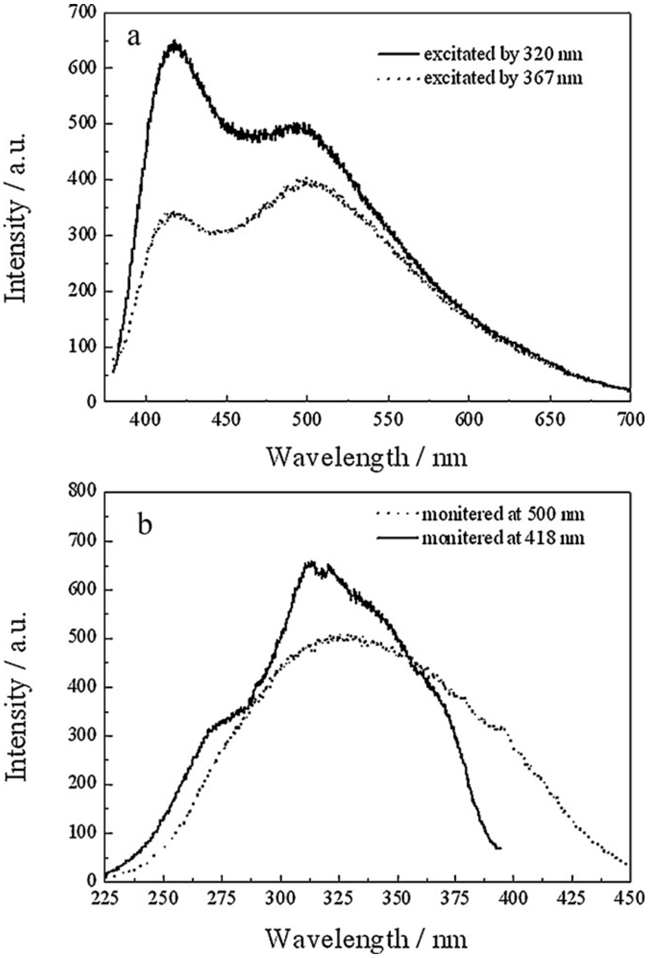

Fig. 2. (a) Emission spectra of $Sr_{2.97}La(PO_4)_3:0.03Eu^{2+}$; (b) excitation spectra of $Sr_{2.97}La(PO_4)_3:0.03Eu^{2+}$.

3.3. Crystal surroundings of Eu^{2+} ions in $Sr_3La(PO_4)_3$ lattice

It is well-known that there are two sites of Sr^{2+} ions in $Sr_3La(PO_4)_3$ lattice, one is nine-coordinated and the other is six-coordinated [32]. When $Sr_3La(PO_4)_3$ doped with Eu^{2+} ions, activator ions may occupy both kinds of Sr^{2+} sites and form two different luminescent centers. The purple emission band (418 nm) and cyan emission band (500 nm) originate from the allowed $4f5d^1 \rightarrow 4f^7$ electric dipole transition of Eu^{2+} ions in different crystal field.

According to the report of Van Uitert [33], for most divalent and some trivalent rare earth ions in suitable matrices, such as sulfide, oxide, halide and aluminates, the following experiential equation provides a good fit to the emission peak for Eu^{2+} and Ce^{3+}:

$$E(\mathrm{cm}^{-1}) = Q\left[1 - \left(\frac{V}{4}\right)^{1/V} \times 10^{-(n-ear)/8}\right] \qquad (1)$$

Table 1
Position of low d-band edge in energy for Eu^{2+} in $Sr_3La(PO_4)_3$.

n	ea/eV	r/nm	E/cm^{-1}	λ_{em}/nm (calculated)	λ_{em}/nm (observed)
9	2.6	0.131	24,049	416	418
6	2.6	0.118	19,844	504	500

where E represents the position of the d-band edge in energy for rare earth ions (cm^{-1}), Q is the position in energy for the lower d-band edge for the free ions, V is the valence of the activator, n is the number of anions in the immediate shell about the activator, r is the radius of the host cation replaced by the activator (nm), and ea is the electron affinity of the atoms that form anion (eV).

For crystal $Sr_3La(PO_4)_3$:Eu^{2+}, the value of Q is 34,000 cm^{-1}, $V = 2$, $ea = 2.6$ eV. The radius of nine-coordinated Sr^{2+} ion is 0.131 nm and radius of six-coordinated Sr^{2+} ion is 0.118 nm [26,27]. By substitution the data into the above formula, results are listed in Table 1.

The experimental results basically correspond with theoretical calculation. From the table, we can infer that the purple emission at 418 nm is due to nine-coordinated Eu^{2+}(I) luminescence center and the cyan emission at 500 nm is attributed to six-coordinated luminescence center.

Fluorescence decay time of $Sr_3La(PO_4)_3$:Eu^{2+} monitored at 418 nm and 500 nm are shown in Fig. 3. Both curves are excited at 375 nm and are exponential decaying. As we can seen in Fig. 3, two curves are not coincide with each other, which indicates that the two emission band have different decay time. This also confirms that Eu^{2+} ions occupy two different Sr^{2+} sites in $Sr_3La(PO_4)_3$ lattice.

3.4. *Effect of Eu^{2+} concentration on emission spectra*

The purple emission band (418 nm) and the cyan emission band (500 nm) are assigned to 5d → 4f transition of nine-coordinated Eu^{2+} ions and six-coordinated Eu^{2+} ions, respectively. Fig. 4 shows the dependence of the emission spectra of $Sr_{(3-x)}La(PO_4)_3$:$3xEu^{2+}$ phosphors on the doping concentration of Eu^{2+}. It is observed that an increase in Eu^{2+} concentration affects the shape of the emission spectra. With Eu^{2+} concentration increasing (x from 0.002 to 0.03), the purple emission intensity increases continuously, while the cyan emission intensity first increases then decreases. Table 2 exhibits the relative intensity of purple and cyan emission peaks with different doping concentration and excite wavelength. The ratio of purple emission intensity and cyan emission intensity increases with increasing Eu^{2+} doping concentration. It can be explained as Eu^{2+} ions are likely to form Eu^{2+}(II) luminescent centers at lower doping concentration and Eu^{2+}(I) centers at higher doping concentration.

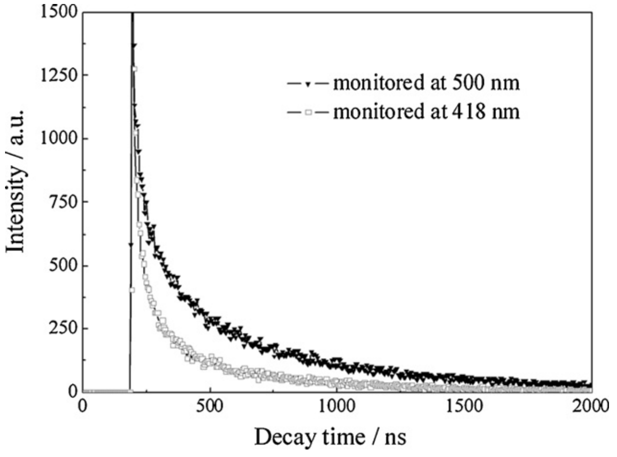

Fig. 3. $Sr_3La(PO_4)_3$:Eu^{2+} fluorescence decay.

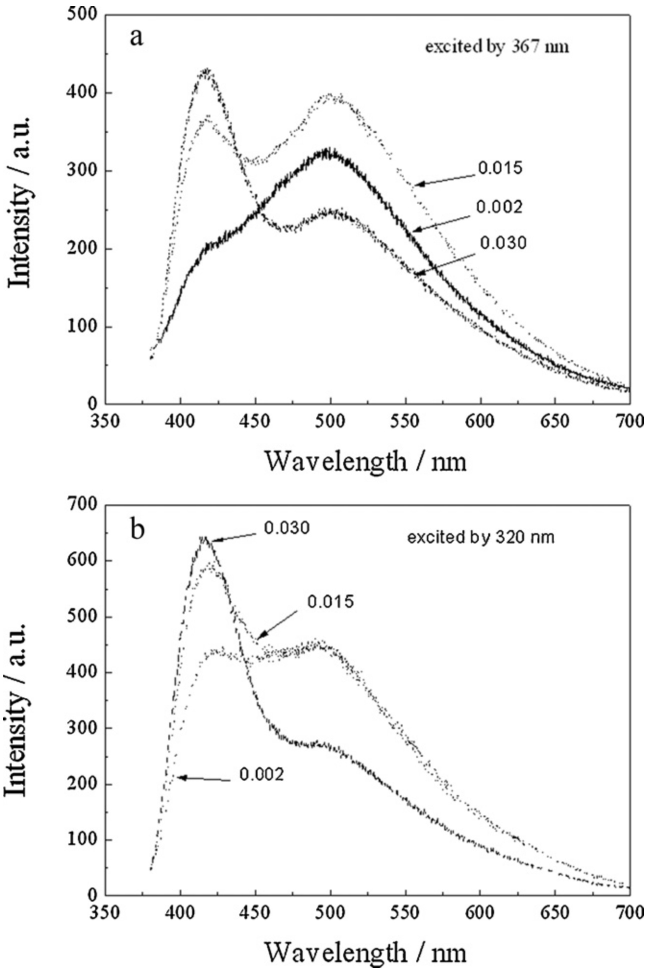

Fig. 4. Eu^{2+} concentration affect on emission spectrum: (a) excited by 367 nm; (b) excited by 320 nm.

Table 2
Ratio of purple peaks and cyan peaks with different doping concentrations.

λ_{ex}	x	I_p	I_c	I_p/I_c
367 nm	0.002	202.0	322.5	0.6264
367 nm	0.015	365.3	397.1	0.9202
367 nm	0.030	427.9	248.5	1.7219
320 nm	0.002	438.4	450.0	0.9742
320 nm	0.015	591.6	451.2	1.3112
320 nm	0.030	644.8	266	2.4241

λ_{ex}, excite wavelength; x, Eu^{2+} concentration; I_p, purple emission intensity; I_c, cyan emission intensity.

4. Conclusion

In summary, a series of $Sr_3La(PO_4)_3$:Eu^{2+} phosphors were prepared by convenient solid-state reaction. $Sr_3La(PO_4)_3$:Eu^{2+} materials can be excited effectively by the light range from 300 nm to 375 nm. Eu^{2+} ions occupy two different Sr^{2+} sites in $Sr_3La(PO_4)_3$ lattice and form two kinds of luminescent centers. Nine-coordinated Eu^{2+} luminescent centers (Eu^{2+}(I)) emit purple light centered at 418 nm and six-coordinated Eu^{2+} luminescent centers (Eu^{2+}(II)) emit cyan light located at 500 nm. As the Eu^{2+} doping concentration increasing, it likely to form Eu^{2+}(I) luminescent centers and emit purple light.

Acknowledgments

The authors would like to acknowledge the financial support from Natural Science Foundation of China (No. 50902042) and Hebei Natural Science Foundation (No. F2009000217).

References

[1] G. Blasse, J. Solid State Chem. 2 (1970) 27.
[2] W. Rehwald, R. Widmer, J. Phys. Chem. Solids 34 (1973) 2269.
[3] F. Rogemond, C. Pedrini, B. Moine, G. Boulon, J. Lumin. 33 (1985) 455.
[4] A.A. Kaminskii, O. Schultze, B. Hermoneit, S.E. Sarkisov, L.L.J. Bohm, P. Reichter, R. Ehlert, A.A. Mayer, Y.A. Lomonov, V.A. Balashov, Phys. Status Solidi A 33 (1976) 737.
[5] F. De Notaristefani, P. Lecoq, M. Schneegans, Heavy Scintillators, Editions Frontières, Gif-sur-Yvette, Paris, 1993.
[6] X.Z. Xiao, S. Xu, B. Yan, J. Alloys Compd. 429 (2007) 255.
[7] H.B. Liang, Y. Tao, J.H. Xu, H. He, H. Wu, W.X. Chen, S.B. Wang, Q. Su, J. Solid State Chem. 177 (3) (2004) 901.
[8] T.W. Kuo, T.M. Chen, J. Electrochem. Soc. 157 (6) (2010) 216.
[9] M.F. Hoogendorp, W.J. Schipper, G. Blasse, J. Alloys Compd. 205 (1994) 249.
[10] T. Znamierowskaa, W. Szuszkiewicza, J. Hanuzab, J. Alloys Compd. 341 (2002) 371.
[11] J. Zhang, Y.H. Wang, Electrochem. Solid-State Lett. 13 (2010) 35.
[12] S. Xu, X.Z. Xiao, B. Yan, J. Optoelectron. Adv. Mater. 10 (2008) 2727.
[13] B. Han, H.B. Liang, H.H. Lin, W.P. Chen, Q. Su, G.T. Yang, G.B. Zhang, J. Opt. Soc. Am. B 25 (12) (2008) 2057.
[14] Z.C. Wu, J. Liu, M.L. Gong, Chem. Phys. Lett. 466 (1–3) (2008) 88.
[15] W.B. Im, H.S. Yoo, S. Vaidyanathan, K.H. Kwon, H.J. Park, Y. Kim, D.Y. Jeon, Mater. Chem. Phys. 115 (1) (2009) 161.
[16] W.B. Im, Y.-I. Kim, J.H. Kang, D.Y. Jeon, Solid State Commun. 134 (11) (2005) 717.
[17] Z.C. Wu, J.X. Shi, J. Wang, M.L. Gong, Q. Su, J. Solid State Chem. 179 (8) (2006) 2356.
[18] Z.P. Yang, G.W. Yang, S.L. Wang, J. Tian, X.N. Li, Q.L. Guo, G.S. Fu, Mater. Lett. 62 (12–13) (2008) 1884.
[19] K.Y. Jung, H.W. Lee, H.-K. Jung, Chem. Mater. 18 (9) (2006) 2249.
[20] X. Sun, J. Zhang, X. Zhang, Y. Luo, X. Wang, J. Rare Earths 26 (3) (2008) 421.
[21] Z.P. Yang, S.H. Wang, G.W. Yang, J. Tian, P.L. Li, X. Li, Mater. Lett. 61 (30) (2007) 5258.
[22] R.J. Xie, Hirosaki S N., T. Suehiro, F.F. Xu, M. Mitomo, Chem. Mater. 18 (23) (2006) 5578.
[23] Y.S. Hu, W.D. Zhuang, H.Q. Ye, S.S. Zhang, Y. Fang, X.W. Huang, J. Lumin. 111 (3) (2005) 139.
[24] H.D. Ju, X.Y. Su, S.Q. Xu, Y. Zhang, D.G. Deng, S.L. Zhao, H.P. Wang, B.L. Wang, L.Z. Sun, Mater. Lett. 63 (15) (2009) 1275.
[25] T. Aitasalo, J. Hölsä, H. Jungner, M. Lastusaari, J. Niittykoski, J. Phys. Chem. B 110 (10) (2006) 4589.
[26] P.L. Li, Z.P. Yang, Z.J. Wang, Z.C. Zhang, Q.L. Guo, X. Li, C.Y. Liu, Acta Photonica Sin. 37 (10) (2008) 2001.
[27] R.S. Liu, S.F. Wu, D.S. Shy, S.F. Hu, D.A. Jefferson, Phys. C: Supercond. 222 (1994) 278.
[28] G. Blasse, J. Solid State Chem. 62 (207) (1986).
[29] H.S. Jang, Y.H. Won, S. Vaidyanathan, D.H. Kim, D.Y. Jeon, J. Electrochem. Soc. 156 (6) (2009) J138.
[30] S.K. Jong, H.P. Yun, M.K. Sun, C.C. Jin, L.P. Hong, Solid State Commum. 133 (2005) 445.
[31] Z.P. Yang, Y.F. Liu, Acta Phys. Sin. 55 (9) (2006) 4946.
[32] J. Barbier, J.E. Greedan, T. Asaro, J. Solid State Inorg. Chem. 27 (1990) 855.
[33] L.G. Van Uitert, J. Lumin. 29 (1) (1984) 1–9.