Journal of Alloys and Compounds 509 (2011) 9897–9900

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Synthesis and luminescence properties of Bi^{3+}-doped YVO_4 phosphors

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ARTICLE INFO

Article history:
Received 13 June 2011
Accepted 23 July 2011
Available online 29 July 2011

Keywords:
Luminescence
YVO_4:Bi^{3+}
Phosphors

ABSTRACT

YVO_4:Bi^{3+} phosphors have been prepared by a convenient high-temperature solid-state method. X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence (PL) technologies are used to study the luminescence properties of YVO_4:Bi^{3+} phosphors. The emission and excitation spectra of Bi^{3+} in the YVO_4 lattice have been investigated at room temperature. The excitation band peaks at 330 nm in a region among 250–400 nm, and the emission spectrum exhibits an intense yellowish-white broad emission centered at about 543 nm covering from 400 nm to 800 nm. The full width at half maximum (FWHM) is about 144 nm. The color coordinates of the as-synthesized YVO_4:Bi^{3+} phosphors are in a range of $x = 0.358–0.374$, $y = 0.482–0.496$. The dependence of the luminescence intensity on Bi^{3+} concentrations and heat treatment condition has also been discussed. In addition, we found that a little amount of flux NH_4Cl could enhance the Bi^{3+} luminescence intensity.

1. Introduction

Many papers on the luminescence properties of the bismuth have been published [1–4]. Bismuth can exist in materials in different valence states, such as 0, +1, +2, +3, +5, or even mixed valence states of +1 and +5. In the past few decades, some researchers have investigated the luminescence properties of Bi^{3+}- or Bi^{2+}-doped crystals and glasses [5–8]. Recently, bismuth-doped multicomponent glasses can be used for optical amplification with super-broadband emission in the near-infrared range [9,10]. In all of these valence states only Bi^{3+} is normally most stable in most host materials. The luminescent properties of Bi^{3+} ions and energy transfer among Bi^{3+} ions or from Bi^{3+} to another activator have been discussed profoundly [11–13]. Usually, the emission peaks of Bi^{3+} occur in the ultraviolet, green, or even red wavelength regions with variation of host materials. For example, red luminescence is observed in $Bi_4Ge_3O_{12}$ at low temperature [14], while in other materials such as $GaBO_3$:Bi^{3+} or La_2SO_6:Bi^{3+}, UV emission is observed [15]. In $LnNbO_4$:Bi^{3+} the Bi^{3+} shows a blue emission band [16].

It is well-known that yttrium orthovanadate (YVO_4) is a good lattice which exhibits a high luminescence efficiency [17,18]. Bi^{3+} can be used as not only an activator but also a sensitizer of luminescence. Many works have been done on the energy transfer from Bi^{3+} ion to another activator such as Eu^{3+}, Dy^{3+}, Sm^{3+} in YVO_4 host lattice when Bi^{3+} acts as a sensitizer [19,20]. However, few reports solely discussed the luminescence properties of Bi^{3+} as an activator in YVO_4 host lattice. In this paper YVO_4:Bi^{3+} phosphors were synthesized by a convenient high-temperature solid-state method. Bi^{3+} exhibits an intense yellowish-white broad emission in YVO_4 host lattice. We systematically study the synthesis, luminescence properties and the application of YVO_4:Bi^{3+} phosphors as well as flux NH_4Cl effect on the Bi^{3+} luminescence intensity.

2. Experimental

2.1. Synthesis of YVO_4:Bi^{3+} phosphors

All materials were purchased from commercial sources (analytical grade) and used without further treatment. The mixture of Y_2O_3, NH_4VO_3 and Bi_2O_3 were weighted essentially in a stoichiometric proportion. After the mixture was ground sufficiently, the powder was placed in the alumina crucible and transferred into the furnace. The samples were heated at a rate of 5 °C/min up to different temperatures from 800 to 1200 °C and then kept there for 4 h before being taken out of the furnace. When cooled to room temperature, the samples were milled into powders for the measurements and applications.

2.2. Characterization

All experiments were taken at room temperature. X-ray powder diffraction (XRD) pattern was recorded by using a Japan Regaku D/max çA X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation ($\lambda = 1.5418$ Å) irradiated with a scanning rate of 4° min^{-1}. The morphology of the phosphors was studied by scanning electron microscopy (HITACHI S4800 operated at 3 kV). The optical properties of as-prepared samples were investigated by photoluminescence (PL) and photoluminescence excitation (PLE) spectra, which were taken on a VARIAN Cary-Eclipse 500 fluorescence spectrophotometer equipped with a 60 W xenon lamp as the excitation source.

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doi:10.1016/j.jallcom.2011.07.079

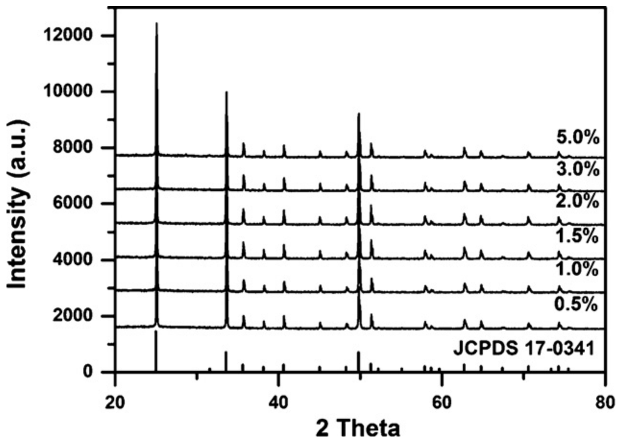

Fig. 1. The XRD patterns of $Y_{1-x}Bi_xVO_4$ (x = 0.005, 0.01, 0.015, 0.02, 0.03, 0.05) Phosphors prepared at 1000 °C for 4 h.

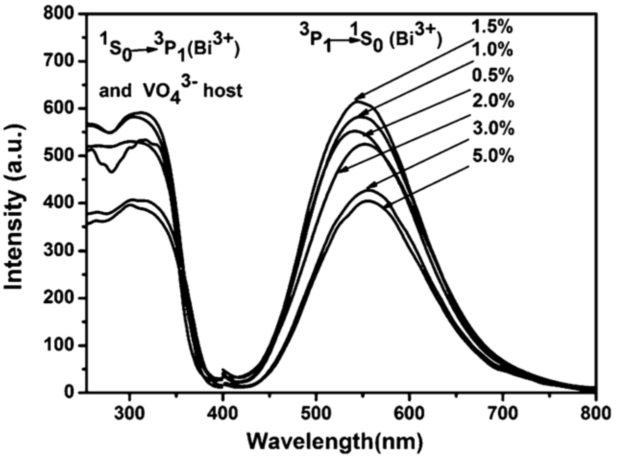

Fig. 3. Room temperature PL (under 330 nm excitation) and PLE spectra of YVO_4:Bi^{3+} at different concentrations.

3. Results and discussion

3.1. Preparation of phosphors YVO_4:Bi^{3+}

Fig. 1 shows the XRD patterns of $Y_{1-x}Bi_xVO_4$ (x = 0.005, 0.01, 0.015, 0.02, 0.03, 0.05) powers synthesized at 1000 °C for 4 h. According to Committee on Power Diffraction Standards (JCPDS) card 17-0341, YVO_4 has a tetragonal structure and its unit cell parameters are a = 7.119 Å, b = 7.119 Å, c = 6.289 Å. As shown in Fig. 1, most all of the diffraction peaks of YVO_4:Bi^{3+} powers can be indexed to tetragonal crystalline phase YVO_4 with lattice contents $a = b$ = 7.12 Å and c = 6.29 Å (JCPDS 17-0341). Only a small shift was observed because of the introduction of Bi^{3+} ions. The strong peaks indicate the high crystalline of the as-prepared products, which is very beneficial for obtaining bright luminescence. Because of the introduction of Bi^{3+} ions, the (2 0 0) diffraction peaks at $2\theta = 25°$ shift slightly toward lower 2θ values with respect to the standard card. This observation results from the fact that the ionic radius of Y^{3+} (0.088 nm) is smaller than that of Bi^{3+} (0.196 nm) [21]. Obviously, the introduction of Bi^{3+} ions did not influence the crystal structure of the host matrix, indicating that we have synthesized successfully the YVO_4 host lattice.

Fig. 2 shows the SEM micrographs of YVO_4:1.5% Bi^{3+} powders obtained at 1000 °C for 4 h. From the pictures we can observe that the particles have a very narrow size distribution with a slight agglomerate phenomenon, and the edge angles of the grains are smooth. Their sizes are in the range of 1–2 μm. Such morphology can be useful for the application of the phosphors.

3.2. The factors influencing the luminescence properties of the Bi^{3+}-doped YVO_4 phosphors

The luminescence properties of the Bi^{3+}-doped YVO_4 phosphors were examined. Fig. 3 presents the PLE and PL spectra of YVO_4:Bi^{3+} phosphors at different concentrations sintered at 1000 °C for 4 h. Strong yellowish-white broad emission band centered at about 543 nm is observed that results from the ${}^3P_I-{}^1S_0$ transition. The excitation spectrum is very broad extending from 254 nm to 400 nm due to the Bi^{3+} ${}^1S_0-{}^3P_I$ transition and VO_4^{3-} host. The trivalent Bi^{3+} ion has a configuration $6s^2$ and belongs to ions

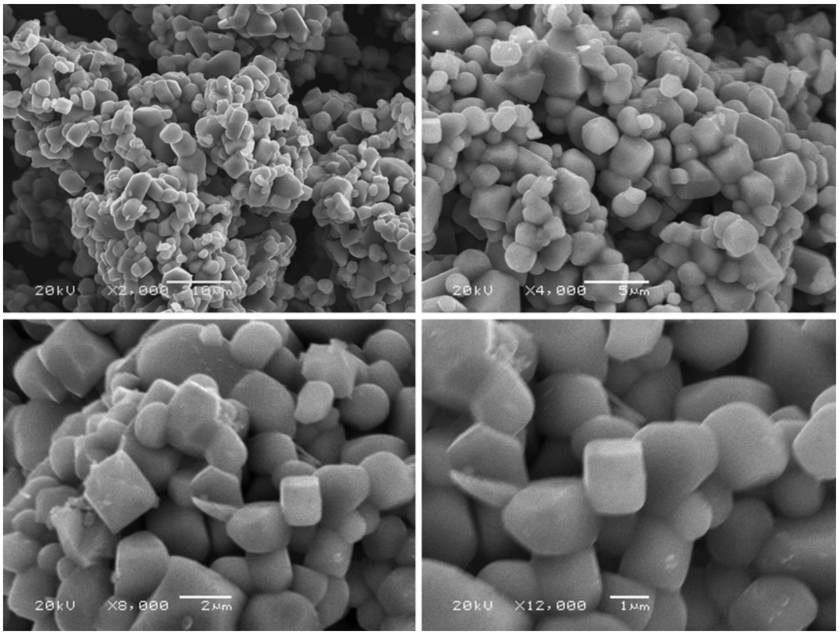

Fig. 2. Scanning electron microscope micrographs of YVO_4:1.5% Bi^{3+} powders obtained at 1000 °C for 4 h.

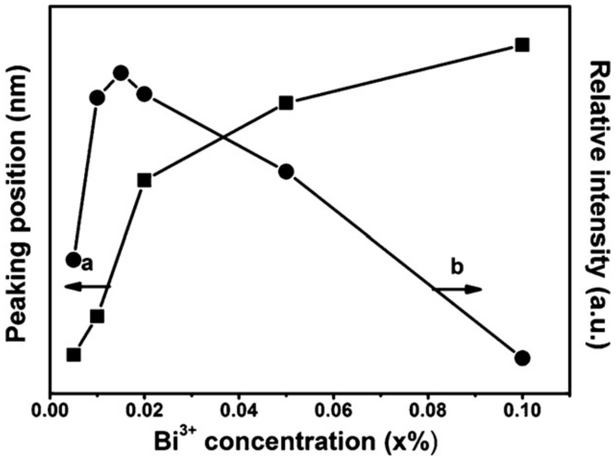

Fig. 4. (a) The relationship between Bi^{3+} concentration and emission peaks. (b) The dependence of emission intensity on Bi^{3+} concentration.

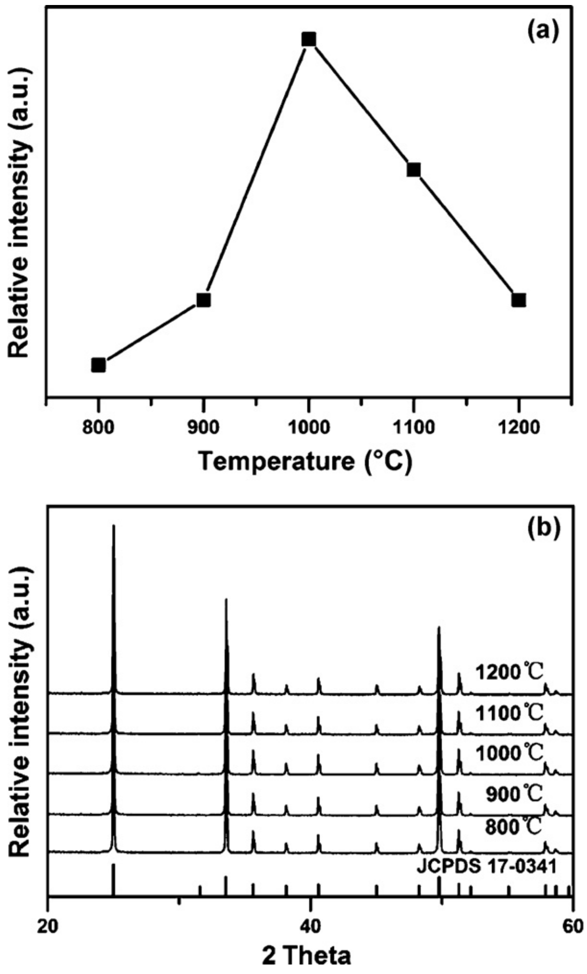

Fig. 5. (a) The dependence of emission intensity of YVO_4:1.5% Bi^{3+} on the sintering temperatures. (b) The XRD patterns of YVO_4:1.5% Bi^{3+} phosphors prepared at different temperatures.

with ns^2 configuration. Rare earth doped-YVO_4 phosphors show line emission where transitions among the $4f^6$-electron energy levels come up because the shielding effects of outer electrons minimize the perturbing influence of the crystal field. However, YVO_4 phosphors activating with ions show broad emission bands which involve s-, p-, or d-electrons where considerable perturbation occurs. Hence, under ultraviolet excitation we observe a single intense broad emission band extending from 400 nm to 800 nm corresponding to the allowed $^3P_1$–$^1S_0$ transition of Bi^{3+} ions. The ground state of the free Bi^{3+} ion is $^1S_0$ and the excited states are $^3P_0$, ^3P_l, $^3P_2$, and $^1P_1$ in order of increasing energy [1]. As an activator, excitation usually occurs from the $^1S_0$ ground state to the $^3P_1$ or ^1P_l excited state because the $^1S_0$–$^3P_0$ and $^1S_0$–$^3P_2$ transitions are strongly forbidden. The emission of Bi^{3+} ions originates from the $^3P_0$ state at low temperatures, while at higher temperatures the emission occurs mainly from the $^3P_1$ level, in which transition is allowed by spin–orbit mixing of the $^3P_1$ and $^1P_1$ states.

Fig. 4(a) shows the relationship between Bi^{3+} concentration and emission peaks. With the increasing of Bi^{3+}concentration, the emission peaks move slightly toward longer wavelength, namely, about from 543 nm to 555 nm. As mentioned earlier, with the change of the distance among Eu^{2+} ions, the probability of energy transfer from Eu^{2+} ions at higher levels of 5d to those at the lower 5d levels increases which makes it possible to shift the emission peak to the longer wavelength with Eu^{2+}concentration increasing [22]. In YVO_4 lattice the Bi^{3+} may show the same characteristics which may be aroused because of the Bi^{3+} 6s6p → $6s_2$ orbit transition.

The concentration quenching of the Bi^{3+} ions was studied on powder samples. The intensity of $^3P_1$–$^1S_0$ transition of Bi^{3+} ions in YVO_4 host is shown in Fig. 4(b) as a function of the Bi^{3+} concentration. Bi^{3+} was substituted for Y^{3+} in YVO_4 lattice in various concentrations. The incorporated amount of Bi^{3+} was always lower than the weighted amount of Bi^{3+}, resulting from the loss by vaporization. In view of problems of this kind it was not possible to obtain a complete range of compounds with continuously varying Bi^{3+} concentration. In this paper, all the Bi^{3+} concentrations were calculated on the basis of theory values. We observed that the concentration quenching started between 0.5% and 2.5% Bi^{3+} ions. The energy transfer between Bi^{3+} ions can be expected to be very efficient in YVO_4 lattice. Former works have investigated about the concentration quenching of Bi^{3+} ions in some hosts. The critical concentration of Bi^{3+} ions for concentration quenching is always lower though there is a little difference for differing hosts. Kellendonk proposed that the concentration quenching in $YA1_3B_4O_{12}$ started between 0.5% and 1% Bi^{3+} ions [1]. In YVO_4 lattice, with the increasing of Bi^{3+} concentration, the Bi^{3+} emission intensity increase because of the efficient $VO_4{}^3$–Bi^{3+} energy transfer. The emission intensity reaches its maximum at $x = 0.015$. When Bi^{3+} ion concentration is more than 1.5 mol%, efficient Bi^{3+}–Bi^{3+}energy transfer would take place due to the near distance between Bi^{3+} ions, resulting in the concentration quenching effect.

There are several factors which may influence the Bi^{3+} luminescence intensity in YVO_4 host. We found that the intensity of the Bi^{3+} emission in YVO_4 host was obviously temperature dependent. From Fig. 5(a) we can observe that 1000 °C is the optimum sintering temperature for their preparation. The as-synthesized powders obtained after heat treatment at different temperatures were characterized by XRD (Fig. 5(b)). From Fig. 5(b), the diffraction peaks of all powers obtained at different temperatures can be indexed to tetragonal crystalline phase YVO_4 (JCPDS17-0341). The peak position did not change with the change of heating temperatures, but the peak intensity increased slightly at 1000 °C, indicating the best crystalline at 1000 °C. However, the diffraction peak intensity did not change obviously, so we deduce that vaporization at higher temperatures could make the Bi^{3+} luminescence intensity come down because the Bi^{3+} concentration decrease.

The flux NH_4Cl on the effect of fluorescence intensity of YVO_4:1.5% Bi^{3+} phosphors also was investigated. From Fig. 6 we found that when the flux NH_4Cl is 1–5% of the whole samples quality the Bi^{3+} emission intensity can increase clearly. The optimum content of NH_4Cl is about 1% of the whole sample mass which

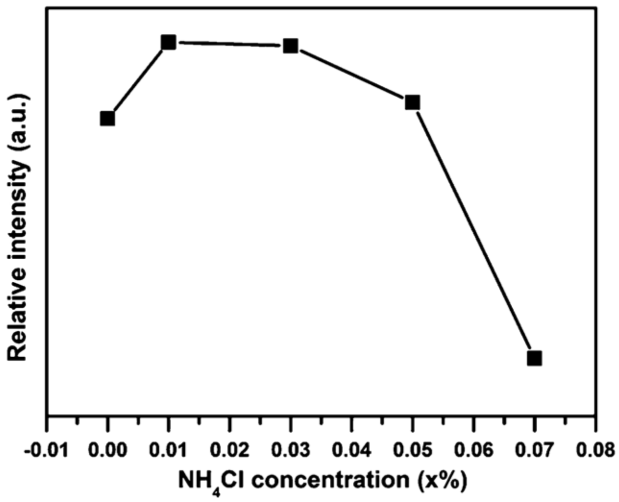

Fig. 6. The flux NH_4Cl on the effect of luminescence intensity of YVO_4:1.5% Bi^{3+} phosphors obtained at 1000 °C for 4 h.

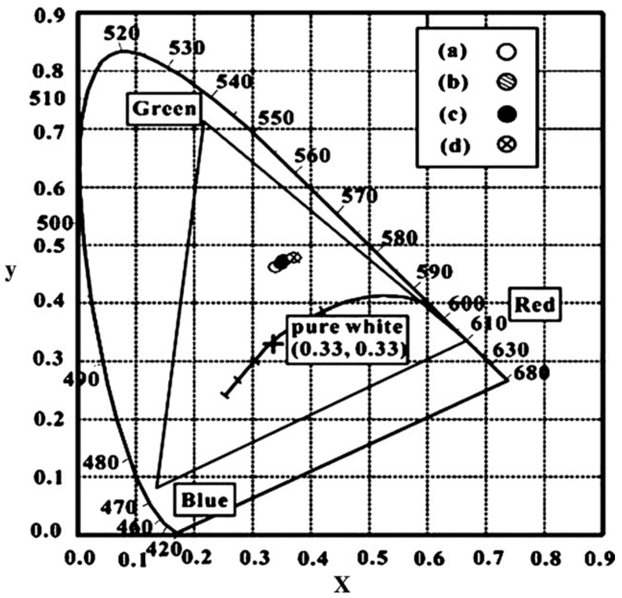

Fig. 7. CIE color coordinates of $YVO_4:Bi^{3+}$ phosphors obtained at different concentrations: (a) 0.5% Bi^{3+} (0.359, 0.482), (b) 1% Bi^{3+} (0.364, 0.487), (c) 1.5% Bi^{3+} (0.366, 0.491) and (d) 3% Bi^{3+} (0.374, 0.496).

increases the relative emission intensity of the YVO_4:1.5% Bi^{3+} by about 6%. The results show that the use of NH_4Cl as flux can help to crystallize the phosphor, and enhances the intensities of the excitation and emission spectra of the YVO_4:1.5% Bi^{3+} phosphors. The flux mechanism for the improvement of the photoluminescence characteristics of the YVO_4:1.5% Bi^{3+} phosphors may result from the fact that NH_4Cl melts at a low temperature to form liquid phase, which accelerates the velocity of the chemical reaction, prompting the Bi^{3+} ions to enter the YVO_4 lattice through grain boundary diffusion and improving the morphology of particles, endowing them with smooth surfaces and well-proportioned distribution, resulting in the improvement of the photoluminescence [23].

Emission color was analyzed with the help of CIE (Commission Internationale de l' Eclairage) chromaticity coordinates diagram. The color coordinates of the as-synthesized $YVO_4:Bi^{3+}$ phosphors are in a range of $x = 0.358–0.374$, $y = 0.482–0.496$. The color coordinates of $Y_{1-x}Bi_xVO_4$ ($x = 0.005, 0.01, 0.015, 0.03$) are shown in detail in Fig. 7. We found that with the increasing of Bi^{3+}concentration the color coordinates move toward top right corner, namely the color becomes yellowish-green. It is clear from the figure that color coordinates of the as-synthesized samples are located near to white region on the chromaticity diagram.

4. Conclusions

The yellowish-white $YVO_4:Bi^{3+}$ phosphors were synthesized by a convenient high-temperature solid-state method, 1.5% Bi^{3+} the optimum concentration and 1000 °C being the optimum sintering temperature for their preparation. When the flux NH_4Cl is 1% of the whole samples quality the Bi^{3+} emission intensity can increase by about 6%. The Bi^{3+} shows an intense wide emission band with FWHM of 144 nm and broad excitation band ranging form 200 to 370 nm, so they may be hopeful in the use of high pressure mercury lamp and tricolor conversion phosphors. In addition, Bi^{3+}-doped YVO_4 phosphors, which have a wide emission band including the blue region and the green region ranging from 400 nm to 800 nm, can make the useful visible white spectrum.

Acknowledgments

This work was financially supported by Innovation Program of Shanghai Municipal Education Commission (10YZ70, 09ZZ136), Science Foundation of Shanghai Normal University (SK201002), Shanghai Science and Technology Development Fund (Nos. 09520500500, 11ZR1426500) and the Key Laboratory of Resource Chemistry of Ministry of Education of China.

References

[1] F. Kellendonk, T. Van den Belt, G. Blasse, J. Chem. Phys. 76 (1982) 1194.
[2] M. Ilmer, B. Grabmaier, G. Blasse, Chem. Mater. 6 (1994) 204–206.
[3] A. Srivastava, Mater. Res. Bull. 37 (2002) 745–751.
[4] E. Oomen, G. Blasse, J. Solid State Chem. 75 (1988) 201–204.
[5] J. Bao, S. Zhou, G. Feng, X. Wang, X. Qiao, J. Qiu, J. Alloys Compd. 456 (2008) 239–242.
[6] W. Minquan, F. Xianping, X. Guohong, J. Phys. Chem. Solids 56 (1995) 859–862.
[7] S. Zhou, N. Jiang, B. Zhu, H. Yang, S. Ye, G. Lakshminarayana, J. Hao, J. Qiu, Adv. Funct. Mater. 18 (2008) 1407–1413.
[8] M. Peng, L. Wondraczek, Opt. Lett. 34 (2009) 2885–2887.
[9] H.T. Sun, A. Hosokawa, Y. Miwa, F. Shimaoka, M. Fujii, M. Mizuhata, S. Hayashi, S. Deki, Adv. Mater. 21 (2009) 3694–3698.
[10] M. Peng, G. Dong, L. Wondraczek, L. Zhang, N. Zhang, J. Qiu, J. Non-Cryst. Solids (2010).
[11] G. Blasse, A. Bril, J. Chem. Phys. 47 (1967) 1920–1926.
[12] P. Zhiwu, S. Qiang Zhang, Solid State Commun. 86 (1993) 377–380.
[13] W.J. Park, M.K. Jung, S.J. Im, D.H. Yoon, Colloids Surf. A 313–314 (2008) 373–377.
[14] G. Blasse, C. Timmermans, J. Solid State Chem. 52 (1984) 222–232.
[15] V. Dotsenko, N. Efryushina, I. Berezovskaya, Mater. Lett. 28 (1996) 517–520.
[16] X. Xiao, B. Yan, J. Alloys Compd. 421 (2006) 252–257.
[17] A. Huignard, T. Gacoin, J.-P. Boilot, Chem. Mater. 12 (2000) 1090–1094.
[18] A.K. Levine, F.C. Palilla, Appl. Phys. Lett. 5 (1964) 118–120.
[19] Z. Xia, D. Chen, M. Yang, T. Ying, J. Phys. Chem. Solids 71 (2010) 175–180.
[20] V. Natarajan, A.R. Dhobale, C.-H. Lu, J. Lumin. 129 (2009) 290–293.
[21] W.J. Park, M.K. Jung, D.H. Yoon, Sens. Actuators B: Chem. 126 (2007) 324–327.
[22] J. Qiu, K. Miura, N. Sugimoto, K. Hirao, J. Non-Cryst. Solids 213–214 (1997) 266–270.
[23] L. Cheng, H. Zhong, J. Sun, X. Zhang, Y. Peng, T. Yu, X. Zhao, J. Rare Earths 26 (2008) 211–214.