ISSN : 0974 - 7486 Volume 11 Issue 8

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 11(8), 2014 [261-266]

Synthesis of red phosphors $NaLa(MoO_4)_2:Eu^{3+}$ by sol- gel method assisted by microwave and effect of doping PO_4^{3-} on the structure and luminescent properties

Yong-Qing Zhai[1]*, Yao-Xuan Cui[1], Jia-Jia Zhao[1], Jian Ma[1], Qiang Zheng[1], Jia Qiao[2]
[1]College of Chemistry and Environmental Science, Hebei University, Baoding 071002, (P.R.CHINA)
[2]College of Mechanical and Electrical Engineering, Agricultural University of Hebei,
Baoding 071001, (P.R.CHINA)
E-mail: zhaiyongqinghbu@163.com

ABSTRACT

Red phosphors $NaLa_{0.95}Eu_{0.05}(MoO_4)_2$ have been synthesized by sol-gel method assisted by microwave. X-ray diffraction and fluorescence spectrophotometer were used to analyze and investigate the phase structure and luminescent properties of phosphors, respectively. The results show that the as-synthesized sample belongs to tetragonal scheelite-structure. The excitation spectrum of $NaLa_{0.95}Eu_{0.05}(MoO_4)_2$ is composed of two major parts: one is the broad band between 200 and 350 nm, which belongs to the charge transfer of Mo-O and Eu-O; the other consists of a series of sharp lines between 350 and 500 nm, ascribed to the f-f transition of Eu^{3+}. The main emission peak is at 616 nm, which is ascribed to the transition of $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+}. Moreover, the luminescent intensity of $NaLa_{0.95}Eu_{0.05}(MoO_4)_2$ can be greatly enhanced with incorporation of PO_4^{3-} and charge compensator Li^+.

KEYWORDS

Phosphors;
Luminescence;
$NaLa_{0.95}Eu_{0.05}(MoO_4)_2$;
Doping negative ions;
Sol-gel preparation;
Microwave.

INTRODUCTION

White light-emitting diodes (w-LEDs) can offer a lot of benefits in terms of higher efficiency, longer lifetime, lower power consumption and environmental protection[1,2]. In recent years, blue-, green- and red tricolor phosphors are used and combined with a NUV InGaN chip (350–410 nm) to generate white light in order to solve the problem of low color-rendering index for yellow-blue combination. Therefore, these phosphors excited effectively by NUV-LED chips attract extensive attentions[3].

Recently, rare earth ions doped molybdate as a kind of new w-LEDs phosphors has been widely applied in the field of luminescent materials[4-6]. Especially, double molybdates with scheelite-like structure show excellent thermal and hydrolytic stabilityÿand are regarded as promising host materials for phosphors[7-9]. To date, rare earth ions doped double molybdate phosphors have been prepared by different routes. Wang et al[10] synthesized a series of Eu^{3+}-doped double molybdate red phosphors $NaLn_{1-x}Eu_x(MoO_4)_2$, $AEu(MoO_4)_2$ (Ln=La, Gd and Y, A=Li, Na and K) and $A_{0.5}A'_{0.5}Eu(MoO_4)_2$ (A, A'=Li, Na and K) by traditional solid state reaction method, and studied the relationship between the structures and the photo-luminescent properties of the phosphors. Zhou et al[11] prepared $LiY_{1-x}Eu_x(MoO_4)_2$ red-emitting phosphors by sol-gel process and investigated the effect of Eu^{3+} concentration, annealing temperature and the molar ratio of citric acid to the total metal cations on the fluorescent properties of as-synthesized samples. Wang et al[12] synthesized $NaEu(MoO_4)_2$ phosphors by the combustion method, and compared the photo-luminescent of samples with that prepared by the solid state reaction. However, the enhancement of luminescent intensity of rare earth double molybdates by doping negative ions has been rarely studied.

In the present work, double molybdate red phosphors $NaLa_{0.95}Eu_{0.05}(MoO_4)_2$ have been prepared by sol-gel method assisted by microwave. Gelling and drying time were shortened greatly by microwave radiation. As-synthesized red phosphors can be excited effectively by UV, NUV and blue light, showing good prospect for red phosphors of white LED. The influence of doping negative ions PO_4^{3-} into the $NaLa_{0.95}Eu_{0.05}(MoO_4)_2$ phosphors on the structure and luminescent properties of $NaLa_{0.95}Eu_{0.05}(MoO_4)_2$ were studied. Meanwhile, Li^+ was introduced as charge compensator in order to enhance luminescent intensity.

EXPERIMENTAL

$NaLa_{0.95}Eu_{0.05}(MoO_4)_2$ phosphor was synthesized by sol-gel method assisted by microwave. Firstly, Eu_2O_3(99.99%) and La_2O_3(99.99%) were dissolved respectively in appropriate HNO_3(A.R.) to prepare $Eu(NO_3)_3$ and $La(NO_3)_3$ solution, then the accurate concentrations were determined by EDTA complexing titration to ensure a desired stoichimetry. According to the stoichiometric ratio of target product, $NaNO_3$(A.R.), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$(A.R.), citric acid(A.R.), $Eu(NO_3)_3$ solution, $La(NO_3)_3$ solution and appropriate amount of distilled water were added into a 100 ml ceramic crucible. Then, the mixture was stirred to make the materials dissolve completely. Subsequently, a small amount of aqueous ammonia was added to adjust the pH value of the solution to 2~3. Next, the resulting solution was treated by ultrasonic wave for 5 min to make raw materials mix uniformly. Then the mixture was put into a WG700SL2011-KG microwave oven, and heated under the power of middle-high fire for 6.5 min to evaporate superfluous water fast, and form a transparent gel. Then the gel was dried in a drying oven at 90 °C. After drying, the dry white loose and porous sample (which was called the precursor) was obtained. Finally, the precursor was ground into fine particles, and calcined in muffle furnace at 800 °C for 3 h to obtain the goal product.

The preparation procedure of $NaLa_{0.95}Eu_{0.05}(MoO_4)_{2-x}(PO_4)_xLi_x$ are similar to above process. PO_4^{3-} is from $(NH_4)_3PO_4\cdot 3H_2O$(A.R.), and Li^+ is supplied by $LiNO_3$, which is obtained by the reaction of Li_2CO_3(A.R.) and HNO_3.

Phase structure and crystallization of synthesized samples were characterized by X-ray diffraction analysis (XRD) with a Y2000 diffractometer using Cu-Kα radiation source (30 kV × 20 mA, λ=0.154178 nm). The excitation and emission spectra of the samples were recorded on an F-380 fluorescence spectrophotometer. All measurements were performed at room temperature.

RESULTS AND DISCUSSIONS

XRD analysis

Figure 1 shows the XRD patterns of the as-synthesized samples. It can be seen that all of the peaks can be indexed to the $NaLa(MoO_4)_2$ nearly, which agrees well with the JCPDS card (No.24-1103). According to that, the samples are all pure tetragonal phase $NaLa(MoO_4)_2$ with space group $I4_1/a$. In these patterns, the peaks of the reactants cannot be found, which proves that Eu^{3+}, PO_4^{3-} and Li^+ ions have entered into the crystal lattice and have little effect on the crystal structure of the host $NaLa(MoO_4)_2$. It can be found that all the diffraction peaks shift toward the high angle side. This can be explained by the Bragg equation, $\lambda=2d\sin\theta$ (d is the distance between two crystalplanes, θ is the diffraction angle of an observed peak, and λ is the X-ray wavelength). Since the radii of Eu^{3+} (0.106 nm) is smaller than that of La^{3+} (0.116 nm), and the radii of P^{5+} (0.17 nm) is smaller than that of Mo^{6+} (0.41 nm)[13]. When the La^{3+} and MoO_4^{2-} ions in $NaLa(MoO_4)_2$ host lattice are partially substituted by Eu^{3+} and PO_4^{3-} ions respectively, the crystal lattice constants as well as dspacing decrease (shown in TABLE 1), hence, the diffraction angles shift to the higher angle side.

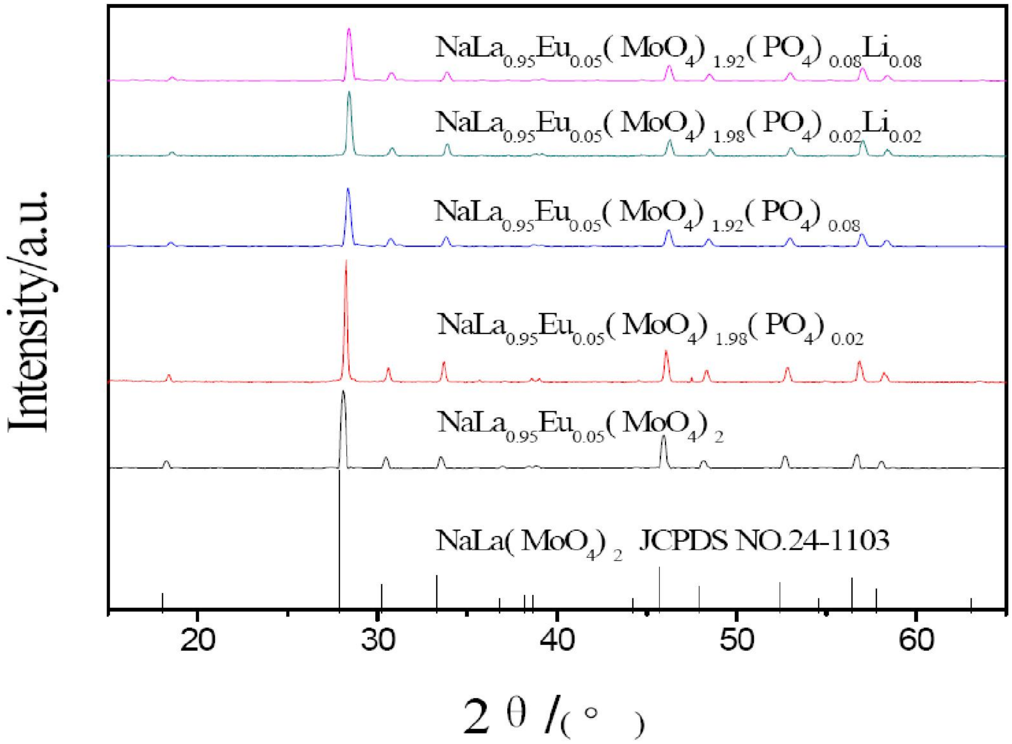

Figure 1 : XRD patterns of samples

TABLE 1 : The calculated lattice parameters of samples

	a(Å)	c(Å)	Cell volume (Å^3)
$NaLa(MoO_4)_2$ (JCPDS No.24-1103)	5.343	11.743	335.240
$NaLa_{0.95}Eu_{0.05}(MoO_4)_2$	5.333	11.718	333.320
$NaLa_{0.95}Eu_{0.05}(MoO_4)_{1.98}(PO_4)_{0.02}$	5.320	11.693	330.970
$NaLa_{0.95}Eu_{0.05}(MoO_4)_{1.92}(PO_4)_{0.08}$	5.309	11.668	328.930
$NaLa_{0.95}Eu_{0.05}(MoO_4)_{1.98}(PO_4)_{0.02}Li_{0.02}$	5.308	11.658	328.480
$NaLa_{0.95}Eu_{0.05}(MoO_4)_{1.92}(PO_4)_{0.08}Li_{0.08}$	5.304	11.654	327.870

Effect of co-doped PO_4^{3-} ions on the luminescent properties of $NaLa_{0.95}Eu_{0.05}(MoO_4)_2$

Figure 2 shows the excitation spectra of $NaLa_{0.95}Eu_{0.05}(MoO_4)_{2-x}(PO_4)_x$ with different concentration (x) of PO_4^{3-}. It can be seen that all the excitation spectra are composed of a broad band and a series of sharp lines. The broad band in the range 200 nm~350 nm can be ascribed to the charge transfer band (CTB) of Mo-O and Eu-O, and the main peak is at 301 nm. The sharp lines between 350 nm and 500 nm are due to intra-configuration 4f-4f transition of Eu^{3+} in the host lattice. Among them, the peaks at 395 nm ($^7F_0$-$^5L_6$) and 464 nm ($^7F_0$-$^5D_2$) are stronger than others[14,15]. Therefore, the phosphors can be excited by UV (301 nm), NUV (395 nm), and blue light (464 nm) very well. So, it can match well with UV-, NUV- and Blue-LED, showing a great potential for practical applications. Moreover, it can be found that the CTB shift toward the long wavelength side along with the doping of PO_4^{3-}. The possible reason is as follows. The radii of P is smaller than that of Mo, and the electronegativity of P (2.19) is stronger than that of Mo (2.16), so doping negative ions PO_4^{3-} leads to the bond length of Mo-O being shortened. As a result, it requires less energy to transfer an electron from an O^{2-} to Mo^{6+}, resulting in the CTB shift towards lower energy, i.e., the long wavelength side.

The emission spectra (in Figure 3) show that the PO_4^{3-} concentration (x) has little effect on the shape and position of emission peaks. All the emission spectra are mainly composed of two strong emission peaks. The emission peak at 616 nm is ascribed to the electric dipole transition from $^5D_0$ to $^7F_2$ of Eu^{3+}, while the emission peak near 592 nm is assigned to the magnetic dipole transition from $^5D_0$ to $^7F_1$ of Eu^{3+}[16,17]. The PO_4^{3-} concentration (x) has great effect on the intensity of emission peaks. When PO_4^{3-} doping concentration x<0.04, the emission intensity at 616 nm increases with the increase of x; the emission intensity is up to the strongest when x=0.04, which is about 1.3 times of the un-doped sample; if x>0.04, the emission intensity begins to decrease. The reason may be that the electronegativity of P is stronger than that of Mo. The incorporation of PO_4^{3-} leads to the enhancement of covalent degree of Mo^{6+}-O^{2-} bond. Therefore, the energy stored in MoO_4^{2-} is decreased, while the energy transferred to Eu^{3+} from MoO_4^{2-} is enhanced, and then the fluorescence intensity of the sample is enhanced. However, when exceeding the optimum concentration, superfluous PO_4^{3-} ions may cause oversize distortion of the lattice, and then lead to fluorescence quenching. Thus, the optimum concentration of PO_4^{3-} x=0.04.

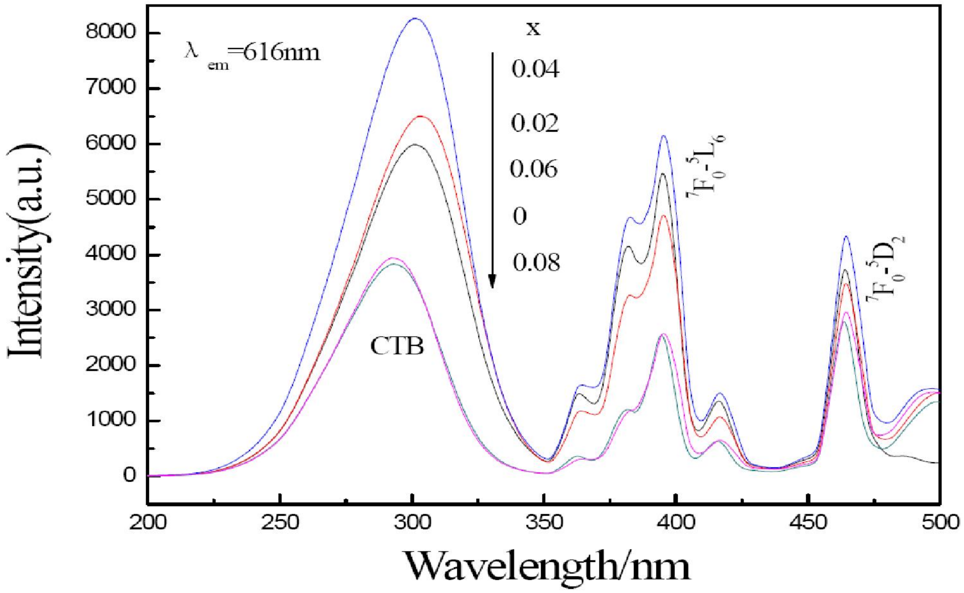

Figure 2 : Excitation spectra of $NaLa_{0.95}Eu_{0.05}(MoO_4)_{2-x}(PO_4)_x$ samples

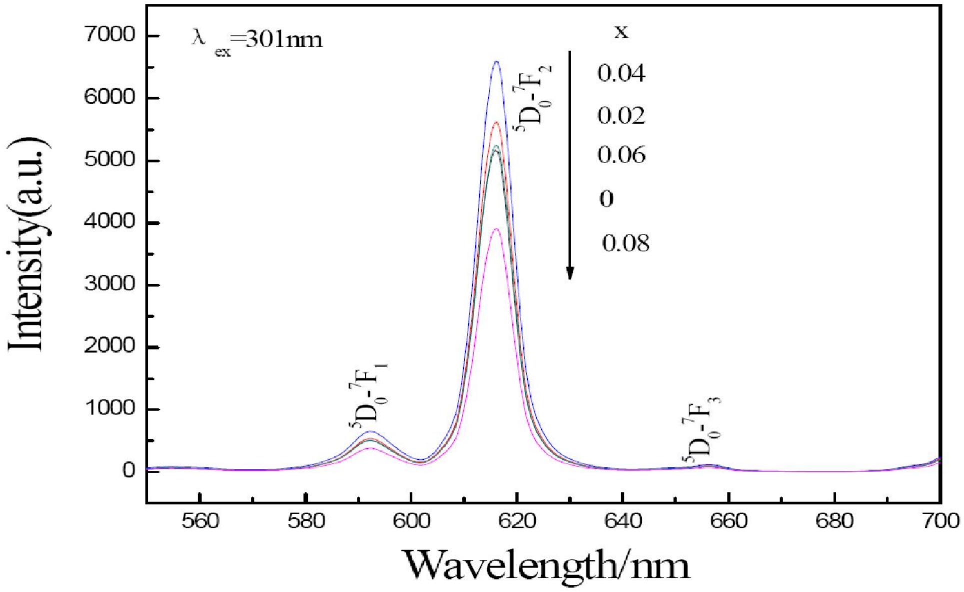

Figure 3 : Emission spectra of $NaLa_{0.95}Eu_{0.05}(MoO_4)_{2-x}(PO_4)_x$ samples

Effect of charge compensation agent on the luminescent properties of $NaLa_{0.95}Eu_{0.05}(MoO_4)_{2-x}(PO_4)_x$

In $NaLa_{0.95}Eu_{0.05}(MoO_4)_{2-x}(PO_4)_x$ phosphors, MoO_4^{2-} ions are substituted partially by PO_4^{3-} ions. An extra negative charge will be formed because of the unbalanced charge between PO_4^{3-} and MoO_4^{2-}, therefore, appropriate charge compensation is needed to keep charge balance[18].

In our present work, Li^+ was introduced as the charge compensator. The emission spectra of $NaLa_{0.95}Eu_{0.05}(MoO_4)_{2-x}(PO_4)_xLi_x$ are shown in Figure 4. It can be known that doping small amount Li^+ has little effect on the shape and position of emission peaks, but has obvious effect on the intensity. Compared with Figure 3, under the same concentration of PO_4^{3-}, the luminescence intensity of samples doped with Li^+ is all enhanced, and the emission intensity is up to the strongest when x=0.04. The possible reason for above result is as follows. The incorporation of appropriate charge compensator Li^+ ions makes the charge keep balance, and meantime cause the distortion of the crystal lattice, improving the probability of transition emission of Eu^{3+}, and then enhancing the emission intensity of $NaLa_{0.95}Eu_{0.05}(MoO_4)_{2-x}(PO_4)_x$ phosphor.

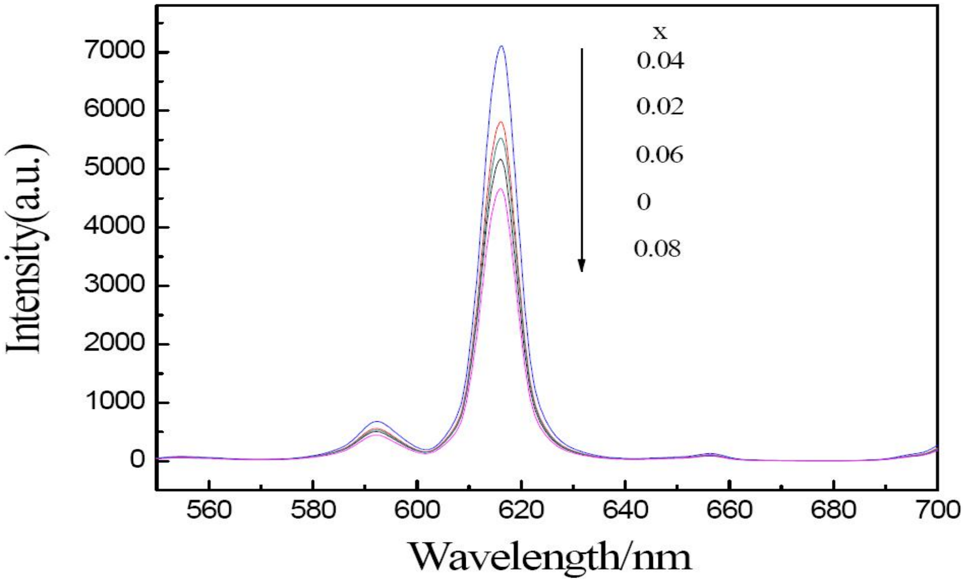

Figure 4 : Emission spectra of $NaLa_{0.95}Eu_{0.05}(MoO_4)_{2-x}(PO_4)_xLi_x$ samples

CONCLUSION

In this work, red-emitting phosphor $NaLa_{0.95}Eu_{0.05}(MoO_4)_2$ with tetragonal scheelite-structure was successfully synthesized by sol-gel method assisted by microwave. This method has many advantages of short gelling and drying time, low calcination temperature, energy saving, easy operation, uniform composition, and so on. The phosphor can be excited effectively by UV-, NUV- and Blue-emitting LED chip due to their broad excitation band extending from 250 nm to 500nm. Therefore, $NaLa_{0.95}Eu_{0.05}(MoO_4)_2$ shows good prospect for red phosphors of white LED. The emission intensity of $NaLa_{0.95}Eu_{0.05}(MoO_4)_2$ is enhanced significantly by doping negative ions PO_4^{3-}, and reach the maximum at the doping concentration x=0.04. Moreover, Li^+ was doped as the charge compensator, and improved the luminescent intensity of $NaLa_{0.95}Eu_{0.05}(MoO_4)_{2-x}(PO_4)_x$ samples.

REFERENCES

[1] J.Y.Sun, X.Y.Zhang, H.Y.Du; J.Rare Earths, **30(2)**, 118-122 **(2012)**.

[2] A.Xie, X.M.Yuan, F.X.Wang, et al; J.Alloys Compd., **501**, 124-129 **(2010)**.

[3] Y.S.Hu, W.D.Zhang, H.Q.Ye, et al; J.Lumin., **111(3)**, 139-145 **(2005)**.

[4] X.X.Ju, X.M.Li, W.L.Li, et al; Mater.Lett., **77**, 35-37 **(2012)**.

[5] Md.Masuqul Haque, Dong-KuK Kim; Mater.Lett., **63(9-10)**, 793-796 **(2009)**.

[6] Z.M.Li, Y.J.Zhang, S.K.Gao; J.Rare Earths, **30(10)**, 990-994 **(2012)**.

[7] X.H.Qian, X.P.Pu, D.F.Zhang, et al; J.Lumin., **131**, 1692-1695 **(2011)**.

[8] L.Guan, W.Wei, S.Q.Guo, et al; J.Electrochem.Soc., **159(4)**, D200-203 **(2012)**.

[9] F.W.Mo, L.Y.Zhou, P.Qi, et al; Ceram.Int., **38(8)**, 6289-6294 **(2012)**.

[10] Z.L.Wang, H.B.Liang, M.L.Gong, et al; J.Alloys Compd., **432**, 308-312 **(2007)**.

[11] X.J.Zhou, T.H.Zhou, Y.M.Li, et al; J.Rare Earths, **30(4)**, 315-318 **(2012)**.

[12] Z.L.Wang, H.B.Liang, M.L.Gong, et al; Mater.Lett., **62**, 619-622 **(2008)**.

[13] G.Jia, S.W.Ding, C.M.Huang, et al; Opt.Mater., **35**, 285-291 **(2012)**.

[14] E.D.Bacce, A.M.Pires, M.R.Davolos; J.Alloys Compd., **344(1-2)**, 312-315 **(2002)**.

[15] G.Blasse; Chem.Phys.Lett., **20(6)**, 573-574 **(1973)**.

[16] X.G.Wang, Z.Y.Yu, M.Na, et al; Chin.J.Inorg. Chem., **24(4)**, 571-575 **(2008)**.

[17] G.Jia, M.Yang, Y.H.Song, et al; Cryst.Growth Des., **9(1)**, 301-307 **(2009)**.

[18] L.H.Tian, S.I.Mho; Solid State Commun., **125(11-12)**, 647-651 **(2003)**.