



A Preliminary Study on Pb^{2+} Ion as Site Probe in SrAl_2O_4

Jinsheng Shi,^{a,b} Lili Wang,^b Qiang Sun,^b Qianqian Wei,^b Liangliang Cui,^b and Yangdong Hu^{a,z}

^aCollege of Chemistry and Chemical Engineering, Ocean University of China, Qingdao, 266100, Shandong, China.

^bDepartment of Applied Chemistry, Institute of Chemistry and Pharmacy, Qingdao Agricultural University, Qingdao, 266109, Shandong, China

Site occupation in SrAl_2O_4 was probed just by doping Pb^{2+} ion, and a new route to investigate site occupation in luminescence materials was put forward. $\text{SrAl}_2\text{O}_4:\text{Pb}^{2+}$ samples obtained through sol-gel method were investigated and its excitation spectrum had two bands at lower temperatures. These two bands are closely related to two Sr sites. Environment factor h_e of two Sr sites were calculated and the energy E_A of Pb^{2+} were obtained making use of our pre-bulit empirical formula, i.e. $E_A = 7.223 - 3.271h_e$. It was concluded that the excitation band peaking at 253 nm is from Sr(1) site and the excitation band peaking at 264 nm Sr(2) site. There is one possibility that using Pb^{2+} ion as site probe in SrAl_2O_4 host or other host materials.

© 2011 The Electrochemical Society. [DOI: 10.1149/2.053111jes] All rights reserved.

Manuscript submitted February 23, 2011; revised manuscript received August 11, 2011. Published October 5, 2011.

Location of activator in host lattice of luminescent materials has been the object of great interest. Site occupation of activators in host lattice has been investigated through different methods or from different perspectives. From the standpoint of covalency, Cao et al.¹ investigated site occupation of Sm^{2+} in KMgF_3 by substituting Mg^{2+} with Be^{2+} , Ca^{2+} respectively. He concluded that Sm^{2+} did not enter Mg site but entered K site based on that position of emission bands will shift due to different covalency. Lin and Su² studied site occupation of Eu^{3+} in $\text{Me}_2\text{Y}_8(\text{SiO}_4)_6\text{O}_2$. Two sites (4f and 6h sites) are available, and 6h sites were more covalently bonded than 4f sites. Therefore, the lower energy of two $^5\text{D}_0\text{--}^7\text{F}_0$ lines was assigned to Eu^{3+} (6h) and the higher energy was assigned to Eu^{3+} (4f); Folkerts et al.³ investigated luminescent property of Pb^{2+} in several calcium borates. Two Ca sites in $\text{Ca}_4\text{LaO}(\text{BO}_3)_3$ are available, and covalency of Ca(1) site is higher owing to having a “free” oxygen ion to coordinate. Based on this, the emission band at 410 nm is ascribed to Pb^{2+} on Ca(1) site and the emission band at 370 nm to Pb^{2+} on Ca(2) site.

Variation of lattice parameters of unit cell was utilized to study the problem of site occupation. Inaguma et al.⁴ investigated site occupation of Pr in Pr-doped perovskite-type lithium ion-conducting oxides. Lattice parameters of Pr-doped $\text{Sr}_{0.6}\text{Li}_{0.3}\text{Ti}_{0.5}\text{Ta}_{0.5}\text{O}_3$ decreased with the Pr content. Taking ionic radius into consideration at the same time, it is concluded that Pr^{3+} occupied Sr^{2+} site at $x < 0.5\%$ and Pr^{3+} primarily occupied Sr^{2+} site, partially occupied Ti^{4+} and Ta^{5+} sites at $x > 0.5\%$.

Regularity of site also be used to investigate site occupation. Folkerts et al.⁵ studied luminescence of Pb^{2+} in BaAl_2O_4 . Two different Ba^{2+} sites are available. Ba(2) site is less regularly coordinated and occurs three times more frequently. Therefore, less intense emission band was assigned to a transition on Pb^{2+} ion occupying Ba(1) site, the more intense to Pb^{2+} ion on Ba(2) site.

Although several methods have been utilized to investigate site occupation of activator in host lattice of luminescent materials, due to lack of quantitative methods or tools, the work to assign the source of excitation bands makes slow progress. A simple, exact, quantitative method is sorely needed.

SrAl_2O_4 is one of most efficient host for long-lasting phosphorescence materials.^{6,7} It exists in two crystallographic forms, monoclinic structure in lower temperature and hexagonal structure in higher temperature. There are two different crystallographically sites in monoclinic structure and they have identical coordination number (i.e. 6) and similar Sr-O distance.⁸ Folkerts et al.⁵ observed that the two sites occur in equal amounts in SrAl_2O_4 and two emissions bands gave similar intensity. All these make the problem of site occupation of Pb^{2+} after being doped into SrAl_2O_4 more complex.

Pb^{2+} belongs to ns^2 ions and its luminescent properties were easily influenced by crystalline environment of host of luminescent

materials.^{9–12} In our recent studies, we have investigated the quantitative relationship between sp energy level of Pb^{2+} and environmental factor h_e in different hosts. Corresponding empirical formula has been obtained.¹³ Although two Sr sites in SrAl_2O_4 are similar, it is expected that excitation bands of Pb^{2+} at different sites can be distinguished. Therefore, we explored the feasibility using Pb^{2+} as site probe in SrAl_2O_4 .

In this paper, $\text{SrAl}_2\text{O}_4:\text{Pb}^{2+}$ phosphor was synthesized and its spectral data have been obtained. Origin of two excitation bands related to Pb^{2+} in two Sr sites were assigned successfully. This work can provide a novel idea that use Pb^{2+} ion or other ns^2 ions to explore site occupation when some other activator ions are doped in some host materials.

Experimental

Synthesis.—The raw materials are SrCO_3 , $\text{Pb}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Citric acid, Nitric acid. All the materials are analytical pure. Firstly, $\text{Sr}(\text{NO}_3)_2$ solution was prepared by dissolving SrCO_3 in dilute HNO_3 solution under heating and was isovolumed in a 100-ml volumetric flask. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Citric acid and $\text{Pb}(\text{NO}_3)_2$ were dissolved in distilled water respectively and also isovolumed in 100-ml volumetric flasks to prepare aqueous solutions. These four aqueous solutions were measured in stoichiometric $\text{Sr}_{0.985}\text{Al}_2\text{O}_4:\text{Pb}_{0.015}$ and added into a beaker. After stirring, ammonia solution was dropped into the above solution until $\text{pH} = 3.5$. After heating for about 2 h, yellow, transparent and sticky gel formed. The obtained gel was dried at 60°C in air to remove water and calcined at 1000°C for 2 h in muffle furnace.

Characterization.—The samples were characterized by X-ray powder diffraction using a Rigaku D/max 2200 vpc X-ray Diffractometer with $\text{Cu K}\alpha$ radiation at 40 kV and 30 mA. The photoluminescence (PL) spectra of $\text{SrAl}_2\text{O}_4:\text{Pb}^{2+}$ phosphor was investigated by a Fluorolog-3 spectrofluorometer (Jobin Yvon Inc/specx) equipped with a 450 W Xe lamp and double-excitation monochromators.

Results and Discussion

The X-ray diffraction pattern.—Figure 1 shows the results of the X-ray diffraction of the product after calcination at 1000°C for 2 h. It can be found that the peak positions of the XRD patterns fit well with those of the monoclinic phase SrAl_2O_4 (JCPDS No. 34-0379). No raw materials or other products can be observed, indicating that the composition of the product is pure monoclinic phase. At the same time, a little amount of doped Pb^{2+} has no obvious influence on the structure of the host, and it can be attributed to the similar ionic radius of Sr^{2+} (1.18 Å) and Pb^{2+} (1.19 Å).

^z E-mail: ydhuhd@ouc.edu.cn

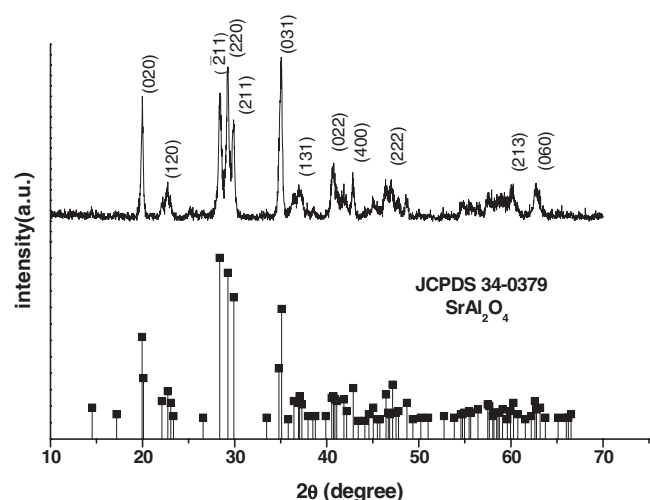


Figure 1. XRD pattern of $\text{Sr}_{0.985}\text{Al}_2\text{O}_4:\text{Pb}^{2+}_{0.015}$. The standard data of pure monoclinic phase SrAl_2O_4 (JCPDS 34-0379) are presented in the figure for comparison.

Luminescence properties.— Excitation spectrum of $\text{SrAl}_2\text{O}_4:\text{Pb}^{2+}$ is shown in Figure 2 and the detective wavelength is 320 nm. Excitation spectrum at lower temperature suggests that there are two excitation bands. The two excitation bands can be found peaking at 252 nm and 263 nm. Based on excitation spectrum at lower temperature, we chose 252 nm and 263 nm as excitation wavelength. In addition, more interestingly, when the monitor wavelength is 390 nm, a new excitation band peaking at 271 nm can be found (see Figure 3). Therefore, emission spectra of Pb^{2+} in SrAl_2O_4 under 252, 263 and 271 nm excitation at various temperatures are shown in Figure 4–6, respectively.

Two emission bands with maximum at 320 and 390 nm are observed. With increasing temperature these maxima shift to shorter wavelengths and intensity of the 320 nm peaks increases. Under 271 nm excitation, intensity of the emission band peaking at 320 nm increases at the expense of intensity of another band peaking at 390 nm.

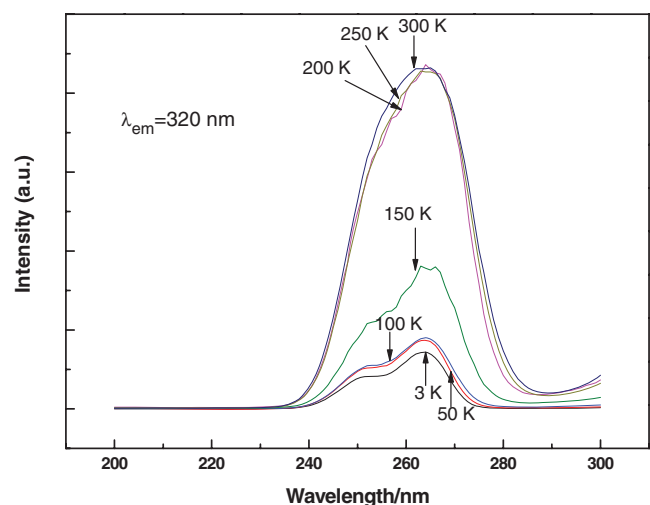


Figure 2. Excitation spectra of $\text{Sr}_{0.985}\text{Al}_2\text{O}_4:\text{Pb}^{2+}_{0.015}$ samples at various temperatures from 3 K to 300 K under 320 nm monitor wavelength.

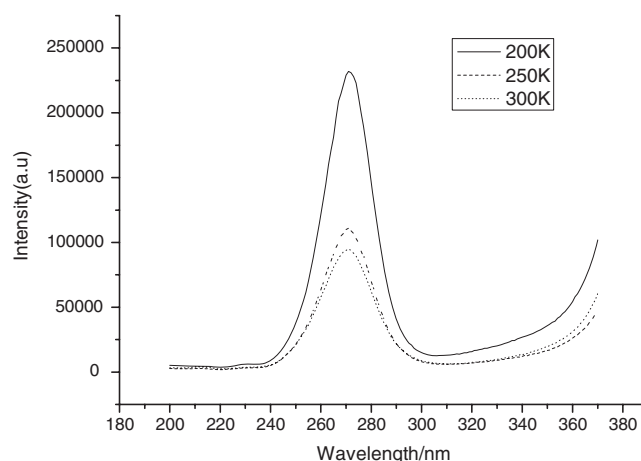


Figure 3. Excitation spectra of $\text{Sr}_{0.985}\text{Al}_2\text{O}_4:\text{Pb}^{2+}_{0.015}$ samples at various temperatures from 200 K to 300 K under 390 nm monitor wavelength.

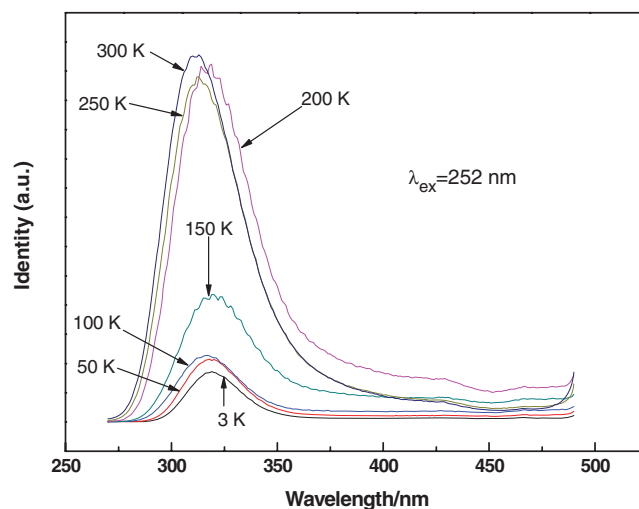


Figure 4. Emission spectra of $\text{Sr}_{0.985}\text{Al}_2\text{O}_4:\text{Pb}^{2+}_{0.015}$ samples at various temperatures from 3 K to 300 K under 252 nm excitation.

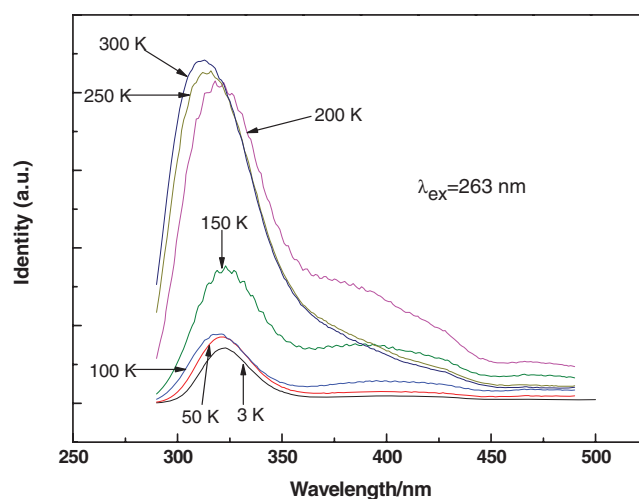


Figure 5. Emission spectra of $\text{Sr}_{0.985}\text{Al}_2\text{O}_4:\text{Pb}^{2+}_{0.015}$ samples at various temperatures from 3 K to 300 K under 271 nm excitation.

Table I. Environmental factors h_e of Sr(1) and Sr(2) site for SrAl_2O_4 as well as experimental and theoretical calculation value of A band of Pb^{2+} ion

Host	n	Bond	f_c^μ	$\alpha_b^\mu (\text{\AA}^3)$	Q_B^μ	C.N.	h_e	$E_{A,\text{exp}}/\text{eV}$	$E_{A,\text{cal}}$	$\Delta_{\text{error}}(\%)$
SrAl_2O_4	1.647	Sr(1)—O(1)	0.0789	0.6028	1.333	1	0.732	4.901	4.829	1.46
		Sr(1)—O(2)	0.0787	0.6123	1.333	1				
		Sr(1)—O(3)	0.1542	0.8344	1	1				
		Sr(1)—O(4)	0.0802	0.5045	1.333	1				
		Sr(1)—O(7)	0.079	0.5879	1.333	2				
		Sr(2)—O(1)	0.0776	0.7129	1.333	1				
		Sr(2)—O(2)	0.0784	0.6322	1.333	1				
		Sr(2)—O(4)	0.0795	0.5482	1.333	1				
		Sr(2)—O(5)	0.1544	0.8173	1	1				
		Sr(2)—O(6)	0.1531	0.8833	1	1				
		Sr(2)—O(8)	0.1537	0.8544	1	1				

$$\Delta_{\text{error}} = (E_{A,\text{exp}} - E_{A,\text{cal}})/E_{A,\text{exp}}$$

Excitation spectrum for 320 nm emission peak is shown in Figure 2. There is only a broad band at higher temperatures. While, two excitation bands can be found at lower temperatures, which are similar to the results that Folkerts⁵ had observed. We made the assignment of the source of A band of Pb^{2+} ion with the aid of our empirical formula obtained before as follows:

Calculation and assignment of A band of Pb^{2+} ion.— The environmental factor designated by the symbol h_e can be expressed as:¹⁴

$$h_e = \left[\sum f_c(i) \alpha(i) Q(i)^2 \right]^{1/2} \quad [1]$$

where $f_c(i)$ is the fractional covalency of chemical bond from centre ion to i th ligand, $\alpha(i)$ is the polarizability of the i th chemical bond volume, $Q(i)$ is the charge presented by the i th neighbouring anion in the bond subformula. The three chemical bond parameters can be calculated using chemical bond theory for complex crystals. The detailed theoretical method was expressed elsewhere.^{15,16}

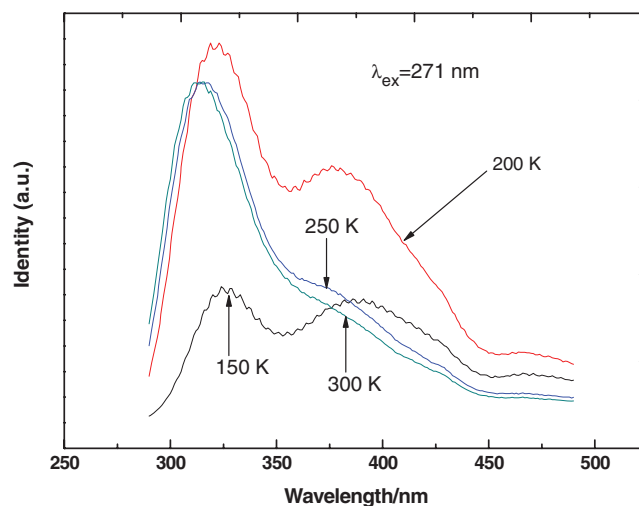
The detailed structure of SrAl_2O_4 crystal has been reported.¹⁷ By means of the dielectric theory of chemical bond for complex crystals, we performed decomposition of subformula equations of SrAl_2O_4 :

$$\begin{aligned} \text{SrAl}_2\text{O}_4 &= \text{Sr}(1)_{1/2}\text{Sr}(2)_{1/2}\text{Al}(1)_{1/2}\text{Al}(2)_{1/2}\text{Al}(3)_{1/2}\text{Al}(4)_{1/2}\text{O}(1)_{1/2}\text{O}(2)_{1/2}\text{O}(3)_{1/2}\text{O}(4)_{1/2}\text{O}(5)_{1/2}\text{O}(6)_{1/2}\text{O}(7)_{1/2}\text{O}(8)_{1/2} \\ &= \text{Sr}(1)_{1/12}\text{O}(1)_{1/8} + \text{Sr}(1)_{1/12}\text{O}(2)_{1/8} + \text{Sr}(1)_{1/12}\text{O}(3)_{1/6} + \text{Sr}(1)_{1/12}\text{O}(4)_{1/8} + \text{Sr}(1)_{1/6}\text{O}(7)_{1/4} \\ &\quad + \text{Sr}(2)_{1/12}\text{O}(1)_{1/8} + \text{Sr}(2)_{1/12}\text{O}(2)_{1/8} + \text{Sr}(2)_{1/12}\text{O}(4)_{1/8} + \text{Sr}(2)_{1/12}\text{O}(5)_{1/6} + \text{Sr}(2)_{1/12}\text{O}(6)_{1/8} \\ &\quad + \text{Sr}(2)_{1/12}\text{O}(8)_{1/6} + \text{Al}(1)_{1/8}\text{O}(2)_{1/8} + \text{Al}(1)_{1/8}\text{O}(4)_{1/8} + \text{Al}(1)_{1/8}\text{O}(6)_{1/6} + \text{Al}(1)_{1/8}\text{O}(8)_{1/6} \\ &\quad + \text{Al}(2)_{1/8}\text{O}(1)_{1/8} + \text{Al}(2)_{1/8}\text{O}(3)_{1/6} + \text{Al}(2)_{1/8}\text{O}(5)_{1/6} + \text{Al}(2)_{1/8}\text{O}(8)_{1/6} + \text{Al}(3)_{1/8}\text{O}(1)_{1/8} \\ &\quad + \text{Al}(3)_{1/8}\text{O}(4)_{1/8} + \text{Al}(3)_{1/8}\text{O}(5)_{1/6} + \text{Al}(3)_{1/8}\text{O}(7)_{1/8} + \text{Al}(4)_{1/8}\text{O}(2)_{1/8} + \text{Al}(4)_{1/8}\text{O}(3)_{1/6} \\ &\quad + \text{Al}(4)_{1/8}\text{O}(6)_{1/6} + \text{Al}(4)_{1/8}\text{O}(7)_{1/8} \end{aligned}$$

Refractive index n of SrAl_2O_4 was already known¹⁸ and making use of the chemical bond theory for complex crystals, chemical bond parameters were calculated and listed on Table I. Using expression (1), we obtained environmental factor h_e for Sr(1) and Sr(2) site, i.e. 0.732 for Sr(1) site and 0.810 for Sr(2) site.

Our empirical formula obtained before¹⁵ is:

$$E_A = 7.223 - 3.271h_e \quad [2]$$

**Figure 6.** Excitation spectra of $\text{Sr}_{0.985}\text{Al}_2\text{O}_4:\text{Pb}^{2+}_{0.015}$ samples at various temperatures from 3 K to 300 K.

By aid of expression (2), E_A of Pb^{2+} in Sr(1) and Sr(2) site were calculated, 4.829 eV for Sr(1) site and 4.573 eV for Sr(2) site. The expression is shown that E_A decreases as h_e increases. Therefore, higher energy excitation band at 253 nm is from Pb^{2+} on Sr(1) site and lower energy excitation band at 264 nm is from Pb^{2+} on Sr(2) site. Experimental results are 4.901 eV for Sr(1) site and 4.696 eV for Sr(2) site. Calculation values agreed well with experimental results and the

relative errors for the two sites were 1.46% and 2.63%, respectively, which were almost in the same order of magnitude with experimental errors.

After accomplishing the work above, we solved the site selection problem in $\text{SrAl}_2\text{O}_4:\text{Pb}$ phosphors successfully. More importantly, if other ions were doped in some host materials and its site selection is unclear, we can introduce Pb^{2+} ion into this kind of host materials and repeat the stages above. After that, source of excitation bands can be assigned quantitatively and site occupation of Pb^{2+} in these host materials can be explored. By aid of the information, when introduce other ions to this host, site selection can be threw light on to a certain degree.

Conclusions

Two excitation bands in the excitation spectrum of Pb^{2+} doped SrAl_2O_4 at lower temperatures were discovered. By using our empirical formula obtained before, we got the $E_{A,cal}$ of Pb^{2+} in Sr(1) site is 4.829 eV, and in Sr(2) site is 4.573 eV. Based on the calculation values, we concluded that excitation band peaking at 253 nm is from Sr(1) site and excitation band peaking at 264 nm Sr(2) site. From what has been discussed above, we verified our pre-built empirical formula and enlarged its application, that is to say, using Pb^{2+} ion as site probe in some host materials. And it may be practicable to other ns^2 ions.

Acknowledgment

This work was supported by the Project of Shandong Province Higher Educational Science and Technology Program (J10LD10) and

Promotive research fund for excellent young and middle-aged scientists of Shandong Province (BS2010CL022).

References

1. Z. C. Cao, C. S. Shi, and J. Z. Ni, *Chin. J. Rare Earths*, **11**, 112 (1993).
2. J. Lin and Q. Su, *Mater. Chem. Phys.*, **38**, 98 (1994).
3. H. F. Folkerts and G. Blasse, *J. Mater. Chem.*, **5**, 273 (1995).
4. Inaguma, Yoshiyuki, Okamoto, Mami, Tsuchiya, Takeshi, Katsumata, and Tetsuhiro, *Solid State Ionics*, **179**, 788 (2008).
5. H. F. Folkerts, F. Ghianni, and G. Blasse, *J. Phys. Chem. Solids*, **57**, 1659 (1996).
6. Q. Xiao, L. Y. Xiao, Y. L. Liu, X. B. Chen, and Y. D. Li, *J. Phys. Chem. Solids*, **71**, 1026(2010).
7. Y. F. Xu, D. K. Ma, M. L. Guan, X. A. Chen, Q. Q. Pan, and S. M. Huang, *J. Alloys. Compd.*, **502**, 38 (2010).
8. F. Clabau, X. Rocquefelte, S. Jobic, P. Deniard, M. H. Whangbo, A. Garcia, and T. Le Mercier, *Chem. Mater.*, **17**, 3904 (2005).
9. A. Wolfert, E. W. J. L. Oomen, and G. Blasse, **31-32**, 308(1984).
10. A. Wolfert, E. W. J. L. Oomen, and G. Blasse, *J. Solid State Chem.*, **59**, 280 (1985).
11. G. Blasse, *Prog. Solid State Chem.*, **18**, 79 (1988).
12. A. van Dijken, H. F. Folkerts, and G. Blasse, *J. Lumin.*, **72-74**, 660 (1997).
13. Q. Sun, J. Wang, and J. S. Shi, *J. Solid State Chem.*, **183**, 1174 (2010).
14. J. S. Shi and S. Y. Zhang, *J. Phys.: Condens. Matter*, **15**, 4101 (2003).
15. S. Y. Zhang, *Chin. J. Chem. Phys.*, **4**, 109 (1991).
16. D. F. Xue and S. Y. Zhang, *J. Phys. Chem. A*, **101**, 5547 (1997).
17. A. R. Schulze and Hk. Müller Buschbaum, *Z. anorg. allg. Chem.*, **475**, 205 (1981).
18. M. J. Weber, *Handbook of Optical Materials*, pp. 87, CRC Press, Boca Raton, FL (2002).