

Research Article

Fluorescence Properties and Synthesis of Green-Emitting Tb³⁺-Activated Amorphous Calcium Silicate Phosphor by Ultraviolet Irradiation of 378 nm

Yoshiyuki Kojima, Masaaki Numazawa, Shinnosuke Kamei, and Nobuyuki Nishimiya

Department of Materials and Applied Chemistry, Faculty of Science and Technology, Nihon University, 1-8, Kanda-Surugadai, Chiyoda-ku, Tokyo 101-8308, Japan

Correspondence should be addressed to Yoshiyuki Kojima, ykojima@chem.cst.nihon-u.ac.jp

Received 27 September 2011; Accepted 31 October 2011

Academic Editor: Gong Ru Lin

Copyright © 2012 Yoshiyuki Kojima et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The excitation wavelength of conventional Tb³⁺-activated phosphor is near 270 nm. This study describes novel green-emitting Tb³⁺-activated amorphous calcium silicate by ultraviolet excitation at 378 nm. The Tb³⁺-activated amorphous calcium silicate was prepared by heating a sample of Tb³⁺-activated calcium silicate hydrate (CSH) at 900°C for 30 minutes. The emission wavelength of the resulting phosphor was 544 nm. The optimum excitation wavelength within the range 300–400 nm was 378 nm. The Tb³⁺-activated amorphous calcium silicate emitted green by ultraviolet irradiation. The optimum initial Tb/Ca atomic ratio of this phosphor was about 0.5. A mechanism for the action of the phosphor is proposed, in which Tb³⁺ ions existing in the layer of the CSH lead to loss of water molecules and OH groups.

1. Introduction

In recent years, white light emitting diodes (LEDs) have been used as an alternative to fluorescent lamps. The method of manufacture of white LEDs is determined by the mode of operation, which can be divided into three types as follows: (1) blue LED + yellow phosphor, (2) blue LED + green and red phosphors, and (3) near-ultraviolet LED + red, green and blue phosphors. However, the emission intensities of the red- or green-emitting LED is weaker than that of the blue-emitting [1, 2]. A white color is obtained by mixing blue-emitting phosphor with a yellow-emitting phosphor, and the emission intensity of a blue-emitting phosphor was stronger than other color (red or green) phosphors [3, 4]. To obtain true white emission, the emission intensity of green-emitting and red-emitting phosphors must have a strong. We reported on synthesis and fluorescence properties of novel red-emitting amorphous calcium silicate (not glassy system compounds, powder state) phosphor [5]. Eu³⁺-activated amorphous calcium silicate phosphor was produced by heating Eu³⁺-activated CSH

phosphor at 870°C. The emission intensity of Eu³⁺-activated amorphous calcium silicate phosphor was about half for that of the commercial BAM (BaMgAl₁₀O₁₇:Eu²⁺) phosphor, and the phosphor was expected for the application in white LED. Furthermore, the authors reported on synthesis and fluorescence properties of the phosphors which was reduced Eu³⁺-activated amorphous calcium silicate phosphor and was used alkaline-earth metal ions substitution for Ca²⁺ ion [6, 7]. We tried the synthesis of amorphous calcium silicate phosphor which was green emitting by using Tb³⁺ ion in substitution for Eu³⁺ ion in this paper.

In these applications, the Eu³⁺ ion is mainly used as the phosphor activator for red emitting, and the Tb³⁺ ion is often known as activator of the green-emitting phosphor. Eu³⁺ ion emits in the red for irradiation in the near ultraviolet at 395 nm. However, Tb³⁺ ion does not emit in the green for irradiation in the near ultraviolet at 395 nm. The ultraviolet of near 270 nm was emitted Tb³⁺ ion as a luminescence center. In this way, the improvement of the phosphor was necessary, since Tb³⁺-activated phosphor was not emitted in the ultraviolet irradiation at 378 nm. As example, the

wavelength for exciting Ce^{3+} and Tb^{3+} -codoped phosphor was about 320 nm [8, 9].

The level of doping at which concentration quenching begins differs depending on the types of host crystal. For example, the doping limit before concentration quenching occurs is about 5 mol% in CaCO_3 and 0.01 mol% in CaS [10, 11]. However, the quantity of activator in the phosphor for white LED should be abounding.

However, we found the Tb^{3+} -activated phosphor which was green-emitting by the ultraviolet irradiation at 378 nm. This study describes synthetic conditions of green emitting Tb^{3+} -activated amorphous calcium silicate phosphor by ultraviolet irradiation for white LEDs.

2. Experimental

The raw materials used for synthesis were 95% CaCl_2 , Na_2SiO_3 , and 99.0% $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$. All reagents were obtained from Kanto Kagaku Co., Ltd. (Japan).

The initial Tb^{3+} -activated calcium silicate hydrate (CSH) phosphor was synthesized by adding 0.1 mol/dm³ Na_2SiO_3 solution to a solution of 0.1 mol/dm³ CaCl_2 and a given concentration of TbCl_3 , with the initial Tb/Ca and initial $(\text{Ca} + \text{Tb})/\text{Si}$ atomic ratio set from 0.1–0.7 and 1, respectively. The mixture was heated at 50°C for 0.5 hours. The as-prepared Tb^{3+} -activated CSH phosphor was then heated at 600–900°C under atmospheric pressure to increase the emission intensity. This heating resulted in the production of Tb^{3+} -activated amorphous calcium silicate phosphor.

The final sample was characterized by X-ray diffraction and inductively coupled plasma (ICP) spectrometry. The fluorescence properties of the sample were measured using a Hitachi F-4500 spectrophotometer. All measurements were carried out at room temperature. In this paper, 100% emission intensity is relative to the 422 nm emission intensity of calcium tungstate, which was irradiated in the ultraviolet at 254 nm. The calcium tungstate reference was prepared by Nakaraitesuku Co., Ltd. (Japan). The emission intensity of calcium tungstate as a standard phosphor was measured at the same time as measurement of emission intensity of the sample phosphor. The internal quantum efficiency was measured by a multichannel photodetector (MCPD-7000, Otsuka electronics Co., Ltd.) with an integrating sphere. To determine Tb/Ca atomic ratio in the phosphor, the Tb^{3+} -activated calcium silicate hydrate was dissolved in hydrochloric acid, and analyzed using ICP spectrometry.

3. Results and Discussion

Figure 1 shows the structure of calcium silicate hydrate (CSH). The structure of CSH resembles that of the tobermorite. CSH is intercalation compound. In the layer, Ca^{2+} ions and interlayer water exist. The Ca^{2+} ions are exchanged to Tb^{3+} ions. In TG-DTA curves, when CSH heated at near 950°C, β -wollastonite was formed by the transfer of CSH. CSH becomes an amorphous condition on the eve of transfer. It is because SiO_3 chain is broken. The formation of

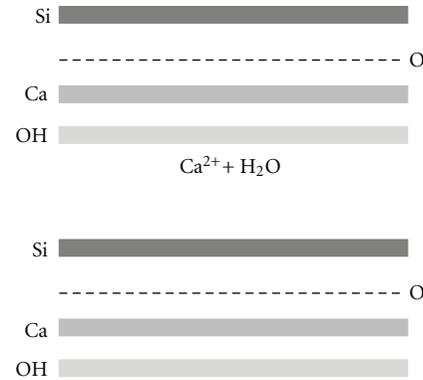


FIGURE 1: Structure of CSH.

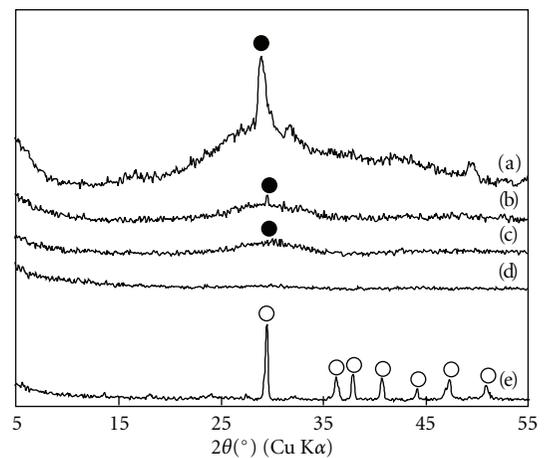


FIGURE 2: X-ray diffraction patterns of products prepared by heating Tb^{3+} -activated calcium silicate hydrate (CSH) phosphor. Tb/Ca atomic ratio, (a) 0, (b)–(e) 0.5. Heating temperature (°C), (a), (b) room temperature, (c) 800, (d) 900, and (e) 1000. ●: CSH, ○: β -Wollastonite.

wollastonite is due to the rearrangement of the broken SiO_3 chain.

X-ray diffraction patterns of products prepared by heating the Tb^{3+} -activated CSH phosphor are shown in Figure 2 along with the CSH before the Tb^{3+} -activating. For the compound without the Tb^{3+} ion, a diffraction peak of low crystallinity is observed corresponding to the CSH structure (Figure 2(a)). However, for the CSH phosphor synthesized at an initial Tb/Ca atomic ratio of 0.50, this diffraction peak was not observed (Figure 2(b)); that is, the diffraction peak of terbium silicate was not observed, suggesting that the Tb^{3+} ions were included in the layer of CSH structure. After heating the Tb^{3+} -activated CSH at 800°C, the product showed a low crystallinity due to removing interlayer water (Figure 2(c)). The product obtained by heating at 900°C was in an amorphous state (Figure 2(d)). The X-ray diffraction pattern showed that the phosphor was in an amorphous condition as a result of rearrangement of the silicate ion, before forming β -wollastonite upon further heating. However, this phosphor was not in a glassy state. In addition,

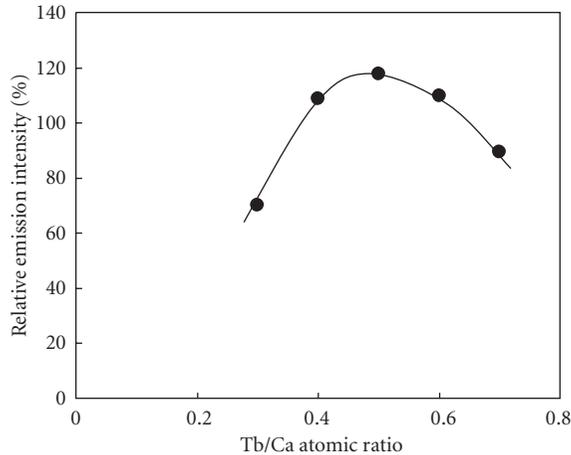


FIGURE 3: Effect of initial Tb/Ca atomic ratio on the emission intensity of the phosphor heated at 700°C.

X-ray diffraction peaks indicating crystalline β -wollastonite were observed when the phosphor was heated further at 1000°C (Figure 2(e)).

As expected, the initial Tb^{3+} -activated CSH phosphor barely emitted in the green under near-ultraviolet irradiation. However, it was shown that the emission intensity of the CSH phosphors increased with increasing temperature.

We next examined the effect of the initial Tb/Ca atomic ratio on the emission intensity of the phosphor heated at 700°C, as shown in Figure 3. Generally, the concentration quenching for the calcium carbonate phosphor irradiated in the ultraviolet region below 320 nm occurred at a Tb/Ca-atomic ratio of 0.05 (5 mol%) [8]. The amount of activated Tb^{3+} ion in another phosphor was approximately 25 mol% at the maximum [12] although concentration quenching was apparent above 20 mol%. The emission intensity of the phosphor increased with an increase of Tb/Ca atomic ratio. The phosphor was found to have maximum emission intensity at an initial Tb/Ca atomic ratio of 0.5. In the present paper, Tb^{3+} could be activated in the phosphor up to 33 mol%. However, the emission intensity of the phosphors decreased at value of above 0.5 of Tb/Ca atomic ratio. This was caused by the concentration quenching; that is, it was guessed that Tb^{3+} ions substituted with Ca^{2+} ions except the layer of CSH structure. Generally, the Ca/Si ratios of CSH changed into 0.6–1.5 [13, 14]. Quantity of Ca^{2+} ions in layers was influenced by the Ca/Si ratio of CSH. There were Ca^{2+} ions abundantly between the layers of the CSH. The ion radius of Tb^{3+} is 0.092 nm. This value was similar to that of Ca^{2+} . In the previous paper, it reported that Eu^{3+} ions entered precedence in layer of CSH [5]. In the present paper, there was Tb^{3+} ions abundantly between the layers of the CSH. The concentration quenching happened to hinder energy transfer by resonance of two activators by lattice vibration. The lattice vibration was difficult to travel in Tb^{3+} ions which were existed in the layer of CSH structure.

Actually, the chemical composition of Tb^{3+} -activated CSH phosphor was measured using ICP. In the case of initial Tb/Ca atomic ratio of 0.3, the chemical composi-

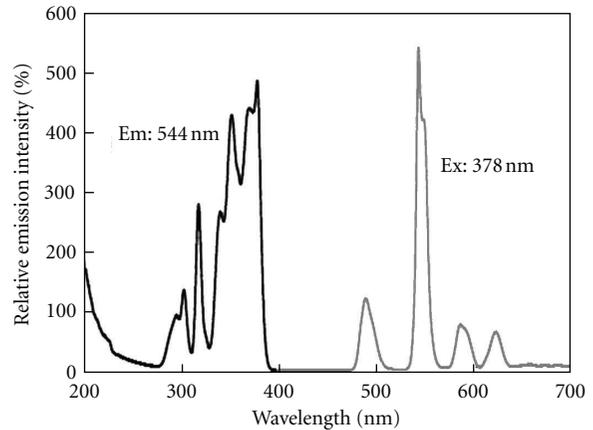


FIGURE 4: Spectra of excitation and emission of heated Tb^{3+} -activated calcium silicate phosphor at room temperature.

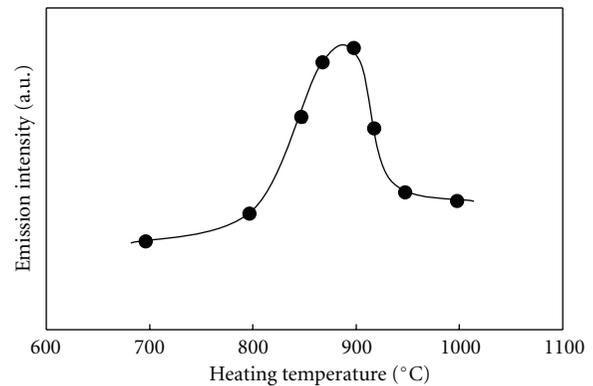


FIGURE 5: Effect of heating temperature on emission intensity of Tb^{3+} -activated amorphous calcium silicate phosphor.

tion of the CSH phosphor was $CaO/Tb_2O_3/SiO_2/H_2O = 21.1/29.3/38.5/17.3$ mass%. The chemical composition of the phosphor obtained for an initial Tb/Ca atomic ratio of 0.5 was $Na_2O/CaO/Tb_2O_3/SiO_2/H_2O = 0.4/12.5/31.8/28.0/17.3$ mass%. The content of Na^+ increased with the increase in the Tb/Ca atomic ratio. The above results indicated the compositions for the phosphor of $Ca_{0.59}Tb_{0.25}SiO_{2.97}$ and $Na_{0.07}Ca_{0.37}Tb_{0.27}SiO_{2.76}$, respectively.

The spectra of excitation and emission of heated Tb^{3+} -activated calcium silicate phosphor at room temperature are shown in Figure 4. In the emission spectrum under excitation of 378 nm, the emission spectrum exhibited four major emission bands at 488, 544, 593, and 616 nm, which were attributed to the $^5D_4 \rightarrow ^7F_6, \rightarrow ^7F_5, \rightarrow ^7F_4,$ and $\rightarrow ^7F_3$ typical transitions of Tb^{3+} ions, respectively [15]. These peaks commonly observed with phosphors activated Tb^{3+} . Generally, the excitation photoluminescence shows the peak at 272 nm responsible for $Tb^{3+} 4f^8 \rightarrow 4f^75d$ transition [16]. However, the excitation spectrum for 544 nm exhibited four major excitation bands at 318, 351, 378, and 484 nm. In the excitation band below 300 nm, light emission of the

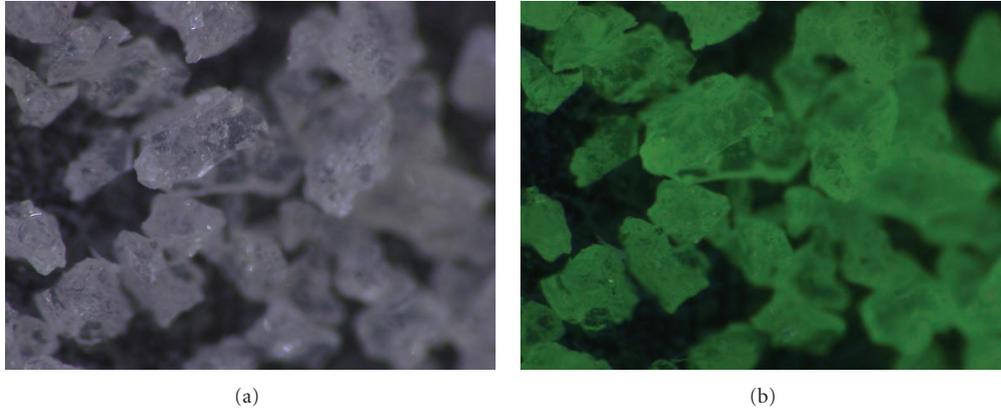


FIGURE 6: Appearance of green-emitting Tb^{3+} -activated amorphous calcium silicate phosphor by black-light irradiation. (a) before black-light irradiation, (b) during black-light irradiation.

green was not observed. The excitation bands of 340–378 nm corresponded to the $4f \rightarrow 4f$ absorptivity [15, 17].

The effect of heating temperature, on emission intensity of Tb^{3+} -activated amorphous calcium silicate phosphor is shown in Figure 5. As clear from X-ray diffraction patterns at 700, 800°C, the emission intensity is lowered by presence of water molecule or OH group in layer of CSH structure [5]. However, the emission intensity abruptly increased water molecule or OH group in layer dried up at around 800°C [18]. The amorphous state was obtained by heating Tb^{3+} calcium silicate hydrate at 900°C. The emission intensity of the Tb^{3+} -activated amorphous calcium silicate attained a maximum value of 540% for initial Tb/Ca atomic ratio of 0.50. While emission intensity decreased with an increase of heating temperature the diffraction peaks of β -wollastonite by heating Tb^{3+} -activated calcium silicate hydrate at 1000°C were observed (Figure 1(e)). The lowering of the emission intensity was because the Tb^{3+} ion was taken in the structure of β -wollastonite.

Figure 6 shows the appearance of green emitting Tb^{3+} -activated amorphous calcium silicate phosphor by black light irradiation. The phosphor which was heated at 900°C was observed by a microscope. As a result, an amorphous particle was transparent. The phosphor, which was irradiated with black light, emitted light in green. The emission of light was uniform in an amorphous particle.

The internal quantum efficiency commercial phosphor such as red-emitting CASN ($CaAlSiN_3:Eu^{2+}$), blue-emitting BAM ($BaMgAl_{10}O_{17}:Eu^{2+}$), and green-emitting BSON ($Ba_3Si_6O_{12}N_2:Eu^{2+}$) was 80%, 83%, and 84%, respectively. The internal quantum efficiency of Tb^{3+} -activated amorphous calcium silicate phosphor in this paper was 37% of the half of commercial phosphors. The half width of CASN, BAM, BSON, and phosphor in the present paper was 89, 63, 56, and 12 nm. That of amorphous calcium silicate phosphor was very narrow. The internal quantum efficiency depended on peak area of emission spectrum and emission intensity. When emission peak was wide, the emission color was not bright. When emission peak was narrow, the emission color was bright.

4. Conclusions

We reported on synthesis and fluorescence properties of Eu^{3+} -activated amorphous calcium silicate phosphor. In this paper, it used Tb^{3+} ion instead of Eu^{3+} ion. Tb^{3+} -activated calcium silicate hydrate (CSH) phosphor was synthesized by liquid-liquid reaction. The amorphous state phosphor was obtained by heating Tb^{3+} -activated CSH at 900°C. Then, the emission intensity of Tb^{3+} -activated amorphous calcium silicate phosphor was a maximum at initial Tb/Ca atomic ratio of 0.50. The excitation wavelength of Tb^{3+} -activated amorphous calcium silicate phosphor was 378 nm. The study on the phosphor with excitation wavelength of 378 nm was very few. Since there were Tb^{3+} ions in the layer of CSH structure, the excitation wavelength of Tb^{3+} -activated phosphor was changed to ultraviolet at 378 nm. The emission wavelength was 544 nm, and the emission color was green.

References

- [1] S. Nakamura, T. Mukai, and M. Senoh, "Candela-class high-brightness InGaN/AlGaIn double-heterostructure blue-light-emitting diodes," *Applied Physics Letters*, vol. 64, no. 13, pp. 1687–1689, 1994.
- [2] S. Nakamura, "Present status and future prospects of GaN-based light emitting devices," *The Japan Society of Applied Physics*, vol. 65, no. 7, pp. 676–685, 1996.
- [3] Y. Hu, W. Zhuang, H. Ye, D. Wang, S. Zhang, and X. Huang, "A novel red phosphor for white light emitting diodes," *Journal of Alloys and Compounds*, vol. 390, no. 1-2, pp. 226–229, 2005.
- [4] R. Mueller-Mach, G. O. Mueller, M. R. Krames, and T. Trotter, "High-power phosphor-converted light-emitting diodes based on III-nitrides," *IEEE Journal on Selected Topics in Quantum Electronics*, vol. 8, no. 2, pp. 339–345, 2002.
- [5] Y. Kojima, S. Kamei, and N. Nishimiya, "Preparation and fluorescence property of red-emitting Eu^{3+} -activated amorphous calcium silicate phosphor," *Materials Research Bulletin*, vol. 45, no. 2, pp. 121–123, 2010.
- [6] S. Kamei, Y. Kojima, and N. Nishimiya, "Preparation and fluorescence properties of novel alkaline earth silicate phosphors by reduction treatment of Eu^{3+} to Eu^{2+} ," *Journal of the Ceramic Society of Japan*, vol. 118, no. 1380, pp. 758–761, 2010.

- [7] S. Kamei, Y. Kojima, and N. Nishimiya, "Preparation and fluorescence properties of novel red-emitting Eu^{3+} -activated amorphous alkaline earth silicate phosphors," *Journal of Luminescence*, vol. 130, no. 11, pp. 2247–2250, 2010.
- [8] Y. Kojima, K. Machi, T. Yasue, and Y. Arai, "Synthesis of Ce^{3+} and Mn^{2+} codoped calcium carbonate phosphor emitting by black light irradiation and its fluorescence property," *Journal of the Ceramic Society of Japan*, vol. 108, no. 9, pp. 836–841, 2000.
- [9] Y. Kojima, S. Doi, and T. Yasue, "Synthesis of cerium (III) and terbium(III) codoped vaterite phosphor emitting by black light irradiation and its fluorescence property," *Journal of the Ceramic Society of Japan*, vol. 110, pp. 755–760, 2002.
- [10] Y. Kojima, K. Aoyagi, and T. Yasue, "Effect of lithium ion addition on afterglow time of green-emitting Ce^{3+} and Pr^{3+} codoped CaS phosphor by black light irradiation," *Journal of Luminescence*, vol. 115, no. 1-2, pp. 13–18, 2005.
- [11] Y. Kojima, K. Aoyagi, and T. Yasue, "Afterglow mechanism and thermoluminescence of red-emitting $\text{CaS}:\text{Eu}^{2+}, \text{Pr}^{3+}$ phosphor with incorporated Li^+ ion upon visible light irradiation," *Journal of Luminescence*, vol. 126, no. 2, pp. 319–322, 2007.
- [12] Z. Li, J. Zeng, G. Zhang, and Y. Li, "A new promising phosphor, $\text{Na}_3\text{La}_2(\text{BO}_3)_3:\text{Ln}$ ($\text{Ln}=\text{Eu}, \text{Tb}$)," *Journal of Solid State Chemistry*, vol. 178, no. 12, pp. 3624–3630, 2005.
- [13] A. Nonat, "The structure and stoichiometry of C–S–H," *Cement and Concrete Research*, vol. 34, no. 9, pp. 1521–1528, 2004.
- [14] J. J. Chen, J. J. Thomas, H. F.W. Taylor, and H. M. Jennings, "Solubility and structure of calcium silicate hydrate," *Cement and Concrete Research*, vol. 34, no. 9, pp. 1499–1519, 2004.
- [15] S. Komarneni, R. Roy, and D. M. Roy, "Pseudomorphism in xonotlite and tobermorite with Co^{2+} and Ni^{2+} exchange for Ca^{2+} at 25°C," *Cement and Concrete Research*, vol. 16, no. 1, pp. 47–58, 1986.
- [16] N. J. Coleman, "Interactions of Cd(II) with waste-derived 11 Å tobermorites," *Separation and Purification Technology*, vol. 48, no. 1, pp. 62–70, 2006.
- [17] X. Zhao, X. Wang, B. Chen, Q. Meng, B. Yan, and W. Di, "Luminescent properties of Eu^{3+} doped $\alpha\text{-Gd}_2(\text{MoO}_4)_3$ phosphor for white light emitting diodes," *Optical Materials*, vol. 29, no. 12, pp. 1680–1684, 2007.
- [18] Y. Kojima, S. Kamei, T. Toyama, and N. Nishimiya, "Preparation of novel phosphor using intercalation of tobermorite," *Journal of Luminescence*, vol. 129, no. 7, pp. 751–754, 2009.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

