

Combustion synthesis of $X_{3.5}Mg_{0.5}Si_3O_8Cl_4$ ($X_{3.5} = Sr, Ba$): Eu^{2+} blue emitting phosphors

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ABSTRACT

Eu^{2+} luminescence in novel $Sr_{3.5}Mg_{0.5}Si_3O_8Cl_4$ and $Ba_{3.5}Mg_{0.5}Si_3O_8Cl_4$ phosphors is reported in this paper. These were synthesized by combustion method at $550^{\circ}C$ furnace temperature. The prepared phosphors shows PL emission spectra at 445 nm, due to $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ions by monitoring excitation at 358 nm for Sr and Ba host lattice. Phase purity was checked by using XRD-pattern. The prepared phosphors have potential applications for solid-state lighting purpose. Copyright © 2011 VBRI press.

Keywords: Phosphors; combustion synthesis; solid-state lighting; photoluminescence; XRD.



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Introduction

Investigation on suitable phosphor for light-emitting diode (LED) based solid-state lighting is continuously going on. White LEDs offer the advantages of high brightness, low power consumption and longer life time compared to conventional light bulbs and fluorescent lamps [1, 2]. The most common approach involves combining a blue GaInN LED chip (460nm) with a yellow-emitting phosphor, $Y_3Al_5O_{12}:Ce^{3+}$. This system has a low color rendering index because of its deficiency in the red region of the visible spectrum. Other approach to overcome this drawback is to add a red-emitting phosphor to compensate the deficiency [3–5]. Another approach is to develop a new white LED system consisting of ultraviolet (UV) LEDs (300–410nm) with red, blue, and green phosphors [6–8]. This system is suitable for white LEDs with an excellent color-rendering index and high color tolerance. To advance this technology, phosphors with desirable color emission and high efficiency under UV excitation must be developed. Optical transitions of divalent europium ($4f-5d$) have been investigated in many silicate and other phosphors [9–14]. Spectra of Eu^{2+} -doped compounds are due to electric dipole transitions with parity allowed so that they occur with high transition probabilities. The emission colors vary from ultraviolet to red depending on the host lattice [9, 15]. The luminescence of Eu^{2+} activated phosphors usually results from the ground $4f^7(8S_{7/2})$ level

to the $4f^65d$ excited configuration and therefore, has a broad character that depends strongly on the nature of the host lattice. The emission color of Eu^{2+} can vary in a broad range from ultraviolet to red. Since the $4f-5d$ transition is an allowed electrostatic dipole transition, the absorption and emission of Eu^{2+} are very efficient in many hosts, which makes the Eu^{2+} -doped phosphors good candidates for photonic sources [16]. Covalence, the size of the cation, and the crystal-field strength influence the emission color of Eu^{2+} . Oxide-based phosphors activated with Eu^{2+} are promising candidates for white-light-emitting diodes pumped by ultraviolet-light-emitting diode [17, 18]. The phosphors with better optical properties are still in development. Rare-earth-ions-doped silicate hosts have demonstrated good photoluminescence properties and chemical-physical stabilities. Eu^{2+} in such kinds of host may emit various colors demanded by white lighting. In the 20th century studies on halosilicates ($\text{Ca}_3\text{SiO}_4\text{Cl}_2$) were carried out by Winkler and Wieker [19]. Halide and silicate are the excellent matrices for Eu^{2+} activated phosphors. The halo silicate has several advantages, like low synthetic temperature, high chemical and physical stability. To the best of our knowledge, there have been no investigations regarding the synthesis and luminescence in blue emitting $\text{Sr}_{3.5}\text{Mg}_{0.5}\text{Si}_3\text{O}_8\text{Cl}_4:\text{Eu}^{2+}$ and $\text{Ba}_{3.5}\text{Mg}_{0.5}\text{Si}_3\text{O}_8\text{Cl}_4:\text{Eu}^{2+}$ phosphors by combustion method till now. Though they have prepared successfully and photoluminescence properties show that the phosphors have potential application for solid-state lighting purpose.

Experimental

Synthesis of the halosilicate phosphors were carried out by combustion method at 550°C furnace temperature. The starting materials for the preparation of $\text{Sr}_{3.5}\text{Mg}_{0.5}\text{Si}_3\text{O}_8\text{Cl}_4:\text{Eu}^{2+}$ and $\text{Ba}_{3.5}\text{Mg}_{0.5}\text{Si}_3\text{O}_8\text{Cl}_4:\text{Eu}^{2+}$ phosphors used were $\text{Sr}(\text{NO}_3)_2$ Merck (99.99% purity), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.99% purity), $\text{Ba}(\text{NO}_3)_2$, Merck (99.99% purity), SiO_2 (A.R.), $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck's 99.9%), $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck's 99.9%), urea ($\text{NH}_2\text{-CO-NH}_2$, Merck) and Eu_2O_3 (99.99%). All the ingredients were mixed according to stoichiometric ratio in agate mortar and a pasty solution was formed, the solution was then transferred to silica crucible and kept inside a muffle furnace which is maintained at a constant temperature 550°C . The flame with the foamy powder was formed. The powder was collected and analyzed by XRD and photoluminescence measurement. The X-ray diffraction (XRD) technique was used to identify the phase composition, structure. Their crystallinity were characterized by XRD pattern using a PAN-analytical diffractometer with $\text{Cu K}\alpha$ radiation (1.5405 \AA) operating voltage at 40 kV, 30mA and scan step time at 10.3377 s. The morphology of the phosphor was examined by scanning electron microscopy (SEM, JED-2300) equipped with an energy-dispersive spectrometry attached to the JEOL 2300.

Results and discussion

X-ray diffraction pattern

XRD-pattern for $\text{Sr}_{3.5}\text{Mg}_{0.5}\text{Si}_3\text{O}_8\text{Cl}_4$ phosphor is shown in

Fig. 1. It indicates well crystalline nature and was well matched with standard JCPDS file no.40-0074. **Fig. 2** shows XRD-pattern of $\text{Ba}_{3.5}\text{Mg}_{0.5}\text{Si}_3\text{O}_8\text{Cl}_4$ phosphors. There is no standard JCPDS data to match this compound; we reported this for the first time. The grain size of the prepared $\text{X}_{3.5}\text{Mg}_{0.5}\text{Si}_3\text{O}_8\text{Cl}_4$ ($\text{X} = \text{Sr}, \text{Ba}$) phosphors was calculated by using Debye Scherrer formula

$$0.9\lambda / \beta \cos\theta \quad (1)$$

It comes out to be approximately 85 nm and 72 nm respectively for Sr and Ba hosts from equation (1). The cation Sr^{2+} is coordinated by 9 oxygen ions [20] in $\text{Sr}_{3.5}\text{Mg}_{0.5}\text{Si}_3\text{O}_8\text{Cl}_4$, whereas Ba^{2+} is relatively larger with 12 oxygen ions coordinated [21, 22] in $\text{Ba}_{3.5}\text{Mg}_{0.5}\text{Si}_3\text{O}_8\text{Cl}_4$. The structure data also indicate that Sr^{2+} site has lower symmetry (C_1) than Ba^{2+} site (D_{6h}). The 9 Sr-O bond lengths for Sr^{2+} site are all different and vary from 2.45 to 3.22 \AA while for the Ba^{2+} site there are only two types of bond lengths, Ba-O 1×6 , 3.3251 \AA and Ba-O 2×6 , 3.8781 \AA . It is well known that crystal field strength can be represented by the parameter Dq , which is inversely proportional to the 5th power of the bond length R [23].

$$Dq \propto 1/R^5 \quad (2)$$

From the above formula (2), shorter bond length denotes stronger crystal field strength. The average bond length of Sr-O in $\text{Sr}_{3.5}\text{Mg}_{0.5}\text{Si}_3\text{O}_8\text{Cl}_4$ is 2.80 \AA and that of Ba-O in $\text{Ba}_{3.5}\text{Mg}_{0.5}\text{Si}_3\text{O}_8\text{Cl}_4$ is 3.60 \AA , thus it is believed that crystal field strength at Sr^{2+} site is stronger than that at Ba^{2+} site.

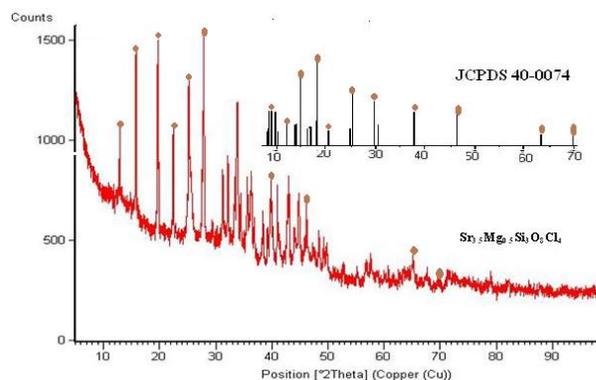


Fig. 1. XRD-pattern of $\text{Sr}_{3.5}\text{Mg}_{0.5}\text{Si}_3\text{O}_8\text{Cl}_4$ phosphor.

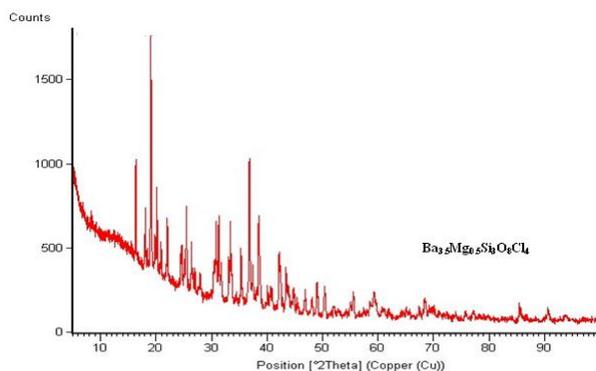


Fig. 2. XRD-pattern of $\text{Ba}_{3.5}\text{Mg}_{0.5}\text{Si}_3\text{O}_8\text{Cl}_4$ phosphor.

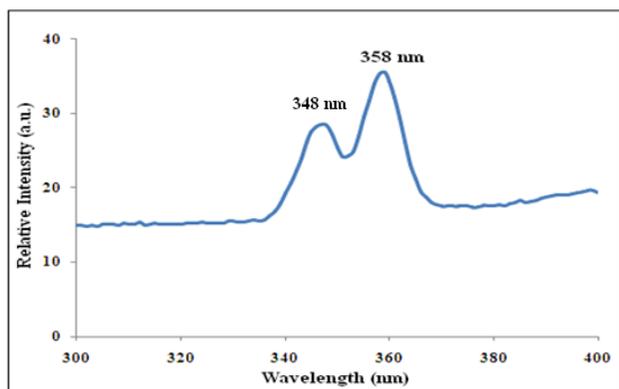


Fig. 3. Excitation spectra of $X_{3.5}Mg_{0.5}Si_3O_8Cl_4$ ($X = Sr, Ba$) phosphors $\lambda_{em} = 445$ nm.

Eu^{2+} luminescence in $X_{3.5}Mg_{0.5}Si_3O_8Cl_4$ ($X = Sr, Ba$) phosphors

The photoluminescence properties of the phosphor (excitation and emission) were measured using a Shimadzu RF5301PC Spectrofluorophotometer at room temperature keeping slit-width at 1.5 nm for both emission and excitation. The same amount of phosphor materials were used in each case. PL emission spectra of both $Sr_{3.5}Mg_{0.5}Si_3O_8Cl_4$ and $Ba_{3.5}Mg_{0.5}Si_3O_8Cl_4$ phosphors are illustrated in Fig. 4 and Fig. 5 which shows the emission band peaking at 445 nm corresponding to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ions, keeping excitation at 358 nm (Fig. 3). There is a possibility of Eu^{2+} ions getting incorporated into the crystal structures of $Sr_{3.5}Mg_{0.5}Si_3O_8Cl_4$ and $Ba_{3.5}Mg_{0.5}Si_3O_8Cl_4$, to substitute all cationic site Sr^{2+} or Ba^{2+} , and Si^{4+} . However, considering the irrespective ionic radii and allowed oxygen-coordination number, it is difficult for Eu^{2+} ions to substitute Si^{4+} ions. Therefore, it is clear and reasonable that Eu^{2+} ions substitute for only Sr^{2+} or Ba^{2+} ions in $Sr_{3.5}Mg_{0.5}Si_3O_8Cl_4$ and $Ba_{3.5}Mg_{0.5}Si_3O_8Cl_4$ host lattice. The different size of cations Sr^{2+}/Ba^{2+} causes different crystal symmetry and there are several polymorphs of feldspars for each alkaline earth halosilicates. Although Sr^{2+} is coordinated by approximately four O atoms and four Cl atoms in the $Sr_{3.5}Mg_{0.5}Si_3O_8Cl_4$ host and the sites of Sr^{2+} can be substituted by Eu^{2+} whichever factors like radius or charge are considered. So the value of coordination number is eight, and the radius of Sr^{2+} under this coordination environment is 0.126 nm. $Sr_{3.5}Mg_{0.5}Si_3O_8Cl_4:Eu^{2+}$ exhibits (Fig. 5) a emission-peak at wavelength of 445 nm, corresponding to $22,026\text{ cm}^{-1}$ in energy. Based on the above-mentioned data, the value of energy is calculated as $21,264\text{ cm}^{-1}$ and the difference can be interpreted as the vibration of crystal field and covalence strength. Where as possible sites for Eu^{2+} incorporation into $Ba_{3.5}Mg_{0.5}Si_3O_8Cl_4$ lattice were the Ba^{2+} sites or Si^{4+} sites. Si (0.026 nm) was small, so Eu^{2+} (0.112 nm) ions could hardly incorporate into a tetrahedral SiO_4 . Thus depending on the ionic radii as mentioned above Eu^{2+} could only occupy Ba^{2+} sites in the $Ba_{3.5}Mg_{0.5}Si_3O_8Cl_4$ lattice. In the excitation spectra there are two different excitation peaks were observed at wavelengths of 348 and 358 nm, the emission spectra are located at 445 nm for both Sr^{2+} and

Ba^{2+} host, consistent with this fact that there is only one kind of Sr and Ba site in the host material $Sr_{3.5}Mg_{0.5}Si_3O_8Cl_4$ and $Ba_{3.5}Mg_{0.5}Si_3O_8Cl_4$. The main excitation peaks which will be peaking at 358 nm have higher PL intensity than 348 nm; we monitor the emission wavelength at 445 nm, which indicate the phosphor is very suitable for a color converter using UV lights as the primary light source. It can be used as a blue phosphor excited by UV-LED chip and would have applications in the solid-state lighting field.

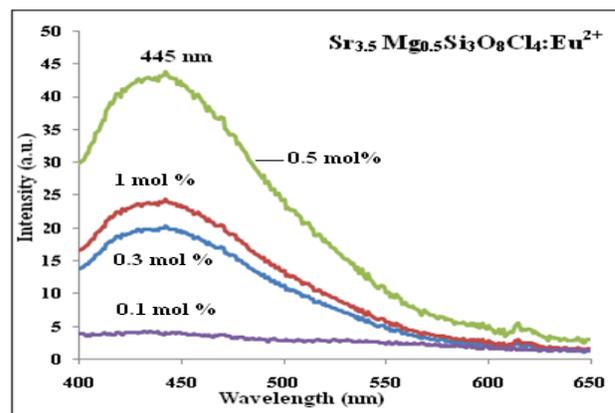


Fig. 4. Emission spectra of $Sr_{3.5}Mg_{0.5}Si_3O_8Cl_4:Eu^{2+}$ phosphor $\lambda_{ex} = 358$ nm.

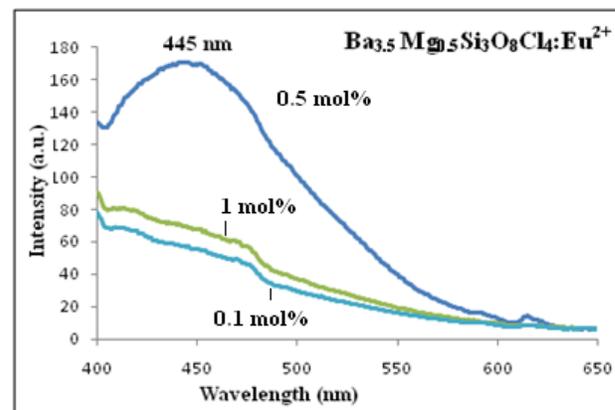


Fig. 5. Emission spectra of $Ba_{3.5}Mg_{0.5}Si_3O_8Cl_4:Eu^{2+}$ phosphor $\lambda_{ex} = 358$ nm.

Conclusion

The present work reported Eu^{2+} luminescence in $X_{3.5}Mg_{0.5}Si_3O_8Cl_4$ ($X = Sr, Ba$) phosphors were synthesized by combustion method. Phosphors of $X_{3.5}Mg_{0.5}Si_3O_8Cl_4:Eu^{2+}$ where $X_{3.5} = Sr, Ba$, showed excitation peaking at 358 nm, which is excellent for near UV-LED. The emission peak was also broad centered at 445 nm for Sr and Ba host containing phosphors. In particular, the maximum emission intensity for Eu^{2+} 0.01-1 mol% occurs at 0.5 mol%. The XRD pattern indicates that $X_{3.5}Mg_{0.5}Si_3O_8Cl_4$ ($X = Sr, Ba$) phosphors were of good crystalline nature and observed grain size is 85 nm (Sr host) to 72 nm (Ba host) range for white light emitting phosphor-LED devices. From the luminescence investigation it is to be concluded that the

prepared $X_{3.5}Mg_{0.5}Si_3O_8Cl_4$ ($X = Sr, Ba$) phosphors may be useful to design near UV excited w-LED.

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Reference

- Zukauskas, A. : Shur, M.S. : Gaska, R. *MRS Bull.* **2001**,26 ,764.
DOI: [10.1557/mrs2001.225](https://doi.org/10.1557/mrs2001.225).
- Narukawa, Y.: Narita, J.: Sakaomto, T. : Yamada, T. : Narimatsu, H.: Sano, M. : Mukai, T. *Phys. Status Solidi (a)*.**2007**,204,2087.
DOI: [10.1002/pssa.200778428](https://doi.org/10.1002/pssa.200778428).
- Piao, X. : Machida, K.I. : Horikawa, T.: Hanzawa, H. : Shimomura, Y. : Kijima, N. *Chem. Mater.* **2007**,19,4592.
DOI: [10.1021/cm070623c](https://doi.org/10.1021/cm070623c).
- Uheda, K.: Hirosaki, N.: Yamamoto, Y. : Naito, A. : Nakajima, T.: Yamamoto, H. *Electrochem. Solid State Lett.* **2006**,9,22.
DOI: [org/10.1149/1.2173192](https://doi.org/10.1149/1.2173192).
- Hirayama, M. : Sonoyama, N. : Yamada, A. : Kanno, R. *J. Lumin.* **2008**,128,1819.
DOI: [10.1016/j.jlumin.2008.05.005](https://doi.org/10.1016/j.jlumin.2008.05.005).
- Sheu, J.K.: Chang, S.J.: Kuo, C.H.: Su, Y.K.: Wu, L.W.: Lin, Y.C.: Lai, W.C.: Tsai, G.C. Chi, J.M. : Wu, R.K. *IEEE Photonics Technol. Lett.* **2003** ,15,18.
DOI: [10.1109/LPT.2002.805852](https://doi.org/10.1109/LPT.2002.805852).
- Jung, K.Y.: Lee, H.W.: Jung, H.K. *Chem. Mater.***2006**,18,2249.
DOI: [10.1021/cm060003w](https://doi.org/10.1021/cm060003w).
- Okamoto, S. : Yamamoto, H. *Electrochem. Solid State Lett.* **2007**,10,139.
DOI: [org/10.1149/1.2767003](https://doi.org/10.1149/1.2767003).
- Doren bos, P. *J. lumin.***2003**,104,239.
DOI: [10.1016/S0022-2313\(03\)00078-4](https://doi.org/10.1016/S0022-2313(03)00078-4)
- Thejo Kalyani, N.: Dhoble , S.J.: Poda, R.B. *Adv. Mat. Lett.* **2011**,2,65.
DOI: [10.5185/amlett.2010.10169](https://doi.org/10.5185/amlett.2010.10169).
- Deshmukh, A. D. : Dhoble, S. J.: Dhoble, N.S.: *Adv. Mat. Lett.* **2011**,2,38.
DOI: [10.5185/amlett.2010.10171](https://doi.org/10.5185/amlett.2010.10171).
- Shinde, K. N.: Dhoble, S. J. *Adv. Mat. Lett.***2010**,1,254.
DOI: [10.5185/amlett.2010.916](https://doi.org/10.5185/amlett.2010.916).
- Dhoble, S. J.: Pawade, V. B.: Shinde, K.N. *E.P.J. Applied Phys.***2010**,52,11104.
DOI: [10.1051/epjap/2010122](https://doi.org/10.1051/epjap/2010122).
- Poort, S.H.M.: Janssen, W. : Blasse, G. *J. Alloys Compounds.***1997**,260,93.
DOI: [10.1016/S0925-8388\(97\)00140-0](https://doi.org/10.1016/S0925-8388(97)00140-0).
- Kim, J.S.: Jeon, P.E.: Choi, J.C.: Park, H.L.:*Solid State Commun.* **2005**,133,187.
DOI: [10.1016/j.ssc.2004.10.017](https://doi.org/10.1016/j.ssc.2004.10.017).
- Shinoya, M.: Yen, W. M. *Phosphor Handbook*, p. 192, CRC Press, Washington, D.C. **1999**.
URL: pubs.acs.org/doi/abs/10.1021/jp109988a.
- Pawade,V.B.:Dhoble,S.J.,*OpticsCommunications.***2011**,284,4185
DOI: [10.1016/j.optcom.2011.05.015](https://doi.org/10.1016/j.optcom.2011.05.015).
- Kim, J.S. : Jeon, P.E. : Park, Y.H. : Choi, J.C. : Park, H.L. *Appl. Phys. Lett.***2004** ,85,3696.
DOI: [10.1063/1.1808501](https://doi.org/10.1063/1.1808501).
- Winkler, A.: Wieker, W. *Z. Chem.* **1982**,22,52.
DOI: [10.1002/zaac.19824900110](https://doi.org/10.1002/zaac.19824900110).
- Takeuchi, Y. *Mineral. J.***1958**,2,311.
DOI: [10.1039/JR9640002296](https://doi.org/10.1039/JR9640002296).
- Chiari, G.: Calleri, M. : Bruno, E. : Ribbe, P.H. *Am. Mineral.***1975**,60,111.
DOI: [abs/10.1021/ic7004166](https://doi.org/abs/10.1021/ic7004166).
- Takeuchi, Y. *J. Am. Ceram. Soc.***1951**,34,283.
DOI: [10.1111/j.1151-2916.1995.tb08037](https://doi.org/10.1111/j.1151-2916.1995.tb08037).
- Henderson,B.:Imbush, G.G. *Optical Spectroscopy of Inorganic Solids*, Clarendon, Oxford, **1989**.
DOI: [aip.org/link/APPLAB/84/2931/1](https://doi.org/aip.org/link/APPLAB/84/2931/1).

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