Photoluminescence Properties of Impurities Doped Silicate-Based Phosphors: A Review

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Abstract

This review work provides a systematic study of the silicate-based phosphors, which provides the better understating about the synthesis process of various silicate-based phosphors. In this paper we review numerous techniques for synthesizing the rare-earth-doped phosphor materials. It also focused on the brief study of photoluminescence properties of various silicate-based phosphors and discuss their possible application for the generation of WLEDs.

Keywords: WLEDs, Photoluminescence, Thermoluminescence, Luminescence, Phosphor, Excitation.

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Introduction

PC-WLEDs (phosphor-converted white light-emitting diodes) are a next-generation solid-state lighting technology that could replace traditional lighting sources such as incandescent lamps, fluorescent lamps, halogen lamps, and backlights for liquid crystal displays. High luminous efficiency, low power consumption, durability, environmental friendliness, and extended operational life are just few of the wonderful benefits that phosphor-converted light emitting diodes (pc-LEDs) offer over other conventional forms of illumination. Fluorescence is a process that converts blue light to white light by using a blue LED with a phosphor coating. Various methods are available in order to fabricate white light emitting diodes. Some of these methods are by combining red, blue, and green LEDs. The intensity of the individual red, blue, and green chips is adjusted to produce white light. PC-LEDs use phosphors that are coated on the LED chip or the walls are encapsulant and may be stimulated by the UV or blue light generated by the chip. The fundamental need for a phosphor to be used in a pc-LED is that it exhibits substantial absorption in the UV or near-UV region and effective emission in the visible light range. It is also critical that the transitions responsible for emission and excitation are not prohibited. The methods used in the synthesis of phosphors and their fabrication in a pc-LED are summarized in this review work. There is also a brief mention of the various properties of phosphors used in pc-LEDs. [1,2]

Silicate materials can be used in a variety of applications. The manufacture of certain silicate phosphors by combustion is discussed. The reaction of urea with ammonium nitrate is exothermic, and heat is transferred to the reactants as a result. The combustion synthesis, it is believed, is a simple and quick way of creating silicate minerals. Excellent luminescence responsiveness and a high colour rendering index Silicate phosphors are suited for photonic applications, opening up new pathways for solid-state lighting, fluorescent lamps, cathode ray tubes, scintillators, and so on, and They can also be crucial components for phosphor-converted LED. The silicate minerals are the most important mineral class because they are the most abundant rock-forming minerals. This group is based on the silica (SiO_4) tetrahedron structure, in which a silicon atom is covalently bonded to four oxygen atoms at the corners of a triangular pyramid shape. When pure, silica minerals are colorless and transparent, with a vitreous luster. [3,4]

They are both diamagnetic and nonconductors of electricity. All are hard and strong, and when subjected to stress, they fail by brittle fracture. Silica is used in the production of concrete materials such as glasses. The most common application for these silicates is in the production of silica refractory bricks. They're very high-quality bricks. Silicate, as a host of phosphor materials, offers excellent thermal, chemical, and mechanical stability, as well as structural variability. Lately, silicate compounds have been widely explored as host lattices for phosphors, which display distinctive, intriguing light features when doped with rare earth ions. This in turn expressed that the silicate-based phosphors act as an excellent material to be used as a host structure for developing an efficient phosphor.[5,6,7]

The overall discussion and advantage of rare earth doped phosphors drew considerable attention to study of their photoluminescence properties. This review work provides systematic study of the silicate-based phosphors, which provides the better understating about the synthesis process of various silicate-based phosphors, their structural characterization as well as to optical characterization, to find their possibility to applicable as pc-LED.

Materials and Methods

There are numerous techniques for synthesizing the rare-earth-doped phosphor materials.

In this investigation, three separate approaches (solution combustion, sol-gel, and solid-state reaction procedures) were employed to synthesize Ho^{3+}/Yb^{3+} -co-doped YVO4 phosphor. The samples are created using combustion and sol-gel techniques. Portions of these samples are heated to 973 and 1473 K. The solid-state reaction technique is then used to create Ho^{3+}/Yb^{3+}-co-doped YVO_4 phosphor at 1473

K. All of the samples' optical and structural qualities are compared. It is found that phosphor samples synthesized using the sol-gel approach exhibit superior optical behavior than phosphor samples synthesized using combustion or solid-state reaction techniques.[8]

To the best of our knowledge, comparative investigations of structural and optical characteristics in phosphors produced using diverse processes are rarely documented. Some of the phosphors synthesized via different synthesis routes are summarized in table I.

Table I Silicate-based phosphors synthesized via different routes

Phosphors	Methods	Doping	Author name
$Sr_3MgSi_2O_8$	solid-state technique	Ce^{3+}, Dy^{3+}	Hong. Yu et al.
{Ca2}[Sc,Ga](Al,Ga, $Si_2)O_{12}$	Hydrothermal crystallization method	Ce^{3+}	N. Khaidukov et al.
$Ca_2Al_2SiO_7$	Solid –state reaction	Sm^{3+}	Minhong Li, et.al
$Ca_2Al_2SiO_7$	Solid-state reaction	Bi^{3+}, Eu^{3+}, Tb^{3+}	P. Yang et al.
$Sr_2ZnSi_2O_7$	Sol-gel method.	Tb^{3+}	Vijay singh
$Ba_2MgSi_2O_7$	Solid- state reaction technique	Dy^{3+}	Sanjay Kumar Sao
$Sr_2Al_2SiO_7$	Solid state reaction	Eu^{2+}	Yuelei Ding et.al
$Ca_2Al_2SiO_7$	Solid state reaction technique	Ce^{3+}, Dy^{3+}	Do Thanh Tien
$Ca_2Al_2SiO_7$	combustion technique.	Dy^{3+}	Geetanjali Tiwari et. Al.
$MY_2Al_4SiO_{12}$	combustion synthesis	Ce^{3+}	P.P. Lohe et.al.

Brief review on PL properties of silicate-based phosphors

Y. Ding et al. [9] $Sr_2Al_2SiO_7:Eu^{2+}$ and $Sr_2Al_2SiO_7:Eu^{2+}$, Dy^{3+} phosphors were prepared and compared. When triggered by UV light, the silicate phosphors made utilising a solid-state reaction sequence emitted a wide blue emission with a peak at 484nm. Its bluish-green emission is caused by Eu^{2+} intrinsic +'s 4f-5d transitions. Both samples displayed long-lasting phosphorescence that could be observed with the naked eye in full darkness after the Ultraviolet source was switched off. Using a solid reaction sequence, long-lasting silicate phosphors, Eu single doped and Eu/Dy codoped $Sr_2Al_2SiO_7$ phosphors with extended afterglow were created in a reducing environment. Reitveld refinement confirmed that the doped ions, Eu and Dy, were integrated into the $Sr_2Al_2SiO_7$ lattice. The blue green emission of phosphors is caused by the intrinsic 4f-5d transitions of Eu^{2+}.

M. Li et al. [10] synthesized $Ca_2Al_2SiO_7$: Sm^{3+}, Bi^{3+}, and Tb^{3+} which is red, green and blue luminescent spectrum respectively. However, the red area has a low luminescence intensity. Bi^{3+} and Tb^{3+} ions were added to $Ca_2Al_2SiO_7$:Sm^{3+} phosphors to enhance the red-emitting of Sm^{3+} in accordance with the energy transfer theory. By using a high temperature solid state process, a series of CASO:Bi3+, Tb3+, and Sm3+ phosphors with tunable-luminescence from blue to red have been created. Crystal structure and XRD patterns were used to describe the structure and phase purity. Inorganic luminescence is doped with rare earth metals due to characteristics emission spectra such as white light emitting diodes (wLEDs), Field emission displays (FEDs) etc. Recently, white LEDs have improved the Luminous of red phosphorus due to characteristics emission Spectra of red light activated phosphor. Phosphor is based on energy transfer. These findings all point to the importance of the terbium branch mechanism in increasing the intensity of the luminescence of the activators

Le Ngoc Liem et al. [9] present result on Luminescent and transfer from Ce^{3+} to Dy^{3+} ion in $Ca_2Al_2SiO_7$ lattice. Lighting and displays technology, Luminescent material has an important role in manufacturing fluorescent lamps and LED which are highly efficient and energy saving. In recent years white LEDs were excited by near ultraviolet radiation. Rare earth metals doped luminescent materials are widely used in various applications because they are non-toxic environmental friendliness and have high luminosity and life expectancy. By using a solid-state process at 12800C for one hour, Ce^{3+} and Dy^{3+} ions doped $Ca_2Al_2SiO_7$ (CAS) phosphors were created. Tetragonal crystalline structure was verified by the X-ray diffraction patterns [10]. The Ce^{3+} and Dy^{3+} phosphors' luminous spectra have a broad band with a peak at 420 nm that corresponds to their luminescence and thin lines that come from Dy^{3+} ions. Presentation and discussion of the energy transfer from the Ce^{3+} ion to the Dy^{3+} ion.

N. khaidukov et al. [11] studied that, in the last two decades the lamps were based on white light emitting diodes (w-LEDs) as a traditional source of light due to the high Luminous efficiency, energy saving, long lifetime and environmental friendliness. At the present a, WLEDs manufactured blue chips. The first silicate garnets are worked on Ce^{3+} ion which is doped by ceramic phosphor. We have various properties of Ce^{3+} with Si^{4+} garnets. The cation concentration at the dodecahedral, octahedral and tetrahedral sites of the garnet lattice caused differences in the spectroscopic characteristics of Ce3+ ions in the aforementioned Ca^{2+}-Si^{4+} garnet hosts, which we have observed. These findings may be helpful in the development of a new generation of ceramic phosphor converters for white LEDs based on the investigated garnet compounds. These results can be useful for a new generation of ceramic phosphor converted White-LEDs based on the garnet compounds under study.

Zefeng Xu et al. [13] aimed to synthesize the $Ca_2Al_2SiO_7$ phosphor co-doped with Eu^{2+} and Eu^{3+} and study their photoluminescence properties and Judd-Ofelt study were performed in order to find the intensity parameters and efficiency. The author finds that by adjusting the doping concentration and excitation wavelength color tenability was obtained. Kubelka- Munk function was applied to evaluate the bang gap value of $Ca_2Al_2SiO_7$ doped with different concentration of Eu. A series of Eu3+/Eu2+ codoped Ca2Al2SiO7 were synthesized by traditional solid-state synthesis in reducing atmosphere. In this study, XRD powder diffraction demonstrated that the sample produced was pure. Excitation, emission spectra, and decay curves all serve to describe the characteristics of photoluminescence. By altering excitation wavelength and concentration, double centre emission is produced. The emission spectra of Ca2Al2SiO7: Eu phosphors show two bands at the blue emission of the 4f5d-4f transition coming from Eu2+ ion and the red emission of the 4f-4f transition coming from Eu3+ ion, respectively, under the 394 nm excitation.

Guanghuan Li et al. [14] aimed to synthesized and study the luminescence properties of $Sr_2Al_2SiO_7$ co-doped with Ce^{3+} and Eu^{2+}. PLE spectra exhibit a broad band extending from 280-450 nm while emission spectra exhibit a blue band centered at 415 nm. Energy transfer arises in between Ce^{2+} to Eu^{3+} via dipole-dipole interaction. The $Sr_2Al_2SiO_7$:Eu^{2+}, Ce^{3+} phosphors are potential phosphors for warm-white light-emitting diodes due to their effective excitation in the near ultraviolet region. CIE chromaticity co-ordinates vary from deep blue to greenish region with the variation of concentration of Eu^{2+}. The Eu^{2+} and Ce^{3+} co-doped phosphors have been synthesized by a high temperature solid–state reaction.

V. Singh et al. [15] Prepared deals with green-emitting Tb-doped $Sr_2ZnSi_2O_7$ phosphors. The $Sr_2ZnSi_2O_7$:Tb^{3+} the sol-gel technique is used to produce phosphor. The structural characterization of the $Sr_2ZnSi_2O_7$:Tb^{3+} phosphors were conducted using the SEM and XRPD analyses. The spectra of emission and excitation signified that the phosphor could be effectively activated by a 239-nm ultraviolet excitation, and a green emission that is centered at 543 nm and that corresponds to the $^5D_4 \rightarrow {}^7F_5$ transition was exhibited. Sound green emissions with the chromaticity coordinates of the CIE (0.2661, 0.43204) could be achieved. The $Sr_{1.95}ZnSi_2O_7$:$Tb_{0.05}$ powder demonstrated the maximum emission intensity for the 239-nm excitation, indicating its potential use in lighting and displays [16-19]. The strong emission peak centered at 543 nm is optimal for producing a phosphor with high color purity. The excitation and emission intensities increased with the addition of Tb^{3+} content, with the $Sr_{1.95}ZnSi_2O_7$: $Tb_{0.05}$ sample achieving the highest intensity [20-21].

Conclusion

In this review work, we have successfully reviewed the synthesis and photoluminescence properties of various silicate-based phosphors synthesized via various synthesis techniques such as solid-state reaction method, sol-gel, hydrothermal, and auto combustion route. Finally from the reviewed work, it is concluded that a solid-state reaction is suitable for the formation of pure phase. Secondly, it is found that doping of different rare earth in different hosts will leads to the generation of visible light in different regions and consequently suitable for the fabrication of PC-LEDs in respective regions.

Reference

[1]. Iida, D., Zhuang, Z., Kirilenko, P., Velazquez-Rizo, M., & Ohkawa, K. (2020). High-color-rendering-index phosphor-free InGaN-based white light-emitting diodes by carrier injection enhancement via V-pits. *Applied Physics Letters*, *117*(17), 172103.

[2]. Nair, G. B., Swart, H. C., & Dhoble, S. J. (2020). A review on the advancements in phosphor-converted light emitting diodes (pc-LEDs): Phosphor synthesis, device fabrication and characterization. *Progress in Materials Science*, *109*, 100622.

[3]. Klein, C., & Hurlbut Jr, C. S. (1985). *Manual of Mineralogy*, pp. 430–434.

[4]. Deer, W. A., Howie, R. A., & Zussman, J. (1992). An introduction to the rock-forming min er als.

[5]. Fernández-Rodríguez, L., Durán, A., & Pascual, M. J. (2021). Silicate-based persistent phosphors. *Open Ceramics*, *7*, 100150.

[6]. Kazemi Shariat Panahi, H., Dehhaghi, M., Kinder, J. E., & Ezeji, T. C. (2019). A review on green liquid fuels for the transportation sector: a prospect of microbial solutions to climate change. *Biofuel Research Journal*, *6*(3), 995-1024.

[7]. Dwivedi, A., Rai, E., Kumar, D., & Rai, S. B. (2019). Effect of synthesis techniques on the optical properties of Ho3+/Yb3+ Co-doped YVO4 phosphor: a comparative study. *ACS omega*, *4*(4), 6903-6913.

[8]. Yuelei, D., Yixuan, Z., Zhiyu, W., Wen, L., Dali, M., Haibo, H., & Chengkang, C. (2009). Photoluminescence of Eu single doped and Eu/Dy codoped Sr {sub2} Al {sub2} SiO {sub7} phosphors with long persistence. *Journal of Luminescence*, *129*.

[9]. Li, M., Wang, L., Ran, W., Ren, C., Song, Z., & Shi, J. (2017). Enhancing Sm3+ red emission via energy transfer from Bi3+→ Sm3+ based on terbium bridge mechanism in Ca2Al2SiO7 phosphors. *Journal of Luminescence*, *184*, 143-149.

[10]. Son, N. M. (2019, May). Energy Transfer between Ce3+-Dy3+ In Ca2Al2SiO7: Ce3+, Dy3+ Phosphor. In *IOP Conference Series: Materials Science and Engineering* (Vol. 540, No. 1, p. 012001). IOP Publishing.

[11]. Khaidukov, N., Zorenko, et.al. (2017). Synthesis and luminescent properties of prospective Ce3+ doped silicate garnet phosphors for white LED converters. *Journal of Luminescence*, *192*, 328-336.

[12]. Kashyap, P., Diwakar, A. K., Singh, S., & Verma, A. (2022). Gd3+ Co-Doping in Al2MgSiO4: Eu2+ Photoluminescence Properties of Eu2+ and Gd3+ Phosphors Presence. *Journal of Optoelectronics Laser*, *41*(6), 243-247.

[13]. Xu, Z., Zhu, Y., Luo, Q., Pan, Y., Wang, W., Liu, X., & Li, L. (2019). Anomalous preparation, intense 5D0→ 7F4 emission and adjustable double center emission of Eu3+ and Eu2+ codoped Ca2Al2SiO7. *Ceramics International*, *45*(16), 20405-20413.

[14]. Li, G., et. al. (2011). Luminescent properties of Sr2Al2SiO7: Ce3+, Eu2+ phosphors for near UV-excited white light-emitting diodes. *Materials Letters*, *65*(23-24), 3418-3420.

[15]. Singh, V., Kaur, S., Rao, A. S., & Jeong, H. (2021). Green-emitting Tb3+ doped LaP3O9 phosphors for plasma display panel. *Optik*, *244*, 167323.

[16]. Verma, A., Diwakar, A. K., Richhariya, T., Singh, A., & Chaware, L. (2022). Aluminum Oxide Used Between Molybdenum Trioxide and Poly (3, 4-Ethylene Dioxy Thiophene) Polystyrene Sulfonate In Organic Solar Cells By Indium Tin Oxide Free Structures. *Journal of Optoelectronics Laser*, *41*(6), 230-233.

[17]. Hagenmuller, P. (Ed.). (2012). *Preparative methods in solid state chemistry*. Elsevier.

[18]. Bhatkar, V. B., Omanwar, S. K., & Moharil, S. V. (2007). Combustion synthesis of silicate phosphors. *Optical materials*, *29*(8), 1066-1070.

[19]. Singh, S., Diwakar, A. K., Kashyap, P., & Verma, A. (2022). Synthesis, Characterization & Luminescence Properties of Rare Earth Nano Phosphors Doped Eu2+ &Gd3+. *Journal of Optoelectronics Laser*, *41*(6), 238-242.

[20]. Chopra, V., Kadam, A. R., Swart, H. C., & Dhoble, S. J. (2022). Introduction to luminescence and radiation dosimetry techniques. In *Radiation Dosimetry Phosphors* (pp. 1-27). Woodhead Publishing.

[21]. Kashyap, P., Diwakar, A. K., Verma, A. (2022). Photosensitive Behavior Studies of the Ba3CaSi2O8:Eu3+ and NaCeSiO4:Eu3+ Luminescence Material Synthesis. *International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)*, 2 (1), 160-165.