

Structural and Optical Properties of Eu- Doped Silicate Phosphors: A Review

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Abstract

In the Nineteenth century the traditional sulphide based phosphor has improved greatly but they applied only in some commercial fields because the sulphide series phosphors are very poor stability. The long afterglow property and brightness is not good enough. That is the reason the researcher is trying to the research on the other phosphors. The researcher got the aluminate based phosphors at beginning the Nineties. These phosphors show the better luminescent, brightness, high stability and long afterglow character over sulphide series phosphors. The drawback of the aluminate based phosphors is single luminescent color, production cost was higher, bad anti-moisture character & strict restriction over the raw materials purity. Silicate based phosphors solve these problem, the invention provides a new kind of rare earth doped alkaline earth silicates phosphors. In this review, we present an outline of the important silicate based phosphors of known luminescent materials based on Eu-doping and how they were prepared, and we take a closer look at the mechanisms and applications that have been suggested to explain intense afterglow in various compounds.

Keywords: Luminescence; europium; after-glow; phosphors

1. INTRODUCTION

The word ‘phosphor’ comes from the Greek language and means ‘light bearer’, to describe light-emitting or luminescent materials; barium sulfide is one of the earlier known naturally occurring phosphors. A phosphor is luminescent, that is, it emits energy from an excited electron as light. The excitation of the electron is caused by absorption of energy from an external source such as another electron, a photon or an electric field. An excited electron occupies a quantum state whose energy is above the minimum energy ground state [1-2]. The materials of inorganic luminescent are currently in these days broadly utilized in numerous display devices. These materials can introduce excitabilities in region of ultraviolet, which empowers them in fluorescent lamps of new era (with no mercury), field emission displays, projection televisions and cathode ray tubes etc.

In the recent years, much consideration has been centered around on luminescent materials which are based on oxide because of their business applications in scintillations, X-ray phosphors and fluorescent tubes. As of late different phosphor materials have been effectively explored for enhancing their properties of luminescent and to meet the advancement of various luminescence and display devices. Inorganic compounds doped with rare ions of earth form a critical class of phosphors as they have a couple of fascinating attributes, for example, flexible colors of emission with various activators, high efficiency of luminescence and incredible chemical stability. There is developing enthusiasm for the improvement of new full shading emitting materials of phosphor that join chemical and thermal stability in air with high outflow yield of quantum at room temperature [3]. Silicate was chosen as a host due to its special properties, such as low cost, easy preparation, excellent thermal and chemical stabilities, and especially the strong absorption in the near-UV region. Therefore, in this paper, we have reported the structural characterization and luminescence properties of different Eu/Dy activated silicate based phosphors.

2. EXPERIMENTAL FINDINGS

The best known persistent luminescent silicate is $\text{Sr}_2\text{MgSi}_2\text{O}_7$: Eu^{2+} , Dy^{3+} , first reported by Lin *et al.* in 2001 [4], but a long afterglow has also been discovered in a number of other silicate compounds listed in Table 1. The family of materials $\text{M}_2\text{MgSi}_2\text{O}_7$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$), also called alkaline earth akermanites, plays a role similar to that of MAl_2O_4 in the aluminate group. They are often used as an example material when presenting afterglow mechanisms and they are the most widely studied persistent luminescent silicates. A solid-state reaction at 1200–1400 °C is the most common way to prepare $\text{M}_2\text{MgSi}_2\text{O}_7$ samples, but recently co-precipitation [5] and combustion methods [6] were also applied successfully.

Table 1. List of some known silicate compounds [7].

Host Materials	Dopants	Fluorescence maximum (nm)
Sr ₂ MgSi ₂ O ₇	Eu ²⁺ , Dy ³⁺	470 (blue)
Sr ₃ MgSi ₂ O ₈	Eu ²⁺ , Dy ³⁺	460 (blue)
Ca ₃ MgSi ₂ O ₈	Eu ²⁺ , Dy ³⁺	470 (blue)
Ba ₃ MgSi ₂ O ₈	Eu ²⁺ , Dy ³⁺	440 (blue)
CaMgSi ₂ O ₆	Eu ²⁺ , Dy ³⁺	445 (blue)
CaAl ₂ Si ₂ O ₈	Eu ²⁺ , Dy ³⁺	435 (blue)
Sr ₂ Al ₂ SiO ₇	Eu ²⁺ , Dy ³⁺	485 (blue/green)
Sr ₂ ZnSi ₂ O ₇	Eu ²⁺ , Dy ³⁺	460 (blue)
Sr ₂ SiO ₄	Eu ²⁺ , Dy ³⁺	480 (green)

Omara et al. [8] presented experimental results on Photoluminescence properties of Eu³⁺ doped low cost zinc silicate based glass ceramics. They synthesized Zn₂SiO₄:xEu³⁺ phosphors with different concentrations of Eu³⁺ ions (x = 1,3 and 5 wt.%) by using waste bottle glasses as silicate source. The structure, morphology, and luminescent properties of the phosphors were characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and photoluminescence (PL) spectroscopy. The XRD analysis revealed that addition of dopant increased the crystallinity of the samples, and then were decreased dramatically when the dopant concentration further to 5 wt.%. The FESEM images showed the samples have irregular in shapes while their emission and excitation peak of Zn₂SiO₄:xEu³⁺ phosphor was observed at 600 and 400 nm, respectively.

Ye et al. [9] studied a series of Sr₂Al₂SiO₇ phosphors with fixed Eu²⁺ concentration and various Tm³⁺ concentrations via a high temperature solid state reaction. The structure and luminescence properties of the samples were characterized by X-ray powder diffraction (XRD), photoluminescence (PL) spectra, decay curves, thermoluminescence (TL) glow curves as well as the photostimulated luminescence (PSL) spectra. Sr₂Al₂SiO₇: Eu²⁺, Tm³⁺ phosphors exhibited strong green phosphorescence and photostimulated luminescence originating from 4f⁶5d¹-4f⁷ transition of Eu²⁺ after ultraviolet light stimulation. Deep traps were found by analyses on the phosphorescence decays and thermoluminescence spectra. It was also found that with increasing the time interval between UV excitation turn-off and stimulation turn-on, the photostimulated luminescence became stronger. This phenomenon resulted from the fact that the captured electron was retrapped by the

deep traps. Compared with the Tm³⁺ free sample, it was found that the PSL intensity was strongly enhanced in Tm³⁺ codoping samples.

In a follow-up work, Huidong et al. [10] adopted similar synthesis method to synthesize Eu²⁺ doped K₂MgSi₃O₈ phosphors. The phase formation of as-prepared samples was characterized by X-ray powder diffraction. The luminescence properties were investigated by the photoluminescence excitation and emission spectra, decay curve and CIE coordinates. The phosphor showed bluish-green emission centered at 460 nm under the excitation of UV and near UV light with the wavelength range of 250–430 nm. Two Eu²⁺ emission centers existed in the K₂MgSi₃O₈: Eu²⁺ phosphor according to the luminescence spectra and the decay curves. The critical quenching concentration of Eu²⁺ doping was determined to be 3.0 mol.% and the concentration quenching mechanism was dipole-dipole interactions between Eu²⁺ ions. These results suggested that K₂MgSi₃O₈: Eu²⁺ was a potential bluish-green phosphor candidate for white UV-LED.

Omara et al. [11] characterized the structures, morphologies, and properties of Eu³⁺ doped Zn₂SiO₄ phosphors using X-ray diffractometer (XRD), Field emission scanning electron microscope (FESEM), Fourier transform infrared spectrometer (FTIR) , and UV-vis spectrophotometer. The density of doped zinc silicate shows the trend of increment when the sintering temperature increases. The XRD pattern shows that the material was highly crystalline; having sharp peaks, while the FESEM image reveals the presence of densely packed grains as sintering temperature increased 600 °C up to 1000 °C. The increase of transmission band intensities at 3443, 1630, 980, 650, 530 cm⁻¹ confirmed the crystallization of Zn₂SiO₄ crystal in the glass matrix with increasing sintering temperature. Lastly, the increment of energy band gap after sintering temperature at 900° C was related to the stabilization of α-Zn₂SiO₄ phase in material.

Xia et al. [12] synthesized and studied the new bromosilicate Ca₃SiO₄Br₂ crystal. The crystal structure characters have been discussed preliminarily, which can be used to explain the asymmetry emission band. The luminescence of Ca₃SiO₄Br₂:Eu²⁺ upon the 365 nm UV lamp gives a broad emission band centered at 469 nm with some asymmetry on the long wavelength side. The double-exponential decay behaviors for the two fitted emission centers further support that there are two different Eu²⁺ sites in Ca₃SiO₄Br₂. The activation energy of thermal quenching in Ca₃SiO₄Br₂:Eu²⁺ is calculated as 0.374 eV. The above results indicate that Ca₃SiO₄Br₂:Eu²⁺ is a good candidate for blue component in w-LEDs.

Suresh et al. [13] studied the effect of concentration of Eu³⁺ doped on the photoluminescence properties of CaMgSiO₄ is discussed. Interesting behavior, such as the presence of sharp bands centered at 324, 367, 384 and 396 nm of Eu³⁺ ion were observed along with CT band centered at 267 nm. Among these bands the Eu–O

charge transfer band (CTB) is a strong and broad band with FWHM 36 nm, and the 396 nm sharp band with FWHM 2 nm is also stronger one which can be used as excitation source for the generation of white light. This is an interesting multifunctional phosphor. The excitation spectra displayed that this phosphor could be effectively excited by 267 nm wavelength so that they could be used as red component for the generation of white light in display and lamp devices and as well the ($^5D_0 \rightarrow ^7F_1$) 590 and ($^5D_0 \rightarrow ^7F_2$) 615 nm red line becomes the most intense with no other emission lines, could be used as red components for white light-emitting diodes under nUV (396 nm) excitation. The results in this work demonstrate that this phosphor is a good candidate luminescent material for use in display and light emitting diodes.

The adjustment of microwave synthesis conditions found by Turkin et al. [14] to provide a control over the phase composition, luminescence spectra, and color coordinates of Eu-doped silicate phosphors. Sol-gel preparation of the charge mixture instead of mechanical mixing resulted in ~35% increase of luminescence brightness. The phosphor prepared under optimal conditions exhibit “warm” white luminescence color in combination with high brightness. Generally, the considered synthesis procedure is promising for the manufacture of efficient phosphors.

3. CONCLUSIONS AND FUTURE PERSPECTIVES

Macroscopic quantification of the silicate phosphors is of key importance for determination of composition-structure-property of the phosphors. However, quantitative characterization of the phosphors content still remains a challenge. As discussed, target phosphors contents utilized during processing are not necessarily the measured values of synthesized materials. So far, EDS and XRD measurements provided valuable information in that regard. Yet, those techniques are limited to localized surface measurements. Furthermore, as EDX measurements demonstrated, surface hydrocarbon contamination is predominant in phosphors. Although TEM and SEM measurements demonstrated crystalline morphologies, XRD measurements so far did not validate such results nor displayed characteristic peaks.

Another important issue is thermal stability of silicate compounds in high melting temperatures of constituents. Most studies showed improvement in structural and optical properties of phosphors. However, reasons for these improvements are not yet fully understood. Also, upon heat treatment, phosphors were observed to lose such improved structural and optical properties. So, to establish structural and optical property comparison, both phosphors and parent materials should be processed under same thermal conditions. Another critical need is to understand effects processing parameters during the phosphors preparing on properties so these materials could reach their optimum performance.

In summary, silicate phosphors have promising physical properties surpassing those of the corresponding rare earths. With so far demonstrated characteristics, phosphors possess potential to address needs in cutting-edge applications. However, further research is needed before that can be fully accepted and used in industrial applications.

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