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SYNTHESIS AND PHOTOLUMINESCENCE STUDY OF SCANDIUM BASED SILICATE PHOSPHOR ($\text{RbBaScSi}_3\text{O}_9:\text{Eu}^{2+}$) BY AMORPHOUS METAL COMPLEX METHOD

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ABSTRACT

The scandium based silicate phosphors with the compositions $\text{RbBa}_{(1-x)}\text{Eu}_x\text{ScSi}_3\text{O}_9$ have been synthesized by an advanced solution based method employing an water soluble silicon compound. The high quantum efficiency of the phosphors owe to the synthesis methodology heat treatment at H_2/N_2 atm. To demonstrate its potential application, we fabricated a warm white light-emitting diode LED using the $\text{RbBaScSi}_3\text{O}_9:\text{Eu}^{2+}$ phosphor. These Scandium based silicate phosphor can be excited by a near-UV and blue light irradiation and give green and bluish green emission. The $\text{RbBaScSi}_3\text{O}_9:\text{Eu}^{2+}$ phosphor can be excited by a near-UV and blue light irradiation and presents a bluish green band centered at 500 nm due to the allowed transition from $^4\text{f}_6\ ^5\text{d}_1$ to $^4\text{f}_7$ of Eu^{2+} . RBS Compound which reflects the good color rendering index and color temperature.

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INTRODUCTION

As new light source for next generation illumination, white light emitting diodes (LEDs) have been developed extensively and are commercially available due to their excellent advantages such as high energy efficiency, durability, reliability and safety and most importantly energy saving. In general, commercial white LEDs consist of blue-light-emitting LEDs and broad-band yellow phosphors, which result in the formation of “artificial” white light. $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG: Ce^{3+}) has frequently been used as a broad-band yellow phosphor because it exhibits a high emission intensity excited by blue LEDs.[1] However, the color rendering index of such white LEDs is low owing to a lack of a red light region. In order to enhance the color rendering index, other white LEDs that consist of blue-light-emitting LEDs and two broadband green (or yellow) and red phosphors, or UV LEDs with three broad-band blue, green and red phosphors, have been proposed, and are currently available as commercial LED lamps. Therefore, the development of high-efficiency phosphors with various colors is one of the most important issues that need to be addressed to improve the performance of white LEDs. Eu^{2+} activated phosphors are most suited to obtain emissions of various colors (from the blue to the red region), because the emission resulting from the $^4\text{f}_6\ ^5\text{d}_1 \rightarrow ^4\text{f}_7$ electronic

transition is strongly correlated with the energy gap between 5d and 4f orbital's, which are strongly affected by both the nephelauxetic and crystal field effects of Eu^{2+} ions. [2] We consider two key points for the appearance of high efficiency phosphor emissions owing to the $^4\text{f}_6\ ^5\text{d}_1 \rightarrow ^4\text{f}_7$ electronic transitions of the Eu^{2+} activators in the phosphors, which are (a) the selection of the appropriate host compounds and (b) the uniform dispersion of Eu^{2+} activators in the host compounds. In the case of the former, silicon-based oxides and nitrides, [3-5] aluminates, [6] and sulfides, [7,8] are the most appropriate host compounds for such high-efficiency phosphors.

Host selection is an important factor in this development process. For the exploration of a new phosphor we adopt a “mineral inspired methodology”. Among different possible matrices, silicates are good candidates to serve as the host structure due to several merits such as excellent chemical and thermal stability and their abundance in nature, they constitute approximately 90% of the crust of the earth. Interestingly, the number of known inorganic silicates is over 14 000, most of which have been derived from natural minerals, and this substantiates the significance of the mineral inspired approach. For example, rankinite ($\text{Ca}_3\text{Si}_2\text{O}_7$), [9] jervisite ($\text{NaScSi}_2\text{O}_6$), [10] wastromite ($\text{BaCa}_2\text{Si}_3\text{O}_9$), [11] akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$), [12] anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), [13] or pyrope ($\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$),

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[14] doped with a rare-earth ion, can act as an efficient phosphor. The large number of phosphors derived from minerals evidences the fact that this “mineral inspired methodology” for developing a new phosphor is advantageous and less time-consuming than the combinational method developed by a generic algorithm. [15]

The obstacle in the artificial syntheses of compounds containing silicon imitating minerals comes from the lack of an appropriate silicon source that is required when an advanced solution technology has to be employed to obtain high-quality Si-containing ceramic materials. In fact, the only silicon sources that can be used in a given solution process are “volatile” tetra alkoxy silanes (TAS). However, the use of TAS is not recommended, since TAS evaporates when subjected to repeated heat treatment, as a result of which the composition changes greatly from the original. For this reason, the discovery of new phosphors from silicon-containing compounds regarded as cornucopia of functions is challenging. We systematically synthesized silicon-containing phosphors. [16-23] using nonvolatile and nonflammable Propylene glycol-modified silane (PGMS) [16], which was uniformly dispersed in water.

In this work, we report a process for exploring new phosphors by the Amorphous Metal Complex (AMC) method based on a mineral inspired approach. Specifically, we detail the discovery of new phosphors of scandium based silicate minerals the RbBaScSi₃O₉: Eu²⁺ phosphor was synthesized by utilizing water-dispersible PGMS, and the photoluminescence properties of the RbBaScSi₃O₉:Eu²⁺ was characterized in detail.

Experimental

In this paper, we report a process for exploring new phosphors by the AMC method based on a mineral-inspired approach. First, we extract silicate-based substances of mineral origin from the database. That mineral specifically based on alkaline-earth/alkali metals and silicates, the standard composition was created by removing water of crystallization (“•nH₂O”) from original mineral compositions. Specifically, we detail the discovery of new phosphors of silicate mineral RbBaScSi₃O₉ by the AMC method utilizing water-dispersible PGMS. We have first described the method for the synthesis of PGMS, followed by the importance of the use of PGMS in the AMC method.

Until now, we reported on the synthesis of silicon-containing phosphors [15-21] through the aqueous solution method involving PGMS obtained by reacting tetra ethoxy silane (TEOS) a typical silicon alkoxide with glycol. For example, silane modified with propylene glycol (PG) (propylene-glycol-modified-silane; PGMS) can be synthesized in the presence of hydrochloric acid as a catalyst by reacting TEOS with PG at 80°C for 1 h. PGMS has a distinct property of reacting with water to form silicon clusters [8], such as Si(OH)₄ and (OH)₃-Si-O-Si(OH)₃, and of distributing uniformly in water, unlike other conventional Si compounds such as TEOS. While PGMS is important in the synthesis of silicon-containing phosphor, it is indispensable in the discovery of new silicon-containing

phosphors by the SPS method. PGMS formation reaction shown in figure 1.

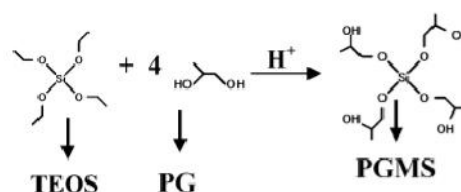


Fig. 1 Reaction between TEOS and PG in the presence of an acid catalyst to produce PGMS

In RBS compound Eu²⁺ doped RbBaScSi₃O₉ phosphor powders have been synthesized by AMC method. In this process, required amount of Rubidium carbonate (RbCO₃) salts and Barium carbonate (BaCO₃) are dissolved in an aqueous solution of citric acid in RBS compound. Then both compound desired amount of europium and scandium nitrates solutions are added to it. The temperature of the solution has been increased to 80°C and kept for 2 h. Then the temperature has been increased gradually to 130°C followed by the addition of required amount of WSS solution. After complete evaporation of the solution a transparent gel has been formed. Then the gel has been subjected to pyrolysis at 550°C for 4 h. The resultant product has been heat treated for 800°C for 4 h to get the precursor. Finally, the precursor was reduced in H₂/N₂ atmosphere at 1150°C for 3 h to get the required sample.

All Phase identification of samples by X-ray diffraction measurement and the evaluation of photoluminescence properties by excitation and emission-spectrum measurement were performed to choose promising phosphors. In the specific case of Eu²⁺ doped RBS /Si-oxide systems, further reduction of a stable trivalent europium (Eu³⁺) to a less stable divalent europium (Eu²⁺) was found to be necessary. In order to reduce Eu³⁺ to Eu²⁺ completely, additional heat-treatment under a strongly reducing atmosphere was carried out by passing N₂/H₂ (95/5 mol%) gas at 1150°C for 3 h.

Material characterization

The crystal structure of the as-synthesized sample was identified by using powder X-ray diffraction (XRD) analysis with a Bruker AXS D8 advanced automatic diffractometer with Cu-Kα radiation (λ = 1.5418 Å), over the angular range 10° ≤ 2θ ≤ 80°, operating at 40 kV and 40 mA. The photoluminescence (PL) and PL excitation (PLE) spectra of the samples were analyzed by using a Spex Fluorolog-3 Spectrofluorometer equipped with a 450-W Xe light source. The temperature dependent PL spectra were obtained with a spectrophotometer (Jobin-Yvon Spex, Model FluoroMax-3).

RESULTS AND DISCUSSION

The XRD patterns of the RbBaScSi₃O₉: 2%Eu²⁺ RBS compound phosphors are shown in Fig. 3. The XRD patterns of all samples were identical to a single phase of the monoclinic RbBaScSi₃O₉ structure with high crystallinity, samples exhibited relatively high intensities and narrow peak widths, indicating that all the samples and there is no diffraction peak corresponding to any impurities in the patterns.

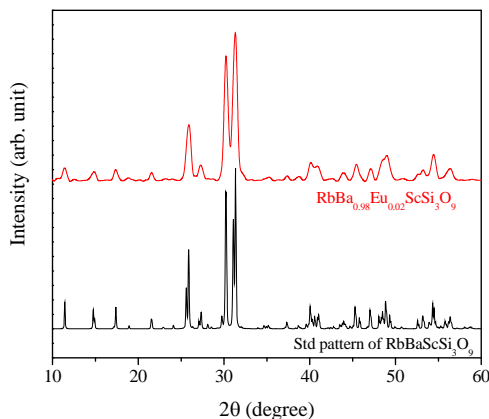


Fig.3 Powder XRD patterns of RbBaScSi₃O₉:Eu²⁺

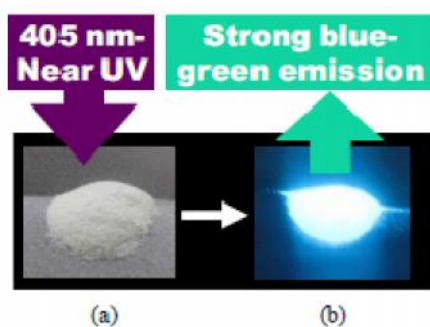


Fig. 4 Appearance of phosphor of powder of RBS:Eu²⁺ (a) and its emission by illumination of short UV

After careful inspection of the result obtained by the AMC experiment, the RBS:Eu²⁺ phosphor, emitting blue green light(500 nm). The light emission when irradiated with 405nm of near ultraviolet light is shown in figure 4.

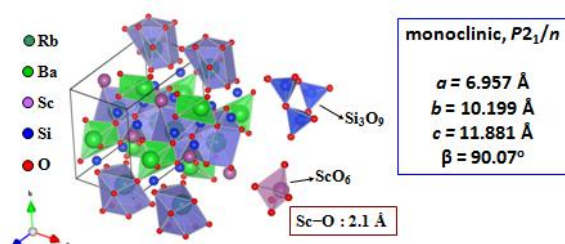


Fig.5 Crystal Structure of RbBaScSi₃O₉

Figure 5 explain the crystal form of RbBaScSi₃O₉ adopts a monoclinic structure [24], in which tetrahedral SiO₄ and octahedral ScO₆ connected to form a rigid three-dimensional structure and the Rb⁺ and Ba²⁺ ions are located in the three-dimensional framework, as illustrated in Fig. 5. In the case of present phosphor, the doping Eu²⁺ may be preferably occupy the Ba²⁺ site in the crystal structure, because the ionic radius of Eu²⁺ (0.120 nm for 7 coordination and 0.125 nm for 8 coordination) is similar to that of Ba²⁺ (0.138 nm for 8 coordination), and the valences of Eu²⁺ is same to that of Ba²⁺.

Figure 6 explain the dependence of the photoluminescence emission peak intensities on the Eu²⁺ concentrations in the RbBaScSi₃O₉ : 2% Eu²⁺ phosphors under excitation wavelength at 405 nm is shown in Figure Fig. 6 presents the

photoluminescence excitation and emission spectra of the RbBaScSi₃O₉ : 2 mol%Eu²⁺ phosphor. The excitation spectrum of the phosphor is consisted of a broad band covering from the UV to blue light region. This indicates that the phosphor can be applied in the white LEDs which including near-UV LED chip and blue LED chip as an excitation source. The emission spectra exhibit a broad bluish green band centering at 500 nm, corresponding to the allowed transition from ⁴F₆³d₁ to ⁴F₇ of Eu²⁺, under excitation wavelength at 405 nm.

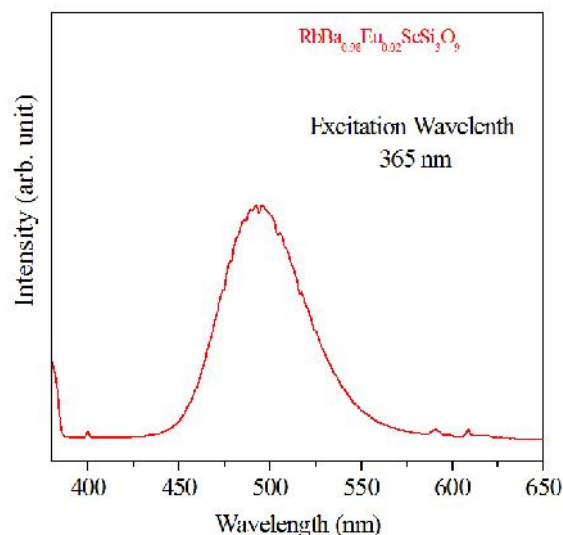


Fig 6 PL emission spectra Eu²⁺ doped RbBaScSi₃O₉ sample

CONCLUSION

We believe that research involving exploration for new phosphors is still in infancy. In this paper, we described the process parameters involved in the exploration of new phosphors using the AMC method based on a mineral-inspired approach. We would like to reiterate the importance of propylene glycol-modified silane (PGMS) in the implementation of the AMC method for preparing new phosphors from silicates. Using this method, we recently found Eu²⁺-activated oxide phosphor that emitted bluish green band centering at 500 nm when excited with blue light

This high luminescence intensity of the phosphor may owe to the synthesis procedure based on AMC method which helps in the homogeneous distribution of Eu²⁺ ions in the matrix as well as the double annealing in graphite and H₂/N₂ reducing atmosphere.

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