Preparation and Luminescent Properties of Eu$^{3+}$ Doped Barium Strontium Orthosilicate (SrBaSiO$_4$) Phosphor

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ABSTRACT

Europium doped BaSrSiO$_4$ phosphors were prepared by high temperature modified solid state diffusion method. The starting materials Strontium carbonate SrCO$_3$ Barium carbonate BaCO$_3$ and silicate SiO$_3$ are used to prepare BaSrSiO$_4$ Phosphor and its optical properties were studied. XRD analysis suggests direct reaction between SrCO$_3$ and SiO$_2$ powders. The crystallite size of powders samples were calculated from X-ray peak broadening of the diffraction using Scherer’s formula. The calculated average crystallite size of the BaSrSiO$_4$ phosphor is 25 nm. The XRD patterns of the powders revealed that the structure of BaSrSiO$_4$ is orthorhombic. The photoluminescence of the obtained phosphors were studied. The conversion ratios of the BaSrSiO$_4$ starting materials are calculated from the weight loss. The CIE co-ordinates for the Eu doped BaSrSiO$_4$ phosphors were $x=0.30$ and $y=0.31$. From the CIE chromaticity diagram for the emissions of Eu$^{3+}$ doped BaSrSiO$_4$. This phosphor having color tenability and this phosphor has an important candidate of the lighting system.

Keywords: XRD, Modified solid state diffusion method, SEM, Photoluminescence, Phosphor.

1. INTRODUCTION

Alkaline earth silicate is a important luminescent material, so it has been widely applied in phosphor for lamp. Since it can be excited efficiently by LED chips, there have been
many reported about this material applied in phosphor for white LED\textsuperscript{1-4}. However, it has troubles of low color stability with increasing applied current, low color rendering index, and low color reproducibility\textsuperscript{5,6}. Another new type of phosphor: Sr\textsubscript{2}SiO\textsubscript{4}:Eu\textsuperscript{2+} has attracted researchers’ attention\textsuperscript{7-9}. Sr\textsubscript{2}SiO\textsubscript{4} provides the broadband absorption in UV/Blue region due to low symmetry of the crystallographic sites. In addition, the Sr\textsubscript{2}SiO\textsubscript{4}:Eu\textsuperscript{2+} phosphor has a higher luminous efficiency, CRI and color stability than YAG\textsuperscript{10,11}, and giving rise to a new phosphor approach for white LED applications. Phosphor materials are essential due to their emerging expertise with solid state lighting (SSL), SSL is the recent revolution in the lighting technology, wherein the low power light emitting diodes (LEDs) are used for lighting applications\textsuperscript{12}.

Information of the fundamental reaction kinetics and mechanism are important when optimizing the solid-state process for phosphor applications\textsuperscript{14}. Sr\textsubscript{2}SiO\textsubscript{4} is a suitable host lattice for phosphor applications Sr\textsubscript{2}SiO\textsubscript{4} powder is usually prepared in a solid-state reaction by heating mixed strontium and silicon salts at elevated temperatures\textsuperscript{15}. The main benefit of solid state reaction method is, the ending production solid form is structurally pure with the desired properties depending on the final sintering temperatures. This technique is environment friendly and no toxic or unwanted waste is produced after the solid state reaction is complete. In this method the powders produced from solid state reaction is very fine as well as the cross contamination is very less.\textsuperscript{13}

In this study, BaSrSiO\textsubscript{4} powders were prepared via modified solid-state reaction by heating mixed precursors at elevated temperatures. The purpose of this study is to explain the reaction mechanism and reaction kinetics of formation of BaSrSiO\textsubscript{4} in a solid-state reaction. The precursors were examined using thermal and X-ray diffraction analysis to determine the optimum reaction range. The isothermal analysis was adopted to understand the reaction mechanism and kinetics. Using the micro structural observations accompanied by the kinetics, a reaction model for the formation of BaSrSiO\textsubscript{4} via the solid-state reaction is proposed.

2. MATERIALS AND METHOD

Barium Strontium Orthosilicate (SrBaSiO\textsubscript{4}) Phosphor was synthesized by the modified solid state reaction method. Strontium carbonate (SrCO\textsubscript{3}, Aldrich Chemicals, 99.9%), Barium carbonate BaCO\textsubscript{3} and silicon dioxide (SiO\textsubscript{2}, Aldrich Chemicals, 99.6%) were mixed in their stoichiometric ratio according to the BaSrSiO\textsubscript{4} chemical formula. A Stoichiometric mixture of these powders was thoroughly homogenized in agate mortar for 1hr. and then transferred to alumina crucibles. The homogenized mixture was heated in air at 1200 °C for 4h in a muffle furnace with heating rate of 300 °C/hr. Finally cool down to room temperature by furnace shut off. All samples were prepared by same technique.

Thermo gravimetric analysis (TGA) of precursor of BaSrSiO\textsubscript{4} was carried out in nitrogen atmosphere in 30–12000 C temperature range using a Perkin Elmer, Diamond TG/DTA instrument. The initial mass of sample taken for recording the TGA curves was 64.778 mg and hold for 1.0 min at 300 C, and then heating rate was maintained at 100 C/min. The phase composition and phase structure were characterized by X-ray diffractograms (XRD)
using an automated Rigaku Miniflex X-ray diffractometer (D Max III VC, Japan). The photoluminescence excitation and emission spectra were measured by Spectrofluorophotometer (SHIMADZU, RF – 5301 PC) equipped with a 150 W Xenon lamp as excitation source. All the spectra were recorded at room temperature. The emission and excitation spectra of BaSrSiO₄ phosphor were recorded for excitation at 254 nm and for emission at 468 nm.

3. RESULTS AND DISCUSSION

TGA curves for the BaSrSiO₄ precursors heated at rate of 10 °C/ min shows in Fig. 1. The TG analysis showed two stages of weight loss accompanied by two endothermic peaks. The corresponding endothermic peak at 100 and 450 °C in DTA curve, corresponding to the weight loss shown in TG, was due to precursor dehydration. An apparent weight loss occurred at around 700 °C, and no further weight loss was found at temperatures higher than 980 °C. To explain the broad endothermic peak at around 820 °C, the TG analysis for pure strontium carbonate and silicon dioxide (SiO₂) were also performed. According to our experimental results, the silicon dioxide seemed to be stable in comparison with strontium carbonate in the range of 25 °C to 1000 °C.

The total weight loss measured from TG experiment amounted to 24.7%, which was closed to the theoretical weight loss of this reaction. The net equation of the reaction involving SrCO₃ and SiO₂ is given in Eq. (1).

$$\text{BaCO}_3 + \text{SrCO}_3 + \text{SiO}_2 \rightarrow \text{BaSrSiO}_4 + 2\text{CO}_2$$  \hspace{1cm} (1)

![Fig. 1 TG of Precursor of BaSrSiO₄.](image)

During the reaction indicated in Eq. (1), the conversion ratio of BaSrSiO₄ can be calculated from the weight loss of the samples. The detailed calculations are described as follows.

Take the dehydration of precursors into consideration; the weight loss was 0.92% in TG experiment, hence, the exact conversion of the reaction is revised as

\[ \alpha = (W\% - 0.92\%) / 24.77\% \]  

(2)

As deduced from Fig. 1 for the reaction to proceed, the temperature should be higher than 700 °C. Therefore, the reaction temperatures were chosen at 700 °C, 750 °C and 800 °C, respectively. The mixed BaSrSiO₄ precursors were isothermally heated at these temperatures for various periods of time and then quenched to room temperature. The weight difference \( W \) of each specimen before and after the heating process was recorded. The conversion ratio of BaSrSiO₄ formation under each heating condition was calculated by Eq. (2). The reaction was nearly completed at 1000 °C after 60 min. In addition, it was noted that for the same reaction period, the conversion increased with a rise in the heating temperature. Heating specimens at 700 °C for 120 min increased conversion ratio to about 71%. After reacting for 120 min, the conversion ratios at 750 °C and 1000 °C were 95% and 97%, respectively.

The structure and phase purity of the synthesized BaSrSiO₄ phosphor was investigated by X-Ray Diffraction Method. Results are shown in Fig. 2 and all diffraction peaks can be well indexed based on the JCPDS data card No. 39-1256.

![XRD of BaSrSiO₄: Eu³⁺](image)

Fig. 2 XRD of BaSrSiO₄: Eu³⁺

All diffraction patterns were obtained using Cu Kα radiation (\( \lambda = 1.54051 \) A°), at 30 kV and 15 mA. Measurements were made from 2θ = 10° to 80° with steps of 0.02°. The
crystallite size of powders samples were calculated from X-ray peak broadening of the diffraction using Scherer’s formula. The calculated average crystallite size of the BaSrSiO₄ phosphor is 29 nm. The XRD patterns of the powders revealed that the structure of BaSrSiO₄ is orthorhombic.

Fig. 3 shows the SEM images of the BaSrSiO₄: Eu³⁺ phosphors at 1.5% concentrations of Eu³⁺. The Ba doping also has a strong influence on the microstructure of the produced powders. According to the SEM images in Fig. 3, the fine BaSrSiO₄: Eu³⁺ powder consists of small spherical particles with smooth and round surfaces whereas increasing the Ba content cause in the powder to become bigger and to take an irregular shapes and sharp edges. The cause for this change in the crystal structure and the surfaces of the particles is the structural heterogeneity and the chemical complexity¹⁶.

![Fig. 3. SEM Photograph of Eu³⁺ doped BaSrSiO₄](image-url)
The excitation spectra recorded at 613 nm emission shows peak around 361 nm is due to charge transfer band between O$_2$— Eu$^{3+}$. The electron transfers to partially filled 4f orbit of Eu$^{3+}$ from 2p full orbit. This transfer leads to oxidation of O$_2$ to O$\cdot$ and reduction of Eu$^{3+}$ to Eu$^{2+}$. Thus the phosphor can be efficiently excited by mercury lamp$^{13}$. Peaks at 376, 382, and at 393 nm are due to $^7F_0 \rightarrow ^5G_2$, $^7F_0 \rightarrow ^5G_5$ and $^7F_0 \rightarrow ^5G_6$ respectively as shown in fig. 3. In Eu$^{2+}$ there are two types of excitation charge transfer band and 4f-4f transition. The filled $^5S_2$ and $^5P_6$ orbital shield the 4f orbital. Thus the influence on the optical transition by host lattice within the 4fn configuration is small and 4f-4f transition is sharp lines$^{14}$.

Fig. 4 shows the excitation and emission spectra of BaSrSiO$_4$: Eu$^{3+}$. The emission spectrum was recorded with 254 nm excitation.

Most lighting specifications refer to colour in terms of the 1931 CIE chromatic colour coordinates which recognize that the human visual system uses three primary colours: red, green, and blue. In general, the colour of any light source can be represented on the (x, y) coordinate in this colour space. The colour purity was compared to the 1931 CIE Standard Source C (illuminant Cs (0.3101, 0.3162)). The dominant wavelength is the single monochromatic wavelength that appears to have the same colour as the light source. The dominant wavelength can be determined by drawing a straight line from one of the CIE white illuminants (Cs (0.3101, 0.3162)), through the (x, y) coordinates to be measured, until the line intersects the outer locus of points along the spectral edge of the 1931 CIE chromatic diagram.$^{17-19}$
The CIE co-ordinates for the BaSrSiO$_4$: Eu$^{3+}$ phosphors were $x=0.31$ and $y=0.30$ Fig. 5. Illustrates the CIE chromaticity diagram for the emissions of Eu$^{3+}$, (1.5 mol %) doped BaSrSiO$_4$. This phosphor having colour tenability from blue to white light and this phosphor has an application in the lighting system.

**Table 1 CIE coordinates for BaSrSiO$_4$: 1.0 % Eu$^{3+}$**

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>Excitation (nm)</th>
<th>Strong Emission (nm)</th>
<th>(x,y) Coordinate</th>
<th>Color region</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaSrSiO$_4$: 1.0 % Eu$^{3+}$</td>
<td>254</td>
<td>Tricolor</td>
<td>(0.31, 0.30)</td>
<td>white</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

The reaction mechanism and kinetic analysis for the formation of BaSrSiO$_4$: Eu$^{3+}$ are investigated in this study. The process of formation of BaSrSiO$_4$: Eu$^{3+}$ is assumed to be a direct reaction between BaCO$_3$, SrCO$_3$ and SiO$_2$ via the TG and XRD analysis. The conversion of BaSrSiO$_4$: Eu$^{3+}$ from the starting materials increases with an increase in the heating temperature and heating time. For the ceramic reaction involving SrCO$_3$ and SiO$_2$, the three-dimensional solid-state reaction model is considered. The formation of BaSrSiO$_4$: Eu$^{3+}$ is confirmed to be governed by a diffusion controlled mechanism via reaction kinetic isothermal analysis. From the emission spectra, the peaks at 589-593, 613-619 and 702 nm are due to
radiative transitions from $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_4$. Broad band along with small peak appears around 431 nm in the blue region. The CIE co-ordinates for the Eu$^{3+}$ doped BaSrSiO$_4$ phosphors were x=0.31 and y=0.30. As seen in the SEM images, the BaSrSiO$_4$: Eu$^{3+}$ powder consisted of small spherical particles with smooth and round surfaces. The BaSrSiO$_4$:Eu$^{3+}$ phosphors have a wide range of applications as blue emission phosphors for white light and can be applied to backlight unit of LCD.

REFERENCES