Synthesis and Characterization of a Near-ultraviolet Converting Cyan Emitting $NaBaScSi_2O_7$: Eu^{2+}Phosphor for the application in White Light Emitting Diode

J.Rawat[1], S.Ray[2]

[1,2]*Department of Physical Science, Rabindranath Tagore University*

***Abstract** - To facilitate the next generation of White Light Emitting Diodes (WLEDs) with higher color rendering and warm lighting, the development of inorganic phosphor for efficient conversion of photons from blue/ n-UV light to other visible wavelengths is essential. In this regard, we demonstrate a systematic, cost effective, solution-processable, easily scalable and fully controllable synthesis a new cyan emitting scandium silicate based phosphor$NaBaScSi_2O_7$:$Eu^{2+}$with 86% internal quantum efficiency under n-UV excitation. The concept as well as the methodology of using a "Mineral Inspired Approach" emerges as a new blueprint for the rational design of novel phosphor for phosphor converted WLEDs.Impact of synthesis methodology on the optimization of photoluminescence emission intensity of $NaBaScSi_2O_7$:Eu^{2+} phosphor has also been studied and reported. The results evidence the importance of the synthesized phosphor for phosphor converted WLEDs industry.*

***Keywords:** WLEDs, Inorganic phosphor, n-UV, Cost effective, $NaBaScSi_2O_7$:Eu^{2+}, Photoluminescence emission.*

I. INTRODUCTION

The advent of 21st century has been coined as the age of solid-state photonics because compact and rugged solid-state lamps based on light emitting diodes (LEDs) are replacing conventional fluorescent lamps.[1] This replacement promises an enormous decrease in power consumption, with vast economic and ecological consequences. White light LEDs (WLEDs)represent a promising next-generation illumination source, because of their merits of a long operation lifetime, energy saving capabilities and high material stability.[2The] phosphor-converted light emitting diode (pc-LEDs) combine a GaN - based LED with down - converting phosphor and emits light in the visible spectral region.[3The] combination of luminescence from the phosphor excited by LED and emission from the LED generate white light.[4]

One strategy to make LEDs by coating a near-ultraviolet (n-UV) emitting LED chip (380–420 nm) with a mixture of blue, green and red emitting phosphors, which exhibits smoother spectral distribution over the whole visible range and therefore can obtain high quality white light.[5Undoubtedly], phosphors play a crucial role for governing the color characteristics of white LEDs including color rendering in the lighting and color reproduction in the backlight.[4The] eventual performance of white LED-based devices strongly depends on the luminescence properties of the phosphors used, as a consequence, research on new phosphors excitable by blue or n-UV light is rapidly increasing and has become one of the most fascinating research topics in the phosphor community.[6The] high luminescence intensity of phosphor contributes to the high efficiency of white LEDs. Although the conventional white LED phosphor, YAG:Ce, has a high luminescence intensity, the luminescence spectrum is not suitable for high-color-rendering white LEDs used for lighting, and the matching to the color filter is not suitable in the backlight.[4]

II. MATERIALS AND METHOD

$NaBaScSi_2O_7$doped with 2% Eu^{2+}samples have been synthesized by amorphous metal complex (AMC) method of an aqueous solution process7[,8]. Stoichiometric amount of $BaCO_3$dissolved in citric acid was added in a beaker followed by the addition of required amount of $NaNO_3$, $Sc(NO_3)_3$ and $Eu(NO_3)_3$ solutions. Citric acid was used for the complexation of metal ions. The molar ratio of [all metals]: [citric acid] was maintained as 1:5. Propylene glycol-modified silane, which was used a source of Si, was obtained by alkoxy group exchange reaction in tetrahydroxy silane in the presence of an acid as a catalyst[9]. The beaker containing all metal solutions along with citric acid was kept on a digital hot plate at 80 ^oC under 2 hours stirring conditions for the complexation reaction. Then the temperature of the hot plate was increased to 130 ^oC followed by the addition of PGMS in order to promote the poly-esterification. This heat treatment resulted in the formation of a transparent gel-like substance. This gel-like matter was heated at 450 ^oC for 12 h and then heated at 550 ^oC for 4 h to remove the organic matters. The resultant product was then heated at 800^oC for 5 h to obtain the precursor. Finally the precursor was heat treated at 1150 ^oC for 3 h under graphite reduction condition. Due to the volatilizing tendency of Na, three compounds with 10%, 20% and 30% excess $NaNO_3$ have been synthesized in the similar way. The samples have been collected and one part of the sample synthesized with 30% excess $NaNO_3$ was again reduced in H_2/Ar atmosphere at 1150 ^oC for different times like 10 min, 20 min and 1 h to synthesize the required samples. We denote the sample reduced in graphite atmosphere followed by the reduction in H_2/Ar atmosphere for 10 min as sample A, 20 min as sample B and 1 h as sample C.

It is noteworthy that the uniform distribution of activator ions into the host matrix is the key factor responsible for the enhancement of luminescence intensity of the phosphor. In this context, the above-mentioned “AMC” method has several advantages as follows:

1) Complexation of the cations by citric acid greatly improved the stability of the initial solution against hydrolysis or precipitation, which increases the local activator concentration and eventually diminishes the emission intensity of the phosphor.

2) The water evaporation generates the formation of a gel with high viscosity, in which, the mobility of the metal ions get lowered, which, in turn is responsible for the prohibition of the undesirable segregation of metal ions. It is important to mention that an aqueous solution of PGMS solution undergoes self-gelation and solidify if the hydrolysis of PGMS proceeds very slowly**.** To get the improved uniformity of the dopant ion into the matrix, self-gelation of PGMS is detrimental as it would increase the local activator concentration. In AMC method, after the addition of PGMS, two competitive gelation processes takes place simultaneously, reaction of PGMS with metal-citrate precursor along with self-gelation of PGMS. It has been reported that the hydrolysis of PGMS proceeds quickly with the enhancement of temperature, which in turn decreases the self-gelation of PGMS.[16] For this reason, the temperature of the hot plate was raised to 130 ^oC to suppress the self-gelation process at the expense of reaction of PGMS with metal-citrate precursor.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the XRD patterns of the samples synthesized under graphite reduction conditions. fig, it is evident that the samples synthesized in the presence of 20% and 30% excess amount of $NaNO_3$, constitute of a single phase of $NaBaScSi_2O_7$whereas the XRD pattern of the samples synthesized with stoichiometric amount and 10% excess $NaNO_3$ contain small amount of $NaScSi_2O_6$ as impurity phase.

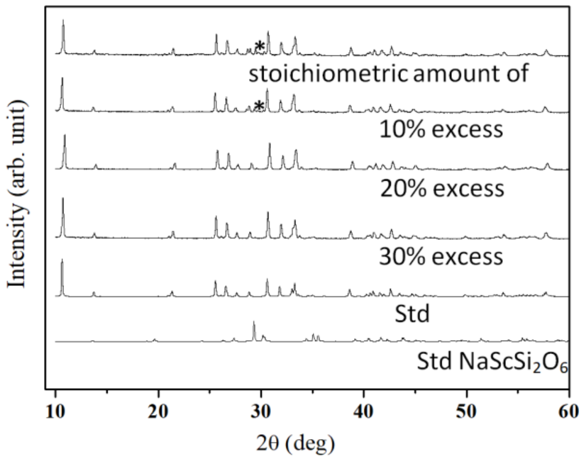
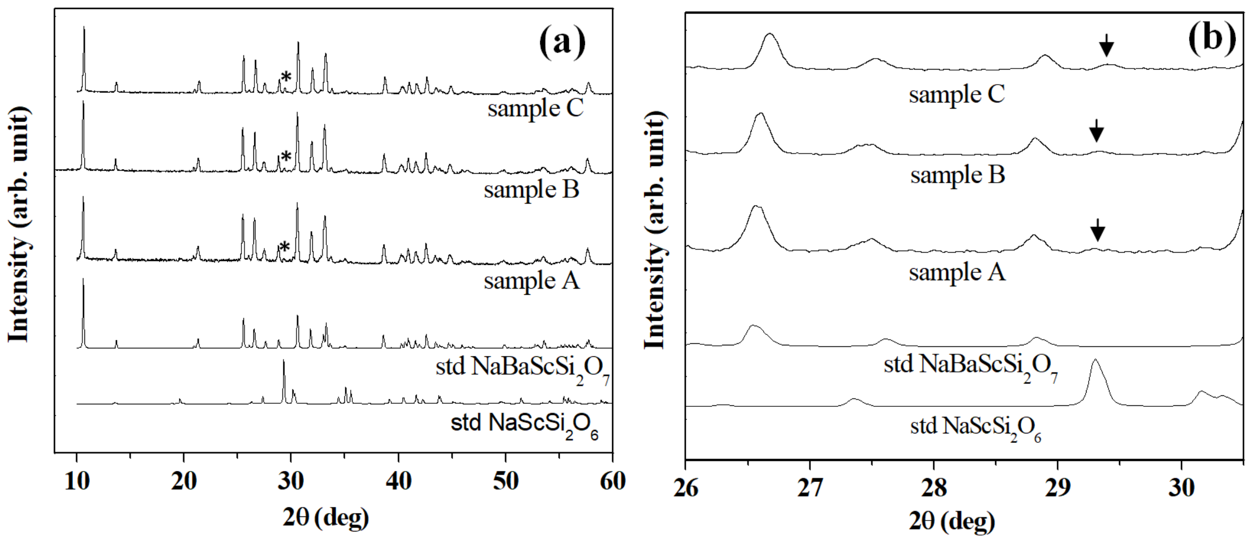


Fig. 1 XRD patterns of $NaBa_{0.98}Eu_{0.02}ScSi_2O_7$synthesized under graphite reduction condition.

Fig. 2(a) presents the full range XRD patterns of sample A, B and C. Fig. 2(b) shows the small range (2θ = 26^o – 30.5^o) XRD patterns of the samples. From these two figures, the formation of pure phase of $NaBaScSi_2O_7$ is evident for all three samples as the amount of impurity is almost negligible as depicted from Fig. 2(b).



Figs. 2(a) Full range (b) and small range (2θ = 26^o – 30.5^o) (b) XRD patterns of sample A, B and C.

IV. CONCLUSION

In this study a cyan-green emitting $NaBaScSi_2O_7:Eu^{2+}$ phosphor has been successfully synthesized by an advanced solution method. AMC method produces phosphors with high phase purity and very high luminescence intensity. As compared with $YAG:Ce^{3+}$, sample C produces 1.23 times higher PL intensity at the excitation wavelength of 440 nm, which makes this blue-excitable green emitting phosphor a very promising candidate for its application in white LEDs. This high luminescence intensity of the phosphor may owe to the synthesis procedure based on AMC method which helps in the homogeneous distribution of Eu^{2+} ions in the matrix as well as the double annealing in graphite and H_2/Ar reducing atmosphere. The internal quantum efficiency of the phosphor was calculated to be 86%.

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