

Photoluminescence properties Eu³⁺activated NaCaPO₄ phosphors by Combustion synthesis.

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ABSTRACT

The preparation of NaCaPO₄ doped with rare earth (RE) ions Eu³⁺ by combustion synthesis method was described. When NaCaPO₄:Eu³⁺ phosphor was excited at 362 nm, the emission spectrum showed intense bands at 571 and 594 nm. The prepared phosphor characterized by X-ray diffraction, SEM of host lattice, FTIR and photoluminescence behaviour of NaCaPO₄ doped with Eu. Thus, the photoluminescence behaviour of rare earth Eu³⁺ activated in this host is strongly suggested that potential candidate for near-UV white light-emitting diodes (LEDs).

Keywords: combustion synthesis; photoluminescence; phosphor; solid state lighting; rare earths.

INTRODUCTION

Solid-state lighting using light-emitting diode (LED) and phosphor material to generate white light is the current research focus in the lighting industry. Solid-state lighting technology has several advantages over conventional fluorescent lamps such as reduced power consumption, compactness, efficient light output, and longer lifetime. Solid-state lighting will have its impact on reducing the global electricity consumption. White light-emitting diodes (LEDs) can save about 70% of the energy and do not need any harmful ingredient in comparison with the conventional light sources,

such as incandescence light bulbs and the luminescent tubes, thus white LEDs have a great potential to replace them and are considered as next generation solid state light devices[1,2]. The phosphors based on phosphate host matrices have become the subject of great interest for an extensive investigation due to their wide applications in lighting and displays.

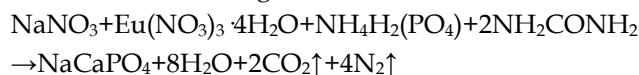
In this paper, the Eu^{3+} activated NaCaPO_4 phosphor was synthesized by combustion method and its luminescent properties were also investigated, which demonstrated that NaCaPO_4 is potential phosphor near-UV white light - emitting diodes (LEDs).

METHODOLOGY

The Eu^{3+} activated NaCaPO_4 phosphors were prepared via combustion synthesis method. The starting AR grade materials (99.99% purity) were taken, where calcium nitrate tetra hydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Merck), ammonium di-hydrogen phosphate ($\text{NH}_4\text{H}_2(\text{PO}_4)$, Merck), sodium nitrate (NaNO_3 , Merck), europium oxide (Eu_2O_3 , REI 99.9%), and urea (NH_2CONH_2 , Merck) was used as fuel. The reagents were mixed and crushed about 30 min. to obtain a homogeneous solution (It becomes in Jelly form). Eu^{3+} ions were introduced as of $\text{Eu}(\text{NO}_3)_3$ solution by dissolving Eu_2O_3 into dil. HNO_3 solution. For the preparation of $\text{NaCaPO}_4:\text{Eu}^{3+}$ phosphor. For various compositions of the calcium nitrates (oxidizers), the amount of urea (fuel) was calculated maintaining total oxidizing and reducing valences of the components equal to unity, so that the heat liberated during combustion is maximum. After stirring for about 30 min, precursor solution was transferred in to crucible and it put into a furnace preheated to 600–700 °C and the porous products were obtained. The stoichiometric amount of redox mixture, when heated rapidly at ~650 °C was boiled, underwent dehydration followed by decomposition generating combustible gases such as oxides of N_2 , H_2O and nascent oxygen. The volatile combustible gases ignite and burn with a flame and thus provide conditions suitable for the formation of phosphor lattice with dopants. Large amounts of escaping gases dissipate heat and prevent the material from sintering and thus provide conditions for the formation of crystalline phase. Rare earth ion doped NaCaPO_4 phosphors were prepared by introducing

Eu ions as $\text{Eu}(\text{NO}_3)_3$ solution respectively with different concentrations and repeated the procedure as explained above.

Chemical reaction is given as follows:



RESULTS AND DISCUSSION

Several complementary methods were used to characterize the prepared phosphor. The prepared host lattice was characterized for their phase purity and crystallinity by X-ray powder diffraction (XRD) using a PAN-analytical diffractometer (CuK α / 1.541862 Å radiation) at a scanning speed of 10° per minute, in the 2 θ range from 10° to 80°; the average crystallite size was calculated from the broadening of the X-ray line (311) using Scherer's equation. The photoluminescence measurement of excitation and emission were recorded on a Shimadzu RF5301PC spectrofluorophotometer. The same amount of sample, 2g, was used for each measurement. Emission and excitation spectra were recorded using a spectral slit width of 3 nm. The morphology of the products were examined by a scanning electron microscope (SEM, JEOL 6380A) also Fourier Transform Infrared Spectroscopy (FTIR) of the sample is taken.

NaCaPO_4 has an orthorhombic crystal structure (Buchwaldite) and their lattice parameters values are $a=0.6797$ nm, $b=0.9165$ nm and $c=0.5406$ nm [3]. Fig. 1 shows the XRD pattern of NaCaPO_4 and it agrees well with Joint Committee on Powder Diffraction Standards (PDF Card No.: 9004559). The XRD pattern did not indicate presence of the constituents like, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, NaNO_3 or $\text{NH}_4\text{H}_2\text{PO}_4$ and other likely phases, which is a direct evidence for the formation of the desired compound. These results indicate that the final product was formed in crystalline and homogeneous form. It is clearly seen that the grains are irregular in shape of particles with a size of about 0.5–2 μm . This shows that the combustion reactions of the mixtures took place well [4].

The typical morphological images are presented in Fig. 2 The particles possess foamy like morphology

formed from highly agglomerated crystallites and the particles are globular in appearance. An average crystallite size is in sub-micrometer range and formation of sphere type structure is seen in SEM images. This indicates that this experimental processing is favourite for the crystalline growth of Buchwaldite type of crystal structure [4].

The main goal of FT-IR spectroscopic analysis is to understand the chemical functional groups in samples, which absorb characteristic frequencies of IR radiation. Thus, FT-IR spectroscopy is an important and powerful tool for structural elucidation and compound identification.

FTIR spectrum of the Eu^{3+} ions doped NaCaPO_4 phosphor prepared via combustion method in open air is shown in Fig.3. The peak observed at 471 cm^{-1} could be assigned to the symmetric stretching of the P-O-P bonds in the P_2O_7 group [5]. Usually, the IR absorption band of $(\text{PO}_4)_3$ has two regions of $1120\text{--}940\text{ cm}^{-1}$ [6]. The $1200\text{--}800\text{ cm}^{-1}$ range shows the PO_4 and P_2O_7 stretching modes. It could perhaps be a little specific by noting that the imperfectly strong bands near 4879243 cm^{-1} is attributed to the diphosphates ($\nu\text{P-O-P}$) groups [7]. The $550\text{--}3500\text{ cm}^{-1}$ range corresponds to the OH modes of HPO_4 groups characterized by two broad bands of weak intensity [7]. All the rest kinks at about 981 to 1498 cm^{-1} may be related to P-O-H, which may be brought by air moisture during the preparation of KBr pellets for IR measurements [8]

Eu^{3+} ions emit a characteristic yellow light with several narrow lines due to the $4f \rightarrow 4f$ ($^5\text{D}_0 \rightarrow ^7\text{F}_i=0,1,2,3,4$) transitions [9,10]. The luminescence spectrum of Eu^{3+} ion is slightly influenced by surrounding ligands of the host material because the transitions of Eu^{3+} involve only a redistribution of electrons within the inner $4f$ sub-shell [11]. Fluorescence spectra of Eu^{3+} doped NaCaPO_4 were measured at room temperature (Fig. 4 and 5), the following emission transitions are observed: $^5\text{D}_0 \rightarrow ^7\text{F}_2$ at 571 nm and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ at 594 nm between them, the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is the strongest.

Due to the magnetic dipole transitions $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and electric dipole transitions $^5\text{D}_0 \rightarrow ^7\text{F}_2$, this phosphor

exhibits yellow color emission [4]. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition should be relatively strong when the Eu^{3+} ions occupying version center sites, while the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition must be relatively weak. Also, according to Rambabu et al. [12] and Yu et al. [13], the transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ displayed more intensity than $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition due to the localized energy transfer. The intensity of these emission transitions are usually used to gauge the quality of the luminescent material. The highest intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition indicates that Eu^{3+} ions have Centro-symmetrical environment structure [4].

The transitions are found to be split into components depending on the host matrix composition. Due to the dependency between $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emissions and the crystal field, $^7\text{F}_1$ associated with one site symmetry can split into three Stark lines in the crystal field and the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} can split into, at most, five lines in the crystal field [14]. In our case, the photoluminescence excitation spectra of the prepared Eu activated NaCaPO_4 phosphor are shown in Fig. 4. The prominent excitation band at 362 nm may be due to the $f\text{--}f$ transitions of Eu^{3+} ion. The PL excitation spectrum is broad and maximizes at 362 nm in the LED phosphors excitation region. The PL emission spectrum ($\lambda_{\text{ex}} = 362\text{ nm}$) consists of the intense peak at 571 nm (yellow) that can be ascribed to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} ion and other peaks at 594 nm (red) which can be associated with the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, respectively of Eu^{3+} ion respectively. The 571 and 594 nm emission of Eu^{3+} ion in host of NaCaPO_4 material was very applicable as a yellow/red phosphor for the solid state lighting. The excitation of this phosphor is 362 nm is far away to Hg excitation as well as this excitation is main characteristic of solid state lighting (in the range $360\text{--}395\text{ nm}$ near UV region) in the lamp industry. The broadness of the excitation spectrum means that the phosphors can be well excited by near-ultraviolet light in the range $360\text{--}395\text{ nm}$, matching well with the emission bands of the near-UV LED chips [14]. The excitation spectra shows that these phosphors can be well excited by near UV-light which is exactly required by ultra-violet chip pumped multi-phosphor converted white LEDs. Therefore, this phosphor is one candidate of yellow /red phosphor for LED lighting.

The PL intensity increased with concentration from 0.3 mol.% to 0.5 mol.% and it decreased at more than 0.5 mol.% probably due to concentration quenching effect. For Eu^{3+} ion, the relative intensity of the 571 nm to the 594 nm peaks strongly depends on the local site symmetry around the Eu^{3+} ions. The PL intensity of

Eu^{3+} emission at 594 nm is less as compared to 571 nm peaks. The increase of PL emission intensity observed may be due to the decrease of cross-relaxation between Eu^{3+} ions (in this process, excited ion transfers only part of energy to another ion) in case of higher concentration of Eu^{3+}

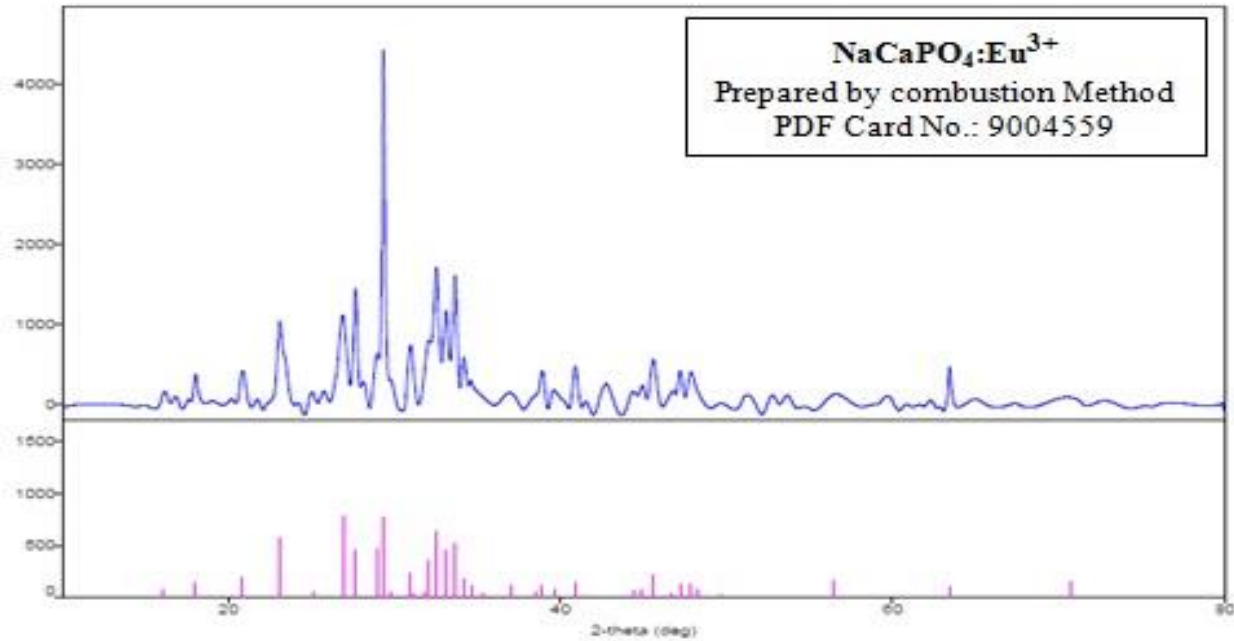


Fig 1: X-Ray Diffraction Pattern of $\text{NaCaPO}_4:\text{Eu}^{3+}$ synthesized at 700°C

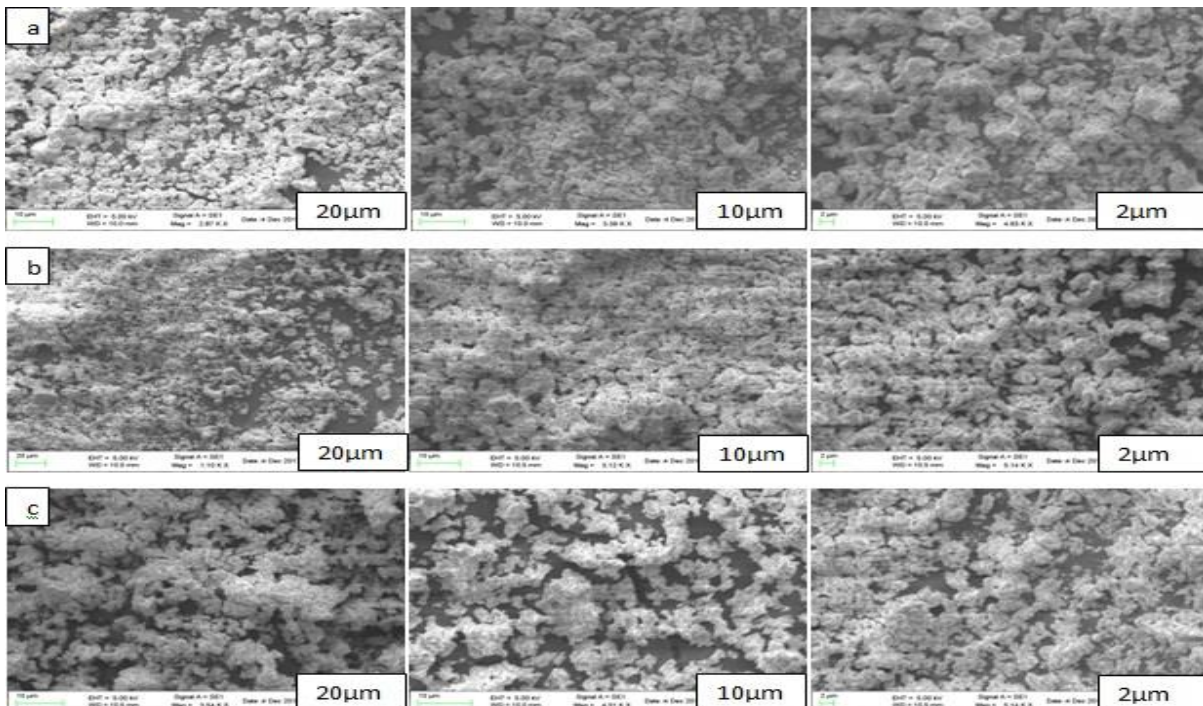


Fig 2: SEM images of the $\text{NaCa}_{1-x}\text{PO}_4:\text{Eu}_x$ powders with x (a) 0.3, (b) 0.5 and (c) 1.0

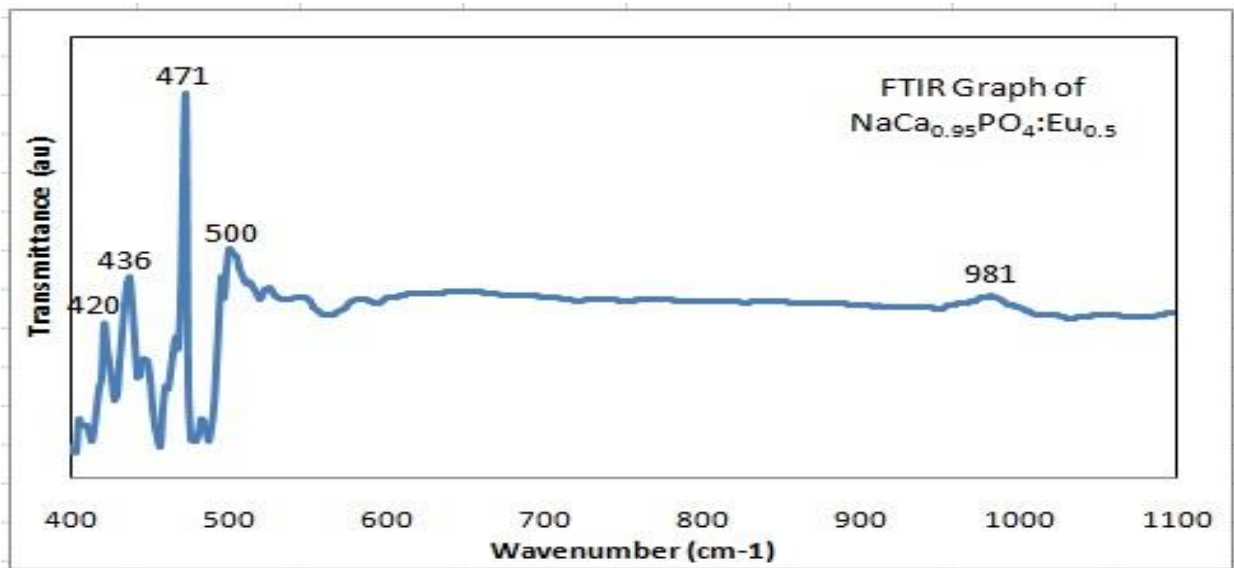


Fig 3: Fourier Transform Infrared Spectroscopy Graph of NaCaPO₄:Eu³⁺

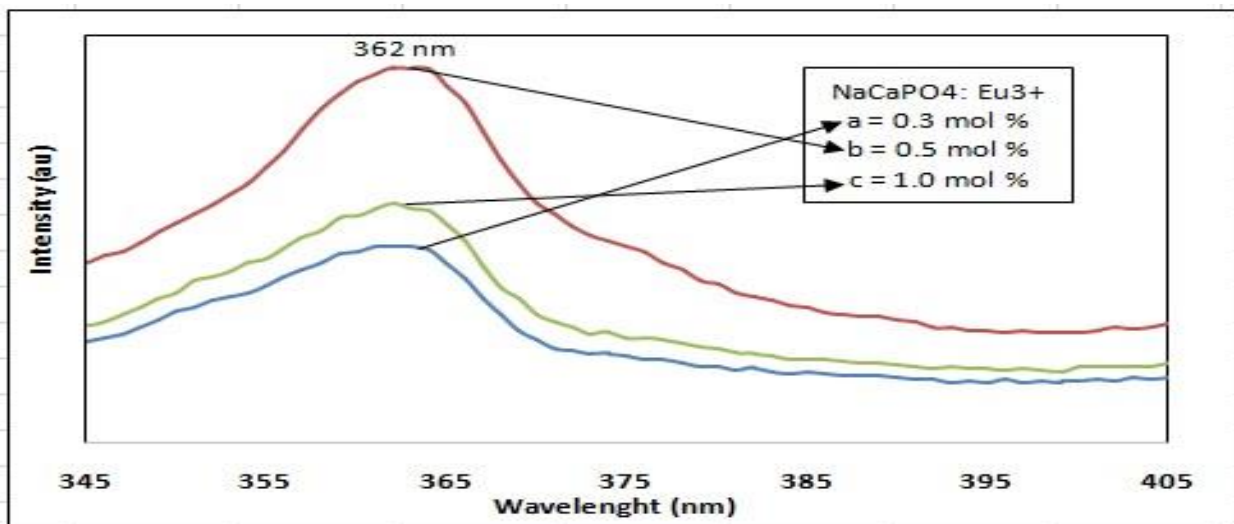


Fig 4: PL Excitation Spectrum of NaCaPO₄:Eu³⁺ Monitored at λ_{em} =571 nm and 594 nm

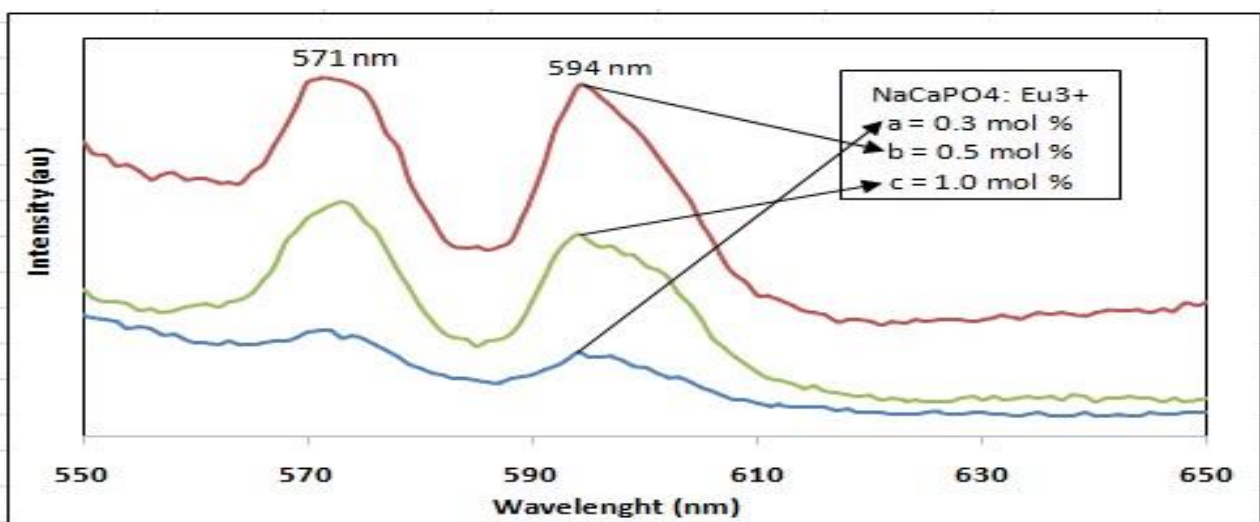


Fig 5: PL Emission Spectrum of NaCaPO₄:Eu³⁺ obtained under excitation λ_{ex} =362 nm

CONCLUSION

In this paper, sodium calcium phosphate doped with rare earth ion Eu^{3+} prepared by combustion method and confirmed by XRD was described. The photoluminescence characterization of prepared phosphors showed role of rare earth ion in the host lattice. The PL spectroscopic characterizations of the prepared phosphors were done using excitation and emission spectra. Eu activated NaCaPO_4 phosphor the emission spectrum shows a dominant peak at 571 nm (yellow) while other are at 594 nm (red) when excited at 362 nm. Eu^{3+} activated NaCaPO_4 phosphors showed the excitation in 362 nm. LED excitation and emission was observed in the yellow and red region of the spectrum. This result showed that the NaCaPO_4 : Eu^{3+} phosphors could be applicable for LED phosphors. This paper included synthesis of efficient phosphate based phosphors via combustion method, characterized by X-ray diffraction (XRD) pattern, morphological examination by SEM and photoluminescence behaviour of NaCaPO_4 doped with Eu^{3+} . Results showed that this phosphor had potential applications in the field of LED based lighting.

Conflicts of interest: The authors stated that no conflicts of interest.

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