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ORIGINAL RESEARCH ARTICLE

Study on structural and luminescence properties of Eu-doped CBP phosphors

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ABSTRACT

Europium (Eu) doped Calcium borophosphate (CBP) phosphors were synthesized via the solid-state diffusion method. The prepared Europium (Eu) doped Calcium borophosphate (CBP) powder was heated up to 600 °C for 6 h for a complete diffusion of ions in the powder system. XRD results showed that the prepared phosphors exhibit a well-crystallized hexagonal phase. The complete diffusion inside the CBP/Eu powder system has been confirmed by the presence of elements such as P, O, Bi, Ca, C, Eu, and B. Apart from that, the synthesized powder system has shown a down-conversion property where the Eu^{3+}-activated ion was excited at 251 nm. Under the excitation of 251 nm, CBP/Eu phosphor showed intense emissions peaking at 591,617, and 693 nm due to the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, and $^5D_0 \rightarrow {}^7F_4$ transition of Eu^{3+} ions. The obtained results suggest that the CBP/Eu phosphors have the potential for spectral response coating materials to improve photovoltaic (PV) panel efficiency.

Keywords: rare earth materials; phosphor; photoluminescence; europium (Eu); spectral response

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1. Introduction

Phosphors are known for their low effective atomic number, non-toxicity, and good fluorescent properties such as up-and-down conversion[1]. So far, a variety of phosphor materials have been explored and reported in phosphate, sulfate, oxides, nitride, oxynitride, vanadate, molybdate, borate, and silicate form Mehare et al.[2]. Among the types of phosphors, phosphate-based phosphors are established with outstanding properties such as ease of preparation, efficient luminescence output, and good thermal and chemical stability[3]. Rare earth elements (REE) are used as dopants, which exhibit excellent luminescence properties. Rare earth-activated phosphors are extremely efficient materials because of their outstanding luminescence properties as well as their environmental friendliness[4]. Luminescence occurs when sharp emission lines are exhibited from the ultraviolet (UV) or infrared (IR) region and transform to the visible region via 4f–4f and 4f–5d electronic transitions of rare earth ions (REIs)[5].

In recent times, many researchers have initiated the study of the luminescence properties of REI-doped phosphate-based phosphors as well as identified their potential applications. Because of its huge band gap, strong thermal and chemical stability, moderate phonon energies, and low sintering temperature, the phosphate group makes excellent host materials for luminescence[6]. The PL properties of Ho^{3+} and Pr^{3+}-doped CBP were recorded for potential green and red emission material applications[7]. Besides, the PL properties of Nd^{3+} and Er^{3+}-doped CBP were observed, which are expected to be used for green emission applications[8]. Another study is based on the enhancement of luminescent down-shifting of Eu-doped phosphors by incorporating plasmonic silver nanoparticles to improve the efficiency of silicon solar cells[9].

The luminescence properties of REIs are able to modify the wavelength of the solar spectrum to match the wavelength range of solar cells and improve the photoelectric conversion efficiency of the solar cells. Generally, spectral conversion is divided into two common types, such as up-conversion (Uc) and down-conversion (DC)[10]. The UC materials usually absorb low-energy (>800 nm) photons and convert them into one high-energy photon. However, DC materials are able to absorb high-energy photons (250 nm–500 nm) and transform them into two or more photons[11]. This causes the solar cells' spectral response to match the sunlight spectrum that is being incident upon them, greatly increasing the efficiency of silicon solar cells[4]. Among REEs, Europium (Eu) has a good energy level structure and exhibits high luminescence efficiency with high emission bands in the region from 550 to 750 nm[5,12]. Therefore, Eu is widely used as a dopant material to enhance the luminescence properties of phosphor materials for various applications[11].

The structural and luminescent characteristics of rare-earth-doped CBP hosts have not been extensively studied. In this work, CBP/Eu phosphors are synthesized by the solid-state reaction method. The purpose of this work is to report the targeted properties of Eu-doped CBP phosphors and check the suitability of the materials to develop spectral response coatings for solar cell applications. The incorporation of Eu and CBP as phosphor materials might be an advanced and novel material in the field of spectral response coating fabrication. The morphology, structural, and luminescence properties of Eu in the CBP host have not been reported so far, to the best of our knowledge. The structural and luminescence properties of Eu-doped CBP phosphor were investigated in this present work. XRD, SEM, and EDX characterized the synthesized CBP/Eu phosphor for structural and morphological studies. The emission and excitation of CBP/Eu phosphor were also studied in detail via the PL test. The present investigation explores the reported phosphor as a new candidate in the phosphor group.

2. Experimental work

2.1. Materials and preparation

The 1.0 mol% (Europium) Eu-doped calcium boro phosphate (CBP) phosphor with the formula ($2CaO$-B_2O_3-P_2O_5: 1.0% Eu) has been synthesized by using the solid-state reaction method[6]. Raw materials such as $CaCO_3$, H_3BO_3, $NH_4H_2PO_4$, and Eu_2O_3 have a purity of 99.99% and are used to prepare CBP/Eu phosphor powder. 10g of CBP/Eu powder was weighed and mixed together as mentioned in **Figure 1**. The powder mixture was ground using a hand grinder for 30 min. Then, the powder mixture was pressed into tablet shape using a manual hydraulic tablet machine at an applied pressure of 8 MPa. The prepared tablet was transferred into a porcelain crucible and then heated in a muffle furnace (Model: JSMF-30T) at 600 °C for 6 h to achieve complete diffusion of ions in the powder mixture. Finally, the CBP/Eu tablet was ground back to powder form before undergoing further characterization.

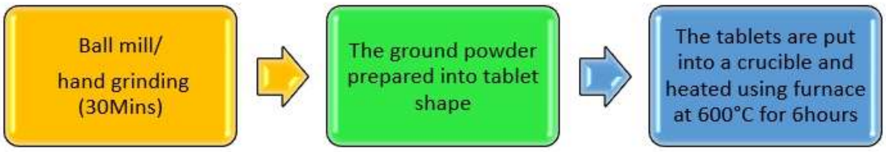

Figure 1. The flowchart of solid-state reaction method.

2.2. Characterization

The surface morphology of CBP/Eu has been analyzed using Scanning Electron Microscopy (Model: Tescan Vega3) at a magnification of 20 µm with EDX mapping. The EDX mapping is employed to detect the desired elements on the prepared CBP-doped Eu powder surface. The crystalline structure and diffraction phase of CBP/Eu phosphor were examined using powder X-ray diffraction (XRD) at the diffraction angle range of 20º–80º via the XPERT-PRO X-Ray Diffractometer. The synthesized Eu-doped CBP powder was characterized by the photoluminescence technique to identify luminescence properties. The photoluminescence excitation and emission spectra were recorded in the FP-8650 NIR Spectrofluorometer with a Xenon flash lamp (150 W).

3. Results and discussion

3.1. Crystallization phase of CBP/Eu powder

The structure and phase purity of the produced phosphors were investigated using the XRD technique. XRD patterns of 1.0 mol% Eu doped CBP phosphor were measured in the range from 20° to 80°, as shown in **Figure 2**. It was observed that the XRD pattern of the CBP/Eu powder sample matches well with standard diffraction JCPDS card No. 0-018-0283 since the position of all diffraction peaks is almost similar to standard diffraction data of the host material, CBP[5,7]. From the X-ray diffractogram, the sharp peaks indicate the crystalline phase at (110), (112), (104), (202), (006), (300), (112), and (206) at the diffraction angles of 24.32°, 29.9°, 32.75°, 35.54°, 38.26°, 46.64°, 49.21°, and 52.23°, respectively, as shown in **Table 1**. The strongest diffraction peak observed at 29.9° corresponds to the (112) plane. Hence, no secondary phases were observed with Eu^{3+} doped into CBP phosphors. This XRD result shows the pure crystalline phase of CBP/Eu powder, which indicates that the dopant material (Eu) insignificantly contributes to the original structure of CBP when incorporated with each other. It becomes clear from this that the addition of Eu^{3+} did not affect the phase or crystal structure of the host material, CBP.

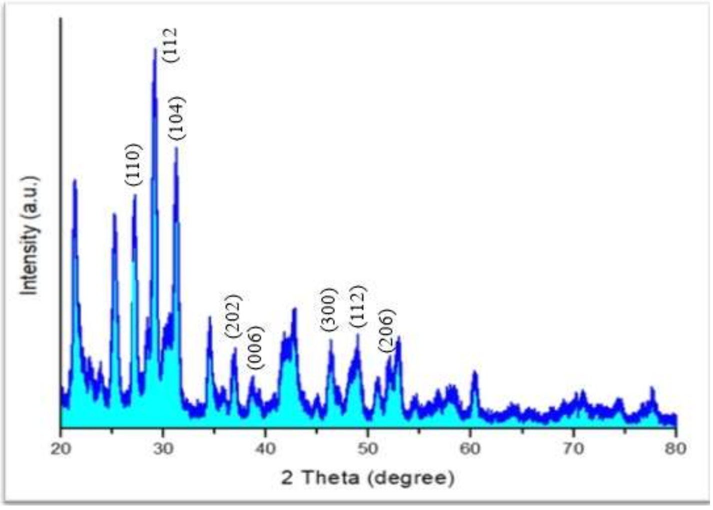

Figure 2. XRD profiles of Eu (1.0 mol %) doped CBP phosphors.

Table 1. XRD profile of Eu doped CBP phosphor.

Powder system	2θ (degree)	(hkl)
CBP/Eu	24.32	(110)
	29.91	(112)
	32.75	(104)
	35.54	(202)
	38.26	(006)
	46.64	(300)
	49.21	(112)
	52.23	(206)

3.2. Morphology and elemental analysis

The morphology of the prepared samples was examined by scanning electron microscopy (SEM). The morphology of CBP/Eu powder was examined under a magnification of 5 µm, as shown in **Figure 3**. From **Figure 3**, it has been observed that the particles of the synthesized powder system exhibit irregular shapes and inhomogeneous sizes due to the heterogeneous combination of phosphor powder and lanthanide particles. Since the luminescence properties of phosphors depend on particle size and crystallinity, the micro-sized particles of CBP/Eu powder could demonstrate the luminescence properties as verified in the photoluminescence analysis.

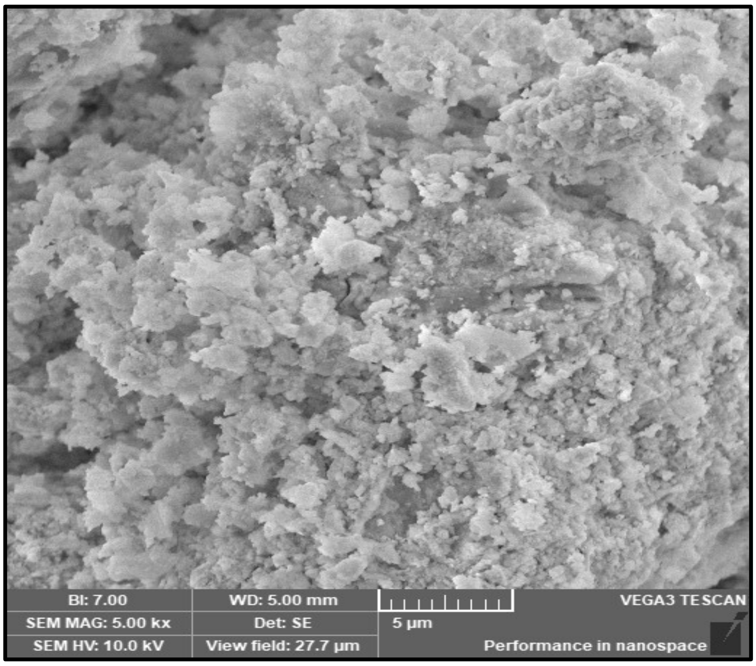

Figure 3. The surface morphology of CBP/Dy phosphors.

Figure 4 shows the quantitative analysis of elements based on the EDX result. The weight percentage (w%) of CBP/Eu was determined, and the data were recorded in **Table 2**. **Figures 4(a–h)** shows the corresponding elemental mapping profile of CBP/Eu phosphors, and the obtained results confirm the uniform distribution of constituent elements of the CBP/Dy. The O element has recorded the highest weight percentage (wt.%) of 31.47%, indicating the high composition of phosphate, PO_4, in the CBP/Eu. The Bi, C, Ca, P, B, and Eu elements exhibited around 25.86, 16.91, 10.80, 10.32, 3.92, and 0.72 wt.%, respectively. The weight percentage of Eu elements around 0.72 wt.% has shown the presence of the activator ion, Eu, that acts as a catalyst for photoluminescence properties.

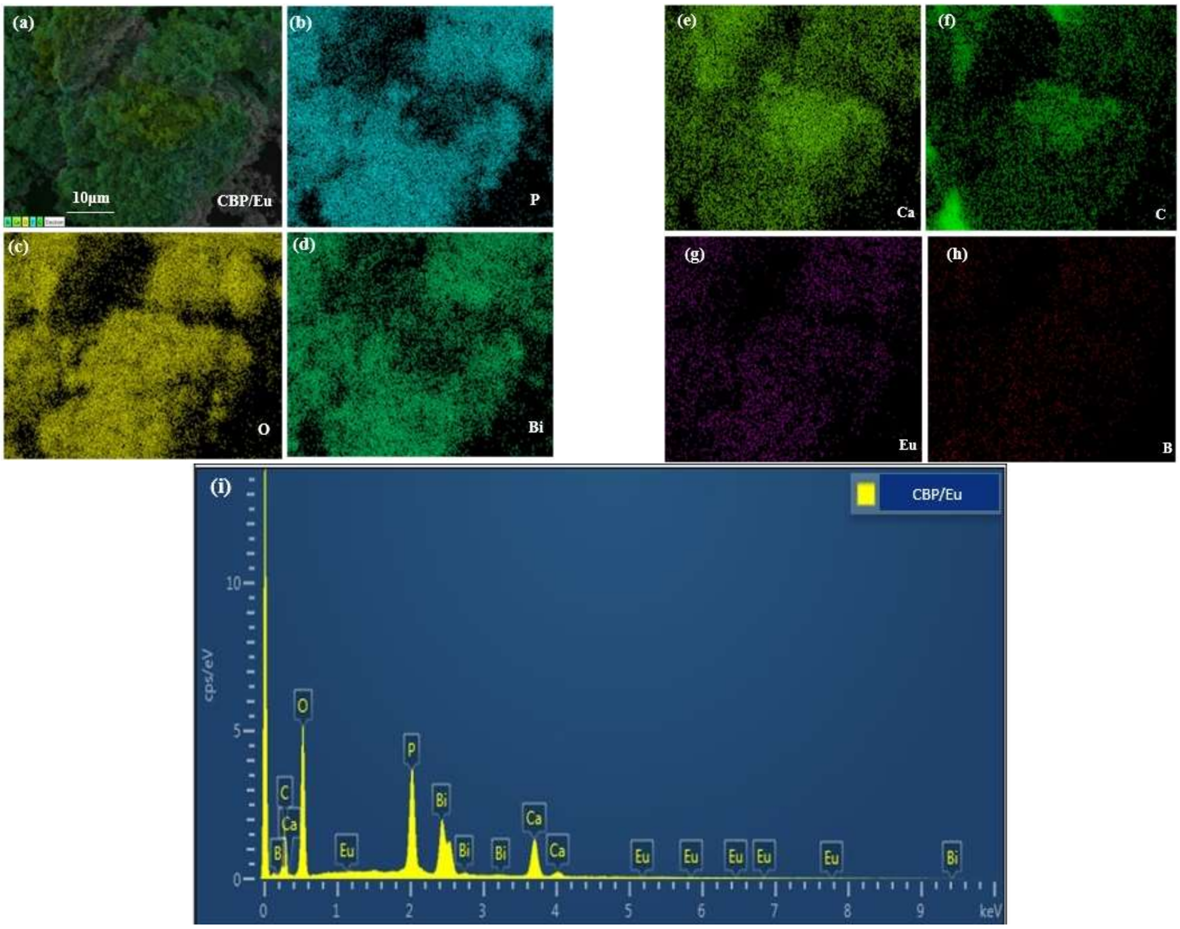

Figure 4. (a–h) elemental mapping profiles of CBP/Eu phosphor; **(i)** the EDX image of CBP/Eu phosphor.

The EDX spectra provided additional proof that the CBP/Eu phosphor contained the expected Ca, B, O, P, and Eu elements, as shown in **Figure 4(i)**. The EDX result did not provide information about any other peaks of impurity elements in the CBP/Eu powder sample, which gives more strength to the XRD analysis above. The details of the weight percentage of chemical elements in CBP/Eu are presented in **Table 2**.

Table 2. The weight percentage of chemical elements in CBP/Eu.

Elements	**(Wt%)**
Ca	10.80
C	16.91
O	31.47
B	3.92
P	10.32
Eu	0.72
Bi	25.86

3.3. Photoluminescence properties

The PL excitation spectra of $CaCO_3$: CBP were monitored at the 591 nm emission wavelength, as shown in **Figure 5**. The spectra contain an intense and broad excitation peak centered at 251 nm, corresponding to $O^{2-} \rightarrow Eu^{3+}$ transitioning electrons from the oxygen (2p state) to the Eu^{3+} (4f state), which is known for the charge transfer band (CTB), as shown in **Figure 6**[13,14]. The charge transfer band (CTB) excitation is the excitation through the energy transfer from the host lattice (CBP) to the activator (Eu) centre, Eu. The valence electrons move from the host anion to a partially filled orbital of the lanthanide ions. This transition forms a broad absorption in the UV region (200–350 nm). The CTB transition significantly improves the photoluminescence properties of phosphor materials due to broad absorption in the UV region. Therefore, better emission is obtained by charge transfer excitation[15].

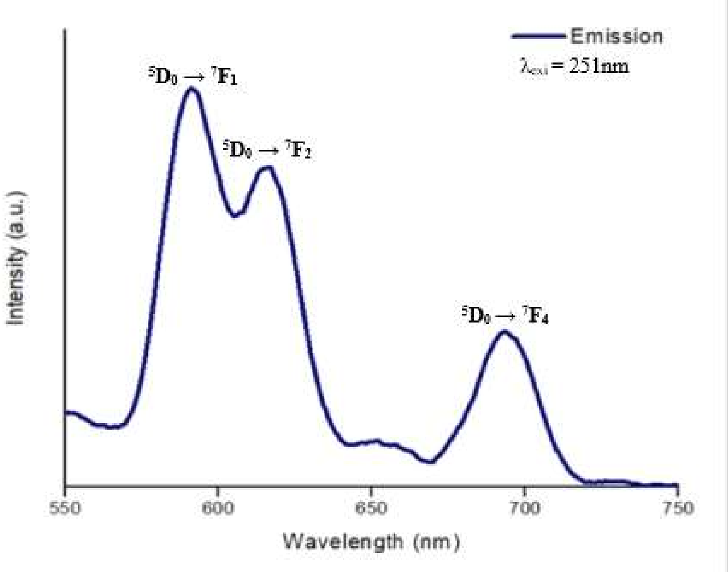

Figure 5. Emission spectrum of Eu (1.0 mol %) doped CBP phosphor.

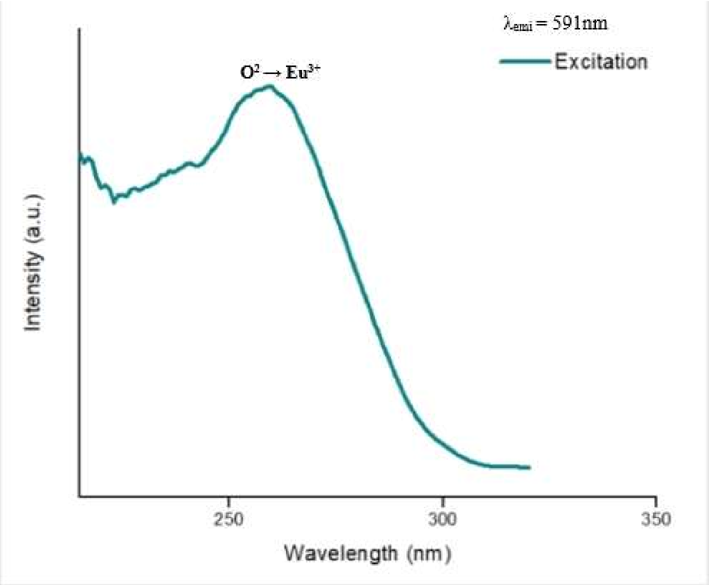

Figure 6. Excitation spectrum of Eu (1.0 mol %) doped CBP phosphor.

PL emission spectra of Eu-doped CBP were observed in the range of 550 to 750 nm on the excitation wavelength of 251 nm, as shown in **Figure 5**. The powder sample emits three emission peaks, which are observed at 591, 617, and 693 nm and were assigned to the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, and $^5D_0 \rightarrow {}^7F_4$ transitions of the Eu^{3+} ion respectively[13,14]. Among the three emission peaks, the PL intensity of the 591 nm emission peak is higher than the emission peaks at 617 and 693 nm. All these excitation and emission peaks are matched with the excitation and emission wavelengths corresponding to the transitions and energy levels of the Eu^{3+} ions. The $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions are assigned as magnetic dipole type and electric dipole type transitions respectively. It is generally known that the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition will predominate when Eu^{3+} ions occupy crystallographic sites with inversion symmetry, whereas the electric dipole $^5D_0 \rightarrow {}^7F_2$

transition will predominate when Eu^{3+} ions occupy sites without inversion symmetry. The obtained data gives information about the asymmetrical nature of the prepared powder sample[5].

Apart from that, the excitation peak is monitored in a spectral range from 230 nm to 330 nm where the region is in the UV range, while emission peaks are observed in a spectral range from 550 nm to 750 nm where the region belongs to the visible range. **Figure 7** illustrates the energy transfer process of Eu^{3+} ions in CBP/Eu. The transfer process of Eu^{3+} ions has shown the suitability of CBP/Eu powder as the host lattice to transform high-energy spectra/photons into low-energy spectra/photons. The down-conversion process occurs when the rare earth ions modify the incident short-wavelength photon and then emit two or more long-wavelength photons via the photoluminescence process. So it is proven that Eu-doped CBP phosphor material is able to absorb photons in the UV range and emit them in the visible region by transforming their energy and wavelength.

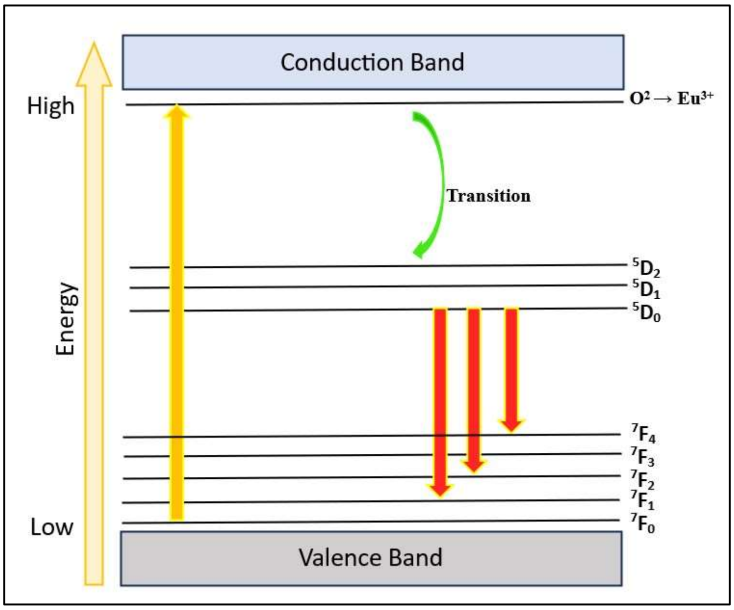

Figure 7. The schematic energy level diagram and energy transfer process of Eu^{3+} ions in CBP/Eu.

Therefore, CBP/Eu has the potential to be used as a filler in a polymer binder in order to synthesize a spectral response coating. Since CBP/Eu powder has the potential to absorb more photons via photoluminescence, this will help to overcome the low-efficiency issue in solar cells due to spectral mismatch. CBP/Eu phosphor modifies the energy of absorbed photons and then matches them with the energy band gap of the solar cell (1.1 eV) via the photoluminescence process. In conclusion, when more photons are absorbed by the solar cell, more electrical energy can be converted; hence, the efficiency is improved.

4. Conclusion

CBP/Eu phosphor powder is prepared by the solid-state reaction method. The XRD result of Eu-doped CBP exhibits well-crystallized hexagonal symmetry. The SEM image shows a morphology with irregular particle shapes due to Eu ion incorporation. The PL spectrum represents broad excitation and broad emission spectra. PL excitation spectra were observed in the range of 250 nm to 450 nm under the 591 nm emission wavelength due to the $O^2 \rightarrow Eu^{3+}$ transition of the Eu^{3+} ion. PL emission spectra were observed in the range of 550 nm to 750 nm under 251 nm excitation spectra due to the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, and $^5D_0 \rightarrow {}^7F_4$ transitions of Eu^{3+} ion. The synthesized Eu-doped CBP phosphors demonstrate excellent photoluminescence characteristics and exhibit down-conversion features. Therefore, Eu-doped phosphor may be a promising candidate for spectral response material to enhance the efficiency of solar cells. According to the above results, the Eu^{3+} ion-activated CBP phosphor is an environmentally friendly, UV-excited, efficient luminescent material and has good potential for use as a UV-to-visible converter in solar cell applications.

Author contributions

Conceptualization, KKK and ASBAJ; methodology, SJD; validation, RS, RK and VB; formal analysis, KKK; investigation, KKK; resources, YST and AKP; data curation, KKK and ASBAJ; writing—original draft preparation, KKK; writing—review and editing, ASBAJ, RS and RK; visualization, ASBAJ; supervision, VB; project administration, VB and ASBAJ; funding acquisition, NAR. All authors have read and agreed to the published version of the manuscript.

Conflict of interest

The authors do not have any conflict of interest.

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