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Influence of Calcination Temperature on Crystal Growth and Optical Characteristics of Eu$^{3+}$ Doped ZnO/Zn$_2$SiO$_4$ Composites Fabricated via Simple Thermal Treatment Method

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Abstract: This research paper proposes the usage of a simple thermal treatment method to synthesis the pure and Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ based composites which undergo calcination process at different temperatures. The effect of calcination temperatures on the structural, morphological, and optical properties of ZnO/Zn$_2$SiO$_4$ based composites have been studied. The XRD analysis shows the existence of two major phases which are ZnO and Zn$_2$SiO$_4$ crystals and supported by the finding in the FT-IR. The FESEM micrograph further confirms the existence of both ZnO and Zn$_2$SiO$_4$ crystal phases, with progress in the calcination temperature around 700–800 °C which affects the existence of the necking-like shape particle. Absorption humps discovered through UV-Vis spectroscopy revealed that at the higher calcination temperature effects for higher absorption intensity while absorption bands can be seen at below 400 nm with dropping of absorption bands at 370–375 nm. Two types of band gap can be seen from the energy band gap analysis which occurs from ZnO crystal and Zn$_2$SiO$_4$ crystal progress. It is also discovered that for Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ composites, the Zn$_2$SiO$_4$ crystal (5.11–4.71 eV) has a higher band gap compared to the ZnO crystal (3.271–4.07 eV). While, for the photoluminescence study, excited at 400 nm, the emission spectra of Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ revealed higher emission intensity compared to pure ZnO/Zn$_2$SiO$_4$ with higher calcination temperature exhibit higher emission intensity at 615 nm with 700 °C being the optimum temperature. The emission spectra also show that the calcination temperature contributed to enhancing the emission intensity.

Keywords: thermal treatment; ZnO; Zn$_2$SiO$_4$; europium ion; composite

1. Introduction

For the past decades, there has been a lot of studies regarding the luminescence material for the optical-electronic industry [1]. Luminescent materials such as phosphors are the substances that emit light in the electromagnetic waves (EM) spectrum after the conversion of the absorbed energy from an energy source. These materials may be classified according to the wide range of excitation energy sources and excitation trigger [2–4]. Essentially, photoluminescence is a phenomenon where the emission of light happens when a material for the optical-electronic industry [1] is excited by short-wavelength light, usually ultraviolet (UV) light or visible light [5]. Among many types of phosphors research, zinc silicate (Zn$_2$SiO$_4$) doped transition metal ions, as well as rare-earth ions have been one of the most popular host materials [6–8]. These numerous interests in zinc silicate phosphor also due to their interesting properties, having
good thermal and chemical stability [9], excel in water resistance with better resistance to nuclear radiation [10]. Zinc silicate also exhibits excellent luminescence properties when homogenously grows with an inorganic oxide crystal [11–15].

In this work, zinc oxide (ZnO) crystal has been chosen as a crystal to be grown with zinc silicate (Zn$_2$SiO$_4$) crystal due to its ability to develop semiconductor material with huge direct transition allowed optical band gap energy (3.37 eV) [16] as well as high exciton binding energy (more than 60 meV) [17] added with exceptionally good thermal and chemical stability [18]. Therefore, ZnO crystal can be a proper application as a phosphor host in light-emitting diodes [19]. Several studies have been reported on the fabrication of ZnO/Zn$_2$SiO$_4$. The solid-state reaction had been used to fabricate ZnO/Zn$_2$SiO$_4$ [20] with the fabricated sample showed broader visible range emissions compared to Zn$_2$SiO$_4$ and ZnO. Fabrication of ZnO/Zn$_2$SiO$_4$ doped Eu$^{3+}$ by sol–gel spin coating technique has also been reported [21]. PL study showed that the highest emission spectra obtained is around 610 nm which is at the red region due to the existence of Eu$^{3+}$ ions in the sample and the emission intensity increased with the increment of calcination temperature. Recently, the Eu$^{3+}$ ions are widely used as an energetic luminescent ion for the reason of its main sharp red emission at 615 nm, which results from the hypersensitive ($^5D_0 \to ^7F_2$) electronic dipole transition [22].

To fabricate pure and doped zinc silicate-based phosphor, various methods and techniques have been conducted. However, most of the fabrication techniques including solid-state reaction [23], sol–gel [24], and chemical methods [25] are hard to be utilized due to the high production cost. In addition, these methods are usually required high production energy with complex synthesis experimental techniques and often require long preparation time as well as a potentially environmental-harmful by-product. Hence, a novel developed simple reaction method has been applied to prepare Eu$^{3+}$ doped Zn$_2$SiO$_4$/ZnO composite due to the material handling simplicity, low energy consumption, and environmentally friendly [26]. The simple thermal treatment method has been used for the past few years to synthesis zinc selenide [27], (CuO)$_{0.6}$(CeO$_2$)$_{0.4}$ [28], nickel ferrite nanocrystals [29], zinc oxide [30,31], and amorphous silica [32]. A simple thermal treatment method has also been used to fabricate ZnO-SiO$_2$ [33] and Zn$_2$SiO$_4$ by impregnating ZnO with amorphous SiO$_2$ [34].

The main objective of this research work is to study the effect of different calcination temperatures on morphological, optical, and photoluminescence properties of undoped and Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ composite synthesized via a simple thermal treatment method. The crystal growth, phase transformation, and microstructure of the composite samples were evaluated using XRD, FTIR, and FESEM micrograph. UV-visible absorbance and PL spectroscopy were used to evaluate the optical and photoluminescence properties of the composite samples. The excellent results in optical properties shown that the new composite samples can be proposed to be used as a red phosphor in optoelectronic applications. The novelty of this work is the usage of a new simple thermal treatment method to synthesis ZnO/Zn$_2$SiO$_4$ and the introduction of Eu$^{3+}$ ion as doping in the system.

2. Materials and Methods
2.1. Preparation of ZnO/Zn$_2$SiO$_4$ Composite

To produce ZnO/Zn$_2$SiO$_4$ based composites, the starting materials such as zinc acetate dihydrate as well as silicon tetraacetate was used as the precursors. The polyvinyl pyrrolidone (PVP) was added to the solution as the capping agent, for the purpose to reduce agglomeration and stabilize the composite particles. In this work, europium (III) acetate hydrate was used as a dopant. All the chemicals used were from Sigma Aldrich with 99.9% purity. Deionized water was used as a solvent. Firstly, 0.1 mmol (0.21951 g) of zinc acetate dihydrate (zinc source) followed by 0.1 mmol (0.26426 g) of silicon tetraacetate (silicon source) were added into an aqueous solution of 100 mL of deionized water. Next, 4 g of poly(vinyl) pyrrolidone (capping agent) was added to the solution. Then, 1 mol.% (0.003291 g) of europium (III) acetate hydrate which acts as the dopant was then added into
the solution and left for stirring for 2 h with the temperature of 80 °C to ensure the mixing of the solution [35]. The solution was then poured into petri dishes and left for drying in the oven at 120 °C for 24 h. After the drying process, the deposited residue which is yellow in colour at the wall of the dishes was scraped using a spatula and crushed into powder using pestle and mortar before heat-treated at different calcination temperatures; 600 °C, 700 °C, and 800 °C for 3 h.

2.2. Characterization

In this study, the undoped and Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ samples undergo different analyses for structural, morphological, and optical properties of the samples. By employing X-ray diffraction (XRD) as well as Fourier-transform infrared spectroscopy (FTIR), structural properties of Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ could be studied. The selected range of 2θ angles (degree) for the XRD analysis was specified within a Bragg angle (20°–80°). The crystalline phase of the samples was analyzed by utilizing the XRD machine from (Philips, Model: PW 3040/60 MPD XPERT PRO PANalytical, Philips, Almelo, The Netherlands), with copper, Cu K$_\alpha$ radiation at 40 kV and 30 mA of the input current. The results were then examined using PANalytical X’Pert High Score software (PANalytical, Malvern, UK). While, for FTIR, these samples were analyzed using an FTIR spectrometer (Thermo Nicolet, Model: Nicolet 6700, Waltham, MA, USA) in the wavenumber range 200–4000 cm$^{-1}$. Field emission scanning electron microscopy (FESEM) was used to study the morphological behavior of Eu$^{3+}$ doped ZnO-Zn$_2$SiO$_4$ samples. The specified properties of samples were viewed using (FEI, Model: Nova NanoSEM 230, Hillsboro, OR, USA) with 5 kV acceleration voltage. The gold coating was applied on top of the samples to prevent the charging effect from non-conductive specimens, with gold or platinum are usually chosen due to their thermal stability and the ability for a thin layer to form on the surface of the specimen.

For optical properties, ultraviolet-visible spectroscopy (UV-vis), band gap analysis, and photoluminescence (PL) analysis were used to analyze the Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ samples. In this study, the absorbance of UV radiation was obtained through the diffuse reflectance technique using the UV/Vis/NIR spectrophotometer (SHIMADZU, Model: UV-3600, Kyoto, Japan). For optical band gap analysis, the model used was the Kubelka–Munk function which was proposed in 1931 by Kubelka and Munk [36]. By applying the Kubelka–Munk function, the measured reflectance spectra can be transformed to the corresponding absorption spectra as followed [37]:

$$F(R_\infty) = \frac{\alpha}{s} = \frac{(1 - R_\infty)^2}{2R_\infty},$$

where $R_\infty = \frac{R_{\text{sample}}}{R_{\text{standard}}}$ is the reflectance of an infinitely thick specimen, while $\alpha$ and $s$ represent the absorption and scattering coefficients, respectively. Thus, the equation above could become

$$(F(R_\infty)\cdot hv)^{\frac{1}{\gamma}} = B(hv - E_g),$$

where $h$ represents the Planck constant, $\nu$ represents the photon’s frequency, $E_g$ represents the optical band gap energy, and $B$ represents the energy constant. The $\gamma$ factor depends on the nature of the electron transition [38]. While for photoluminescence properties, the pure and Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ based composites were analyzed using the photoluminescence spectrometer (PERKIN ELMER, Model: LS 55, Waltham, MA, USA). 350 nm was chosen as the excitation wavelength to study the effect of different calcination temperatures on photoluminescence properties of undoped samples while for Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ based composites, 400 nm was chosen as the excitation wavelength.

3. Results and Discussion

3.1. X-ray Diffraction (XRD) Analysis

To study the crystalline substances present, the XRD test has been carried on the samples. Figure 1 shows the XRD finding of silicon tetraacetate, Si source for the samples.
The broad spectrum and absence of peaks indicates that the silicon tetraacetate is in an amorphous state. Figure 1 also shows the XRD peak of zinc acetate which acts as the Zn source for the samples. The peaks available propose the existence of ZnO crystals in zinc acetate. Figure 1 also presents ZnO/Zn$_2$SiO$_4$ samples spectrum which undergoes a calcination process with different temperatures; 600 °C, 700 °C, and 800 °C for 3 h. As can be seen from the graph, the pattern from 600 °C calcination temperature exhibits a handful of sharp peaks which suggest the crystallinity of the ZnO peaks which present the existence of ZnO element in the samples. This corresponds with the findings from the previous study [25].

![Figure 1. XRD spectrum of ZnO/Zn$_2$SiO$_4$ sample calcined at various temperatures for 3 h.](image)

The existence of the Zn$_2$SiO$_4$ crystal peak can also be discovered at around 31.5° which shows the formation of Zn$_2$SiO$_4$ as ZnO and SiO$_2$ fused during the calcination process. While the XRD spectra of samples heat-treated at 700 °C show the diffraction patterns which belong to zinc silicate (Zn$_2$SiO$_4$) phases (JCPDS No. 37-1485) at 25°, 28°, 31.5°, 48°, and 56°. Several phases containing ZnO (JCPDS No. 36-1451) also can be seen in the spectra at 32°, 34°, 36.5°, 53°, 63°, and 68.5°. SiO$_2$ peaks at 24.5° and 28.7° are low and can almost be neglected. At this calcination temperature, the intensity of the ZnO peak at 36.5° is higher than the Zn$_2$SiO$_4$ peak at 31.5°. It is also found that at this calcination temperature, the number of ZnO peaks decreased while the amount of Zn$_2$SiO$_4$ peaks increased compared to the lower temperature. This is due to the higher energy provided during the calcination process which led to high surface mobility of Zn and Si ions for the formation of Zn$_2$SiO$_4$ in the samples [39]. As the calcination temperature progressed further...
to 800 °C, the intensity of the Zn$_2$SiO$_4$ peaks at 28° and 31.5° increased which indicates that the increment of calcination temperatures will affect better crystallization process which will also lead to the increment of the diffraction peak intensity [40–42]. By further observing the graph, the diffraction peak sharpness tends to increase with the increment of calcination temperatures with the full width at half maxima (FWHM) value become lower which decrease from 0.2273 to 0.1624. Usually smaller FWHM means the progress of larger particle size. This is because the enhancement of the crystallization process in the samples will leads to a sharper diffraction peak. Based on the previous report, the rate of ions diffusion in the samples increases at higher calcination temperature which accelerates the crystal’s growth rate and produces larger crystals size in the samples [43]. From Figure 2, not many differences can be seen in the spectrum pattern of the Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ as compared to the undoped spectrum. However, at the calcination temperature of 700 °C, the intensity of the Zn$_2$SiO$_4$ peak at 31.5° is higher than the ZnO peak at 36.5°. This shows that at this temperature, the addition of Eu$^{3+}$ in the sample may help for the formation of Zn$_2$SiO$_4$ in the samples; however, further increasing the calcination temperature may affect the diffraction peak of Zn$_2$SiO$_4$ to become lower due to the possibility of lattice distortion in the structural system in the samples [44]. From Figure 2, it is also observed that there are no Eu$_2$O$_3$ peaks or any other peak besides ZnO and Zn$_2$SiO$_4$ can be seen in the graph indicated that the dopant was well dissolved in the ZnO/Zn$_2$SiO$_4$ crystal lattice.

![Figure 2. XRD spectrum of Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ composites calcined at different temperatures for 3 h.](image-url)
3.2. Fourier Transform Infrared (FT–IR) Spectroscopy

To study the functional group and the phase composition of the ZnO/Zn$_2$SiO$_4$ samples after the calcination process, FT-IR spectroscopy was used. Figures 3 and 4 below show the spectra for the functional group and phase composition of the undoped and Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ based composites respectively, which undergo different calcination temperatures which are 600, 700, and 800 °C for 3 h. The main peaks of the compounds in the spectra fall in the frequency range of 400–2500 cm$^{-1}$. Essentially, both figures show the same pattern where, the spectrum display absorption peaks at 462, 500, 580, 620, 700, 802, 884, 989, 1002, and 1100 cm$^{-1}$. The absorption peak at a wavenumber of 462, 500, and 580 cm$^{-1}$ indicated the symmetric stretching vibration of the ZnO$_4$ group [21,38,41,45]. Absorption peaks present at 620 and 700 cm$^{-1}$ ascribed to the ZnO$_4$ asymmetric stretching and SiO torsional vibrations whereas peaks at 812 and 884 cm$^{-1}$ were assigned to the SiO$_4$ symmetric stretching vibration [21,38,41,42,45,46]. The absorption peak around 989 cm$^{-1}$ was assigned to the SiO$_4$ asymmetric stretching vibration [15,45,47]. The existence of the vibrations of SiO$_4$ and ZnO$_4$ groups being evidence of the formation of the Zn$_2$SiO$_4$ phase [47–49]. The vibrational band observed at 1110 cm$^{-1}$ ascribed to the Si-O-Si asymmetric stretching vibrations [15,20]. From the Figures 3 and 4, it is found that the increment in the absorption peak intensity at 580 cm$^{-1}$ which implied the enhancement of ZnO$_4$ group unit by replacing the Si atoms [48]. Next, from the same figures, the dropping in the peak intensity at 620 and 1110 cm$^{-1}$ can be seen which indicates the decrement of the asymmetrical stretching of ZnO$_4$ and Si-O-Si due to the breaking of ZnO$_4$ and Si-O-Si bonds during the formation of Zn$_2$SiO$_4$ [49]. Table 1 further simplified the absorption band and the corresponding assignment band of the ZnO/Zn$_2$SiO$_4$ composites. The absence of the peaks in the range of 2000–2500 cm$^{-1}$ in the spectrum indicates that there are no C-O mode and C=H stretching mode of organic sources [29]. With the increase in the calcination temperature, the spectrum shifts slightly to the lower wavelength in the vibrational bands which favors ZnO/Zn$_2$SiO$_4$ composites crystallization and formation [45]. The addition of Eu$^{3+}$ in the sample may not affect much to the pattern, as a similar pattern can be seen for both figures.

![Figure 3. FT-IR spectra of ZnO/Zn$_2$SiO$_4$ composites calcined at different temperatures (°C) for 3 h.](image-url)
Table 1. FT-IR absorption bands and the corresponding assignment bands of ZnO/Zn$_2$SiO$_4$ composites.

| Wavenumber (cm$^{-1}$) | Assignment of Vibrational Mode                        | Reference(s)       |
|-----------------------|-------------------------------------------------------|---------------------|
| 462–580               | ZnO$_4$ symmetric stretching vibration                 | [21,38,41]          |
| 620                   | ZnO$_4$ asymmetric stretching vibration                 | [21,41,42,46]       |
| 700                   | SiO torsional vibrations                               | [41]                |
| 812–884               | SiO$_4$ symmetric stretching vibration                  | [38,42,45–47]       |
| 989                   | SiO$_4$ asymmetric stretching vibration                 | [15,45,47]          |
| 1100                  | Si-O-Si asymmetric stretching vibration                 | [15,20]             |

3.3. Field Emission Scanning Electron Microscope (FESEM) Analysis

To understand the characteristics of the surface morphology and elemental composition of ZnO/Zn$_2$SiO$_4$ based composites, FESEM analysis has been done. Below are the figures for FESEM images of pure and Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ based composites heat-treated at various calcination temperatures at 3 h holding time. Figure 5a shows the separated tiny particles in the structure in the sample at 600 °C of calcination temperature. As the calcination temperature increased, the surface energy in the samples also tends to become higher which caused smaller particles to fuse with the neighboring particles thus, forming larger crystallite sizes [50–52]. From Figure 5c, the existence of several necking-like shape particles can be seen in the sample with 800 °C calcination temperature. For Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ based composites, a similar pattern can be seen. As the calcination temperature progresses further to 800 °C, a lot of dumbbell-like structures can be seen with a higher particle size as in Figure 5f. This is maybe due to the effect of the agglomeration of neighboring particles by further increasing the calcination temperature which will enhance the diffusion between particles by melting their surfaces, thus forming the dumbbell-like structure in the sample [25].

3.4. Ultraviolet-Visible Spectroscopy (UV-Vis)

The effects of calcination temperatures on the optical properties, specifically the light absorption characteristic of ZnO/Zn$_2$SiO$_4$ samples has been studied by undergoing the Ultraviolet-visible spectroscopy (UV-vis) in the UV-visible range of 250–800 nm. The below figures show the absorption spectrum of pure and Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ based composites undergo different calcination temperatures, which are 600 °C, 700 °C, and
800 °C for 3 h. Figure 6 shows the absorption spectra of undoped ZnO/Zn$_2$SiO$_4$ with different calcination temperatures for 3 h. From the graph, it is observed that undoped ZnO/Zn$_2$SiO$_4$ has an absorption band of below 400 nm with higher calcination temperature contributed to higher absorption intensity. This happened due to the scattering of Zn$_2$SiO$_4$ crystals in the samples [53,54]. The absorption bands displayed the red-shift pattern due to the process of crystallization during the calcination process. Dropping of absorption edge also can be seen around 370 nm, which due to the possibility of ZnO structure collapse thus formed the Zn$_2$SiO$_4$ structure [54]. By observing Figure 7, the absorption spectrum of Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ shows quite a similar pattern to those of undoped samples, with an absorption band of below 400 nm. The absorption spectrum of the doped ZnO/Zn$_2$SiO$_4$ shows that the absorption band is having red-shift as the calcination temperature increased, due to the enhancement of crystallization in the samples which also show that the absorption edge has been enhanced. The UV-vis spectrum of Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ also show the pattern of higher calcination temperature affect to higher absorption intensity, due to the scattering of Zn$_2$SiO$_4$ crystals in the samples while, the dropping of absorption edge can be seen at around 375 nm, thanks to the reason of ZnO structure collapse which formed the Zn$_2$SiO$_4$ structure, as associated with XRD findings.

![FESEM images of ZnO/Zn$_2$SiO$_4$ calcined for 3 h.](image)

**Figure 5.** FESEM images of ZnO/Zn$_2$SiO$_4$ calcined for 3 h with (a) 0% Eu$^{3+}$ at 600 °C, (b) 0% Eu$^{3+}$ at 700 °C, (c) 0% Eu$^{3+}$ at 800 °C, (d) 1% Eu$^{3+}$ at 600 °C, (e) 1% Eu$^{3+}$ at 700 °C, (f) 1% Eu$^{3+}$ at 800 °C.

### 3.5. Optical Band Gap Analysis

The effect of calcination temperature on the optical band gap energy ($E_g$) of ZnO/Zn$_2$SiO$_4$ synthesized between 600 and 800 °C was determined by applying the Kubelka-Munk function using diffuse reflectance technique. The $\gamma$ factor value used is $\gamma = 1/2$, which is a direct allowed transition. The figures below show the optical band gap spectra of pure and Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ based composites undergo different calcination temperatures which are 600, 700, and 800 °C for 3 h. Essentially, two different band gap values were observed and calculated for each ZnO/Zn$_2$SiO$_4$ composite sample. This is due to the existence of two phases in the composite, which is the ZnO phase and Zn$_2$SiO$_4$ crystal phase, under XRD and FESEM findings.
temperature affect to higher absorption intensity, due to the scattering of Zn$_2$SiO$_4$ crystals.

3.5. Optical Band Gap Analysis

Figure 7. UV-vis absorption spectra of Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ composites calcined at different temperatures (°C) for 3 h.

From Figure 8, the direct energy band gap value of the undoped ZnO/Zn$_2$SiO$_4$ observed by extrapolating the linear portion of the optical absorption plot is between 3.21 and 3.17 eV for ZnO crystal and 5.21 to 4.09 eV for Zn$_2$SiO$_4$ crystal which are tabulated in Table 2. It is observed that for both the crystals phase, the optical band gap value produced is decreasing with the increment of calcination temperature. This is due to the reason of ZnO structure collapse which formed the Zn$_2$SiO$_4$ structure, as the calcination temperature increased. This is maybe due to the possibility of ZnO crystals became deteriorated as the calcination temperature became higher [56]. However, the energy band gap value of Zn$_2$SiO$_4$ crystal is decreasing (5.11–4.71 eV) as the calcination temperature increases. This is caused by the crystallization process that occurred in the
The effect of calcination temperature on the optical band gap... at different temperatures (°C) for 3 h.

Figure 8. Plot of $(F(R_\infty)h\nu)^2$ against $h\nu$ of ZnO/Zn$_2$SiO$_4$ composites calcined at different temperatures (°C) for 3 h.

Table 2. Optical band gap energy $(E_g)$ value for undoped and Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ composites.

| Sample       | Calcination Temperature (°C) | ZnO $E_g$ (eV) | Zn$_2$SiO$_4$ $E_g$ (eV) |
|--------------|-------------------------------|----------------|--------------------------|
| undoped      | 600 °C                        | 3.21           | 5.21                     |
| undoped      | 700 °C                        | 3.19           | 5.18                     |
| undoped      | 800 °C                        | 3.17           | 5.09                     |
| Eu$^{3+}$ doped | 600 °C                        | 3.27           | 5.11                     |
| Eu$^{3+}$ doped | 700 °C                        | 3.68           | 4.93                     |
| Eu$^{3+}$ doped | 800 °C                        | 4.07           | 4.71                     |

Figure 9. Plot of $(F(R_\infty)h\nu)^2$ against $h\nu$ of Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ composites calcined at different temperatures (°C) for 3 h.
3.6. Photoluminescence (PL) Analysis

PL analysis was done to study and understand the photoluminescence properties of undoped and Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ composite samples. The measured emission spectra of the ZnO/Zn$_2$SiO$_4$ samples are between 450 and 700 nm. Figure 10 shows the emission spectra of undoped ZnO/Zn$_2$SiO$_4$ based composites excited under 350 nm while Figure 11 shows Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ samples excited under 400 nm [57]. From Figure 10, several emission peaks can be seen at 460, 485, and 575 nm which are associated with violet-blue, blue, and green regions, respectively. The emission peak at around 460 nm is indicated to the transition of an electron from Zn interstitial to the valence band and from conduction band to oxygen defects in the region of violet-blue and commonly referred to as blue emission while at the emission wavelength of 485 nm, the peak is associated to the zinc interstitials [57,58]. Located within the green region, the emission peak of 575 nm was associated with the transition of electrons between the valence band and conduction band [56]. From the same figures, it is also observed that as the calcination temperature increases from 600 °C to 700 °C, the emission peaks also increases. This is due to the enhancement of the crystal quality in the material [59].

![Figure 10. Photoluminescence (PL) spectra of ZnO/Zn$_2$SiO$_4$ composites calcined at different temperatures (°C) for 3 h.](image)

![Figure 11. PL spectra of Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ composites calcined at different temperatures (°C) for 3 h.](image)
For the Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$, Figure 11 shows three major emission peaks in the emission spectra which are at 578, 590, and 615 nm, attributed to the electronic transitions $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, and $^5D_0 \rightarrow ^7F_2$ of Eu$^{3+}$ ion, respectively [21]. However, before that, the broad emission peak at 485 nm can be related to the transition from the ionized oxygen vacancies to the valence band [60]. The blue-green emission peak can be due to the transition of an electron from interstitial zinc to zinc vacancies or interstitial oxygen as well as the transition originated from a complex defect level of oxygen vacancies and interstitial zinc to the valence band. The red-shift of the peak is mainly due to the unlike crystalline phases between the samples and thus the different host crystal field. Generally, during the heat-treatment process, the formation of ZnO and Zn$_2$SiO$_4$ crystals may affect the local environment of Eu$^{3+}$ ions, which indicate that Eu$^{3+}$ ions may be incorporated both into the ZnO and Zn$_2$SiO$_4$ lattice where the coordination number of Eu$^{3+}$ may intensely influence the emission color of the ZnO and Zn$_2$SiO$_4$ crystal lattice to produce red emission color [21]. This can be discovered from FESEM images, where no Eu$^{3+}$ structure can be seen in the images regardless of the concentration of Eu$^{3+}$, which shows that Eu$^{3+}$ has been incorporated into both crystals sites.

Next, the $^5D_0 \rightarrow ^7F_0$ transition at the emission peak of 578 nm belongs to the 4f-4f transitions, which is principally forbidden according to the standard selection rules of the Judd–Ofelt theory [61]. Hence, the peak should be inexistent or very weak in the PL emission spectrum, however, due to the possibility of the majority of Eu$^{3+}$ ions occupy the interstitial sites with much lower local symmetry in the ZnO/Zn$_2$SiO$_4$ host, hence affect to the occurrence of $^5D_0 \rightarrow ^7F_0$ transition [62,63]. While the emission peak at 590 nm with the electronic transitions $^5D_0 \rightarrow ^7F_0$ is attributed to the magnetic allowed transitions ($\Delta l = 1$) with an insensitive magnetic dipole transition to the environment [21,64,65]. As shown in the figure, the prominent emission peak is found at 615 nm with the electronic transitions $^5D_0 \rightarrow ^7F_2$. This transition is ascribed to the allowed transitions of an electric dipole ($\Delta l = 2$) with hypersensitive electric dipole transition to the crystal field environment [21,66]. At 615 nm, the strong emission peak of Eu$^{3+}$ which is characteristically red emission was attributed to magnetic dipole (MD) transitions. This peak shows that the Eu$^{3+}$ ions had occupied the non-centrosymmetric site in the Zn$_2$SiO$_4$ crystal lattice [67]. The peak in the emission spectra was also almost similar to the emission peak of the commercial red phosphors (Y$_2$O$_3$:Eu from Nichia Corporation, Japan) which show that the highest emission peak is around 615 nm, which support the emission peak of this work having the highest emission peak at 615 nm [68]. From the graph, it was also shown that the 700 °C samples produced higher emission peaks as compared to 600 °C and 800 °C. This shows that 700 °C was the optimum calcination temperature for the red emission and will emit the brightest red color when excited under the UV lamp.

4. Conclusions

Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ based composite has been successfully fabricated using the simple thermal treatment method. The XRD results confirmed the existence of two crystal phases; ZnO phase and Zn$_2$SiO$_4$ phase with the highest peak at 36.5° (ZnO) and 31.5° (Zn$_2$SiO$_4$), supported by FT–IR and FESEM. Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ calcined at 700 °C showed higher Zn$_2$SiO$_4$ peak (31.5°) compared to ZnO peak (36.5°) and further increment of calcination temperature may cause the Zn$_2$SiO$_4$ peaks to drop due to the lattice distortion occurred. FESEM micrograph suggested that increment in the calcination temperature may affect to the existence of dumbbell-like structures to appear in the sample, indicates that the agglomeration of neighboring particles happen in the composite. Next, absorption band intensity tend to become higher as calcination temperature increased. Furthermore, the crystallization process during calcination had affected the occurrence of red shift in the absorption spectra. Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ based composite also possessed two band gap energy which are ZnO crystal $E_g$ value (3.271 to 4.07 eV) and Zn$_2$SiO$_4$ crystal $E_g$ value (5.11 to 4.71 eV). The $E_g$ value for Zn$_2$SiO$_4$ crystal calculated become lower with increment of calcination temperature. PL study showed that Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ calcined at 700 °C is the optimum condition for red phosphor by
emitting the highest emission intensity at ~615 nm. We believed the fabricated Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ via simple thermal treatment method are suitable to be used for red phosphor for several applications such as LEDs for its good emission intensity in the red region and the simplicity of the technique. In the presented work, the structural, morphological, and optical properties of Eu$^{3+}$ doped ZnO/Zn$_2$SiO$_4$ composites has been presented. However, the thermal and electrochemical properties of the material need to be studied and verified in the future.

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