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Microwave-assisted combustion synthesis of $(\text{Gd}_{x}\text{Y}_{2-x})\text{O}_3$:Eu$^{3+}$

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Abstract

$(\text{Gd}_{x}\text{Y}_{2-x})\text{O}_3$:Eu$^{3+}$ nanoparticles were synthesized from stoichiometric metal nitrates mixture (oxidizer) and glycine (fuel) by microwave-assisted combustion method. $(\text{Gd}_{x}\text{Y}_{2-x})\text{O}_3$:Eu$^{3+}$ nanoparticles were fully crystalized in solution combustion step by microwave irradiation. These nanoparticles were thermally treated at 300, 500, 700, 900, and 1100 °C for about 30 min to release the combustion-induced stresses. The nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), energy dispersive X-ray (EDX), and photoluminescence spectroscopy (PL) techniques. Based on the XRD spectra, the as-synthesized sample was crystalline and single-phase. The crystallinity of nanoparticles was further improved after additional thermal treatment. The main PL peaks intensity (PLI) at 612 nm and 590 nm (relating to ${^5}\text{D}_0-^7\text{F}_2$ electric bipolar and ${^5}\text{D}_0-^7\text{F}_1$ magnetic dipole transitions, respectively) were increased upon thermal treatment above 300 °C. The PLI was increased about twice of the as-synthesized sample upon thermal treatment at 1000 °C.
˚C. The Chromaticity coordinates diagram of the emission were evaluated based on the 1931 CIE chromaticity diagram. TEM images confirmed the grain growth from ~25 nm to over 100 nm after thermal treatment. The substitution of Eu$^{3+}$ instead of Y$^{3+}$ or Gd$^{3+}$ was also confirmed by EDX point analysis in (Gd$_x$Y$_{2-x}$)O$_3$:Eu$^{3+}$ structure. Crystallographic planes of the synthesized samples were investigated using SAED patterns. Crystallinity of samples with increasing the heat-treatment temperature was promoted. Also AFM images confirm the enhancement of particles size with increasing temperature.

**Keywords**: Luminescence, Solution Combustion Synthesis, (Gd$_x$Y$_{2-x}$)O$_3$:Eu$^{3+}$, nanoparticles, heat treatment, crystallinity.

1. **Introduction**

Luminescence is an optical property of the material that refers to the emission of visible, ultraviolet, or infrared light regardless of its thermal radiation. From nanoseconds to several hours after removing the excitation source [1]. The prerequisite for the luminescence phenomenon is the excitation of material. If the excitation source is a kind of light (ultraviolet or visible), subsequently the phenomenon is called Photoluminescence (PL). Due to the particular properties of the synthesized luminescent materials, new generations of displays have been developed, such as electro-luminescence displays, vacuum fluorescent displays, plasma displays, and field emission displays. Phosphors are still consumed in conventional applications, such as fluorescent lamps, cathode-ray tubes, X-ray lamps, etc [2,3]. Quantum mechanics theory is used to explain luminescence phenomena in atoms and molecules of solids. In quantum mechanics, the electron energy is confined in an atom or a molecule, then
absorption and radiation of light occur discretely with specific values [1,4–7].

One of the most important mechanisms of luminescence is transitions between various energy levels of impurity atoms in the host structure. These localized defects are the main luminescence centers in the crystal which are strongly bonded to crystal atoms. Transition-metals or rare-earth elements are typically used as impurity atoms, known as dopants [8]. Generally, the principal cause of luminescence mechanisms is "defects" in the structure. They can be classified into intra-defect transitions, inter-defect transitions, and band-defect transitions [1,6,7]. Changing into the feature of defects by changing dopants, mechanical or heat treatment instantly, can make different energy levels of defects. Therefore, intensity or even type of emission wavelength are altered.

Wet chemical methods are very common in the production of luminescent compounds due to the uniform size and shape of the produced particles[9,10]. The combustion synthesis technique as a kind of wet chemical methods is a straightforward and low-cost approach to synthesize nanostructured materials. One of the advantages of this method is its high processing speed and good crystallinity of the product due to the high combustion reaction temperature. Practically, there is no need for heat treatment after combustion. Although, the desired crystalline structure can be improved with slight post-combustion heat treatment. The optimal time and temperature of heat treatment in this method are less than other methods. In the combustion synthesis method, a mixture of fuel and oxidizer is required which is initially heated and then combusted spontaneously. For the combustion synthesis of oxides, metal nitrates are conventionally used as oxidizers while organic compounds based on hydrazine, urea, glycine, etc. are used as fuels. The ratio of fuel to metal nitrate is usually calculated according to the reaction stoichiometry. The valence of C, H, V, B, and O elements after combustion is +4, +1, +5, +3, and -2, respectively,
while nitrogen has a neutral charge due to conversion to gaseous nitrogen. These rules, known as propellant chemistry, are used to calculate the stoichiometric ratio of fuel to oxidizer in a combustion reaction. If the fuel concentration is higher than the earned value, the combustion temperature will increase and usually leads to grain growth, while if it is lower, the released heat during the combustion process will not be sufficient and the produced material will not have enough crystallinity [11–17].

In this study, (Gd_xY_{2-x})O_3:Eu^{3+} nanoparticles with a specific molecular ratio of oxidizer to fuel (glycine) (ψ) were synthesized via solution combustion reaction using the microwave oven. Whereas heat treatment effects were not so available in combustion synthesis, especially for luminescence nanoparticles in this study, the particle size and the luminescence intensity were analyzed before and after heat treatment. The effect of grain growth and crystallinity during heat treatment on the intensity of the luminescence was also investigated.

2. Experimental

2.1. Materials and Methods

Analytical grade of yttrium oxide (Y_2O_3), gadolinium oxide (Gd_2O_3), europium oxide (Eu_2O_3), glycine (C_2 H_5 NO_2 ), 65% nitric acid (HNO_3), and 25% ammonia (NH_4OH) solution were obtained from MERCK as a precursor. The structure and crystallinity of as-prepared and heat-treated samples were characterized by X-Ray diffraction (XRD, Siemens D500) and diffractometer using Cu Kα radiation (0.15406 nm) in the 2θ = 10-80° at a scan step size of 0.013° and step time of 1.0 s. The photoluminescence (PL) analysis was performed on Perkin-Elmer LS55 at the rates of 15 and 20 nm/s. The colour chromaticity coordinates were obtained according to Commission International de l’Eclairage (CIE) using MATLAB software. The
nanostructure morphology was analyzed by the atomic force microscopy (AFM) technique and
the Philips CM-200 Transmission Electron Microscope (TEM) with a 200kV source and field
emission gun. The Energy Dispersive X-ray (EDX) analysis was performed by EDX detector
coupled with CM200 FEG microscope. TEM selected area electron diffraction (SAED)
technique was used to record the crystallographic pattern of the samples.

2.2. Experimental procedure

As we reported earlier[18], (Gd₀.₄₈₅Y₀.₅₇Eu₀.₀₄)O₃:Eu³⁺ nanoparticles were prepared by solution
combustion synthesis method from nitrate solutions of Gd, Y, and Eu. Initially, specific amounts
of Y₂O₃, Gd₂O₃, and Eu₂O₃ were dissolved in dilute nitric acid (65 vol.%%) to obtain nitrate
solutions of Gd, Y, and Eu with the desired molar ratio as the oxidant and the source of cations.
Then glycine fuel as a reducing agent was added to the solution. The oxidizer to fuel ratio (ψ)
was determined 1.667 according to propellant chemistry as follows.

\[
2aGd(NO₃)₃ + 2(1-a-b)Y(NO₃)₃ + 2bEu(NO₃)₃ + 2ΨC₂H₅NO₂ → (GdₐY₁₋ₐ₋bEuₙ)₂O₃ + 4ΨCO₂ + 5ΨH₂O + (3+1Ψ)N₂, \quad [a=0.485, \ b=0.03]
\]

The solution was then heated at 80°C to remove the excess water to obtain a viscose gel. The
combustion reaction was carried out in a microwave oven operating at 900 W/2.45 GHz for 1
min. The combusted sample was divided into six equal portions. One of them was used as-
synthesized while the other five samples were treated thermally in the furnace at 300, 500, 700,
900, and 1100 °C for 30 minutes to remove residual carbon and combustion thermal stresses and
strains. Heat treatment was also developed a diffusion network of dopant into the ordered
crystalline structure matrix.
3. Results and discussion

3.1. Structural analysis

The transparent precursor solution was initially dehydrated in the microwave oven with the evolution of gases. The combustion reaction is initiated through the sudden burning of semi-solid transparent precursors with a large amount of fume and heat. The combustion reaction intensity practically depends on the degree of reaction exothermicity. Considerably, glycine combustion intensity was high during the combustion reaction such that a part of the synthesized powder was spread out of the beaker. It was concluded that the glycine combustion was a self-propagated reaction with a high reaction temperature.

![Figure 1](image)

Figure 1: a) XRD spectra of the as-synthesized and heat-treated samples, b) JCPDS cards of standard database, c) compression of XRD spectra of samples with JCPDS cards of standard database of database in 2θ around the (222) plane.

Figure 1a shows the crystalline phases of the as-synthesized and the heat-treated samples at
different temperatures. Intensity, ratio and position of XRD peaks of all the samples (as-synthesized and the heat-treated) are accurately consistent with some JCPDS cards database of gadolinium-yttrium oxide and europium-yttrium oxide. The heat-treated powders are a single-phase cubic crystalline structure and no secondary-phase peaks are detected in all the samples. This shows, crystallization process is occurred in samples. This confirms that single-phase sample is formed during one-step combustion reaction even without any heat treatment. Hence, the combustion reaction temperature is high enough to promote gadolinium-yttrium-europium oxide crystallization in one step combustion process.

According to our literature review, there is no XRD standard database of triple-component of Y, Gd and Eu oxides. Figure 1b is expansion of the JCPDS cards from standard database in X’pert software. It shows the JCPDS cards database of Y, Gd and Eu oxides component and mixed oxides component of Y-Gd, Y-Eu and Gd-Eu. The XRD pattern of single and mixed oxide of Y, Gd and Eu indicate single cubic phase with space group Ia-3 (No. 206) without any impurity phases. The XRD peaks of as-synthesized and the heat-treated samples are matched with the mixed oxides component of JCPDS card’s references (Yttrium-Gadolinium Oxide or Yttrium-Europium Oxide) with a minor peak-shift.

Figure 1c shows the main (222) XRD peaks of database and samples. According to Bragg's Law[19], the diffraction angle of 2θ is increased by lattice constant decreasing. Effective ionic radiuses of Y$^{3+}$, Gd$^{3+}$ and Eu$^{3+}$ are 1.019, 1.053 and 1.066 Å respectively[20]. Therefore, the main peak of (GdY)O$_3$ at 28.87$^\circ$ is shifted toward lower diffraction angles due to the expansion of the (222) plane caused by the better substitution of Eu$^{3+}$ instead of Y$^{3+}$ or Gd$^{3+}$ in the structure. The larger radius of the Eu$^{3+}$ is increased the plane distances [19,21,22]. In Figure 1c, the main peak (222) of sample are shifted toward the higher diffraction angels. Whereas it is
expected that the main XRD of samples are appeared in Δ2θ region in Figure 2c according to the standard cards of \((Gd_{0.63}Y_{0.37})_2O_3\) and \((Gd_{0.37}Y_{0.63})_2O_3\).

Table 1: Structural and optical characteristics of \((Gd_xY_{2-x})O_3:Eu^{3+}\) samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(I_{(222)}/I_{(440)}) [XRD diagram]</th>
<th>(I_{610nm}(^{5}D_0^{-7}F_2)/I_{590nm}(^{5}D_0^{-7}F_1)) [PL diagram]</th>
</tr>
</thead>
<tbody>
<tr>
<td>JCPDS No. 01-081-2219</td>
<td>3.25</td>
<td>—</td>
</tr>
<tr>
<td>JCPDS No. 01-081-2218</td>
<td>3.04</td>
<td>—</td>
</tr>
<tr>
<td>JCPDS No. 00-025-1011</td>
<td>2</td>
<td>—</td>
</tr>
<tr>
<td>as-synthesized</td>
<td>2.57</td>
<td>5.34</td>
</tr>
<tr>
<td>300</td>
<td>2.42</td>
<td>5.30</td>
</tr>
<tr>
<td>500</td>
<td>2.66</td>
<td>5.05</td>
</tr>
<tr>
<td>700</td>
<td>2.75</td>
<td>5.13</td>
</tr>
<tr>
<td>900</td>
<td>2.5</td>
<td>5.59</td>
</tr>
<tr>
<td>1100</td>
<td>2.52</td>
<td>5.48</td>
</tr>
</tbody>
</table>

\(I_{(222)}/I_{(440)}\) ratios of the samples are shown in Table 1. \(I_{(222)}/I_{(440)}\) ratios of standard JCPDS No. 01-081-2219 \((Gd_{0.63}Y_{0.37})_2O_3\) and JCPDS No. 01-081-2218 \((Gd_{0.37}Y_{0.63})_2O_3\) cards are 3.25 and 3.04 respectively. \(I_{(222)}/I_{(440)}\) ratios of standard JCPDS No. 00-025-1011 \((Y_{0.95}Eu_{0.05})_2O_3\) card is equal to 2.

As seen in Table 1, \(I_{(222)}/I_{(440)}\) ratios of samples is neither matched with \(I_{(222)}/I_{(440)}\) ratios standard cards of \((Gd_{0.63}Y_{0.37})_2O_3\) and \((Gd_{0.37}Y_{0.63})_2O_3\) nor \(I_{(222)}/I_{(440)}\) ratios with standard JCPDS No. 00-025-1011 \((Y_{0.95}Eu_{0.05})_2O_3\) card. It is concluded that Eu3+ is doped in the structure of yttrium oxide and gadolinium oxide.
Figure 2 compares the position and intensity of peaks between 28 to 33 degrees of the two main peaks with (222) and (400) planes for as-synthesized and heat treated samples. As shown in Figure 2a, peak intensity and sharpness of samples is enhanced at higher heat treatment temperatures. Figures 2b and 2c shows peak shift of samples upon heat treatment. XRD peaks are shifted to higher angles as heat treatment temperatures is increased. Heat treatment is eased the diffusion Eu ion in a mixed oxide lattice [19,20]. The nano strain is released from lattice matrix and hence lattice parameter is decreased. This reduces dislocation defects[23,24]. Therefore, heat-treated samples are shown sharper and more intense XRD peaks than the as-synthesized sample. This shows that the heat treated samples’ crystallinity is improved upon additional heat treatment.
Figure 3 shows the average crystallite size of the samples based on Debye-Scherrer formula [25]. The average crystallite size of the as-synthesized sample is 18 nm. The average crystallite size of the as-synthesized sample is reduced to 16 nm upon thermal treatment at 300 °C. At 500 and 700 °C thermal treatment, the average crystallite size is about 18 nm. The crystallite size is increased to 20 and 24 nm at 900 and 1100 °C respectively. This shows that the required thermal driving force for grain growth is developed above 700 °C. So, it is concluded that the thermal combustion stress is initially removed from the structure at temperatures at 300 °C. The average crystallite size is increased with further heat treatment increase.

3.2. Photoluminescence properties

Figure 4 illustrates the PL spectra of as-synthesized and the heat-treated samples of (Gd$_x$Y$_{2-x}$)O$_3$:Eu$^{3+}$ nanoparticles. As shown in Figure 4, luminescence peak intensity is generally increased with thermal treatment temperature in all wavelengths. The highest luminescence peak
intensity is observed at 1100°C, where it is twice of the luminescence intensity of as-synthesized. According to the XRD results, crystal size growth is occurred with sample heat treatment. This follows with the reduction of crystal defects in the structure. According to our experimental results and literature review [26–29], luminescence intensity is enhanced with increasing the thermal treatment temperature. It is observed that luminescence intensity is initially reduced at 300°C and then increased at higher thermal treatment temperature with maximum radiation at 612nm. Unlike other synthesis methods, the relation between thermal treatment temperature and luminescence intensity is not linear in the combustion synthesis method.

Figure 4: PL spectra of the as-synthesized and heat-treated samples.

The peaks in the 570-700 nm range are attributed to the $^5D_0-\Sigma^7F_j$ ($j = 0,1,2,3 \ldots$) transitions. Also, the band range of 530-570 nm is assigned to the $^5D_1-^7F_1$ transition. The main peak is
known as the $^5D_0-^7F_2$ electric bipolar transition that appears at 612 nm. However, the smaller peak at 590 nm is associated with the $^5D_0-^7F_1$ magnetic bipolar transition. The weaker peaks at 650 and 700 nm are related to $^5D_0-^7F_3$ and $^5D_0-^7F_4$ electron transitions. All emission peaks approximately followed Gaussian distribution [30,31].

Figure 5: The substitution positions in the structure of yttrium oxide [32].

In the structure of yttrium (or gadolinium) oxide, there are two positions for $Y^{3+}$ (or $Gd^{3+}$), as shown in Figure 5. If the $Y^{3+}$ (or $Gd^{3+}$) substitutes with $Eu^{3+}$ at position $C_2$, high-intensity luminescence spectra are associated with $^5D_0-^7F_2$ transition. However, this transition will not occur unless the Eu ion enters the $C_{3i}$ position. It is because the $Eu^{3+}$ ion is affected by the crystal field at position $C_2$. As shown in Figure 5, the effect of the crystal electric field is negligible due to oxygen vacancy symmetry in the $C_{3i}$ position, [32–36]. The $I_{610nm}$ ($^5D_0-^7F_2$) /$I_{590nm}$ ($^5D_0-^7F_1$) ratio is representative of dopant replacement in the electric field to magnetic field position at the host structure.

The colorimetric data of the as-synthesized and heat-treated samples are simulated from emission spectra. The locus diagram of the mentioned samples has been illustrated in Figure 6. The color chromaticity coordinates are well-matched with the red color coordinates of Yttrium and Gadolinium as a host matrix with Europium dopant [37–39].
Figure 6: Chromaticity coordinates diagram of the as-synthesized and heat-treated samples.

Chromaticity coordinates shows that the as-synthesized and heat-treated samples chromaticity are not of much difference. However, the main trend from T300 toward T1100 sample is emitted from red to orange color. Indeed, a higher ratio of electric dipole ($^5D_0-^7F_2$) intensity in PL spectra in the red region shift the chromaticity to the magnetic dipole transition ($^5D_0-^7F_1$) intensity to the orange region. As shown in Figure 5, the Eu$^{3+}$ ion is placed in the $C_{3i}$ position rather than $C_2$ in samples which is treated at higher temperature. In the as-synthesized sample, magnetic positions are more active than electric sites.

3.3. Morphological studies

Figure 7 shows AFM images of as-synthesized sample and heat-treated sample at 1100°C. In distribution diagrams of samples for both 20×20 μm$^2$ and 50×50 μm$^2$ scanning areas, average peak height of as-synthesized sample are 39 and 135 nm. Average peak height of heat-treated sample at 1100°C are 142 and 359 nm in 20×20 μm$^2$ and 50×50 μm$^2$ scanning areas images,
Therefore, the average particle size of heat-treatment sample is higher than as-synthesized sample.

Figure 7: AFM images of 20*20 μm² and 50*50 μm² scanning areas with their distribution of particles: (a1),(b1),(a2) and (b2) for as-synthesized sample, (c1),(d1),(c2) and (d2) for heat-treated sample at 1100 °C.

Figure 8(a,b) shows TEM images of microwave synthesized samples before and after heat
treatment. The particle size of the as-synthesized sample is in the range between 25 to 35 nm as shown in Figure 8a, where a narrow size distribution of particles is obtained via the combustion method.

Figure 8: TEM images of (a) as-synthesized sample, heat-treated samples at (b) 900 and (c) 1100 °C, (d) HRTEM images of the distance between crystal planes.

Figure 8b shows the particle size after heat treatment at 900°C, which confirms particle size growth (50 to 78 nm) during heat treatment. At 1100°C, particle size is increased to more than 100 nm as shown in Figure 8c. At 1100°C heat treatment, the particle size growth is 3 to 4 times of the as-synthesized sample particle size. It can be concluded that an adequate Ostwald ripening activation force is exerted on the particles at this temperature [40,41]. The particle size growth is consistent with the results obtained from XRD and PL spectra. The distance between crystal lattice planes and crystal structure is shown in the TEM high-resolution image in Figure 8d.
EDX elemental analysis and diffraction pattern of the as-synthesized sample are shown in Figure 9. The EDX point analysis is used to detect the Europium element as a dopant in the sample using a 2nm electron probe diameter. EDX elemental analysis shows the existence of Eu element along with Y and Gd elements in the combustion synthesized sample.

The SAED dotted ring pattern of the as-synthesized sample is an indication of the well-crystallized nature of the nanoparticles. The SAED dotted ring pattern is also shown the nanosize nature as-synthesized sample. The obtained Miller index from the SAED pattern is consistent with the XRD results. This shows that the solution combustion method is the single-step synthesized method with commercialization potential.

4. Conclusion

In this study, \((\text{Gd}_x\text{Y}_{2-x})\text{O}_3:\text{Eu}^{3+}\) nanoparticles were synthesized via a solution combustion
method using glycine as a fuel. The synthesized samples were treated at 300, 500, 700, 900, and 1100°C. XRD analysis showed that not only all the synthesized samples were single-phase and crystalline but also crystallinity and particle size were obtained after thermal treatment. In PL spectra, the main peak was observed clearly at 612 nm (\(5D_0-7F_2\) electric bipolar transition). the smaller peak at 590 nm (\(5D_0-7F_1\) magnetic bipolar transition). PL peak intensity was enhanced due to crystallinity improvement and particle size growth of samples heat-treated at higher temperatures. The reduction of initial PL peak intensity occurred due to the release of trapped structural thermal stresses induced during the combustion reaction. Crystallinity improvement and particle size growth were also investigated by AFM and TEM images, which were in good accordance with XRD and PL data. EDX chemical analysis confirmed the presence of Eu\(^{3+}\) ion in the \((Gd_{x}Y_{2-x})O_3\) structure.

A particular characteristic of the solution combustion reaction is a rapid temperature rise for a few seconds and then followed by a subsequent sudden temperature drop. Consequently, thermal stress is induced to the crystal structure of \((Gd_{x}Y_{2-x})O_3:Eu^{3+}\) nanoparticles during the sharp fluctuation of temperature. The trapped thermal stress develops energy sublevels transition within the crystal structure, which activates intra- or inter-defect luminescence transitions. The electron transitions of these extra sublevels enhance slightly luminescence properties. During the thermal treatment, these trapped thermal stresses are slowly released from the structure, and hence the corresponding relevant sublevels of electron transitions are eliminated. Therefore, in low temperatures of thermal treatment (less than about 500°C) a little reduction in the PL intensity has been observed. But diffusion mechanisms are activated at higher temperatures of thermal treatment. Hence, the rapid enhancement of the luminescence intensity is occurred.
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5. References


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