Synthesis of Mg$_2$SiO$_4$:Eu$^{3+}$ by combustion method and investigating its luminescence properties

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In this study, nanocrystalline forsterite (Mg$_2$SiO$_4$) powder was synthesized via two-step combustion–calcination procedure. Mixtures of citric acid and glycine were used as fuel and nitrate ions were used as oxidizers. The samples were synthesized with different fuel to nitrate (F/N) molar ratios. The synthesized sample was characterized by X-ray diffraction, transmission electron microscopy, scanning electron microscopy and photoluminescence spectroscopy. The effect of fuels on formation of the forsterite phase was studied. The X-ray diffraction (XRD) patterns of the samples revealed that the forsterite was formed as a major phase for all the samples containing citric acid. The crystallite size was found to be in the range of 18–50 nm. Photoluminescence spectra showed that the luminescent intensity of Mg$_2$SiO$_4$:Eu$^{3+}$ particles were much higher than that of MgO:Eu$^{3+}$ ones.

1. Introduction

Forsterite (Mg$_2$SiO$_4$) is an important material in the magnesia-silica system with many notable properties, such as high melting point, chemical stability even at high temperatures, great electrical and refractory characteristics, as well as good mechanical properties, bioactivity and biocompatibility [1]. Therefore, it has found commercial applications in many industrial areas, e.g. electronics as insulators working at high frequencies [1], refractory industry [2], advanced technologies such as SOFC (solid oxide fuel cells) [3], biomedicine [4] and luminescent technology [5].

Forsterite can be made through solid state reaction but necessarily at high temperature and long reaction time. Meanwhile, low chemical homogeneity and large crystal sizes of the sintered power have led to preference of the “solution based” methods. However, the synthesis of pure nanocrystalline forsterite with controlled particle size has still remained challenging [6]. Therefore, many alternative synthesis techniques have been reported for the synthesis of pure forsterite including the citrate–nitrate method [7], combined mechanical activation [8], molten-salt approach [9], polymer precursor method [10], mechano-thermal synthesis [11], mechano-chemical synthesis [12], Flame Spray Pyrolysis [13], combustion synthesized [14] and sol-gel techniques [1,15,16].

Patil et al. [17] invented the combustion method in order to synthesize different oxide nanopowders. Recently, an important part of researches in the field of synthesis of oxide nanoparticles has been focused on microwave-assisted combustion process because of its advantages of rapid reaction velocity, uniform heating, and efficient energy utilization [18–20]. On the other hand, one of the most important parameters in this process is the kind of fuel. Some researchers have employed citric acid [7,21] and glycine [22,23] as suitable fuels in the combustion method. More recently, a mixture of citric acid and glycine has been used [24,25] to recognize co-effect of these fuels. The main reasons of this selection are the simultaneous effect of chelating agent and flammability in the former and the high rate of ignition in the later. Although using the citric acid contributes to formation of more uniform particles, the intense ignition of the glycine fuel creates better structures.

Recently, rare-earth ion doped luminescent materials have received an extensive attention due to the unique characteristic of RE dopants, as well as their stability and potential applications in the fields of luminescence devices, optical transmission, biochemical probes, medical diagnostics, and so forth [26]. Emission of light from the RE ions is mainly due to electric and magnetic dipole optical transitions with $^4f_n$ energy manifolds and may also involve $^4f_{n-2}$-$^2d$. In recent years, new luminescent nanomaterials have seemed promising, since nanostructures exhibit interesting luminescent properties [26,27].

In this work, two-step combustion–calcination processes were applied for the synthesis of forsterite nanoparticles. To the best
of our knowledge, the effect of F/N molar ratio on particle size, uniformity, morphology and structure of forsterite nanoparticles have not been reported. Moreover, Tetraethyl orthosilicate (TEOS) was utilized as the precursor of silica instead of other silica species (like colloidal silica) to synthesize forsterite by this process. Furthermore, luminescent intensity of the samples which were doped with Eu\(^{3+}\) has been investigated. Modification of the luminescent properties is the main goal of solution combustion in the presence of fuel mixtures.

2. Experimental details

All materials used in this study were of chemical grade, supplied by Merck Company. Experimental procedure was on the basis of propellant chemistry which was presented by Pati et al. [17]. In the propellant chemistry, chemistry balance is established between fuel and oxidant compounds [25]. In this study, the mixture of fuels is balanced by magnesium nitrate as oxidant. For example, the combustion reaction which leads to the formation of forsterite in the presence of glycine and citric acid could be described as Eq. (1).

\[
16\text{Mg(NO}_3\text{)}_2 + 2\text{C}_6\text{H}_8\text{O}_7\text{COOH} + 9\text{C}_3\text{H}_6\text{O}_3 + 8\text{H}_2\text{O} \rightarrow 8\text{Mg}_2\text{SiO}_4(\text{s-amorphous}) + 58\text{CO}_2(g) + 50\text{H}_2\text{O}(g) + 17\text{N}_2(g)
\]

(1)

Tetraethyl orthosilicate (TEOS) starts hydrolysis in the presence of citric acid. Probably, it hydrolyses to \(\text{Si-O-Si}\) species before adding the glycine. It is expected that the source of silicate during the ignition of combustion causes the formation of \(\text{MgO-SiO}_2\) systems. Nominal equation of reaction for citric acid and glycine as fuels are given by Eqs. (2) and (3), respectively.

\[
2\text{Mg(NO}_3\text{)}_2 + 2\text{C}_6\text{H}_8\text{O}_7\text{H}_2\text{O} \rightarrow 8\text{Mg}_2\text{SiO}_4(\text{s-amorphous}) + 12\text{CO}_2(g) + 10\text{H}_2\text{O}(g) + 2\text{N}_2(g)
\]

(2)

\[
5\text{Mg(NO}_3\text{)}_2 + 2\text{HN}_{2}\text{CH}_2\text{COOH} + (\text{CH}_3\text{CH}_2\text{O})_3\text{Si} + 4\text{H}_2\text{O} \rightarrow 5\text{MgO}(\text{periclase}) + \text{SiO}_2(\text{s-amorphous}) + 12\text{CO}_2(g) + 15\text{H}_2\text{O}(g) + 6\text{N}_2(g)
\]

(3)

The amount of oxidant was kept constant in all samples. As a typical example, 2.5 g magnesium nitrate, 1 cc TEOS, 10 ml ethanol and a known amount of citric acid were dissolved in 5 ml distilled water (Table 1) and mixed together for 2 h. pH value of the final solution was set to the range of 3–4. A stoichiometric amount of \(\text{Eu(NO}_3\text{)}_3\) solution was added to the previous solution. The resulting solution was kept in a reflux system at 80 °C for 1 h. The final solution was aged for 24 h. Schematic chart of the experimental procedure is illustrated in Fig. 1.

A given amount of glycine calculated based on the propellant chemistry was added to the aged solution. Then, the solution temperature was reached up to 80 °C. Transparent gel was obtained by keeping the temperature constant for 1 h. The obtained gel was finally transferred to a microwave oven to complete the combustion reaction. Time of combustion reaction was about 50 s and the samples were prepared by high speed ignition with a large amount of exhaust gases. At last, the obtained powders were calcined at 800 °C for 1 h. Samples were coded based on the weight contents of citric acid and glycine (according to Eq. (1)). The amount of fuels in AC100 and G100 samples were calculated according to Eqs. (2) and (3), respectively (Table 1).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>G/N</th>
<th>C/N</th>
<th>F/N</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC100</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>100% AC</td>
</tr>
<tr>
<td>G10–AC90</td>
<td>0.009</td>
<td>0.359</td>
<td>0.368</td>
<td>10% G + 90% AC</td>
</tr>
<tr>
<td>G20–AC80</td>
<td>0.018</td>
<td>0.319</td>
<td>0.337</td>
<td>20% G + 80% AC</td>
</tr>
<tr>
<td>G30–AC70</td>
<td>0.024</td>
<td>0.299</td>
<td>0.323</td>
<td>30% G + 70% AC</td>
</tr>
<tr>
<td>G40–AC60</td>
<td>0.033</td>
<td>0.256</td>
<td>0.289</td>
<td>40% G + 60% AC</td>
</tr>
<tr>
<td>G50–AC50</td>
<td>0.045</td>
<td>0.206</td>
<td>0.253</td>
<td>50% G + 50% AC</td>
</tr>
<tr>
<td>G100</td>
<td>0.4</td>
<td>-</td>
<td>0.4</td>
<td>100% G</td>
</tr>
</tbody>
</table>

Table 1 Composition of mixture of fuels.

G: glycine, AC: citric acid.

Fig. 1. Schematic flow chart of the synthesis of forsterite nano-powder.

3. Results and discussion

3.1. Crystal structures of synthesized samples

Fig. 2 depicts the XRD patterns of the as-synthesized samples with calculations process. It can be observed that AC100 sample is generally amorphous with no distinguishable phases in its pattern. However, crystalline structures are formed by increasing glycine content of the fuel mixtures. It can be observed that the samples obtained at the lowest content of glycine fuel (G10–AC90) display patterns of Mg(NO\(_3\))\(_2\)-6H\(_2\)O phase (JCPDS No. 00-001-0349), while periclase (MgO) phase (JCPDS No. 01-087-0651) is appeared at higher contents of glycine. It is believed that the amount of energy which is released by citric acid during the synthesis is not sufficient to form crystalline phases [24]. On the other hand, glycine shows high ignition intensity possibly due to the presence of amine-groups in the chemical composition [28]. It
clic fuel transforms the mixture of Mg\(^{2+}\) and TEOS to the periclase phase. The F/N ratio significantly affects the formation of forsterite. The glycin amount of F/P belongs to G20–AC80 sample. It indicates that the forsterite phase is the main phase along with minor phase of crystalline SiO\(_2\) (JCPDS No. 01-076-0941) and forsterite. It seems that the absence of citric acid hinders the hydrolysis of TEOS which can be inferred from the patterns that the non-calcined samples are not crystallized properly and calcination plays a key role in formation of the crystalline structure in different samples.

Fig. 3 illustrates the XRD patterns of the calcined samples with different amounts of glycine and citric acid. The results indicate that the structure of all samples except G100 and G50–AC50 has been converted to forsterite (JCPDS No. 00-001-1290). However, the structure G50–AC50 sample consists of periclase (JCPDS No. 01-087-0651) as the major phase along with minor phase of crystalline SiO\(_2\) (JCPDS No. 01-076-0941) and forsterite. It seems that the absence of citric acid hinders the hydrolysis of TEOS which can be attributed to the low content of acid catalysis. Therefore, glycine is not able to adjoin Mg and Si ions together [26].

Forsterite has been formed according to the heterogeneous reaction between Mg ions and Si(OH) species which are produced by the hydrolysis of TEOS in the presence of acid citric [27]. By increasing the amount of acid citric and decreasing the amount of glycine, the intensity of forsterite is increased and that of periclase is decreased.

As mentioned previously, the samples prepared via two-step combustion-calcination stages (CC) were essentially consisted of forsterite and periclase phases. Fig. 4 shows variations of F/(1 2 0) (the main peak of forsterite phase)/P(2 2 0) (the main peak of periclase phase) ratio with respect to the fuel ratios. The greatest amount of F/P belongs to G20–AC80 sample. It indicates that the F/N ratio significantly affects the formation of forsterite. The glycine fuel transforms the mixture of Mg\(^{2+}\) and TEOS to the periclase phase while the combustion process is activated. In this situation, TEOS will probably fail to be hydrolyzed completely. Furthermore, the ignition intensity of glycine is rather high [25]. Subsequently, Mg\(^{2+}\) ions are transformed to periclase following Eq. (3).

Fig. 3. X-ray diffraction patterns of the samples obtained by different F/N ratio after calcination at 800 °C for 1 h.

Table 2 Effect of F/N ratios on crystallite size and luminescent intensity of forsterite phase.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Average crystallite size calculated by XRD</th>
<th>Luminescence intensity at 614 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC100</td>
<td>43.9</td>
<td>178</td>
</tr>
<tr>
<td>G10–AC90</td>
<td>44.4</td>
<td>253</td>
</tr>
<tr>
<td>G20–AC80</td>
<td>27.3</td>
<td>305</td>
</tr>
<tr>
<td>G30–AC70</td>
<td>26.6</td>
<td>176</td>
</tr>
<tr>
<td>G40–AC60</td>
<td>26.5</td>
<td>149</td>
</tr>
<tr>
<td>G50–AC50</td>
<td>18.8</td>
<td>152</td>
</tr>
<tr>
<td>G100</td>
<td>–</td>
<td>126</td>
</tr>
</tbody>
</table>

Saberi [15] reported that the forsterite formation starts at 730 °C, while it is poorly crystallized. Also, the forsterite phase only can be detected in samples which are calcined at higher temperatures (800–1000 °C). But in current work, the XRD patterns of G100 obtained from CC method showed that the major phase was periclase. This can be assigned to the absence of Si(OH) groups beside Mg ions. However, the periclase phase has become the minor phase in other F/N ratio.

Table 2 summarizes the average crystallite size of forsterite phase in the samples prepared via CC method. The evaluation of crystallite size was determined based on Scherrer equation. The main diffraction peaks, namely (1 2 0), (2 1 1) and (2 2 2) were selected to measure the crystallite size. The forsterite crystallites provide a wide range of size from 18 to 50 nm due to their oriental growth of them. According to the obtained results, sample G20–AC80 forms more uniform particles with narrow size distribution (25–50 nm).

3.2. Microstructure of synthesized samples

Fig. 5 depicts TEM micrographs, particle size distribution (PSD), selected area electron diffraction (SAED) pattern and EDS analysis of G20–AC80 sample. Fig. 5a and c demonstrate that morphology of the synthesised powder has a semi-sphere shape with crystallite size distribution in the range of 20–50 nm (Fig. 5b) which is in agreement with the XRD patterns. However, Fig. 5c shows a small amount of some larger particles. EDS analysis (Fig. 5f) reveals that the smaller particles are forsterite, while the larger ones are periclase (Fig. 5e). The SAED pattern (Fig. 5g) which was taken from the smaller particles also verifies that these particles are forsterite.

SEM images (Fig. 6) illustrate the powders produced using much higher contents of citric acid have fine and loosely agglomerated particles with uniform size as compared to those produced with higher contents of glycine. This indicates that citric acid has a better effect on producing powders with proper distribution and less agglomeration as the chelating agent.

The high-resolution of the regions indicated by arrows (insets in Fig. 6) show that glycine has reduced the size of individual particles because of the greater energy released from glycine. Nevertheless, the glycine has localized heat on the particle boundaries during the combustion process which results in semi-sintered particles [24]. Therefore, samples with higher contents of glycine will have hard and large agglomerate after the calcination process.

Eqs. (1)–(3) indicate that a large amount of exhaust gasses are produced during the combustion process. Probably, the huge amount of exhaust gases in the G20–AC80 sample leads to better reaction of ingredients and thus production of more uniform morphologies [29].

3.3. Photoluminescence properties of synthesized samples

Fig. 7 shows excitation and emission spectra of Mg\(_2\)SiO\(_4\):Eu\(^{3+}\) particles synthesized in different F/N ratios. As it can be seen from
Fig. 7a, the excitation peaks of samples are distributed within 240–289 nm and the maximum peaks are located at 245 and 393 nm. The former maximum peak can be attributed to the charged-transfer band of Eu\(^{3+}\) which corresponds to the electronic transition from 2p orbital of O\(^2-\) to 4f orbital of Eu\(^{3+}\) and the later is assigned to the f–f transitions from \(^7F_0\) ground state to \(^5L_6\) excited state [6]. Intensity of the photoluminescence results (Fig. 7b) is impressively high in G20–AC80 sample which has the maximum amount of forsterite phase. Rare-earth (RE) ions like Eu\(^{3+}\) are very attractive luminescent centers owing to their high color purity and luminescence efficiency [30]. Most europium doped inorganic oxides show the characteristic red emission located at 611 nm, but some researchers have reported the red shift at 611 nm [31,32]. Previous works carried out on europium doped forsterite reveal that the wavelength location of the characteristic emission could be varied with respect to the change of crystal field resulting from type of the synthesis method [6,33,34]. In current work, the wavelength of red emission from Mg\(_2\)SiO\(_4\):Eu\(^{3+}\) is located at 614 nm. The luminescence intensity of samples at 614 nm is shown in Table 2. The emission spectrum of MgO:Eu\(^{3+}\) (synthesized by combustion method) is also presented to be compared with the results. It is clear that just the characteristic emission line \(^{5}D_0\rightarrow^{7}F_2\) is appeared in the MgO:Eu\(^{3+}\) spectrum, while more characteristic emission lines are presented in the spectra of the samples obtained via CC method.

The Mg ion occupies two non equivalent octahedral sites in the crystalline structure of Mg\(_2\)SiO\(_4\): one (M1) with inversion symmetry (C\(_i\)), and the other (M2) with mirror symmetry (C\(_s\)). When RE\(^{3+}\) ions were doped into the host, they could probably occupy the both sites. However, the PL results show that RE\(^{3+}\) ion in Mg\(_2\)SiO\(_4\) is mainly situated more at the low symmetry sites [6]. Because of the largely different in ionic radius of Mg\(^{2+}\) and Eu\(^{3+}\), it is suggested that only a minor fraction of the total amount of RE\(^{3+}\) goes into Mg substitution sites and a larger amount may be precipitated into Mg\(_2\)SiO\(_4\):RE\(^{3+}\) clusters, or even separated as a rare earth oxide phase. The excess amount of RE\(_2\)O\(_3\) will likely reside on either surface or grain boundaries of the nanocrystals to yield optimum strain relief [35]. On the other hand, Yang et al. have reported that the Eu\(^{3+}\) ions only replace the Mg\(^{2+}\) ions in M2 (C\(_s\)) site [33]. Therefore, situation at such low-symmetry local sites for RE\(^{3+}\) ions leads to transition emission \(^{4}F_9/2\rightarrow^{4}I_{13/2}\). Therefore, Eu\(^{3+}\) ions in the forsterite structure exhibit a bright red emission at 614 nm.
4. Conclusions

Nanocrystalline forsterite (Mg$_2$SiO$_4$) was synthesized via two-step combustion–calcination stages in the presence of different ratios of glycine and citric acid. It was shown that citric acid can be used as a fuel to synthesize forsterite phase, but the glycine just forms periclase one. For all samples calcination of the precursor was required to obtain a crystalline forsterite, whereas the periclase phase formation was completed during the combustion by using glycine as a fuel. The greatest amount of forsterite was observed in G20–AC80 sample. The crystallite size of the powder calcined at 800 °C was in the range of 18–50 nm. Photoluminescence spectra revealed that the luminescent intensity of Mg$_2$SiO$_4$:Eu$^{3+}$ particles were much higher than that of MgO:Eu$^{3+}$ ones.

Fig. 6. SEM micrographs of samples with different fuel mixtures (after calcinations): (a) G50–AC50, (b) G30–AC70, (c) G20–AC80 and (d) G10–AC90.

Fig. 7. (a) Excitation ($\lambda_{ex} = 614$ nm) and (b) emission ($\lambda_{em} = 245$ nm) spectra of samples obtained with different F/N ratios after calcination at 800 °C for 1 h.

4. Conclusions

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