Influence of pH on the physical and electromagnetic properties of Mg–Mn ferrite synthesized by a solution combustion method

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The synthesis of nano-crystalline Mg–Mn ferrites by a solution combustion method using citric acid and ammonia was investigated by varying the pH of the precursor solution, which played an important role in controlling the morphology of the synthesized powders. The phase formation, microstructure and electromagnetic properties were studied using X-ray diffraction, scanning electron microscopy, impedance analyzer and vibrating sample magnetometer. Single phase pure spinel Mg–Mn ferrite powders were obtained for all the samples at different pH (~1, 3, 5, 7, 9). The results showed that an increase of pH improves the crystallinity of the Mg–Mn ferrite nanoparticles. The average grain size of sintered samples was found to decrease from 2 μm to 0.5 μm with increasing pH values from pH < 1 to pH 9, respectively. The dielectric constant of the samples with different pH is in the range of 7–12 from frequencies of 1 MHz to 1 GHz. The highest saturation magnetization (30.04 emu/g) was obtained for the sample with pH < 1.

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1. Introduction

Ferrites are magnetic ceramics containing iron oxide as a major constituent and which are used in a wide range of modern technology. These ferrites are now a very well established group of magnetic materials. In the present day, ferrites are employed in a wide variety of applications and have contributed to the advances in electronics. Even though improvements and innovations continue to take place, many new applications, theories and preparation technologies are currently under development in the field of ferrites.

Spinel ferrites are prepared through various chemical methods such as co-precipitation, hydrothermal and sol–gel. These methods have some disadvantages which include multiple step pathways that are time consuming and require expensive alkoxide precursor materials. In contrast, the solution combustion method has the advantages of using inexpensive precursors and low external energy consumption, thus resulting in the formation of nano-sized, homogeneous and highly reactive powders [1].

Several researchers prepared Mg–Mn ferrites, including various other ferrites like MgCuZn [2], MgZn [3] and NiZn [4–5], by the auto-combustion method to produce nano-ferrite powders. Generally, metal nitrate salts are used as reactants whilst glycine, urea and citric acid are used as fuels in the auto combustion method. Citric acid is preferred because both glycine and urea contain the element nitrogen which releases an extra amount of pollutant N₂ gas during the combustion reaction. The solution combustion process has been proven to be a simple and economic way to prepare nano-scale ferrite powders [6]. Although the solution combustion technique gives more promising results in the synthesis of nano-ferrites, several preparation conditions such as dilution, fuel/oxidant ratio, pH and temperature can have an influence on the formation of the ferrites and their properties [7].

Therefore, an attempt has been made in the present work to investigate the effect of pH on the phase formation, microstructure, density–porosity and electromagnetic properties of Mg–Mn ferrites by the solution combustion method.

2. Experimental procedure

In order to prepare Mg–Mn ferrites by the solution combustion method, Mg(NO₃)₂·6H₂O, Mn(NO₃)₂·4H₂O, Fe(NO₃)₃·9H₂O and citric acid were first dissolved in minimum amount of deionized water. The molar ratio of fuel (citric acid) to metal nitrates was taken as 1:1. The pH was adjusted to 3, 5, 7 and 9 using ammonia (NH₄OH-25%). The results showed that an increase of pH improves the crystallinity of the Mg–Mn ferrite nanoparticles. The average grain size of sintered samples was found to decrease from 2 μm to 0.5 μm with increasing pH values from pH < 1 to pH 9, respectively.
heated at 80 °C to obtain a dense gel. Upon the formation of a dense sticky gel, the temperature was increased to 120 °C for the dehydration process. The temperature was then increased rapidly and when it reached approximately 130 °C, large amounts of gases (CO₂, H₂O, N₂) were liberated, and a dark brown ferrite powder was produced through the combustion process. Finally, the as-burnt powder was calcined at 500 °C for 5 h with a heating rate of 5 °C/min to obtain the Mg–Mn fer-

Fig. 1. Schematic presentation of powder preparation technique for the pure phase Mg–Mn ferrite.

Fig. 2. XRD spectra of as-prepared powders at (a) pH < 1, (b) pH = 3, (c) pH = 5, (d) pH = 7 and (e) pH = 9 prepared by the solution combustion method.

density and apparent porosity of sintered specimens were determined by the Archimedes principle. The morphology and microstructure of the samples were observed under a field emission scanning electron microscope (FESEM-Zeiss Supra 55VP). A vibrating sample magnetometer (model-7410, Lake Shore) was used to measure the magnetic properties of the samples at room temperature. The electrical properties such as dielectric constant and dielectric loss were measured by an impedance/ materials analyzer (HP/Agilent 4291B RF).

3. Results and discussion

The phase analysis of the as-prepared ferrite powders is shown in Fig. 2. The powders are in a crystalline state and reveal single-phase spinel ferrite structure. There is no metal oxide phase in the as-prepared powders produced at different pH values. The crystallite sizes of the powders are in the range of 6–10 nm. The sample prepared with pH < 1 shows significant broad peaks in the XRD patterns due to the very small crystallite size or the nature of fine particles. However, the peaks become sharp and intense with increasing pH values, indicating an increase in crystallite size. In this study, it is found that the degree of crystallinity is affected by the control of pH.

The as-prepared powders at different pH were calcined at 500 °C for 5 h to improve the crystallinity of the spinel phase and XRD patterns of the calcined powders are shown in Fig. 3. The crystallite size of the calcined powders is in the range of 10–26 nm. The variation of average crystallite size with different pH values is presented in Fig. 4. The XRD
results show that as the pH increases, the diffraction maxima become sharper and more pronounced. This indicates that the crystallinity and the average crystallite size are increased as the pH increases. Due to the rapid combustion rate and high flame temperature with increasing pH, higher pH produces larger crystallite size and good crystallinity. It has been experimentally observed by some researchers that nanocrystalline powders are quite susceptible to the formation of interparticle London–van der Waals bonds either in the wet or in the dry state due to their very fine particle size [8]. The magnetic interaction with high reactivity can cause the powder particles to bond together into agglomerates during handling, drying or storage. It can also be seen that the pH has more effect on the phase formation and crystal growth.

All the calcined powders were then subjected to sintering at 1250 °C and the XRD traces of those samples are shown in Fig. 5. The XRD pattern of sintered Mg₀.₉Mn₀.₁Fe₁.₈O₄ ferrite is compared to its as-prepared and calcined powders in Fig. 2 and Fig. 3. It is found that the broadening of diffraction peak decreases from the as-prepared, calcined and sintered products, respectively. The crystallite size increases with successive heat treatments of the ferrite [60 to 75 nm] and it is revealed in Fig. 4. According to the XRD patterns shown in Fig. 5, phase formation is stable and no secondary phase is detected in the sintered ferrite samples produced at different pH values.

The TEM images of Mn-doped Mg ferrites heat-treated at 500 °C are presented in Fig. 6. The micrographs clearly show that the ferrite particles have a tendency to hold together, forming agglomerates because of the strong magnetic interactions between ferrite particles during preparation [9]. The average particle sizes are in the range of 9 to 23 nm. In Fig. 7, we can observe the variation of average particle sizes with different pH values of Mg–Mn ferrites. It can be seen that the particle growth of Mg–Mn ferrites is enhanced in basic medium. A similar phenomenon was observed in zinc oxide nano-particles synthesized by the sol–gel method with variation of pH reported by Radyum et al. [10]. We believe that the size dependence on pH value may be due to the rapid and large amount of heat combustion. At higher pH values, the rate of heat combustion is greater than at lower pH.

The microstructures of the fractured pellet samples prepared from different pH and sintered at 1250 °C are shown in Fig. 8. Similar fracture surface is observed for samples sintered at the same temperature with different pH values. The SEM images show clearly the change in morphology as the pH of the solution increases from 3 to 9. By increasing

![Fig. 5. XRD spectra of sintered pellets at 1250 °C for different powders prepared at (a) pH < 1, (b) pH = 3, (c) pH = 5, (d) pH = 7, and (e) pH = 9.](image)

![Fig. 6. TEM micrographs of Mg₀.₉Mn₀.₁Fe₁.₈O₄ powders heat-treated at 500 °C (a) pH < 1, (b) pH = 3, (c) pH = 5, (d) pH = 7 and (e) pH = 9.](image)
the pH value, the average grain size decreases to some extent. The formation of pores and voids in the samples can be attributed to the release of large amounts of gases during the synthesis combustion process since the rate of combustion is increased significantly with increasing pH values. The average grain size (2 to 0.5 μm) is slightly decreased with increasing pH values. The influence of pH values on the grain size is depicted in Fig. 7. This is probably associated with the use of ammonia which is used to vary the pH value. Typically, the degree of hydrolysis increases significantly with the intensification of pH value and during the combustion process, the metal hydroxide converts to crystal easier than unhydrolyzed water-dissolving metal salt.

However, when the pH increases, the growth in truncated octahedron shape gradually increases. Hence, the grain size seems to be smaller as the pH increases. Faster rate of solidification could occur at higher pH values during sintering, resulting in more nucleation points and smaller grains. Transgranular fracture mode was observed for all compositions investigated. Transgranular fracture is characterized by the appearance of planar, crystallographic cleavage planes which give sharp contrast [11]. There were few pores at the grain boundaries and the grain growth is non-uniform.

The EDX analyses of Mg–Mn ferrites synthesized at different pH and sintered at 1250 °C are shown in Fig. 9. All indicate the presence of Mg, Mn, and Fe and O in the sintered ferrite samples. The results shown in this figure show that there are no other elements present except for Mg, Mn, Fe and O. Upon close scrutiny, the compositions of the samples show a slight difference in the amounts of Mg, Mn, Fe and O. The slight deviations may be due to the possible evaporation of Mg and Mn during the synthesis at elevated temperatures, and to the formation of a mixture of metastable ferrites after gel combustion.

Fig. 10 expresses the density and porosity of Mg$_{0.9}$Mn$_{0.1}$Fe$_{1.8}$O$_4$ ferrites with different pH values. Based on the microstructure observations and density measurements, it is confirmed that the highest density and less porosity are found at a condition without pH modification (original solution pH < 1). After modifying the pH value, the density is slightly

![Fig. 7. Variation of average particle size and grain size with different pH values of Mg-Mn ferrites calculated from (a) TEM micrographs, and (b) SEM micrographs.](image)

![Fig. 8. SEM micrographs of Mg$_{0.9}$Mn$_{0.1}$Fe$_{1.8}$O$_4$ ferrites sintered at 1250 °C (a) pH < 1, (b) pH = 3, (c) pH = 5, (d) pH = 7 and (e) pH = 9.](image)
decreased compared to the solution without pH modification. However, the density is subsequently increased when the pH of the solution is increased from 3 to 9.

The electrical properties of Mg$_{0.9}$Mn$_{0.1}$Fe$_{1.8}$O$_4$ ferrites sintered at 1250 °C for different pH values prepared by the solution combustion method were measured using the impedance analyzer. The variation of dielectric constant of the pellets with different pH is shown in Fig. 11. The purpose of setting the frequency range to 1 MHz–1 GHz is to investigate the dielectric properties at microwave frequencies. The dielectric constant of the samples with different pH is in the range of 7–12 from frequency 1 MHz to 1 GHz.

The obtained dielectric constant values in this study are very low and it shows the semiconducting behavior of the ferrite materials. Normally, there is a strong correlation between conduction mechanism and the dielectric behavior of ferrites. This can be explained by the fact that an increase in frequency induces either weakening or disappearance of...
ionic polarization, and consequently decreases the dielectric constant values [12]. For the ferrite materials, the dielectric properties will be affected by many factors such as the content of the individual crystalline phase, formation of the phases, level of porosity and degree of densification [13]. In fact, all these factors could rely on the variation of pH values in the solution. Density plays an important role in the variation of dielectric constant [14]. Higher porosity and lower density result in lower dielectric constant. However, it is also observed that all the samples show no significant frequency dependent phenomenon, i.e. the permittivity maintains an almost constant value at higher frequency.

Fig. 12 illustrates the dielectric loss or loss tangent as a function of frequency for sintered pellets of Mg0.9Mn0.1Fe1.8O4 ferrites at different pH. Low dielectric loss is desirable for reducing heat generation at high frequency, and for high resistivity. It was observed that there was no maximum dielectric loss within the measured frequency range until 1 GHz.

Fig. 13 illustrates the magnetization curve for the sintered samples prepared at different pH value. The magnetic moment per unit cell, nB was calculated from magnetization data using Eq. (1) and the values of Ms, Mr, and Hc are also shown in Table 1. The variation of Ms, Mr, Hc, and nB of Mg0.9Mn0.1Fe1.8O4 ferrites with pH is revealed in Fig. 14.

\[
\text{nB} = \frac{\text{molecular weight (Mw)} \times \text{saturation magnetization (Ms)}}{5585}
\]

It is found that the Ms value of the sample (pH < 1) is higher than the samples prepared with pH modification. It could be related to density,
Table 2

<table>
<thead>
<tr>
<th>pH</th>
<th>Occupation of cations</th>
</tr>
</thead>
<tbody>
<tr>
<td>A site</td>
<td>B site</td>
</tr>
<tr>
<td>pH &lt; 1</td>
<td>Mg$^{2+}$, $0.15$Fe$^{3+}$</td>
</tr>
<tr>
<td>pH = 3</td>
<td>Mg$^{2+}$, $0.12$Fe$^{3+}$</td>
</tr>
<tr>
<td>pH = 5</td>
<td>Mg$^{2+}$, $0.15$Fe$^{3+}$</td>
</tr>
<tr>
<td>pH = 7</td>
<td>Mg$^{2+}$, $0.45$Fe$^{3+}$, $0.55$</td>
</tr>
<tr>
<td>pH = 9</td>
<td>Mg$^{2+}$, $0.45$Fe$^{3+}$, $0.55$</td>
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The ferrite powders showed good sinterability at pH < 1. The sample with the pH < 1 provided higher dielectric constant with low dielectric loss and the highest values of $M_b$ and $M_r$ (30.04 emu/g and 4.93 emu/g). In this study, the variation of pH values of the mixed precursor solutions has a significant influence on the phase formation and the morphology of the ferrite products as well as its effect on the electromagnetic properties.

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