Structural and Magnetic Properties of \( \text{Ba}_3[\text{Cu}_{0.8-x}\text{Zn}_x\text{Mn}_{0.2}]_2\text{Fe}_{24}\text{O}_{41} \) Z-Type Hexaferrites

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Received 18 August 2018; Accepted 9 September 2018; Published 1 October 2018

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We report on the synthesis and characterization of \( \text{Ba}_3[\text{Cu}_{0.8-x}\text{Zn}_x\text{Mn}_{0.2}]_2\text{Fe}_{24}\text{O}_{41} \) \((x = 0.0, 0.2, 0.4, 0.6, \text{ and } 0.8) \) barium hexaferrites. The samples were prepared by high-energy ball-milling technique and double-sintering approach. The effects of Zn substitution for Cu on the structural and magnetic properties of the prepared samples were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), and vibrating sample magnetometer (VSM). XRD patterns of the samples revealed the presence of a major Z-type hexaferrite phase, together with secondary M-type and Y-type phases. The magnetic results indicated that the saturation magnetization increased slightly with increasing the Zn content, while the coercivity and magnetocrystalline anisotropy field exhibited a decreasing tendency with the increase of Zn content. The magnetic interactions revealed the complex magnetic structure of the prepared samples and confirmed that the Curie temperature of the magnetic phases decreased with increasing \( x \) as a result of the reduction of the strength of the superexchange interactions.

1. Introduction

The demands of rapidly developing modern technologies have driven and directed the efforts of a large sector of scientists and engineers toward the search for new materials with improved performance for miniaturized high-frequency devices [1]. Hexaferrites belonging to an important class of magnetic oxides have demonstrated potential for a plethora of permanent magnets as well as soft magnetic materials applications due to their favorable properties including chemical stability, low eddy current losses, and cost-effectiveness [2–10]. Z-type hexaferrites had attracted a great attention due to their high permeability in frequency regions higher than 300 MHz, and cutoff frequency up to 2 GHz, rendering these materials promising for inductive core at microwave frequencies, and ultrahigh-frequency communications devices [1, 11–13].

Synthesis of a pure phase of Z-type barium hexaferrite is a difficult process which involves a progressive transformation through intermediate ferrites before achieving the final complex crystalline structure [14–16]. This structure can be viewed as the sum of two simpler hexagonal ferrites, namely, M-type (BaFe_{12}O_{19}) and Y-type (Ba_2Me_2Fe_{12}O_{22}), which crystallize prior to the formation of the Z phase through solid-state reaction [11]. Accordingly, realization of the Z-type ferrite may occur through topotactic reaction involving alternate stacking of platelets of simpler hexagonal ferrite phases [2, 17].

The magnetic and dielectric properties of hexaferrites can be tuned by controlled substitution scenarios for the divalent (Me^{2+}) or trivalent (Fe^{3+}) ions [12, 16]. It was reported that specific choices of divalent metal ions in Z-type hexaferrite may improve their properties [12, 18–23]. Specifically, the substitution of Co^{2+} by Cu^{2+}, Zn^{2+}, and Ni^{2+} ions was adopted for enhancing the electromagnetic properties of Co_2Z for miniaturized antenna applications [24], where the substitution of Zn^{2+} improves the saturation magnetization, while the substitution of Cu^{2+} lowers the sintering temperature. Also, Cu and Zn-substituted Co_2Z hexaferrite demonstrated improved properties for multilayer...
chip inductor applications [25, 26]. In addition, various scenarios of Cu and/or Mn substitutions were adopted in the synthesis of M-type and Y-type hexaferrites (which are intermediate components of Z-type hexaferrites) and were reported to modify the magnetic properties of these hexaferrites for potential practical applications [27–37]. Also, the substitution of Co by Zn in Co₂Z hexaferrite demonstrated an increase in saturation magnetization, initial permeability, and resistivity, which makes Zn-substituted Co₂Z hexaferrites potentially important materials for high-frequency microchip inductor components [38, 39]. Further, the substitution of Mn for Fe in Co₂Z was reported to induce a shift of the relaxation peak in the dielectric behavior of Co₂Z hexaferrites toward higher frequencies [22].

Previous experimental results revealed that the optimal sintering temperature for the synthesis of Z-type hexaferrites using conventional solid-state method was in the range of 1200°C–1350°C [40]. Lower sintering temperatures of 1150°C–1200°C, however, were sufficient for the production of Z-type hexaferrites using wet chemical methods [13, 24, 40, 41]. The difficulty of obtaining a pure Z-type phase, and its tendency to coexist with other (M-, Y-, and W-type) hexaferrites and spinel phases, has led to adopting different modified synthesis routes, where synthesis of pure Co₂Z hexaferrite was reported to be achieved at 1250°C sintering temperature [42, 43]. Also, it was reported that a Z-type phase can be obtained using two-step solid-state reaction where precursor materials are initially sintered at temperatures between 980 and 1180°C, then ground, and again sintered at about 1230–1300°C [23, 44].

In this study, divalent ion dopants Zn²⁺ and Mn²⁺ were incorporated into the structure of Cu₂Z hexaferrite to enhance the magnetic properties. The samples were prepared using two-step sintering solid-state reaction of raw materials. This method is suitable to produce high-quality samples, since intermediate M and Y phases are formed at ~1000°C, and topotactical reaction of these intermediate phases at higher sintering temperature is expected to lead to crystallization of the Z-type phase.

2. Experimental Techniques

Precursor powders of Ba₃[Cu₀.₈₋ₓZnₓMn₀.₂]₂Fe₂₄O₄₁ (x = 0, 0.2, 0.4, 0.6, and 0.8) were prepared by ball-milling stoichiometric ratios of the starting Fe₂O₃, CuO, ZnO, MnO, and BaCO₃ powders. The starting powder mixtures were milled for 16 h at a rotational speed of 250 rpm in a planetary ball-mill, using a powder to ball ratio of 1:12. The resulting powder was preheated to 1000°C, and then ground for 1 h and pressed into disks of ~1 cm diameter and ~2 mm thickness under a force of 50 kN. The disks were then sintered at 1200°C for 2 h in air using a heating rate of 10°C/min.

The structure of the samples was investigated by X-ray diffraction (XRD), using a 7000 X-ray diffractometer, with Cu-Kα radiation (λ = 0.154 nm). XRD patterns for the samples were recorded over the angular range 20° < 2θ < 70° with a scan speed of 0.01° and a scan speed 0.5 deg./min. A powder diffraction software package was used to identify the structural phases in the prepared samples. The morphology of the prepared samples was examined using scanning electron microscope (SEM), and the sample composition was examined by energy-dispersive X-ray spectroscopy (EDX). The magnetic measurements were carried out at room temperature in an applied field up to 10 kOe using a vibrating sample magnetometer (VSM). The sample for VSM measurements was needle-shaped to reduce sample shape anisotropy.

3. Results and Discussion

3.1. XRD Results. Figure 1 shows the diffraction patterns of Ba₃[Cu₀.₈₋ₓZnₓMn₀.₂]₂Fe₂₄O₄₁. Rietveld analysis of the patterns using FullProf software indicated that the samples generally consisted of mixtures of the BaM hexaferrite phase, Y-type hexaferrite phase, and Z-type hexaferrite phase. The diffraction peaks corresponding to M- and Y-type intermediate phases were relatively strong in the sample with x = 0, and their intensities seemed to be weakened by Zn substitution for Cu, especially at x = 0.2–0.6, indicating the production of Z-type hexaferrites with higher purity at these compositions. Although noticeable changes of the relative intensities of the diffraction peaks of Z-type hexaferrites were observed as a consequence of Zn and Mn substitution, the structure remained consistent with the standard pattern. These results indicated that while the high-purity Z-type phase was not successfully achieved in the two-end binary compounds [Cu₀.₈Mn₀.₂]₂Z and [Zn₀.₈Mn₀.₂]₂Z, the ternary [Cu₂ZnMn]₂Z ferrites crystallized with high purity at sintering temperature of 1200°C, which is lower than the sintering temperature of 1250°C, 1300°C used for the production of the Z-type hexagonal phase by the sol-gel auto combustion method and ball-milling method, respectively [45]. The enhancement of the relative intensity of the (0018) reflection at 30.8° in comparison with the relative intensity of the corresponding reflection in the standard powder diffraction pattern is an indication that the possibility of crystallographic texture along the c-axis in these samples cannot be excluded. This result is consistent with the results reported by others [1, 46].

The refined lattice parameters and cell volume of the Z-type hexaferrite phase in the samples, as well as the bulk density and X-ray density, are listed in Table 1. The bulk densities of the samples were measured using Archimedes’ principle, while the X-ray density of each sample was determined using the relation:

$$\rho_x = \frac{Z(M_w)}{N_A V},$$

where Z is the number of molecules per unit cell, M_w is the molecular weight, V is the cell volume, and N_A is Avogadro’s number.

The lattice parameter a of the Z-type phase remains almost constant (5.88 ± 0.02 Å) with substitution, while c revealed a maximum value at x = 0.4. The cell volume (V) fluctuated (within ~1.5%) with a tendency to increase with the increase of x. The increasing trend of cell parameters and cell volume can be associated with the substitution of Cu²⁺.
by Zn$^{2+}$ with larger ionic radius [47], whereas the un-systematic fluctuations of these parameters can be associated with uncontrolled lattice distortions in the respective samples [32].

The bulk density of sintered disk samples was found to be in the range of (4.91 ± 0.06) g/cm$^3$ for all samples except that with $x = 0.2$, which demonstrated a relatively higher density of 5.22 g/cm$^3$. The X-ray density remains almost constant in the range (5.37 ± 0.04) g/cm$^3$ for the Z phase in all samples. These results indicated that our synthesis route yielded highly dense magnets (≥ 90% of theoretical density) for all compositions. The small decrease in X-ray density for the sample with $x = 0.4$ can be attributed to the small increase in the cell volume. The X-ray density of the Z-type phase in the samples is consistent with the reported value of 5.37 g/cm$^3$ for Zn$_2$Z hexaferrite [48].

### Table 1: The lattice parameters ($a$ and $c$), cell volume ($V$), bulk density ($\rho_b$), and X-ray density ($\rho_x$) for the Ba$_3$[Cu$_{0.8-}Zn_xMn_{0.2}$]$_2$Fe$_{24}$O$_{41}$ samples.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a = b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ (Å$^3$)</th>
<th>$\rho_b$ (g/cm$^3$)</th>
<th>$\rho_x$ (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>5.87</td>
<td>52.16</td>
<td>1554</td>
<td>4.89</td>
<td>5.41</td>
</tr>
<tr>
<td>0.2</td>
<td>5.89</td>
<td>52.27</td>
<td>1569</td>
<td>5.22</td>
<td>5.36</td>
</tr>
<tr>
<td>0.4</td>
<td>5.90</td>
<td>52.37</td>
<td>1577</td>
<td>4.86</td>
<td>5.33</td>
</tr>
<tr>
<td>0.6</td>
<td>5.88</td>
<td>52.29</td>
<td>1568</td>
<td>4.97</td>
<td>5.37</td>
</tr>
<tr>
<td>0.8</td>
<td>5.89</td>
<td>52.34</td>
<td>1571</td>
<td>4.85</td>
<td>5.36</td>
</tr>
</tbody>
</table>

3.2. SEM and EDX Results. Typical SEM images were collected for each sample to investigate the particle shape and particle size distribution. Furthermore, EDX measurements at randomly selected spots of the samples were carried out to identify the particular hexaferrite phase to which the measured particle belongs. In some cases, the results of EDX measurements on different spots of the same sample were discussed for comparison, limiting our discussion to special cases for brevity purposes, and clarification of the main findings.

Figure 2(a) shows SEM image for the Ba$_3$[Cu$_{0.8-}Zn_xMn_{0.2}$]$_2$Fe$_{24}$O$_{41}$ sample. The SEM image shows platelets with varying sizes in the range of 4 to 11 µm, including a large hexagonal platelet with sharp edges. Discontinuous grain growth (DGG) could be responsible for the occurrence of anomalously large hexagonal crystals in this sample [2]. Also, the SEM image shows small irregular particles which could be due to poor crystallization of starting components or as a result of the fractured surface of the sample.

To check the chemical composition of the particles, EDX spectra were collected at different spots of the sample. A typical spectrum collected from the encircled spot is shown in Figure 2(b), and the atomic ratios are presented in Table 2. The observed Ba : Fe atomic ratio of 1 : 8.04 is in excellent agreement with the stoichiometric ratio of 1 : 8.00 for Ba$_3$[Cu$_{0.8}$Mn$_{0.2}$]$_2$Fe$_{24}$O$_{41}$ hexaferrite. Also, the observed
Ba: Cu and Ba:Mn atomic ratios of 1:0.66 and 1:0.10 are close to the stoichiometric ratios of 1:0.53 and 1:0.13, respectively, for Ba₃[Cu₀.₈Mn₀.₂]₂Fe₂₄O₄₁ hexaferrite.

For reproducibility purposes, EDX measurements were carried out at two different spots of the same sample. The measured Ba:Fe atomic ratios were 1:9.00 and 1:7.00, the Ba:Cu ratios were 1:0.64 and 1:0.80, and the Ba:Mn atomic ratios were 1:0.17 and 1:0.12. The average ratio of Ba:(Fe+Cu+Mn) in the two regions is 1:8.87, which agrees well with the theoretical value of 1:8.67 for Ba₃[Cu₀.₈Mn₀.₂]₂Fe₂₄O₄₁ hexaferrite.

Figure 3 shows two SEM images (a, b) for Ba₃[Cu₀.₈−ₓZnₓMn₀.₂]₂Fe₂₄O₄₁ (x = 0) sample. Sharp-edged hexagonal platelets with in-plane dimensions of several micrometers are observed in Figure 3(a), while much larger hexagonal platelets evolving through the DGG process are observed in Figure 3(b). The majority of the sample, however, is composed of large, nonparticulate masses, which may explain the appreciable increase in sample density. EDX spectra (not shown) were collected at different measuring spots to examine the chemical composition of the sample. The observed Ba:Fe atomic ratios at two different measuring spots were (1:7.00) and (1:8.00), while the atomic ratios of Ba:Zn were 1:0.22 and 1:0.14, the atomic ratios of Ba:Cu were 1:0.56 and 1:0.52, and the atomic ratios of Ba:Mn were 1:0.15 and 1:0.16. These atomic ratios are in agreement with the stoichiometric Ba:Fe ratio of 1:8.00, Ba:Zn ratio of 1:0.13, Ba:Cu ratio of 1:0.40, and Ba:Mn ratio of 1:0.13 for Ba₃[Cu₀.₈Zn₀.₂Mn₀.₂]₂Fe₂₄O₄₁ hexaferrite. Also, the average Ba:metal, Ba:(Fe + Zn + Cu + Mn) ratio was 1:8.4, which is close to the theoretical value of 1:8.7 for Ba₃[Cu₀.₆Zn₀.₂Mn₀.₂]₂Fe₂₄O₄₁ hexaferrite.

The SEM image for Ba₃[Cu₀.₈−ₓZnₓMn₀.₂]₂Fe₂₄O₄₁ (x = 0.4) sample in Figure 3(c) shows that a large fraction of the sample consists of sharp-edged hexagonal platelets with typical in-plane size of few micrometers, in addition to some larger particles and nonparticulate masses which may have evolved through DGG process. EDX measurements on a selected spot of the sample revealed that the Ba:Fe atomic ratio is 1:5.20, the Ba:Zn atomic ratio is 1:0.38, the Ba:Mn atomic ratio is 1:0.10, and the Ba:Cu atomic ratio is 1:0.47. These ratios are lower than the stoichiometric metal ratios in the Z-type phase and are closer to the stoichiometric Ba:metal ratios of 1:6.0, 1:0.4, 1:0.2, and 1:0.4, respectively, in Ba₂Cu₀.₆Zn₀.₄Mn₀.₄Fe₂₂O₄₂ Y-type hexaferrite. This result confirmed the presence of Y-type hexaferrite crystallizing in the form of separate particles.

Figure 3(d) shows a typical SEM image for the samples with x = 0.6, which also revealed the presence of a large fraction of sharp-edged hexagonal platelets with a typical in-plane size in the range of 1.5 to 4 µm, in addition to large layered formations which may have evolved through the DGG process and topotactical reactions. EDX measurement on a selected spot of the sample revealed that the atomic ratio of Ba:Fe was 1:8.0, while the atomic ratios of (Ba:Cu, Zn, Mn) were 1:0.16, 1:0.28, and 1:0.07, respectively. These ratios are in agreement with the Ba:Fe, Cu, Zn, and Mn atomic ratios of 1:8.0, 1:0.13, 1:0.40, and 1:0.13 for

Table 2: Atomic concentrations and atomic ratios of the different elements in the sample Ba₃[Cu₀.₈−ₓZnₓMn₀.₂]₂Fe₂₄O₄₁ (x = 0).

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (C)%</th>
<th>Atom/mol.</th>
<th>Stoichiometric ratio Metal:Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>3.84</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Fe</td>
<td>30.87</td>
<td>8.04</td>
<td>8.00</td>
</tr>
<tr>
<td>Cu</td>
<td>2.54</td>
<td>0.66</td>
<td>0.53</td>
</tr>
<tr>
<td>Mn</td>
<td>0.40</td>
<td>0.10</td>
<td>0.13</td>
</tr>
<tr>
<td>O</td>
<td>62.36</td>
<td>16.2</td>
<td>13.7</td>
</tr>
</tbody>
</table>

Figure 2: (a) SEM image and (b) EDX measurement for the Ba₃[Cu₀.₈−ₓZnₓMn₀.₂]₂Fe₂₄O₄₁ (x = 0) sample.
Ba₃[Cu₀.₂Zn₀.₆Mn₀.₂]₂Fe₂₄O₄₁ hexaferrite. EDX measurement on a different spot of this sample, however, revealed that the Ba:Fe ratio was 1:6.59, which is close to the Ba:Fe ratio of 1:6.0 in Y-type hexaferrite. This could be evidence of the presence of traces of the Y-type hexaferrite phase in the form of separate particles.

Figure 3(e) shows a typical SEM image for the sample with \( x = 0.8 \), which revealed crystallization of mainly hexagonal platelets with almost similar in-plane particle sizes in the range from 1.67 to 2.3 \( \mu \)m. EDX measurements on a selected spot of the sample demonstrated that the atomic ratios of Ba:Fe, Zn, and Mn were 1:7.0, 1:1.0, and 1:0.10. The Ba:Zn ratio is consistent with Zn₂Y (Ba₂Zn₂Fe₁₂O₃₂) stoichiometry, while the observed Ba:Fe and Ba:Mn ratios are between their corresponding stoichiometric ratios in Zn₂Y and Ba₃Zn₁.₆Mn₀.₄Fe₂₄O₄₁ Z-type hexaferrite, which may indicate that the measured region of the sample contained a mixture of Y-type and Z-type hexaferrite phases.

Figure 3: SEM images for the Ba₃[Cu₀.₈₋ₓZnₓMn₀.₂]₂Fe₂₄O₄₁ \( (x = 0.2, 0.4, 0.6, \text{and } 0.8) \) samples.
3.3. VSM Results

3.3.1. Isothermal Magnetization. The magnetic properties of Ba$_3$[Cu$_{0.8-x}$Zn$_x$Mn$_{0.2}$]$_2$Fe$_{24}$O$_{41}$, $x=0$, 0.2, 0.4, 0.6, and 0.8 samples were studied by VSM at room temperature in an applied field up to 10 kOe. The hysteresis loops of all samples (Figure 4) were typical smooth S-shaped curves revealing characteristics of relatively soft magnetic materials. An expanded view of the loops is shown in Figure 5, from which the remnant magnetization and coercive field for each sample were obtained directly. The saturation magnetization, however, was determined by applying the law of approach to saturation in the high-field range. In this range, the magnetization of the sample is dominated by magnetization rotation processes of the magnetic domains, where the magnetization is given by [49–51]:

\[
M = M_s \left(1 - \frac{A}{H} - \frac{B}{H^2}\right) + \chi H, \tag{2}
\]

where $M_s$ is the spontaneous saturation magnetization of the domains per unit volume, $A$ is a constant representing the contributions of inclusions and microstress, $B$ is a constant representing the contributions of magnetocrystalline anisotropy, and $\chi H$ is the forced magnetization term. For hexagonal crystals, the constant $B$ is given by

\[
B = \frac{H_s^2}{15}. \tag{3}
\]

A plot of $M$ versus $1/H^2$ in the field region 8 kOe < $H$ < 10 kOe for each sample gave a straight line, indicating that the magnetization in this field range is dominated by the magnetocrystalline term. According to Equation (2), the intercept of the straight line with the $M$-axis determines the saturation magnetization, while the slope determines the constant $B$, from which the anisotropy field ($H_a$) can be determined using Equation (3). The magnetic parameters derived from the hysteresis loops are presented in Table 3. The metallic ions (Fe$^{3+}$, Mn$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$) in the Z-type hexaferrite phase occupy 10 nonequivalent crystallographic sites, listed in Table 4 together with the number of metal ions per formula unit and magnetic sublattice spin orientation. The partial substitution of Cu$^{2+}$ ions in Cu$_2$Z by Zn$^{2+}$ or Mn$^{2+}$ ions may lead to complex magnetic structure determined by the cationic preferential site occupation. The preferred site for Cu$^{2+}$ ion is the tetrahedral site, while that for both the Mn$^{2+}$ ion is the octahedral site [52]. The Zn$^{2+}$ ion generally prefers to occupy 4f$_{IV}$ tetrahedral site, with some tendency to enter the 4f$_{VI}$ octahedral site due to the large ionic diameter (0.74 Å) [53].

Figure 6 shows the effect of zinc content on the saturation magnetization and the coercivity of Ba$_3$[Cu$_{0.8-x}$Zn$_x$Mn$_{0.2}$]$_2$Fe$_{24}$O$_{41}$. The saturation magnetization $M_s$ for the sample with $x=0.0$ was found to be 45 emu/g, which is close to the value of 46 emu/g reported for Cu$_2$Z hexaferrite [48]. As $x$ increases, the saturation magnetization demonstrated increasing tendency, reaching the value of 53 emu/g for the sample with $x=0.8$. While this value is in good agreement with recently reported values of 52.9 emu/g for Zn$_2$Y hexaferrite [45], it is lower than previously reported values of 58-59 emu/g [38, 48, 54]. Considering that the Zn-rich samples consist of a mixture of stoichiometric ratios of Zn$_2$Z, Zn$_2$Y, and M-type hexaferrites, with Zn$_2$Z = Zn$_2$Y + M,
Table 4: Crystallographic sites of small metal ions in Z-type barium ferrite, their coordination, position in the unit cell, occupancy, and spin orientation of magnetic ions in the site [52].

<table>
<thead>
<tr>
<th>Site</th>
<th>Coordination</th>
<th>Block</th>
<th>Number of ions/formula</th>
<th>Spin orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>12kVI</td>
<td>Octahedral</td>
<td>R-S</td>
<td>6</td>
<td>Up</td>
</tr>
<tr>
<td>2dI</td>
<td>Five fold</td>
<td>R</td>
<td>1</td>
<td>Up</td>
</tr>
<tr>
<td>4eV</td>
<td>Octahedral</td>
<td>R</td>
<td>2</td>
<td>Down</td>
</tr>
<tr>
<td>2eV</td>
<td>Octahedral</td>
<td>T</td>
<td>2</td>
<td>Down</td>
</tr>
<tr>
<td>4eV</td>
<td>Tetrahedral</td>
<td>S</td>
<td>2</td>
<td>Down</td>
</tr>
<tr>
<td>4f</td>
<td>Tetrahedral</td>
<td>T</td>
<td>2</td>
<td>Down</td>
</tr>
<tr>
<td>4f*V</td>
<td>Tetrahedral</td>
<td>T</td>
<td>2</td>
<td>Down</td>
</tr>
<tr>
<td>4f*VI</td>
<td>Octahedral</td>
<td>S</td>
<td>2</td>
<td>Up</td>
</tr>
<tr>
<td>12k*VI</td>
<td>Octahedral</td>
<td>T-S</td>
<td>6</td>
<td>Up</td>
</tr>
<tr>
<td>2aVI</td>
<td>Octahedral</td>
<td>T</td>
<td>1</td>
<td>Up</td>
</tr>
</tbody>
</table>

The saturation magnetization of the sample can be calculated from the following formula:

\[
M_s = \frac{M_M}{M_Z} (M_{x})_M + \frac{M_Y}{M_Z} (M_{y})_Y
\]

where \(M_M\), \(M_Y\), and \(M_Z\) are the molecular weights of BaM, Zn2Y, and Zn2Z hexaferrites, respectively, and \((M_{x})_M\) and \((M_{y})_Y\) are the saturation magnetizations of BaM and Zn2Y hexaferrites, respectively. Using typical values of the saturation magnetization of 72 emu/g for BaM [55] and 35.2 emu/g for Zn2Y [56], the calculated value of the saturation magnetization of the sample is \(\sim 51\) emu/g. The fluctuations (of \(\sim 5\%\)) of the observed values of Zn-substituted samples about the calculated value can be attributed to the presence of Cu and Mn ions in the lattice.

Figure 6 also shows that the coercivity decreased sharply at all levels of Zn substitution for Cu. In light of the XRD results, the magnetically hard BaM hexaferrite was one of the observed structural components of the sample with \(x = 0\), which could be responsible for the relatively high coercivity of the sample. The significant reduction of the coercivity of the Zn-substituted samples could therefore be associated with the transformation of the hard BaM magnetic phase to the soft Z-type phase, whereas the fluctuations of the coercivity of the Zn-substituted samples could be due to differences of the microstructure and particle size as demonstrated by SEM imaging.

Figure 7 shows the behavior of the anisotropy field \(H_a\) with increasing Zn concentration (\(x\)). The value of \(H_a\) demonstrated decreasing tendency with zinc substitution, recording values of 5.61 and 6.05 kOe at \(x = 0.4\) and \(x = 0.6\), respectively. These values are in good agreement with the reported value of 5.6 kOe for Zn2Z hexaferrites [54]. Also, the values of 8.58 kOe and 7.92 kOe for the samples with \(x = 0.2\) and 0.8 are in reasonable agreement with previously reported values of 6.66 and 7.0 kOe for Zn2Z hexaferrites [45].

The initial susceptibility \(\chi_i\) and magnetic permeability \(\mu_i\) of each sample was determined from the initial magnetization curve (not shown for brevity). The obtained values of these magnetic parameters are also listed in Table 3 for all samples under investigation. The data indicated that the magnetic permeability improved by zinc substitution for Cu, and the improvement reached 55% at \(x = 0.8\). This improvement could be potentially important for microwave applications of these materials.

3.3.2. Thermomagnetic Measurements. Figure 8 shows thermomagnetic curves for Ba\(_{1-x}\)Cu\(_x\),Zn\(_{0.5}\)Mn\(_{0.5}\),Fe\(_{24}\)O\(_{41}\) samples at constant applied field of 100 Oe. A homogeneous sample with sharp magnetic phase-transition at the Curie temperature \(T_c\) should give a sharp peak in the derivative of the thermomagnetic curve at that temperature. The thermomagnetic curve for the sample with \(x = 0.0\) exhibited magnetic transition at 336°C, and a second magnetic transition at 440°C, preceded by a Hopkinson peak at \(T = 424\) °C, which is an indicator of the existence of some small particles with superparamagnetic behavior near the Curie temperature [57]. In light of the reported values for the Curie temperatures of various pure hexaferrite phases (Table 5), the phase transition at 440°C is associated with the ferromagnetic-to-paramagnetic transition of the Cu2Z phase. On the contrary, the magnetic transition associated with the peak in the derivative curve at 336°C is close to the reported magnetic transition temperature of Mn2Y, where the difference between our value and those reported for the Mn2Y phase could be due to the insufficiency of Mn and Cu content to form pure Mn2Y. In addition, since the substitution of Fe by Cu in BaM was found to result in a decrease of the Curie temperature [32], the peak structure around 440°C could also be associated with ferromagnetic-to-paramagnetic transition in Cu-partially substituted BaM.

The derivative curve for the sample with \(x = 0.2\) exhibited a relatively strong and sharp peak at 370°C, which is associated with the Curie temperature of the Zn2Z phase. The observed higher transition temperature (compared to reported value of 360°C), and the occurrence of another small peak at 402°C, could be associated with sample
inhomogeneity, where different phases of Cu-substituted Zn$_2$Z coexist with Curie temperatures between the characteristics of Zn$_2$Z and Cu$_2$Z. Furthermore, the small peak at 440°C could be associated with magnetic transitions of BaM and pure Cu$_2$Z phases, and the small peak at 294°C is in good agreement with the transition temperature of the Mn$_2$Y phase.

The derivative curve for the sample with $x = 0.4$ exhibited a strong peak at 356°C, which is associated with the transition temperature of the pure Zn$_2$Z phase. Also, the small peak at 396°C is associated with the transition temperature of the (Cu,Zn)$_2$Z (Zn-substituted Cu$_2$Z) phase. On the

**Table 5:** Curie temperature $T_c$ (°C) for the hexaferrite phases observed in the samples [48].

<table>
<thead>
<tr>
<th>Phase</th>
<th>BaM</th>
<th>Zn$_2$Z</th>
<th>Cu$_2$Z</th>
<th>Zn$_2$Y</th>
<th>Mn$_2$Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$ (°C)</td>
<td>450</td>
<td>360</td>
<td>440</td>
<td>130</td>
<td>290</td>
</tr>
</tbody>
</table>

**Figure 7:** The anisotropy field as a function of Zn concentration ($x$).

**Figure 8:** Thermomagnetic curves and their derivatives for the Ba$_3$(Cu$_{0.8-x}$Zn$_x$Mn$_{0.2}$)$_2$Fe$_{24}$O$_{41}$.
contrary, the transition temperature at 227°C lies between the transition temperatures of Zn$_2$Y (130°C) and Mn$_2$Y (290°C) and could therefore be associated with the (Mn, Zn)$_2$Y phase.

The magnetic transition at 338°C for the sample with $x = 0.6$ could be associated with the Zn$_2$Y phase, while the magnetic transition at 383°C is associated with the (Cu, Zn)$_2$Z phase. Also, the thermomagnetic curve exhibited a small peak at 183°C, which can be associated with the transition temperatures of Zn$_2$Y (130°C) and Mn$_2$Y (329°C) could be associated with BaM with partial substitution for Fe.

The observed Curie temperatures of the different magnetic phases in the samples are listed in Table 6.

<table>
<thead>
<tr>
<th>$x$</th>
<th>Curie temperature $T_c$ (°C)</th>
<th>Magnetic phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>336 — 440</td>
<td>Mn$_2$Y, BaM, Cu$_2$Z</td>
</tr>
<tr>
<td>0.2</td>
<td>294 370 402 440</td>
<td>Mn$_2$Y, Zn$_2$Z, Cu$_2$Z</td>
</tr>
<tr>
<td>0.4</td>
<td>227 356 396</td>
<td>(Mn,Zn)$_2$Y, Zn$_2$Z, (Cu,Zn)$_2$Z</td>
</tr>
<tr>
<td>0.6</td>
<td>183 338 383</td>
<td>(Mn,Zn)$_2$Y, Zn$_2$Z, (Cu,Zn)$_2$Z</td>
</tr>
<tr>
<td>0.8</td>
<td>146 329 383 431</td>
<td>Zn$_2$Y, Zn$_2$Z, BaM</td>
</tr>
</tbody>
</table>

4. Conclusion

The double-sintering process was successful in producing high-density [$\text{Cu}_{0.8-x}\text{Zn}_{0.2}\text{Mn}_{0.2}$]$_2$Z hexaferrites at a relatively low temperature of 1200°C. Intermediate levels of Zn substitution for Cu (0.2 ≤ $x$ ≤ 0.6) was found to be suitable for the production of a highly pure Z-type phase with increased saturation magnetization and reduced coercivity and magnetocrystalline anisotropy. All samples were highly dense, with a record density of 97% observed for the sample with $x = 0.2$. DGG, and topotactical reactions were responsible for growth of large particles and nonparticulate masses in the samples. The thermomagnetic curves demonstrated the complexity of the fabricated materials and indicated that the samples consisted of different magnetic phases with Curie temperatures generally decreasing with the increase of Zn concentration, which leads to the reduction of the superexchange interactions.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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