Size dependent structural and magnetic properties of Al substituted Co–Mg ferrites synthesized by the sol–gel auto-combustion method

Imran Ahmad a,*, Tahir Abbas b, A.B. Ziya a, Ghazanfar Abbas c, Asghari Maqsood d

a Department of Physics, Bahauddin Zakarya University, Multan 60800, Pakistan
b Centre for Solid State Physics, University of the Punjab, Lahore 54560, Pakistan
c Department of Physics, Comsats Institute of Information Technology, Islamabad 44000, Pakistan
d Centre for Emerging Sciences, Engineering & Technology (CESET), I I U, Islamabad 45320, Pakistan

Article history:
Received 11 April 2013
Received in revised form 13 December 2013
Accepted 1 January 2014
Available online 8 January 2014

Keywords:
A. Magnetic materials
B. Chemical synthesis
C. X-ray diffraction
D. Magnetic properties

Abstract
Single phased nanocrystalline Co0.7Mg0.3FeAlO4 ferrites having low coercivity were synthesized by the sol–gel auto-combustion route. The subsequent powder materials were sintered in a temperature range of 800–1200 °C for 2 h. The effects of sintering temperatures on the structure, morphology and magnetic properties of the prepared soft magnetic material were studied. X-ray diffractometer (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), and magnetic property measurement system (MPMS) were used to characterize the samples. X-ray diffraction analysis confirmed a single-phase cubic spinel structure and ruled out the presence of impurities like hematite. The higher sintering temperatures have caused in enhanced mark of crystallinity and bigger average grain size of the nanocrystals. A slight decrease in lattice parameters was noticed with a rise of grain size. Magnetic measurements revealed that grain size increase led to a decrease in the coercivity and, in difference, an increase in the saturation magnetization.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The replacement of several magnetic and non-magnetic ions at different sub-lattices in ferrite components has provided fascinating magnetic structures and electrical properties. Spinel ferrites are more striking among them as they have a variety of magnetic disorder and frustration. The presence of unsatisfied bonds results in magnetic dilution, and generates a variety of structures because of the competition between the various exchange interactions [1–3]. Co–Mg ferrite nanomaterials have been widely used for the electronic devices because of their large permeability at high frequency, high electrical resistivity, chemical strength and cost efficiency. The enhanced dielectric and decent magnetic properties due to the nanometer size establishment make them superb materials for high frequency and microwave application devices. Rehman et al. [4] prepared nanocrystalline Mg–Co ferrites by the sol–gel method. Based on dielectric and magnetic measurements, they reported that these materials were capable constituents for the diminishment of the size of antennas. Ahmed et al. [5] found the correlation between the structure and magnetic interaction by interpreting the lattice parameters, Curie temperature and magnetic susceptibility assuming cation distribution, for Mg-substituted Co ferrites. Kulkarni et al. [6] synthesized the spinel solid solution series Mg₅Co₁₋ₓFeₓO₄ by co-precipitation method and based on a.c. susceptibility and Mossbauer spectral reports, studied that fine particles gave rise to the unusual magnetic properties within the system, like superparamagnetism. Diamagnetic exchange in simple and mixed ferrites has established a great deal of considerations over the previous few years [7]. The existence of nonmagnetic ions in spinel lattice makes over the magnetic and electrical properties of the material. Such isomorphic interactions in iron oxides significantly decrease the magnetic interactions, causing lesser magnetic ordering temperatures and reduced magnetic-field super transfer [8]. The octahedral B-site preference is testified for Al³⁺ ions in the aluminum substituted ferrites [9,10]. Zakaria et al. [11] used neutron diffraction to refine the crystal structure of the spinel system Zn₀.₆Co₀.₄Al₀.₄Fe₂₋ₓO₄ and reported a monotonous decrease in the saturation magnetization, and the Curie temperature with increasing Al substitution. Different methods such as a ceramic method [12], co-precipitation method [13], sol–gel method [14], microemulsion method [15], hydrothermal method [16], citrate method [17], and combustion method [18], have been used for the synthesis of spinel ferrites. The aim of this work was to...
synthesize a decent soft magnetic material, with modified magnetic properties (low hysteresis loss) for high-frequency application and to study the effects of sintering temperatures on the structural and magnetic properties of the prepared materials. Therefore, to achieve the said objectives, we substituted a proper amount of diamagnetic Al$^{3+}$ in place of Fe$^{3+}$ in the Co–Mg spinel lattice. Although the substitution of Al$^{3+}$ for Fe$^{3+}$ in many ferrites has been reported, but in most of the cases, consequent materials were not a single phase material \cite{8.12}. In the current exploration, the sol–gel auto-combustion method has been employed for the synthesis of single phased Co$_{0.7}$Mg$_{0.3}$FeAlO$_4$ nanoparticles. Solution–gelation is the most useful method for the synthesis of nanomaterial due to its several benefits like high homogeneity and purity of products, low processing temperature, controlled size and morphology of the resulting particles. The impact of sintering behaviors, microstructural features and magnetic properties of sintered ferrites are inspected. The fallouts are being described and discussed.

2. Experimental

2.1. Synthesis

Co$_{0.7}$Mg$_{0.3}$FeAlO$_4$ ferrite nanocrystals were prepared by the sol–gel (auto-combustion) method. At first, a mixed solution was formed by dissolving stoichiometric quantities of the analytically pure grade Mg (NO$_3$)$_2$·6H$_2$O, Co(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, and CuH$_2$O$_2$·H$_2$O, into deionized water. The uniform distribution and segregation of the metal ions were attained using the citric acid (chelating agent) by fixing the molar ratio of the nitrates to citric acid as 1:2. In order to speed up the reaction and to attain the large surface area of the particles, the pH of the solution was maintained equal to 7.5 by the drop wise addition of ammonia solution (base catalyst). Then, the solution was persistently stirred at room temperature using a magnetic stirrer until a condensation reaction between the metal nitrates, and the citrate was accomplished and a polymer complex was formed. The resulting sol was heated at 80 °C for 12 h on a hot plate under steady stirring to condensate it into a dry gel. Further rise of temperature up to 270 °C led to the ignition of the dry gel. Consequently, a fluffy nanoferrite powder was obtained by burning of the gel in a self-propagating combustion mode. The NO$_3^{-}$ ions play a significant role in the auto-combustion of nitrate–citrate dried gel. Combustion is an oxidation–reduction reaction, during which a redox mixture of the nitrates (oxidant) and carboxyl groups (reductant) collapses exothermically, along with the removal of a large amount of gases such as N$_2$, H$_2$O, and CO$_2$. The prepared powder samples were then sintered for 2 h at different temperatures from 800 °C to 1200 °C in order to enhance the crystallinity.

2.2. Characterization techniques

X-ray diffractometer (PANalytical X’ pert Pro) with CuKα as a radiation source was used to analyze the phase constitutes of the product materials. The scan was performed through the angle (2θ) range of 20–80° keeping the step size equal to 0.02. The microstructure and the grain sizes were estimated by the field emission scanning electron microscope (FE-SEM, PHILIPS XL30S FEG) and transmission electron microscope (TEM, JEOL JEM-2100F). The powders were distributed in a solution of oleic acid in heptane. One droplet of the suspension was placed on carbon film of the microscopic grid, and the solvent was vanished at room temperature. Magnetic properties were measured using a squid magnetometer MPMS-7 (Quantum Design) under an applied field of 7 T (70,000 Oe) at room temperature.

![Fig. 1. XRD patterns of Co$_{0.7}$Mg$_{0.3}$FeAlO$_4$ ferrites sintered at (a) 800 °C, (b) 900 °C, (c) 1000 °C, (d) 1100 °C and (e) 1200 °C.](image)

3. Results and discussion

3.1. Structural analysis

X-ray diffraction patterns of the Co$_{0.7}$Mg$_{0.3}$FeAlO$_4$ samples sintered at different temperatures are displayed in Fig. 1. The diffractograms reveal the specific reflections of the cubic (Fd-3 m) spinel phase and there is no sign of the formation of mixed phases. Fig. 1 also indicates that the peaks become sharper and thinner with the increase of sintering temperature, showing the improvement of crystallinity. A minor decrease in the unit cell parameters was observed by the increase of sintering temperature and hence with grain size. This slight lattice expansion with the decrease of grain size may be attributed due to the reduction in valence states and distribution of cations among the lattice sites within the spinel structure \cite{19}. Lattice parameter values calculated using the standard equation ($a = d(h^2 + k^2 + l^2)^{1/2}$) are given in Table 1. The results obtained for investigated samples are in good agreement with the previous literature \cite{10,19}. The average crystallite sizes (D) were calculated from XRD peak broadening of the (3 1 1) diffraction peak using the Scherrer’s formula \cite{20}: $D = 0.9 \lambda / \beta \cos \theta$, where D is the crystallite size, $\lambda$ the X-ray wavelength, $\beta$ the full width at half maximum intensity and $\theta$ is the Bragg’s angle. The average XRD crystallite size (Table 1) increased from 20 nm to 70 nm as the sintering temperature was raised from 800 °C to 1200 °C. This grain growth is due to the increase in sintering temperature.

3.2. Morphology analysis

The scanning electron micrographs (Fig. 2) clearly indicate that the samples are composed of homogeneously distributed nanoparticles of well-defined shape with distinct grain boundaries and

<table>
<thead>
<tr>
<th>Table 1: Lattice parameter, crystallite size, saturation magnetization, coercivity and magnetic moment values of Co$<em>{0.7}$Mg$</em>{0.3}$FeAlO$_4$ nanoparticles.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sintering</strong></td>
</tr>
<tr>
<td><strong>temperature</strong></td>
</tr>
<tr>
<td><strong>(°C)</strong></td>
</tr>
<tr>
<td>900</td>
</tr>
<tr>
<td>1000</td>
</tr>
<tr>
<td>1100</td>
</tr>
<tr>
<td>1200</td>
</tr>
</tbody>
</table>
the grain size increases with growing sintering temperature. The grain size evaluated from SEM micrographs was found to vary from 55 nm to 395 nm for the samples sintered at 900–1200 °C. TEM analysis (Fig. 3) was also performed for the verification of the grain sizes. At the sintering temperatures of 900 °C and 1000 °C the observed TEM grain sizes were 60 nm and 65 nm, respectively. Moreover, these TEM particle sizes were in good agreement with those estimated by SEM (55–70 nm) and XRD (42–55 nm). At the higher sintering temperatures (i.e., 1100 °C and 1200 °C) the larger size of the particles was observed in comparison of the sizes calculated by the Scherrer equation. This may be caused by the agglomeration and coalescence of the particles with each other, as on sintering, two or more particles look like to fuse together by melting of their surfaces.

3.3. Magnetic properties

Room temperature magnetic hysteresis curves, recorded for all the samples sintered at different temperatures, are presented in Fig. 4. From the M–H loops, it can be observed that the samples behave as soft magnetic materials with low hysteresis loss. Magnetic behavior of the powders also exhibited that the
saturation magnetization ($M_s$) increased somewhat, and coercivity decreased continuously with increasing sintering temperature. The variation in the magnetic properties can be ascribed due to the adaptation of grain sizes dependent on the sintering temperature. The increase in saturation magnetization with the rise of temperature is mainly related to the grain growth, development of domain walls in the particles and alignment of the atomic spins in the direction of the applied magnetic field. Furthermore, it may also be due to the small reduction in unit cell parameter, enhancement of crystallinity and decreased inert surface layer effects of the crystals when the crystals expose to elevated temperatures [19,21]. As the coercivity depends on the particle size so variation of coercivity can be explained assuming domain structure and critical diameter of the particles [22]. By taking into account the critical diameter, the nanoparticles can be classified under three categories, superparamagnetic particles, single-domain particles, and multi-domain particles. In the superparamagnetic class of the particles (particle size < 10 nm) when the thermal energy becomes higher than the anisotropy energy barrier, coercivity becomes zero due to the random fluctuation of the magnetization. In addition, in the single-magnetic domain particles, coercivity increases gradually and reaches to its maximum at the threshold of the single to multi-domain state with increasing particle size. This is because of the lack of domain walls and dominance of thermal effects, and the demagnetization caused by the magnetic domain rotation. On the other hand, in multi-magnetic domain particles, coercivity decreases with the increase of particle diameter due to the domain wall displacement.

According to the previous reports, the critical diameter of a single domain of CoFe$_2$O$_4$ and MgFe$_2$O$_4$ is below 50 nm [20,23,24]. In the samples under study, observed grain size range is 55–395 nm, which is beyond the critical size of a single domain. Thus, within the sintering temperature range of 900–1200 °C, only the growth of the multi-domain particles occurred and transformation from single to multi domain phase could not be observed. In the multi-domain particles, there is no hindrance, and domain wall movement becomes dominant with the increase of particle size. That is why coercivity decreases with the increase of grain size because of the displacement of domain walls. Similar results of the saturation magnetization (21.0 emu/g) and coercive field (78 G) are reported [11] for Co$_{0.6}$Mg$_{0.4}$AlFeO$_4$. The possible reason behind the low values of saturation magnetization and coercivity of our samples is the presence of non-magnetic Mg$^{2+}$ and a large content of Al$^{3+}$, which causes magnetic dilution and a decrease in anisotropy. The magnetic moment ($\mu_B$) values (Table 1) are also calculated from the saturation magnetization data using the relation ($\mu_B = M_w \times M_s / 5585$) [25]. Where, $M_w$ is the molecular weight to the sample, and $M_s$ is the saturation magnetization in emu/g. The value of magnetic moment per formula unit obtained from M–H curve increases a little with the sintering temperature and grain size. This is due to the slight increase of saturation magnetization.

4. Conclusion

Pure phased Co$_{0.6}$Mg$_{0.4}$AlFeO$_4$ cubic nanocrystals were prepared by the sol–gel method. Size and crystallinity dependent structural and magnetic properties of the synthesized materials were studied. The higher sintering temperatures resulted in better degree of crystallinity and bigger mean particle size. The room-temperature magnetic measurement showed that due to the multi-domain nature (size >50 nm) of the synthesized particles, the saturation magnetization increased and coercivity decreased with the increment of grain size, and the sintering temperature. From the hysteresis loops as determined by the field dependence of magnetization, it is perceived that the samples perform as soft magnetic materials with low hysteresis loss.

Acknowledgments

The financial support under the Indigenous 5000 scholarship scheme from Higher-Education Commission (HEC) of Pakistan is acknowledged. Pohang University of Science and Technology South Korea is also acknowledged for the facilities and equipment to carry out this study.

References