The effect of the Doping with Cobalt Transition Metal on the Dielectric and Structural Properties of Fe\textsubscript{0.5}Co\textsubscript{x}Mg\textsubscript{0.95-x}O Nanoparticles Synthesized by Sol-Gel Assisted Auto-Combustion

Tagreed M. Al-Saadi\textsuperscript{1}, Omar A. Ahmed\textsuperscript{2}, Imad H. Khaleel\textsuperscript{3}, T.A.AL.- Dhahir\textsuperscript{4}

\textsuperscript{1,3}Collage of Education for Pure Science -Ibn Al-Haitham/University of Baghdad, Baghdad, Iraq.
\textsuperscript{2}The General Directorate for Education in Diyala, Diyala, Iraq.
\textsuperscript{4}Madenat Alelem University College.

E-mail: taghreed.m.m@ihcoedu.uobaghdad.edu.iq

Abstract. The compound Fe\textsubscript{0.5}Co\textsubscript{x}Mg\textsubscript{0.95-x}O where (x= 0.025, 0.05, 0.075, 0.1) was prepared via the sol-gel technique. The crystalline nature of magnesium oxide was studied by X-ray powder diffraction (XRD) analysis, and the size of the sample crystals, ranging between (16.91-19.62nm), increased, while the lattice constant within the band (0.5337-0.4738 nm) decreased with increasing the cobalt concentration. The morphology of the specimens was studied by scanning electron microscopy (SEM) which shows images forming spherical granules in addition to the presence of interconnected chips. The presence of the elements involved in the superposition was confirmed by energy-dispersive X-ray (EDX) analysis. The results showed that the dielectric constant decreases with increasing the cobalt concentration, while the dielectric loss factor and AC conductivity increase.

Keywords: Dielectric properties, MgO, Sol-Gel, Nanoparticles, SEM, EDX

1. Introduction

Metal oxides such as magnesium oxide have attracted great interest due to their ease of preparation with different crystal shapes and sizes and being unstable in harsh processes but are safe for humans and animals [1]. The magnesium oxide (MgO) is an alkaline earth metal oxide that has a large band gap and structure of rock-salt of 4-5 volts. It has many applications for its ionic nature, surface quality, and high reactivity and these results in high efficiency in various reactions [2, 3]. There are many fields that use magnesium oxides, including sterilization, superconductor products, display panels, heat-resistant glass, fuel oil additives, toxic waste remediation, and insulation applications due to its low heat capacity and high melting point [4-7]. The minerals have the ability to form multiple oxides with various properties and ease of modification. These properties are through the doping process for use in multiple fields. Various crystal defects in the magnesium oxide structure give the deformation process a significant change in structural and electrical properties [6].
research aims to study the effect of doping the nanostructured MgO compound with the transition metal cobalt ion on the structural and dielectric properties.

2. Experimental details

The sol-gel method of spontaneous combustion was used in preparing the compound (Fe$_{0.5}$Co$_x$Mg$_{0.95-x}$O), and the four samples (X= 0.025, 0.05, 0.075, 0.1) were prepared, and in each preparation, the molar ratio of the fuel used was (citric acid), with the proportion of mineral salts at 1:1. The analytical grade metal nitrates, i.e., Mg(NO$_3$)$_2$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O and Co(NO$_3$)$_2$·6H$_2$O, were taken as the starting materials. The sol-gel spontaneous combustion method was used to prepare the compound. Metal nitrate and citric acid are dissolved separately in distilled water according to the molar ratios calculated for each sample. The nitrate solution is mixed with the acid solution in a suitable heat-resistant flask, and the components are mixed by a magnetic mixer, and the acid function (pH) is adjusted until about (7) is reached, by adding ammonia to the solution in the form of drops. The ingredients were mixed for (30 minutes) to ensure the homogeneity of the solution and a good distribution of the ingredients at room temperature. The temperature is raised and fixed at (80 °C) for all proportions, and after a short period the gases start to rise and leave the reaction and the stirring will be continuous until reaching the gel form. After a period of half an hour, the jelly starts to burn to form a dry gel, which is grounded with an agate mortar. The resulting powder for each sample was placed in a container in the oven. For the purpose of calcination at a temperature of (600 °C) for two hours at an rising rate (10 deg/min), in order to get rid of the reaction residues that may still be stuck, such as water residues, and carbon dioxide residues arising from Combustion, and obtaining the required phase.

3. Results and discussion

3.1. XRD Phase Analysis

The results of the examination with X-ray diffraction technology of the compound Fe$_{0.5}$Co$_x$Mg$_{0.95-x}$O, which are shown in Fig.1, showed that the prepared compound was of the cubic type for all of the samples (X= 0.025, 0.05, 0.075, 0.1) and the appearance of peaks of planes, (111), (200), (220),(311) and (222). When comparing the locations and intensities of the peaks with the JCPDS card for MgO numbered (45-0946) [8], we found that they are somewhat similar. Some additional peaks appeared in the XRD spectra for the secondary phases corresponding to Fe$_2$O$_3$ (JCPDS card No. 00-040-1139). Where we note that the intensity of the magnesium oxide peaks increases with increasing the concentration of cobalt. This result confirms that the crystallization ratio has increased due to the decrease in the width of the curve of the middle of the great peak (FWHM), as the increase in the height of the peaks is evidence of increasing crystallization and reducing crystalline defects by giving the material atoms potential energy to rearrange themselves in the lattice [9]. The lattice constant (a) with respect to the cubic structure is calculated according to the relationship (1) [10], where (hkl) is the Miller indices and d is the vertical distance between the planes of crystal.

\[
\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \\
\text{...... (1)}
\]

The average crystal size (D) of samples was calculated using the (Formula Williamson-Hall) method according to the relationship [11] (2).

\[
\beta \cos \theta = \frac{k\lambda}{D} + 4\varepsilon \sin \theta \\
\text{...... (2)}
\]

Where K is the constant (0.94), \(\beta\) Full width at Half Maximum (FWHM) measured in radial units, \(\theta\) Bragg angle , \(\varepsilon\) the strain, \(\lambda\) the wavelength of the X-rays incident upon the target = 1.5406 Å.
The X-ray diffraction in Fig. 2 showed a decrease in the lattice constant with an increase in the concentration of cobalt ions. This is a result of the gradual replacement of magnesium ions with a larger ionic radius (0.89 Å) with cobalt ions with a small ion radius (0.58), which led to the deformation of the lattice and expansion [1-4]. As shown in Table 1, the full width value at half the maximum (FWHM) of the peaks decreased and the crystallite size of the samples increased with increasing x-values. It is noted that the full width value at half maximum (FWHM) of the peak (200) decreased from 0.53370 Å to 0.48280 Å and the crystallite size increased from 16.91 nm to 19.61 nm with increasing cobalt concentration, which means that the surfactant increased the crystallite size [14].
Table 1: Lattice parameter, crystallite size and FWHM for peak (200).

| Composition (x) | FWHM (200) | Lattice parameter a[Å] | Crystallite size [nm] |
|-----------------|------------|------------------------|-----------------------|
| 0.025           | 0.5337     | 4.225                  | 16.91                 |
| 0.05            | 0.5013     | 4.224                  | 18.07                 |
| 0.075           | 0.4738     | 4.220                  | 18.16                 |
| 0.1             | 0.4828     | 4.222                  | 19.62                 |

Fig.3. Hall–Williamson plots for samples Fe_{0.5}Co_{x}Mg_{0.95-x}O for (X= 0.025, 0.05, 0.075, 0.1).

3.2. SEM and EDX analysis

The SEM images in Fig. 4 show the formation of semi-spherical granules in addition to the presence of interconnected chips with no clear boundaries between them due to accumulation of nanoparticles and an increase in the randomness and porosity with increasing cobalt concentration. It was found that the average grain size of the compound ranged between (36.9-59.8 nm) with increasing cobalt concentration. Fig. 5 show the histogram of the particle size of Fe_{0.5}Co_{x}Mg_{0.95-x}O samples.
Fig. 5. Histogram of the particle size of Fe$_{0.5}$Co$_x$Mg$_{0.95}$O samples.

The initial composition of Fe$_{0.5}$Co$_x$Mg$_{0.95}$O was observed in samples via energy dispersive spectroscopy. The diagrammatic consequence for EDX is appeared in Figure (6). It can be seen that
the predominant peaks concern magnesium, oxygen, iron, and cobalt, which appear the superimposed nanoparticles of these elements.

![EDX spectra](image)

**Fig. 6.** EDX spectra of Fe$_{0.5}$Co$_x$Mg$_{0.95}$O ($X = 0.025, 0.05, 0.075, 0.1$).

3.3. Dielectric Properties

The dielectric properties of the composite samples Fe$_{0.5}$Co$_x$Mg$_{0.95}$O were studied as a function of the alternating electric field frequency within the range (50Hz-1MHz) and at room temperature, which included dielectric constant, dielectric loss coefficient and alternating conduction.

Fig. 7 shows the change of the dielectric constant with the electric field frequency applied for all ratios of cobalt addition to the compound Fe$_{0.5}$Co$_x$Mg$_{0.95}$O. It can notice that the decrease of the dielectric constant with the increase of the frequency. It is because at low frequencies the dipoles in the dielectric have sufficient time to orient themselves completely in parallel to the applied electric field. When the frequency of the electric field increases, the dipoles lag behind in rotation and regularity with the electric field and this leads to a decrease in polarization and thus lower values of the dielectric constant [15]. That means the dielectric constant decreases with increasing the concentration of cobalt ions in the samples. Theoretically, the dielectric constant of the compound should be increased because the ion polarization of cobalt ions is greater than that of the magnesium ions, thus increasing the overall ionic polarization of the composite Fe$_{0.5}$Co$_x$Mg$_{0.95}$O with values of x [16]. There are two main reasons taken into consideration in the decrease of the dielectric constant. Replacement of cobalt ions with magnesium ions, which led to the lattice deformation and expansion, thus increasing the porosity [12], which in turn reduces the relative density. On the other hand, the cobalt content is very low and thus does not cause a rise in the constant of dielectric [17].
Fig. 7. Variation of dielectric constant with the frequency of \( \text{Fe}_{0.5}\text{Co}_x\text{Mg}_{0.95}\text{O} \).

Fig. 8 shows that the dielectric loss factor decreases with the frequency and there is a stable relationship between the emergence of dielectric and the conduction mechanism. There are several factors that can affect the dielectric loss factor such as the synthesis method, calcination temperature and formation. The variation of dielectric loss in the low frequency range can be explained by the Maxwell-Wagner model [15,18]. The greater amount of the dielectric loss at lower frequency is due to the jump among \( \text{Mg}^{2+} \), \( \text{Co}^{2+} \), and \( \text{Fe}^{3+} \) and the applied field monitors by the electrons. The electrons with increasing the frequency are not able to follow the higher applied frequency that reduces the jump among \( \text{Mg}^{2+} \), \( \text{Co}^{2+} \), and \( \text{Fe}^{3+} \). Thus, the loss of the applied field is minimal at the larger frequencies [19].

Fig. 9 shows a non-linear behaviour between AC conductivity (\( \sigma_{ac} \)) and frequency which shows that the amount of ac conductivity rises with frequency. Different conductivity operations, for instance tunnelling, jumping and free-range connection etc. participate in increasing the value of the alternating conductivity. It has been found that the adding of Co ions increases the conductivity of superposition [20].
Conclusions

The structural and dielectric properties of Fe$_{0.5}$Co$_x$Mg$_{0.95}$O were studied. Where it was found that the lattice parameter decreases due to the small ionic diameter of the cobalt ions compared to the ionic radius. For iron ions and the ionic radius of magnesium ions, the crystal size increases with increasing cobalt ion concentration. The EDX results confirm the presence of elementary elements to form the compound. SEM images showed the formation of semi-spherical granules and an increase in randomness and porosity associated with an increase in the concentration of cobalt in the compound. It was noticed that the dielectric constant decreases with the increase in the ratio of cobalt ions, although the ionic polarization of cobalt ions is greater compared to the magnesium ions. The dielectric loss factor and the alternating conductivity increases with the increase in the cobalt ions concentration.

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