Preparation, Structural and Dielectric Behaviors of $\text{Co}_x\text{Mn}_{1-x}\text{Mn}_2\text{O}_4$ ($0 \leq x \leq 1$) Nanoparticles

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Abstract: Cobalt-manganese oxide nanoparticles become remarkable metal oxides due to their physical characters, for example, their electrical properties. In this paper, we report the synthesis of $\text{Co}_x\text{Mn}_{1-x}\text{Mn}_2\text{O}_4$ ($0 \leq x \leq 1$) nanoparticles via a precipitation method. The structural and dielectric properties were investigated by means of X-ray diffractometer (XRD) and LCR-meter. From the data analysis, it was found that the $\text{Co}_x\text{Mn}_{1-x}\text{Mn}_2\text{O}_4$ particles structured spinel cubic with the particle size ranging from 22.7 to 28.6 nm. Increasing $\text{Co}^{2+}$ ions led to declining lattice and crystal volume of the $\text{Co}_x\text{Mn}_{1-x}\text{Mn}_2\text{O}_4$ nanoparticles. Such phenomenon was originated from the substitution process of $\text{Co}^{2+}$ ions that change the metal construction both at the octahedral and tetrahedral sites. Furthermore, the $\text{Co}^{2+}$ ion substitution resulted in an increase in the dielectric properties of the $\text{Co}_x\text{Mn}_{1-x}\text{Mn}_2\text{O}_4$ nanoparticles regarding with dipole moment. Interestingly, the increase was also influenced by reducing the particle size and crystal volume of the $\text{Co}_x\text{Mn}_{1-x}\text{Mn}_2\text{O}_4$ nanoparticles.

Keywords: $\text{Co}_x\text{Mn}_{1-x}\text{Mn}_2\text{O}_4$, dielectricity, nanoparticles, and nanostructure.

1. Introduction

Over recent decades, investigations on nanomaterials, especially on metal oxides have been widely performed by many researchers and engineers regarding preparations, characterizations, and applications of the metal oxides. One of the various metal oxides that play an essential role in sophisticated technology is hausmannite ($\text{Mn}_3\text{O}_4$) nanoparticles. $\text{Mn}_3\text{O}_4$ nanoparticles constructed in a spinel system with tetragonal structure have been fabricated in various sizes, forms, and morphologies to enhance their application performance. Some literature showed that the hausmannite had been utilized for many applications as supercapacitor [1, 2], superior anode materials for Li-ion batteries [3], highly efficient hydrogen evolution [4], electro-oxidation of ethanol and propanol [5], nonenzymatic glucose sensor [6], superior sunlight photocatalysts [7], and so forth.

In order to develop the sophisticated applications of the $\text{Mn}_3\text{O}_4$ nanoparticles, many researchers have made various efforts, especially which are generally started by developing nanoparticle synthesis methods. The methods have been conducted to produce the $\text{Mn}_3\text{O}_4$ nanoparticles in various shapes or nanostructure. Several papers presented that the $\text{Mn}_3\text{O}_4$ nanoparticles have been successfully prepared by ultrasonic irradiation assisted by co-precipitation method [8], auto-
combustion method [9], one-pot method [10], ultrasonic method [2], co-precipitation method [11], and others. In this experiment, based on the methods mentioned above, we apply the co-precipitation method due to its simplicity and effectiveness in producing the nanomaterials. By using such method, the Mn$_3$O$_4$ nanoparticle can be prepared without a high temperature in relatively short time.

One of the exciting properties of the Mn$_3$O$_4$ nanoparticles is related to their electrical properties such as dielectric property. In nanometric size, the nanomaterials have entirely different electrical properties from those of their bulk counterparts [11]. Furthermore, in order to enhance the dielectric property of the Mn$_3$O$_4$ nanoparticles, it is also essential to substitute several metal ions in the Mn$_3$O$_4$ particles. Theoretically, the substitution can be conducted by inserting some metals such as Fe, Zn, Mn, Cr, Co, and other metals. Therefore, in this work, we propose the substitution of Co ion in Mn$_3$O$_4$ to form Co$_x$Mn$_{1-x}$O$_4$ (0 ≤ x ≤ 1) nanoparticles. The range of x value is determined to keep the samples in spinel system with a tetragonal structure. In this paper, we report the preparation of the Co$_x$Mn$_{1-x}$O$_4$ nanoparticles using a simple coprecipitation route. Moreover, the structural and dielectric properties of the samples are also presented.

2. Materials and methods
The materials used in this experiment were MnCl$_2$.4H$_2$O, CoCl$_2$.6H$_2$O, NH$_4$OH, H$_2$O, and alcohol. In the first stage, the MnCl$_2$.4H$_2$O and CoCl$_2$.6H$_2$O were weighed based on the stoichiometric composition (x value) to form Co$_x$Mn$_{1-x}$O$_4$ (0 ≤ x ≤ 1) particles in 5 samples, i.e., x = 0; 0.4; 0.6; 0.8; and 1.0. The MnCl$_2$.4H$_2$O and CoCl$_2$.6H$_2$O were then diluted in H$_2$O (90 mL) using a hot plate magnetic stirrer at 70 °C and followed by wisely dropping NH$_4$OH (30 mL) for 60 min to obtain sediment. The sediment was then filtered and washed with H$_2$O and alcohol for several times until pH condition was obtained. The process was followed by a calcination at 100 °C for 120 min to achieve the Co$_x$Mn$_{1-x}$O$_4$ (0 ≤ x ≤ 1) particles in powders.

The prepared samples were characterized via an X-ray diffractometer (XRD) using Cu-Kα for 2-theta in the range from 20° to 70° with a step size of 0.02°. The X-ray diffraction data were then analyzed using a Rietica program by employing Rietveld method. To investigate the dielectric property as well as a dielectric constant, an LCR-meter was utilized at ambient temperature by varying the frequency in the range of 1 kHz to 200 kHz. The dielectric constant data was then analyzed by comparing the data by x content and frequency with the crystal structure and crystallite size.

3. Results and discussion
X-ray diffraction patterns of the Co$_x$Mn$_{1-x}$O$_4$ particles are presented in Figure 1. It is clear from Figure 1a that a higher value of x corresponds to the increasing Co content and decreasing Mn content. The peaks of the XRD data from small 2-theta present (hkl) planes of respective (112), (200), (103), (211), (004), (220), (105), (312), (303), (321), (224), and (400) which coincides with JCPDS No. 18-0803. Moreover, the figure also indicates a peak is broadening along with the increasing Co content. It could prove that the Co$^{2+}$ ions have been successfully injected into the Mn$_3$O$_4$ without producing new phases or impurities. The wider peak broadening also becomes evident that the increasing Co content resulted in decreasing the particle size of the samples. Moreover, from Figure 1b, it can be seen that the Co$^{2+}$ ions occupied the position of Mn$^{2+}$ ions at the tetrahedral site. In accordance with this work, Salek et al. reported that the Co$^{2+}$ ions mainly occupied the tetrahedral site [12]. Such site is occupied by the metal ions surrounded by four oxygen atoms. Meanwhile, the octahedral site was occupied by the metal ions surrounded by six oxygen atoms [13]. In order to study the crystal structure comprehensively, we analyzed the XRD data using a Rietica program by employing a Rietveld analysis. The output of quantitative data analysis, as well as crystallite size and crystal volume, are presented in Figure 2.
Figure 1. (a) XRD patterns of the $\text{Co}_x\text{Mn}_{1-x}\text{Mn}_2\text{O}_4$ ($0 \leq x \leq 1$) particles and (b) the crystal structure for a certain $x$ composition

Figure 2. Crystallite size and crystal volume of the $\text{Co}_x\text{Mn}_{1-x}\text{Mn}_2\text{O}_4$ ($0 \leq x \leq 1$) particles

The increasing crystal volume as shown in Figure 2 originating from the lattice parameters of the $\text{Co}_x\text{Mn}_{1-x}\text{Mn}_2\text{O}_4$ particles is strongly affected by the incorporation of $\text{Co}^{2+}$ ions. These ions have been successfully inserted into the tetrahedral site that was initially occupied by $\text{Mn}^{2+}$ ions. Because the ionic radii of $\text{Co}^{2+}$ ions (0.74 Å) were lower than those of $\text{Mn}^{2+}$ ions (0.80 Å) [14], the lattice parameters ($a$, $b$ and $c$) of the system became smaller and therefore directly decreased its crystal volume. The results of data analysis also presented that there is not a significant connection between
the c/a ratio and the degree of c-a/a distortion. The ratio of the five samples was around 1.63 and 1.64 that became another evidence that the Co\(^{2+}\) ions successfully substituted the Mn\(^{2+}\) ions and not the Mn\(^{3+}\) ions. Thus, it only disrupted the tetrahedral site while the octahedral site occupied by the Mn\(^{3+}\) ions was not disrupted although the c/a ratio and the degree of c-a/a distortion were strongly influenced by the Jahn-Teller effect, which was purely occupied by Mn\(^{3+}\) ions at the octahedral site. In principle, the crystal field theory could explain the tetrahedral distortion caused by the Jahn-Teller effect [15]. Such distortion caused a lower system of symmetry and degeneration level. If the two ligands in z-axis move away from the core atom in the same directions with the –z and +z axes, the repulsion between the electrons and ligands and the central atom that occupies d orbitals containing z components such as \(d_{xz}, d_{yz}, d_{z^2}\) would decrease. Consequently, the orbitals would stabilize or experience a decrease in energy level. On the contrary, the d orbitals that do not possess any z components, namely \(d_{xy}\) and \(d_{x^2-y^2}\), would be unstable or would have an increasing level of energy.

The smallest crystallite size of 22.77 nm was obtained on \(x = 1\) sample, and the largest was 28.61 nm on \(x = 0\) sample. Meanwhile, the \(x = 0.4\) sample had 26.88 nm crystallite size, the \(x = 0.6\) sample had 24.62 nm crystallite size, and the \(x = 0.8\) sample had 23.99 nm crystallite size. Figure 2 shows such information in detail. The results are in good agreement with the initial prediction about the peak area of the X-ray diffraction pattern in a nanometric size. From such explanation, it could be concluded that the Mn\(_{1.3}\).Co\(_{0.7}\)O\(_4\) nanoparticles have been successfully prepared. The crystallite size of the Mn\(_{1.3}\).Co\(_{0.7}\)O\(_4\) nanoparticles for \(x = 1\) in this experiment is relatively similar to that of the sample prepared by a newly adopted hydrothermal route [16]. The data analysis via Scherer’s equation obtained a continuously decreasing crystallite size along with the increasing composition of the Co\(^{2+}\) ions. It related to the concept of the compound formation when Mn\(_{1.3}\)O\(_4\) is treated at a certain temperature while simultaneously added with a composition of another material, in this case, a Co\(^{2+}\) dopant. Therefore, it requires a longer period to form a new compound when the dopant composition increased. As a result, the formation of the new compound of Co\(_x\)Mn\(_{1-x}\)O\(_4\) would be imperfect, which resulted in a smaller crystallite size as a higher amount of Co\(^{2+}\) dopant was added.

Figure 3 presents the dielectric constant of Co\(_x\)Mn\(_{1-x}\)O\(_4\) nanoparticles for 0 ≤ \(x\) ≤ 1 as a function of frequency. The figure shows the increasing value of dielectric constant along with the increasing Co\(^{2+}\) content. It means that the Co\(^{2+}\) incorporation into the tetrahedral site in the system contributed significantly to enhancing the dielectric constant of the Co\(_x\)Mn\(_{1-x}\)O\(_4\) nanoparticles. Theoretically, it can be explained that the Co\(^{2+}\) ions with the smaller ionic radii than those of Mn\(^{2+}\) ions contributed to reducing valence electron of the Co\(_x\)Mn\(_{1-x}\)O\(_4\) nanoparticles and followed by increasing their dipole moments. The increasing dipole moments could be reflected by lowering the crystal volume of the Co\(_x\)Mn\(_{1-x}\)O\(_4\) nanoparticles that directly increased the dielectric constant. The decreasing crystal volume of the Co\(_x\)Mn\(_{1-x}\)O\(_4\) nanoparticles was started by a declining crystal volume of the tetragonal structure.

The interesting phenomenon in this work is a decreased dielectric constant along with the increasing frequency. Figure 3 illustrates the dielectric constant of the same sample, i.e., for similar \(x\) composition, the constant dielectric lead to a decrease in frequency. The phenomenon can be explained by the physical concept that relates to the correlation between capacitance and frequency as shown in Equation 1 [17].

\[
C = C_g \frac{\omega \tau}{1 + \omega^2 \tau^2}
\]

Where \(C\) is capacitance, \(C_g\) is geometrical capacitance, \(S\) is conductance, \(\tau\) is time relaxation for a dipole, and \(\omega\) is angular frequency. The equation guides us that the capacitance decreases by an increase in frequency. Implicitly, it could be explained by the polarization mechanism of a charge carrier in the Co\(_x\)Mn\(_{1-x}\)O\(_4\) nanoparticles by increasing the frequency. Therefore the polarization would decrease following the decreasing dielectric constant [17]. Rathore and co-workers reported that dielectric polarization happens as ionic, electronic, dipolar, or interfacial polarization. The dipole will no longer be able to rotate sufficiently fast when the frequency is increased. Furthermore, the dipole will be unable to follow the field when the frequency is further increased, and the orientation
polarization will stop. Therefore, at higher frequencies, the dielectric permittivity of the samples decreases and tends to be constant. Such phenomenon is believed originating from the vanished space charge or interfacial polarization [18].

![Figure 3. Dielectric constant of the Co$_x$Mn$_{1-x}$Mn$_2$O$_4$ (0 ≤ x ≤ 1) nanoparticles as a function of frequency.](image)

Another work reported that the effect of increasing frequency could be expressed by considering samples composing of well-conducting grains separated by poorly conducting grain boundaries [19]. Furthermore, the charge displacement can explain the microscopic mechanism in the material. The electric dipole movement caused by the electrical field in the material that is still in the range of short transition since the valency electrons could not move freely due to the addition of Co$^{2+}$ ions to the Co$_x$Mn$_{1-x}$Mn$_2$O$_4$ nanoparticles. Therefore, it strengthens the core bond towards the outermost electron resulting in a larger dipole moment. As a consequence, the dielectricity of the material will increase. Besides, the growing dielectric constant also could be seen from the comparison between the polarization and crystal volume based on the Equation 2.

$$
P = \sum \frac{p_i}{V}$$

Where $P$ is the polarization, $p_i$ is the dipole moment, and $V$ is the volume [20]. The equation shows that the volume is inversely proportional to the polarization so that the increasing amount of Co$^{2+}$ ions in the Co$_x$Mn$_{1-x}$Mn$_2$O$_4$ nanoparticles will cause its volume to shrink resulting in a growing polarization and dielectric constant. Moreover, polarization at the tetrahedral complex in the spinel structure of the Co$_x$Mn$_{1-x}$Mn$_2$O$_4$ nanoparticles also contributes to the increasing dielectricity. The polarization at such tetrahedral complex has a particular value (not zero) even though the sample has not obtained the electric field yet.

From Figure 2 and 3, it is shown that the declining crystal volume is proportional to the increase of dielectric constant. It shows that the Co$^{2+}$ ions contributing in the tetrahedral site that increases the
dielectricity of the material. A dielectric constant of nanoparticles could be influenced by the technique of synthesis, particle size, and cation distribution. It is known in this research that besides the ionic radii of a dopant that is smaller than the parent ion, the dielectric constant of the Co$_x$Mn$_{1-x}$O$_4$ nanoparticles is also affected by its crystallite size. It is in good agreement with the statement of Raghavender and Jadhav that the smaller the size of a crystal, the higher the dielectric constant value of it [21]. Based on Figure 2 and 3, the crystallite size tends to decline and result in an increase of the dielectricity of the samples. Such increase in the value of the dielectric constant at a certain frequency was found to be significant, namely 126 %. The samples with $x = 0.8$ and $x = 1.0$ had an almost similar percentage of the dielectric constant increase, i.e., 134 %. The percentage of such increase is affected by the declining crystallite size. Such facts are in good agreement with others work that a small crystallite size would have a high value of dielectric constant. The increase of the dielectric constant as the decrease of the crystallite size can be described by the correlated barrier hopping model. In principle, the ions or charge carriers be supposed to be separated by anisotropy barrier or potential well and to jump from one to another position over the potential well [18]. In this condition, when the particle size becomes smaller as a single-domain in nanometric size, a weak field is necessary to overcome the potential well and then finally to increase the dielectric permittivity of the samples. Furthermore, the Coulombic interaction mechanism could be stronger due to the shrinking crystal volume that tends to contributes more in the dielectric constant value rather than in the development of the crystallite size, which is relatively small. The comprehensive explanation of the size effect on dielectric constant can be found in the literature [19,22]. As a final remark, in order to investigate the hierarchical nanostructure in more detail of the Co$_x$Mn$_{1-x}$O$_4$ nanoparticles in 3-dimensions, it is necessary to conduct a further experiment by employing small angle scattering using neutron or synchrotron sources.

4. Conclusions
Based on the data analysis, it can be concluded that the Co$_x$Mn$_{1-x}$O$_4$ particles have been successfully prepared via a precipitation route. The Co$_x$Mn$_{1-x}$O$_4$ particles constructed spinel cubic structures with the particle size ranging from 22.7 nm to 28.6 nm. Increasing Co$^{2+}$ ions with ionic radii larger than those of Mn$^{2+}$ ions caused declining lattice parameters and crystal volume of the Co$_x$Mn$_{1-x}$O$_4$ nanoparticles. Interestingly, the Co$^{2+}$ ion substitution results in an increasing dielectric property of the Co$_x$Mn$_{1-x}$O$_4$ nanoparticles regarding dipole moment. Moreover, the increase was also influenced by the shrinking particle size and crystal volume of the Co$_x$Mn$_{1-x}$O$_4$ nanoparticles. Finally, the dielectric constant was also affected by the variation of frequency during characterization.

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