Synthesize and Characterization of Ca Substituted Co-Zn Ferrites by Micro-Emulsion Technique

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Co-Zn ferrites have great magnetostriction, high corrosion resistivity and excellent chemical stability. We can control the ferromagnetic properties and paramagnetic properties of Co-Zn ferrites by changing its particle distribution and particle size. There are different types of techniques are available to synthesis Co-Zn ferrites like co-precipitation, sol gel and auto-combustion method etc. In this research, we will synthesize Co-Zn ferrites by micro-emulsion technique and substitute Ca in it with different composition. XRD results showed that samples were in single phase ferrite. Particle size was between the ranges of 34-14nm. Average lattice constant were 8.11-8.18Å. FT-IR confirm the results obtained by XRD. SEM confirm the morphology of the samples and its grain size. Grain size decreased with increased of the concentration of Ca in Co₀.₆₋ₓZn₀.₄CaₓFe₂O₄. TGA results were found in agreement with previous literatures.

Keywords:
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1. Introduction

Ferrites have gained immense significance in current moment. Ferrites are comparatively steady, low cost and a wide range in different logical applications in MRI, sensors, magnetic recording and so forth. So, it is concluded that any other magnetic materials cannot replace by spinal ferrites. These days, these materials are largely synthesized in nanometric scale for new and enhanced properties. Fe₂O₃ and metallic oxides are the main constituents of the ferrites (Raghasudha, Ravinder, & Veerasomaiah, 2013).

The value of ferrite material has been known to mankind for many centuries. Ferrites were very famous in Chinese nation in early 12th century in form of compass for navigation purpose. Ferrites have high electric resistivity, less eddy current, mediocre permittivity and high saturation magnetization Ms (Li, Yang, Bao, Meng, & Lou, 2013). Basically, ferrites are magnetic oxides and there is no such material that can replace ferrites due to high range properties that it’s have. Accordingly, ferrites are exclusive magnetic materials which locate applications in approximately all fields.

Ferrite’s have great electrical and magnetic properties; that’s way they have great importance in technological devices (Arulmurugan, Jeyadevan, Vaidyanathan, & Sendhilnathan, 2005). Ferrites can be used in magnetic recording, computer technology, used as permanent magnets, transformer cores and memory chips etc (Zhang, Zhong, Yu, Liu, & Zeng, 2009). there are two types of ferrites in general named as Soft (Spinel) ferrites and Hard (Hexagonal) ferrites.
2. Method and Material

Ca doped Co-Zn ferrite were prepared by the micro-emulsion technique by using, Fe (NO$_3$)$_2$. 9H$_2$O, Ca (NO$_3$)$_2$. 6H$_2$O, Zn (NO$_3$).6H$_2$O, Co (NO$_3$).6H$_2$O, Cetyl-trimethyl-ammonium bromide (CTAB), as raw materials. Firstly, all solutions were prepared according to calculated volume in distilled water. CTAB will mix up in the solution. 6 grams of NaOH was dissolved in appropriate amounts (50ml) of distilled water and mixed it in the solution to obtained pH value near to 12. Solution stirred constantly by using magnetic stir and maintained temperature about 50°C-55°C. After 3h stirring, solution becomes a homogeneous solution. By washing solution with distilled water reduced solution pH to value 7. After that, solution was dried into oven at temperature 85°C for 24h to get dried powder form. After grinding the dry solution, very fine and brown colored Ca doped Co-Zn ferrite was synthesized. To study its magnetic and structural properties, samples were annealed at 900°C for 5h. After that temperature slowly down up to room temperature and samples again grind to get more structure powder (Gilani et al., 2017).

![Figure 1: Solution stirred constantly](image1)

![Figure 2: Homogeneous solution after string](image2)

To study the crystal size and it phases, generally XRD, Fourier transform infrared (FT-IR) spectroscopy, Thermo-geometry analysis (TGA), scanning electron microscope (SEM) is used.

Due to extremely outstanding electrical and magnetic properties, cubic ferrites (which are synthesized at nano scale) intensively investigated in these recent years. These cubic ferrites are using in different areas of daily life, for example: recording disks or tapes, magnetic devices, active components of ferro-fluids and microwave absorbers. The purpose to synthesized the Ca doped Co-Zn ferrite is that to study it effect on different properties of Co-Zn ferrites like corrosion resistivity, anisotropy, magneto-optical, magneto-crystalline and chemical stability (He, 2011).

Now a days, different techniques are using to synthesized Ca doped Co-Zn ferrite. However, we synthesis Ca doped Co-Zn ferrite is limited through micro-emulsion technique. In this research, we try to synthesis Ca doped Co-Zn ferrite by micro-emulsion technique and study the effect on it morphology, magnetic and electrical properties.
Figure 3: Dried solution into oven at temperature 85°C

3. Result and Discussion of Structural Properties

In our research experiment, we try to synthesize Ca doped Co-Zn ferrite by micro-emulsion technique using Cetyl-trimethyl-ammonium bromide (CTAB) as a template. After making solution of Ca doped Co-Zn ferrite, samples are dry at 85°C in drying oven and annealed in furnace at 850°C for 5h. After XRD characterization, following pattern are obtained (Gilani et al., 2017).

The XRD pattern of Ca doped Co-Zn ferrite \(\text{Co}_{0.6-x}\text{Zn}_{0.4}\text{Ca}_x\text{Fe}_2\text{O}_4\) \((x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5)\) shows that samples are in the single phase and have spinel structure without any impurity. Diffraction peaks \((220), (311), (422)\) and \((511)\) are clear verification of spinel ferrite (Kumar, Singh, Mandal, & Kotnala, 2015).

The \(d\) spacing for each peak is record by automatic software (Match; version: 3.4.2, Build96), then lattice parameter \((a)\) is calculate from following relation:

\[
a = d_{hkl} (h^2+k^2+l^2)^{1/2}
\]  

(1)

Results show that lattice constant always depends on the concentration of Ca after doping in Co-Zn ferrite. In \(\text{Co}_{0.6-x}\text{Zn}_{0.4}\text{Ca}_x\text{Fe}_2\text{O}_4\), lattice constant increased from 8.41 to 8.53 at \(x=0.1-0.4\) but decreased to 8.42 at \(x=0.5\).
Figure 4: XRD patterns for all samples

Figure 4 shows Co$_{0.6-x}$Zn$_{0.4}$Ca$_x$Fe$_2$O$_4$ XRD patterns. From graph, it is confirms the following peaks for samples in phase with some extra peaks; (220), (311), (422) and (511) and also confirms their cubic spinal structural formation. From experiment, we find alter plane distance d, lattice constant (a) unit (Å$^0$) and volume of the unit cell (Å$^0$)$^3$ and particle size from full width half maxima (FWHD) method (Arulmurugan et al., 2005; Nazim et al., 2016; Urcia-Romero, Perales-Pérez, & Gutiérrez, 2010).
Results shows that with the increase of the concentration of Ca in Co-Zn ferrite, the lattice constant increase from 8.11-8.18 Å and particle size decreased from 34-14nm with increase of Ca concentration.

Figure 5: FTIR graphs for all samples from 450cm\(^{-1}\)-4000cm\(^{-1}\)

Figure 5 shows FTIR spectra for Ca doped Co-Zn ferrite at room temperature in the range of 450-4000cm\(^{-1}\) respectively. The obtained result confirms the cubic structure. Results show two bands \(v_1\) and \(v_2\) that referred to the intrinsic vibration of tetra-hedral and octa-hedral complexes. The bond vibration between tetra-hedral metal ion (O-M\(_{\text{tetra}}\)) and oxygen ion is assigned for \(v_1\). The bond vibration between octa-hedral ion (O-M\(_{\text{octa}}\)) and oxygen is assigned for \(v_2\).

**Co\(_{0.5}\)-Zn\(_{0.4}\) Ca\(_{0.1}\) Fe\(_2\)O\(_4\)**

**Co\(_{0.3}\)-Zn\(_{0.4}\) Ca\(_{0.3}\) Fe\(_2\)O\(_4\)**
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Figure 6: SEM spectra for Ca doped Co-Zn ferrite

The SEM images clearly show the materials are small size in nano-region (Sathishkumar, Venkataraju, & Sivakumar, 2011). SEM results shows that the crystal is spinal ferrite.

Figure 7: TGA results for all samples from temperature to 1000°C

Figure 7 shows the TGA results for Co$_{0.6}$-Zn$_{0.4}$Fe$_2$O$_4$, Co$_{0.4}$-Zn$_{0.4}$Ca$_{0.2}$Fe$_2$O$_4$ and Co$_{0.1}$-Zn$_{0.4}$Ca$_{0.5}$Fe$_2$O$_4$ nano ferrites from room temperature to 1000°C. Weight loss is gradually decreased from 117°C-231°C for Co$_{0.6}$-Zn$_{0.4}$Fe$_2$O$_4$ and a sharp weight loss is in the region of 233-346 °C and 669-732 °C. For Co$_{0.4}$-Zn$_{0.4}$Ca$_{0.2}$Fe$_2$O$_4$, gradually weight loss region is between 117-212 °C and sharp weight loss region is 223-450 °C and 611-729 °C. For Co$_{0.1}$-Zn$_{0.4}$Ca$_{0.5}$Fe$_2$O$_4$, gradually weight loss region is between 107-233 °C and sharp weight loss region is 223-450 °C and 644-701 °C (Arulmurugan et al., 2005; Nazim et al., 2016).

4. Conclusion

In our research work, we investigated that Ca doped Co-Zn ferrite (Co$_{0.6-x}$Zn$_{0.4}$Ca$_x$Fe$_2$O$_4$ where x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5) nanoscale particles were synthesized by micro-emulsion method where CTAB was used as template. All samples were sintered at
850°C. The following characterization were used to study the samples; XRD, FT-IR, SEM and TGA. XRD results showed that samples were in single phase ferrite. Crystalline size was between the ranges of 34-14nm. Average lattice constant were 8.11-8.18Å. FT-IR conform the results obtained by XRD. SEM conform the morphology of the samples and its grain size. Grain size decreased with increased of the concentration of Ca in Co0.6-xZn0.4Fe2O4. TGA results were found in agreement with previous literatures (Nazim et al., 2016).

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