Structural and Dielectric Properties of Cr\textsuperscript{3+}-Cu\textsuperscript{2+} Substituted Cobalt Ferrites

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Abstract:

The current paper examined the impact of Cu\textsuperscript{2+}-Cr\textsuperscript{3+} substitution on the structural and dielectric possessions of nanoparticles of cobalt ferrites with the composition Co\textsubscript{1-x}Cu\textsubscript{x}Fe\textsubscript{2-x}Cr\textsubscript{x}O\textsubscript{4} (x=0.0, 0.1, 0.2), synthesized via sol-gel auto-combustion technique and calcinated for 4 hours at 700°C. The XRD patterns display large peaks suggesting nanocrystalline for inverse spinel ferrite formation. FTIR indicate the formation of spinel ferrites by revealing the presence of a typical absorption band in range 390-410 cm\textsuperscript{-1} and 540-560 cm\textsuperscript{-1}, respectively. FESEM reveals that the specimen is plate and sponge-like structure. In the frequency assortment 1 KHz - 5 MHz, dielectric analysis at room temperature was performed and described on the foundation of the phenomenological theory of Koop and the theory of Maxwell Wagner. The result shows the highest dielectric constant without doping is 128.5. The experiment showed low dielectric loss i.e.1.8 with x=0.2.

Keywords: Cobalt ferrites, FTIR, spinel ferrites, XRD, FESEM, AC conductivity.

1. Introduction

Ferrites nanoparticles due to their excellent dielectric, magnetic and catalytic properties have been attracted scientists and researcher’s attention over the years. [1-6]. These properties are vital for application such as microwaves absorbers, electronic devices, magnetic adsorbents, computer
memories, telecommunication, magnetic refrigeration, catalysis and high frequency transformer [7-11]. The versatile structure of the spinel permits the insertion of diverse metallic cations deprived of distorting the crystal structure of the spinel [12-14]. Cobalt ferrite exhibits an inverse spinel structure having the general structural formula \([\text{Fe}^{3+}_8]^{\text{Co}^{2+}_2\text{Fe}^{3+}_{2-\delta}\text{O}_4^{2-}}\), with the square bracket representing the octahedral site and the parenthesis representing tetrahedral site respectively and \(\delta\) indicates the level of inversion [2]. Different synthesis procedures were employed for the preparation of nanoparticles materials such as hydrothermal, micro-emulsion, citrate-precursor, chemical co-precipitation, sol-gel, organic-precursor and chemical reduction but sol gel method is one of the best methods to harvest material in a satisfactory specific mode [11,15-23]. Keeping in mind, the simplicity, high purity, low environmental pollution, highly reproducible method, ability to control the composition with good precision and convenience in operation such as low processing time and less external energy consumption, sol-gel auto-combustion method is employed for present work [2][17]. Pandav et al prepare nickel ferrite manganese base using the sol-gel technique and studied its magnetostructural properties [22]. Senthil et al and Vishal synthesize cobalt doped nickel ferrite nanostructures for magnetic applications [17, 23]. So, in the present paper more emphasis has been given to dielectric properties of cobalt ferrite nanoparticles.

2. Experimental procedure

Using sol-gel technique at room temperature, cobalt ferrite with chemical composition \(\text{Co}_{1-x}\text{Cu}_x\text{Fe}_{2-x}\text{Cr}_x\text{O}_4\) (\(x=0.0, 0.1, 0.2\)), with \(x=0.0\) sample assigned a code RR1, \(x=0.1\) to RR2 and \(x=0.2\) to RR3, respectively were prepared. The metal nitrate (AR grade) have been used as the preliminary materials in equal ratios and liquified in de-ionized water. The 9 gm of Polyvinyl pyrrolidone (PVP k-30, M.W-40000 LOBA Chemie) was added to serve as the auto-combustion agent. The solution was continuously stirred and heated by forming a brown gel at a temperature of 80-100°C until the water evaporated completely. The obtained brown gel was placed on a hot plate and heated to a temperature range of 280-300°C for 3 hours in order to obtain the precursor. The precursor material was then calcined at a temperature of 700°C for 4 hours.

3. Details of the characterisation

The structural chattels were examined using the X-ray diffraction with Cu-K\(\alpha\) radiation collected at 20°-80° with phase size 0.01°. The FTIR spectrum was attained using the Nicolet 100 IR spectrometer. The FESEM (Joel 6390LV) was used to examined the surface morphology and composition of elements. The dielectric belongings were analysed with an impedance analyzer (Wayne Kerr 6500B) operating between 1 KHz and 5MHz frequency range.

4. Results and discussions

4.1 The analysis OF XRD

The spinel phase establishment of \(\text{Co}_{1-x}\text{Cu}_x\text{Fe}_{2-x}\text{Cr}_x\text{O}_4\) (\(x=0.0, 0.1, 0.2\)) was inveterate by XRD patterns. Also, the obtained values of lattice constants for CoFe\(_2\)O\(_4\) were in agreement with the standard JCPDS card 22-1086, which depict the formation of the inverse spinel ferrite. The broad peaks signifying nanocrystalline nature. Table 1 present the calculated values of the crystallite size, constant of lattice and unit cell volume using equations (1), (2) and (3) respectively [24].

\[
D = \frac{0.93 \lambda}{\beta \cos \theta}
\] (1)
The constant of lattice (a) and the unit cell volume (V_{cell}) increase and then decrease with doping of Cu^{2+}-Cr^{3+}. The imperfection found in these parameters can be caused by residual pressure by chemical reaction processes or by an increase in dopant concentration Cu^{2+}-Cr^{3+} \cite{25, 26}.

![XRD spectra of Co_{1-x}Cu_{x}Fe_{2-x}Cr_{x}O_{4} (x=0.0, 0.1, 0.2)](image)

Table 1 presents the calculated values of the crystallite size, constant of lattice and unit cell volume.

| Sample Codes | 2θ (°) | d_{hkl} (Å) | β (rad) | a (Å) | D (nm) | V_{cell} (Å^3) | ρ_{XRD} (g/cm^3) |
|--------------|--------|-------------|---------|-------|--------|----------------|-----------------|
| RR1          | 35.55  | 2.5229      | 0.212   | 8.3675| 39.351 | 585.85         | 6.674           |
| RR2          | 43.14  | 2.0952      | 0.225   | 8.3808| 37.967 | 588.65         | 5.2967           |
| RR3          | 43.27  | 2.0895      | 0.176   | 8.3580| 48.559 | 583.86         | 5.2236           |

4.2 FTIR Analysis

FTIR spectra of Co_{1-x}Cu_{x}Fe_{2-x}Cr_{x}O_{4} (x=0.0, 0.1, 0.2) recorded between 4000 and 400 cm^{-1} is shown in Fig. 2. Two absorption bands observed in ferrites were attributed to the spatial arrangement of the oxygen closest neighbours. The absorption band \( \nu_1 \) is aligned with the stretching and vibration of \( \text{Fe}^{3+} - \text{O}^{2-} \) in tetrahedral complexes and the absorption band \( \nu_2 \) is induced by the bending and vibration of octahedral complexes. The locations and intensities change slightly for the tetrahedral and octahedral sites owe to the variance in the Fe^{3+} – O^{2-} distances. In this work absorption band \( \nu_1 \) is observed near at 540-560 cm^{-1}. While the other absorption...
band $v_2$ appears near at 390-410 cm$^{-1}$. Both $v_1$ and $v_2$ are shifted towards lower frequency with the substitution of Cu$^{2+}$-Cr$^{3+}$. The broad spectra observed for all the samples, confirm the formation of the inverse spinel ferrites[27][7].

![FTIR Spectra for Co$_{1-x}$Cu$_x$Fe$_{2-x}$Cr$_x$O$_4$ (x=0.0, 0.1 and 0.2)](image)

**Fig. 2** FTIR Spectra for Co$_{1-x}$Cu$_x$Fe$_{2-x}$Cr$_x$O$_4$ (x=0.0, 0.1 and 0.2)

### 4.3 The analysis of morphology

The synthesized sample’s surface morphology (Fig.3,4) indicates the formation of cumulative due to agglomeration of nanoparticles, which may result from the particle’s magnetostatics interaction. The particle size first decreases and then increases with the substitution of Cu$^{2+}$ -Cr$^{3+}$ with a structure-like feature of plates and sponge and many pores that could be attributed to the immiscible nature of cobalt with copper[7][28].
Fig. 3 FESEM micrograph of Co$_{1-x}$Cu$_x$Fe$_{2-x}$Cr$_x$O$_4$ (x=0.0 and 0.1)
Fig. 4 EDX spectra and mapping for $\text{Co}_{0.1-x}\text{Cu}_x\text{Fe}_{2-x}\text{Cr}_x\text{O}_4$ ($x=0.0$ and 0.1) (a) RR1, (b) RR2

4.4 The analysis of Dielectric

The properties and function of the dielectric are clarified on the core of the premise that the dielectric polarization mode is alike to that of electrical conduction. As the frequency increases, the dielectric loss ($\tan \delta$) and dielectric constant ($\varepsilon'$) decrease, Figure. 5(a) and (b) respectively. This is due to the separation of the good conductive grains within the material and the limits of the poorly conducted grains. Due to the high resistance at the boundary, electrons primarily enter the grain boundary through the hopping process, pile up at the grain boundary and cause polarization effects. The upsurge in the frequency with external field reverses the electron movement direction and this reduces the chances of electrons reaching the boundaries and thus reduces the effect of polarization. [29]. Fig. 5 (c) describes the variance of the AC conductivity at room temperature for $\text{Co}_{1-x}\text{Cu}_x\text{Fe}_{2-x}\text{Cr}_x\text{O}_4$ ($x=0.0$, 0.1 and 0.2). All the nanoparticles synthesized show independent frequency behaviour. The AC conductivity at lower frequencies, based on the Maxwell-Wagner method, is responsible for the behaviour of the grain boundary. Whereas at higher frequencies the phenomenon of dispersion may be owe to the conductivity of the grain and electrons hopping of $\text{Fe}^{3+}$-$\text{Fe}^{2+}$ ions [30, 31].
Fig. 5(a) Dielectric loss variance with frequency for Co<sub>1-x</sub>Cu<sub>x</sub>Fe<sub>2-x</sub>Cr<sub>x</sub>O<sub>4</sub> (x=0.0, 0.1 and 0.2)

Fig. 5(b) Variation of dielectric constant with frequency for Co<sub>1-x</sub>Cu<sub>x</sub>Fe<sub>2-x</sub>Cr<sub>x</sub>O<sub>4</sub> (x=0.0, 0.1, 0.2)
Fig. 5(c) AC conductivity variance with frequency for $\text{Co}_{1-x}\text{Cu}_x\text{Fe}_{2-x}\text{Cr}_x\text{O}_4$ ($x=0.0, 0.1 \text{ and } 0.2$)

5. Conclusion

The chemical composition of spinel ferrite (cobalt) $\text{Co}_{1-x}\text{Cu}_x\text{Fe}_{2-x}\text{Cr}_x\text{O}_4$ ($x=0.0, 0.1 \text{ and } 0.2$) was successfully prepared using the sol-gel method. XRD analysis shows the formation of the phase of the inverse cubic spinel. At low frequency (100 Hz), the synthesized nanoparticle shows low dielectric loss which enhanced its application in wireless communication and numerous others electronic devices. [32-33]

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