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Structural and Electrical Properties of Sol-Gel Synthesized CoFe2O4 Nanoparticles

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Abstract

In this present work, synthesis and characterization of $CoFe_2O_4$ nanoparticles has been carried out by using sol-gel method. The prepared nanoparticles were characterized by using XRD, SEM, EDAX and FT-IR . The XRD patterns confirms the single-phase spinal structure and the crystallite size as calculated by Scherer's formula is 30nm. Micro-structural and morphological studies were carried out by scanning electron microscope technique and energy dispersive spectrum. The FTIR was used to study the presence of functional groups. The frequency-dependent electrical properties of the sample were investigated in the temperature range 30ºC - 700ºC and in a frequency range of 42 Hz – 0.5 MHz. The appearance of peak in the real and imaginary part of impedance (Z″) for each sample and shifting of this peak with temperature towards higher frequency side indicated that the presence of electric relaxations. The plots of Z' vs. Z" (Z' is the real part of impedance and Z" is the imaginary part) for Zn doped $CoFe_2O_4$ were recorded. All samples have a semicircle arc originating at the origin.

Keywords: Sol-gel Method , $CoFe_2O_4$ nanoparticles, Electrical Properties.

Introduction

Spinal ferrites (AFe_2O_4) materials have been found in a broad range of applications in many areas. Nanostructured spinal ferrites have a great attention regarding to their effective particle size dependent electronic, magnetic, chemical, mechanical and electrical properties [1–2]. Due to these properties make Fe containing oxides acceptable for numerous device applications, including magnetic materials (circulators, oscillators, phase shifters for microwave region), sensors, magneto-optic sensors,anode materials for batteries, catalysts, sensors in space applications, lasers, phosphorescent sources, microwave and electrochemical devices, black and brown pigments. Since these magneto-particles have also been shown to be non-cytotoxic, they would be suitable for biotechnological applications [3-7].Nanostructured iron-containing transition metal Spinal ferrites have the general formula AFe_2O_4 (where A2+ = Co, Ni, Zn, Mg, etc.) and the unit cell contains 32 oxygen atoms in cubic cross-link packing with 8 tetrahedral (Td) and 16 octahedral (Oh) occupied sites. Altering the divalent cation type and level content in the ferrites, enable us to obtain a large range of different physical and magnetic properties [8]. The basic uses of these spinal ferrites depend on the inherent properties. In the literature synthesis and investigation of magnetic properties of spinel cobalt ferrite nanoparticles have been carried out by several workers [9, 10]. The large number of researchers has reported magnetic properties of cobalt ferrite nanoparticles with a view to understand magnetism at nano scale and their possible practical applications. However, very less attention has been paid to study the electrical properties of cobalt ferrite nanoparticles. The study of electrical properties of cobalt ferrite nanoparticles are important from the point of view of its use in electrical and electronic applications. The goal of the present work is to synthesize cobalt ferrite nanoparticles by sol-gel method and to study the structural and electrical properties. The sol-gel method is most useful, low cost, low temperature and less time, produces analogous particles of uniform size. The porosity of the spinel ferrite produced by sol-gel method is high which leads to increases in the resistivity. In the present work, we describe the structural and electrical properties of cobalt ferrite ($CoFe_2O_4$) nanoparticles. The synthesized cobalt ferrite ($CoFe_2O_4$) nanoparticles were studied using XRD, FTIR, SEM, EDAX and impedance spectroscopy in order to study the structural and electrical properties.

II. Experimental Method

Nano crystalline $CoFe_2O_4$ powder was synthesized by using sol–gel citrate method. High purity nitrates were used for the preparation. A stoichiometric mixture cobalt nitrate and Ferric nitrate were used as raw materials. A stoichiometric mixture of nitrates was mixed with citric acid and ethylene glycol and stirred magnetically at 80°C for 3hrs to obtain a homogenous mixture; the solution was further heated in a pressure vessel at about 130°C for 12 hrs and there after kept at 350°C for 3 hrs in muffle furnace and then milled to a fine powder. The dried powder was then calcined in the range of 350°C to 750°C for 6 hrs in order to improve the crystallinity of the powder .The impedance measurement were done on the pellets (the pellets of 13.2 mm diameter and15.45 mm thickness were made by applying a pressure of 8 tons on the powered sample) by using an LCR meter. Impedance measurement were carried out in the frequency range 42 Hz-500 MHz and at temperature range 37 to 700°C.

Result and Discussion

3.1 X-Ray Diffraction (Xrd)

Fig. 1 shows the XRD patterns of pure $CoFe_2O_4$ (CFO) nanoparticles prepared using sol gel process and calcined at 550°C. The XRD pattern represent the scattering form of the plane of Miller indices (*hkl*): (220), (311), (400), (440), and (533), confirming the formation of well-crystallized single phase $CoFe_2O_4$ (JCPDS card 22-1086) [11]. The nanoparticle has a spinel crystal structure with group space of Fd3m. The highest intensity of the diffraction peak was taken place in (311) with a diffraction angle 2θ of 36.23°. In fig.1 there is no other peaks connected to cobalt oxide, iron oxide or other phases which indicate that we have pure cubic spinal $CoFe_2O_4$.The crystallite size for $CoFe_2O_4$ was found to be 30nm.

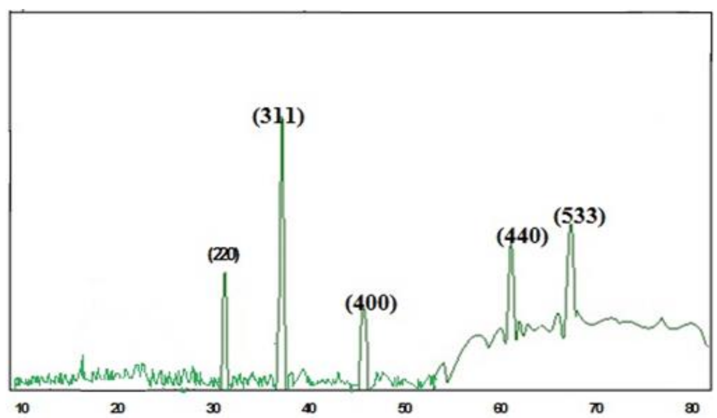


Fig. 1: X-ray diffraction pattern of the synthesized $CoFe_2O_4$ calcined at 550°C.

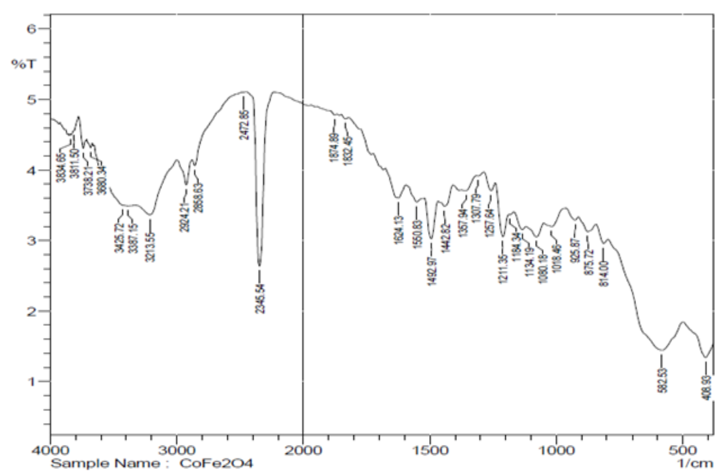


Fig. 2: FTIR spectrum of the prepared $CoFe_2O_4$ nanoparticles.

FT-IR spectra is a important tool to investigate the stretching and bending vibrations of tetrahedral and octahedral complexes of ferrites Since cobalt ferrite ($CoFe_2O_4$) has a spinel structure, so it characterized by octahedral and tetrahedral site. FTIR spectra give good information about the distribution of cations between octahedral and tetrahedral sites in the spinal ferrite. Fig. 2 shows that the FTIR spectrum of $CoFe_2O_4$ has two distinct absorption bands around 408.93 cm^{-1} and 582.53 cm^{-1}. The absorption band around 408.93 cm^{-1} distinguishes the stretching vibration frequency of the metal-oxygen at the octahedral site from the stretching vibration of the metal-oxygen at the tetrahedral site which has absorption band around 582.53 cm^{-1}.[12] These two absorption bands observed with in this limit reveal the formation of single-phase spinel structure having two sub-lattices, tetrahedral (A) site and octahedral [B] site. The absorption band at 925.87cm^{-1} and 1018.86 cm^{-1} may be assigned to the bending vibration of C-H and stretching vibration of C-N, respectively. 1018.86cm^{-1} may be corresponding to the nitrate traces. [13] The band at 1442 cm^{-1} was assigned to symmetric vibration (COO-) of the carboxyl ate group bonded to the nanoparticle surface. The 1624.13cm^{-1} band is due to the deformation mode of absorbed H_2O molecules, assigned to the bending vibration. [14] The sharp band with a maximum around 2345.54cm-1 assigned to C-O stretching vibration .The absorption band of symmetric and asymmetric vibrations of CH_2 groups appeared at 2924 and 2858 cm-1,respectively, which can be attributed to organic residues . The broad band with a maximum around 3425.72 cm−1 assigned to O–H stretching vibration of the surface adsorbed water from moisture content in the sample. [15]

SEM Analysis

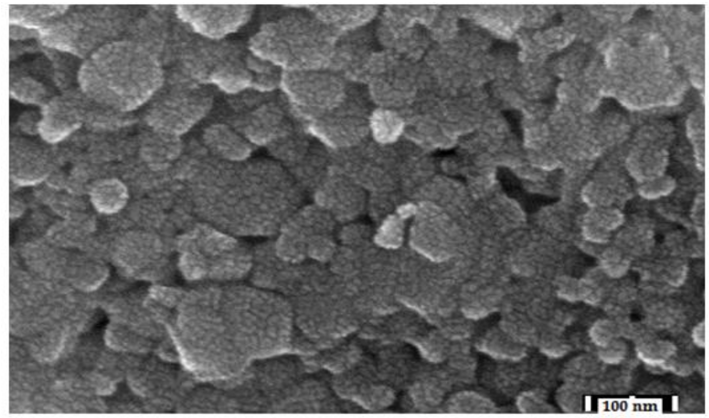


Fig. 3: SEM image of $CoFe_2O_4$ nanocomposites. Scanning Electron microscopy was used for the study of morphology and particle size.

To prove nano-particles and particle size distribution SEM images has used. The particle size of the images was calculated by the ImageJ software. Fig.3 shows the SEM image of the sample $CoFe_2O_4$. It is clear from the image that uniformly distributed; less cluster and homogenous spherical particles have been formed in a controlled environment by sol-gel method. According to the image, the most distribution of particle size is 30 nm which is corresponded to X-ray diffraction pattern results that calculated by Scherer equation. The homogeneity of shape and grain size largely affects the electrical and magnetic properties of ferrites.

Energy Dispersive X-ray (EDAX) Spectroscopy Analysis

EDAX examination was done in order to decide the chemical composition on the surface of the sample to support our observations on the structure of $CoFe_2O_4$. Fig.5 Shows the Energy dispersive X-ray spectroscopic (EDS) analysis shows that there are elements of Co, Fe, and O in the sample. It is noteable from

Fig. 5 the atom ratio of Co; Fe; O is , which is close to that of

$CoFe_2O_4$ formula. All of the above investigation confirm that the synthesized sample is $CoFe_2O_4$ without any impurities.

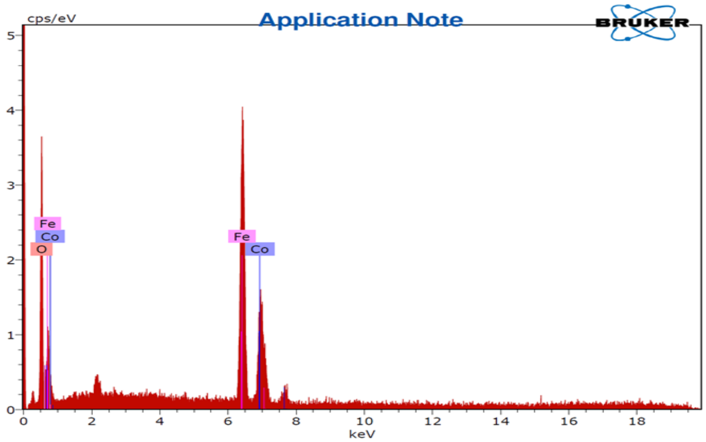


Fig. 5: EDAX pattern of $CoFe_2O_4$ nanocomposites

Electrical Properties

The electrical properties of $CoFe_2O_4$ include the dielectric properties, A.C conductivity and Impedance spectroscopy.

Dielectric constant

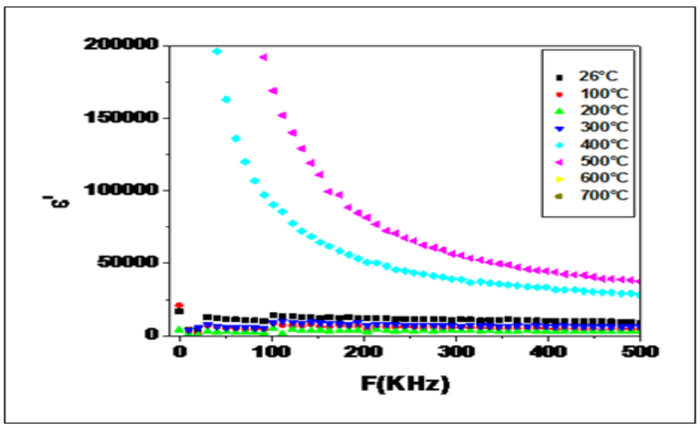


Fig. 6: Dielectric constant of the nanocrystalline $CoFe_2O_4$ at different temperatures.

Nanocrystalline spinel ferrites are virtuous dielectric materials, depending upon the particle size, cation distribution and method of synthesis. Dielectric constant (Ɛ') were carried out using an ac impedance analyzer. The variation of dielectric constant with temperature is shown in Fig 6. From graph it is observed that at lower frequency the Dielectric constant of the nanocrystalline $CoFe_2O_4$ sample calcinated at 550 °C is varies but with increase in frequency the Dielectric constant of the nanomaterial is nearly same and it is increases with the increase in temperature. This is due to the thermal activity and mobility of the electrical charge carriers apropos to the hopping or tunneling mechanism.

Conductivity

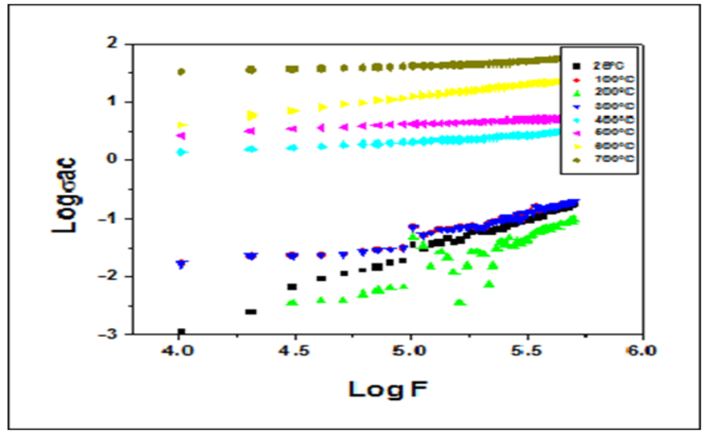


Fig. 7: Variation of ac conductivity with frequency for CoFe2O4

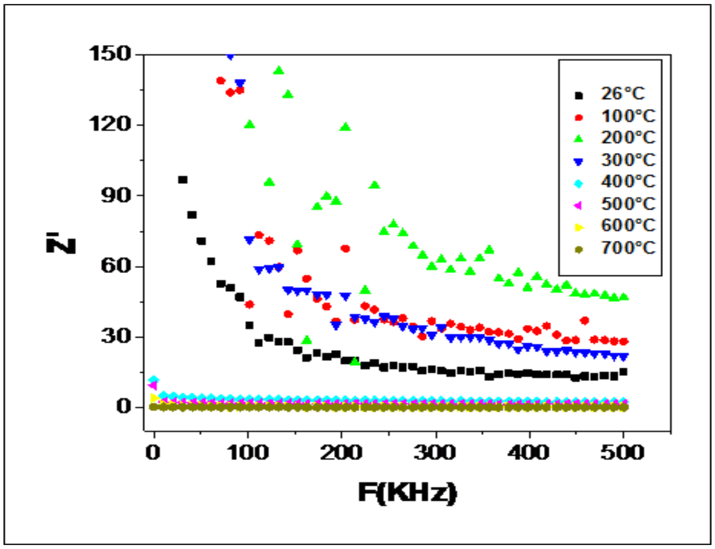
The ac conductivity increases with increase of the frequency and temperature applied in the experiment. The variations of A.C electrical conductivity of bulk CoFe2O4 with frequency is shown in fig.7 It Can be noted the A.C conductivity σa.c(ω) increases with increases in the frequency and temperature is common response for semiconductor material. Which is the normal behavior of ferrites this agrees with the result [16]. As mentioned above the conduction in ferrites mainly due to exchange of electrons amongst Fe^{3+} and Fe^{2+} ions. The boost in frequency of the connected fields expands the bouncing of charges bearers bringing about4 increase in conductivity and lessening of resistivity. Typical conduct of ferrites is the ordinary conduct of ferrites.

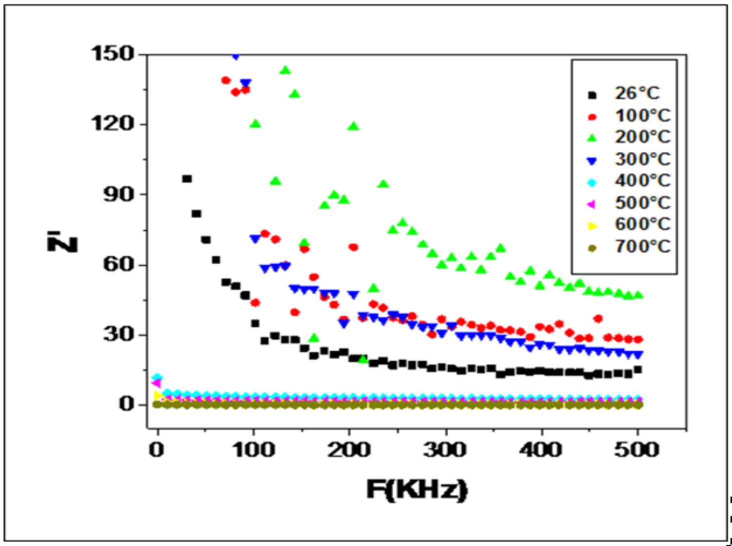
Impedance spectroscopy

Impedance describes a measure of opposition to alternating current (a.c.) . Electrical impedance extends the concept of resistance to a.c. circuits, describing not only the relative amplitudes of the voltage and current, but also the relative phases. Impedance analysis is useful to completely understand the electrical properties of spinel type ferrites and give us the data for both resistive (real part) and reactive (imaginary part) contribution to conductivity on the application of AC field. When the circuit is driven with direct current (d.c), there is no distinction between impedance and resistance; the latter can be thought of as impedance with zero phase angles. The symbol for impedance is usually *z* . The term impedance was invent by Oliver Heaviside et al. [17] and Kennelly et al.[18] was the first to represent impedance with complex numbers in 1893. Impedance is a frequency dependent measure of the opposition to current flow in an electric circuit. The magnitude of the complex impedance is the ratio of voltage to current amplitude. Complex impedance spectrum (CIS) is a non-destructive and powerful experimental technique for the characterization of micro structural and electrical properties of some electronic materials over a wide range of frequency and temperature [19]. There are many ways by which CIS data may be plotted. In CIS field, where capacitive rather than inductive effects dominate, conventionally one plots Im*(Z)*' ≅ −*Z*" on the *y*-axis vs. Re*(Z)* ≅ *Z*' on the *x*-axis to give a complex-plane impedance plot. Such graph shave been termed as SyQuest plots. But, it has the disadvantage of not indicating frequency response directly, but may nevertheless be very helpful in identifying conduction processes that all present. Complex impedance plane plots were drawn to study the electrical properties of CoFe2O4. The real (Z/) and imaginary (Z//) parts of impedance were calculated using the relations,

$$Z' = Z\cos\theta$$
$$Z'' = Z\sin\theta$$

Where Theta is the phase angle measured from LCR meter. Fig. 8 shows the variation of *Z*' with frequency at different measuring temperatures LMO and LSMO at different temperature The value of *Z*′ is higher at lower frequency region and as the frequency increases, the value of *Z*′ decreases monotonically and attains a constant value at high frequency region at all temperatures. The decrease in the *Z*′ value at low frequency region in all the compounds indicate that the conductivity of these compounds increases with the increase of frequency due to the increase of hopping of charge carriers between the localized ions. At low frequency, the value of *Z*′ for these compounds decreases with the increase of temperature and these values merge at high frequency region due to the increase of ac conductivity i.e. existence of negative temperature coefficient of resistance (NTCR) in the compounds. Decrement of *Z*′ with the increase of temperature and frequency suggests a possible release of space charge and consequently lowering of barrier properties in these materials.





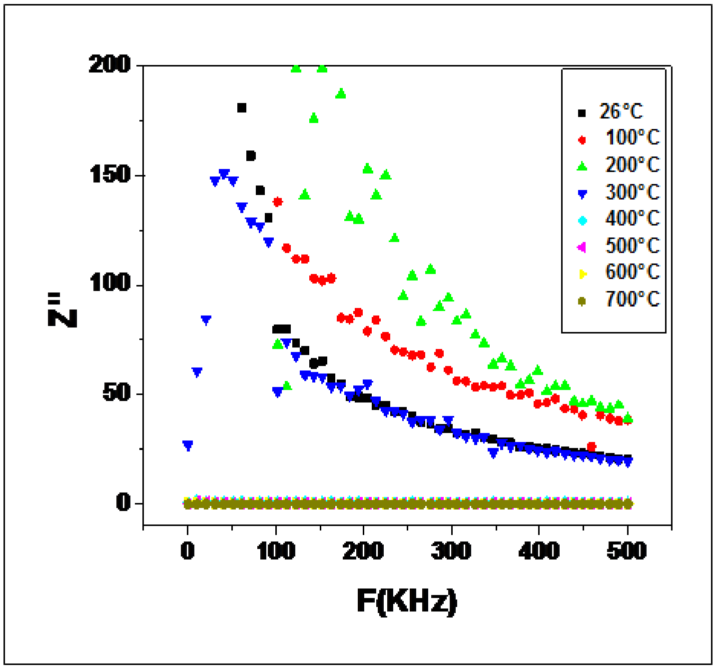


Fig. 9: Frequency dependence of imaginary parts of impedance Z'' for $CoFe_2O_4$

Impedance details of nanocrystalline $CoFe_2O_4$ calcined at 550°C have been measured in the temperature range from 100 to 700 °C. Fig. 10 manifest the Nyquist plot of the impedance measurements. The decrease of resistance with increasing temperature is a well-known property of semiconducting materials. Almost all measurements on this particle size show semicircle indicating that the single conduction mechanism is involved in the composite system. This single conduction mechanism may be assign to grain site or may be due to the mobility of free charges

induced by increase in temperature. The semicircle obtained decreases gradually with the increase of temperature showing that the sample is more conductive at higher temperature. From Nyquist plots, these semi circle arcs represent different relaxation processes. Usually semi circle at lower frequency represents grain boundary relaxation process and the one at higher frequencies gives the information on grain relaxation. It is noticeable from Nyquist plots that grains are contributing to the physical properties of the polycrystalline sample.

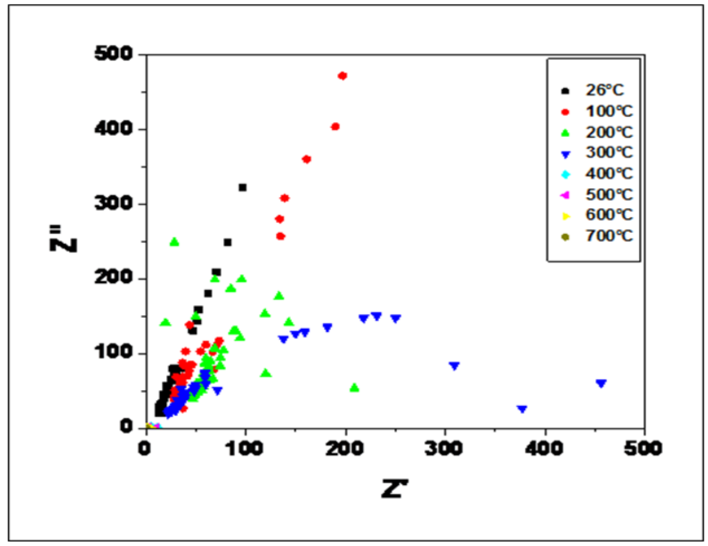


Fig. 10: Nyquist Plot of $CoFe_2O_4$ at different temperatures.

Conclusions

Sol–gel method was used to prepare $CoFe_2O_4$. The sharp and single diffraction peaks of XRD confirm the formation of polycrystalline $CoFe_2O_4$ nanomaterials. The electrical conductivity studies showed the NTCR character of $CoFe_2O_4$. The ac conductivity found to obey universal power law and showed the negative temperature coefficient of resistance character. The frequency variation of ac conductivity at different temperatures indicates that the conduction process is thermally activated.

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References

1. Y. Z. Donga, S. H. Piaoa, K. Zhangb, H. J. Choi, Colloids and Surfaces A **537**, 102 (2018)
2. J. Dong, Y. Zhang, X. Zhang, Q. Liu, J. Wang, Materials Letters **120**, 9 (2014).
3. G., Tang, S., Xu, B., Gu, B., Du, Y. Synthesis of CoFe2O4 Nanowire Arrays by Sol-Gel Template Method Chemical Physics Letters 379 2003: pp. 484 – 489.

4. Khan, A., Chen, P., Boolchand, P., Smirniotis, P. G. Modified Nano-crystalline Ferrites for High-temperature WGS Membrane Reactor Applications Journal of Catalysis 253 2008: pp. 91 – 104.
5. Srivastava, M., Ojha, A. K., Chaubey, S., Materny, A. Synthesis and Optical Characterization of Nanocrystalline NiFe2O4 Structures Journal of Alloys and Compounds 481 2009: pp. 515 – 519.
6. Wang, X., Wang, L. Y., Lim, I. I. S., Bao, K., Mott, D., Park, H. Y., Luo, J., Hao, S. L., Zhong, C. J. Synthesis, Characterization and Potential Application of MnZn Ferrite and MnZn Ferrite@Au Nanoparticles Journal of Nanoscience and Nanotechnology 9 2009: pp. 3005 – 301
7. Mouli, K. C., Joseph, T. Ramam, K. Synthesis and Magnetic Studies of Co-Ni-Zn Ferrite Nano Crystals Journal of Nanoscience and Nanotechnology 9 2009: pp. 5596 – 5599.
8. M. Sertkol, Y. Köseoglu, A. Baykal, H. Kavas, A. M. S. Bozkurt, M. S. Toprak, J. Alloys Compd. **486**, 325 (2009).
9. Y. Ichiyanagi, M. Kubota, S. Moritake, Y. Kanazawa, T. Yamada and T. Uehashi, "Magnetic properties of Mg-ferrite nanoparticles" J. Magn. Magn. Mater. 310 (2007) 2378.
10. Lawrence Kumar and Manoranjan Kar, "Influence ofAl3+ion concentration on the crystal structure and magnetic anisotropy of nanocrystalline spinel cobalt ferrite" J. Magn. Magn. Mater. 323 (2011) 2042.
11. Suwanchawalit C, Somjit V (2015) A facile hydrothermal synthesis of magnetic CoFe2O4 nanoparticles and photocatalytic performance. *Dig J Nanomater Bios* 10: 705–713.
12. Vasundhara, K., S. N. Achary, S. K Deshpande, P. D. Babu, S. S. Meena and A. K. Tyagi, 2013.Size dependent magnetic and dielectric properties of nano CoFe2O4 prepared by a salt assisted gel-combustion method. J. Appl. Phys. 113, 194101.
13. Sangmanee, M., S. Maensiri, 2009. Nanostructures and magnetic properties of cobalt ferrite (CoFe2O4) fabricated by electrospinning. Appl Phys A 97: 167–177
14. Li, X.-H., C.-L. Xu, X.-H. Han, L. Qiao, T. Wang and F.-S. Li, 2010. Synthesis and Magnetic Properties of Nearly Monodisperse CoFe2O4 Nanoparticles Through a Simple Hydrothermal Condition. Nanoscale ResLett 5, 1039–1044.
15. Trad, T. M., R. M. Alvarez, E. J. McCumiskey, and C. R. Taylor, 2011. Capped CoFe204 nanoparticles: nonhydrolytic synthesis, characterization, and potential application as magnetic extractants and in ferrofluids. J. of Advances in Nanomaterials and Nanostructures, 155-162.
16. P.A. Noorkhan and S. Kalayne,"Synthesis, Characterization Ac Conductivity of Nickel Ferrite", *Journal of Engineering Research and Applications,2, 2012, 681-685.*
17. Oliver Heaviside 1886 The Electrician, p. 212, 23rd July 1886,
18. Kennelly Arthur 1893 Impedance (IEEE)
19. Ivanova V V, Kapyshev A G, Venevtsev Yu N and Zhadanov G S Izv. ANSSSR, Ser. Fiz. **26** 354(1962)