Impedance Studies on Chromium substituted Cobalt Nano ferrites

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Abstract: Chromium substituted cobalt nano ferrites with the chemical composition CoCrₓFe₂₋ₓO₄ (x=0.0, 0.5, and 1.0) were synthesized by Citrate-gel auto-combustion method. X-ray diffraction analysis of all the chromium substituted cobalt ferrites confirmed the formation of a homogeneous single phased cubic spinel with a crystallite size of the particles in the range of 6-12nm. The impedance measurements were used to study the effect of grain size and grain boundary on the electrical properties of the synthesized samples. The impedance measurements of the Co-Cr nano ferrites were carried out at room temperature in the frequency range of 100Hz to 1MHz. One semicircle observed in the Cole-Cole impedance plots of the ferrite compositions indicates that the conduction mechanism is solely due to the grain boundary.

Key words: Nano ferrites, Citrate gel method, Impedance study, Cole-Cole impedance plots

1. Introduction
Ferrites in nano regime show unique properties compared to their bulk materials [1], spinel ferrites are important due to their technological applications. They are very good dielectric materials with a wide range of applications ranging from microwave to radio frequencies [2]. Method of preparation, nature of metal ion substitutions, size of the particle, etc. will influence the electrical properties of the spinel ferrites [3]. They are used as excellent materials for applications in high frequency microwave devices, computer memories, transformers and magnetic recordings, etc. [4].

Impedance spectroscopy is a powerful tool for investigating the electrical behavior in spinel ferrites [5]. Microstructure of the ferrites will influence its properties to a greater extent. The microstructure can be determined by the two main components viz., the grain and grain boundary. Impedance analysis is used to investigate the electrical transport properties in detail by considering their resistive (real) and reactive (imaginary) components separately [6].

The authors have prepared chromium substituted cobalt ferrites through citrate-gel method by analyzing the room temperature impedance data with varying frequencies and results are reported in the present work.

2. Experimental
2.1. Materials and synthesis
Co-Cr Nano ferrites with the chemical composition CoCrₓFe₂₋ₓO₄ (where x=0.0, 0.5, 1.0) were synthesized via Citrate-Gel auto combustion technique by using Cobalt Nitrate, Ferric Nitrate, Chromium Nitrate, Citric acid and Ammonia of high purity chemicals as starting materials. The detailed procedure for the synthesis of ferrites under investigation was reported in our earlier publication [7].

2.2. Characterization
X-ray diffraction (XRD) analysis was carried out to identify the phase and crystal structure of the synthesized ferrites using Phillips X-ray diffractometer at room temperature by continuous scanning in the range of 20° to 85°. The prepared ferrite powders were pressed to form pellets of 13mm diameter and 2mm thickness and were sintered at 500°C for four hours. Silver paste was applied on both sides of the pellets to have good electrical contact for carrying out impedance measurements. The impedance measurements as a function of frequency at room temperature were made using Impedance analyzer in the frequency range 100Hz to 1MHz.

3. Results and discussion
XRD patterns and the crystalline phases were identified by comparison with reference data from the ICSD card No. 22-1086 for Cobalt ferrites (CoFe₂O₄). The XRD patterns of all the Chromium substituted cobalt ferrites showed a homogeneous single phased cubic spinel belonging to the space group Fd₃m (confirmed by ICSD Ref 22-1086). The X-ray diffraction patterns of all the samples were shown in Fig 2. The calculated crystallite size was in the range of 6-12nm as reported in our earlier publication [7].

The impedance measurement gives us the information about the resistive (real part, dented by superscript “”) and reactive (imaginary part, denoted by superscript “”) components of a material. The Cole-Cole plot or Nyquist or complex impedance plot was drawn for complex parameter, impedance (Z”). The grain, grain boundary and grain-electrode effects
appear as semi circles in a Cole-Cole plot. The lower frequency arc corresponds to the resistance of grain boundaries, while the high frequency arc represents the resistance of the grain or bulk properties [8].

Fig 2 shows the Cole-Cole plot as a function of frequency at room temperature for each individual composition of CoCr<sub>x</sub>Fe<sub>2-x</sub>O<sub>4</sub> with x=0.0, 0.5, 1.0. From the figure it is clear that as the Cr composition is increased, the curves attain larger curvature and become perfect semicircles. Larger diameter of the semicircle shows the greater resistance. The obtained plots show only one semicircular arc corresponding to the conduction due to the grain boundary volume in the frequency range, which suggests that the conduction mechanism takes place predominantly through the grain boundary volume. Further the contribution of the grains was not well resolved in the samples. The major contribution of the grain boundary can be due to the decrease in Fe<sup>3+</sup> content, increase in surface to volume ratio and disordered atomic arrangement near the grain boundary.

**Figure 2.** XRD patterns of Co-Cr Nano ferrites with x=0.0, 0.5, 1.0

4. Conclusion
Nano particles of CoCr<sub>x</sub>Fe<sub>2-x</sub>O<sub>4</sub> (0≤x≤1) system with an average crystallite size between 6 and 12 nm were synthesized through Citrate-gel method. Cole – Cole plots obtained from the impedance data as a function of frequency at room temperature for nano ferrites under investigation suggests that the conduction mechanism in the ferrites is solely due to the grain boundary contribution.

**References**