Structural and Electrical Characterization of Chromium Substituted Copper Spinel Ferrite

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Abstract

Chromium substituted cupper spinel ferrite nanoparticles with nominal composition CuCrxFe2-xO4 (for x =0.0 & 0.2) have been synthesized by the sol-gel auto combustion technique. The XRD and TEM were employed to evaluate the structure properties of CuCrxFe2-xO4 nanomaterials. The XRD analysis confirms the single phase formation. The various parameters such as lattice constants ('a' and 'c'), cell volume and crystallite size have also been calculated from the XRD data. From Debye Scherrer formula, the crystallite size is found in the range of 30–57 nm, which was supported by TEM studies. The DC electrical conductivity was measured as a function of temperature from 303 K to 650 K and found to behave like semiconductor. The electrical behavior of synthesized nano-spinel ferrites may be explained by polarons and hopping mechanism.

Keywords: Nanoparticle, sol-gel combustion technique, XRD, TEM, dc electrical conductivity etc.

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1. Introduction

Nanocrystalline ferrites are currently the subject of interest of its wide application in industrial as well as research areas. They are attractive because of their importance in ferrofluids, magnetic drug delivery, hyperthermia for cancer treatment etc [1]. An interesting example is that of CuFe2O4 which has got some peculiar properties like structural, electrical etc with the various substitutions allows tunable change in its properties. CuFe2O4 has an inverse spinel structure with Co+2 ions in octahedral sites and Fe3+ ions equally distributed between octahedral and tetrahedral sites [2]. The presence of nonmagnetic ions in spinel was found to alter their electrical properties and studies revealed useful information on the nature of exchange interaction, cation exchange, etc. Reddy et al [3] have been studied the electrical conductivity zinc –substituted cobalt ferrites as a function of composition and temperature. The electrical conductivity was found to increase with increasing temperature with a change of the slope at transition. It has been well understood that the electrical conductivity of the spinel is due to the movement of charge carrier between different valence cations on octahedral sites.

2. Experimental

2.1 Materials and Powder Preparation

The synthesis of CuCrxFe2-xO4 was performed by a sol-gel auto combustion method. The raw materials used to form the precursors are cupper nitrate, chromium nitrate, ferric nitrate & urea. The appropriate amounts of reactant were weighed out in a stoichiometric proportion. All the reactant dissolves in a deionized water. This solution of homogenous mixture was put onto the magnetic hot plate at the temperature of 80^0C. After sometime, the

solution transformed in to gel. The gel form of the solution ignited and fired in a specially designed microwave oven on 600 watt for 7 min. The gel was burnt out completely forming ash. The resulting ash was grinded with a pestle mortar to obtain the ultra fine ferrite powder. The synthesized sample was calcined at 800^0C for about 8 hours in the electric furnace to obtain monophase cubic ferrite.

2.2 Characterization Techniques

X-ray diffraction (XRD) analysis of the powdered samples was carried out by Bruker X-ray diffractometer equipped with a CuKa radiation source (λ=1.54Å).

To obtained detailed information on the morphology and verify the particle size of calcium substituted hexaferrites, a set of micrographs were taken by TEM-CM 200at the operating voltage of 20-200 KV with the resolution of 2.4 Å.

The samples were pressed in form of discs and rubbed with silver paste as contact material. Electric measurements as a function of temperature in the range 300- 673 K at constant frequency of 100 Hz were carried out using the Precision Impedance Analyzer 6500 B.

3. Results and Discussion

XRD patterns showed that the CuCrxFe2-xO4 samples consisted of single phase spinel, which was confirmed to be the same cubic structure as shown in figure 1. The lattice parameters depend on the Cr/Fe cation ratio, because the ionic radii of Cr^{+3} (0.640 Å) has smaller ionic radii as compared to Fe^{+3} (0.690 Å). The average particle size of the samples calculated by Debye Scherrer formula was to be found in the nanometer range. The X-ray density as a function of Co concentration is tabulated in table No. 1.

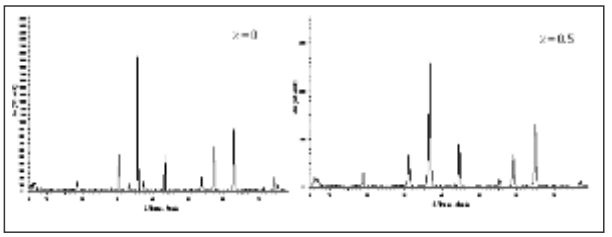

Figure 1: X-ray powder diffraction patterns of the CuCrxFe2-xO4 system

Sr. No	Conc. (x)	a (Å)	V (Å3)	ρx (gm/cm3)	ρx (gm/cm3)	P(%)	Particle Size by Scherrer formula (nm)
01	x = 0.0	8.1286	537.09	5.916	3.254	44.99	57
02	x =0.1	8.3379	579.65	5.437	3.102	42.94	30

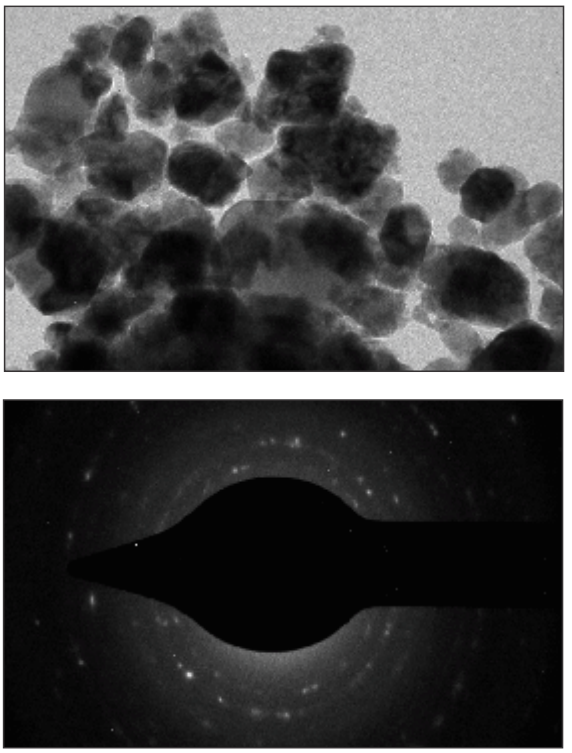

Figure 2: TEM images pattern of the CuCrx Fe2-xO4 system

Figure 2 shows the TEM images of the samples calcinated at 800 °C, from the micrographs we observe that the oxides particles are finely dispersed and spherical in shape within narrow size range. The micrographs shows spherical particles with the particle size distribution of below 100 nm. It seems that the size of the

particles is below 100 nm which resembles with the measurement of the crystallite size of sample by D Scherrer formula as between 30-57 nm [4].

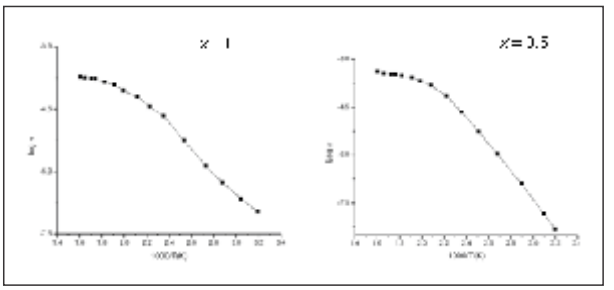

Figure 3: Plot of log σ vs temperature of the CuCrxFe2-xO4 system

The plots of conductivity with temperature for, is shown in fig 3. From these plots it can be seen that the conductivity increase slowly. This conduction can be attributed to localized charge carriers. According to localized model the electronics are strongly localized on cations. Theoretical work by several over the years has provided some understanding of conduction in oxides and transition metal compounds. For these materials, the interaction between electrons and optical phonons is strong and conduction is explained on the basis of polarons. The treatment of conduction by polarons is discussed by several workers [5, 6, 7]. Polarons belonging to two categories large and small polarons. In the large polaron model, the conductivity is by band mechanism at all temperatures and the conductivity decreases with frequency. The small polaron conduct in band like manner up to a certain temperature, and the conductivity increases with frequency. At higher temperature, the conduction is by thermally activated hopping mechanism. The localization may be attributed to electron-phonon interaction or strong magnetic interaction between carriers and magnetic sub – lattice [8]. An additional localization Fe^{2+} ions may arise from inhomogeneous distribution of ions over octahedral and tetrahedral sites in spinel lattice' The experimental results in present case also shows a trend expected for small polaron conduction.

4. Conclusions

From the XRD spectra, the structure of CuCrxFe2-xO4 is a single phase normal spinel. TEM analysis revealed that the particles are nearly spherical. The particle size determined from TEM was found to be in close agreement with the XRD studies. From the electrical conductivity measurement it was found conduction mechanism is due to the small polaron hopping mechanism on the octahedral cation.

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