Structural and dc electrical transport study of Cu-Zn ferrialuminates prepared by chemical route.

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Abstract. Ferrimagnetic ionic crystalline materials, with general formula AB₂O₄ are termed as spinel phase ferrites. Electro – magnetic properties, concentration of different ions and surface morphology of mixed-metal oxides shows significant applications in the various fields. In above work, Cu doped Zn ferrialuminate were prepared by sol-gel auto-combustion route. Purity of the synthesized materials were confirmed by XRD analysis which reveals the formation spinal phase structure and by applying the Debye-Scherer’s formula. Nanocrystalline nature of the samples were studied by transmission electron microscopy (TEM). The particle was found in the nanorange. The temperature dependent DC electrical conductivity was studied by two probe method. Semiconductor behavior with the rise in temperature were found in all the samples.

Keywords: Ferrimagnetic; XRD; Nano-sized particle; semiconductor;

1. Introduction
Nanostructured spinel ferrites, nominally AFe₂O₄ where A is a bivalent metal ion and often a transition metal ion, play a significant role in technologies, viz. high frequency transformers, antennae, various microwave and radar systems, high speed digital tape recording devices, catalysis and magnetic equipments [1-6]. The different physico-chemical properties of the ferrospinel having resourceful structure as well as proportional composition play a vibrant role to mark them applicable in several ways. Its spreading over tetrahedral (A) and octahedral (B) sites is key factor to make them tailor made material. These compounds have good ability to tune their electrical and magnetic properties which mainly depend upon the selection of metal ions, its distribution and their processing conditions [7-11].

Various magnetic properties of spinels are due to the strong interaction of metal ions, distributed over tetrahedral (A) and octahedral (B) sites [12-20]. They have strong potential to absorb high frequency
radiations and hence are applicable in radio frequency devices [21-25]. Ferrsospinels are high resistivity materials and are suitable for microwave appliances also [26-30].

Our literature review expose that, numerous research reports on ternary system containing diamagnetic transition metal ion distributed over different sites but very limited reports on various composition system having four number of ions in single composition with single phase. With an assessment to study the four different element containing series of Zn\(^{2+}\) ion substituted Cu - ferrialuminates were formulated by soft chemical route using citric acid and investigated by various characterization tools.

2 Experimental Methodology

Cu-Zn ferraluminate \([\text{Cu}_{1-x}\text{Zn}_x\text{FeAlO}_4 (0.0 \leq x \leq 1.0)]\) system with various compositions having nanoscale particle size were synthesized by one-step citrate sol–gel method using citric acid as oxidant as well as fuel [22]. Stoichiometric amount of Cu(NO\(_3\))\(_2\).5H\(_2\)O, Zn(NO\(_3\))\(_2\).6H\(_2\)O, Fe(NO\(_3\))\(_3\).9H\(_2\)O, Al(NO\(_3\))\(_3\).9H\(_2\)O, liquor ammonia and Citric acid (C\(_6\)H\(_8\)O\(_7\)) were uses as starting material. All the metal salts were dissolved in deionized double distilled water. The molar concentration of metal salts and fuel-oxidant (citric acid) were maintained as 1:2. Aqueous solutions of metal nitrates were added to the citric-acid solution and stirred for 2 Hrs to get homogenous mass. With the help of ammonia solution, the pH of the solution was maintained about 8. The above homogenous mass was heated slowly on hotplate at about 80°C to convert solution into gel with continuous stirring. Finally colored gel was further heated to convert into floopy powder by auto- combustion. Finely grinded powder form samples were analyzed by diffractometer by X-rays (XRD) and electron beams of transmission electron microscope (TEM) to focus on sample to produce images and confirm nanostructure techniques. The temperature dependent dc resistivity study was followed using two probe method and investigated in detail.

3 Characterization

3.1 Phase formation by XRD

The as prepared middle composition Cu\(_{0.5}\)Zn\(_{0.5}\)FeAlO\(_4\) of the mentioned series was sintered at different temperature (500 – 900°C). Their X-ray pattern was scanned on Philips PW 1710 diffractometer with CuK\(_{\alpha1}\) radiation (1.5406Å). Figure 1 shows that 700°C is desired temperature to get single phase spinel compound. Hence all the composition of the series was sintered at same temperature (Figure 2). All the samples show the presence of face centered cubic spinel structure. The peaks were indexed to plane (111), (220), (311), (222), (400), (411), (511), and (440) of pure single phase nanocrystalline structure. Lattice constant ‘a’ was seen to vary from 8.41 Å to 8.48 Å with increase in Zn\(^{2+}\) ion concentration (x = 0.0 to 1.0). It's because of large ionic radii of Zn\(^{2+}\) ion (0.82 Å) [31] compared to that of Cu\(^{2+}\) ion (0.72 Å). Well known Debye-Scherer’s equation was followed to determine crystallite size and it’s in the range of 56-76 nm.
3.2 Electrical resistivity

The liner plots without any disruption of log ρ vs 1000/T (Figure 3) reveals the semiconducting nature of all the samples. The dc electrical resistivity of all the samples varied from 10⁷ - 10¹⁰Ωcm while activation energy values differs from 0.46 to 0.81eV.

The nonlinear trend in electrical resistivity with respect to increase in concentration of diamagnetic Zn²⁺ ions is due to distribution of same or different ions over two different sites (tetrahedral and octahedral). The site preference energy of various ions is also accountable for its anomalous behavior. These plots of Figure 3, shows that, dc electrical resistivity increases gradually as Zn²⁺ ion concentration increases up to x = 0.5 (Cu₀.₅Zn₀.₅FeAlO₄) and then drops to lowest value at x = 0.75 (Cu₀.₂₅Zn₀.₇₅FeAlO₄). The last composition of the system ZnFeAlO₄ (x=1.0) shows most dc electrical resistivity. The hopping mechanism in the oxides helps to explain the conduction in mixed-metal oxides which takes place through charge carries over different sites (tetrahedral and octahedral) as well as probable variable oxidation states of same / different ions. In the initial compositions (up to x = 0.5) there will be absence of Fe²⁺ ions [32] to show continuous increase in resistivity while in further compositions, Cu₀.₂₅Zn₀.₇₅FeAlO₄ & ZnFeAlO₄, Zn²⁺ ions strongly desire tetrahedral (A) sites & Cu⁺² ions favor the octahedral (B) sites while Fe⁺²/³ ions moderately locate mutually A and B sites [2, 33-40]. Gradual increase in Zn²⁺ ion concentration (at A site) results decrease in the Cu⁺² ions concentration at B site which is responsible for relocation of some Fe⁺²/³ ions from tetrahedral (A) site to octahedral (B) site with reduction in content of Cu²⁺ ions from B sites. As a consequence of it, amount of ferrous and ferric ions at B site increases, which are responsible for conduction in ferrite by hopping mechanism.
3.3 Surface Morphology

TEM images of CuFeAlO$_4$ and ZnFeAlO$_4$ are shown in Figure 4 (a) and (b) respectively. Particle dimensions of both the samples are in nanorange and found to be of 50 - 70 nm. The content of zinc ions and sintering temperature aids for interaction amongst grain to develop them appropriately. The higher energy barrier of CuFeAlO$_4$ than that of ZnFeAlO$_4$ results the large particles of Cu-ferrialuminates than Zn-ferrialuminates.

![Figure 4. Transmission electron microscopic images of samples: (a) CuFeAlO$_4$, (b) ZnFeAlO$_4$.](image)

4. Conclusion

Soft and low temperature chemical route (sol-gel auto-combustion) is employed for synthesis of Cu-Zn-Fe-Al quaternary oxides with good stoichiometry. We are successful to get single-phase FCC spinel structure. DC resistivity is linearly increases with increase in concentration of zinc reveals the
The semiconducting nature of all the compositions. The hopping mechanism of electrons between the Fe$^{+2}$ and Fe$^{+3}$ ions explicates the deviation of dc conductivity with temperature. The investigated material has desirable electrical resistivity for use in microwave appliances.

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