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Variation of Porosity with Copper Content in Copper Cobalt Ferrite

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Summary:

Nano-particle size polycrystalline aluminum substituted copper cobalt ferrite samples $Cu_xCo_{1-x}Fe_{2-2y}Al_{2y}O_4$ (where x= 0.0, 0.2 0.4, 0.6, 0.8, 1.0 ; y = 0.05, 0.15 and 0.25) have been prepared by standard ceramic technique. The effects of aluminium and copper on structural properties of cobalt ferrite are studied. A universal testing machine as well as Archimedes's method was applied for determining the physical properties of the samples. Phase formation is investigated using X-ray diffraction, Infrared absorption technique and Scanning electron microscope technique. Ionic radii $R_A$and bond lengths (A-O) on both sites are found decreases with Al^{3+} and copper content. The Lattice constant 'a', physical density as well as X-ray density of samples goes on increasing with Al^{3+} and copper content. The ratio c/a is found increasing when addition of copper content and decreases with aluminium content. It means that Al^{3+} and copper acquire the tetragonal prolate type distortions on B site and hence (c/a) ratio increases and automatically crystal lattice turned from tetragonal spinel to cubic spinel. It can be seen from the micrographs that the average grain size decreases with increasing substitution of doping concentration of Al^{3+} in copper cobalt ferrite which decrease in porosity.

Keywords: Polycrystaline, nanoparticle size, standard ceramic technique and Inverse cubic spinel

INTRODUCTION:

Cobalt ferrite is a partially inverse spinel with formula $[Cu_xFe_{1-x}]^A$ $[Cu_{1-x}\ Fe_{1+x}\ ]^B\ O_4$ where A and B are the tetrahedral and octahedral sites respectively [1-3]. Vaingankar et.al (4) has reported that cobalt is 74% inverse spinel. Degree of inversion is found to vary with heat treatment and quenching [5]. The cation distribution may also differ at surface and no surface atoms [6]. Copper cobalt ferrite is having high coercive force field. Mechanical hardness and chemical stability is magnetic recording, magneto-optical recording and electronic devices [7]. Magnetic properties of nanoparticles find wide technological applications such as high density recording, magnetic refrigeration, Ferro-fluids, spintronics and drug delivery etc.[8]. Several researchers have reported on Cd, Cr, Mn, Ti, Zn, Gd, and Nd. Substituted cobalt ferrite [9-11]. Raghavendra et. al. [12] have synthesized aluminium doped cobalt ferrite by the sol-gel method and reported the results on particle size. The estimated values of the porosity of the samples lie between 4.5% and 16.2% in Magneto electric composites with composition (x) $Ni_{0.2}Co_{0.8}Fe_2O_4$ (ferrite) + $(1-x)PbZr_{0.8}Ti_{0.2}O_3$[13]. In this present work we report the standard ceramic synthesis, structural properties of Al^{3+}substituted copper cobalt spinel ferrite nanoparticles.

EXPERIMENTAL:-

Materials:

High purity starting materials are used as

Cobalt Oxide (CoO):- 74.9326 gm, Copper Oxide (CuO) :- 74.5454 gm, Ferric oxide(Fe_2O_3):- 159.6922 gm, Aluminum Oxide (Al_2O_3):- 101.9612 gm

Preparation of ferrite:

Nano crystalline powder samples of $Cu_xCo_{1-x}Fe_{2-2y}Al_{2y}O_4$ (where x= 0.0, 0.2, 0.4, 0.6, 0.8, 1.0; y = 0.05, 0.15 and 0.25) were prepared by the standard ceramic technique. Starting materials CuO, CoO, Fe_2O_3 and Al_2O_3 of AR grade obtained from Sigma – Aldrich, India were used. These samples were heated at ramping rate of 80 $^0C\ hr^{-1}$ at 1000^0C for 48 hours. XRD and IR analysis revealed the cubic spinel structure of the synthesized samples and functional groups in the samples respectively. The absence of any extra line confirms the formation of single phase ferrite. The average particle size 'D' was determined from line broadening (311) reflection using the Debye Scherer formula discussed elsewhere [14]. Calculations of lattice constant, physical density, X-ray density, porosity, site radii and ionic bond lengths on both sites were calculated by using formulae discussed elsewhere [15] and graphically shown in fig.4.

Infrared absorption spectra of powdered samples were recorded in the range 350-800 cm^{-1} using Perkin-Elmer FTIR spectrum and spectrometer by KBr pellet technique and presented in (fig.2). The scanning electron microscopes are shown in fig.3

Results and discussion:

The X-ray diffraction patterns of the samples are presented in (fig.1). Powder X-ray diffractometer of the ferrite samples reveals the single phase spinel structure, as well defined reflection is observed without any ambiguity. The diffraction peaks are corresponding to (200), (311), (400), (422), (333/511), (440) and (533) planes. The lattice constants 'a' and 'c' for all prepared samples are calculated by using prominent (311) XRD peak. The calculated and observed values of inter planer distance (d) are found in good agreement with each other for all reflections. The physical density (dB), x-ray density (dx), and porosity (p), are calculated from the formulae given by Gadkari et.al [16].

From the calculations of lattice constants 'a' and 'c' for all the prepared ferrites it is observed that c >a and tetragonality ratio (c/a) is found in the range of 1.03 to 1.07. This result is in good agreement with previous report [17-18].In this present report tetragonality ratio for copper ferrite is 1.06. It means 70% copper resides on B site and it exhibits prorate type distortions in the crystal lattice. The previous report [19] well supports the present results reported this communication. Both Fe^{3+} and Cu^{2+} are John-Teller ion which produces prolate type distortions on (B) site and hence c >a and (c/a) = 1.06. Therefore copper ferrite exhibits tetragonal spinel structure in host crystal lattice of cobalt ferrite. In addition of copper content in tetragonality ratio is found increasing but due to addition of aluminium tetragonality ratio deceases. It means that Al^{3+} and copper suppress the tetragonal prolate type.

The crystallite sizes (t) of all the prepared samples were computed by Scherer rule utilizing the peak width at one-half intensity of the maximum intensity peak (311). The Al (y = 0.05-0.25) doped copper cobalt ferrite samples show a higher grain growth and the crystallite size (t) lies in the extent of 52.53-94.4 nm. The mean particle size calculated from diffractograms is in the range of 50 to 100 nm. That suggest the particles in the ferrites samples are fine and there is continuous grain growth in all compositions. It gives the confirmation of suitable microstructure formation in all compositions. The width of the reflection peak (311) for all the compositions is approximately the same due to the nearly equal particle size.

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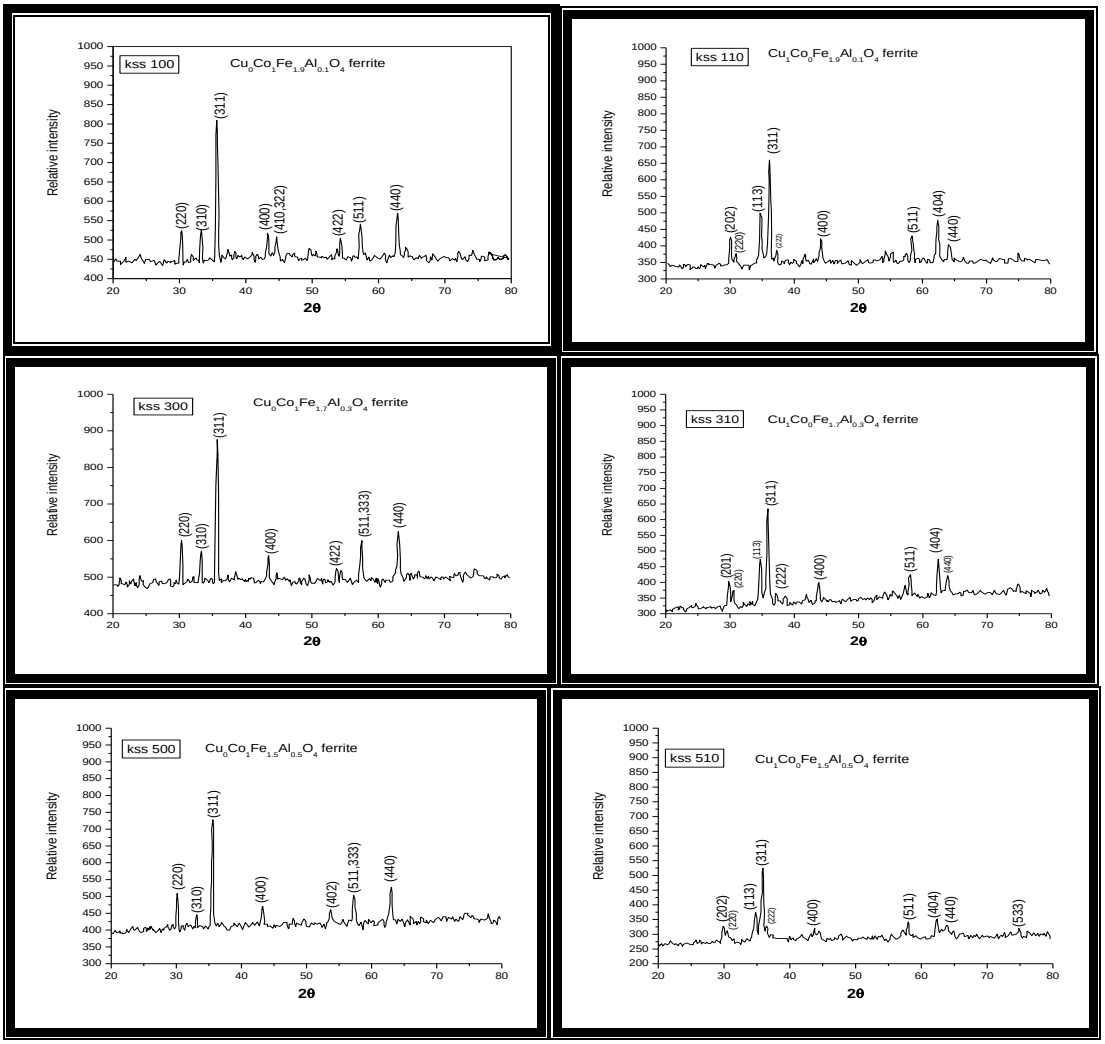

Fig: 1 XRD patterns of system $Cu_xCo_{1-x}Fe_{2-2y}Al_{2y}O_4$

The infrared absorption spectra are showing two distinct absorption bands ν_1 due to tetrahedral (A) site interstitial voids near 600 cm^{-1} and other ν_2 due to octahedral (B) site interstitials voids near 400 cm^{-1}. Our results in this present communication are well supported by previous reports [20, 21].

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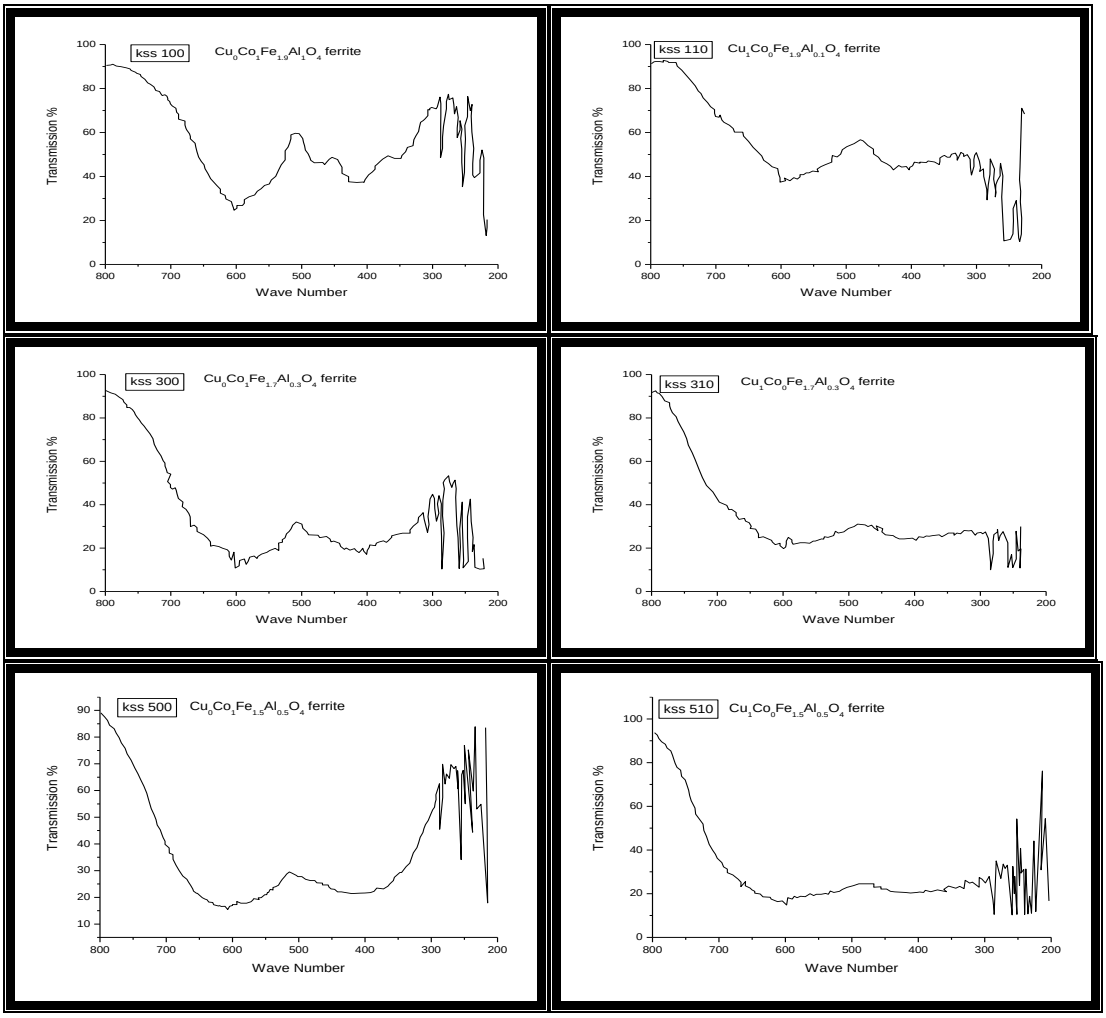

Figure 2: Absorption spectra for system $Cu_xCo_{1-x}Fe_{2-2y}Al_{2y}O_4$

The close inspection of all micrographs revealed that there is continuous grain growth with well – defined grain boundaries formed. The present system shows multi domain behavior. No exaggerated grain growth is observed in any composition. The average grain size is found to decrease with increase in Al content in copper cobalt ferrite. However in the present system the grain growth shows generally a decreasing trend with aluminum content, which is rather expected because of multi-domain behavior of these compositions in copper cobalt ferrite. Grain growth is almost accompanied with grain size, which is increasing with copper and aluminum content. So it appears that copper and aluminum content favors the grain growth. The scanning electron micrographs shown below

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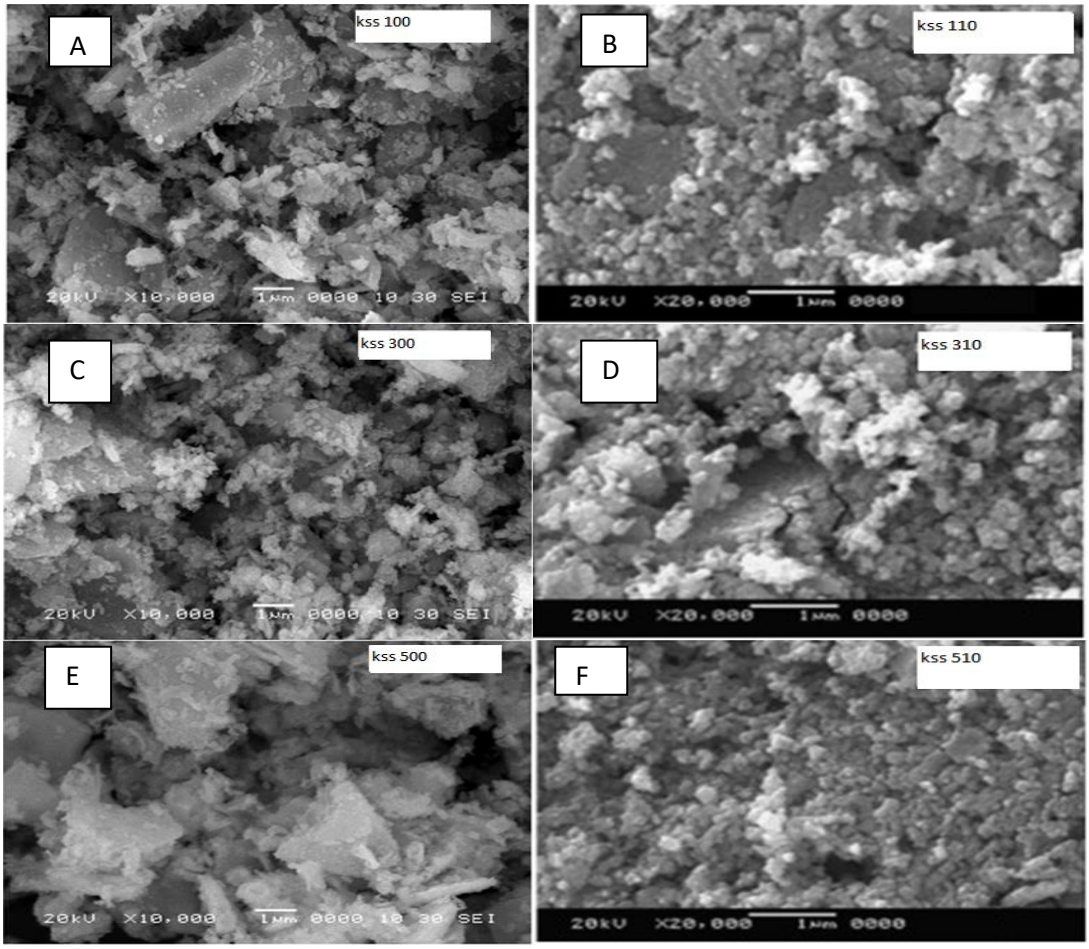

Fig: 3 scanning electron microscopes of $Cu_xCo_{1-x}Fe_{2-2y}Al_{2y}O_4$: (A) KSS 100-$Cu_0Co_1Fe_{1.9}Al_{0.1}O_4$, (B) KSS 110- $Cu_1Co_0Fe_{1.9}Al_{0.1}O_4$, (C) KSS 300- $Cu_0Co_1Fe_{1.7}Al_{0.3}O_4$, (D) KSS 310- $Cu_1Co_0Fe_{1.7}Al_{0.3}O_4$, (E) KSS 500- $Cu_0Co_1Fe_{1.5}Al_{0.5}O_4$ & (F) KSS 510- $Cu_1Co_0Fe_{1.5}Al_{0.5}O_4$

From the fig.4, it is detected that the size of particle rises with concentration Al^{3+} content increment. The particle size occurs in the nano range 50nm to 100nm.The particle size is a very important parameter in terms of ferrite. It has a substantial function in finding out the magnetic and electric phenomenon of ferrites. The change of the particle size with copper as well as Al^{3+} content for different ferrite samples is shown in figure 4.

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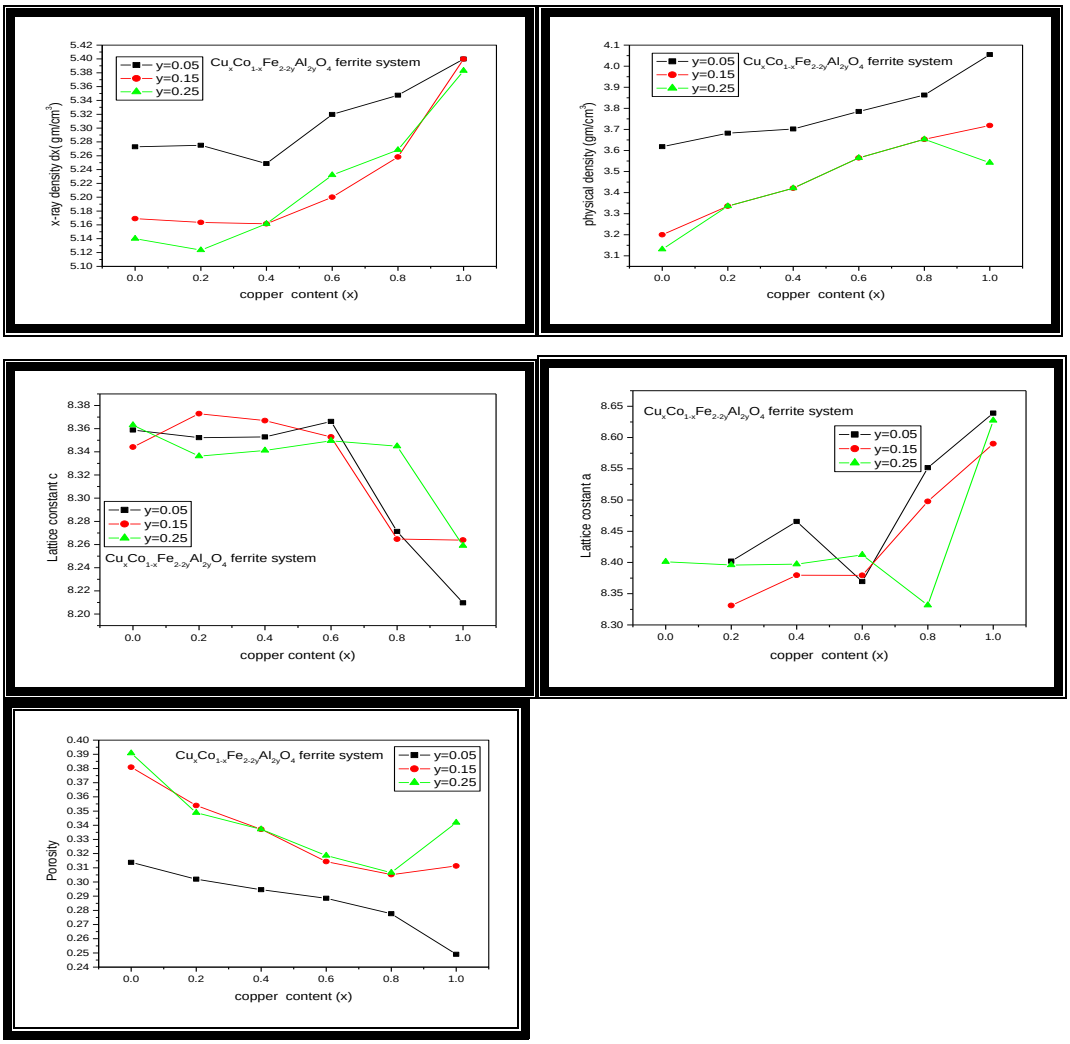

Fig: 4: Variation of lattice constant a, lattice constant c, x-ray density, physical density and porosity with copper content and aluminum content.

CONCLUSIONS:

The lattice constant obtained from XRD data shows non-linear behaviour. The lattice constants 'a' and 'c' for all the prepared ferrites it is observed that c >a and tetragonality ratio (c/a) is found in the range of 1.03 to 1.07. The infrared absorption spectra showing two distinct absorption band ν_1 due to tetrahedral (A) site interstitial voids near 600 cm^{-1} and other ν_2 due to octahedral (B) site interstitials voids near 400 cm^{-1} It can be seen from the SEM micrographs that the average grain size decreases with increasing substitution of doping concentration of Al^{3+} in copper cobalt ferrite which decrease in porosity.

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