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Microcrystalline parameters of Cu-Zn ferrites using X-ray line profile analysis

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Cu-Zn ferrites are synthesized by double sintering ceramic method. X-ray analysis of Cu-Zn ferrite shows the single phase spinel structure. The structural and microstructural parameters have been computed using X-ray diffraction data. Using CheckCell program, the Bragg reflections have been indexed. The estimated microstructural parameters have been correlated with the reported physical parameters. In the present paper, an analytical asymmetric function like exponential distribution function was used to describe the paracrystalline statistics of column length distribution in Cu-Zn ferrites and a good convergence was observed with this function.

Keywords: Ferrites, *dc* Conductivity, Activation energy, Microstructural parameters

1 Introduction

Crystalline Cu-Zn spinel ferrites have been investigated extensively due to their potential applications in non-resonant devices, radio frequency circuits, high quality filters, rod antennas, transformer cores, read/write heads for high-speed digital tapes and operating devices[1]. Also the polycrystalline Cu-Zn ferrites are very good dielectric materials, having very high dielectric constants which are useful in designing good microwave devices such as isolators, circulators etc. Here, the ferrite powders are sintered under slightly reducing conditions, the divalent iron ions formed in the body lead to high conductivity grains. When such a material is cooled in an oxygen atmosphere, it is possible to form layer of very low conductivity over the constituent grains[2]. The variations of crystallite size along the particular direction of the crystallographic axis , also with the chemical compositions and external conditions have been studied systematically in the present paper.

Ferrites with formula $FeO.Fe_2O_3$ where the divalent iron metal element can occupy either tetrahedral (A) sites or octahedral (B) sites in cubic spinel type structure. The chemical composition for the Cu-Zn ferrites is $Cu_xZn_{1-x}Fe_2O_3$ where x represents the degree of inversion (defined as the fraction of (A) sites occupied by the Fe^{3+} cat ions, x=0.0, 0.2, 0.4, 0.6, 0.8, 1.0). For this purpose, slowly cooled $Mg\text{-}Fe_2O_3$ ferrites have been used. The distribution of cations among the lattice sites depends on the preparation of material. This often leads to variation in the unit cell dimensions. Both variations are seen as broadening and/or shift in the diffraction lines position. Since the ionic radii of Mg^{2+} and Fe^{3+} are quite different, different distributions of cat ions will also lead to different lattice strains. All these effects are accounted here using line profile analysis of the profiles recorded in the X-ray powder diffraction patterns.

2 Experimental Details

It is common to ascribe the line broadening effects observed in X-ray powder diffraction patterns to various microstructure features like crystallite finiteness micro strain and stacking faults. Cu-Zn ferrites have been investigated for line profile analysis (LPA). The electrical conductivity of all these samples measured up to a temperature of 600 K starting from room temperature. The *dc* conductivity is useful to calculate different activation energies for given ferrite system from the slope of conductivity as a function of temperature[3-5].

(i) Materials and methods — Mixed Cu-Zn ferrites were synthesized using standard double sintering ceramic technique. The samples were taken in the stoichiometric proportions and mixed in the agate mortar for 4 hr. The final products are taken in the fused silica crucible and pre-sintered in air in an electronically controlled furnace at 1200°C for six hours. The grinding process was repeated before pressing this powder into a disc shaped pellets with a diameter of 1cm and the thickness in the range 0.05-0.1 cm. The pressed samples were annealed at 1000°C. Higher temperature more than 1000°C will

help in reducing the porosity of the samples. Later the samples are slowly cooled to room temperature.

(ii) Electrical conductivity measurement — The *dc* electrical conductivity σ (mho/cm) was measured using source metes Keithly 2400 and its variation with temperature was carried out using two-probe method over various temperature range. A calibrated thermocouple was used to measure the temperature of the specimen. The specimens were painted with conducting silver paint for providing good electrical contact and clamped firmly between two silver electrodes for measurement. By knowing the geometry of the sample, voltage drop across the sample and current through the sample, the conductivity (σ) can be calculated using the formula:

$$\sigma=1/\rho=IL/VA \quad \ldots\text{mho/cm}$$

(iii) X-ray diffraction pattern — The X-ray diffraction patterns of the samples were recorded using X-pert Philips Diffractometer employing X-ray radiation (λ CuKα=1.5418Å) provided with the copper anode. The data recording of X-ray diffraction lines were performed by step scanning method in 2θ in the range 5°-80° in steps of 0.02°.

3 Theory

The scan of X-ray diffraction profile (Fig. 1) obtained from Cu-Zn ferrites was used for the estimation of microcrystalline parameters like crystal size and lattice distortion. The crystal size D ($=N.d_{hkl}$) and lattice distortion g are related through the Fourier coefficients $A(n)$ of the X-ray profile intensity $I(s)$ which is given by[6,7]:

$$I(s)=\sum_{n=-\infty}^{\infty} A(n)\cos\{2\pi nd(s-s_0)\} \quad \ldots(1)$$

Also Fourier coefficients can be factorized into size $A_s(n)$ and disorder $A_d(n)$:

$$A(n)=A_s(n).A_d(n) \quad \ldots(2)$$

Various analytical forms for the distribution of crystallite sizes have been investigated by Hall and Somashekar[8]. Using asymmetric exponential distribution function, Hall and Somashekar[8] arrive at the following expression:

$$A_s(n)=A(0)\,(1-n/\langle N\rangle);\ n\le p \quad \ldots(3)$$

$$A_d(n)=A(0)\,[\exp\{-\alpha(n-p)\}/\alpha\langle N\rangle];\ n\ge p \quad \ldots(4)$$

where p is the smallest crystal size.

$$A_d(n)=\exp(-2\pi^2m^2ng^2) \quad \ldots(5)$$

$A_d(n)$ is the disorder coefficient for a para crystal having a Gaussian distribution of standard deviation σ, m is the order of reflection and g is the para crystallinity parameter of lattice distortion. Initial values of $\langle N\rangle$ and g were obtained using the method of Nandi *et al*[9]. Using these values in Eqs (1-5), the corresponding values for the distribution function are obtained. Here, we also compute:

$$\Delta^2=[I_{cal}-(I_{exp}+BG)]^2/\text{number of points} \quad \ldots(6)$$

4 Results and Discussion

It is found from Table 1 that in paramagnetic region, the activation energy is higher than that of the ferromagnetic region. This value was found to

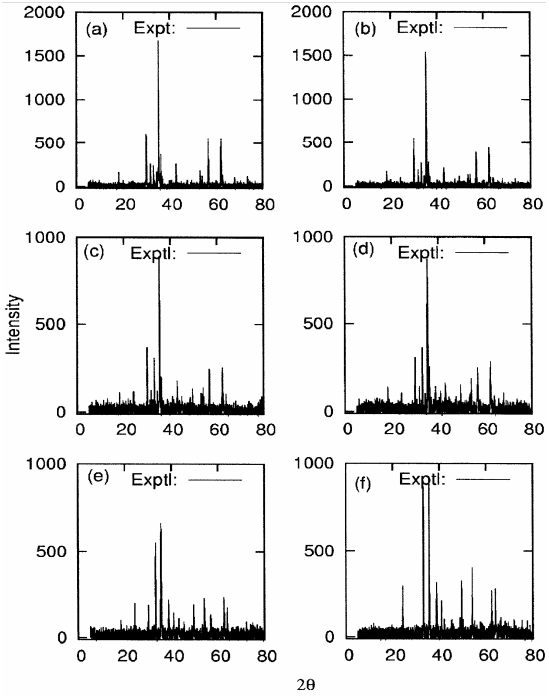

Fig. 1 — X-ray diffraction patterns of Cu-Zn ferrites [a] S1(x=0.0) [b] S2(x=0.2) [c] S3(x=0.4) [d] S4(x=0.8) [e] S5(x=0.8) [f] S6(x=1.0)

Table 1—Activation energy and Curie temperature data obtained from *dc* conductivity measurements

Samples	Activation Energy ΔE (eV)		Curie temperature T_c, K.
	Below transition temperature T_a	Above transition temperature T_a	
S1(x=0.0)	0.058	0.44	469
S2(x=0.2)	0.033	0.83	465
S3(x=0.4)	0.026	0.60	420
S4(x=0.6)	0.120	1.52	413
S5(x=0.8)	0.047	0.41	403
S6(x=1.0)	0.025	0.78	398

decrease with addition of Cu^+ ions in the samples. Same observations were reported by earlier researchers[10,11]. The transition temperature was determined by studying the temperature variation of *dc* conductivity. For the sake of completeness, we have included the variation of *dc* conductivity for a particular concentration (x=0.4) in Fig. 2. Near the transition temperature, there is discontinuity in the conductivity value (Fig. 2). Using Arrhenius equation, activation energy has been estimated. The calculated microstructural parameters are presented in Table 2. The standard deviation in all the cases is given as δ. The goodness of the fit between the experimental and stimulated profiles (Fig. 3) was less than 5% of the mean value using exponential distribution function. The computed microstructural parameters have been projected in two-dimensional plane and the corresponding shape of crystallite shape domains is shown in Fig 4. It is evident from Fig. 4 that the crystallite shape has maximum area for x=0 in the chemical formula $Cu_xZn_{1-x}Fe_2O_4$, which essentially implies that the presence of Cu^+ ions induce disorder in the lattice. Such disorders do change the perfect periodic potential seen by the electrons and tend to have a change in *dc* conductivity, which results in variation of activation energy below and above the transition temperature. This also leads to localization

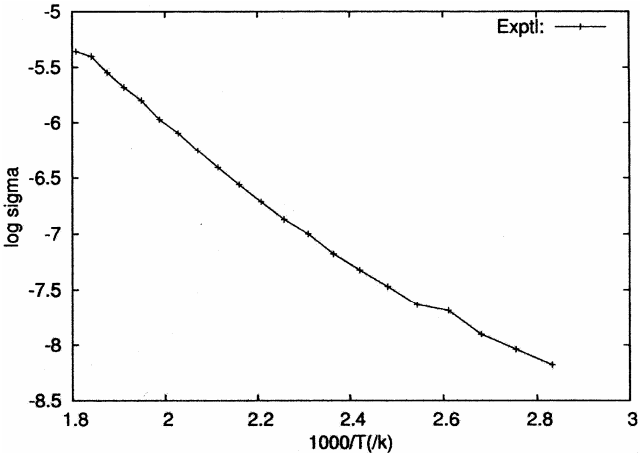

Fig. 2 — Variation of *dc* conductivity (σ) with temperature

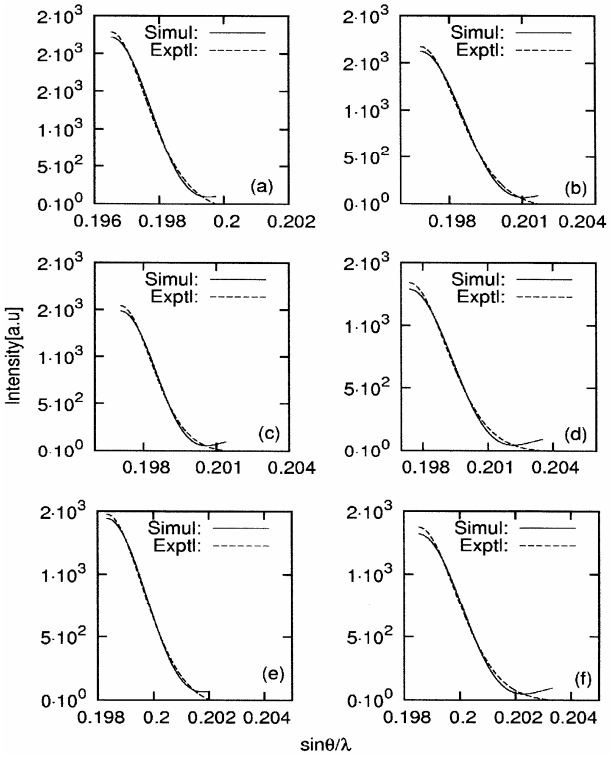

Fig. 3 — Experimental and simulated profiles of prominent reflection using exponential size distribution function [a] S1(x=0.0) [b] S2(x=0.2) [c] S3(x=0.4) [d] S4(x=0.8) [e] S5(x=0.8) [f] S6(x=1.0)

Table 2 — Micro structural parameters calculated for the prominent reflection (311 and 440) of the samples using exponential size distribution function

Samples	2θ	*hkl*	<*N*>	*P*	*g* (in %)	d_{hkl}	Surface area of crystallites $(nm)^2$
S1(x=0.0)	35.27	311	66.45±2.1	66.44±2.0	0.2	2.54	240.66
	62.23	440	95.91±3.4	95.89±3.4	0.1	1.49	
S2(x=0.2)	35.33	311	46.32±1.6	46.31±1.5	0.2	2.54	133.53
	62.32	440	76.17±1.5	76.08±1.5	0.1	1.49	
S3(x=0.4)	35.37	311	56.08±2.5	56.06±2.4	0.2	2.54	194.17
	62.37	440	91.49±2.5	91.47±2.5	0.1	1.49	
S4(x=0.6)	35.43	311	41.14±1.9	41.12±1.9	0.1	2.54	114.46
	62.41	440	73.25±2.1	73.51±2.1	0.1	1.49	
S5(x=0.8)	35.61	311	57.38±1.7	57.36±1.7	0.1	2.54	180.81
	62.59	440	83.27±1.9	83.20±1.8	0.1	1.49	
S6(x=1.0)	35.65	311	53.09±2.5	53.07±2.5	0.2	2.54	172.09
	62.58	440	85.65±2.1	85.51±2.1	0.1	1.49	

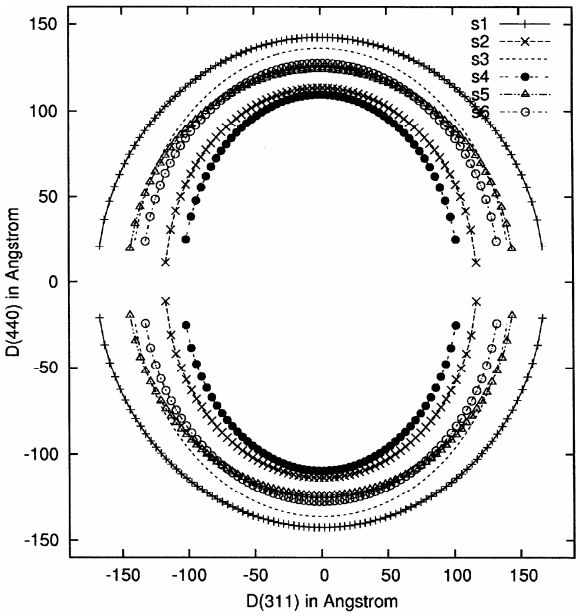

Fig. 4 — Ellipticity of crystallites observed in Cu-Zn ferrites at different concentrations

of electrons, which is normally described as metal-insulator transition. Essentially, with the addition of copper there is metal-insulator transition, which is associated with decrease in crystallite shape area. Further, it is evident from Table 1 that the transition temperature is higher in the samples with x=0, which is in agreement with the fact that such samples have larger ordered crystallite like area, which requires a little thermal energy than for samples with copper because of interactions and non-localized behaviour of electrons. It is also observed that exponential distribution; an asymmetric function gave a better fit with the experimental profiles of the samples. Hence, it is concluded that the lattice distortion plays an insignificant role in determining the conductivity behaviour of ferrites. All these samples show a single spinel structure.

5 Conclusions

The following conclusions emerge from our investigations: Ferrites with the presence of Cu, leads to decrease in activation energy and decrease in conductivity because of the reason that there is a significant decrease in crystallite shape area. The presence of Cu in ferrites leads to disorder and hence to localization of electrons leading to metal-insulator transition like properties of Anderson model. The lattice disorder plays a significant role in determining *dc* conductivity behaviour of such ferrites. In fact, a plot of Activation energy versus crystallite shape area shows, on an average, a decreasing trend, which indicates the instability of the samples with increase in crystalline area. The crystallite shape area has a maximum value without copper and has a minimum value where x=0.6

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