

A.c. susceptibility study of CaCl₂ doped copper–zinc ferrite system

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Abstract. Polycrystalline soft ferrites, Zn_xCu_{1-x}Fe₂O₄ ($x = 0.30, 0.50, 0.70, 0.80$ and 0.90), doped with controlled amount of calcium chloride (CaCl₂) were prepared by standard ceramic route and studied for a.c. susceptibility. X-ray diffraction studies of the compositions reveal formation of single-phase cubic spinel. The values of lattice constant increase as doping percentage of CaCl₂ increased from 0.01% to 0.05% and afterwards decrease slightly. The presence of chlorine ions is confirmed by absorption peak in far IR spectra near 650 cm⁻¹ for all the samples. The variation of a.c. susceptibility with temperature shows the existence of single domain structure for $x = 0.3$ and exhibits transition from single domain to multidomain structure with increased Ca²⁺ contents from 0.01 to 0.1%. The composition, $x = 0.5$, shows multidomain structure independent of Ca²⁺ content. The samples for $x = 0.70, 0.80$ and 0.90 show paramagnetic behaviour at and above room temperature.

Keywords. Polycrystalline ferrites; a.c. susceptibility; Curie temperature; magnetic properties with CaCl₂ doping; effect of additives.

1. Introduction

Curie temperature is one of the important parameters of any ferrite system. The ferromagnetic materials show quite resemblance in their magnetic properties to those of ferromagnetic class. These materials show hysteresis and susceptibility below transformation temperature i.e. Curie temperature. It is intrinsic property of the spinel ferrites, which can be controlled by preparation conditions, sintering temperature and doping of additives (Sattar and El-Shokrofy 1997; Rezlescu *et al* 2000). The microstructure, porosity and grain size play dominant roles in deciding the a.c. susceptibility. Depending on the size of grains the domain structure is classified into three types: multidomain (MD), single domain (SD) and superparamagnetic (SP). The domain structure of spinel ferrite is found to alter on substitution or doping of additives (Vasambekar *et al* 1994; Ladgaonkar *et al* 2000; Rezlescu *et al* 2000). Porosity is the basic need of the humidity sensor. One main advantage of ferrites is that they are porous materials (Vaingankar *et al* 1997). Okamoto *et al* (1986) have shown that the good humidity dependent properties are exhibited by the zinc ferrites having small proportion of alkali salts. Vaingankar *et al* (1997) have reported the humidity dependent resistivity of CaCl₂ doped copper–zinc ferrites. No studies of the magnetic a.c. susceptibility of CaCl₂ doped Cu–Zn ferrite system have been carried out as function of temperature. Therefore, a detailed

investigation of the compositions of the a.c. susceptibility at various temperatures was carried out. In the present communication the temperature dependent variation of a.c. susceptibility for alkali salt, CaCl₂, doped Zn_xCu_{1-x}Fe₂O₄ ferrite system is reported.

2. Experimental

Polycrystalline compositions of the series, Zn_xCu_{1-x}Fe₂O₄, ($x = 0.30, 0.50, 0.70, 0.80$ and 0.90) system doped with calcium chloride (0.01%, 0.05% and 0.10%) in bulk were prepared by standard ceramic technique using AR grade oxides: ZnO, CuO and Fe₂O₃. The compositions were wet milled with acetone as a base and presintered at 700°C for 12 h. After milling, compositions were subjected to sintering wherein it was controlled at 950°C for 30 h. Rate of cooling was 80°C/h. Sintered powder was crushed into fine powder. Molecular weight percentage of salt, CaCl₂, was mixed into ferrite powder and wet milled. The mixture was heated to 500°C for 12 h. The pellets of different compositions were finally sintered at 725°C for 30 h. The compositions were characterized by X-ray powder diffractometer, and IR absorption spectroscopy.

A.c. susceptibility of powdered samples was measured in the range 25–500°C on Helmholtz double coil setup operated at 263 Hz with the constant field of 7 Oe (Raadhakrishnamurty *et al* 1978). The Curie temperature was also measured by the modified Loria–Sinha method (Ladgaonkar *et al* 2001).

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3. Results and discussion

3.1 X-ray diffraction studies

The X-ray diffractograms of all the powdered compositions, doped with CaCl_2 , suggest formation of single-phase cubic spinel ferrite showing well-defined peaks. Similar results are reported in literature (Rezlescu and Rezlescu 1996; Lipare *et al* 1999, 2002a). The typical X-ray diffractogram for the composition of $\text{Zn}_{0.30}\text{Cu}_{0.70}\text{Fe}_2\text{O}_4$ with 0.05% doped CaCl_2 is presented in figure 1. The variation of lattice constants against Zn^{2+} concentration (x) is as depicted in figure 2. It can be seen that the variations

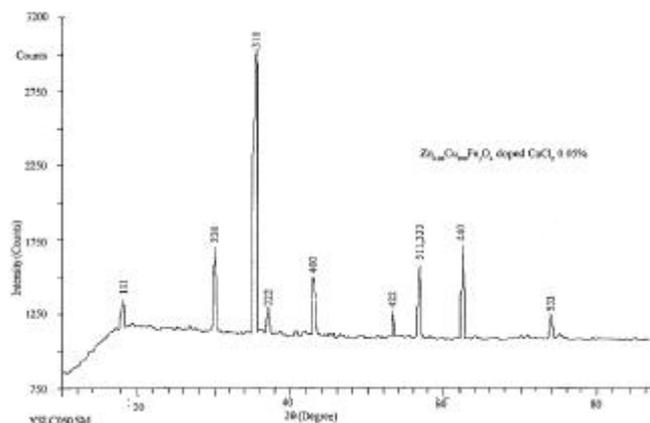


Figure 1. X-ray diffraction pattern for the composition, $\text{Zn}_{0.30}\text{Cu}_{0.70}\text{Fe}_2\text{O}_4$, doped with CaCl_2 (0.05%).

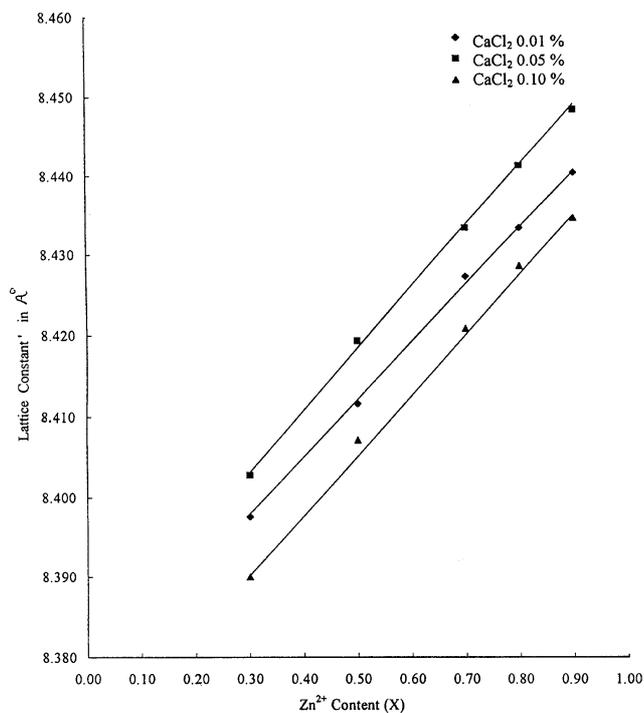


Figure 2. Variation of lattice constant against Zn^{2+} concentration for the composition, $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$, doped CaCl_2 .

of lattice constants ' a ' show linear relationship with Zn^{2+} concentration, obeying Vegard's law. The values of lattice constant increase as the doping percentage of CaCl_2 is increased from 0.01% to 0.05%, when Ca^{2+} ions introduced in the spinel, occupy A-site (Pasnicu *et al* 1983; Rezlescu *et al* 1992; Kulkarni 1995; Rezlescu and Rezlescu 1995, 1996; Ali *et al* 2000; Lipare *et al* 2003a). Ionic radius of $\text{Ca}^{2+} = 0.94 \text{ \AA}$ (Ali *et al* 2000), which is more larger than $\text{Zn}^{2+} = 0.74 \text{ \AA}$ (Kulkarni *et al* 1986), $\text{Cu}^{2+} = 0.70 \text{ \AA}$ (Ul-Islam *et al* 2002) and $\text{Fe}^{3+} = 0.60 \text{ \AA}$ (Patil and Kulkarni 1979), hence lattice constant ' a ' is found to increase (Kulkarni 1995; Rezlescu and Rezlescu 1995, 1996; Ali *et al* 2000; Lipare *et al* 2003a). When the doping percentage of CaCl_2 is increased from 0.05% to 0.10%, the value of lattice parameter again decreases slightly. This is probably due to the fact that for higher concentration, the Ca^{2+} occupy interstitial sites (Rezlescu and Rezlescu 1995; Lipare 2002; Lipare *et al* 2002a, 2003a, b).

3.2 Infrared absorption studies

The IR spectra of all the compositions were obtained in the wave number range from $200\text{--}800 \text{ cm}^{-1}$, using Perkin-Elmer Spectrophotometer, Model 783, wherein KBr is used as reference. The band, n_1 , is assigned to the tetrahedral group complexes, while the band, n_2 , is attributed to the octahedral group complexes. Figure 3 shows the typical IR absorption spectrum for the composition of $\text{Zn}_{0.30}\text{Cu}_{0.70}\text{Fe}_2\text{O}_4$ with 0.05% doped CaCl_2 . As usual the band, n_1 , near 600 cm^{-1} arises due to tetrahedral complexes and n_2 near 400 cm^{-1} , due to octahedral complexes. However, IR spectra of the composition show additional absorption peak near 650 cm^{-1} , which is attributed to the existence of chlorine bond (Lipare *et al* 2002a; 2003a, b). Thus the presence of chlorine after sintering is also confirmed. The intensity of absorption peak

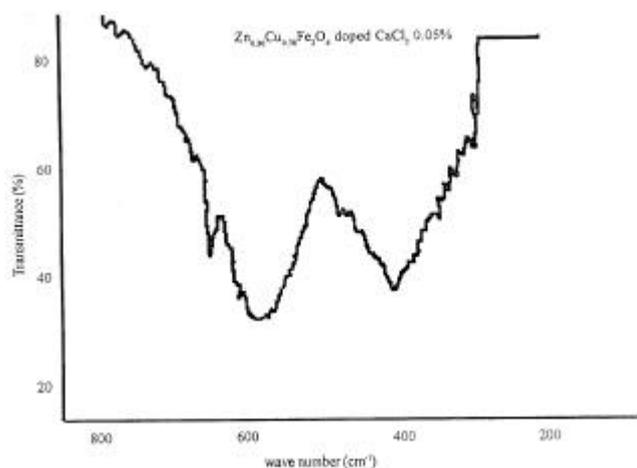


Figure 3. Infrared absorption pattern for the composition, $\text{Zn}_{0.30}\text{Cu}_{0.70}\text{Fe}_2\text{O}_4$, doped with CaCl_2 (0.05%).

corresponding to chlorine bond near 650 cm^{-1} is probably due to lower doping percentage of CaCl_2 . Further, this peak is found to vanish for the undoped samples and gives direct proof for existence of chlorine. Similar result is reported by Kulkarni (1995), Bellamy (1959), Miller and Carlson (1960) and Klemperer and Norris (1961).

3.3 Compositional and doping dependent magnetic a.c. susceptibility study

The temperature dependence of normalized susceptibility, $c_{a.c.}/c_{RT}$, for $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$, doped with CaCl_2 in molecular weight proportion in bulk for $x = 0.30$ and 0.50 is shown in figures 4 and 5, respectively. The sharp fall of normalized susceptibility, $c_{a.c.}/c_{RT}$, beyond blocking temperature shows single-phase formation of the ferrites (Vasambekar *et al* 1998; Lipare 2002), which is also confirmed from XRD studies where no impurity lines were detected.

From figure 4, in Cu–Zn ferrites having lower concentration ($\text{Zn}^{2+} = 0.30$) doped with CaCl_2 , it can be seen that a small peak occurs in the $c_{a.c.}/c_{RT}$ plot. The peak intensity is highest for lowest doping (0.01%) of CaCl_2 and it decreased with increasing doping percentage (0.05%). It exhibits single domain (SD) structure. The intensity of peak decreases with increasing doping (0.10%), indicating multi domain (MD) in the sample. The plot further shows the sharp drop at Curie temperature after blocking temperature (Lipare 2002).

From figure 5, in Cu–Zn ferrite having equal concentration of Cu^{2+} and Zn^{2+} ($x = 0.50$) doped with CaCl_2 , it can be seen that the temperature dependence of normalized susceptibility, $c_{a.c.}/c_{RT}$, is approximately constant for large temperature range up to ‘blocking temperature’ and has sharp drop at Curie temperature. The plot do not show any peak, hence it can be concluded that the exis-

tence of multi domain (MD) are present in these samples (Lipare 2002).

From figures 4 and 5, it can be seen that for Cu–Zn ferrites ($x = 0.30$ and 0.50) there is decrease in Curie temperature for increased doping percentage from 0.01 to 0.05%. For further increase in doping percentage from 0.05 to 0.10%, Curie temperature increases slightly. When the doping percentage of CaCl_2 is small (0.01%), very negligible Ca^{2+} ions go into the spinel and hence the number of magnetic ions on A-site is comparatively larger. Therefore, the A–B interaction is comparatively stronger resulting in high Curie temperature (T_C) (Kulkarni 1995; Lipare 2002), whereas with increased doping percentage from 0.01 to 0.05%, the number of non magnetic ions (Ca^{2+}) occupy A-sites reducing magnetic moment of A site (Lipare 2002; Lipare *et al* 2002a). Therefore, A–B interaction becomes weaker causing reduction in Curie temperature (Pasnicu *et al* 1983; Kulkarni 1995; Rezlescu and Rezlescu 1995; Lipare 2002). The trend of Curie temperature obtained by a.c. susceptibility is similar to the Curie temperature obtained by modified Lorria–Sinha technique. For further increase in doping percentage from 0.05 to 0.10%, the value of T_C is found to increase slightly. It may be due to the fact that non-magnetic ions (Ca^{2+}) enter into the interstitial sites for higher percentage of doping and the magnetic moment of A-site again increases, which results into stronger A–B interaction and hence Curie temperature increases (Lipare 2002; Lipare *et al* 2003a). The values of Curie temperature are presented in table 1.

The compositions for $\text{Zn}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.70, 0.80$ and 0.90) doped with CaCl_2 are paramagnetic at and above room temperature. The values of Curie temperature measured by modified Lorria–Sinha technique (Ladgaonkar *et al* 2001) are in good agreement with those observed by susceptibility technique (Lipare 2002; Lipare *et al* 2003a).

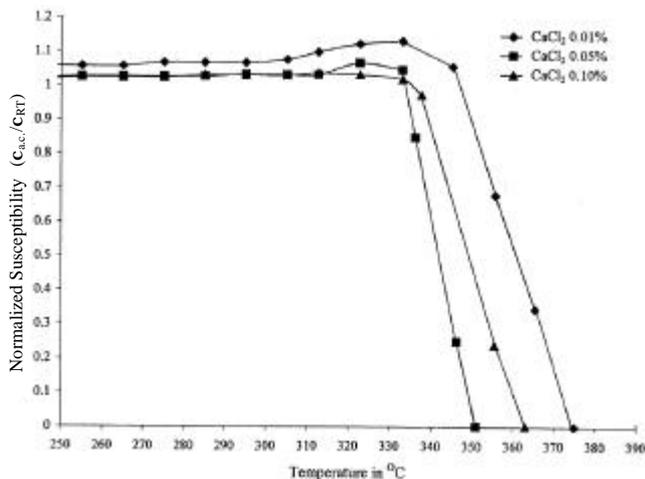


Figure 4. Temperature dependence normalized susceptibility for the composition, $\text{Zn}_{0.30}\text{Cu}_{0.70}\text{Fe}_2\text{O}_4$, doped with CaCl_2 .

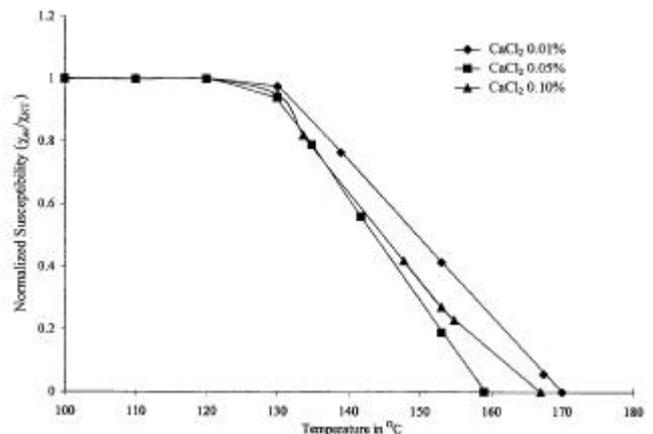


Figure 5. Temperature dependence normalized susceptibility for the composition, $\text{Zn}_{0.50}\text{Cu}_{0.50}\text{Fe}_2\text{O}_4$, doped with CaCl_2 .

Table 1. Curie temperature for the composition, $Zn_xCu_{1-x}Fe_2O_4$ ($x = 0.30, 0.50, 0.70, 0.80$ and 0.90) system doped with calcium chloride (0.01%, 0.05% and 0.10%) in bulk.

x	y	Doped CaCl ₂ (%)	Curie temperature (°C)		
			By d.c. resistivity	By a.c. susceptibility	By modified Loria–Sinha
0.30	0.70	0.01	370	375	374
		0.05	356	351	349
		0.10	366	363	365
0.50	0.50	0.01	170	170	171
		0.05	166	159	157
		0.10	168	167	169

The compositional study of the series, $Zn_xCu_{1-x}Fe_2O_4$ ($x = 0.30, 0.50, 0.70, 0.80$ and 0.90), shows decrease in Curie temperature with increase in Zn^{2+} concentration. We know that Zn^{2+} ions occupy A-site (Kato 1958; Sawant and Patil 1981; Ladgaonkar *et al* 1999; Lipare *et al* 2002a). In copper–zinc ferrite system the concentration of Zn^{2+} ions go into the spinel on A-site, therefore reducing magnetic moment of A-site, hence magnetic A–B interaction becomes weaker and therefore Curie temperature decreases (Lipare 2002; Lipare *et al* 2003a). This type of result is also reported by Ravinder (1999).

The Curie temperature measurement was carried out by a.c. susceptibility and modified Loria–Sinha technique at lower humidity in summer (40% relative humidity) and at higher humidity in rainy season (93% relative humidity). It is observed that magnetic property like susceptibility is not affected by relative humidity. Similar results are reported for temperature sensitive ferrites by Seki *et al* (1988) and Vaingankar *et al* (1997). They have found that only resistivity (conductivity) changes due to humidity whereas the susceptibility remains practically constant for lower (40% RH) and higher humidity (93% RH).

Our aim is to develop humidity sensor using soft ferrites. Vaingankar *et al* (1997), Lipare *et al* (1999) and Lipare *et al* (2003b) have reported the electrical properties of sensor dependent on relative humidity. However, the magnetic properties do not show any change even if the %RH is changed from 40% to 95% (Seki *et al* 1988). Basically ferrites are temperature sensitive. Electrical properties can be used for humidity sensing and magnetic properties can be used for temperature sensing with a single device. Details regarding humidity sensor device are described in Lipare *et al* (2002b).

4. Conclusions

X-ray diffractogram of all the compositions doped with CaCl₂, suggest formation of single-phase cubic spinel structure. The variation of lattice constants shows linear relationship with Zn^{2+} concentration, obeying Vegard's law. Increase and decrease of lattice constant may be due to occupation of Ca^{2+} ions on A-site. The presence of

chlorine ions is confirmed by absorption peak in IR spectra near 650 cm^{-1} for all the samples. The variation of a.c. susceptibility with temperature shows the existence of single domain structure for $x = 0.30$ and exhibits transition from single domain to multidomain structure with increased Ca^{2+} contents from 0.01 to 0.1%, and for the $x = 0.50$ shows multidomain structure with independent of Ca^{2+} contents. The samples for $x = 0.70, 0.80$ and 0.90 show paramagnetic behaviour at and above room temperature. As the doping percentage of Ca^{2+} is increased, Curie temperature decreases, and further increases slightly, which may be due to weaker and stronger interaction between A–B sites. The magnetic properties like Curie temperature, permeability and magnetization are not affected by humidity.

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