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Bulk magnetic properties of Co–Zn ferrites prepared by the co-precipitation method

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The alternating current (a.c.) susceptibility versus temperature and magnetization measurements are reported for the disordered spinel ferrite system $Zn_x\ Co_{1-x}\ Fe_2\ O_4$ prepared by a wet chemical method before and after high temperature annealing. The low field a.c. susceptibility measurements indicate that the low temperature synthesis of wet prepared Co–Zn ferrites aids the formation of spin-clusters and thereby increases the magnetic inhomogeneity. The X-ray analysis shows that the samples are single phase spinels and the variation of lattice constant with zinc concentration deviates from Vegard's law [1]. The high temperature annealing changes the wet prepared ferrites into the ordered magnetic structure of the ceramic ferrites.

1. Introduction

Ferrites with spinel structure, such as Ni–Zn, Co–Zn, Li and Co ferrites, have been the subject of many studies because of their magnetic properties resulting from a particular configuration of the cations in the lattice. It is well known that the method of preparation influences the cation distribution between tetrahedral (A) and octahedral (B) sites of the spinel lattice.

The usual ceramic preparation of ferrites proceeds through a high temperature (~ 1000 °C) reaction between finely milled oxide (or carbonate) powders followed by shaping, successive pressing and sintering. Materials of the same composition but with very different properties can be prepared at lower temperatures (55 °C) as wet ferrites by co-precipitation method from aqueous solutions of the corresponding hydroxides [2]. In the case of ferrite preparation by the conventional ceramic method, the morphological characteristics of the raw materials, mainly of the iron oxide, x, (dimensions and shape of particles) are important factors for obtaining some final reproducible properties [3, 4]. The preparation of ferrite powders by the oxidation method consists of oxidation by bubbling air through an aqueous solution containing ferrous ions and other divalent ions after an alkaline solution has been added

$$Fe^{2+} + M^{2+} + ROH + O_2 \rightarrow M_{1-x}Fe_{2-x}O_4$$

Where ROH is NaOH, KOH, NH_4OH etc. Thus, ferrite powders with high homogeneity and purity are obtained.

With the exception of a few works [2–5], wet prepared ferrites have, however, not been extensively studied and only in the past years have comparative studies on ceramic and wet ferrites appeared in the literature for Mg Fe_2O_4 [6] and $Zn_xMn_{1-x}\ Fe_2O_4$ [7].

The Co–Zn ferrite with the chemical formula $Zn_x\ Co_{1-x}Fe_2\ O_4$ have been prepared by ceramic method and extensively studied by a number of workers [8–10]. Materials of the same composition can be prepared by the wet chemical (co-precipitation) method over a very wide range of compositions between cobalt and zinc ferrite. No information exists in the literature for chemically wet prepared Co–Zn ferrites.

The Fe^{3+}, Co^{2+} and Zn^{2+} cations are distributed among octahedral (B) and tertrahedral (A) interstitial sites of the face centred cubic oxygen lattice. $Zn_xFe_2O_4$ ($x = 1$) is generally assumed to be normal spinel with all Fe^{3+} ions on B sites and all Zn^{2+} ions on A sites. In Co Fe_2O_4 ($x = 0$), the site preferences lead to a predominantly inverse structure with Co^{2+} ions mainly on B sites and Fe^{3+} ions distributed almost equally between A and B sites. The inversion is not complete in Co Fe_2O_4 and the degree of inversion depends on the previous heat treatment of the material. As zinc replaces cobalt between $x = 0$ and $x = 1$, Zn^{2+} ions appear to preferentially enter tetrahedral positions while the Fe^{3+} ions displaced from these tetrahedral sites enter the octahedral sublattice. Assuming that a fraction of Co^{2+} ions, (y) occupy the A site [8], the cation distribution can be described by the chemical formula

$$(Zn_xFe_{1-x-y}Co_x)^A \quad [Co_{1-x-y}Fe_{1+x+y}]^BO_4$$

Here the parentheses refer to ions in tetrahedral and the square brackets to ions in octahedral sites. However, exact cation distributions have not been determined experimentally.

The aim of the present work is to prepare mixed Co–Zn ferrites by the co-precipitation method and to study the structural and bulk magnetic properties of the products. Magnetization measurements were undertaken to investigate the variation of the saturation magnetization with zinc concentrations. The variation of low field a.c. susceptibility with temperature

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of wet Co–Zn ferrites was studied to determine the Curie temperatures and to explore the possibility of magnetic phase transition. X-ray diffractometry was employed to obtain the crystal structure.

2. Experimental procedure

Variable composition ($x = 0.1$–1.0) Co–Zn ferrites were prepared by air oxidation of an aqueous suspension containing Co^{2+}, Zn^{2+} and Fe^{2+} cations in stoichiometric proportions. The starting solutions were prepared by mixing 50 ml of aqueous solutions of $FeSO_4 \cdot 7H_2O$, $CoSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 7H_2O$ in proper proportions. A 2 M solution of NaOH was prepared as a precipitant. It has been suggested [11] that the solubility product constant (K_{sp}) of all the constituents is always exceeded when the starting solution is added into the precipitant (K_{sp} for hydroxides of Co^{2+} Zn^{2+} and Fe^{2+} are 1.6×10^{-15}, 1.2×10^{-17} and 8×10^{-16}, respectively). Therefore, in order to achieve simultaneous precipitation of all the hydroxides, $Co(OH)_2$, $Zn(OH)_2$ and $Fe(OH)_2$, the starting solution (pH value about 3.5) was added to the solution of NaOH and a suspension (pH = 11.25) containing dark green intermediate precipitates was formed. Then the suspension was heated and kept at a temperature of 55 °C, while oxygen gas was bubbled uniformly into the suspension to stir it and to promote the oxidation reaction, until all the intermediate precipitates changed into the dark brownish precipitates of the spinel ferrite. The samples were filtered, washed and dried at 150 °C under vacuum.

The wet samples of Co–Zn ferrites were annealed in air at 1000 °C for 24 h. After high temperature annealing, the wet samples exhibit weight loss (around 2%) because of the removal of water and the absorption or chemical combination of the hydroxyl ions, even after the drying process.

The X-ray powder patterns were recorded using Fe*k* radiation on a Philips diffractometer. The saturation magnetization of each sample was carried out using the high field hysteresis loop techniques. The low field a.c. susceptibility measurements on powdered samples were made in the temperature range 77–800 K using double coil set-up [12] operating at a frequency of 263 Hz and in the RMS field of $39.8\ Am^{-1}$.

3. Results and discussion

The X-ray diffraction pattern showed that all the samples were single phase spinels. No amorphous phase was detected. The plot of lattice constant versus zinc content is depicted in Fig. 1. The lattice constant gradually decreases on increasing Zn content, shows a minimum at $X \sim 0.5$ and then increases on further dilution. Usually, in a solid solution of spinels within the miscibility range, a linear change in the lattice constant with the concentration of the components (Vegard's law) [1] is observed. Non-linear behaviour, on the other hand, has been reported for systems which are not completely normal or inverse like Co–Zn ferrites [13]. The X-ray densities of both sets of samples have been calculated from molecular weight and volume of the unit cell and values are given in Table I.

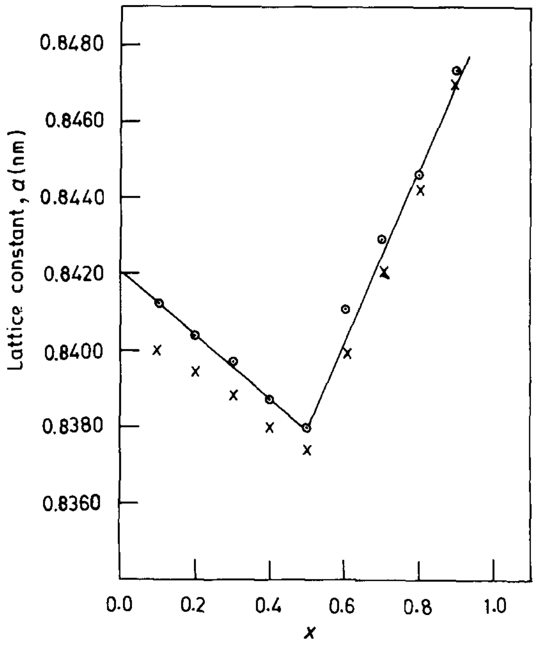

Figure 1 Lattice constant versus zinc content for $Zn_xCo_{1-x}Fe_2O_4$, ferrite system: (x) wet prepared; (⊙) annealed wet.

The wet samples of Co–Zn ferrites are characterized by smaller values of lattice constant than that of the annealed wet samples. After high temperature annealing the lattice constants of wet samples are found to increase. The smaller values of the lattice constant for wet samples cannot be explained solely on the basis of rearrangement of cations in the spinel lattice due to different formation conditions. It may also be due to the different degrees of crystallinity of wet and annealed wet samples resulting from the differences in the temperature of crystallinity. The X-ray diffraction lines were found to be slightly broader in the case of wet samples, because of particle size effects. The average particle size determined from full width at half maxima of the diffraction lines for wet Co–Zn ferrites was within the range 30–50 nm. The X-ray diffraction lines of annealed wet samples were sharp. This indicates that the high temperature annealing (~ 1000 °C) of the wet samples has increased the crystallite size up to the order of ceramic ferrites.

The values of saturation magnetizaton (σ_s) for wet and annealed wet samples are listed in the Table I. The lower values of saturation magnetization for wet samples compared to the annealed wet samples of Co–Zn ferrites is due to the stronger covalency effects arising from smaller cationic site dimensions. The magneton number, i.e., saturation magnetization per formula unit in Bohr magneton (n_B) at 298 K initially increases and then decreases as x is increased (Fig. 2). Since the diamagnetic Zn^{2+} ions replace the magnetic Fe^{3+} ions at tetrahedral sites and due to the prominent inter-sublattice A–B superexchange interaction (up to $X \leqslant 0.3$) the net magnetic moment per formula unit is increased. The Neel's theory [14] which is able to account for the initial rise, is, however, unable to

TABLE I The X-ray density, ρ, saturation magnetization, σ, Curie temperature, T_c and blocking temperature T_b for wet prepared (W) and annealed wet (AW) samples of $Zn_x Co_{1-x}Fe_2O_4$

X	ρ ($g cm^{-3}$) W	AW	σ_s ($emu g^{-1}$) W	AW	T_c (K) W	AW	T_b (K) AW
0.1	5.29	5.25	62	81	748	748	700
0.2	5.31	5.28	74	85	713	723	680
0.3	5.33	5.31	76	90	650	663	600
0.4	5.36	5.34	70	83	565	573	525
0.5	5.38	5.36	49	71	490	495	–
0.6	5.35	5.33	24	52	440	455	–
0.7	5.32	5.31	08	28	–	400	–
0.8	5.30	5.29	03	02	–	–	–
0.9	5.27	5.26	–	–	–	–	–

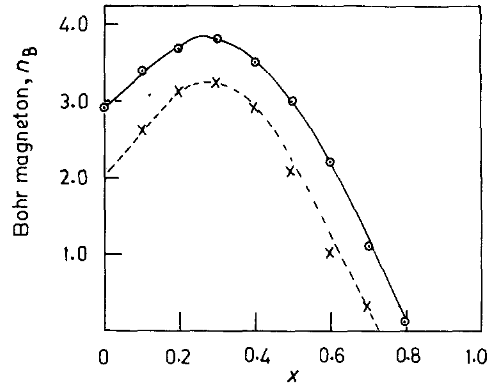

Figure 2 n_{13} versus temperature for $Zn_xCo_{1-x}Fe_2O_4$, ferrite system; key as Fig. 1.

account for the subsequent decrease. The reason for this decrease after $X = 0.3$, can be explained in terms of a uniform Yafet–Kittel [15] triangular-type magnetic ordering of spins on the B sublattice. But for a chemically disordered system such as $Zn_x Co_{1-x} Fe_2O_4$, it is quite possible that the canting is not uniform but instead is locally dependent upon the statistical distribution of non-magnetic neighbouring ions. Therefore, the decrease in magnetization of these materials after $X = 0.3$ is primarily associated with canting of the magnetic moments.

The plots of thermal variation of normalized (χ/χ_{RT}) low field a.c. susceptibility (χ) for wet and annealed wet samples of $Zn_x Co_{1-x} Fe_2O_4$, are shown in Figs 3 and 4. The first hump observed in the χ-T curve of annealed wet ferrites (Fig. 3) is referred to as the isotropic peak [16]. This peak can be clearly seen for a magnetic material in multi-domain (MD) state and only if the material has a temperature at which the magnetocrystalline anisotropy is zero. Beyond the temperature at which isotropic peak occurs, the coercive force due to the shape anisotropy will still be dominant for single domains (SD). If the temperature of such an SD particle is further increased it may so happen that the thermal energy may become comparable to the effective magnetic anisotropy when the magnetization direction spontaneously fluctuates between the easy axes of the grain. In such a state, a particle is said to be exhibiting superparamagnetism (SP). The specific temperature at which the SD to SP transition for a particle of volume V takes place is known as the blocking temperature, T_b, and the relation governing this is given by

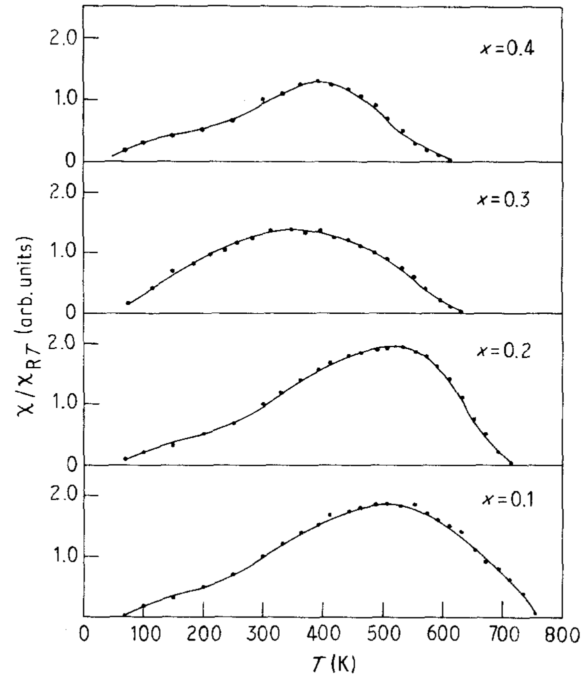

Figure 3 Thermal variation of low field a.c. susceptibility for wet $Zn_xCo_{1-x}Fe_2O_4$ ferrite system.

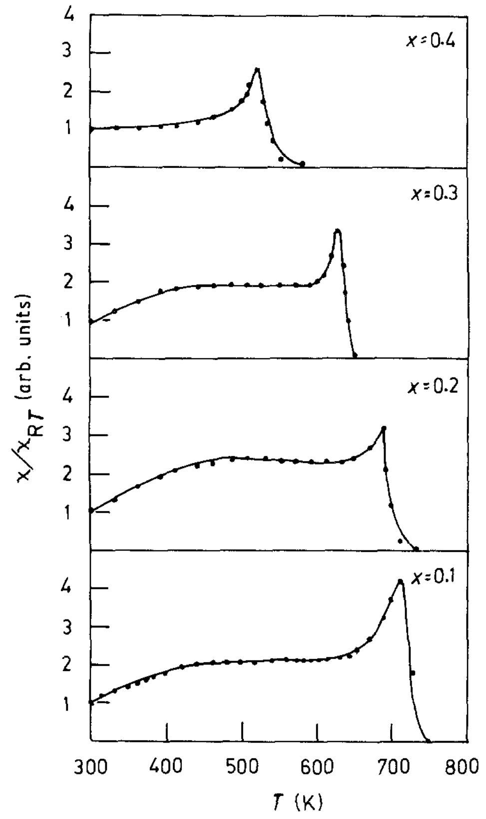

Figure 4 Thermal variation of low field a.c. susceptibility of annealed wet samples of $Zn_xCo_{1-x}Fe_2O_4$.

$$V J_s H_c = 2 k T_b$$

where J_s is the saturation intensity, H_c is the coercive force of the material and k is the Boltzmann constant.

For SD particles H_c is large whereas it tends towards zero for SP particles [17]. Thus susceptibility, which is inversely proportional to H_c, is large for SP of the same material and hence there is a peak in χ–T curve at T_b.

Plots of χ–T curves for wet samples are shown in Fig. 4. A broad maximum is observed in χ–T curve of all the samples which may be taken to be composed of several narrower peaks representing the response of SD particles of various sizes as they undergo SD–SP transition. The Curie temperatures determined through the high temperature susceptibility measurements are listed in Table I. The observed decrease in Curie temperature with small additions of zinc is due to the decreasing A–B superexchange interactions resulting from replacement of Fe^{3+} by Zn^{2+} at A sites.

It is believed that these results are related to the preparation conditions. The low temperature synthesis of the wet prepared Co–Zn ferrites leads to the disordered system and inhibits the formation of uniform size of SD particles (i.e., spin-clusters). The high temperature annealing changes the wet prepared ferrites into the ordered magnetic structure of the ceramic ferrites.

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