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Letter

Cation distribution of titanium substituted cobalt ferrites

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ABSTRACT

Polycrystalline titanium substituted cobalt ferrites with general formula $CoFe_{2-x}Ti_xO_4$ where x varies from 0.00 to 0.30 in steps of 0.05 have been prepared by standard ceramic method and characterized by X-ray diffraction. All the titanium containing cobalt ferrite compositions have shown $TiFe_2O_5$ (monoclinic) secondary phase besides spinel structure. Saturation magnetization, dc resistivity and Curie temperature studies have been made with a view of developing suitable compounds for magnetic stress sensors. Cation distribution of these materials has been proposed on the basis of magnetization and resistivity measurements and the same has been established from lattice constant calculations.

1. Introduction

Although there exist many useful properties, the usage of cobalt ferrite is limited due to its high magnetic anisotropy and consequent magnetomechanical hysteresis for sensing applications [1]. As magnetic anisotropy is known to approach zero close to Curie temperature of a system [2], it is always desirable to bring down the Curie temperature into the vicinity of operating temperature of the sensor device which can be accomplished by incorporating suitable substituents in the material. Substitution of tetravalent diamagnetic ions in ferrites has been known to produce lower Curie temperatures, lower magnetic anisotropy [2] and higher dc resistivity [3]. A decrease in magnetic anisotropy has been reported with increasing titanium content in cobalt–cadmium ferrite system [4]. Although many researchers dealt with the modification of both cobalt and titanium ions in cobalt ferrite, the direct substitution of titanium in place of iron has not been reported yet. The present investigation is aimed at providing cation distribution of titanium substituted cobalt ferrite in elucidating the controlled nature of magnetic and electrical properties.

2. Experimental details

Samples having the general composition $CoTi_xFe_{2-x}O_4$ where x varies from 0.00 to 0.30 in steps of 0.05 were processed through conventional ceramic method. The starting materials were analytical reagent grade cobalt, iron and titanium oxides. Suitable proportions of these oxides were thoroughly ground in the presence of acetone into fine homogeneous powder. The resulting mixture was calcined in air for 2 h at 900 °C. This calcined powder was further ground for another 2 h to obtain in the form of pellets by adding a small quantity of 15% polyvinyl alcohol as binder. The pellets were sintered in air for 2 h at 1250 °C and subsequently cooled to room temperature. In order to remove any oxide layer formed on the surface of the pellets, necessary grinding of the pellets was made. The observed single phase spinel structure in basic cobalt ferrite from X-ray diffraction pattern confirmed the procedure adopted for processing the series was correct one.

X-ray diffraction patterns of all the samples were recorded using Rigaku Miniflex X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å). Saturation magnetization for all the samples was measured using Ponderometer method [5]. Curie temperature was determined using Soohoo method [6]. DC resistivity was estimated using two-probe method by measuring current accurately with the help of digital nanoammeter model DNM-121.

3. Results and discussion

3.1. Lattice constant

X-ray diffraction patterns of all the compositions (Fig. 1) confirmed spinel structure. Titanium containing samples showed an extra peak ($2\theta = 33.63°$) corresponding to an increasing $TiFe_2O_5$ (monoclinic) phase with titanium concentration [7]. Lattice constant has been determined from the observed Bragg angles considering Nelson–Riley function to minimize the error in its determination. Variation in lattice constant with increasing titanium concentration has been shown in Fig. 2.

The observed change in lattice constant with increasing titanium concentration indicates that titanium occupying the lattice and replaces Fe^{3+} ions from tetrahedral (A) or octahedral (B) or both the sites. The replacement of iron ion by a titanium ion in any site demands the formation of Fe^{2+} ions to maintain the charge neu-

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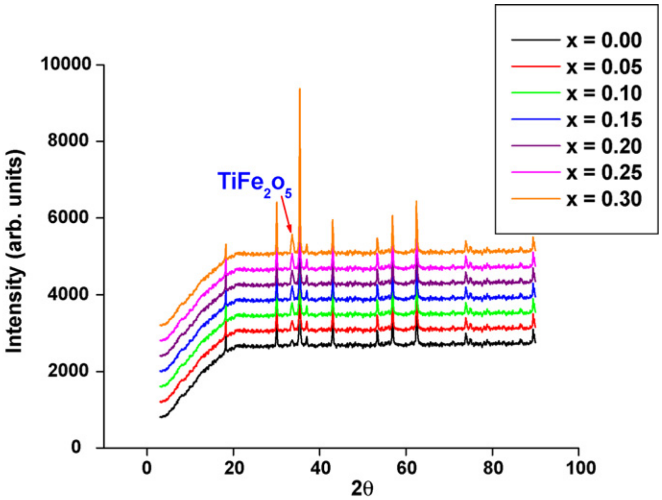

Fig. 1. X-ray diffraction patterns of $CoTi_xFe_{2-x}O_4$ ($x = 0.00–0.30$ in steps of 0.05).

trality requirement by a process where one Fe^{3+} ion gets modified to Fe^{2+} ion and another is replaced by Ti^{4+} ion. In other words, the process can be thought of replacing 2 Fe^{3+} ions by a Ti^{4+}–Fe^{2+} pair. It is well known that the presence of Fe^{2+} ions at tetrahedral site has been ruled out [8] because of their larger ionic radii. Further, the closeness of ionic radii of titanium and the available octahedral site promotes the occupancy of titanium into octahedral sites.

The observed variation in lattice constant can be understood on the basis of average ionic radii of displaced Fe^{3+} ions as well as displacing Ti^{4+}–Fe^{2+} pair. From Vegard's law, if the radius of displacing ion is larger than the displaced ion, the lattice gets expanded and the lattice constant increases. Reverse will hold if a smaller ion replaces a metal ion of the regular lattice [9]. Hence, the observed increase in lattice constant can be attributed to a higher value of average ionic radius of Ti^{4+}–Fe^{2+} pair (0.69 Å) over that of Fe^{3+} ion (0.645 Å).

3.2. Saturation magnetization

Fig. 3 shows a systematic linear fall in specific saturation magnetization with increasing titanium concentration. It is well established [10] in cobalt ferrite that A–B exchange interaction is predominant because nearly 20% cobalt occupies A-site. The observed decrease in magnetization in present system can be understood on the basis of Neel model [11]. According to this model, A–B exchange interaction in ferrites is stronger and effective than A–A and B–B superexchange interactions and the net magnetic moment of the ferrite lattice as a whole is equal to the difference between the magnetic moments of A and B sublattices, i.e. $M = M_B - M_A$.

As thought in earlier section, the diamagnetic titanium entry into A-sublattice dilutes its magnetic moment without affecting the magnetic moment of B-sublattice and leading to an increase in net magnetic moment of the sample. Contrary to expectation, the observed linear decrease in specific saturation magnetization clearly establishes the fact that titanium prefers to occupy only octahedral sites.

3.3. Curie temperature

A gradual decrease in Curie temperature with increasing concentration of titanium is shown in Fig. 4. The observed variation can be explained on the basis of exchange interactions. It is obvious that the exchange interaction between the magnetic ions would increase with both the density of magnetic ions and their magnetic moments. It is therefore, expected that greater amount of thermal energy will be required to off-set the effects of exchange interaction in cases having magnetic ions of larger magnetic moments. As stated, the diamagnetic titanium replaces octahedral iron ions and thereby reduces the magnetic moment of the B-sublattice. This explains the decrease in Curie temperature with increas-

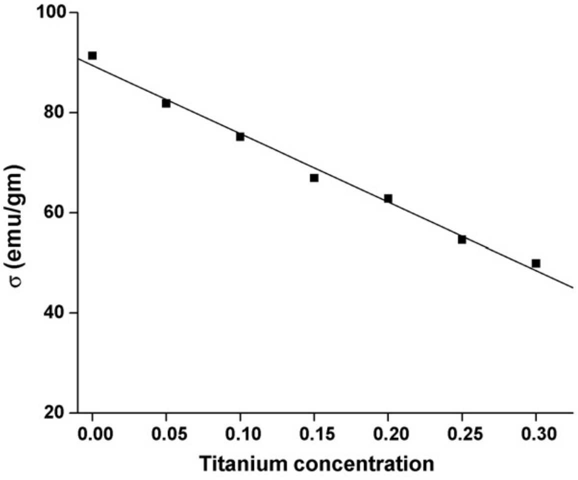

Fig. 3. Variation of saturation magnetization per unit mass with titanium concentration.

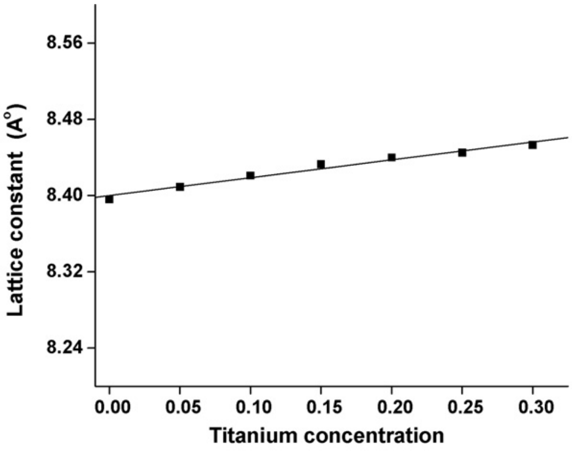

Fig. 2. The variation of lattice constant with titanium concentration.

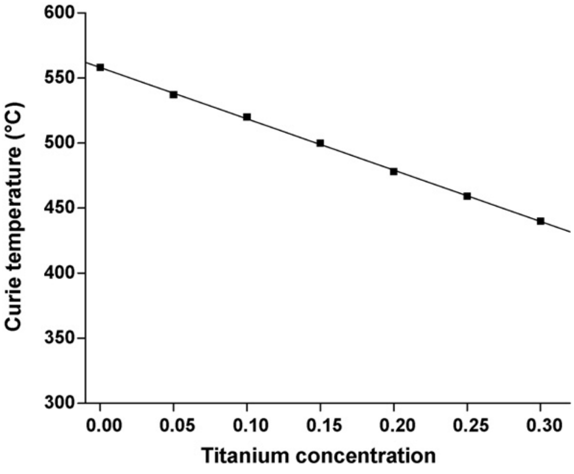

Fig. 4. Variation in Curie temperature as a function of titanium concentration.

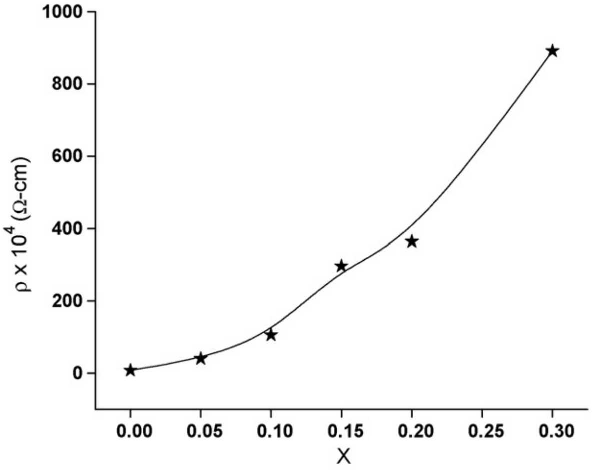

Fig. 5. Room temperature dc resistivity as a function of titanium concentration.

ing concentration of titanium ions. The observed gradual and smaller variation in Curie temperature suggests that A–B exchange interaction weakens but not drastically with increasing titanium concentration.

3.4. DC resistivity

Observed variation in room temperature dc resistivity as a function of titanium concentration is depicted in Fig. 5. The resistivity has been observed to increase throughout the concentration studied and its variation can be explained on the basis of Verwey mechanism [12]. According to this mechanism, the electronic conduction in ferrites is primarily due to hopping of electrons between the ions of the same element present in more than one valance state distributed randomly over crystallographically equivalent lattice sites. The distance between two metal ions in B-sites is smaller than the distance between a metal ion at B-site and another metal ion at A-site in ferrites. The electron hopping between B–A sites under normal conditions, therefore, has a very small probability compared to that of hopping between B–B sites. Hopping between A–A sites does not exists for the simple reason due to the absence of Fe^{2+} ions at A-sites and any Fe^{2+} ions formed during processing preferentially occupy B-sites only.

As discussed earlier, the occupancy of titanium into B-site promotes the formation of Fe^{2+} ions with increasing concentration of titanium in which a decrease in dc resistivity can be expected in the material. However, the observed increase in dc resistivity suggests the formation of Ti^{4+}–Fe^{2+} locking pairs [13,14]. For lower concentration of titanium ($x \leq 0.1$), the observed low value of dc resistivity might be due to the presence of generated Fe^{2+} ions at elevated sintering temperature in the sample in spite of the presence of Ti^{4+}–Fe^{2+} pairs. With increasing titanium concentration, Ti^{4+}–Fe^{2+} pairs become significant in expanding the lattice and reducing the hopping probability between Fe^{2+} and Fe^{3+} ions by increasing their separation at B-sites and contributing to the steep rise in resistivity. Besides, the presence of second phase $TiFe_2O_5$ might also contribute for the observed rise in dc resistivity at higher concentrations of titanium. Similar observations in this aspect have been reported by Zaspalis and Eleftheriou [15].

Temperature dependence of dc resistivity for all the samples has been given in Fig. 6 as log ρ versus $1/T$ plots. Activation energy values in the range of 0.31–0.47 eV also establish the presence of locking mechanism between Ti^{4+}–Fe^{2+} pairs. Electron hopping mechanism between $Fe^{2+} \Leftrightarrow Fe^{3+}$ ions has been ignored since the activation energies needed for the process lie around 0.2 eV [16,3].

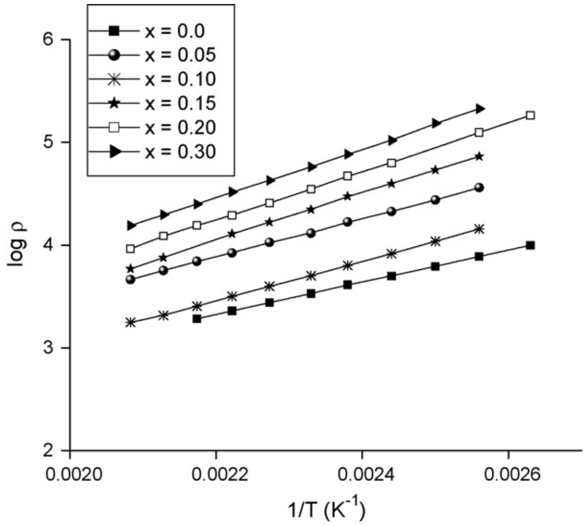

Fig. 6. Log ρ vs. $1/T$ graphs for the titanium substituted cobalt ferrite.

Table 1
Proposed cation distribution of $CoFe_{2-x}Ti_xO_4$.

Titanium content (x)	Proposed cationic distribution
0.00	$(Co^{2+}_{0.2}Fe^{3+}_{0.8})[Co^{2+}_{0.8}Fe^{3+}_{1.2}]O^{2-}_4$
0.05	$(Co^{2+}_{0.2}Fe^{3+}_{0.8})[Co^{2+}_{0.8}Fe^{2+}_{0.05}Ti^{4+}_{0.05}Fe^{3+}_{1.1}]O^{2-}_4$
0.10	$(Co^{2+}_{0.2}Fe^{3+}_{0.8})[Co^{2+}_{0.8}Fe^{2+}_{0.1}Ti^{4+}_{0.1}Fe^{3+}_{1.0}]O^{2-}_4$
0.15	$(Co^{2+}_{0.2}Fe^{3+}_{0.8})[Co^{2+}_{0.8}Fe^{2+}_{0.15}Ti^{4+}_{0.15}Fe^{3+}_{0.9}]O^{2-}_4$
0.20	$(Co^{2+}_{0.2}Fe^{3+}_{0.8})[Co^{2+}_{0.8}Fe^{2+}_{0.2}Ti^{4+}_{0.2}Fe^{3+}_{0.8}]O^{2-}_4$
0.25	$(Co^{2+}_{0.2}Fe^{3+}_{0.8})[Co^{2+}_{0.8}Fe^{2+}_{0.25}Ti^{4+}_{0.25}Fe^{3+}_{0.7}]O^{2-}_4$
0.30	$(Co^{2+}_{0.2}Fe^{3+}_{0.8})[Co^{2+}_{0.8}Fe^{2+}_{0.3}Ti^{4+}_{0.3}Fe^{3+}_{0.6}]O^{2-}_4$

3.5. Cation distribution

Cation distribution for the series of samples has been proposed on the basis of above discussion and given in the Table 1.

From the proposed distribution, theoretical lattice constant for each composition has been calculated using the following relations [17].

$$r_A = 0.2 r_{Co^{2+}_A} + 0.8 r_{Fe^{3+}_A}$$

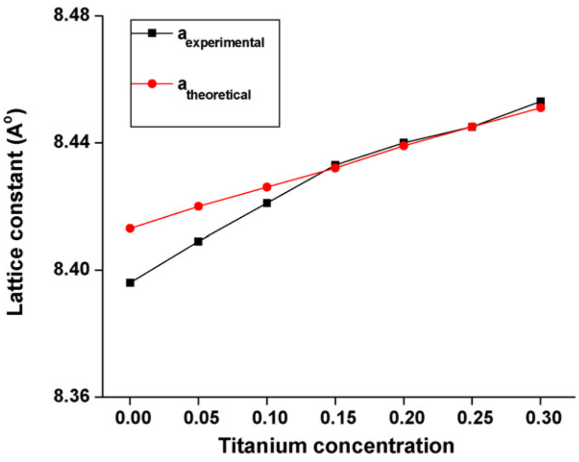

Fig. 7. Lattice constant variations with titanium concentration.

$$r_B = \frac{1}{2}[0.8r_{Co_B^{2+}} + xr_{Ti_B^{4+}} + xr_{Fe_B^{2+}} + (1.2 - 2x)r_{Fe_B^{3+}}]$$

$$a_{th} = \frac{8}{3\sqrt{3}}\left[(r_A + R_o) + \sqrt{3}(r_B + R_o)\right]$$

The close agreement between the calculated and experimentally obtained lattice constants shows that the proposed distributions are correct (Fig. 7).

4. Conclusions

(1) Lattice constant, saturation magnetization and dc resistivity studies of titanium substituted cobalt ferrites have confirmed the occupancy of titanium ions to octahedral site.

(2) Improvement in the electrical resistivity of the titanium substituted cobalt ferrites by three orders in magnitude has been explained on the basis of formation of Ti^{4+}–Fe^{2+} ion locking pairs besides $TiFe_2O_5$ (monoclinic) additional phase.

(3) The reduced Curie temperatures with titanium may help in developing suitable materials with decreased magnetic anisotropy and magnetomechanical hysteresis for stress sensor applications.

(4) Agreement between the experimentally observed and calculated lattice constants indicates that the proposed cation distribution on the basis of magnetization and dc resistivity is correct.

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