Valence of Ti cations and its effect on magnetic properties of spinel ferrites Ti$_x$M$_{1-x}$Fe$_2$O$_4$
($M = Co, Mn$)

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Powder samples of Ti$_x$Co$_{2-x}$Fe$_2$O$_4$ (0.0 $\leq x \leq 0.4$) and Ti$_x$Mn$_{1-x}$Fe$_2$O$_4$ (0.0 $\leq x \leq 0.3$) were synthesized using a conventional method for preparing ceramics. X-ray diffraction analysis confirmed that the samples consisted of a single phase with a cubic (A)[B]$_2$O$_4$ spinel structure. The average molecular magnetic moment ($\mu_{\text{exp}}$) measured at 10 K decreased monotonically with increasing $x$ for two series of samples. According to previous investigations, Ti$^{3+}$ and Ti$^{4+}$ cations are present in these ferrites, but there are no Ti$^{2+}$ cations; the magnetic moments of the Ti$^{2+}$, Ti$^{3+}$, and Mn$^{3+}$ cations are assumed to couple antiferromagnetically with those of the Mn$^{2+}$, Co$^{2+}$, Co$^{3+}$, Fe$^{2+}$, and Fe$^{3+}$ cations whenever they are at the [A] or [B] sublattice. The dependence of $\mu_{\text{exp}}$ of the two series of samples on the doping level $x$ was fitted using a quantum-mechanical potential barrier, and the cation distributions in the two series of samples were obtained.

1 Introduction

Spinel ferrites have received much attention in recent years because of their application in spintronics and multiferroics.$^{1-7}$ In a (A)[B]$_2$O$_4$ spinel ferrite, each unit cell contains eight formula units, in which the 32 larger oxygen anions form a close-packed face-centered-cubic structure with the 24 smaller metal cations occupying two types of interstitial position: the tetrahedral (8a) or (A) sites and the octahedral (16d) or [B] sites,$^{8,11}$ which form the [A] and [B] sublattices.

Many studies were carried out on the magnetic moment of and cation distribution in Ti-doped spinel ferrites.$^{12-16}$ In these investigations, all of the Ti cations were assumed to be tetravalent, but there have been disputes regarding the cation distribution. Dwivedi et al. prepared a series of samples, Co(Fe$_{1-x}$Ti$_x$)$_2$O$_4$ ($x = 0, 0.05$, or $0.1$), by conventional solid-phase reactions; using X-ray photoelectron spectroscopy (XPS) they discovered that all Ti cations went into the octahedral sites.$^{12}$ Srinivasa Rao et al. prepared samples of the CoTi$_x$Fe$_{2-x}$O$_4$ (0.0 $\leq x \leq 0.3$) series; they thought that the Ti$^{4+}$ ions had the tendency to go to the [B] site, which affected the cation distribution in the samples.$^{13}$ Schmidbauer prepared samples of the Fe$_{1-x}$Cr$_{2-x}$Ti$_x$O$_4$ (0 $\leq x \leq 1$) series and concluded that there were Fe$^{2+}$ ions at the (A) and [B] sites, and all Cr and Ti cations occupied the B-sites.$^{14}$ Schmidbauer also prepared samples of two spinel ferrite series, Fe$_{2.4-x}$Cr$_{0.6}$Ti$_x$O$_4$ (0 $\leq t \leq 0.7$) and Fe$_{2.1-x}$Cr$_{0.9}$Ti$_x$O$_4$ (0 $\leq t \leq 0.55$), and assumed that all of the Ti$^{4+}$ ions entered the [B] sites.$^{15}$ However, when Kale et al. prepared Ti$_x$Ni$_{1-x}$Fe$_{2-x}$O$_4$ (0.0 $\leq x \leq 0.7$), they estimated the cation distribution at the (A) and [B] sites using X-ray diffraction and came to the conclusion that the fraction of Ti$^{4+}$ cations entering the [A] sites increased with increasing $x$, and it reached 0.5 when $x = 0.7$.$^{16}$

In order to resolve these discrepancies regarding cation distributions in spinel ferrites, Xu et al. investigated the valence, distribution of cations and the magnetic structure of Ti-doped spinel ferrites$^{17-19}$ by using an O 2p itinerant-electron model.$^{20-22}$ They found an additional antiferromagnetic phase when Ti cations replaced a portion of the Ni or Fe cations in the spinel ferrites Ni$_{0.6}$Fe$_{2.4}$O$_4$ (ref. 17 and 18) and NiFe$_2$O$_4$,$^{19}$ and they offered the following explanation for the phenomenon: most of the Ti cations were Ti$^{2+}$ cations that occupied the [B] sites; the remaining Ti cations were Ti$^{3+}$ cations and there were no Ti$^{4+}$ cations; the magnetic moments of the Ti cations coupled antiferromagnetically with those of Fe and Ni cations whenever they were at the (A) or [B] sites.

The absence of Ti$^{4+}$ in an oxide has been confirmed by theoretical and experimental investigations. Cohen$^{23}$ and Cohen and Krakauer$^{24}$ used density functional theory to calculate the densities of states for valence electrons in the perovskite oxide BaTiO$_3$. Their results indicated that the average valence of Ba is +2, which is the same as the traditionally accepted value, but the average valences of Ti and O are +2.89 and $-1.63$, respectively.
respectively, which are different from the conventional results of +4 and −2, respectively. This calculation result was confirmed by the X-ray photoelectron spectra obtained by Wu et al., who found that the average valence of O anions, \( V_{\text{O}} \), is −1.55, which is close to the value (−1.63) calculated by Cohen. In addition, using XPS analysis, Dupin et al. found that the average valence of O anions is −1.15 for TiO\(_2\), which indicates that there are Ti\(^{2+}\) and Ti\(^{3+}\) cations, but no Ti\(^{4+}\) cations, in TiO\(_2\). Ji et al. proposed a method to estimate the valences of cations and anions in (A)\([B]\)\(_2\)O\(_4\) spinel ferrites; they obtained estimated values between −1.6 and −1.8 for \( V_{\text{O}} \) of spinel ferrites, and they also defined the ionicity of an oxide as \( f_i = |V_{\text{O}}|/2 \), accompanied by calculated values of the ionicity of several cations in spinel ferrites.\(^{27}\)

Taking into account that there are O\(^{1−}\) ions in addition to O\(^{2−}\) ions, our group uses the O 2p itinerant-electron model\(^{28}\) and the quantum mechanical potential barrier method\(^{29,30}\) to investigate the cation distribution in several series of spinel ferrites.\(^{31−33}\) In the study reported here, we prepared spinel ferrite samples of Ti\(_x\)Co\(_{1−x}\)Fe\(_2\)O\(_4\) (0.0 ≤ \( x \) ≤ 0.4) and Ti\(_x\)Mn\(_{1−x}\)Fe\(_2\)O\(_4\) (0.0 ≤ \( x \) ≤ 0.3) and measured the magnetic moment, \( \mu_{\text{exp}} \), of the samples at 10 K. The cation distribution in the samples was estimated by fitting the measured values of \( \mu_{\text{exp}} \).

2 Experimental

2.1 Sample preparation

Spinel ferrites Ti\(_x\)Co\(_{1−x}\)Fe\(_2\)O\(_4\) (0.0 ≤ \( x \) ≤ 0.4; hereafter referred to as the Co-series) and Ti\(_x\)Mn\(_{1−x}\)Fe\(_2\)O\(_4\) (0.0 ≤ \( x \) ≤ 0.3; hereafter referred to as the Mn-series) were prepared using the method of solid-phase reaction.\(^{37}\) The analytical reagent (AR)-grade chemicals CoO, MnO\(_2\), Fe\(_2\)O\(_3\), and TiO\(_2\) were used as the starting materials. First, stoichiometric amounts of each chemical were mixed together, ground for 8 h in an agate mortar, and then calcined at 1173 K for 5 h. The calcined materials were then ground again for 1 h. The ground powder was calcined at 1473 K for an additional 5 h, and then further ground for 1 h. Next, the twice calcined and thrice ground powder was pressed into pellets at a pressure of 10\(^4\) kg cm\(^{−2}\) and then sintered at 1673 K for 10 h in a tube furnace under an argon flow. The sintered pellets were then ground for 30 min in an agate mortar, and the resulting powder was used for the measurements.

2.2 Sample characterization

The crystal structure of the samples was determined by analyzing their X-ray diffraction (XRD) patterns, which were measured with an X-ray diffractometer (X’Pert Pro, PANalytical, The Netherlands) with Cu K\(_\alpha\) (\( \lambda = 1.5406 \) Å) radiation at room temperature. The data were collected in the 2\( \theta \) range of 15−120\(^{°}\) with a step size of 0.0167\(^{°}\). The working current and voltage were 40 mA and 40 kV, respectively. The magnetic hysteresis loops of the samples were measured using a physical properties measurement system (PPMS, Quantum Design Corporation, USA) at 10 and 300 K.

3 Experimental results

3.1 Analysis of X-ray diffraction patterns

Fig. 1(a) and (b) show the XRD patterns of the Ti\(_x\)Co\(_{1−x}\)Fe\(_2\)O\(_4\) (0.0 ≤ \( x \) ≤ 0.4) and Ti\(_x\)Mn\(_{1−x}\)Fe\(_2\)O\(_4\) (0.0 ≤ \( x \) ≤ 0.3) samples, which indicate that they consisted of a single-phase with a cubic spinel structure of space group \( Fd\bar{3}m \). The XRD data were fitted using the X’Pert HighScore Plus software (PANalytical, The Netherlands) and the Rietveld powder-diffraction profile-fitting technique.\(^{36}\) The ions O (32e), A (8b) and B (16c) were located at the positions \((u, u, u)\), \((0.375, 0.375, 0.375)\), and \((0, 0, 0)\), respectively. We obtained the crystal structure data, including the crystal lattice constant, \( a \), the oxygen position parameters, \( u \), the distances from the O anions to the cations at the [A] and [B] sites, \( d_{\text{AO}} \) and \( d_{\text{BO}} \), and the distance between the cations at the [A] sites and those at the [B] sites, \( d_{\text{AB}} \); the data are summarized in Table 1. For the cubic spinel structure, the ideal values (assuming \( u = 0.25 \)) of \( d_{\text{AO}} \), \( d_{\text{BO}} \), and \( d_{\text{AB}} \) are \( \sqrt{3}a/8 \), \( a/4 \), and \( \sqrt{11}a/8 \), respectively; however, the observed values of \( d_{\text{AO}} \) and \( d_{\text{BO}} \) (Table 1) are 1.0400 and 0.9805 (or 1.0918 and 0.9565) times, respectively, of the ideal values for the Co-series (or Mn-series) samples. On the other hand, the observed values of \( d_{\text{AB}} \) are equal to the ideal values for the two series. The volume-averaged crystallite sizes of all samples were calculated using

![Fig. 1 X-ray diffraction patterns of various samples: (a) Ti\(_x\)Co\(_{1−x}\)Fe\(_2\)O\(_4\) (0.0 ≤ \( x \) ≤ 0.4); (b) Ti\(_x\)Mn\(_{1−x}\)Fe\(_2\)O\(_4\) (0.0 ≤ \( x \) ≤ 0.3).](image-url)
Table 1  Rietveld fitting results of XRD patterns of the two series of samples, obtained using the X’Pert HighScore Plus software. $a$ is the lattice parameter; $d_{AO}$ and $d_{BO}$ are the distances from the O anion to the cations at the (A) sites and [B] sites, respectively; and $d_{AB}$ is the distance from the cations at the (A) sites to those at the [B] sites.

| $x$  | $a$ (Å) | $d_{AO}$ (Å) | $d_{BO}$ (Å) | $d_{AB}$ (Å) | $u$ (Å)  |
|------|---------|--------------|--------------|--------------|---------|
| Ti$_x$Co$_{1-x}$Fe$_2$O$_4$  |
| 0.0  | 8.3871  | 1.888        | 2.056        | 3.477        | 0.24503 |
| 0.1  | 8.3987  | 1.891        | 2.059        | 3.482        | 0.24501 |
| 0.2  | 8.4089  | 1.893        | 2.061        | 3.486        | 0.24500 |
| 0.3  | 8.4203  | 1.896        | 2.064        | 3.491        | 0.24499 |
| 0.4  | 8.4343  | 1.898        | 2.066        | 3.497        | 0.24498 |
| Ti$_x$Mn$_{1-x}$Fe$_2$O$_4$  |
| 0.0  | 8.5197  | 2.014        | 2.037        | 3.532        | 0.23856 |
| 0.1  | 8.5190  | 2.016        | 2.038        | 3.531        | 0.23857 |
| 0.2  | 8.5172  | 2.012        | 2.036        | 3.530        | 0.23838 |
| 0.3  | 8.5118  | 2.011        | 2.035        | 3.529        | 0.23839 |

The X’Pert HighScore Plus software, and they were found to be greater than 100 nm. Therefore, surface effects of the crystallites are expected to be very weak in all samples.

Fig. 2 shows the dependence of the lattice parameter $a$ on the Ti-doping level, $x$, in the two series of samples. It can be seen that with increasing $x$, $a$ increased for the Co-series and decreased for the Mn-series. The different trends in the lattice constant were related to the cation radii, magnetic ordering, and cohesive energies of the samples.

3.2 Analysis of magnetic properties of the samples

Fig. 3 and 4 show the magnetic hysteresis loops of the two series of samples measured at 10 and 300 K. From these figures, we obtained the specific saturation magnetization ($\sigma_S$) measured at 10 and 300 K and the magnetic moment ($\mu_{expr}$) per formula unit of each sample at 10 K, as listed in Table 2. It can be seen that the values of $\sigma_S$ for the two series of samples gradually decreased with increasing $x$ at both 10 and 300 K.

4  Estimation of cation distributions by fitting the samples' magnetic moments at 10 K

Following the procedure reported by Xu et al.,16-20 we used the O 2p itinerant-electron model20 and the quantum mechanical potential barrier method21,22 to fit the magnetic moments measured at 10 K as a function of $x$ and estimate the cation distribution in all samples. During the fitting process, the following factors were taken into account:

Factor 1: since there were $O^{1-}$ ions in addition to $O^{2-}$ ions, the ionicity of the cations in the samples was distinctly lower than 1.0, as shown in Table 3; the values listed in Table 3 were calculated using the method reported by Ji et al.21 In [A][B]$_2$O$_4$ spinel ferrites, the total valence and the total number of trivalent cations per formula unit ($N_z$) are both less than the traditional values of 8 and 2, respectively.

Factor 2: the O 2p itinerant-electron model is characterized by certain features:20 (i) In a given sublattice, an O 2p electron with constant spin direction can hop from an $O^{2-}$ anion to the O 2p hole of an adjacent $O^{1-}$ anion, with a cation acting as an intermediary. (ii) The two O 2p electrons in the outer orbit of an $O^{2-}$ anion, which have opposite spin directions, become itinerant electrons in the two different sublattices (the A or B sublattice). (iii) In a given sublattice that is constrained by Hund’s rules and by the fact that an itinerant electron has constant spin direction, the direction of the magnetic moments of cations with the 3d electron number of $n_d \leq 4$ will couple antiferromagnetically to those of the cations with $n_d \geq 5$ at either the (A) sites or the (B) sites of a spinel ferrite. Therefore, the directions of the magnetic moments of Ti$^{3+}$ (3d$^1$), Ti$^{2+}$ (3d$^2$), and Mn$^{3+}$ (3d$^4$) were antiparallel to those of the magnetic

Fig. 2  Curves of lattice constant, $a$, versus the Ti-doping level, $x$, for the two series of samples.

Fig. 3  Magnetic hysteresis loops measured at (a) 10 K and (b) 300 K for samples of Ti$_x$Co$_{1-x}$Fe$_2$O$_4$. 

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Table 2  Estimated values of $\sigma_S$ for the two series of samples.

| $x$  | $\sigma_S$ (Am$^2$/kg) at 10 K | $\sigma_S$ (Am$^2$/kg) at 300 K |
|------|-------------------------------|-------------------------------|
| 0.0  | 4.35                          | 3.85                          |
| 0.1  | 4.25                          | 3.75                          |
| 0.2  | 4.15                          | 3.65                          |
| 0.3  | 4.05                          | 3.55                          |
| 0.4  | 3.95                          | 3.45                          |

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moments of Mn$^{2+}$, Co$^{2+}$, Co$^{3+}$, Fe$^{3+}$, and Fe$^{2+}$ in the same sample at either the (A) sublattice or the [B] sublattice. Therefore, in the following calculations, we set the moment of the cations to the values shown in Table 3.

Factor 3: we assumed that there is a square potential barrier large available space), jumping over an equivalent potential (A) sites (with smaller available space) from the [B] sites (with large e

Factor 4: we considered the Pauli repulsion energy of the electron cloud between adjacent cations and anions. This can be taken into account using the effective ionic radius; smaller ions tend to enter the sites with smaller available space in the lattice. It is worth noting that the volumes of the (A) sites are smaller than those of the [B] sites in spinel ferrites.

Factor 5: during the thermal treatment of the samples, the tendency to balance the electrical charge density forced some of the divalent cations (with large effective ionic radii) to enter the (A) sites (with smaller available space) from the [B] sites (with large available space), jumping over an equivalent potential barrier, $V_{BA}$, because cations at the (A) sites have four adjacent oxygen ions while cations at the [B] sites have six adjacent oxygen ions. $V_{BA}$ is related to the ionization energy, ionic radius, and the thermal-treatment temperature. We assumed $V_{BA}$ of the ferrite samples can be expressed by the following equations:

$$V_{BA} \text{(Fe}^{2+}\text{)} = \frac{V_{BA}(\text{Ti}^{2+})V(\text{Fe}^{3+})r(\text{Fe}^{2+})}{V(\text{Ti}^{3+})r(\text{Ti}^{2+})},$$

$$V_{BA} \text{(M}^{2+}\text{)} = \frac{V_{BA}(\text{Ti}^{2+})V(\text{M}^{3+})r(\text{M}^{2+})}{V(\text{Ti}^{3+})r(\text{Ti}^{2+})}.$$

where $M = \text{Co}$ or Mn; $V(\text{M}^{3+})$, $V(\text{Ti}^{3+})$, and $V(\text{Fe}^{3+})$ are the third ionization energies of Co, Mn, Ti and Fe, respectively; and $r(\text{M}^{2+})$, $r(\text{Ti}^{2+})$, and $r(\text{Fe}^{2+})$ are the effective radii of the divalent cations with coordination number 6, as shown in Table 3.

Table 3 Cation parameters used in the magnetic-moment fitting process, including the second and third ionization energies, $V(M^{2+})$ and $V(M^{3+})$; effective radii, $r$, of the divalent cations with coordination number 6; ionicity, $f_{i}^{27}$ and the magnetic moments of the divalent and trivalent cations, $m_2$ and $m_3$.

| Element | $V(M^{2+})$ (eV) | $V(M^{3+})$ (eV) | $r^2$ (nm) | $f_i^{27}$ | $m_2 (\mu_B)$ | $m_3 (\mu_B)$ |
|---------|-----------------|-----------------|-----------|-----------|----------------|----------------|
| Ti      | 13.58           | 27.49           | 0.0860    | 0.9716    | -1             | -2             |
| Mn      | 15.64           | 33.67           | 0.0830    | 0.8293    | 5              | -4             |
| Fe      | 16.18           | 30.65           | 0.0780    | 0.8790    | 4              | 5              |
| Co      | 17.06           | 33.50           | 0.0745    | 0.8314    | 3              | 4              |

Table 2 Specific saturation magnetization measured at 10 K ($\sigma_{S\text{-}10\text{K}}$) and 300 K ($\sigma_{S\text{-}300\text{K}}$) for the two series of samples; $\mu_{\text{exp}}$ is the experimental magnetic moment per formula unit of a sample, which was calculated using $\sigma_{S\text{-}10\text{K}}$.

| $x$ | $\sigma_{S\text{-}10\text{K}}$ (A m$^{-1}$ kg$^{-1}$) | $\sigma_{S\text{-}300\text{K}}$ (A m$^{-1}$ kg$^{-1}$) | $\mu_{\text{exp}}$ ($\mu_B$ per formula) |
|-----|-----------------------------------------------|-----------------------------------------------|------------------------------------------|
| 0.0 | 77.73                                         | 77.39                                         | 3.266                                    |
| 0.1 | 74.19                                         | 76.32                                         | 3.102                                    |
| 0.2 | 66.30                                         | 67.34                                         | 2.759                                    |
| 0.3 | 59.97                                         | 58.03                                         | 2.484                                    |
| 0.4 | 51.02                                         | 50.12                                         | 2.103                                    |
| 0.0 | 105.23                                        | 74.41                                         | 4.346                                    |
| 0.1 | 92.28                                         | 68.47                                         | 3.799                                    |
| 0.2 | 81.06                                         | 64.31                                         | 3.327                                    |
| 0.3 | 72.91                                         | 58.18                                         | 2.983                                    |
The chemical formulae of the ferrite samples Ti$_x$Co$_{1-x}$Fe$_2$O$_4$ and Ti$_x$Mn$_{1-x}$Fe$_2$O$_4$ are rewritten here as Ti$_x$M$_y$Fe$_{3-x-y}$O$_4$ (M = Co, Mn) so that the cation distributions can be described by the equation

$$
(\text{Ti}_3^{3+}\text{M}_2^{2+}\text{Fe}_3^{3+}, \text{Ti}_2^{2+}\text{M}_1^{3+}\text{Fe}_2^{2+})
$$

$$\text{[Ti}x-x-y_z-2\text{M}_y-x-y_z-2\text{Fe}_2-x-x-y_z-2\text{Ti},$$

$$\text{z}^{3+}\text{M}_z^{2+}\text{Fe}_3^{3+}]\text{O}_4.
$$

(4)

It can be seen from eqn (4) that

$$y_1 + y_2 + y_3 + y_4 + y_5 + y_6 = 1,$$ (5)

$$y_1 + y_2 + y_3 + z_1 + z_2 + z_3 = N_3,$$ (6)

$$N_3 = \frac{8}{3}(f_{\text{Ti},x} + f_{\text{M},y} + f_{\text{Fe},z}(30 - x - x)) - 60,$$ (7)

where $N_3$ is the number of trivalent cations per formula unit. The parameters $f_{\text{Ti},x}$, $f_{\text{Fe},z}$, and $f_{\text{M},y}$ represent the ionicities of the Ti, Fe, and Co (or Mn) ions,$^{27}$ whose values are shown in Table 3. Eqn (7) suggests that when the ionicity of all cations is 1.00, the sum of the valence of all cations is 8.00, while $N_3 = 2.00$. In fact, the ionicity of each cation is lower than 1.00 (see Table 3), resulting in $N_3 < 2.00$. From eqn (4), we have

$$R_{A1} = \frac{x_1}{3 - x_1 - x_2} = \frac{y_1}{y_3},$$

$$R_{A2} = \frac{x_2}{3 - x_1 - x_2} = \frac{y_2}{y_3},$$

$$R_{A4} = \frac{x_1}{3 - x_1 - x_2} = \frac{y_4}{y_3},$$

(8)

where $R_{A1}$, $R_{A2}$, $R_{A4}$, and $R_{A5}$ represent the probability ratios of the Ti$^{3+}$, Co$^{2+}(\text{Mn}^{3+})$, Ti$^{2+}$, Co$^{3+}(\text{Mn}^{2+})$, and Fe$^{2+}$ ions, respectively, with respect to the Fe$^{3+}$ ions at the (A) sites, while $R_{B1}$ and $R_{B2}$ represent the probability ratios of the Ti$^{3+}$ and Co$^{3+}(\text{Mn}^{2+})$ ions with respect to the Fe$^{3+}$ ions at the (B) sites. From eqn (5) and (8), we can obtain

$$y_3 = \frac{3 - x_1 - x_2}{(R_{A1} + R_{A4})x_1 + (R_{A2} + R_{A5})x_2 + (1 + R_{A6})(3 - x_1 - x_2)}. $$

(10)

From eqn (6) and (9), we have

$$z_1 = \frac{N_3 - \left[1 + R_{B1} \frac{x_1}{3 - x_1 - x_2} + R_{A2} \frac{x_2}{3 - x_1 - x_2}\right] y_3}{1 + R_{B1} \frac{x_1}{3 - x_1 - x_2} + R_{A2} \frac{x_2}{3 - x_1 - x_2} + R_{B2} \frac{y_2}{3 - x_1 - x_2} - y_6}. $$

(11)

According to the above-mentioned quantum mechanical potential barrier method for estimating the cation distributions in spinel ferrites,$^{24,25}$ which is similar to eqn (1), the content ratios $R_{B1}$, $R_{B2}$, $R_{A4}$, $R_{A5}$, and $R_{A6}$ at the (A) sites and $R_{B1}$ and $R_{B2}$ at the (B) sites can be rewritten as

$$R_{A1} = \frac{P(\text{Ti}^{3+})}{P(\text{Fe}^{3+})},$$

$$= \frac{V(\text{Fe}^{3+})}{V(\text{Ti}^{3+})} \exp\left\{10.24d_{\text{AO}}\left[V(\text{Fe}^{3+})^{1/2} - c_i V(\text{Ti}^{3+})^{1/2}\right]\right\},$$

(12)

$$R_{A2} = \frac{P(\text{M}^{3+})}{P(\text{Fe}^{3+})},$$

$$= \frac{V(\text{Fe}^{3+})}{V(\text{M}^{3+})} \exp\left\{10.24d_{\text{AO}}\left[V(\text{Fe}^{3+})^{1/2} - V(\text{M}^{3+})^{1/2}\right]\right\},$$

(13)

$$R_{A4} = \frac{P(\text{Ti}^{3+})}{P(\text{Fe}^{3+})},$$

$$= \frac{V(\text{Fe}^{3+})}{V(\text{Ti}^{3+})} \exp\left\{10.24d_{\text{AO}}\left[V(\text{Fe}^{3+})^{1/2} - V(\text{Ti}^{3+})^{1/2}\right]\right\},$$

(14)

$$R_{A5} = \frac{P(\text{M}^{3+})}{P(\text{Fe}^{3+})},$$

$$= \frac{V(\text{Fe}^{3+})}{V(\text{M}^{3+})} \exp\left\{10.24d_{\text{AO}}\left[V(\text{Fe}^{3+})^{1/2} - d_{\text{AO}}c_i V(\text{Ti}^{3+})^{1/2}\right]\right\},$$

(15)

$$R_{A6} = \frac{P(\text{Fe}^{3+})}{P(\text{Fe}^{3+})},$$

$$= \frac{V(\text{Fe}^{3+})}{V(\text{Fe}^{3+})} \exp\left\{10.24\left[d_{\text{AO}} V(\text{Fe}^{3+})^{1/2} - d_{\text{AO}} V(\text{M}^{3+})^{1/2}\right]\right\} - d_{\text{AB}} V_{\text{BA}}(\text{Fe}^{3+})^{1/2}$$

(16)

$$R_{B1} = \frac{P(\text{Ti}^{3+})}{P(\text{Fe}^{3+})},$$

$$= \frac{V(\text{Fe}^{3+})}{V(\text{Ti}^{3+})} \exp\left\{10.24d_{\text{BO}}\left[V(\text{Fe}^{3+})^{1/2} - c_i V(\text{Ti}^{3+})^{1/2}\right]\right\},$$

(17)

$$R_{B2} = \frac{P(\text{M}^{3+})}{P(\text{Fe}^{3+})},$$

$$= \frac{V(\text{Fe}^{3+})}{V(\text{M}^{3+})} \exp\left\{10.24d_{\text{BO}}\left[V(\text{Fe}^{3+})^{1/2} - V(\text{M}^{3+})^{1/2}\right]\right\},$$

(18)

where M = Co or Mn; and $V(M^{3+}), V(M^{2+}), V(Ti^{3+}), V(Ti^{2+}), V(Fe^{3+}),$ and $V(Fe^{2+})$ are the second and third ionization energies of Co, Mn, Ti, and Fe, respectively, as shown in Table 3. The parameter $c_i$ is a barrier shape-correcting constant related to the potential barrier of Ti$^{3+}$ and Ti$^{3+}$ cations; we assume that $c_i = 1.0$ for other cations because the second and third ionization...
energies of Ti cations are distinctly lower than those of other cations. $V_{BA}(M^{2+})$, $V_{BA}(Ti^{2+})$, and $V_{BA}(Fe^{2+})$ are the heights of the equivalent potential barriers [all have a width of $d_{AB}$] which must be transmitted through by the $M^{2+}$, $Ti^{2+}$, and $Fe^{2+}$ ions as they move from the [B] sites to the [A] sites during thermal treatment. The values of, $d_{AC}$, $d_{BC}$, and $d_{AB}$ are the observed values in the XRD patterns, as listed in Table 1.

According to the O 2p itinerant-electron model, the magnetic moments of the $Mn^{3+}$, $Ti^{2+}$, and $Ti^{3+}$ cations are antiparallel to those of $Co^{2+}$, $Co^{3+}$, $Mn^{2+}$, $Fe^{3+}$, and $Fe^{2+}$ cations in the same sublattice of a spinel ferrite (see Table 3). Therefore, we can calculate the average magnetic moment per formula unit of a sample from eqn (4):

$$\mu_C = \mu_{BT} - \mu_{AT},$$

$$\mu_{AT} = -\frac{1}{2} \left( x_1 - y_1 - z_1 - \frac{1}{2} \right) + \frac{1}{2} (5),$$

$$\mu_{BT} = \mu_{B1} + \mu_{B2} + \mu_{B3},$$

where $\mu_C$ is the calculated magnetic moment of a sample; $\mu_{AT}$ and $\mu_{BT}$ are the magnetic moments of the [A] and [B] sublattices; and $\mu_{B1}$, $\mu_{B2}$, and $\mu_{B3}$ are magnetic moments contributed by the $Ti$, $Co$ (or $Mn$), and $Fe$ ions, respectively, at the [B] sublattice.

For each sample, there are 22 parameters: $y_1$, $y_2$, $z_1$, $z_2$, $N_1$; $R_{A1}$, $R_{A2}$, $R_{A3}$, and $R_{B1}$; $V_{BA}(Ti^{2+})$, $V_{BA}(M^{2+})$, and $V_{BA}(Fe^{2+})$; $\mu_{C1}$ and $c_v$. Altogether, there are 20 independent equations, including eqn (2), (3), (5)–(9), and (12)–(19), where eqn (8) contains five equations and eqn (9) contains two equations. Therefore, we needed to obtain the values of at least two independent parameters, such as $c_v$, and $V_{BA}(Ti^{2+})$, in order to fit the observed values of $\mu_{exp}$ of a sample at 10 K.

Using the above parameters and equations, we fitted the dependence of $\mu_{exp}$ on $x$ for the two series of samples. The points and curves in Fig. 5 represent the observed and calculated magnetic moments per formula unit of the (A) and (B) sublattices, respectively and $\mu_C = \mu_{BT} - \mu_{AT}$ is the calculated magnetic moment per formula unit.
calculated magnetic moments, $\mu_{\text{exp}}$ and $\mu_{\text{C}}$, of the samples. It can be seen that the fitted curves are very close to the experimental results. In the fitting process, we obtained the cation distribution and other data, as listed in Tables 4 and 5. The cation distribution is shown as a function of $x$ for the two series of samples in Fig. 6 and 7.

Fig. 6 Distribution of (a) Fe, (b) Ti, and (c) Co cations and (d) the total content percentages of different valence cations at the (A) and [B] sites in samples of $\text{Ti}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ($0.0 \leq x \leq 0.4$).

Fig. 7 Distribution of (a) Fe, (b) Ti, and (c) Mn cations and (d) the total content percentages of different valence cations at the (A) and [B] sites in samples of $\text{Ti}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ ($0.0 \leq x \leq 0.3$).
5 Discussion

From Tables 4, 5, Fig. 6 and 7, we found that the fitting parameters and the cation distribution in the samples had certain characteristics, as discussed in the following subsections.

5.1 Fitting parameters: $c_0$ and $V_{BA}$

During the fitting process, we determined that the potential barrier shape-correcting constant $c_0$ was equal to 1.1 and 1.2 for the pair of ions, Ti–O, in the Co-series and Mn-series, respectively. Both values are reasonable when compared with $c_0 = 1.0$ for other cation–anion pairs.

The Ti$^{2+}$ ions must transmit though the equivalent potential barrier $V_{BA(Ti^{2+})}$ as they moved from the [B] sites to the [A] sites during the thermal treatment. We obtained the values of $V_{BA(Ti^{2+})}$ in the fitting process, and they increased from 1.093 eV ($x = 0.0$) to 1.880 eV ($x = 0.4$) for the Co-series and from 0.896 eV ($x = 0.0$) to 1.140 eV ($x = 0.3$) for the Mn-series. The values of $V_{BA(Fe^{2+})}$, $V_{BA(Fe^{3+})}$, and $V_{BA(Mn^{2+})}$ were calculated from eqn (2) and (3), and they appear reasonable in the context of a physics problem.

5.2 Valence and distribution of Ti cations

(i) The ratio of Ti$^{2+}$ ions at the (A) and [B] sites to the Ti-doping level, $x$, is more than 72% in the Co-series samples (Fig. 6(b)) and about 89% in the Mn-series samples (Fig. 7(b)). This result is similar to that measured using XPS and reported by Dupin et al.; they found that the average O ionic valence is $-1.15$ for TiO$_2$, which suggests that 70% of Ti cations in TiO$_2$ are Ti$^{2+}$ ions. Therefore, the conventional view$^{15-16}$ that all Ti cations in an oxide are Ti$^{4+}$ ions needs to be modified.

(ii) The ratio of Ti$^{2+}$ cations that entered the [B] sites to $x$ increased from 58% ($x = 0.1$) to 63% ($x = 0.4$) in the Co-series samples (Fig. 6(b)), and this ratio remained at 79% from $x = 0.1$ to $x = 0.3$ in the Mn-series samples (Fig. 7(b)). This result is similar to that reported by Xu et al., who found the ratio of Ti$^{2+}$ cations that entered the [B] sites to $x$ was 81% in Ti-doped ferrite Ni$_{0.68}$Fe$_{2.32}$O$_4$.$^{18}$

(iii) The ratio of Ti cations, including Ti$^{2+}$ and Ti$^{3+}$, that entered the [B] sites to $x$ increased from 67% ($x = 0.1$) to 72% ($x = 0.4$) in the Co-series samples (Fig. 6(d)), and this ratio was 85% in the Mn-series samples (Fig. 7(d)). This result appears to be a balance between the contrasting results reported by several authors.$^{12-14}$ Kale et al. concluded that 71% of Ti cations entered the (A) sites in Ti$_x$Co$_{1-x}$Fe$_2$O$_4$,$^{18}$ while other authors assumed that all of the Ti ions entered the [B] sites of the spinel ferrite samples.$^{12-15}$

5.3 Distribution of Co cations in Co-series

(i) The ratio of Co cations, including Co$^{2+}$ and Co$^{3+}$, that entered the [B] sites to the total Co cation content ranged from 76% to 78% (Fig. 6(d)). This ratio is very close to that reported by Shang et al.$^{18}$ for Co$_{1-x}$Cr$_x$Fe$_2$O$_4$. This result is also close to that reported by Wakabayashi et al. for a CoFe$_2$O$_4$ film with thickness of 11 nm, which was based on soft X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) combined with cluster model calculations.$^{28}$

(ii) The ratio of Co$^{2+}$ cations that entered the [B] sites to the total Co cation content increased from 67% ($x = 0.0$) to 73% ($x = 0.4$). This result is similar to that reported by Shang et al., who found that the ratio of Co$^{2+}$ cations that entered the [B] sites ranged from 64% ($x = 0.0$) to 59% ($x = 0.8$) in Co$_{1-x}$Cr$_x$Fe$_2$O$_4$. $^{18}$

5.4 Distribution of Mn cations in Mn-series

The ratio of Mn$^{2+}$ cations that entered the [B] sites to the total Mn cation content was 61%. The ratio of Mn ions, including Mn$^{2+}$ and Mn$^{3+}$ cations, that entered the [B] sites to the total Mn cation content was 73%. This result is similar to that reported by Xu et al.$^{20}$

5.5 Entry of few Co and Mn cations into the (A) sites

It can be seen from Fig. 6(c) and 7(c) that a few of the Co (Mn) cations entered the (A) sites of the Co (Mn) series samples. This is in accordance with the observed results from XRD mentioned in Section 3.1: the ratio of observed to ideal values of A-O distance for MnFe$_2$O$_4$, 1.09, is higher than that for CoFe$_2$O$_4$, 1.04, because the effective radius of Mn is greater than that of Co (see Table 3). This suggested that a few of the Mn (Co) cations entered the (A) sites of MnFe$_2$O$_4$ (CoFe$_2$O$_4$).

6 Conclusions

The single-phase spinel ferrites Ti$_x$Co$_{1-x}$Fe$_2$O$_4$ ($0.0 \leq x \leq 0.4$) and Ti$_x$Mn$_{1-x}$Fe$_2$O$_4$ ($0.0 \leq x \leq 0.3$) were prepared using the conventional method for preparing ceramics. The samples were found to consist of a single phase with a cubic spinel structure. The lattice constant increased in the Co-series samples and decreased in the Mn-series samples with increases in the dopant level, $x$. The values of $\mu_{\text{exp}}$ of the two series of samples, measured at 10 K, decreased approximate linearly with increasing $x$.

The dependence of $\mu_{\text{exp}}$ on $x$ for the two series of samples was fitted using a quantum-mechanical potential barrier method. The fitted magnetic moments were very close to the experimental results. In the fitting process, the cation distributions of the two series of samples were obtained.

The cation distributions and the magnetic structure obtained in this study are distinctly different from those reported by other groups: (i) there were Ti$^{2+}$ and Ti$^{3+}$ ions, but no Ti$^{4+}$ ions, in our samples. (ii) The ratio of Ti$^{2+}$ cations that entered the [B] sites to the Ti-doping level, $x$, increased from 58% ($x = 0.1$) to 63% ($x = 0.4$) in the Co-series samples, and this ratio was 79% from $x = 0.1$ to $x = 0.3$ in the Mn-series samples. (iii) The magnetic moments of Ti$^{2+}$, Ti$^{3+}$, and Mn$^{3+}$ ions (with 3d electron number of $n_d \geq 4$) coupled antiferromagnetically with other cations ($n_d \leq 5$) whenever they were at the (A) or [B] sublattice.
Conflicts of interest

There are no conflicts to declare.

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