



Cite this: *RSC Adv.*, 2018, 8, 302

## Valence of Ti cations and its effect on magnetic properties of spinel ferrites $Ti_xM_{1-x}Fe_2O_4$ ( $M = Co, Mn$ )

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Powder samples of  $Ti_xCo_{1-x}Fe_2O_4$  ( $0.0 \leq x \leq 0.4$ ) and  $Ti_xMn_{1-x}Fe_2O_4$  ( $0.0 \leq x \leq 0.3$ ) 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]<sub>2</sub>O<sub>4</sub> spinel structure. The average molecular magnetic moment ( $\mu_{exp}$ ) measured at 10 K decreased monotonically with increasing  $x$  for two series of samples. According to previous investigations,  $Ti^{2+}$  and  $Ti^{3+}$  cations are present in these ferrites, but there are no  $Ti^{4+}$  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  $\mu_{exp}$  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.

Received 6th November 2017  
Accepted 13th December 2017

DOI: 10.1039/c7ra12163f

rsc.li/rsc-advances

### 1 Introduction

Spinel ferrites have received much attention in recent years because of their application in spintronics and multiferroics.<sup>1–7</sup> In a (A)[B]<sub>2</sub>O<sub>4</sub> 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,<sup>8–11</sup> 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.<sup>12–16</sup> 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,  $Co(Fe_{1-x}Ti_x)_2O_4$  ( $x = 0, 0.05, \text{ or } 0.1$ ), by conventional solid-phase reactions; using X-ray photoelectron spectroscopy (XPS) they discovered that all Ti cations went into the octahedral sites.<sup>12</sup> Srinivasa Rao *et al.* prepared samples of the  $CoTi_xFe_{2-x}O_4$  ( $0.0 \leq x \leq 0.3$ ) 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.<sup>13</sup> Schmidbauer prepared samples of the  $Fe_{1+x}Cr_{2-2x}Ti_xO_4$  ( $0 \leq x \leq 1$ ) 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.<sup>14</sup> Schmidbauer also prepared samples of two spinel ferrite series,  $Fe_{2.4-t}Cr_{0.6}Ti_tO_4$  ( $0 \leq t \leq 0.7$ ) and  $Fe_{2.1-t}Cr_{0.9}Ti_tO_4$  ( $0 \leq t \leq 0.55$ ), and assumed that all of the  $Ti^{4+}$  ions entered the [B] sites.<sup>15</sup> However, when Kale *et al.* prepared  $Ti_xNi_{1+x}Fe_{2-2x}O_4$  ( $0.0 \leq x \leq 0.7$ ), 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  $x = 0.7$ .<sup>16</sup>

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<sup>17–19</sup> by using an O 2p itinerant-electron model.<sup>20–22</sup> They found an additional antiferromagnetic phase when Ti cations replaced a portion of the Ni or Fe cations in the spinel ferrites  $Ni_{0.68}Fe_{2.32}O_4$  (ref. 17 and 18) and  $NiFe_2O_4$ ,<sup>19</sup> 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<sup>23</sup> and Cohen and Krakauer<sup>24</sup> 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,

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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.*,<sup>25</sup> who found that the average valence of O anions,  $V_{\text{alO}}$ , 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  $\text{TiO}_2$ ,<sup>26</sup> which indicates that there are  $\text{Ti}^{2+}$  and  $\text{Ti}^{3+}$  cations, but no  $\text{Ti}^{4+}$  cations, in  $\text{TiO}_2$ . Ji *et al.* proposed a method to estimate the valences of cations and anions in  $(\text{A})[\text{B}]_2\text{O}_4$  spinel ferrites; they obtained estimated values between -1.6 and -1.8 for  $V_{\text{alO}}$  of spinel ferrites, and they also defined the ionicity of an oxide as  $f_i = |V_{\text{alO}}|/2$ , accompanied by calculated values of the ionicity of several cations in spinel ferrites.<sup>27</sup>

Taking into account that there are  $\text{O}^{1-}$  ions in addition to  $\text{O}^{2-}$  ions, our group uses the O 2p itinerant-electron model<sup>20</sup> and the quantum mechanical potential barrier method<sup>21,22</sup> to investigate the cation distribution in several series of spinel ferrites.<sup>28-35</sup> In the study reported here, we prepared spinel ferrite samples of  $\text{Ti}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  ( $0.0 \leq x \leq 0.4$ ) and  $\text{Ti}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$  ( $0.0 \leq x \leq 0.3$ ) 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  $\text{Ti}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  ( $0.0 \leq x \leq 0.4$ ; hereafter referred to as the Co-series) and  $\text{Ti}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$  ( $0.0 \leq x \leq 0.3$ ; hereafter referred to as the Mn-series) were prepared using the method of solid-phase reaction.<sup>17</sup> The analytical reagent (AR)-grade chemicals  $\text{CoO}$ ,  $\text{MnO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{TiO}_2$  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  $10^4 \text{ kg cm}^{-2}$  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  $\text{Cu K}\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation at room temperature. The data were collected in the  $2\theta$  range of  $15\text{--}120^\circ$  with a step size of  $0.0167^\circ$ . 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  $\text{Ti}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  ( $0.0 \leq x \leq 0.4$ ) and  $\text{Ti}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$  ( $0.0 \leq x \leq 0.3$ ) 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.<sup>36</sup> 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

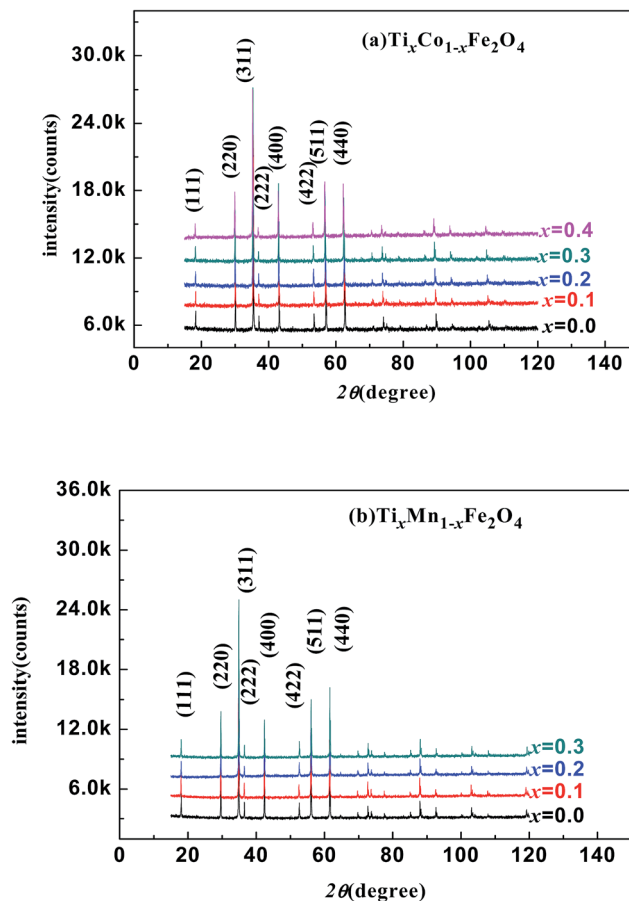
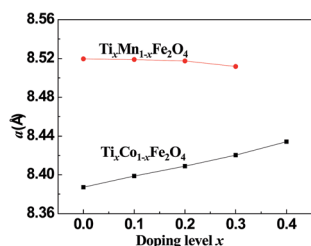


Fig. 1 X-ray diffraction patterns of various samples: (a)  $\text{Ti}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  ( $0.0 \leq x \leq 0.4$ ); (b)  $\text{Ti}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$  ( $0.0 \leq x \leq 0.3$ ).



**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) 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)
<b>Ti<sub>x</sub>Co<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub></b>					
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
<b>Ti<sub>x</sub>Mn<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub></b>					
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	0.23858
0.3	8.5118	2.011	2.035	3.529	0.23859



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

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.

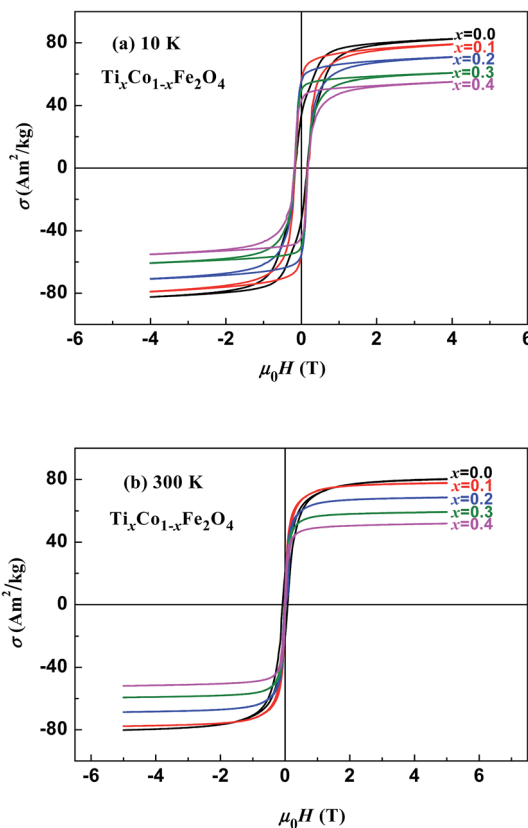
Fig. 2 shows the dependence of the lattice parameter  $a$  on the Ti-doping level,  $x$ , in the two series of samples. It can be seen that with increasing  $x$ ,  $a$  increased for the Co-series and decreased for the Mn-series. The different trends in the lattice constant were related to the cation 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 ( $\mu_{\text{exp}}$ ) 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.*,<sup>18–20</sup> we used the O 2p itinerant-electron model<sup>20</sup> and the quantum mechanical



**Fig. 3** Magnetic hysteresis loops measured at (a) 10 K and (b) 300 K for samples of Ti<sub>x</sub>Co<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub>.

potential barrier method<sup>21,22</sup> 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<sup>1-</sup> ions in addition to O<sup>2-</sup> 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.*<sup>27</sup> In (A)[B]<sub>2</sub>O<sub>4</sub> spinel ferrites, the total valence and the total number of trivalent cations per formula unit ( $N_3$ ) 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:<sup>20</sup> (i) in a given sublattice, an O 2p electron with constant spin direction can hop from an O<sup>2-</sup> anion to the O 2p hole of an adjacent O<sup>1-</sup> anion, with a cation acting as an intermediary. (ii) The two O 2p electrons in the outer orbit of an O<sup>2-</sup> 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<sup>3+</sup>(3d<sup>1</sup>), Ti<sup>2+</sup>(3d<sup>2</sup>), and Mn<sup>3+</sup>(3d<sup>4</sup>) were antiparallel to those of the magnetic



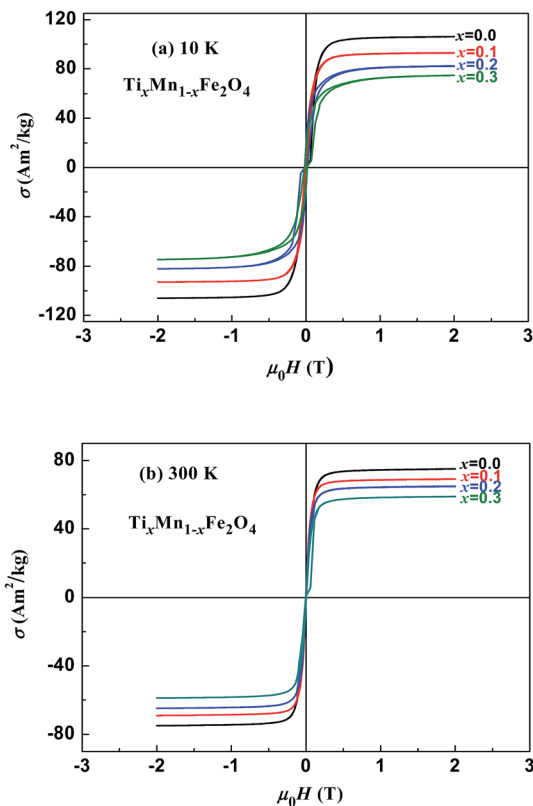


Fig. 4 Magnetic hysteresis loops measured at (a) 10 K and (b) 300 K for samples of  $\text{Ti}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ .

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

$x$	$\sigma_{S-10\text{K}}$ ( $\text{A m}^2 \text{ kg}^{-1}$ )	$\sigma_{S-300\text{K}}$ ( $\text{A m}^2 \text{ kg}^{-1}$ )	$\mu_{\text{exp}}$ ( $\mu_{\text{B}}$ per formula)
<b><math>\text{Ti}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4</math></b>			
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
<b><math>\text{Ti}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4</math></b>			
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

moments of  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Fe}^{2+}$  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 between a pair of anion and cation.<sup>21</sup> The height and the width of the potential barrier are related to the cation ionization energy and the distance between the cation–anion pair. The content ratio ( $R$ ) of the different cations is therefore related to

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

Element, M	$V(\text{M}^{2+})$ (eV)	$V(\text{M}^{3+})$ (eV)	$r^{37}$ (nm)	$f_i^{27}$	$m_2$ ( $\mu_{\text{B}}$ )	$m_3$ ( $\mu_{\text{B}}$ )
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

the probability of the last ionized electrons transmitted through the potential barriers, and the following equation can be obtained:

$$R = \frac{P_C}{P_D} = \frac{V_D}{V_C} \exp \left[ 10.24 \left( r_D V_D^{1/2} - r_C V_C^{1/2} \right) \right], \quad (1)$$

where nanometers (nm) and electron-volts (eV) are used as the units of length and energy;  $P_C$  (or  $P_D$ ) stands for the probability of the last ionized electron of the C (or D) cation jumping to the anions through the potential barrier with the height  $V_C$  (or  $V_D$ ) and the width  $r_C$  (or  $r_D$ ).  $V_C$  and  $V_D$  are the ionization energies of the last ionized electron of the cations C and D, and  $r_C$  and  $r_D$  are the distances from the cations C and D to the anions. The parameter  $c$  is a barrier shape-correcting constant related to the different extents to which the shapes of the two potential barriers deviate from a square barrier. When  $V_C = V_D$  and  $r_C = r_D$ , it is obvious that  $c = 1.0$ .

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:<sup>37</sup> 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,  $V_{\text{BA}}$ , because cations at the (A) sites have four adjacent oxygen ions while cations at the [B] sites have six adjacent oxygen ions.  $V_{\text{BA}}$  is related to the ionization energy, ionic radius, and the thermal-treatment temperature. We assumed  $V_{\text{BA}}$  of the ferrite samples can be expressed by the following equations:<sup>34</sup>

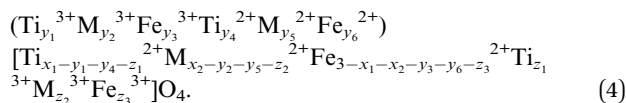
$$V_{\text{BA}}(\text{Fe}^{2+}) = \frac{V_{\text{BA}}(\text{Ti}^{2+})V(\text{Fe}^{3+})r(\text{Fe}^{2+})}{V(\text{Ti}^{3+})r(\text{Ti}^{2+})}, \quad (2)$$

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

where  $\text{M} = \text{Co}$  or  $\text{Mn}$ ;  $V(\text{M}^{3+})$ ,  $V(\text{Ti}^{3+})$ , 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.



The chemical formulae of the ferrite samples  $\text{Ti}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  and  $\text{Ti}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ , are rewritten here as  $\text{Ti}_{x_1}\text{M}_{x_2}\text{Fe}_{3-x_1-x_2}\text{O}_4$  ( $\text{M} = \text{Co}, \text{Mn}$ ) so that the cation distributions can be described by the equation



It can be seen from eqn (4) that

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

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

$$N_3 = \frac{8}{3} [f_{\text{Ti}}x_1 + f_{\text{M}}x_2 + f_{\text{Fe}}(3.0 - x_1 - x_2)] - 6.0, \quad (7)$$

where  $N_3$  is the number of trivalent cations per formula unit. The parameters  $f_{\text{Ti}}$ ,  $f_{\text{Fe}}$ , and  $f_{\text{M}} = f_{\text{Co}}$  (or  $f_{\text{Mn}}$ ) represent the ionicities of the Ti, Fe, and Co (or Mn) ions,<sup>27</sup> whose values are shown in Table 3. Eqn (7) suggests that when the ionicity of all cations are 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

$$\begin{aligned} R_{A1} \frac{x_1}{3-x_1-x_2} &= \frac{y_1}{y_3}, \quad R_{A2} \frac{x_2}{3-x_1-x_2} = \frac{y_2}{y_3}, \quad R_{A4} \frac{x_1}{3-x_1-x_2} \\ &= \frac{y_4}{y_3}, \quad R_{A5} \frac{x_2}{3-x_1-x_2} = \frac{y_5}{y_3}, \quad R_{A6} = \frac{y_6}{y_3}, \end{aligned} \quad (8)$$

$$R_{B1} \frac{x_1 - y_1 - y_4}{3 - x_1 - x_2 - y_3 - y_6} = \frac{z_1}{z_3}, \quad R_{B2} \frac{x_2 - y_2 - y_5}{3 - x_1 - x_2 - y_3 - y_6} = \frac{z_2}{z_3}, \quad (9)$$

where  $R_{A1}$ ,  $R_{A2}$ ,  $R_{A4}$ ,  $R_{A5}$ , and  $R_{A6}$  represent the probability ratios of the  $\text{Ti}^{3+}$ ,  $\text{Co}^{3+}$  ( $\text{Mn}^{3+}$ ),  $\text{Ti}^{2+}$ ,  $\text{Co}^{2+}$  ( $\text{Mn}^{2+}$ ), and  $\text{Fe}^{2+}$  ions, respectively, with respect to the  $\text{Fe}^{3+}$  ions at the (A) sites, while  $R_{B1}$  and  $R_{B2}$  represent the probability ratios of the  $\text{Ti}^{3+}$  and  $\text{Co}^{3+}$  ( $\text{Mn}^{3+}$ ) ions with respect to the  $\text{Fe}^{3+}$  ions at the [B] sites. From eqn (5) and (8), we can obtain

$$y_3 = \frac{3 - x_1 - x_2}{(R_{A1} + R_{A4})x_1 + (R_{A2} + R_{A5})x_2 + (1 + R_{A6})(3 - x_1 - x_2)}. \quad (10)$$

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

$$z_3 = \frac{N_3 - \left[ 1 + R_{A1} \frac{x_1}{3-x_1-x_2} + R_{A2} \frac{x_2}{3-x_1-x_2} \right] y_3}{1 + R_{B1} \frac{x_1 - y_1 - y_4}{3-x_1-x_2-y_3-y_6} + R_{B2} \frac{x_2 - y_2 - y_5}{3-x_1-x_2-y_3-y_6}}. \quad (11)$$

According to the above-mentioned quantum mechanical potential barrier method for estimating the cation distributions in spinel ferrites,<sup>21,22</sup> which is similar to eqn (1), the content ratios  $R_{A1}$ ,  $R_{A2}$ ,  $R_{A4}$ ,  $R_{A5}$ , and  $R_{A6}$  at the (A) sites and  $R_{B1}$  and  $R_{B2}$  at the [B] sites can be rewritten as

$$\begin{aligned} R_{A1} &= \frac{P(\text{Ti}^{3+})}{P(\text{Fe}^{3+})} \\ &= \frac{V(\text{Fe}^{3+})}{V(\text{Ti}^{3+})} \exp\left\{10.24d_{\text{AO}} \left[ V(\text{Fe}^{3+})^{1/2} - c_v V(\text{Ti}^{3+})^{1/2} \right]\right\}, \end{aligned} \quad (12)$$

$$\begin{aligned} R_{A2} &= \frac{P(\text{M}^{3+})}{P(\text{Fe}^{3+})} \\ &= \frac{V(\text{Fe}^{3+})}{V(\text{M}^{3+})} \exp\left\{10.24d_{\text{AO}} \left[ V(\text{Fe}^{3+})^{1/2} - V(\text{M}^{3+})^{1/2} \right]\right\}, \end{aligned} \quad (13)$$

$$\begin{aligned} R_{A4} &= \frac{P(\text{Ti}^{2+})}{P(\text{Fe}^{3+})} \\ &= \frac{V(\text{Fe}^{3+})}{V(\text{Ti}^{2+})} \exp\left\{10.24 \left[ d_{\text{AO}} V(\text{Fe}^{3+})^{1/2} - d_{\text{AO}} c_v V(\text{Ti}^{2+})^{1/2} \right. \right. \\ &\quad \left. \left. - d_{\text{AB}} V_{\text{BA}}(\text{Ti}^{2+})^{1/2} \right]\right\}, \end{aligned} \quad (14)$$

$$\begin{aligned} R_{A5} &= \frac{P(\text{M}^{2+})}{P(\text{Fe}^{3+})} \\ &= \frac{V(\text{Fe}^{3+})}{V(\text{M}^{2+})} \exp\left\{10.24 \left[ d_{\text{AO}} V(\text{Fe}^{3+})^{1/2} - d_{\text{AO}} V(\text{M}^{2+})^{1/2} \right. \right. \\ &\quad \left. \left. - d_{\text{AB}} V_{\text{BA}}(\text{M}^{2+})^{1/2} \right]\right\}, \end{aligned} \quad (15)$$

$$\begin{aligned} R_{A6} &= \frac{P(\text{Fe}^{2+})}{P(\text{Fe}^{3+})} \\ &= \frac{V(\text{Fe}^{3+})}{V(\text{Fe}^{2+})} \exp\left\{10.24 \left[ d_{\text{AO}} V(\text{Fe}^{3+})^{1/2} - d_{\text{AO}} V(\text{Fe}^{2+})^{1/2} \right. \right. \\ &\quad \left. \left. - d_{\text{AB}} V_{\text{BA}}(\text{Fe}^{2+})^{1/2} \right]\right\}, \end{aligned} \quad (16)$$

$$\begin{aligned} R_{B1} &= \frac{P(\text{Ti}^{3+})}{P(\text{Fe}^{3+})} \\ &= \frac{V(\text{Fe}^{3+})}{V(\text{Ti}^{3+})} \exp\left\{10.24d_{\text{BO}} \left[ V(\text{Fe}^{3+})^{1/2} - c_v V(\text{Ti}^{3+})^{1/2} \right]\right\}, \end{aligned} \quad (17)$$

$$\begin{aligned} R_{B2} &= \frac{P(\text{M}^{3+})}{P(\text{Fe}^{3+})} \\ &= \frac{V(\text{Fe}^{3+})}{V(\text{M}^{3+})} \exp\left\{10.24d_{\text{BO}} \left[ V(\text{Fe}^{3+})^{1/2} - V(\text{M}^{3+})^{1/2} \right]\right\}, \end{aligned} \quad (18)$$

where  $\text{M} = \text{Co}$  or  $\text{Mn}$ ; and  $V(\text{M}^{2+})$ ,  $V(\text{M}^{3+})$ ,  $V(\text{Ti}^{2+})$ ,  $V(\text{Ti}^{3+})$ ,  $V(\text{Fe}^{2+})$ , and  $V(\text{Fe}^{3+})$  are the second and third ionization energies of Co, Mn, Ti, and Fe, respectively, as shown in Table 3. The parameter  $c_v$  is a barrier shape-correcting constant related to the potential barrier of  $\text{Ti}^{2+}$  and  $\text{Ti}^{3+}$  cations; we assume that  $c_v = 1.0$  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,  $d_{AO}$ ,  $d_{BO}$ , 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):

$$\left. \begin{aligned} \mu_C &= \mu_{BT} - \mu_{AT}, \\ \mu_{AT} &= -y_1 + m_3y_2 + 5y_3 - 2y_4 + m_2y_5 + 4y_6, \\ \mu_{B1} &= -2(x_1 - y_1 - y_4 - z_1) - z_1, \\ \mu_{B2} &= m_2(x_2 - y_2 - y_5 - z_2) + m_3z_2, \\ \mu_{B3} &= 4(3 - x_1 - x_2 - y_3 - y_6 - z_3) + 5z_3, \\ \mu_{BT} &= \mu_{B1} + \mu_{B2} + \mu_{B3}, \end{aligned} \right\} \quad (19)$$

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:  $y_1$ – $y_6$ ;  $z_1$ – $z_3$ ;  $N_3$ ;  $R_{A1}$ ,  $R_{A2}$ ,  $R_{A4}$ ,  $R_{A5}$ , and  $R_{A6}$ ;  $R_{B1}$  and  $R_{B2}$ ;  $V_{BA}(Ti^{2+})$ ,  $V_{BA}(M^{2+})$ , and  $V_{BA}(Fe^{2+})$ ;  $\mu_C$ ; 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

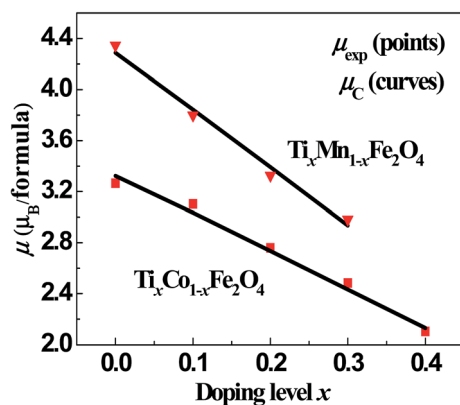


Fig. 5 Fitted magnetic moments,  $\mu_C$  (line), and observed values,  $\mu_{exp}$  (points), as functions of  $x$  for the two series of samples.

Table 4 Cation distributions obtained by fitting the dependence of the magnetic moments in the samples  $Ti_xCo_{1-x}Fe_2O_4$  on  $x$ . The parameters  $V_{BA}(Ti^{2+})$ ,  $V_{BA}(Co^{2+})$ , and  $V_{BA}(Fe^{2+})$  are the heights of the potential barriers that must be transmitted through by the  $Ti^{2+}$ ,  $Co^{2+}$ , and  $Fe^{2+}$  ions when moving from the [B] sites to the (A) sites during thermal treatment of the samples;  $N_3$  is the total average number of trivalent cations per formula unit;  $\mu_{AT}$  and  $\mu_{BT}$  are the 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

$x$	0.0	0.1	0.2	0.3	0.4
$N_3$	0.9070	0.9496	0.9906	1.0297	1.0675
$V_{BA}(Ti^{2+})$ (eV)	1.0933	1.2900	1.4867	1.6833	1.8800
$V_{BA}(Co^{2+})$ (eV)	1.1542	1.3618	1.5694	1.7770	1.9847
$V_{BA}(Fe^{2+})$ (eV)	1.1056	1.3045	1.5034	1.7022	1.9011
<b>A sites</b>					
$Ti^{3+}$	0.0000	0.0168	0.0372	0.0602	0.0849
$Co^{3+}$	0.1164	0.1193	0.1172	0.1106	0.1002
$Fe^{3+}$	0.4159	0.4822	0.5392	0.5864	0.6244
$Ti^{2+}$	0.0000	0.0178	0.0283	0.0332	0.0343
$Co^{2+}$	0.1286	0.0919	0.0637	0.0429	0.0280
$Fe^{2+}$	0.3392	0.2706	0.2121	0.1639	0.1252
<b>B sites</b>					
$Ti^{2+}$	0.0000	0.0578	0.1202	0.1859	0.2536
$Co^{2+}$	0.6674	0.6173	0.5610	0.4992	0.4331
$Fe^{2+}$	0.9578	0.9935	1.0219	1.0424	1.0553
$Ti^{3+}$	0.0000	0.0091	0.0165	0.0228	0.0289
$Co^{3+}$	0.0931	0.0739	0.0586	0.0468	0.0377
$Fe^{3+}$	0.2816	0.2483	0.2219	0.2029	0.1914
$\mu_{BT}$ ( $\mu_B$ per formula)	7.6142	7.2385	6.8574	6.4745	6.0925
$\mu_{AT}$ ( $\mu_B$ per formula)	4.2909	4.2040	4.1225	4.0427	3.9621
$\mu_C$ ( $\mu_B$ per formula)	3.3233	3.0345	2.7349	2.4318	2.1303

Table 5 Cation distributions obtained by fitting the dependence of the magnetic moments in the samples  $Ti_xMn_{1-x}Fe_2O_4$  on  $x$ . The parameters  $V_{BA}(Ti^{2+})$ ,  $V_{BA}(Mn^{2+})$ , and  $V_{BA}(Fe^{2+})$  are the heights of the potential barriers that must be transmitted through by the  $Ti^{2+}$ ,  $Mn^{2+}$ , and  $Fe^{2+}$  ions when moving from the [B] sites to the (A) sites during thermal treatment of the samples;  $N_3$  is the total average number of trivalent cations per formula unit;  $\mu_{AT}$  and  $\mu_{BT}$  are the 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

$x$	0.0	0.1	0.2	0.3
$N_3$	0.8994	0.9373	0.9753	1.0132
$V_{BA}(Ti^{2+})$ (eV)	0.8960	1.0200	1.0800	1.1400
$V_{BA}(Mn^{2+})$ (eV)	1.1348	1.2057	1.2766	1.3476
$V_{BA}(Fe^{2+})$ (eV)	0.9708	1.0315	1.0921	1.1528
<b>A sites</b>				
$Ti^{3+}$	0.0000	0.0042	0.0090	0.0145
$Mn^{3+}$	0.0872	0.0847	0.0808	0.0755
$Fe^{3+}$	0.3319	0.3579	0.3840	0.4101
$Ti^{2+}$	0.0000	0.0104	0.0200	0.0290
$Mn^{2+}$	0.1789	0.1543	0.1312	0.1097
$Fe^{2+}$	0.4019	0.3885	0.3749	0.3612
<b>B sites</b>				
$Ti^{2+}$	0.0000	0.0795	0.1585	0.2371
$Mn^{2+}$	0.6225	0.5566	0.4911	0.4262
$Fe^{2+}$	0.8972	0.8734	0.8489	0.8235
$Ti^{3+}$	0.0000	0.0059	0.0124	0.0194
$Mn^{3+}$	0.1114	0.1044	0.0969	0.0885
$Fe^{3+}$	0.3689	0.3802	0.3922	0.4052
$\mu_{BT}$ ( $\mu_B$ per formula)	8.1005	7.5945	7.0953	6.6036
$\mu_{AT}$ ( $\mu_B$ per formula)	3.8129	3.7513	3.7033	3.6690
$\mu_C$ ( $\mu_B$ per formula)	4.2876	3.8433	3.3921	2.9347



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.

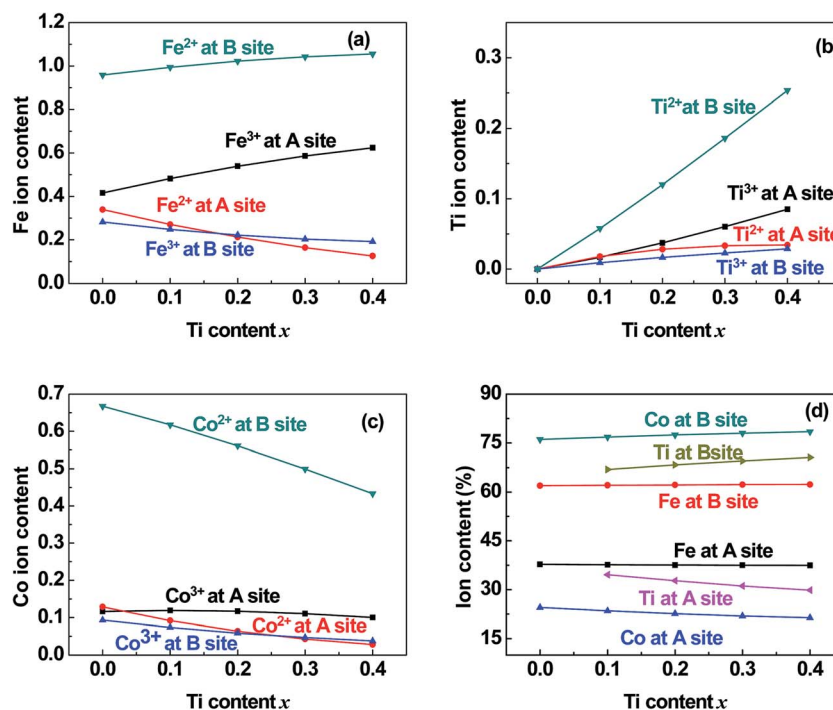


Fig. 6 Distribution of (a) Fe, (b) Ti, and (c) Co cations and (d) the total content percentages of different valence cations at the (A) and [B] sites in samples of  $\text{Ti}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  ( $0.0 \leq x \leq 0.4$ ).

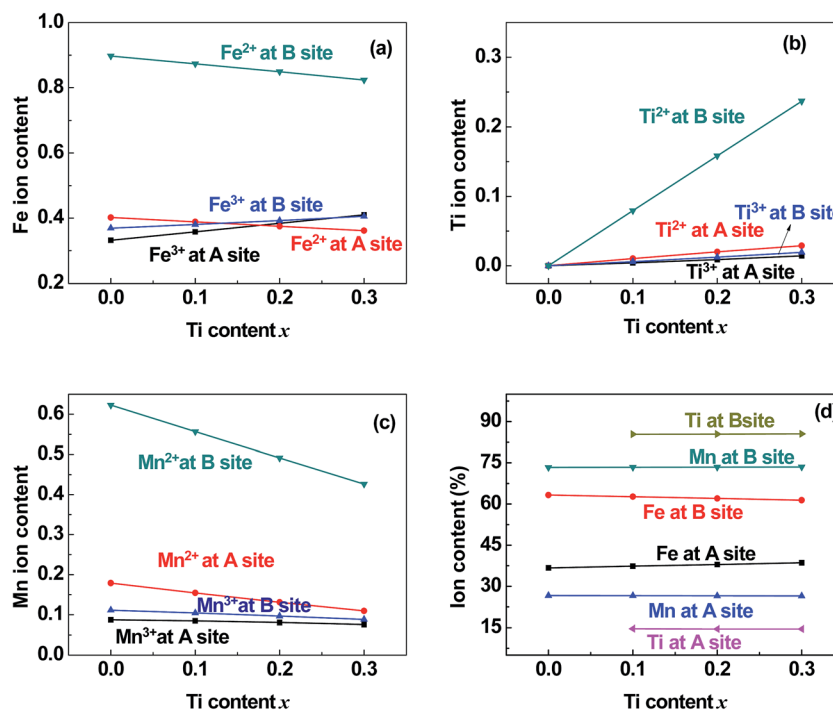


Fig. 7 Distribution of (a) Fe, (b) Ti, and (c) Mn cations and (d) the total content percentages of different valence cations at the (A) and [B] sites in samples of  $\text{Ti}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$  ( $0.0 \leq x \leq 0.3$ ).



## 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: $c_v$ and $V_{BA}$

During the fitting process, we determined that the potential barrier shape-correcting constant  $c_v$  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  $c_v = 1.0$  for other cation–anion pairs.

The  $Ti^{2+}$  ions must transmit through 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  $V_{BA}(Fe^{2+})$ ,  $V_{BA}(Co^{2+})$ , 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.<sup>26</sup> Therefore, the conventional view<sup>12–16</sup> 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  $Ni_{0.68}Fe_{2.32}O_4$ .<sup>18</sup>

(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:<sup>12–16</sup> Kale *et al.* concluded that 71% of Ti cations entered the (A) sites in  $Ti_{0.7}Ni_{1.7}Fe_{0.6}O_4$ ,<sup>16</sup> while other authors assumed that all of the Ti ions entered the [B] sites of the spinel ferrite samples.<sup>12–15</sup>

### 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.*<sup>30</sup> for  $Co_{1-x}Cr_xFe_2O_4$ . This result is also close to that reported by Wakabayashi *et al.* for a  $CoFe_2O_4$  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.<sup>38</sup>

(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  $Co_{1-x}Cr_xFe_2O_4$ .<sup>30</sup>

### 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.*<sup>20</sup>

### 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  $MnFe_2O_4$ , 1.09, is higher than that for  $CoFe_2O_4$ , 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  $MnFe_2O_4$  ( $CoFe_2O_4$ ).

## 6 Conclusions

The single-phase spinel ferrites  $Ti_xCo_{1-x}Fe_2O_4$  ( $0.0 \leq x \leq 0.4$ ) and  $Ti_xMn_{1-x}Fe_2O_4$  ( $0.0 \leq x \leq 0.3$ ) 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  $\mu_{exp}$  of the two series of samples, measured at 10 K, decreased approximately linearly with increasing  $x$ .

The dependence of  $\mu_{exp}$  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  $n_d \leq 4$ ) coupled antiferromagnetically with other cations ( $n_d \geq 5$ ) whenever they were at the (A) or [B] sublattice.





## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work is supported by the National Natural Science Foundation of China (NSF-11174069), the Natural Science Foundation of Hebei Province (A2015205111), the Key item Science Foundation of Hebei Province (Grant No. 16961106D), and the Young scholar Science Foundation of the Education Department of Hebei Province (QN2016015).

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