The valence and site occupancy of substituting metals in magnetite spinel structure \( \text{Fe}_{3-x}\text{M}_x\text{O}_4 \) (\( M = \text{Cr}, \text{Mn}, \text{Co} \) and \( \text{Ni} \)) and their influence on thermal stability: An XANES and TG-DSC investigation

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ABSTRACT

Four series of substituted magnetite \( \text{Fe}_{3-x}\text{M}_x\text{O}_4 \) \( M = \text{Cr}, \text{Mn}, \text{Co} \) and \( \text{Ni} \) were characterized by X-ray diffraction (XRD), X-ray absorption near-edge structure (XANES) spectroscopy, and thermogravimetry and differential thermal analysis (TG-DSC). XRD patterns confirmed the formation of samples with the spinel structure. XANES showed the valence and site occupancy of the substituting cations. Cr cations are in the valence of \( +3 \) and occupy the octahedral sites. The valences of Mn cation are \( +2 \) and \( +3 \). Mn\(^{3+}\) and Mn\(^{4+}\) cations preferentially entered the tetrahedral and octahedral sites, respectively. Both Co and Ni cations have a valence of \( +2 \) and mainly occupy the octahedral sites. The introduction of Cr and Ni cations obviously increases the amount of superficial hydroxyl groups. The incorporation of Mn, Co and Ni enhances the oxidation temperature of magnetite. All the four kinds of substituting cations in this study increase the temperature of phase transformation from maghemite (\( \gamma\text{-Fe}_2\text{O}_3 \)) to hematite (\( \alpha\text{-Fe}_2\text{O}_3 \)). The mechanism of substitution changing the temperatures of oxidation and phase transformation was also discussed.

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1. Introduction

Iron cations \( (\text{Fe}^{2+}/\text{Fe}^{3+}) \) in magnetite \( (\text{Fe}_2\text{O}_4) \) are usually isomorphically substituted by divalent \((\text{Co}, \text{Ni}, \text{Zn}, \text{Cu}, \text{Mn}, \text{etc.})\), trivalent \((\text{Al}, \text{V}, \text{Cr}, \text{etc.})\) and tetravalent \((\text{Ti})\) cations while maintaining the spinel structure \[1\]. Transition metal substituted magnetite has been proved as a promising material in various applications, e.g., catalysis, electromagnetism and thermoelectricity \[2–5\]. The physical and chemical properties (e.g., electrical resistance, magnetic property and catalytic activity) of substituted magnetite strongly depend on the nature of substituting cations in the spinel structure, their valences and distribution over the sites \[6–8\]. For instance, metal substitution (e.g., Cr, Co, Mn, Ni) in magnetite produces systematic variation in magnetic properties, e.g., saturation magnetization, the Curie temperature change, coercivity and electrical resistivity changes \[9\]. The introduction of Co\(^{2+}\), Mn\(^{2+}\), V\(^{3+}\) and Ti\(^{4+}\) in the spinel structure remarkably increases the catalytic activity of magnetite \[10–12\] whereas Ni\(^{2+}\) shows an inhibitory effect \[10\]. Co\(^{2+}\) improves the catalytic activity of magnetite by initiating \( \text{H}_2\text{O}_2 \) decomposition to produce \( \cdot \text{OH} \) (Eq. (1)), while Co\(^{3+}\) is thermodynamically unfavorable for this process. But for Ni\(^{2+}\), it does not participate in the heterogeneous Fenton reaction, because only Ni\(^{2+}\) species are stable and cannot initiate \( \cdot \text{OH} \) generation. The octahedral sites are almost exclusively exposed at the surface of the crystallite and the catalytic activity is mainly related to the octahedral cations \[13\].

\[
\text{Co}^{2+}_{\text{surf}} + \text{H}_2\text{O}_2 \rightarrow \text{Co}^{3+}_{\text{surf}} + \text{OH}^- + \cdot \text{OH} \\
(1)
\]

The experimental determination of the distribution of cations over the spinel structure and their oxidation states is an interesting challenge, though a number of conventional methods have been used to characterize oxidation states and coordination geometries. It is the main demerit that these methods are restricted to certain elements, not element specific or not possible to perform under in situ conditions. For example, electron spin resonance (ESR) spectroscopy is an established method to detect ions having unpaired electrons, but not their counterparts with paired electrons \[14\].
Thermogravimetry is a useful method to measure oxygen loss or gain of crystal structure under heating, however, it is not element specific, i.e., it is unknown which of several ions is oxidized or reduced under heat treatment. Also, X-ray photoelectron spectroscopy (XPS) just focuses on the surface chemical structure. X-ray diffraction (XRD) requires crystal structures or at least a certain ordering of the basic building blocks. But if the sizes of the cations are very similar, a distinction between them is extremely complicated or even impossible. Fourier transform infrared spectroscopy (FTIR) and Mössbauer spectroscopy have also been utilized in relative researches [15,16], and they just provided the structural changes of iron, which would not reflect the occupancy of the substituting cations with enough precision. X-ray absorption near-edge spectroscopy (XANES) is a powerful technique that can be used to investigate all elements in crystals or amorphous structures and is element specific. It can provide information about the local geometry around the absorbing atom and its oxidation state [17,18].

Herein, XANES characterization was carried out to probe the valence and coordination environment of four substituting cations in magnetite. The obtained results can also help resolve an issue in dispute, i.e., the debate whether the substituting cations would exist as incorporated into the magnetite lattice or as its spinel metal oxide with magnetite as the oxide solvent, and since they are two main sources of incorporating cations in natural magnetite [19] and they cannot be easily differentiated by XRD characterization.

Thermal properties of magnetite are also quite important, because ferrite spinels, especially magnetite-like solid materials, are the most important ferrimagnetic materials for industrial applications, e.g., in data storage and as ferrofluids for use in heat transfer, computer system, and levitation of objects [20]. Although natural magnetite with isomorphic substitution is quite common, thermal properties changes of magnetite by substitution have still not received enough attention. Under air atmosphere, magnetite can be oxidized and transformed to maghemite (γ-Fe2O3) with no change in the spinel structure. At higher temperature, a topotactic transformation from γ-Fe2O3 to α-Fe2O3 occurs, which represents the stability limit of maghemite [21]. Actually, the temperatures of these two phase transformations are influenced by substitution to a high extent. Previous studies have revealed that Ti has a stabilization effect on the structure of magnetite and maghemite [11] while both Cr and Mn do not affect the temperature of phase transformation magnetite—maghemite [7,22]. On the other hand, Cr has a stabilization effect on the magnetite structure while Mn has a significantly negative effect [7,22]. Therefore, the influence of isomorphic substitution on the thermal stability of magnetite cannot be ignored, due to the universality of substitution in magnetite structure and high importance of thermal stability for its practical applications. Unfortunately, the magnetite samples reported in most of the previous studies were not prepared by the same method, resulting in that some conclusions are not comparable. This makes it difficult to make a comparison among the substituting metals in terms of their influence on the thermal stability of magnetite.

In this study, four candidates of transition metal substituted magnetite Fe3-xMxO4 (M = Cr, Mn, Co and Ni) were synthesized by a precipitation—oxidation method. XANES measurements were carried out to investigate the valences and occupying sites of substituting cations. And through thermogravimetry and differential thermal analysis (TG-DSC) measurements, a comparison among these substituting cations was made according to their effect on the thermal stability of magnetite. The mechanism of substitution-induced changes in the oxidized and phase transformation temperatures was also discussed. The obtained new insights can be of high importance to a better understanding of the structural and physico-chemical characteristics of magnetite and its industrial applications.

2. Experimental details

2.1. Preparation of Fe3-xMxO4 samples

All chemicals and reagents were of analytical grade. Fe3O4 was synthesized by a precipitation—oxidation method [23]. Suitable amount of ferrous sulfate was dissolved in an HCl solution (total metal cation concentration ≈ 0.90 mol L−1). 1.0 mL of hydradize was added to prevent the oxidation of ferrous ions, and the pH was set low enough (pH < 1) to prevent iron oxidation and hydroxide precipitation. This solution was heated to 90–100 °C. Equal volume of a solution containing 4.0 mol L−1 NaOH and 0.90 mol L−1 NaNO3 was added dropwise (10 mL min−1) into the heated iron solution and the reaction was maintained at 90 °C for 2 h, while stirring at a rate of 500 rpm. Then the solution was cooled to room temperature. It is necessary to emphasize that during the reaction, a N2 flux was passed through to prevent the oxidation of ferrous cations by air. The particles were then separated by centrifugation at 3500 rpm for 5 min and washed with boiling distilled water, followed by an additional centrifugation. After 3–4 washings, the particles were collected and dried in a vacuum oven at 100 °C for 24 h. The Fe3−xCrxO4, Fe3−xMnxO4, Fe3−xCoxO4 and Fe3−xNixO4 samples were prepared following the above-mentioned steps except dissolving a pre-calculated amount of CrCl3, MnSO4, CoCl2 and NiSO4, respectively, while preparing the initial acid solution. All the samples were ground and passed through a 200 mesh screen.

2.2. Characterization of Fe3−xMxO4 samples

The chemical composition of the prepared magnetite samples (Fe3−xMxO4) was obtained by chemical analyses. The determinations of Fe, Cr, Mn, and Ni contents in the synthetic samples were measured spectrophotometrically by the phenanthroline [24], I, 5 diphenylcarboxyhydrate [25], nitroso R salt [26], potassium periodate [27] and dimethylglyoxime [28] methods, respectively. All the samples were denoted as a chemical formula Fe3−xMxO4 (M = Fe, Cr, Mn, Co and Ni) and the value of x was obtained from the chemical analysis results.

X-ray diffraction (XRD) patterns were recorded between 10° and 80° (2θ) at a step of 1° min−1 using a Bruker D8 advance diffractometer with Cu Kα radiation (40 kV and 40 mA). The mean crystal size was determined by applying the Scherrer equation to the XRD patterns.

X-ray absorption near-edge structure (XANES) spectra, taken at the K-edge of substituting metals in Fe3−xMxO4 (M = Cr, Mn, Co and Ni), as well as in reference compounds, were collected at Shanghai Synchrotron Radiation Facility (SSRF), on the new Wiggler beamline BL14W1. The storage ring operating conditions were 3.5 GeV electron energy and 150–300 mA electron current. The used beam size at the sample position was about 200 × 200 μm2. A Si (111) double crystal monochromator was used in these experiments. The alignment of the monochromator set-up tended to drift slightly over time after the initial calibration of the energy. The spectrum of the metal reference foil of the respective measurement was therefore used to compensate for this drift in every sample spectrum. The energy resolution was about 1.2 eV at the Mn K-edge. XANES data for all samples were collected in the transmission mode. Data analyses were performed using IEFIT software package. All the spectra have been normalized to eliminate the influence of the target element content.

Thermogravimetric and differential scanning calorimetry (TG-DSC) analysis was synchronously performed on a Netzsch STA 409 PC Instrument. Pre-weighed finely ground sample (20 mg) was heated in a corundum crucible from 30 to 1000 °C at a heating rate of
of 10 °C min⁻¹ under high pure N₂ or dry air atmosphere (60 cm³ min⁻¹). All data analyses were performed using NETZSCH Proteus Thermal Analysis software.

3. Results and discussion

3.1. Chemical analyses and XRD

From the chemical analysis results (Table 1), it can be seen that the content proportion between substituting metal and iron increases with the content increment of Cr, Mn, Co and Ni, respectively, indicating the substitution of these metals for iron. The chemical formulae of these prepared samples calculated from the chemical analyses results are also shown in Table 1.

X-ray diffraction patterns of Fe₃₋ₓCrₓO₄ (Fig. 1) and other substituted magnetite samples (not shown) correspond to the standard card of magnetite (JCPDS: 19-0629) [29], indicating that all the prepared samples have spinel structure and the introduction of these metal cations does not obviously change the spinel structure of magnetite.

3.2. Valence of substituting metals

In this study, XANES characterization was carried out to probe the valence of the substituting cations in the synthetic samples. Generally, the energy positions of the XANES spectra depend on the binding energy of the absorbing atom, and hence on the oxidation state, but also on other parameters, such as the nature and number of nearest neighbors [30]. A linear relation between the edge shift and the valence state has been established for several cations in samples with the nearest neighbors of the same chemical species. Furthermore, the edge shift can be determined in a straightforward way only for analogical edge profiles. Different environments of the cation, most notably with different site symmetries, result in different K-edge profiles. In such cases, shifts of separate edge or absorption edge features have been proposed to replace the edge shift [31]. Based on this principle, the XANES spectra in this work were evaluated to investigate the valence of substituting metals in the synthetic samples, by comparing the spectra of the samples with each other, and with the spectra of reference compounds. The reference compounds used in the study were metal oxides with ions in single or mixed valence, and spinel standards. The absorption edge is defined as the maximum of derivative at the absorption edge.

Fig. 2 shows the normalized Cr K-edge XANES spectra of Fe₃₋ₓCrₓO₄ and chromium reference compounds. For Cr⁰ in Co foil, its absorption K-edge (Eedge) is at 5989.2 eV, with an obvious shoulder at 5994.6 eV. For Cr³⁺ in Cr₂O₃, its XANES spectrum shows an absorption edge at 5998.5 eV with a weak pre-edge peak (Epre-edge) at 5987.7 eV. For Cr⁶⁺ in CrO₃, its absorption edge locates at 6007.2 eV, followed by a strong pre-edge peak at 5993.7 eV. Their energy positions of absorption edge shift to higher energy values with the increasing valence [32].

<table>
<thead>
<tr>
<th>Table 1 Chemical analyses, crystal size and chemical formula for Cr, Mn, Co and Ni substituted magnetite samples.</th>
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<tbody>
<tr>
<td>Chemical analyses M∕Fe</td>
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<tr>
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</tr>
<tr>
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<tr>
<td>Cr₀.₃₃</td>
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<td>Ni₀.₇₁</td>
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<td>Ni₀.₹₄</td>
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</table>

* M: Cr, Mn, Co or Ni.

Fig. 1. XRD patterns for Fe₃₋ₓCrₓO₄.

Fig. 2. Cr K-edge XANES spectra of Cr foil, Cr₂O₃, FeCr₂O₄ and Fe₃₋ₓCrₓO₄.
octahedral Cr$^{3+}$ in normal spinel FeCr$_2$O$_4$, its absorption edge position lies at 6003.5 eV with a pre-edge peak at 5987.8 eV and a weak shoulder around 6008.2 eV. The absorption edge position is close to that of Cr$^{3+}$ in Cr$_2$O$_3$. For all Cr cations in Fe$_3$-$x$Cr$_x$O$_4$, their absorption K-edges are at 6000.7 eV with pre-edge peaks at 5990.2 eV. The K-edge positions are also quite close to those of Fe$^{3+}$ cations in Cr$_2$O$_3$ and FeCr$_2$O$_4$, but far from those of Cr$_2$O$_3$ and Cr metal. Moreover, the peak profiles of Fe$_3$-$x$Cr$_x$O$_4$ are also identical to that of spinel FeCr$_2$O$_4$ containing octahedral Cr$^{3+}$. These two evidences indicate that Cr cations in synthetic magnetites are mainly Cr$^{3+}$.

In the case of manganese samples, four reference compounds Mn foil, MnO, Mn$_2$O$_3$ and MnO$_2$ having manganese in the valence of 0, +2, +3 and +4, respectively, were measured (Fig. 3). For Mn foil, the absorption edge of Mn atoms locates at 6539.1 eV, with an obvious shoulder at 6542.4 eV. For MnO, its absorption K-edge appears at 6544.0 eV, with a quite weak pre-edge peak observed at 6540.6 eV. For Mn$_2$O$_3$, the absorption edge locates at 6548.4 eV, with a broad pre-edge peak at 6540.4 eV. For pyrolusite MnO$_2$, the absorption edge lies at 6551.7 eV, with a strong pre-edge peak at 6542.4 eV. The absorption edges of manganese oxides shift to higher energy positions with the increment of manganese valence. For spinel Mn$_3$O$_4$ with Mn$^{2+}$ cations at the tetrahedral sites and Mn$^{3+}$ at the octahedral sites, manganese ions have a mean valence of +2.67. Its absorption edge position at 6547.1 eV is between MnO and Mn$_2$O$_3$, but closer to Mn$_2$O$_3$. For MnFe$_2$O$_4$, Fe$^{2+}$ and Mn$^{3+}$ are preferentially located in the octahedral sites while Mn$^{2+}$ occupies the tetrahedral sites [33]. Its manganese ions have a mixed valence of +2 and +3, and the K-edge at 6546.8 eV shifts to higher energy, compared to that of MnO, but lower than that of Mn$_2$O$_3$. For Fe$_{3-x}$Mn$_x$O$_4$, the absorption K-edges locate at 6546.7 eV, with weak but obvious pre-edge peaks at 6540.4 eV. A shoulder peak is also clearly observed at 6551.8 eV. The absorption K-edge positions and peak profiles of Fe$_{3-x}$Mn$_x$O$_4$ are respectively close to MnFe$_2$O$_4$ and Mn$_3$O$_4$, but quite different from MnO and Mn$_2$O$_3$, illustrating that manganese cations in synthetic samples also have a mixed valence of +2 and +3.

Fig. 4 exhibits the normalized Co K-edge XANES of Fe$_{3-x}$Co$_x$O$_4$ and Co reference compounds. For Co foil, an obvious shoulder peak appears at 7713.8 V and the absorption K-edge is at 7709.1 eV. For CoO where Co$^{2+}$ is six-fold coordinated by O$^{2-}$ ions, the absorption K-edge with a weak shoulder peak at 7725.1 eV locates at 7718.2 eV. For Co$_3$O$_4$, its very weak pre-edge peak appears at 7709.7 eV, and the absorption K-edge is at 7724.7 V, companied with a shoulder peak at 7723.7 eV. For Co reference compounds (e.g., Co foil, CoO and Co$_2$O$_3$), a shift of K-edge position with the valence increase can also be observed (Fig. 4). In case of Co$_3$O$_4$ where Co$^{3+}$ is six-fold and Co$^{2+}$ four-fold coordinated by O$^{2-}$, its board pre-edge is at 7709.7 eV, and the k-edge is obvious at 7723.2 eV with a shoulder peak 7728.0 eV. The absorption edge of Co$_3$O$_4$ is between CoO and Co$_2$O$_3$, but closer to Co$_2$O$_3$. For CoFe$_2$O$_4$ with inverse spinel structure, where Co$^{3+}$ occupy the octahedral sites [34,35], its absorption edge at 7718.0 eV is close to that of CoO. For Co cations in Fe$_3$-$x$Co$_x$O$_4$, its absorption K-edge (7717.9 eV) and peak profile are identical to those of CoFe$_2$O$_4$, but far from Co$_3$O$_4$ and Co$_2$O$_3$. With the cobalt content increase, the absorption edge peak profiles of Fe$_{3-x}$Co$_x$O$_4$ show no obvious changes, revealing that the valence of Co cations in the magnetite samples is mainly +2.

In the case of nickel-contained samples, four reference compounds, i.e., Ni foil, NiO, Ni$_2$O$_3$ and NiFe$_2$O$_4$ were used. Both NiO and inverse spinel NiFe$_2$O$_4$ contain octahedral Ni$^{2+}$ [36], and their K-edges are very close as shown in Fig. 5. For Ni$_2$O$_3$, its energy position of absorption edge is higher than those of NiO and NiFe$_2$O$_4$ [37]. For Fe$_{3-x}$Ni$_x$O$_4$ samples, their K-edge positions and shape are quite consistent with those of NiFe$_2$O$_4$, respectively, and the increase of substituting extent does not change the peak profile of Fe$_{3-x}$Ni$_x$O$_4$, indicating that Ni cations exist in the synthetic samples mainly as Ni$^{2+}$.

![Fig. 3. Mn K-edge XANES spectra of Mn foil, MnO, Mn$_2$O$_3$, MnO$_2$, Mn$_3$O$_4$ and Fe$_{3-x}$Mn$_x$O$_4$.](image1)

![Fig. 4. Co K-edge XANES spectra of Co foil, CoO, Co$_2$O$_3$, Co$_3$O$_4$, Fe$_2$CoO$_4$ and Fe$_{3-x}$Co$_x$O$_4$.](image2)
Obviously stronger than that of octahedral one, ascribed to its low symmetry. But the intensity change should also vary with the degree of distortion from centrosymmetry in octahedral site [42].

For Cr foil, Cr atom has a cubic symmetry with eight Cr atoms as the nearest coordinated atoms \((R_{Cr,Cr} = 0.249\, \text{nm})\), its XANES spectrum does not show any pre-edge peak (Fig. 2). For CrO\(_2\), Cr atom occupies a distorted octahedral site, with three oxygen atoms as the nearest coordination \((R_{Cr-O} = 0.196\, \text{nm})\) and other three oxygen atoms as the next nearest coordination \((R_{Cr-O} = 0.211\, \text{nm})\) [30], and its XANES spectrum shows a weak pre-edge peak. For CrO\(_3\), Cr atom occupies a distorted tetrahedral site, with two oxygen atoms as the nearest coordination \((R_{Cr-O} = 0.158\, \text{nm})\) and other two oxygen atoms as the next nearest coordination \((R_{Cr-O} = 0.175\, \text{nm})\), and a strong pre-edge peak can be observed. In the case of chromite \((\text{FeCr}_2\text{O}_4)\) with normal spinel structure [43], Cr\(^{3+}\) cation occupies a distorted octahedral site and its pre-edge peak is quite weak. The observed pre-edge peaks of Cr\(^{3+}\) in the synthetic samples are quite weak, indicating that Cr\(^{3+}\) should mainly occupy the octahedral sites rather than tetrahedral ones. The weak pre-edge is related to the slight octahedral distortion, resulted from the radius difference between Cr\(^{3+}\) (61 pm) and Fe\(^{3+}\) (65 pm). Moreover, the XANES spectra of Fe\(_3\)\(_2\)Cr\(_2\)O\(_4\) are different from those of Cr\(_2\)O\(_3\) and Fe\(_3\)\(_2\)O\(_4\), suggesting that Cr cations hardly exist as Cr\(_2\)O\(_3\) or Fe\(_3\)\(_2\)O\(_4\), but occupy the octahedral sites in the inverse spinel structure (Fig. 6).

For Mn foil, Mn atom has a cubic symmetry with eight Mn atoms as the nearest coordinated atoms and does not show any pre-edge peak (Fig. 3). For MnO, Mn atom has an octahedral symmetry with six oxygen atoms as the nearest coordination \((R_{Mn-O} = 0.222\, \text{nm})\) and it shows a weak pre-edge peak. For MnO\(_2\), Mn atom also occupies the octahedral site with six oxygen atoms as the nearest coordination \((R_{Mn-O} = 0.199\, \text{nm})\). Its XANES spectrum also shows a weak pre-edge peak. For pyrolusite MnO\(_2\), Mn atom has a distorted octahedral coordination, with two oxygen atoms as the nearest coordination \((R_{Mn-O} = 0.188\, \text{nm})\) and other four oxygen atoms as the next nearest coordination \((R_{Mn-O} = 0.189\, \text{nm})\). Herein, Mn atoms in MnO and MnO\(_2\) have nearly regular octahedral symmetry, and their pre-edge peaks are rather weak, while Mn atoms in MnO\(_2\) have a distorted octahedral symmetry, and the XANES shows a relatively strong pre-edge peak. For Mn\(_3\)O\(_4\) with a normal spinel structure, where Mn\(^{2+}\) cations occupy the tetrahedral sites and Mn\(^{3+}\) occupy the octahedral sites [44]. Its XANES spectrum shows a broad pre-edge peak. In the case of manganese ferrite \((\text{MnFe}_2\text{O}_4)\), Fe\(^{3+}\) and Mn\(^{3+}\) are preferentially located in the octahedral sites while Mn\(^{2+}\) occupy the tetrahedral sites [33]. A pre-edge peak can be observed, due to its disordered structure. For Fe\(_3\)\(_2\)Mn\(_2\)O\(_4\), their XANES spectra show an obvious pre-edge peak at the same energy position. The

3.3. Occupying sites of substituting metals

Magnetite is a classical inverse spinel material, which has a ratio of 2:1 for octahedral to tetrahedral site occupancy with Fe ions. In the magnetite structure, Fe\(^{3+}\) shows a strong preference for the octahedral sites while Fe\(^{3+}\) occupy both the octahedral and tetrahedral sites. A number of elements can be incorporated into the magnetite structure by replacing iron ions. It has been proved that the cation with radius about 18% higher or lower than that of high magnetite structure by replacing iron ions. It has been proved that hedral sites. A number of elements can be incorporated into the octahedral sites while Fe\(^{3+}\) Ionic radius (pm) of the cations measured in this study.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
<th>Co</th>
<th>Ni</th>
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<tbody>
<tr>
<td>Valence</td>
<td>+2</td>
<td>+2</td>
<td>+2</td>
<td>+2</td>
<td>+2</td>
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\(^4\text{CN}^a\) coordination number.  
\(^5\text{HS}^b\) high spin.  
\(^6\text{LS}^c\) low spin.

![Fig. 6. The spinel structure of Fe\(_3\)\(_2\)Cr\(_2\)O\(_4\).](image)
shape of these spectra is quite different from those of MnO, Mn₂O₃ and MnO₂, indicating that manganese cations should not exist as the above-mentioned metal oxides. Although manganese cations in Fe₃₋ₓMnₓO₄ have a mixed valence like those in MnFe₂O₄ and Mn₃O₄, but the XANES spectra of Fe₃₋ₓMnₓO₄ are more analogous to that of MnFe₂O₄ than that of Mn₃O₄, revealing that manganese cations are incorporated into magnetite structure, rather than exist as Mn₃O₄. Especially, when manganese content in Fe₃₋ₓMnₓO₄ increases, the shape of XANES gradually becomes identical to that of MnFe₂O₄, illustrating manganese cations have the same occupancy to those in MnFe₂O₄ and the structure becomes more disordered with the increase of manganese content [45].

The XANES spectra of Fe₃₋ₓCoₓO₄ show no obvious variations (Fig. 4) when the cobalt content is increased. The pre-edge peaks on the XANES spectra are quite weak and the shape is quite identical to those of CoO, Co₂O₃ and Co₃O₄, indicating that Co cations are impossible exist as its metal oxides, but occupy the octahedral sites of the spinel structure. The XANES of Fe₃₋ₓNiₓO₄ is quite similar to that of NiFe₂O₄, in which Ni²⁺ ions occupy octahedral sites and the Fe³⁺ ions are equally distributed between tetrahedral and octahedral sites. This suggests that Ni²⁺ mainly occupies the octahedral site. The low intensity of pre-edge feature also supports that Ni²⁺ in the samples is octahedrally coordinated (Fig. 5).

3.4. Surface hydroxyl

Under N₂ atmosphere, two mass losses can be seen on the TG curves for all the magnetite samples. The first mass loss, observed from ca. 30 to 120 °C, corresponds to the dehydration process [47], while the other one, from ca. 150 to 400 °C, is assigned to the dehydroxylation process [48]. Fig. 7 shows the mass loss during the dehydroxylation process (150–400 °C) for all the magnetite samples. It can be seen that the mass loss in the dehydroxylation process increases as the substituting level increases, especially for Cr and Ni series. This suggests that the incorporation of these metal cations increases the surface hydroxyl amount. The surface hydroxyl groups are functional groups of iron oxides due to its vital role in surface adsorption [49], photocatalysis [50] and surface acidity (Bronsted acid) [51]. Under dry conditions, surface Fe cations may be unsaturated in coordination. Because they carry unoccupied atomic orbital surface, Fe atoms are Lewis acids and react with Lewis bases. In aqueous systems, they can coordinate with hydroxyl or water molecules by sharing their ion electron pairs [38,52]. When the external cations substitute iron and enter the spinel structure, they also coordinate with hydroxyl by sharing the unoccupied atomic orbital and build M—OH. The over density of surface hydroxyl is ascribed to the crystal structure and extent of the development of different crystal faces [38]. From XANES results, the incorporation of substituting cations results in distortion of the magnetite lattice, leading to increasing adsorption of hydroxyl group [53]. Moreover, the increase of surface hydroxyl amount by substitution may also be due to the stronger Lewis acid activity of substituting cations than iron.

3.5. Phase transformation magnetite—maghemite

Under air atmosphere, magnetite would be oxidized. Below 300 °C, Fe²⁺ would be oxidized to produce the phase maghemite (γ-Fe₂O₃), with no change in the spinel structure. During the oxidation, the sample mass increases because oxygen is taken up with more vacancies engender [54]. Fig. 8 shows the DSC curves of Fe₃₋ₓCrₓO₄ under air atmosphere. For Fe₃O₄, an exothermic peak appears at 180 °C, related to the Fe²⁺ oxidation and the production of maghemite phase. For the series of Cr contained samples, this exothermic peak also appears with no distinct variation in temperature, just a bit higher than that of pure magnetite (Fig. 8). Another exothermic peak is observed at about 400 °C, related to the Cr³⁺ oxidation. This exothermic peak becomes stronger when the chromium content increases. Fig. 9 also shows the variation in ferrous oxidation temperature for Mn, Co and Ni substituted magnetite. The gradual increase in the content of these substituting cations leads to a rise in the oxidation temperature, especially for the samples containing Co, from 197 to 282 °C.

For Mn, Co and Ni series, as the substituting cation content increases, the temperature of oxidation gradually increases, indicating that these metal cations have a stabilization effect on the magnetite structure. However, for Cr series, the oxidation temperature does not change obviously. It has been pointed out that the temperature of magnetite oxidation mainly depends on morphological (sizes and shape of the particles) and chemical (purity and cation substitution) factors [54,55]. In this study, all the samples

![Fig. 7. Variations of mass loss during dehydroxylation with substituting metal content for Fe₃₋ₓMₓO₄ (M = Cr, Mn, Co and Ni).](image)

![Fig. 8. DSC curves of Fe₃₋ₓCrₓO₄ under air atmosphere (a: Fe₃O₄; b: Fe₂.82Cr₀.18O₄; c: Fe₂.67Cr₀.33O₄; d: Fe₂.53Cr₀.47O₄; e: Fe₂.32Cr₀.68O₄).](image)
were synthesized by the same method and the metal incorporation does not cause obvious changes in the crystallite size (Table 1). Therefore, the influence of particle size should not be the main factor and the changes of oxidation temperature should be ascribed to the nature of substituting cations. On the basis of previous studies, for the oxidation of magnetite to maghemite, the mechanism is based on the diffusion of \( \text{Fe}^{2+} \) cations from the bulk to the surface, where they form new layers with a spinel structure, in combination with \( \text{O}_2 \). The migration of a portion of Fe cations creates vacancies in the bulk [54,56]. The influence of the substitution on the thermal properties can be explained based on this mechanism. Generally, substitution of mono or divalent ions mainly replacing \( \text{Fe}^{3+} \) increases the stability of the spinel phase, ascribed to a decrease in the number of vacancies and an increase in the diffusion factor. From the XANES characterization, both Co and Ni are in the valence of +2 and Mn is partially in the valence of +2, so they increase the thermal stability of magnetite. But the substitution of \( \text{Fe}^{3+} \) by trivalent cations does not cause any variation in the number of vacancies during \( \text{Fe}^{3+} \) oxidation, which would not cause any changes in the oxidation temperature [54]. Therefore, for Cr series, whose Cr valence is +3 from the XANES results, no obvious increase of oxidation temperature is ascribed to the substitution of \( \text{Fe}^{3+} \) rather than \( \text{Fe}^{2+} \) by \( \text{Cr}^{3+} \).

### 3.6. Phase transformation maghemite–hematite

Between ca. 500 and 800 °C, a phase transformation from maghemite (\( \gamma\text{-Fe}_2\text{O}_3 \)) to hematite (\( \alpha\text{-Fe}_2\text{O}_3 \)) is expected to occur. Correspondingly, an exothermic peak would appear on the DSC curve. For \( \text{Fe}_2\text{O}_4 \), this exothermic peak is at 611 °C (Fig. 8) and the incorporation of \( \text{Cr}^{3+} \) in magnetite results in a gradual increase of this temperature, from 582 to 688 °C. The effect of Cr, Mn, Co and Ni substitution on this phase transformation temperature is shown in Fig. 10. Four kinds of substituting cations in this study can enhance the temperature of this phase transformation and have a stabilization effect on the maghemite structure, especially for Co and Ni substitution.

From previous research [54], the phase transformation from maghemite (\( \gamma\text{-Fe}_2\text{O}_3 \)) to hematite corresponds to a lattice rearrangement which takes place by relative sliding of the atomic layers involving the breaking of several Fe–O bonds. The incorporation of these substituting metals can stabilize the spinel structure, by building new bonds (M–O) with oxygen, which may strengthen the Fe–O bond during the lattice rearrangement. Moreover, the XANES spectra of substituted magnetites display weak but obvious pre-edge peaks (Figs. 2–5). The intensity of pre-edge peak varies with the coordination environment and reflects the coordination symmetry. The pre-edge peaks of substituted magnetites are weak but obvious, indicating that these substituting metals have occupied the octahedral sites but created some slight distortion of magnetite lattice, which may prevent the shifting of dislocation. It should be another reason for the increase in the temperature of phase transformation maghemite–hematite.

### 4. Conclusions

This study employed XANES as an effective tool to investigate the valences and site occupancies of substituting metal cations in magnetite. The presented results reveal that Cr cations in the valence of +3 occupy the octahedral sites. Mn cations are in the multi-valence of +2 and +3. Mn\(^{2+}\) and Mn\(^{3+}\) are preferentially located in the tetrahedral and octahedral sites, respectively. Both of Co and Ni cations are mainly in the valence of +2 and occupy the octahedral sites. The substitution of these metals results in an increase of the surface hydroxyl amount, especially for Cr and Ni. The temperature of ferrous oxidation to produce maghemite increases with the increment of Mn, Co and Ni content. Also, the temperature of phase transformation maghemite–hematite is increased by the substitution of Cr, Mn, Co and Ni. The obtained results will be benefit for relative studies on transition metal substituted magnetite and its future practical application in catalyst and heat transfer material.

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