The influence of substituting metals (Ti, V, Cr, Mn, Co and Ni) on the thermal stability of magnetite

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Abstract In this paper, a systematic study on the influence of substituting metals on the thermal stability of magnetite was carried out. Six series of substituted magnetite ($Fe_{3-x}M_xO_4$, M = Ti, V, Cr, Mn, Co and Ni) and Ti–V co-doped magnetite were prepared by a precipitation-oxidation method, followed by the characterization of X-ray diffraction (XRD), X-ray absorption near-edge structure (XANES) spectroscopy and thermogravimetry and differential scanning calorimetry (TG-DSC) analyses. XRD patterns confirmed the formation of samples with spinel structure and XANES probed the valence and site occupancy of the substituting ions. From the TG-DSC analysis results, the substitution of Ti^{4+}, Mn^{2+}, Co^{2+} and Ni^{2+} stabilizes the magnetite structure, while V^{3+} and Cr^{3+} do not show such an effect. For the thermal stability of maghemite, V^{3+} has a negative effect while the other studied ions show a positive effect. In Ti–V co-doped magnetites, the influence of Ti^{4+} and V^{3+} on the thermal

stability of magnetite is similar to the case of their single-metal-substituted magnetites. The mechanism about the thermal stability change of magnetite by metal substitution was also discussed. The obtained results will be of high importance for the industrial applications of magnetite.

Keywords Thermal stability · Magnetite · Substitution · Phase transformation · TG-DSC

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Introduction

Ferrite spinels, especially magnetite-like solid materials, are the most important ferrimagnetic materials for industrial applications [1], e.g., as high-density magnetic recording media [2], microwave devices [3], catalysts in selective catalytic reduction [4] and high temperature water–gas shift reaction [5], and ferrofluids in heat transfer [6]. Certainly for these applications, the thermal stability of magnetite is quite important. Under air atmosphere, magnetite can be oxidized and transformed to maghemite (γ-Fe_2O_3), corresponding to the oxidation of ferrous ions without changes of the spinel structure. At higher temperature, maghemite is transformed to hematite (α-Fe_2O_3) with lattice rearrangement, which represents the stability limit of the spinel structure [7]. Both these two occurrent temperatures of phase transformation can describe the thermal stability of magnetite.

For magnetite in nature, iron ions (Fe^{2+}/Fe^{3+}) are usually isomorphically substituted by divalent (Co, Ni, Zn, Cu, Mn, etc.), trivalent (Al, V, Cr, etc.) and tetravalent (Ti) cations while maintaining the spinel structure unchanged [8]. Some substituting metals can improve the industrial application of magnetite. For instance, the presence of Mn in spinel structure enhances the selective catalytic

reduction of NO with NH_3 over magnetite at low temperature (about 180 °C) [9]. V and Cr increase the catalytic activity of magnetite in high temperature water gas shift reaction [10, 11]. But these substituting ions also alter thermal stability of spinel structure [12–14], which may affect the performance of magnetite in these applications. Among those, Ti^{4+} has a stabilization effect on the structure of magnetite prepared by a precipitation-oxidation method, while both Cr^{3+} and Mn^{2+} do not affect the stability of magnetites that were synthesized by a co-precipitation and then thermal treatment routine. It was also found in these studies that both Ti^{4+} and Cr^{3+} have a stabilization effect on the maghemite structure, whereas Mn^{2+} has a significantly negative effect. Obviously, some of these substituting ions show prominent effects on the thermal property of magnetite, which makes it possible to tune the thermal stability of magnetite for specific applications through introducing some metal ions into the spinel structure. Unfortunately, the tested magnetite samples in most of the relative studies were not prepared by the same method [10, 12, 13, 15], resulting in difficulties in the comparison among the substituting metals in terms of their influence on the thermal stability of magnetite.
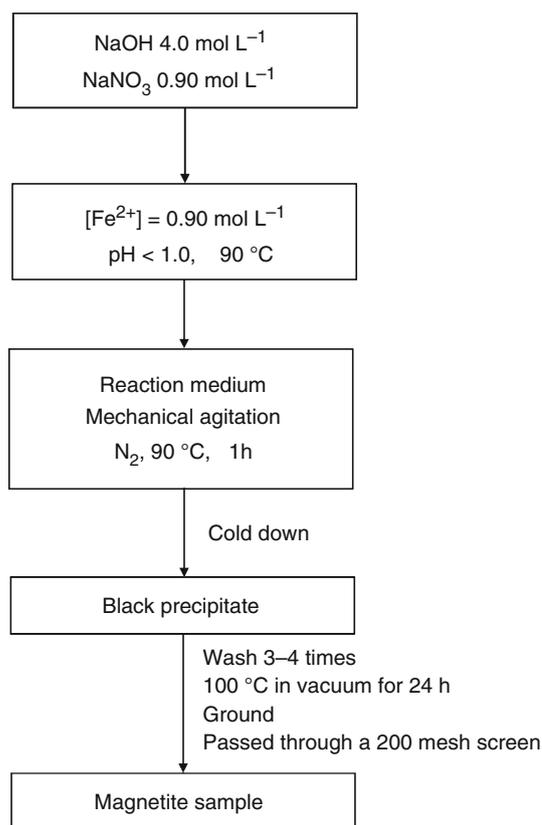
Although many studies have investigated the influence of substituting metals on the thermal stability of magnetite, most of them focused on single-metal-substituted magnetites [12, 15–17]. In fact, in most natural cases, more than two kinds of metals are simultaneously introduced into magnetite in geological processes [18]. The unknown issue about the variations in thermal stability for magnetites with two substituting cations obviously hinders the industrial applications of magnetite. For example, in Panxi region, Southwest China, vanadium titanomagnetite is a kind of widely distributed natural magnetite, in which the iron cations are simultaneously substituted by V^{3+} and Ti^{4+} [18, 19]. The individual effect of V^{3+} and Ti^{4+} on the thermal stability of their single-metal-substituted magnetites has been investigated in previous studies [12, 20]. However, until now it is still unclear how the thermal properties of magnetite change in the presence of both vanadium and titanium in the spinel structure.

In this study, six series of transition metal substituted magnetites $Fe_{3-x}M_xO_4$ (M = Ti, V, Cr, Mn, Co and Ni) and V–Ti co-doped magnetites were synthesized by a precipitation-oxidation method. Through thermogravimetry and differential scanning calorimetry (TG-DSC) analyses, a systematic comparison among these substituting ions was made in terms of their effects on the thermal stability of magnetite and maghemite. Also, the influence of Ti^{4+} and V^{3+} on the thermal properties of their co-doped magnetites was also investigated. The obtained new insights will be of high importance for the industrial applications of magnetite.

Materials and methods

Preparation of magnetite samples

All chemicals and reagents used in this study were of analytical grade. Magnetite samples were synthesized by a precipitation-oxidation routine [21, 22]. The synthesis pathway of Fe_3O_4 is presented in Scheme 1. The $Fe_{3-x}Ti_xO_4$, $Fe_{3-x}Cr_xO_4$, $Fe_{3-x}Mn_xO_4$, $Fe_{3-x}Co_xO_4$, and $Fe_{3-x}Ni_xO_4$ samples were prepared by following the steps in Scheme 1 except dissolving different amounts of $TiCl_4$, $CrCl_3$, $MnSO_4$, $CoCl_2$ and $NiSO_4$ with $FeSO_4$, respectively, in the preparation of the initial acid solution. The $Fe_{3-x}V_xO_4$ series was also synthesized by following the similar routine in Scheme 1 except dissolving different amounts of NH_4VO_3 with NaOH and $NaNO_3$ while preparing the initial alkaline solution. The preparation of vanadium and titanium co-doped magnetite was also achieved by following the steps in Scheme 1 except respectively dissolving different amounts of NH_4VO_3 with NaOH and $NaNO_3$ in alkaline solution and $TiCl_4$ with $FeSO_4$ in acid solution.

| NaOH 4.0 mol L^{-1} |
| NaNO$_3$ 0.90 mol L^{-1} |

↓

| $[Fe^{2+}]$ = 0.90 mol L^{-1} |
| pH < 1.0,   90 °C |

↓

| Reaction medium |
| Mechanical agitation |
| N$_2$, 90 °C, 1h |

↓ Cold down

| Black precipitate |

↓ Wash 3–4 times
100 °C in vacuum for 24 h
Ground
Passed through a 200 mesh screen

| Magnetite sample |

Scheme 1 Flow chart of Fe_3O_4 preparation

Structure characterization of magnetite samples

The contents of Fe, Ti, V, Cr, Co, Mn, and Ni in the synthetic samples were measured spectrophotometrically by the phenanthroline [23], diantipyrylmethane [24], tungstovanadophosphoric acid [25], 1, 5 diphenylcarbohydrazide [26], nitroso R salt [27], potassium periodate [28], and dimethyglyoxime [29] methods, respectively. The chemical formulae of synthetic samples were obtained based on 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).

X-ray absorption near-edge structure (XANES) spectra, taken at the K-edge of the objective substituting metals in magnetite samples, 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 μm^2. A Si (111) double crystal monochromator was used in these experiments. XANES data for all the samples were collected in the transmission mode. Data analyses were performed using IFEFFIT software package. All the spectra have been normalized to eliminate the influence of the target element content.

Thermal analyses of magnetite samples

Thermogravimetric and TG-DSC analysis was synchronously performed on a Netzsch STA 409 PC Instrument. Pre-weighed finely ground sample of about 20 mg was heated in a corundum crucible from 30 to 1,000 °C at a heating rate of 10 °C min^{-1} under dry air atmosphere (60 cm^3 min^{-1}). All data analyses were performed using NETZSCH Proteus Thermal Analysis software.

Results and discussion

Structure characterization of magnetite samples

From the chemical analysis results of the synthetic magnetite samples (not shown), the iron content decreases with the addition of Ti, V, Cr, Mn, Co or Ni, suggesting that these metals have replaced iron and existed in the magnetite structure.

The XRD patterns of $Fe_{3-x}Co_xO_4$ (Fig. 1), $Fe_{3-x}Ti_xO_4$ [12], $Fe_{3-x}V_xO_4$ [20], V–Ti co-doped magnetites [30] and other substituted magnetite samples (not shown) well correspond to the standard card of magnetite (JCPDS:
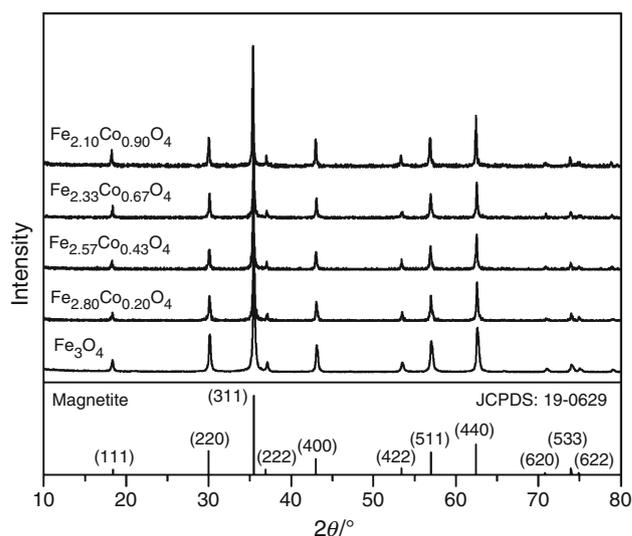

Fig. 1 XRD patterns for $Fe_{3-x}Co_xO_4$

19-0629), indicating that all the prepared samples have spinel structure and the introduction of these metals does not obviously change the spinel structure of magnetite.

The valence and occupying sites of substituting metals in magnetite structure were investigated by XANES characterization, due to the sensitivity of absorption edge position and pre-edge peak intensity to the valence and coordinated environment of substituting metals, respectively [31]. In general, the energy positions of the XANES spectra depend on the binding energy of the absorbing atom, and hence on the oxidation state [31]. 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 [32–34]. 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. Figure 2 shows the normalized Cr K-edge XANES spectra of $Fe_{3-x}Cr_xO_4$ and chromium reference compounds. For Cr^0 in Co foil, Cr^{3+} in Cr_2O_3 and Cr^{6+} in CrO_3, their energy positions of absorption edge are at 5989.2, 5998.5, and 6007.2 eV, respectively, shifting to higher energy values with the increasing valence [34]. And for octahedral Cr^{3+} in normal spinel $FeCr_2O_4$, its absorption edge position (6000.5 eV) is close to that of Cr^{3+} in Cr_2O_3. For all Cr cations in $Fe_{3-x}Cr_xO_4$, their K-edge positions (6000.7 eV) are also quite close to those of Cr^{3+} in Cr_2O_3 and $FeCr_2O_4$, but far from those of CrO_3 and Cr metal. Moreover, the peak profiles of $Fe_{3-x}Cr_xO_4$ are also identical to that of spinel $FeCr_2O_4$ containing octahedral Cr^{3+}. These two evidences indicate that Cr cations in synthetic magnetites are mainly Cr^{3+}. Based on the fact that the pre-edge peak related to tetrahedral site is
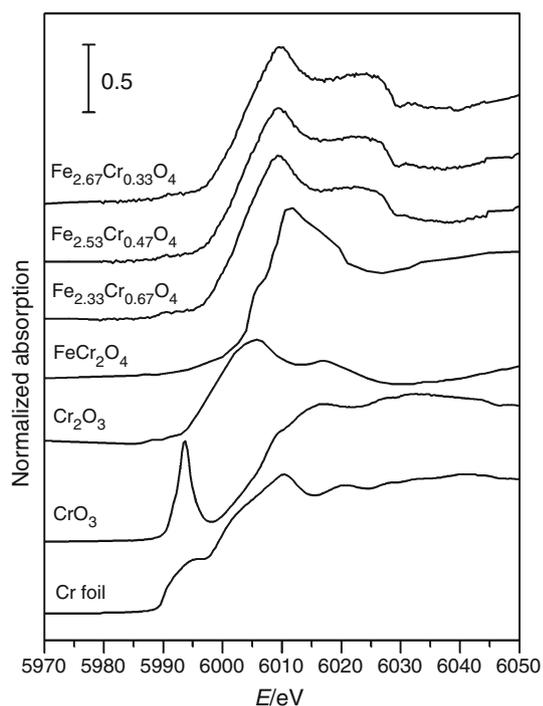
Fig. 2 The XANES spectra of $Fe_{3-x}Cr_xO_4$

Fig. 3 The XANES spectra of $Fe_{3-x}Mn_xO_4$

obviously stronger than that of octahedral one, ascribed to the low symmetry of tetrahedron, Cr^{3+} in $Fe_{3-x}Cr_xO_4$ should mainly occupy the octahedral sites rather than tetrahedral ones, due to their quite weak pre-edge peaks as observed. And similar peak profiles between $Fe_{3-x}Cr_xO_4$ and $FeCr_2O_4$ containing octahedral Cr^{3+} also confirm the octahedral occupancy of Cr in $Fe_{3-x}Cr_xO_4$ samples.

From the XANES characterization of other samples, Ti and V in the valence of +4 and +3, respectively, locate in octahedral sites, which is similar to the case of their co-doped magnetites. And both Co and Ni ions have a valence of +2 and mainly occupy the octahedral sites.

But in the case of $Fe_{3-x}Mn_xO_4$ samples, their XANES results (Fig. 3) look complicated. The Mn K-edge positions of Mn, MnO, Mn_2O_3 and MnO_2 are at 6539.1, 6544.0, 6548.4 and 6551.7 eV, respectively, shifting to higher values with the increasing valence [35]. The absorption K-edge positions (6546.7 eV) and peak profiles of $Fe_{3-x}Mn_xO_4$ are respectively close to those of $MnFe_2O_4$ (6546.8 eV) and Mn_3O_4 (6547.1 eV), but quite different from MnO, Mn_2O_3, and MnO_2, illustrating that Mn ions in synthetic samples have a mixed valence of +2 and +3. For $MnFe_2O_4$, Fe^{2+} and Mn^{3+} are preferentially located in the octahedral sites while Mn^{2+} occupy the tetrahedral sites [35]. Although Mn ions in $Fe_{3-x}Mn_xO_4$ have a mixed valence like those in $MnFe_2O_4$ and Mn_3O_4, but the XANES spectra of $Fe_{3-x}Mn_xO_4$ are more similar to that of $MnFe_2O_4$ than that of Mn_3O_4, revealing that Mn ions are incorporated into magnetite structure, rather than exist as
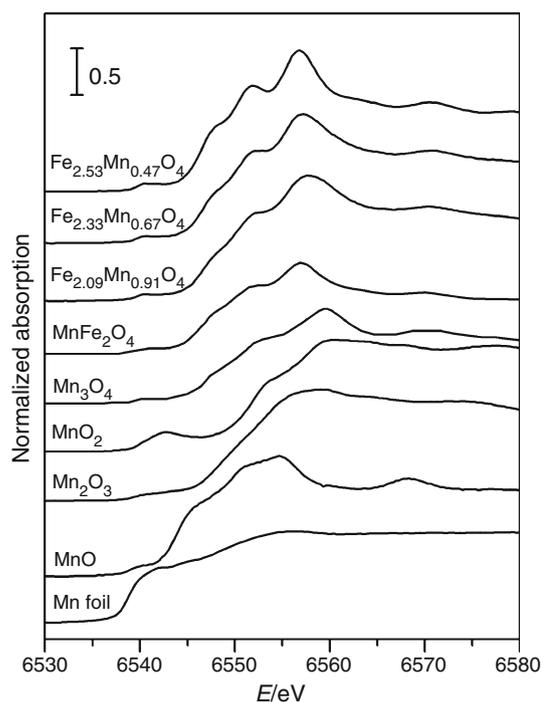
Mn_3O_4. Especially when Mn content in $Fe_{3-x}Mn_xO_4$ increases, the shape of XANES gradually becomes identical to that of $MnFe_2O_4$, illustrating Mn ions have the similar occupancy to those in $MnFe_2O_4$.

Temperature of phase transformation magnetite–maghemite

Figure 4 displays the TG-DSC curves of $Fe_{3-x}Co_xO_4$ under dry air. For Fe_3O_4, its TG curve shows a mass gain from ca. 150 to 300 °C, ascribed to the oxidation of Fe^{2+} to produce the phase maghemite γ-Fe_2O_3. Correspondingly, its DSC curve shows an exothermic peak at 180 °C. A mass loss observed from 300 °C up to 450 °C, accompanied with an endothermic peak at 406 °C, is related to the dehydroxylation process. After Co^{2+} introduction, the mass gain for Fe^{2+} oxidation obviously decreases, due to the substitution of Fe^{2+} by Co^{2+}. For sample $Fe_{2.10}Co_{0.90}O_4$ with the highest cobalt substitution level in this study, its TG curve even does not show any mass gain, because of the nearly complete replacement of Fe^{2+} by Co^{2+}. And the temperature of phase transformation magnetite-maghemite gradually increases from 180 to 287 °C, indicating that Co^{2+} substitution can improve the thermal stability of magnetite. The mass loss for dehydroxylation in 300–450 °C increases with the increment of Co content. Especially for sample $Fe_{2.10}Co_{0.90}O_4$ with the highest Cr substitution level, its mass loss is the highest among the $Fe_{3-x}Co_xO_4$ samples. It indicates that Co substitution increases the surface hydroxyl amount.

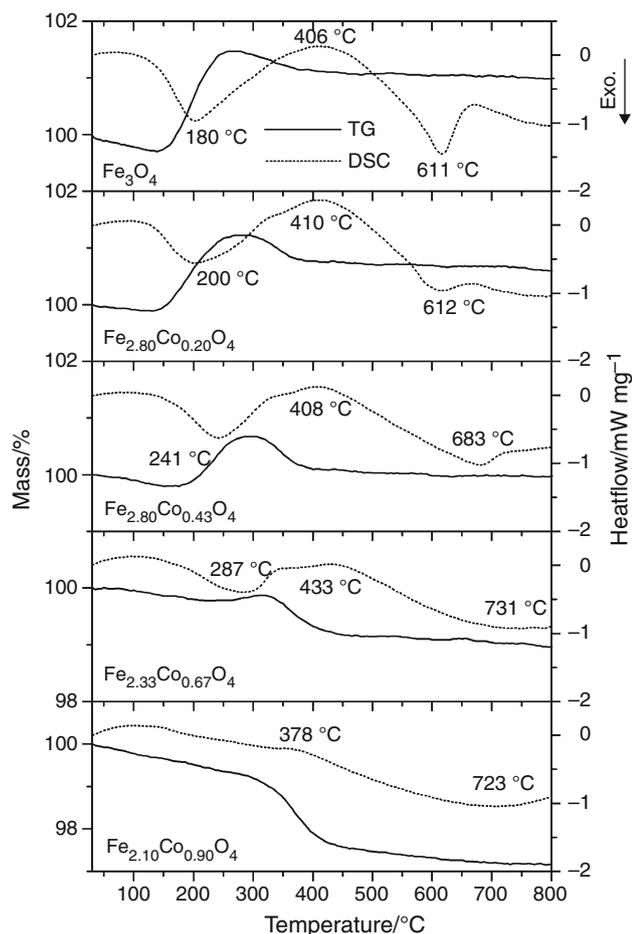**Fig. 4** TG-DSC curves of $Fe_{3-x}Co_xO_4$ ($0 \leq x \leq 0.90$)

Fig. 5 Variations in temperature of phase transformation **a** magnetite–maghemite and **b** maghemite–hematite with contents of Ti, V, Cr, Mn, Co and Ni

From the TG-DSC curves of other five series of $Fe_{3-x}M_xO_4$ (M = Ti, V, Cr, Mn and Ni) (not shown), their temperatures of phase transformation magnetite-maghemite also can be obtained (Fig. 5a). It can be seen that the phase transformation temperature is remarkably enhanced by the introduction of Ti, Mn, Co, and Ni, but not changed obviously by the substitution of V and Cr. The obtained results for effects of V, Cr, and Ni are consistent with the conclusions of studies made by Nohair et al. [36], Magalhaes et al. [13] and Guin et al. [37], respectively, but the Mn effect is contrary to that reported by Oliveira et al. [14]. From the XANES characterization, the valence of Ti is +4 and Co, Ni and partial Mn are in valence of +2 while V and Cr have a valence of +3. Obviously, substituting ions in valence of +2 and +4 can improve the thermal stability of magnetite, while ions in valence of +3 do not show a notable effect. On the basis of previous studies [16, 38], for the oxidation of magnetite to maghemite, the mechanism is based on the diffusion of Fe^{2+} cations from the bulk to the surface, where they form new layers with a spinel structure, in combination with O_2 (Online Resource 1). The migration of a portion of Fe cations creates
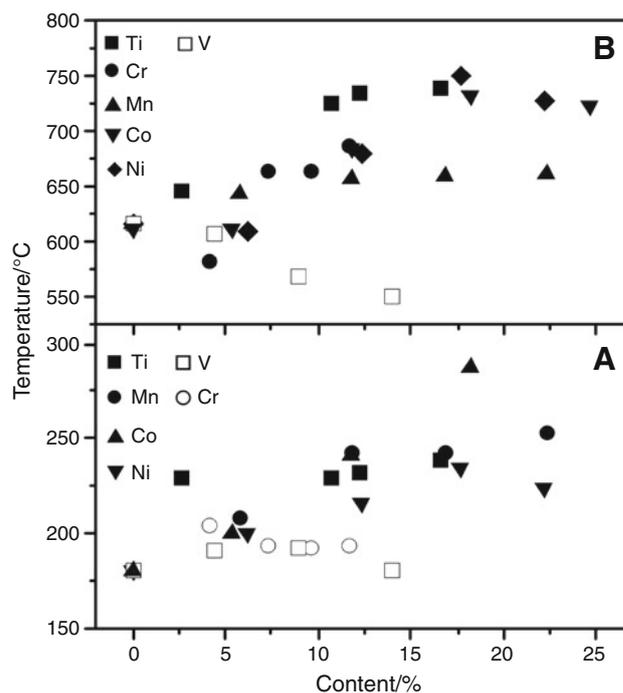
vacancies in the bulk. In this study, the influence of the investigated substituting ions on the thermal properties can be explained based on this mechanism. When metals in the valence of +2 replace Fe^{2+}, i.e., Mn^{2+}, Co^{2+} and Ni^{2+}, the reduce of Fe^{2+} content decreases the number of vacancies during Fe^{2+} migration, resulting in an increase in the diffusion factor and hence improvement in the thermal stability of magnetite. But the introduction of trivalent ions, i.e., V^{3+} and Cr^{3+}, which just substitute Fe^{3+} and do not change the Fe^{2+} content, would not cause any variation in the number of vacancies during Fe^{2+} oxidation. So they do not change the oxidation temperature. For Ti^{4+}, it should replace Fe^{3+} in the spinel structure and meanwhile, the same amount of Fe^{3+} is reduced to Fe^{2+} to keep electrovalent equilibrium. The increase of Fe^{2+} content should increase the vacancy number and decrease the phase transformation temperature. But it is very interesting in this study that Ti^{4+} has increased this temperature, and more investigation needs to be carried out to explain this phenomenon.

Temperature of phase transformation maghemite–hematite

For Fe_3O_4, at higher temperature, i.e., 611 °C, another exothermic peak appears without obvious mass change, ascribed to the phase transformation maghemite-hematite

(Fig. 4). After Co substitution, this phase transformation temperature significantly increases, from 611 to 723 °C, indicating Co^{2+} also has a stabilization effect on the maghemite structure. Figure 5b exhibits the temperature of phase transformation maghemite–hematite for the studied $Fe_{3-x}M_xO_4$. Only V^{3+} reduces this temperature and decreases the thermal stability of maghemite, while other five substituting ions, i.e., Ti, Cr, Mn, Co, and Ni, obviously increase the temperature and stabilize the spinel structure. The Cr effect on maghemite stability in this study is according to the study by Magalhaes et al. [13], but the Mn effect is different from the study by Oliveira et al. [14]. From previous research [16], the phase transformation from maghemite (γ-Fe_2O_3) to hematite (α-Fe_2O_3) corresponds to a lattice rearrangement which takes place by relative sliding of the atomic layers and breaking of several Fe–O bonds. So the effect of metal substitution on the thermal stability of maghemite can be explained by this mechanism. The incorporation of these substituting metals must build new bonds (M–O) with oxygen in the spinel structure, alter the strength of Fe–O bond and accordingly affect the stability of spinel structure during the lattice rearrangement. The comparison in bond strength between M–O and Fe–O bonds leads to their different effects on the thermal stability of maghemite.

Thermal behavior of V–Ti co-doped magnetite

In this study, Ti substitution increases the thermal stability of magnetite and maghemite while V shows different effect, which is obtained from their single-metal-substituted magnetites. But how they affect the magnetite stability, when both ions coexist in the spinel structure, has been yet an unclear but interesting topic. In this paper, this topic was attempted to investigate. Figure 6 shows the TG-DSC curves of V–Ti co-doped magnetite samples. Among these samples, the titanium content gradually decreases while that of vanadium accordingly increases, but iron content shows less variation. For sample $Fe_{2.68}V_{0.32}O_4$, its TG curve shows two mass gain in 150–250 °C and 250–450 °C, related to the oxidation of Fe^{2+} and V^{3+} [36], respectively. Correspondingly, its DSC curve shows two exothermic peaks, centered at 192 and 377 °C, respectively. The former temperature, ascribed to the Fe^{2+} oxidation, is close to that of Fe_3O_4, due to the fact that V^{3+} does not affect the thermal stability of magnetite. At the higher temperature of 525 °C, for the phase transformation maghemite–hematite, is obviously lower than that of Fe_3O_4. But for V–Ti co-doped magnetite, these three temperatures of exothermic peaks show obvious changes, with the increase of Ti content and meanwhile decrease of V content. The first exothermic temperature for Fe^{2+} oxidation, increases from 192 to 229 °C, indicating that Ti

substitution has a stabilization effect on the magnetite structure. For the second temperature for V^{3+} oxidation, its occurrent temperature does not change greatly. But its intensity gradually decreases and this peak even disappears for sample $Fe_{2.31}Ti_{0.69}O_4$, due to the decrease of vanadium content. The third temperature, for sample $Fe_{2.47}Ti_{0.40}V_{0.13}O_4$ and $Fe_{2.50}Ti_{0.42}V_{0.08}O_4$, increases with the increment of Ti content, but is still lower than that of Fe_3O_4, illustrating that V still has a negative effect on the thermal stability of maghemite structure, which is similar to the case of single-metal-substituted magnetite. But for sample $Fe_{2.43}Ti_{0.54}V_{0.03}O_4$ with higher Ti content, its phase transformation temperature is 627 °C, higher than that of Fe_3O_4. It is indicated that Ti still has a positive effect on
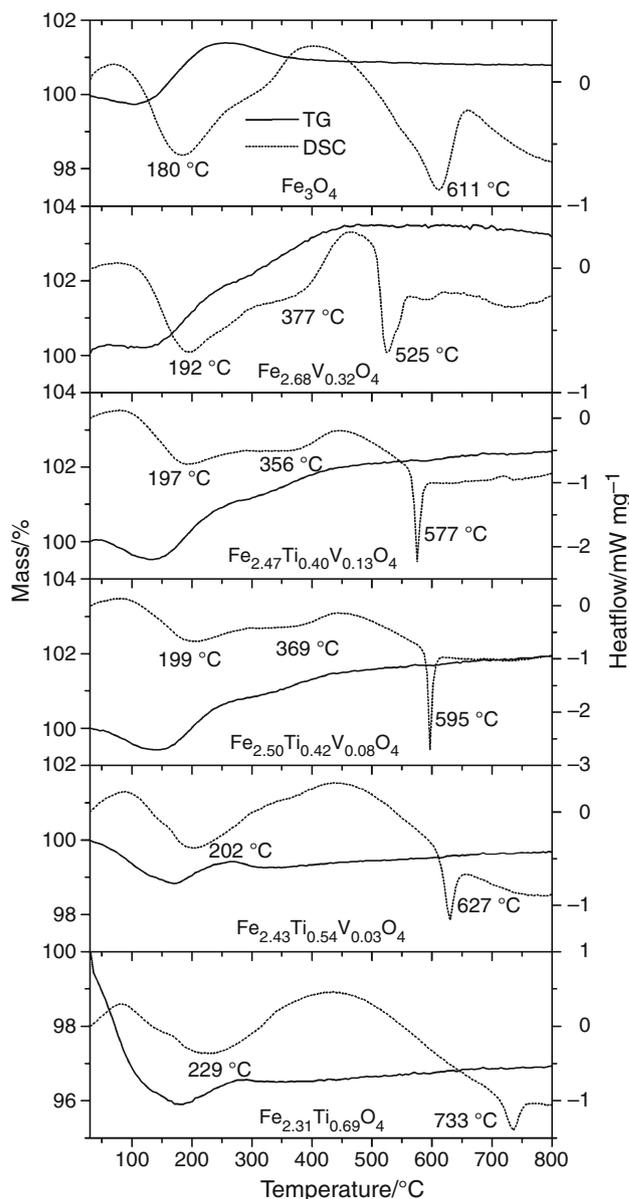

Fig. 6 TG-DSC curves of Ti–V co-doped magnetites

the stability of maghemite when accompanied with vanadium in the spinel structure. In short, in Ti–V co-doped magnetite, Ti increases the thermal stability of magnetite and maghemite while V does not affect the stability of magnetite but has a negative effect on maghemite, which is similar to the case of their single-metal-substituted magnetites. Therefore, the thermal stability of Ti–V co-doped magnetite can be tuned by the vanadium and titanium contents.

Conclusions

This study investigated the thermal stability of substituted magnetite $Fe_{3-x}M_xO_4$ (M = Ti, V, Cr, Mn, Co and Ni) and V–Ti co-doped magnetite. The thermal stability of magnetite is related to the valence of substituting metals. The studied cations in valence of +2 and +4 can improve the thermal stability of magnetite, while cations in valence of +3 do not show a notable effect. V^{3+} has a negative effect on the thermal stability of spinel structure while the other studied ions show a reverse effect. The influence of Ti and V on the thermal stability of their co-doped magnetite is not affected by the co-existent substituting ions. These obtained results will be benefit for the knowledge of thermal stability of magnetite and its industrial applications.

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