Study of electron transition energies between anions and cations in spinel ferrites using differential UV-vis absorption spectra

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ABSTRACT

It is very important to determine electron transition energies (E_{tr}) between anions and different cations in order to understand the electrical transport and magnetic properties of a material. Many authors have analyzed UV-vis absorption spectra using the curve $(\alpha h\nu)^2$ vs E , where α is the absorption coefficient and $E(=h\nu)$ is the photon energy. Such an approach can give only two band gap energies for spinel ferrites. In this paper, using differential UV-vis absorption spectra, $d\alpha/dE$ vs E , we have obtained electron transition energies (E_{tr}) between the anions and cations, Fe^{2+} and Fe^{3+} at the (A) and [B] sites and Ni^{2+} at the [B] sites for the (A)[B]₂O₄ spinel ferrite samples $Co_xNi_{0.7-x}Fe_{2.3}O_4$ ($0.0 \leq x \leq 0.3$), $Cr_xNi_{0.7}Fe_{2.3-x}O_4$ ($0.0 \leq x \leq 0.3$) and Fe_3O_4 . We suggest that the differential UV-vis absorption spectra should be accepted as a general analysis method for determining electron transition energies between anions and cations.

Keywords: Spinel ferrite, Crystal structure, UV-vis absorption spectra, Electron transition energy

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1. Introduction

Recently, spinel ferrites have received considerable attention regarding their morphologies and microstructures because their novel functionalities depend not only on their compositions but also on their microstructures [1–4]. In the (A)[B]₂O₄ spinel ferrites, 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 the two types of interstitial positions: the tetrahedral (8a) or (A) sites, and the octahedral (16d) or [B] sites [4–6].

UV-vis absorption spectra have been used to investigate the band gap energies of (A)[B]₂O₄ spinel ferrites [7–12]. Jagriti Pal et al. studied the characteristics of Co₃O₄ nanocrystals, and gave curves of $(\alpha h\nu)^2$ vs $h\nu$, where α is the UV-vis absorption coefficient, and $h\nu$ is the photon energy. Using this curve, they obtained two band gap energies, 2.28 and 1.57 eV. They claimed that the two band gap energies correspond to electron transitions for $O^{2-} \rightarrow Co^{2+}$ and $O^{2-} \rightarrow Co^{3+}$, respectively [7]. Applying a similar method, Hu et al. investigated the properties of NiCo₂O₄ nanoplates. In their research, two band gap energies were also observed, 2.0 eV and 3.3 eV, which were ascribed to the co-existence of high-spin and low-spin states of Co³⁺ in the NiCo₂O₄ spinel [8]. Cui et al. estimated the band gap energies from O 2p to Co 3d-e_g and Co 3d-t_{2g} for ordinary NiCo₂O₄, and found values of 3.40 and 1.97 eV respectively [9]. Melsheimer et al. studied the band gap energies of heteropoly compounds using differential UV absorption spectra, $d\alpha/dE$ vs E , where $E=h\nu$ is the photon energy [12].

In this paper, we describe how, using differential UV-vis absorption spectra, $d\alpha/dE$ vs E , we obtained the electron transition energies between anions and different cations for the (A)[B]₂O₄ spinel ferrites Co_xNi_{0.7-x}Fe_{2.3}O₄ (0.0 ≤ x ≤ 0.3), Cr_xNi_{0.7}Fe_{2.3-x}O₄ (0.0 ≤ x ≤ 0.3) and Fe₃O₄. This is very important for understanding electrical transport and magnetic properties of a material.

2. Experimental

UV-vis absorption spectra for Co_xNi_{0.7-x}Fe_{2.3}O₄ (0.0 ≤ x ≤ 0.3), Cr_xNi_{0.7}Fe_{2.3-x}O₄ (0.0 ≤ x ≤ 0.3) and Fe₃O₄ samples were measured with a spectrophotometer (SHIMADZU, UV 3600) at room temperature in the wave length range 220-800 nm, with a maximum step size of 2 nm. The samples of Co_xNi_{0.7-x}Fe_{2.3}O₄ and

$\text{Cr}_x\text{Ni}_{0.7}\text{Fe}_{2.3-x}\text{O}_4$ were prepared using a chemical co-precipitation method. The preparation process, heat treatment conditions, crystal structure and magnetic parameters of the samples have been reported elsewhere [13]. The Fe_3O_4 samples were obtained as commercial chemical powders, for which the crystal structure and magnetic parameters can be found in Ref. 14.

3. Result and discussion

The X-ray diffraction (XRD) patterns of the samples are shown in Fig. 1, and indicate that all the samples had a single-phase cubic spinel structure. The XRD data were fitted using the X'Pert HighScore Plus software with the Rietveld powder diffraction profile fitting technique [15]. Table 1 shows the results obtained for the crystal lattice constant a , the distances, d_{AO} and d_{BO} , from the O anions to the cations at the (A) and [B] sites, and the distance, d_{AB} , from the cations at the (A) sites to those at the [B] sites. The volume averaged crystallite sizes of all samples, as estimated using the X'Pert HighScore Plus software, were larger than 100 nm so that surface effects are expected to be very weak in all the samples.

Fig. 2 shows the UV-vis absorption spectra of the samples in the wave length range 220-800 nm, that is the curves of the absorption coefficient (α) versus wave length (λ). It can be seen that there are different slopes at different wave lengths, which can be ascribed to the different electron transitions between the oxygen ions and cations. Using an approach similar to the method reported by Melsheimer et al. [12], we investigated the dependences of the differential absorption coefficient, $d\alpha/dE$, on the photon energy, $E=h\nu$, as shown in Fig. 3.

It can be easily seen from Fig. 3 that for the $\text{Co}_x\text{Ni}_{0.7-x}\text{Fe}_{2.3}\text{O}_4$ samples, the peak intensities at 1.64 eV decrease gradually with decreasing Ni content, while for the $\text{Cr}_x\text{Ni}_{0.7}\text{Fe}_{2.3-x}\text{O}_4$ samples, in which the Ni content is constant, the corresponding peak intensities are constant. Therefore, the peaks at 1.64 eV in Fig. 3(a) and 3(b) are ascribed to the electron transition between Ni and O ions.

It can be easily understood that the peak intensity for a specific ion in Fig. 3 is determined by the cation contents and the distance between the cation and anion. In order to identify how to ascribe the various peaks in Fig. 3 to which transitions, it is necessary to know the distribution of cations at the (A) and [B] sites as a function of the doping level x . Applying the O2p itinerant electron model earlier proposed by our

group, we have estimated the cation distributions for doped spinel ferrites [13,14,16–24]. These cation distributions for $\text{Co}_{0.3}\text{Ni}_{0.4}\text{Fe}_{2.3}\text{O}_4$ [13], $\text{Cr}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$ [13] and Fe_3O_4 [14] are shown in Table 2. It can be seen that the Ni^{2+} cation content at the [B] sites is more than 75% of all Ni cations in the two Ni doped samples. Therefore, the peaks at 1.64 eV in Fig. 3(a) and 3(b) are ascribed to the electron transition between Ni^{2+} and O ions at [B] sites.

For the transition between Fe cations and O anions, on the one hand, it can be seen from Table 2 that the content ratio of Fe cations per formula at the (A) or the [B] sites, $n(\text{Fe}^{2+}_{\text{B}})/n(\text{Fe}^{3+}_{\text{A}})/n(\text{Fe}^{2+}_{\text{A}})/n(\text{Fe}^{3+}_{\text{B}}) = 1.099/0.457/0.403/0.342$ for $\text{Co}_{0.3}\text{Ni}_{0.4}\text{Fe}_{2.3}\text{O}_4$, and $n(\text{Fe}^{2+}_{\text{B}})/n(\text{Fe}^{3+}_{\text{A}})/n(\text{Fe}^{2+}_{\text{A}})/n(\text{Fe}^{3+}_{\text{B}}) = 1.032/0.494/0.269/0.205$ for $\text{Cr}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$. The subscript A or B represents the position of the cation at the (A) or [B] sites. Since the [B] sites have high Fe^{2+} content and low Fe^{3+} content, one of the two peaks with high intensities located at 1.83 or 1.91 eV in Fig. 3(a) and 3(b) should correspond to Fe^{2+} cations at the [B] sites and the peak with low intensity located at 2.60 eV in Fig. 3(a) and 3(b) should correspond to Fe^{3+} cations at the [B] sites. On the other hand, the A-O and B-O distances, d_{AO} and d_{BO} , are about 1.90 and 2.05 Å. For a given cation, the transition energy from the (A) sites to the O sites is therefore lower than that from [B] sites to the O sites, due to the distance d_{AO} being shorter than d_{BO} . On the basis of these two constraints, we can obtain a relationship for the transition energies of Fe cations at the (A) and [B] sites: namely, $E_{\text{tr}}(\text{Fe}^{2+}_{\text{A}}) < E_{\text{tr}}(\text{Fe}^{2+}_{\text{B}}) < E_{\text{tr}}(\text{Fe}^{3+}_{\text{A}}) < E_{\text{tr}}(\text{Fe}^{3+}_{\text{B}})$. We can therefore identify the transition energies of various Fe cations for the $\text{Co}_x\text{Ni}_{0.7-x}\text{Fe}_{2.3}\text{O}_4$ ($0.0 \leq x \leq 0.3$) and $\text{Cr}_x\text{Ni}_{0.7}\text{Fe}_{2.3-x}\text{O}_4$ ($0.0 \leq x \leq 0.3$) samples, as shown in Table 3 and Fig. 3(a) and 3(b).

For Fe_3O_4 , $E_{\text{tr}}(\text{Fe}^{2+}_{\text{A}})=1.66$ eV, $E_{\text{tr}}(\text{Fe}^{2+}_{\text{B}})=1.77$ eV, which are lower than those for the other two groups of samples, roughly $E_{\text{tr}}(\text{Fe}^{2+}_{\text{A}})=1.84$ eV, $E_{\text{tr}}(\text{Fe}^{2+}_{\text{B}})=1.91$ eV. The difference likely results from the fact that the electrons transit along the ionic chain O-Fe-O-Fe-O-Fe-O whether they are in the (A) or the [B] sublattice in Fe_3O_4 , and that the electrons transit along the ionic chain O-Fe-O-M-O-Fe-O in $M\text{Fe}_2\text{O}_4$. This is in accord with the fact that Fe_3O_4 has a lower resistivity than doped spinel ferrites $M\text{Fe}_2\text{O}_4$ [25].

For the $\text{Co}_{0.3}\text{Ni}_{0.4}\text{Fe}_{2.3}\text{O}_4$ sample, we found a weak peak at 1.67 eV, as shown in Fig. 3(a). It is possible that this peak corresponds to Co^{2+} cations at [B] sites for which the content is 0.2 per formula.

We have found no visible peak for Cr^{2+} cations. This may be due to the fact that the maximum content of Cr cations, Cr^{2+} at the [B] sites, is only 0.156 for $\text{Cr}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$, being less than the content ratio for those cations with visible peaks.

Obviously, more information can be obtained using the differential UV-vis absorption spectra than using the method reported in Ref. 7–11, from which only two band gap energies can be obtained.

4. Conclusion

We have obtained the electron transition energies between anions and various cations using differential UV-vis absorption spectra, $d\alpha/dE$ vs E . Specifically, the electron transition energies from the O anions to the cations $\text{Ni}^{2+}_{\text{B}}$, $\text{Fe}^{2+}_{\text{A}}$, $\text{Fe}^{2+}_{\text{B}}$, $\text{Fe}^{3+}_{\text{A}}$ and $\text{Fe}^{3+}_{\text{B}}$ at the (A) or [B] sites in the (A)[B]₂O₄ spinel ferrites $\text{Co}_x\text{Ni}_{0.7-x}\text{Fe}_{2.3}\text{O}_4$, $\text{Cr}_x\text{Ni}_{0.7}\text{Fe}_{2.3-x}\text{O}_4$ and Fe_3O_4 have been determined.

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Figure captions:

Fig. 1. X-ray diffraction patterns for the samples $\text{Co}_x\text{Ni}_{0.7-x}\text{Fe}_{2.3}\text{O}_4$ (a), $\text{Cr}_x\text{Ni}_{0.7}\text{Fe}_{2.3-x}\text{O}_4$ (b) and Fe_3O_4 (c).

Fig. 2. Curves of the UV-vis absorption coefficient, α , vs wave length, λ , for samples $\text{Co}_x\text{Ni}_{0.7-x}\text{Fe}_{2.3}\text{O}_4$ (a), $\text{Cr}_x\text{Ni}_{0.7}\text{Fe}_{2.3-x}\text{O}_4$ (b) and Fe_3O_4 (c).

Fig. 3. Curves of the differential absorption coefficient, $d\alpha/dE$, vs photon energy, $E=h\nu$, for the samples $\text{Co}_x\text{Ni}_{0.7-x}\text{Fe}_{2.3}\text{O}_4$ (a), $\text{Cr}_x\text{Ni}_{0.7}\text{Fe}_{2.3-x}\text{O}_4$ (b) and Fe_3O_4 (c).

Table 1. Rietveld fitting results for the XRD patterns of the Fe_3O_4 and Co, Cr doped $\text{Ni}_{0.7}\text{Fe}_{2.3}\text{O}_4$ samples, where a is the crystal lattice constant, d_{AO} and d_{BO} are the distances from the O anions to the cations at the (A) and [B] sites, 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)
Fe_3O_4	8.388	1.880	2.061	3.478
$\text{Co}_x\text{Ni}_{0.7-x}\text{Fe}_{2.3}\text{O}_4$ [13]				
0.00	8.348	1.894	2.038	3.461
0.10	8.355	1.896	2.040	3.464
0.20	8.359	1.897	2.041	3.465
0.30	8.365	1.898	2.042	3.468
$\text{Cr}_x\text{Ni}_{0.7}\text{Fe}_{2.3-x}\text{O}_4$ [13]				
0.00	8.352	1.895	2.039	3.462
0.05	8.349	1.894	2.038	3.461
0.10	8.347	1.894	2.038	3.461
0.15	8.347	1.894	2.038	3.461
0.20	8.345	1.894	2.037	3.460
0.25	8.343	1.893	2.037	3.459
0.30	8.341	1.893	2.036	3.458

Table 2. Cation distributions in the Fe_3O_4 and Co, Cr doped $\text{Ni}_{0.7}\text{Fe}_{2.3}\text{O}_4$ samples estimated using the O2p itinerant electron model.

	Fe_3O_4	$\text{Co}_{0.3}\text{Ni}_{0.4}\text{Fe}_{2.3}\text{O}_4$	$\text{Cr}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$
(A) site			
Fe^{2+}	0.584	0.403	0.269
Fe^{3+}	0.416	0.457	0.494
Ni^{2+}	---	0.038	0.051
Co^{2+}	---	0.037	---
Cr^{2+}	---	---	0.046
Ni^{3+}	---	0.032	0.070
Co^{3+}	---	0.033	---
Cr^{3+}	---	---	0.070
[B] site			
Fe^{2+}	1.384	1.099	1.032
Fe^{3+}	0.616	0.342	0.205
Ni^{2+}	---	0.300	0.542
Co^{2+}	---	0.200	---
Cr^{2+}	---	---	0.156
Ni^{3+}	---	0.030	0.037
Co^{3+}	---	0.029	---
Cr^{3+}	---	---	0.029
Ref.	[14]	[13]	[13]

Table 3. The electron transition energies of Ni^{2+} , Fe^{2+} , Fe^{3+} cations in Fe_3O_4 and the Co, Cr doped $\text{Ni}_{0.7}\text{Fe}_{2.3}\text{O}_4$ samples. The subscripts A or B represent the position of the cation at the (A) or [B] sites. The energy errors are less than $\pm 0.01\text{eV}$.

sample	$\text{Ni}^{2+}_{\text{B}}$	$\text{Fe}^{2+}_{\text{A}}$	$\text{Fe}^{2+}_{\text{B}}$	$\text{Fe}^{3+}_{\text{A}}$	$\text{Fe}^{3+}_{\text{B}}$
$\text{Co}_x\text{Ni}_{0.7-x}\text{Fe}_{2.3}\text{O}_4$	1.64	1.84	1.91	2.14	2.55
$\text{Cr}_x\text{Ni}_{0.7}\text{Fe}_{2.3-x}\text{O}_4$	1.64	1.83	1.91	2.15	2.56
Fe_3O_4	---	1.66	1.77	2.14	2.57

Fig. 1

Fig. 2

Fig. 3