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Electronic structure studies of the spinel $CoFe_2O_4$ by X-ray photoelectron spectroscopy

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ABSTRACT

The spinel $CoFe_2O_4$ has been synthesized by combustion reaction technique. X-ray photoelectron spectroscopy shows that samples are near-stoichiometric, and that the specimen surface both in the powder and bulk sample is most typically represented by the formula $(Co_{0.4}Fe_{0.6})[Co_{0.6}Fe_{1.4}]O_4$, where cations in parentheses occupy tetrahedral sites and those within square brackets in octahedral sites. The results demonstrate that most of the iron ions are trivalent, but some Fe^{2+} may be present in the powder sample. The Co $2p_{3/2}$ peak in powder sample composed three peaks with relative intensity of 45%, 40% and 15%, attributes to Co^{2+} in octahedral sites, tetrahedral sites and Co^{3+} in octahedral sites. The O 1s spectrum of the bulk sample is composed of two peaks: the main lattice peak at 529.90 eV, and a component at 531.53 eV, which is believed to be intrinsic to the sample surface. However, the vanishing of the O 1s shoulder peak of the powder specimen shows significant signs of decomposition.

1. Introduction

The cobalt ferrite $CoFe_2O_4$ is a very important magnetic materials, which has covered a wide range of applications including electronic devices, ferrofluids, magnetic delivery microwave devices and high density information storage due to its wealth of magnetic and electronic properties, such as cubic magnetocrystalline anisotropy, high coercivity, moderate saturation magnetization, high Curie temperature T_C, photomagnetism, magnetostriction, high chemical stability, wear resistance and electrical insulation, etc. [1–12].

In structure, the spinel cobalt ferrite $CoFe_2O_4$ crystallizes in a face-centered cubic structure with a large unit cell containing eight formula units. There are two kinds of lattices for cation occupancy, A and B sites have tetrahedral and octahedral coordination, respectively. In the normal spinel structure Co is a divalent atom, occupying tetrahedral A sites, while Fe is a trivalent atom, sitting on the octahedral B sites. When A sites being Fe^{3+} ions, while B sites equally populated by Co^{2+} and Fe^{3+} ions, the spinel structure is referred to as the inverse kind [13,14]. Commonly, the $CoFe_2O_4$ material is considered to be mostly an inverse spinel compound with most divalent Co ions occupying octahedral sites [7,15,16]. It means that the Co and Fe cations distribute at both sites. Since the ${Fe_A}^{3+}$–${Fe_B}^{3+}$superexchange interaction is normally different from the ${Co_A}^{2+}$–${Fe_B}^{3+}$ interaction, variation of the cation distribution over the A and B sites in the spinel leads to different magnetic properties of these oxides even though the chemical composition of the compound does not change [14].

The spinel cobalt ferrite $CoFe_2O_4$ materials have been synthesized by different methods [17–19]. In most cases, variation of the magnetic properties was obtained due to the different distribution of the Co and Fe cations over the A and B sites. Thus, investigations on the distribution of the Co and Fe cations over the A and B sites in the spinel cobalt ferrite $CoFe_2O_4$ are important [4,7,13,14].

Quantitative X-ray photoelectron spectroscopy (XPS) gives not only the chemical composition, but also information on the chemical bonding and chemical state. This will help us to understand the distribution of the Co and Fe cations in the spinel cobalt ferrite $CoFe_2O_4$. Thus, in this paper, homogeneous $CoFe_2O_4$ powder and bulk were synthesized by combustion technique, and the XPS was taken to study on the valence of the elements and electronic configuration.

2. Experimental

$CoFe_2O_4$ powder and bulk samples in our experiment were synthesized by combustion technique. In brief description, analytical reagent cobalt (II) nitrate hexahydrate, iron (III) nitrate

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nonahydrate and urea were used. Stoichiometric amounts of the cobalt and iron nitrates were weighed out under dry conditions, intimately mixed in a widemouth vitreous silica basin and heated on a hot blanket inside a fume cupboard, under ventilation. With a rise in temperature, melting occurred and a dark liquid was produced. Soon after the thickened liquid began frothing, ignition took place, leading to rapid increase that propagated in swift ripples to walls of the basin. The reaction produced dry, very fragile foam, which transformed into powder [19]. The powders were ground in an agate mortar and pestle to a fine powder, and then, some powders were cold pressed into disks with diameter of 15 mm and thickness of about 1.4 mm at room temperature under a pressure of 12 MPa. In the final, the compacted powders and the disks were directly put into silica boats separately, and sintered at 1200 °C for 4 h in argon atmosphere.

X-ray diffraction (XRD) patterns were recorded on Bruker D8 ADVANCE powder diffractometer using Cu Kα radiation. The working voltage V, current I and time constant τ were 40 kV, 40 mA and 0.2 s, respectively. X-ray Photoelectron Spectroscopy studies were performed using a KRATOS XSAM-800 ESCA/SIMS/ISS spectrometer with monochromatic Mg Kα (1253.6 eV) radiation, the binding energies of samples has been calibrated by taking the carbon 1s peak as reference (285.0 eV).

3. Results and discussion

Fig. 1 is the X-ray powder diffraction patterns of the $CoFe_2O_4$ powder and bulk. It shows that the powder and bulk samples all have a single spinel phase and all peaks could be indexed according to the standard card of the spinel cobalt ferrite $CoFe_2O_4$ [JCPPS card No. 22-1086].

Fig. 2 gives the wide-scan XPS spectra of the $CoFe_2O_4$ bulk (curve 1) and powder (curve 2) samples in the binding energy of 0–1000 eV. As demonstrated in Fig. 2, the crystals contain Fe, Co, and O elements, and no other impurity element was detected in the spectrum up to 1000 eV except carbon. The carbon on the surfaces of the specimens is probably due to contamination caused by handling or pumping oil, since the samples have been undergone a 1200 °C high-temperature calcinations procedure.

Stoichiometric information can be obtained from core photoemission intensity data. The element composition can be quantified by use of X-ray photoelectron intensity values (I_n) and appropriate sensitivity factors (S_n): $\rho_n = I_n/S_n$. S_{Fe}, S_{Co} and S_O values of 3.8, 4.5 and 0.68 were found by procedures similar to that of Ref. [20]. Because the iron, cobalt and oxygen X-ray photoelectron peaks overlap significantly, the spectrum must first be integrated to obtain the $N(E)$ vs. X-ray photoelectron spectrum and the individual components separated to obtain the integrated XPS intensity for each element independently [21]. Then, ρ_{Co}:ρ_{Fe}:ρ_O = 1:1.8:4.1 and 1:1.9:3.7 to bulk sample and powder sample were obtained separately.

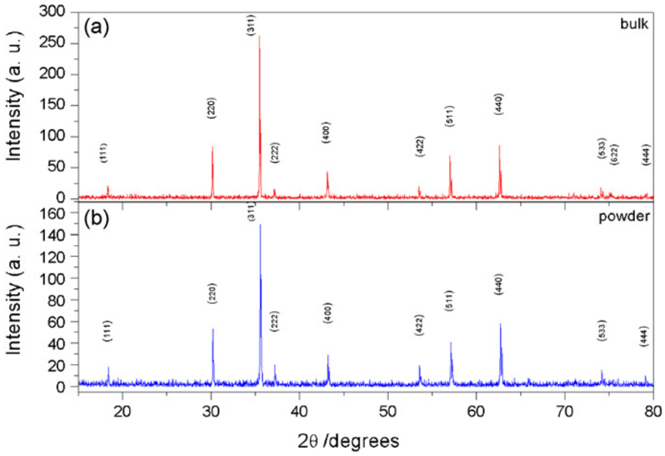

Fig. 1. XRD patterns of the $CoFe_2O_4$, (a) bulk and (b) powder.

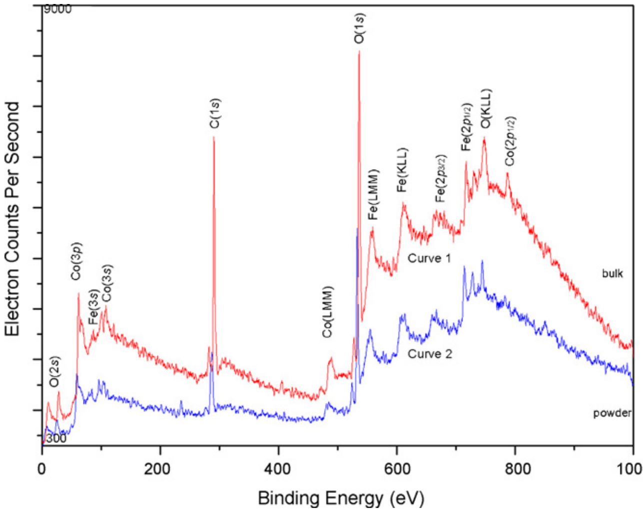

Fig. 2. Wide-Scan XPS spectra of the $CoFe_2O_4$, bulk (curve 1) and powder (curve 2).

Regions in which detailed core spectra were collected including the 2p photoelectron regions of the metallic constituents of the oxides, as well as the oxygen 1s core photoelectron regions. The high-resolution narrow-scan XPS spectra of Fe 2p, Co 2p, and O 1s peaks of the $CoFe_2O_4$ specimen are shown in Figs. 3–5, respectively.

Fig. 3 shows the Fe 2p core-electron spectrum of $CoFe_2O_4$ powder and bulk samples. The peak shape for the two samples is similar, and has an asymmetric shape. The spectrum apparently reveals the presence of two nonequivalent bonds of Fe ions in $CoFe_2O_4$ compounds, which is consistent with that there are two kinds of lattice sites for Fe ions occupancy in $CoFe_2O_4$ compounds. We attempt to resolve the data into two components to represent these two sites. For the $CoFe_2O_4$ powder, it yields Fe $2p_{3/2}$ binding energies of 710.65 and 713.26 eV, and Fe $2p_{1/2}$ binding energies of 724.23 and 725.36 eV. For the $CoFe_2O_4$ bulk, it yields Fe $2p_{3/2}$ binding energies of 710.48 and 713.00 eV, and Fe $2p_{1/2}$ binding energies of 723.60 and 725.70 eV. The doublets in powder and bulk samples can be ascribed to Fe^{3+} ions in octahedral sites and Fe^{3+}

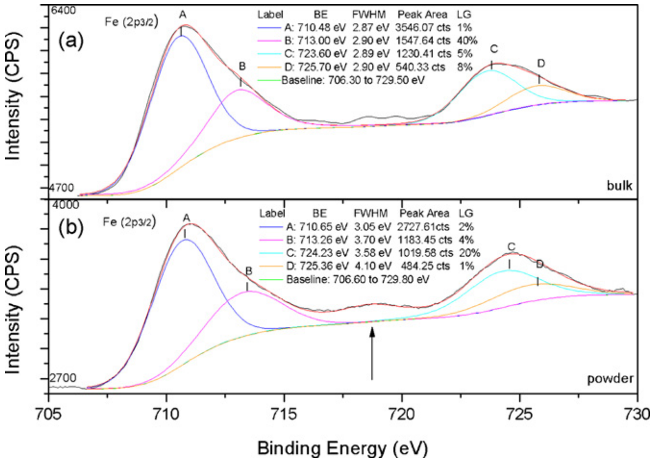

Fig. 3. Fe 2p XPS for bulk (a) and powder (b) samples. (The arrow indicates the approximate position of the satellite characteristic of octahedral Fe^{2+}.)