



Nickel substitution induced effects on gas sensing properties of cobalt ferrite nanoparticles



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ABSTRACT

Ni²⁺ ion induced unusual conductivity reversal and an enhancement in the gas sensing properties of ferrites based gas sensors, is reported. The Co_{1-x}Ni_xFe₂O₄ (for x = 0, 0.5 and 1) nanoparticles were synthesized by wet chemical co-precipitation method and gas sensing properties were studied as a function of composition and temperature. The structural, morphological and microstructural characterization revealed crystallite size of in the range 10–20 nm with porous morphology consisting of nano-sized grains. The Energy Dispersive X-ray (EDX) mapping confirms homogeneous distribution of Co, Ni, Fe and O elements in the ferrites. The non-stoichiometry of the inverse spinel type ferrites and the relative concentration of Ni³⁺/Co³⁺ defects were studied using X-ray photoelectron spectroscopy. It is found that the addition of Ni²⁺ ions into cobalt ferrite shows preferred selectivity towards CO gas at high temperature (325 °C) and ethanol gas at low temperature (250 °C), unlike undoped cobalt ferrite or undoped nickel ferrite, which show similar response for both these gases. Moreover, an unusual conductivity reversal is observed, except cobalt ferrite due to the difference in reactivity of the gases as well as characteristic non-stoichiometry of ferrites. This behavior is highly gas ambient dependent and hence can be well-exploited for selective detection of gases.

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1. Introduction

The ferrites are magnetic semiconductors with widespread technological utility as microwave absorbing materials [1,2], low and high-frequency transformer cores [3], high-density information storage materials [4], magnetorheological devices [5], medical diagnostic tools [6], etc. Both, nickel ferrite (NiFe₂O₄) and cobalt ferrite (CoFe₂O₄) have inverse spinel structure [7], where ideally octahedral sites are shared by Fe³⁺ and Ni²⁺/Co²⁺ ions while the tetrahedral site is occupied by Fe³⁺. Generally Fe²⁺ is also present with Fe³⁺ and shared octahedral site. The presence of the two transition metal ions at one crystallographic site leads to a unique type of hopping conductivity and magnetic coupling.

The charge carriers hopping mechanism between cations in octahedral sites, is responsible for the conduction in these ferrites [8]. This conductivity is strongly influenced by stoichiometry,

cationic interexchange and the creation of oxygen or cation vacancies. During gas sensing, the test gases diffuse through the meso-porous regions and interact with the surface (which generally adsorbs oxygen ions through the surface), altering the charge carrier concentration and hence, the resistivity (or conductivity) of the ferrite. Cobalt ferrite shows p-type conductivity due to the hopping of holes represented as Co²⁺ + h⁺ ↔ Co³⁺. Nickel substitution in these ferrites leads to the shifting of Fe³⁺ from tetrahedral to octahedral site as Ni²⁺ ions occupy both tetrahedral and octahedral sites. Hence, it results in a mixed spinel structure, where divalent and trivalent ions are distributed in the tetrahedral and octahedral sites, which in turn, disturbs the possibility of Co³⁺ formation. The electron transfer in Fe³⁺ + e⁻ ↔ Fe²⁺, gives a n-type conductivity to the material [9].

The well known Metal Oxide (MO) semiconductors used for gas sensing application such as SnO₂, ZnO or WO₃, show high sensitivity, cost effectiveness and ease of fabrication [10,11]. However, their use is limited in devices due to low selectivity and high operating temperatures. Therefore, gas sensors based on ternary transition metal oxides, particularly ferrites, are being explored for

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their expected good sensitivity and selectivity towards a particular gas, due to the selective oxidative catalytic effect [12–17]. Nano-materials based sensors show high sensitivities compared to their bulk counterpart because of their special surface and morphology. Hence, in this paper, we aim to study the effect of substitution of nickel in a cobalt ferrite nanoparticle based gas sensors. We adopt a simple solution based method to synthesize these materials and their structural, morphological and chemical properties are studied to compare their gas sensing properties towards CO and ethanol gases, which are important atmospheric pollutants and hazardous gases.

2. Experimental

Nanoparticles of $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ where $x = 0.0, 0.5, 1.0$ were synthesized by co-precipitation method. Sodium hydroxide and nitrates of nickel, cobalt, ferric were used as the starting materials and oleic acid was used as a surfactant. Aqueous solutions of all nitrates were prepared in de-ionized water and pH level of the solution is maintained at 10–11 by adding NaOH solution slowly with continuous stirring using a magnetic stirrer. The synthesis details are reported elsewhere [18]. The obtained powder was grounded and kept for calcination at temperature 550 °C. The calcined powders were palletized and were sintered for densification again at 550 °C for 2 h.

The structural characterization was done by X-ray Diffraction (XRD 6000, Shimadzu) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54059 \text{ \AA}$) at a scan rate of $1^\circ/\text{min}$ with a step size of 0.02° . The surface morphology was studied by field emission scanning electron microscopy (MIRA3 TESCAN). Additionally, the crystalline size was estimated by using a transmission electron microscope (Model JEOL 2100F, 200 keV) equipped with EDX analyzer. The electronic structure and chemical state of all compositions were investigated by X-ray photoelectron spectroscopy (XPS) with an Axis Ultra DLD high resolution instrument (Kratos). The binding energies reported have an accuracy of $\pm 0.3 \text{ eV}$ and are confirmed using C 1s standard at 284.5 eV.

The details of gas sensing set up and fabrication of sensors are reported elsewhere [19]. The sensing response was studied by exposing the sensors to the different concentrations of test gas vapors diluted with zero air at various temperatures. The response is calculated using the following equations

$$\text{Response} = \frac{\Delta R}{R_g} = \frac{|R_a - R_g|}{R_g} \text{ if } R_g < R_a \quad (1)$$

and,

$$\text{Response} = \frac{\Delta R}{R_a} = \frac{|R_a - R_g|}{R_a} \text{ if } R_g > R_a \quad (2)$$

Where, R_a is the sensor resistance in air and R_g is the sensor resistance in the presence of test gas [20].

3. Result and discussion

3.1. Structural study

Fig. 1(a) shows XRD patterns of $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ samples. All the XRD peaks were indexed to Fd3m space group with cubic spinel structure. The average crystallite size of the samples estimated by Scherrer equation [21], the calculated lattice parameter (a) and X-ray density (d_x) of all samples [22] are tabulated in Table 1.

It is seen from Table 1 that the lattice parameter decreases with increasing Ni^{2+} content in cobalt ferrites. This may be attributed to

the difference in the ionic radius of cations. The ionic radius of Co^{2+} (0.74 Å) is greater than Ni^{2+} radius (0.69 Å). The similar trend in the variation of lattice parameter has also been reported earlier [23]. The X-ray density increases with the increase in Ni^{2+} content in these ferrites as expected.

Fig. 1(b), (c) and (d) show SEM images of the surfaces of the synthesized samples which confirm the microstructures consist of nano-sized grains with high porosity which provides larger specific area for gas sensing applications. There is no significant morphological difference seen for samples with varied nickel contents.

Fig. 2(a)–(f) show the TEM images with respective SAED Pattern in inset and HRTEM images of $x = 0.0, x = 1.0$ and $x = 0.5$ samples, respectively. All the samples exhibit very fine crystallite sizes (~15–25 nm in size) with significant lumps or agglomeration. The SAED patterns shown in set reveals nanocrystalline nature with ring pattern and all have been indexed for reflections of the spinel type of ferrite. The typical crystallite sizes observed from HRTEM image shown in Fig. 2(b), (d) and (f) are nearly 10–15 nm in size and the estimated lattice spacings have been marked which corresponds to several reflections of spinel ferrite. The average crystallite sizes and lattice spacing for corresponding reflections, estimated from HRTEM and XRD are in good agreement with each other.

Fig. 3 shows EDX spectra of CoFe_2O_4 ($x = 0.0$), NiFe_2O_4 ($x = 1$) and mapping in $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.5$) (maps shown inset). The quantification results of elemental contribution from EDX analysis tabulated in Table 2. It is seen that the stoichiometry in the samples are as expected without any trace of impurity. (The signal for Cu and C arises from C coated sample holder grids in TEM) Further, EDX mapping of $x = 0.5$ sample indicated homogeneous distribution of all the constituent elements viz. Co, Ni, Fe and O elements.

3.2. X-ray photoelectron spectroscopy (XPS) study

The existence of multiple oxidation states is inherent to transition metal compounds. Hence, the corresponding XPS peaks are deconvoluted to evaluate the relative contributions of individual oxidation state. The high resolution individual element core level scan (Fig. 4) for Ni 2p, Co 2p, Fe 2p and O 1s were recorded after an initial Ar^+ ion etching for removal of surface contamination, if any. The line shape spectra thus obtained were analyzed by fitting using XPSPEAK41, which is an open source program, the fitting parameters were carefully optimized after a Shirley background evaluation following a few recent literatures [24–27].

Fig. 4(a) shows XPS spectra of Co 2p region of nonsubstituted and Ni substituted cobalt ferrite. The XPS spectra of both the samples contain photopeaks around 778 eV and 779 eV corresponding to Co^{2+} at octahedral and tetrahedral sites, respectively [27], with a shoulder around 781 eV which is assigned to Co^{3+} and a satellite peak around 785 eV. The ratio of the relative concentrations of Co^{2+} and Co^{3+} in the surface region of pure cobalt ferrites is 1:0.63 and 1:0.64 for nickel substituted cobalt ferrites while ratio of the relative concentrations of Co^{2+} at tetra and octa site is 1:0.53 and 1:0.63 for pure and nickel substituted cobalt ferrites, respectively. Fig. 4(b) shows XPS spectra for Ni 2p region of nickel substituted cobalt ferrite ($x = 0.5$) and pure nickel ferrite ($x = 1$). The spectra of both samples contain a main photopeak around 853.1 eV, a shoulder at 854.5 eV assigned to Ni^{2+} and Ni^{3+} defects respectively [28] and a satellite around 859.9 eV. The peak shows asymmetry due to partial non-stoichiometry. The ratio of the relative concentrations of Ni^{2+} and Ni^{3+} in the surface region of samples is 1:1.78 for nickel substituted cobalt ferrite and 1:0.55 for pure nickel ferrite. Thus, the samples containing cobalt exhibit higher contribution of Ni^{3+} . Fig. 4(c) shows XPS spectra of Fe 2p region of all the samples. The Fe 2p photoelectron peak centered around on 708 eV correspond to Fe^{2+} and photoelectron peaks

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