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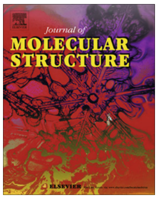

Influence of Cd^{2+} ions on the structural, electrical, optical and magnetic properties of Co–Zn nanoferrites prepared by sol gel auto combustion method

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HIGHLIGHTS

- Cd-doped Co–Zn ferrites synthesized using sol–gel auto combustion method.
- M_s was found to be maximum for the compositional level of Cd having $x = 0.4$.
- Cd^{2+} ions substitution leads to the spin canting phenomenon in ferrites.
- The photo-catalytic degradation enhanced as cadmium ion increased from 0.0 to 1.0.

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ABSTRACT

Cadmium substituted Co–Zn nanoferrites, $Co_{0.5}Zn_{0.5}Cd_xFe_{2-x}O_4$ ($x = 0.0$, 0.2, 0.4, 0.6, 0.8 and 1.0) were synthesized using the sol–gel auto-combustion method. The powder X-ray diffraction patterns of all the ferrite samples confirmed the formation of single-phase cubic spinel structures having Fd-3m space group. The lattice parameter, '*a*' increased with increasing Cd^{2+} ion doping. The d.c resistivity of all the ferrite compositions annealed at 1000 °C decreased as the temperature increased, showing their semiconductor nature. However, decrease in resistivity was observed with increasing cadmium concentration. The drift mobility also increased with increasing temperature as well as cadmium concentration because of the enhanced mobility of charge carriers due to thermal activation. The saturation magnetization (M_s), was found to be maximum for the compositional level of Cd having $x = 0.4$, beyond which it decreased due to the spin canting phenomenon. The photo-catalytic degradation was enhanced as the concentration of cadmium ion increased from 0.0 to 1.0.

Introduction

Cobalt ferrite ($CoFe_2O_4$) has attracted much attention owing to its excellent properties, such as its relatively high saturation magnetization (M_s), high coercivity (H_c), magnetic anisotropy, good chemical stability and good catalytic activity. Its physical properties are strongly dependent on the cation distribution among the tetrahedral (A) and the octahedral (B) sites in the crystal lattice. Depending upon the distribution of the various cation substituents over tetrahedral and octahedral sites, its magnetic and electrical properties can be modified according to the research interest [1,2].

Tremendous work has been reported on the pure and doped cobalt ferrites. Nlebedim et al. [3] have investigated the magnetic and magneto elastic properties of $CoFe_2O_4$ and concluded that the coercive field decreases whereas saturation magnetization (M_s) increases with increase in heat treatment temperature. Synthesis and microstructure of cobalt ferrite nanoparticles have been reported by Ajroudi et al. [4] and it has been found that the particle size varies from 4.0 to 7.5 nm, depending on the cobalt content. Teixeira et al. [5] have reported that sintering at 1400 °C led to "honeycombing" of the ferrite grains in $Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrite. The environment of Fe in $Co_{0.5}Cd_xFe_{2.5-x}O_4$ ($0.0 \leqslant x \leqslant 0.5$) has been studied by Kumar et al. [6] using Mössbauer spectroscopy and observe a decrease in hyperfine magnetic field was observed as the cadmium doping is increased in the A and B sites. Ma et al.

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[7] have synthesized the nano-composites of polyaniline and $Co_{0.5}Zn_{0.5}Fe_2O_4$ in the aqueous solution and found the reflection loss to be about 39.9 dB at 22.4 GHz which is higher than that of polyaniline. In Ni substituted Co–Zn ferrites inversion of cations at both tetrahedral A and octahedral B sites is observed and saturation magnetization decreased with increase in annealing temperature as reported by Suwalka et al. [8]. The effect of solution temperature on the crystallite size and magnetic properties of Zn substituted cobalt ferrites was explored by Mozaffari et al. [9]. It was reported that the crystallite size increased from 6 to 8 nm on increasing the solution temperature from room temperature to 363 K. Singhal et al. [10] have reported an unusual behavior of saturation magnetization in Zn substituted cobalt ferrites, $Co_xZn_{1-x}Fe_2O_4$. The saturation magnetization first increased with Zn doping up to $x = 0.4$, and then decreased with increase in Zn^{2+} concentration. Similar behavior has also been observed by Somaiah et al. [11]. Sharifi et al. [12] have found that $Co_{0.3}Zn_{0.7}Fe_2O_4$ exhibited the super paramagnetic behavior having 97 °C Curie temperature and saturation magnetization and coercivity decrease with increase in the zinc concentration. In aluminum substituted cobalt zinc ferrite $Co_{0.5}Zn_{0.5}Al_xFe_{2-x}O_4$ ($x = 0$, 0.2, 0.4, 0.6, 0.8 and 1.0) the lattice parameter, saturation magnetization and activation energy are found to decrease with increase in the Al^{3+} ion concentration whereas electrical resistivity increases with Al doping as reported by Singhal et al. [13]. Structural, electrical, optical and magnetic properties of chromium substituted Co–Zn nano-ferrites $Co_{0.6}Zn_{0.4}Cr_xFe_{2-x}O_4$ ($0 \leqslant x \leqslant 1.0$) has been discussed by Bhukal et al. [14] and a decreasing trend of saturation magnetization (M_s) with increasing chromium content was observed.

Interestingly the substitution of cadmium ion into the spinel lattice has significant effect on magnetic properties such as spin canting effect. It has been reported that the substitution of Cd^{2+} ions gives rise to spin canting phenomenon and numerous studies have been conducted on such ferrites [15–17]. For instance, Akhter et al. [15] studied the influence of cadmium substitution in lithium-bismuth ferrites of the formula $Li_{0.5-x/2}Cd_xBi_{0.02}Fe_{2.48-x/2}O_4$ and reported that the saturation magnetization increases up to $x = 0.3$ and then it decreases because of the spin canting phenomenon. Similarly, Gadkari et al. [16] synthesized cadmium substituted magnesium ferrites, $Mg_{1-x}Cd_xFe_2O_4$ and found that the saturation magnetization is maximum for $x = 0.4$ owing to the spin canting phenomenon.

Despite of several studies, the influence of Cd^{2+} ion doping on structural, electrical, magnetic and optical properties of Co–Zn spinel ferrites has not been reported yet. Therefore in the present work an attempt has been made to synthesize nanoparticles of cadmium substituted cobalt zinc ferrites, $Co_{0.5}Zn_{0.5}Cd_xFe_{2-x}O_4$ ($x = 0.0$, 0.2, 0.4, 0.6, 0.8 and 1.0) via sol–gel auto combustion method and study of their structural, optical, electrical, magnetic properties and photo catalytic activity was carried out.

Experimental

Preparation of $Co_{0.5}Zn_{0.5}Cd_xFe_{2-x}O_4$ ($x = 0.0$, 0.2, 0.4, 0.6, 0.8 and 1.0) nanoferrites

Synthesis of $Co_{0.5}Zn_{0.5}Cd_xFe_{2-x}O_4$ ($x = 0.0$, 0.2, 0.4, 0.6, 0.8 and 1.0) ferrites was carried out using the sol–gel auto-combustion method. The AR grade ferric nitrate ($Fe(NO_3)_3.9H_2O$), cobalt nitrate ($Co(NO_3)_2.6H_2O$), cadmium nitrate ($Cd(NO_3)_3.9H_2O$), zinc nitrate ($Zn(NO_3)_2.6H_2O$) and citric acid were weighed in their stoichiometric ratios and were dissolved in minimum amount of distilled water. The ratio of metal atoms to citric acid was taken as 1:1. The individual solutions were then mixed together and the pH value was adjusted to ~5–7 by adding NH_4OH solution. The solution was heated and self ignited to obtain ferrite powder. The ferrites were annealed at 400 °C, 600 °C, 800 °C and 1000 °C in a muffle furnace for 2 h.

Physical measurements

Fourier Transform Infrared (FT-IR) spectra was recorded using Perkin Elmer RX-1 FT-IR spectrophotometer with KBr pellets in the range 1000-400 cm^{-1}. Powder X-ray Diffraction (XRD) studies were carried out using a Bruker AXS, D8 Advance spectrophotometer with Cu Kα radiation. Hitachi (H-7500) Transmission electron microscope (TEM), operated at 120 kV was used to record the micrographs of the samples. Wavelength Dispersive X-ray Fluorescence (WD-XRF) spectrometer (Bruker S8-Tiger) was used for the elemental analysis. The electrical properties were studied using a two-probe instrument in the range of 303–373 K. The sintered ferrite samples in powdered form were compressed to pellet of diameter 12 mm and thickness 0.2 mm by applying the pressure of 3 ton. Both the surfaces were polished with silver paint and then the pellet was inserted in the two probe instrument. The values of current were recorded at different temperatures. The magnetic properties were measured at room temperature using a Lakeshore Vibrating Sample Magnetometer (VSM) (7410) up to a magnetic field of ±10 kOe. UV–Vis spectra were recorded using a Hitachi 330 UV–VIS–NIR spectrophotometer.

Results and discussion

FT-IR characterization

The IR spectra shows the bands assign from inter atomic vibrations. The FT-IR spectra of cadmium substituted cobalt zinc ferrites show two dominant absorption bands in the range 570–420 cm^{-1}. The difference in position of the bands for the various compositions is expected because of the difference in the bond length between Fe^{3+} and O^{2-} ion for complexes in each site. The Fe^{3+} - O^{2-} distances in tetrahedral site is 0.189 nm which is smaller than the distance in the octahedral site as 0.199 nm. The high frequency band at ~570 cm^{-1} (υ_1) is assigned to stretching vibrations of the tetrahedral groups and lower frequency band at ~421 cm^{-1} (υ_2) is attributed to the stretching mode of the octahedral M–O groups in the ferrites as shown in Fig. 1. The bands obtained for tetrahedral and octahedral clusters are in accordance with the earlier studies [18–20]. The peak at 720 cm^{-1} is due to the interference of nujol used as mulling agent.

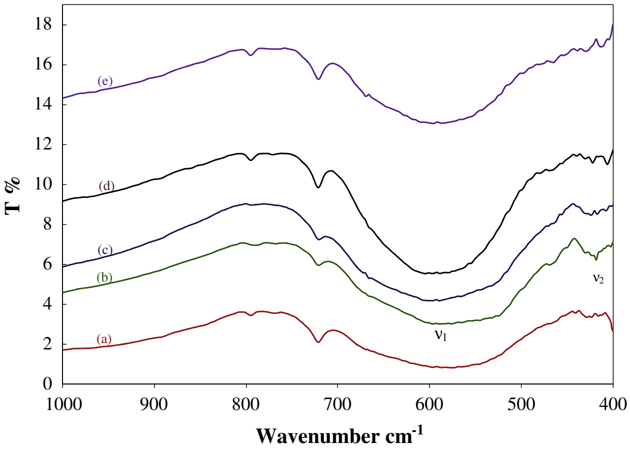

Fig. 1. FT-IR spectra of $Co_{0.5}Zn_{0.5}Cd_xFe_{2-x}O_4$ (a) $x = 0.2$, (b) $x = 0.4$, (c) $x = 0.6$, (d) $x = 0.8$, and (e) $x = 1.0$) annealed at 1000 °C.