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Characterization and spectral studies of Co^{3+}-doped $Cd_{0.4}Mn_{0.6}Fe_2O_4$ ferrites

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Abstract

A series of the $Cd_{0.4}Mn_{0.6}Co_xFe_{2-x}O_4$ ferrites, $0 \leq x \leq 1$, were prepared and studied by using X-ray patterns and Mössbauer and FMR spectra. The lattice parameter, mean ionic radii and hopping and bond lengths and edges are determined and discussed as functions of Co^{3+} content x. The obtained value of oxygen positional parameter was 0.397 for all samples. The recorded FMR and Mössbauer spectra indicated a ferrimagnetic nature of all the samples. The spin–spin relaxation time, the Lande factor (g), line width ΔH and the resonance field are affected by the Co^{3+} additions x. The Mössbauer spectra were analyzed to two sextets attributed to the Fe^{3+} ions at A- and B-sites. The quadrupole and isomer shift values are found to be independent on x, whereas the hyperfine magnetic fields, H_A and H_B, and Mössbauer line widths at the A- and B-sites, respectively, showed dependence on x. Also H_A and H_B were affected by the hopping and bond lengths at these sites.

Keywords: D. Ferrites; Cd–Mn–Co; X-ray; Mössbauer; FMR and magnetic properties

1. Introduction

Ferrites continue to be very attractive materials for technological applications due to their combined properties as magnetic conductors (ferrimagnetic) and electric insulators. Polycrystalline ferrites have applications ranging from simple lifting magnets, microwave frequencies, radio frequencies to the most complex microwave communications to outer space. Many efforts of research have performed in studying the preparation and properties of spinel ferrites [1–10]. Spinel ferrites, by virtue of their structure, can accommodate a variety of cations at different sites enabling a wide variation in electrical and magnetic properties.

Spinel ferrites with cubic crystal structures have interesting structural, physical and magnetic properties. These properties of ferrites strongly depend on the chemical composition, the electronic structure of the magnetic ions, preparation conditions, and the crystal structure of the lattice. The important quantities for technical applications depend also to a great extent on the microstructure of the product [1–10].

The present work is devoted to study the effect of trivalent Co ions substitution for Fe^{3+} ions of spinel ferrites $Cd_{0.4}Mn_{0.6}Co_xFe_{2-x}O_4$, $0 \leq x \leq 1$, on structural, magnetic and site-ionic properties. The techniques used are X-ray patterns, Mössbauer and ferromagnetic resonance spectra.

2. Experimental

A series of the $Cd_{0.4}Mn_{0.6}Co_xFe_{2-x}O_4$ ferrite samples, x=0.0, 0.125, 0.25, 0.375, 0.5, 0.75 and 1, were prepared by the high temperature solid state reaction method. Molar ratios of the high purity CdO, MnO, Co_2O_3 and Fe_2O_3, were mixed together and milling in agate mortar. The final products were pre-sintered at 1000 °C for 24 h and furnace cooled to room temperature. The samples were ground, pelletized and sintered at 1200 °C for 24 h and cooled slowly to room temperature.

X-ray diffraction patterns were recorded using X-ray diffractometer of the type PRUKER-DX and CuK_α radiation.

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The lattice parameter a was calculated using the relation; $a=d(h^2+k^2+l^2)^{1/2}$, where d is the interplanar distance obtained by the Bragg's relation; $2d\sin\theta=n\lambda$, where θ is the diffraction angle and λ is the X-ray wavelength (λ=1.5405 Å).

Ferromagnetic resonance (FMR) spectra of the samples were recorded using JSE-Fe 2xG Jeol EPR spectrometer at room temperature. The FMR spectra were recorded as a first derivative of the absorbed spectra.

A constant acceleration computerized Mössbauer spectrometer and 25 mCi ^{57}Fe radioactive sources diffused in rhodium matrix were used and metallic iron was used for calibration. The obtained spectra were analyzed and fitted using a computer program based on Lorenzian line shapes.

3. Results and discussion

3.1. X-ray analysis

Fig. 1 shows the X-ray diffraction patterns of the $Cd_{0.4}Mn_{0.6}Co_xFe_{2-x}O_4$ ferrites. It is shown that the reflection planes (111), (220), (311), (222), (440), (422), (511), (440), (620), (533), (622) and (444) appeared for all the samples, which prove that these samples are single phase of cubic spinel ferrites [11]. The calculated values of the lattice parameter a lie between 8.5005 and 8.5548 Å, which agree with the previous studies [1,5]. The average values of a are plotted against x as seen in Fig. 2. It is seen that a decreases slowly with x, which is attributed to the substitution of Fe^{3+} ions (0.64 Å) by the smaller Co^{3+} ions (0.61 Å).

Fig. 3 displays that X-ray density D_x and bulk density D increase, while the porosity P decreases with x. The increase in D_x and D with x may be attributed to the substitution of the larger atomic weight Co^{3+} (58.93) by Fe^{3+} (55.85). The decrease in porosity with x may be due to the densification of the samples by sintering process. The X-ray patterns indicated that the peak (311) is a little shifted to higher θ values in samples for $x\geq 0.5$, which may be ascribed to the increase in packing which is emphasized by the porosity.

The mean ionic radii of the A- and B-sublattices (R_A and R_B) can be calculated for all samples using the cation distribution and the relations [6,7];

$$R_A = 0.4r_{Cd^{2+}} + (0.6-y)r_{Mn^{2+}} + zr_{Co^{3+}} + yr_{Fe^{3+}}$$
$$R_B = yr_{Mn^{2+}} + (x-z)r_{Co^{3+}} + (2-y-x)r_{Fe^{3+}}$$

where r denotes to the ionic radius and y and z to the number of Fe^{3+} and Co^{3+}ions at the A-sites, respectively. The calculated values are given in Table 1. It is obvious that the trend of R_A and R_B decrease with x, which may be due to the substitution process. The oxygen positional parameter u can be determined using the relation [6,7];

$$R_A = a\sqrt{3}(u-0.25)-r_O$$

where r_o is the O^{2-} radius. The obtained value of u was 0.397 for all samples. The tetrahedral bond length $d_{AL}(d^{2-}_{A-O})$ and the octahedral bond length $d_{BL}(d^{2-}_{B-O})$ can be calculated by the relations [6,7];

$$d_{AL} = a\sqrt{3}(u-0.25)$$
$$d_{BL} = a\left(3u^2-\frac{11}{4}u+\frac{43}{64}\right)^{1/2}$$

The tetrahedral edge d_{AE} and the octahedral edge d_{BE} and unshared edge d_{BEU} can be determined using the relations [6,7];

$$d_{AE} = a\sqrt{2}(2u-0.5)$$
$$d_{BE} = a\sqrt{2}(1-2u)$$
$$d_{BEU} = a\left(4u^2-3u+\frac{11}{16}\right)^{1/2}$$

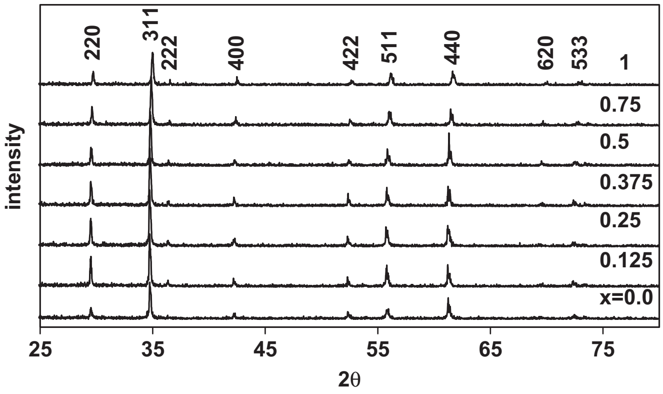

Fig. 1. X-ray diffraction patterns for the system $Cd_{0.4}Mn_{0.6}Co_xFe_{2-x}O_4$.

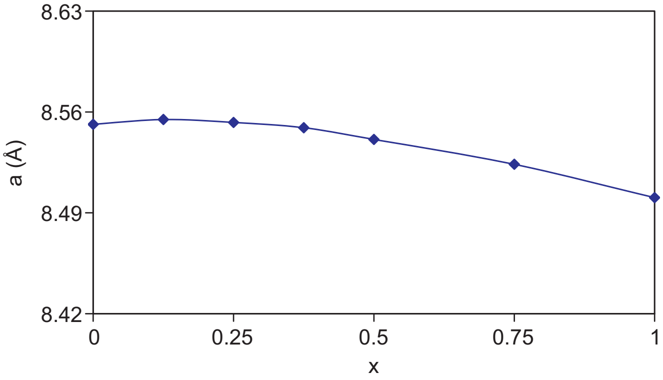

Fig. 2. Dependence of the lattice parameter a on Co^{3+} ion content x.

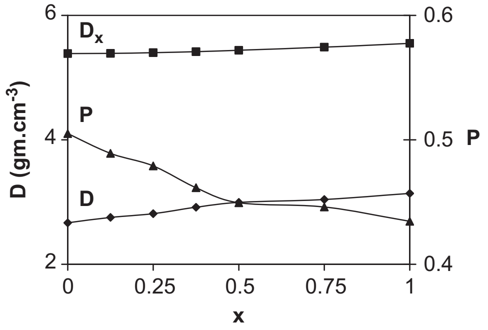

Fig. 3. x dependence of the X-ray density (D_x), bulk density (D) and porosity (P).