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Effect of Cu–Al substitution on the structural and magnetic properties of Co ferrites

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ABSTRACT

In this work copper aluminum substituted cobalt nanocrystalline spinel ferrites having general formula $Co_{1-x}Cu_xFe_{2-x}Al_xO_4$, with $0.0 \leq x \leq 0.8$ have been synthesized by using a co-precipitation method. The Cu–Al substituted samples were annealed at 600 °C and characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM) and vibrating sample magnetometer (VSM). XRD analysis confirmed a single phase spinel structure and the crystalline size calculated using Scherrer's formula found to be in the range of 14 – 24 nm. This crystalline size is small enough to achieve the suitable signal to noise ratio in the high density recording media. The FTIR spectra reveal two prominent frequency bands in the wave number range 350–600 cm^{-1}, which confirm the cubic spinel structure and completion of chemical reaction. Magnetic studies reveal that the coercivity (H_c) attains a maximum value of 1142 Oe at 14 nm. The increasing trend of magnetic parameters (coercivity and retentivity) is consistent with crystallinity. The role played by the Cu–Al ions in improving the structural and magnetic properties are analyzed and understood. The optimized magnetic parameters suggest that the material with composition $Co_{0.6}Cu_{0.4}Fe_{1.6}Al_{0.4}O_4$ may have a potential application for high density recording media. Our simple, economic and environmental friendly preparation method may contribute towards the controlled growth of high quality ferrite nanopowder, potential candidates for recording.

1. Introduction

So much effort is dedicated in recent years on the controlled growth and careful characterization of different cations substituted ferrites due to their widespread fundamental and technological importance [1,2]. Improving the saturation magnetization and obtaining a reasonable value of the coercivity in nanoferrites is the key issue. Another challenges are to reduce the crystalline size and to enhance the electrical resistivity of the materials for diverse applications such as microwave devices [3],recording media [4], gas sensors [5], magnetic fluids [6], high density information storages [7], catalysts [8]and ferro-fluids [9] to cite a few. For these reasons, the spinel nanoferrites with formula AB_2O_4 where A=Ni, Zn, Co and Mg are the most significant magnetic oxides [10]. Influence of various cations such as Co^{2+}, Cu^{2+}, Sn^{4+} and Ti^{4+} on ferrites in improving the electrical and magnetic properties of Co ferrites have been widely studied [11,12]. Cobalt ferrite has an inverse spinel structure with Co^{2+} ions in the octahedral (B) sites while Fe^{3+} ions are equally distributed between tetrahedral (A) and octahedral (B) sites. Therefore, substitution with various metal cations allows some tunable properties of these nanoferrites. The physical properties of such nanocrystalline magnetic materials are highly sensitive to the method of preparation, chemical composition, sintering temperature, grain size and type of substituents and the distribution of cations among tetrahedral and octahedral sites [12–14]. The solid-state reaction being a conventional

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preparation method of ferrites involves the mixing of oxides or carbonates with intermittent grinding followed by high annealing temperature (1200–1700 °C) [15]. Though the process remains simple yet it has several drawbacks such as high energy consumption, long period of production, larger particle size and the presence of various impurities that lead to inhomogeneous ferrite structures. It is the inhomogeneity that resulting the formation of voids and thereby weakens the proper transfer of mechanical signal. Several methods such as sol–gel auto-combustion [16,17], high-energy ball milling [18,19], micro-emulsion technique [20], co-precipitation method [21], hydrothermal [22], combustion method [23], and spray pyrolysis [24,25] have been developed to fabricate nickel ferrite nanoparticles. Chemical co-precipitation method has advantages over other methods due to its processing simplicity, low cost, good control of size, and the efficiency of more homogeneous mixing of the component materials that lead to the formation of nanocrystallites.

Aluminum substituted Co–Cu ferrites due to their high electrical resistivity, low eddy current losses, square nature of hysteresis loops, high stability and high value of saturation magnetization are promising candidates for vast technological application over wide range of frequency [12,26]. Recently, the diamagnetic substitution in mixed ferrites has received special attention. The role-played by the substituents in modifying the physical properties of basic ferrites and the mechanism behind enhanced magnetic response are not widely studied. Fabrication of ferrite materials of high quality, low cost and low loss at high frequency for power applications is ever demanding. This paper reports the concentration dependent effect of Cu–Al ions as dopants on the structural, magnetic and morphological properties of Co ferrites. These ferrites were synthesized using the co-precipitation method and sintered at 600 °C for 10 h with a heating rate of 5 °C/min. The mechanism responsible for the improvement of the magnetic and structural properties was analyzed in detail.

2. Experimental

Ferrites nanoparticles of $Co_{1-x}Cu_xFe_{2-x}Al_xO_4$with $0.0 \leq x \leq 0.8$ were synthesized by the co-precipitation method [27].The chemicals used for the synthesis of cobalt ferrite and its derivatives were $Co(CH_3COO)_2 \cdot 4H_2O$ (99%, Merck), $Cu(NO_3)_2 \cdot 6H_2O$ (98.5%, Merck),Fe $(NO_3)_3 \cdot 9H_2O$ (98.5%, Merck) and Al $(NO_3)_3 \cdot 9H_2O$ (98%, Sigma-Aldrich). All chemicals of analytical grades were used without further treatment. The solutions of the required concentrations were prepared in de-ionized water and heated under constant stirring. As soon as the temperature reached 80 °C, NaOH was added drop wise to maintain the pH above 11 during the co-precipitation process. The co-precipitated products were then washed several times with de-ionized water until the pH of the filtered water reached about 7–8. The precipitates were then filtered and dried over-night in the oven at 200 °C to remove the water content. Finally, the precipitates of the product were ground to fine powder and then annealed at 600 °C in an electric furnace (Vulcan A-550) in air atmosphere with heating rate of 5 °C per minute for 10 h to obtain the pure spinel phase.

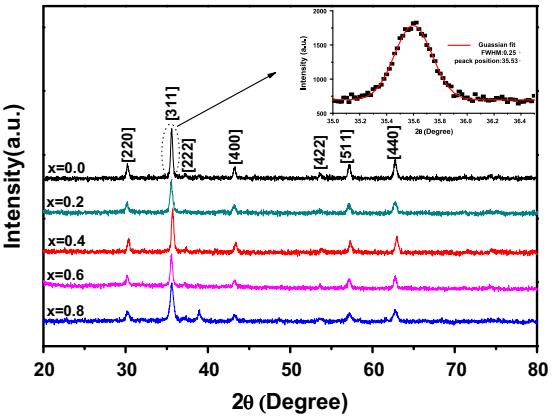

Fig. 1. XRD spectra for $Co_{1-x}Cu_xFe_{2-x}Al_xO_4$NPswith the Gaussian fit of the peak (311)(inset).

For confirmation of the formation of spinel phase and the sample purity, the samples were characterized by using X-ray diffractometer (XRD, D8 Advanced) with CuKα radiations $\lambda = 1.54178$ Å at 40 kV and 10 mA. The speed of scanning was set at ~2°/min with a resolution of 0.011 and 2θ scanning range from 20° to 80°. The Scherrer's equation is used to determine the sizes of ferrite nanoparticles. Fourier transformed infrared (FTIR) spectra were recorded using Perkin-Elmer 5DX FTIR after mixing 1 mg of ferrite sample with 100 mg of potassium bromide (KBr).The contents were thoroughly mixed in mortar for 5 min until a fine mixture was obtained. Pellets of diameter10 mm were then made from these samples. Field emission scan electron microscopy (FESEM) images were recorded using field emission scanning electron microscopy, operated at 120 kV. The room temperature magnetic properties were measured by employing vibrating sample magnetometer (Lake Shore 7303–9309 VSM).

3. Results and discussions

Fig. 1 shows the XRD spectra of all synthesized copper-aluminum substituted cobalt ferrites with concentrations ranging from 0.0–0.8. The XRD spectra confirm the formation of single phased spinel cubic structure (JCPDS no. 22.1086). The lattice constant, '*a*' is determined from the XRD data by using powder-x-software [28]. All samples exhibit a poly-oriented structure with several peaks characteristic of the crystalline planes of 220, 311, 222, 400, 422, 511, and 440 corresponding to the single cubic phase of $Co_{1-x}Cu_xFe_{2-x}Al_xO_4$. The broadening of the X-ray diffraction peaks for as-prepared sample is attributed to the nanocrystalline particle size and lattice strain [28,29]. The absence of any additional peaks related to impurities indicates the high purity of these cobalt–copper ferrite samples. The sizes of the nanocrystallites were estimated from the XRD spectra using Debye–Scherrer's equation [10,30].

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where λ is the wavelength of the X-ray radiation, k is a constant taken as 0.89, β is full width at half maximum (FWHM) of line broadening and θ is the angle of diffraction. The most intense peak (311) is used to estimate the size of