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Structural development and magnetic phenomenon in Zn–Cr–Fe multi oxide nano-crystals

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Abstract

The Cr^{3+} ions doped multi-oxide $ZnFe_{2-x}Cr_xO_4$ ferrite nanoparticles have been synthesized by chemical co-precipitation method. Site occupancies of Zn^{2+}, Cr^{3+} and Fe^{3+} ions were analyzed using X-ray diffraction data and Buerger's method. The effect of the constituent phase variation on the magnetic hysteresis behavior was examined by saturation magnetization which decreases with the increase in Cr^{3+} content in place of Fe^{3+} ions at octahedral B-site. Typical blocking temperature (T_B) around 90 K was observed by zero field cooling and field cooling magnetization study. Room temperature Mössbauer spectra show two paramagnetic doublets (tetrahedral and octahedral sites). The isomer shifts of both doublets decrease whereas quadrupole splitting and relative area of tetrahedral A-site increases with increasing Cr^{3+} substitution. The dielectric constant (measured on compositions $x=0$, 0.4, 0.8 and 1.0) increases when the temperature increases as in the semiconductor. This behavior is attributed to the hopping of electrons between Fe^{2+} and Fe^{3+} ions with a thermal activation.

Keywords: A. Sol–gel processes; C. Dielectric properties; C. Magnetic properties; D. Ferrites

1. Introduction

The magnetic nanoparticles are of great interest, such as the nano-size constituent crystallites used as high-density magnetic storage media [1,2]. Beside, tailoring the properties of nano-spinel ferrite by substitution of different valance cations is most interesting aspect of material chemistry due to their technological importance in the application areas of microwave devices, high speed digital tapes and disk recordings, magneto fluids, catalysis, and magnetic refrigeration systems [3,4]. The synthesis of spinel ferrite nanoparticles has been intensively studied in the recent years and the principal role of the preparation conditions on the morphological and structural features of the ferrites has been discussed by several researchers [5,6]. It is well known that most of the physical and chemical properties of ferrites are strongly depended on their particle size, shape, composition, and cation distribution [7,8]. It is therefore necessary to determine the cation distribution in tetrahedral (A) and octahedral (B) sites of the spinel ferrite. Out of the many transition metal ferrites, the semiconductor zinc ferrite ($ZnFe_2O_4$) has drawn a lot of attention due to its potential applications in radar absorption [9,10]. It has been found that the bulk $ZnFe_2O_4$ has a complete normal spinel structure with tetrahedral A-site occupied by Zn^{2+} and octahedral B-site by Fe^{3+}. The control of $ZnFe_2O_4$ particle size plays a significant role for its magnetic applications.

Substitution of Fe^{3+} by Cr^{3+} in $ZnFe_2O_4$ ferrites affects its structure, electrical and magnetic properties because both are having different ionic size and magnetic moment. Several researchers have studied the effects of Cr^{3+} substitution in the

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spinel ferrites matrix by different methods [11–18]. The ionic magnetic moment of Fe^{3+} and Cr^{3+} ions are 5 μ_B and 3 μ_B, respectively [16]. The Fe^{3+} ($r_{Fe3+}=0.67$ Å) is having higher ionic size compare to Cr^{3+} ($r_{Cr3+}=0.63$ Å) ion [18].

Borhan et al. [16] studied the influence of Cr^{3+} ion substitution on the structural parameters of zinc ferrite synthesized by the sol–gel auto-combustion method and found that the lattice constant and crystallite size slightly decrease with increasing Cr^{3+} content in $ZnFe_{2-x}Cr_xO_4$ (x=0, 0.25, 0.5, 1.0, 1.50 and 2.0) spinel ferrites. The hysteresis loop measurement demonstrated the non-monotonical behavior in saturation magnetization and a coercive field with increasing Cr^{3+} content. The increase in Cr^{3+} content caused a reduction in both magnetic hysteresis loss and dielectric loss at frequencies over 10^5 Hz. Bhargava et al. [17] have synthesized $(Zn_{0.75}Fe_{0.25})[Co_{0.25}Cr_{1.5}Fe_{0.25}]O_4$ ferrite using the conventional solid state route and the spin-glass ordering temperature (T_{sg}) of 25 K in DC field of 200 Oe has been observed.

However, we could not find any reports in the literature related to chemical co-precipitation synthesis of Cr^{3+} substituted zinc ferrites nanoparticles and their magnetic properties. In the present investigation, structural, physical and magnetic properties of co-precipitation produced nanocrystalline zinc ferrite nanoparticles substituted by Cr^{3+} ions in the place of Fe^{3+} ions have been reported. The role of Cr^{3+} substitution in determining structural, dielectric and magnetic properties of Zn–Cr ferrites.

2. Experimental technique

Spinel ferrite nanoparticles $ZnFe_{2-x}Cr_xO_4$ have been prepared by co-precipitation technique. Analytical grade sulfates ($ZnSO_4\cdot 7H_2O$, $Cr_2(SO_4)_3\cdot 6H_2O$,and $Fe(SO_4)_3\cdot 7H_2O$) were used to achieve a $ZnFe_{2-x}Cr_xO_4$ ferrite with x=0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 compositions. Ammonium hydroxide (NH_4OH) was added drop by drop into the solution with stirring until the white precipitates were obtained. After 30 min of stirring, the resultant mixtures were rinsed several times with de-ionized water to remove chlorine and other ionic impurities which may form during the synthesis process.

The resultant precipitations were collected and centrifuged at 6000 rpm and then washed with distilled water and acetone repeatedly and finally dried in air at 80 °C in an oven. A typical flow chart of the synthesis procedure is shown in Fig. 1.

X-ray powder diffraction (XRD) patterns were obtained on a Bruker AXED8 Advance X-ray diffractometer using

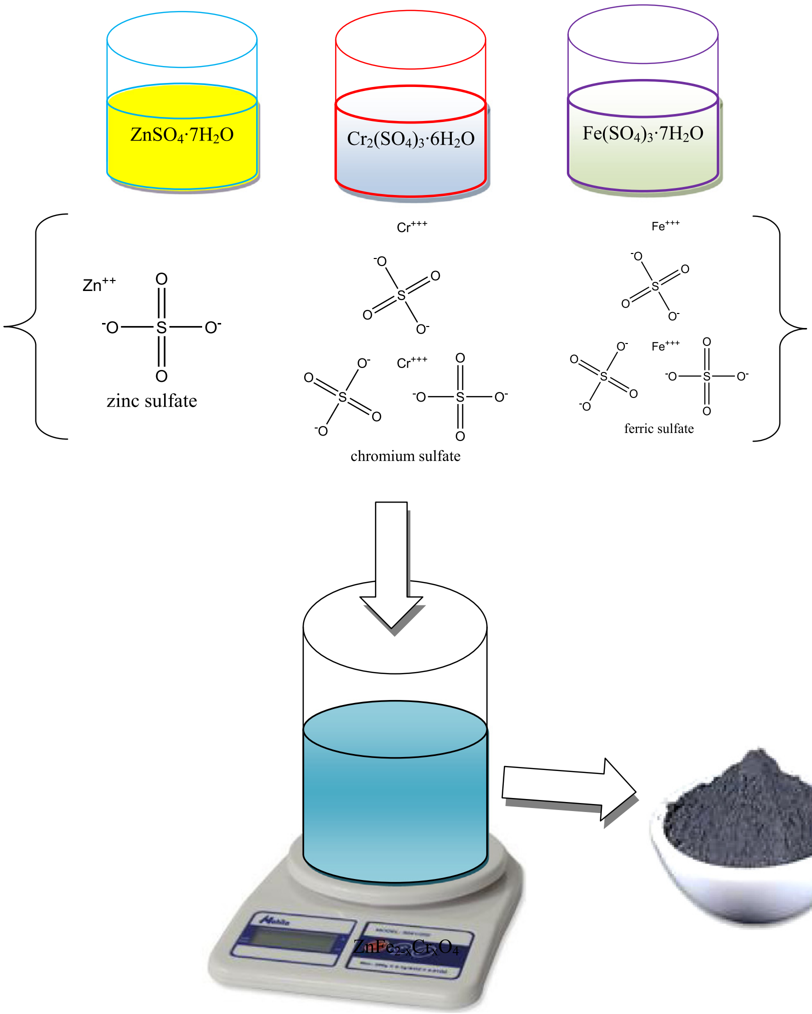

Fig. 1. Flowchart for the preparation of $ZnFe_{2-x}Cr_xO_4$ ferrite nanoparticles by co-precipitation technique.