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Jahn–Teller effect and superparamagnetism in zn substituted copper-gallate ferrite

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Abstract

Spinel ferrite $CuFe_2O_4$ and solid solution of $Cu_{1-x}Zn_xFe_{2-y}Ga_yO_4$ with $0.0 \leqslant x \leqslant 0.5$ are synthesized through the usual ceramic method. X-ray diffraction measurements confirm the presence of single-phase tetragonal structure with $c/a > 1$for $CuFe_2O_4$ and compositions with $x \leqslant 0.1$. The formation of the tetragonal phase in these samples is attributed to the presence of the cooperative Jahn–Teller Cu ion at the octahedral B-site in the spinel lattice. At the compositional parameter $x \geqslant 0.2$, tetragonal-to-cubic transformation occurred and the lattice parameter a for the cubic unit cell is found to decrease with increasing Zn content x. ^{57}Fe Mössbauer measurements at 293 K for these compounds reveal superparamagnetic phase for samples with $0.0 \leqslant x \leqslant 0.2$. In contrast, Mössbauer spectra at 12 K for these materials show well ordered spectra where, the cation distribution and the hyperfine parameters are determined.

Keywords: Jahn–Teller effect; Tetragonal–to-cubic transformation; Mössbauer effect; Superparamagnetism

1. Introduction

In the ideal cubic AB_2O_4 spinel structure the oxygen ions form a cubic close packed lattice with the A and B cations occupying, respectively, $\frac{1}{8}$ of the tetrahedrally and $\frac{1}{2}$ of the octahedrally coordinated interstices. In particular, the phase transformations and Jahn–Teller (JT) distortion in the tetragonal spinels have attracted considerable attention in recent studies [1–4]. The large tetragonal distortion, which occurs in a number of spinels such as $ZnMn_2O_4$, $CuFe_2O_4$, and $CuCr_2O_4$, arises because of JT type distortion in the immediate environment of ions with d^4, d^9 in a high-spin state [5–7]. The cooperative JT effect has also been observed due to the higher concentrations of JT ions in the B-site, which are either isolated from each other or connected in one, two, or three dimensions via common corners, edges, or corners [8]. Copper ferrite, which is tetragonal at room temperature due to a cooperative JT distortion that is driven by the octahedral-site Cu^{2+} ($3d^9$) ions, has led to a number of experimental, and theoretical investigations of this phenomenon [9].

Substitutions of non-magnetic ions in simple and mixed ferrites have received a great deal over the past years [10,11]. The presence of these ions in spinel ferrites is found to alter their magnetic and electric properties. These substitutions in iron oxides are particularly apparent in their Mössbauer spectra, where the magnetic interactions are drastically reduced. This in turn, lower the magnetic ordering temperature and decreases the hyperfine fields [12–15].

The present work reports on preparation procedures, X-ray diffraction (XRD) results, and Mössbauer studies of $CuFe_2O_4$ and Zn^{2+} substituted Cu-gallate spinel ferrite $Cu_{1-x}Zn_xFe_{1.9}Ga_{0.1}O_4$, with $0.0 \leqslant x \leqslant 0.5$ aiming to shed more lights on crystallographic structure and the microscopic picture of the magnetic ordering in these diluted ferrimagnets.

2. Experimental details

Polycrystalline samples $CuFe_2O_4$ and $Cu_{1-x}Zn_xFe_{1.9}Ga_{0.1}O_4$ with $0.0 \leqslant x \leqslant 0.5$ are synthesized through solid-state reactions

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using Fe_2O_3, ZnO, CuO, and Ga_2O_3 (purity $\geqslant$ 99.99%) as starting materials. The mixture of the oxide powders is prefired at 950–1100 °C) depending on the CuO content for 24 h. The product is reground using agate ball-mill and fired again at the same conditions to improve homogeneity. The final powders are pressed into pellets and sintered at 1000–1200 °C for 8 h, then slowly cooled to room temperature. XRD measurements are obtained using CuK_α radiation and their analysis showed that the products are crystallized in a single-phase structure. The Rietveld method [16] is used to determine the phase composition and the lattice parameter of the samples under consideration. The determination of the diffraction domain sizes or crystallite sizes (D) for the powder samples was conducted by line-broadening analysis [17].

Austin Science Mössbauer Spectrometer with constant acceleration drive and data acquisition system is used in a standard transmission setup with a Personal Computer Analyzer (PCA II-card with 1024 channel). The radioactive source is ^{57}Co imbedded in Rh matrix with initial activity of 50 mCi. Metallic iron spectrum is used for the calibration of both observed velocities and hyperfine magnetic fields. For the low-temperature measurements (12 K), the closed-cycle variable temperature cryostat for Mössbauer (Model REF-399-D22) is used. Experimental details for installation, optimization, and utilization of this unit are reported earlier [18]. The Mössbauer spectra are analyzed with a computer program [14], where the areas of both tetrahedral and octahedral subspectra of the Fe^{3+} are used for determination of cation distribution.

3. Results and discussion

Fig. 1 displays the XRD patterns of the prepared samples $CuFe_2O_4$ and $Cu_{1-x}Zn_xFe_{1.9}Ga_{0.1}O_4$ with ($x = 0.2$). The result of indexing XRD patterns has shown that the nominal composition structures with different concentrations are single phase with no additional lines corresponding to any other phase.

Tetragonal structure with space group ($I4_1/amd$) is obtained for $CuFe_2O_4$, $CuFe_{1.9}Ga_{0.1}O_4$, and $Cu_{0.9}Zn_{0.1}Fe_{1.9}Ga_{0.1}O_4$ with $c/a>(\sim 1.4)$ as given in Table 1. This can be explained as follows: the metal sites in most transition metal oxides

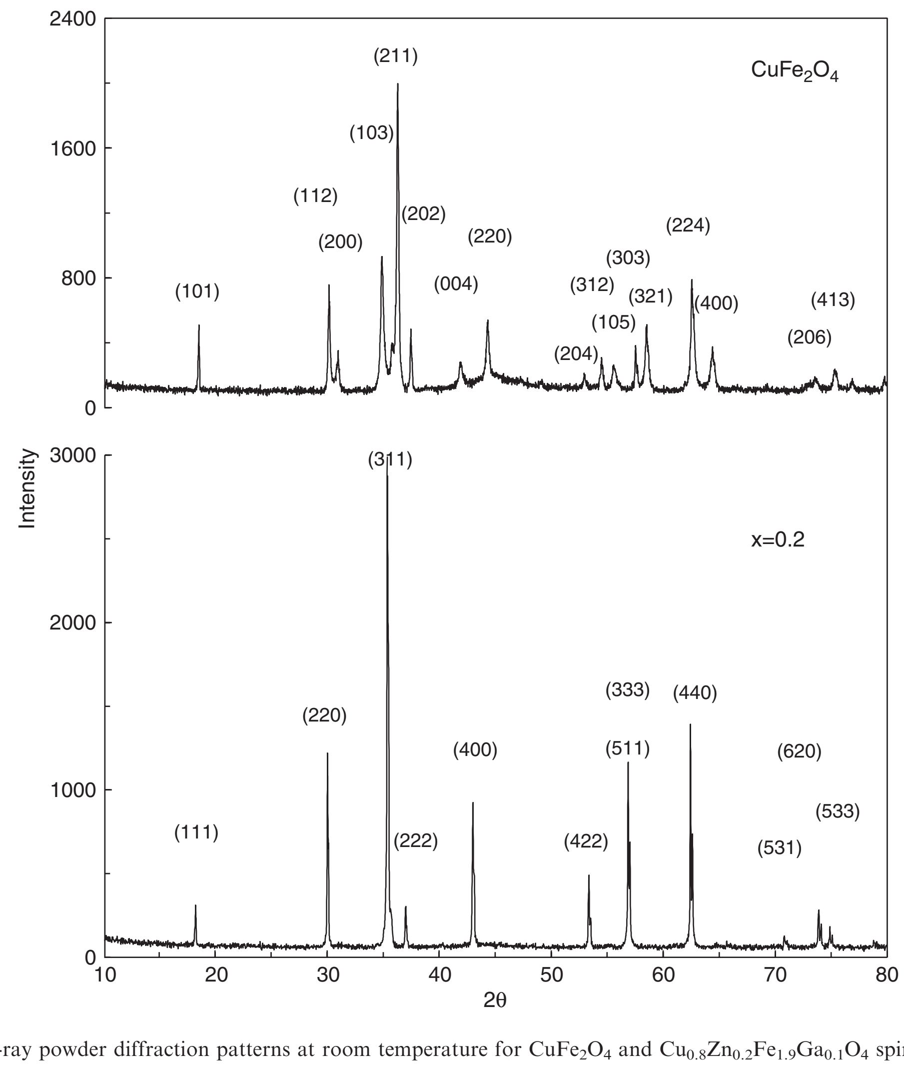

Fig. 1. X-ray powder diffraction patterns at room temperature for $CuFe_2O_4$ and $Cu_{0.8}Zn_{0.2}Fe_{1.9}Ga_{0.1}O_4$ spinel ferrites.