Magnetization Properties Study of $ZnCr_2O_4$ Spinel Normal

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The magnetic properties and crystal structure of Zn chromite spinel normal have been investigated by dc/ac magnetization as a function of temperature and magnetic field. In addition, X-ray powder diffraction and scanning electron microscopy measurements were carried out at room temperature. The structural refinement was performed by means of the Rietveld method and the lattice parameter calculated for this material is 8.327 Å, consistent with those reported for the bulk materials in the literature. The average sizes of the particles were calculated from the Scherrer's equation and compared with the size obtained by scanning electron microscopy. We noticed an increase in the average size of particles with increasing calcination temperature. However, $ZnCr_2O_4$ nanoparticles with grain sizes of about 10–15 nm presents an effective moment of 3.90 μ_B/Cr^{3+}, value slightly higher than expected 3.8 μ_B/f.u., for free ion Cr^{3+}, and a Curie-Weiss temperature of −290 K which implies that this system is geometrically frustrated.

***Index Terms*—Chromite, geometrical frustrated, $ZnCr_2O_4$.**

I. Introduction

In recent years, the investigation of geometrically frustrated magnets has been recognized as an important and exciting area of research [1], [2]. In particular, the AB_2X_4 spinels have been studied due to its natural geometrical frustrated structure. It is known that cations A and B sites both can be occupied by magnetic ions. Coupling between the various magnetic ions gives rise to a number of competing exchange pathways and a multitude of possible ground states. The complexity in the normal AB_2X_4 spinels arises from the frustration effects related to the topological constrains of the pyrochlore lattice of corner-sharing tetrahedral of the B-site magnetic ions. In this geometry, the exchange interaction alone cannot select a unique ground state.

As a result, the magnetic system remains in the disordered state down to temperatures much lower than the scale provided by the exchange interaction. Cr-based spinels ACr_2O_4 (A = Mg, Zn, Cd, and Hg) have attracted much attention because the magnetic $Cr^{3+}S = 3/2$ ions form the most frustrated lattice, a network of corner sharing tetrahedral [3]

Magnetic ground states depend strongly on the A cation in ACr_2O_4 spinels. Non-magnetic A site (for instance A = Zn, Mg, Cd) chromium oxide spinels are highly frustrated [4]. Spin-lattice coupling resolves the large ground state degeneracy by selecting a unique ordered state via a spin Jahn-Teller effect at the magnetic ordering temperature [5]. In magnetic A site spinels (for instance, A = Co, Fe, Cu, Mn), A-O-Cr coupling dominates over frustrated Cr-Cr interactions and non-collinear ferrimagnetic ground states are attained [6]

In $ZnCr_2O_4$ strong direct antiferromagnetic (AFM) Cr-Cr exchange is manifested by the Curie-Weiss temperature of about −400 K, while magnetic order appears around 12 K via a first-order phase transition. At this transition the aforementioned degeneracy is lifted by a structural deformation, which is reported to be tetragonal [7].

The properties of the prepared materials are influenced by the composition and microstructure, which are sensitive to the preparation methodology used in their synthesis. Many methods such as citric acid combustion method, sol-gel auto-combustion method, organic gel-thermal decomposition method, hydrothermal method, coprecipitation method, gel-assistant hydrothermal route, wet chemical coprecipitation technique, self-propagating and microemulsion [10]–[15] have been developed to prepare nanocrystallite $ZnCr_2O_4$.

In this paper, we report magnetization studies on the spin structure of nanoparticles of $ZnCr_2O_4$ prepared by coprecipitation.

II. Experimental Details

Powders of high purity were prepared by the aqueous precipitation method. Chromium (III) nitrate nonahydrate ($Cr(NO_3)3 \cdot 9H_2O$, Sigma-Aldrich 99%) and zinc (II) nitrate hexahydrate ($Zn(NO_3)2 \cdot 6H_2O$, Sigma-Aldrich 99%) were used as the chromium and zinc ions sources respectively, and a dilutes solution of sodium hydroxide (NaOH Sigma-Aldrich 98%) was added with constant stirring until the pH of the solution was adjusted to 13. The precipitate was washed with distilled water until free from chloride and nitrate ions, and then it was dried at 353 K for 2 h. Finally the precipitate was oven dried and calcined at 673 K. A fine powder was obtained by grinding in agate mortar.

X-ray powder diffraction (XRD) patterns were obtained in a Rigaku diffractometer at room temperature. Diffraction patterns were taken from 20 to 80° at a scanning speed of $0.5°/\mathrm{min}$. In order to analyze the structure and morphology of the samples scanning electron microscopy (SEM) images were taken in a JEOL field emission gun SEM JSM 63330 F microscope at the Laboratório de Microscopia Eletrônica at Laboratório Nacional de Luz Sincrotron (LNLS, Brazil). DC/AC magnetization measurements were carried out in a Physical Property measurement system Quantum Design PPMS-9T.

III. Results

Initially, the $ZnCr_2O_4$ nanoparticles were synthesized at 400°C via co-precipitation method and then they were charac-

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