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ORIGINAL ARTICLE

Hydrothermal synthesis, structural and impedance studies of nanocrystalline zinc chromite spinel oxide material

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Abstract Zinc chromite ($ZnCr_2O_4$) nanocrystalline spinel material was synthesized through hydrothermal method by using zinc nitrate 6-hydrate and chromium nitrate 9-hydrate as precursors. The synthesized material was characterized for phase identification, crystallinity and surface morphology by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD results showed that hydrothermally as-synthesized products remained poorly crystalline up to 300 °C. Zinc chromite cubic spinel structure developed after calcination at 600 °C for 4 h. Formation of single-phase cubic structure of $ZnCr_2O_4$ was also confirmed by Rietveld refinement study with lattice parameter $a = 8.2874$ Å, and Fd3m space group. Thermal stability of the developed material was observed by thermogravimetry (TG) and differential thermal analysis (DTA). Thermal study reveals that $ZnCr_2O_4$ is thermally stable above 700 °C. The Fourier transform infrared (FTIR) spectra show the two absorption bands of Cr–O and Zn–O at 490 and 616 cm^{-1} respectively. These bonds were associated with $ZnCr_2O_4$ and indicate the formation of cubic spinel $ZnCr_2O_4$ material. The band gap energy of $ZnCr_2O_4$ powder was determined by absorption spectroscopy in ultraviolet–visible

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range and was found to be 3.771 eV and 3.147 eV for direct and indirect band gap respectively. SEM images show well-faceted crystals of $ZnCr_2O_4$, with the grain size of 50–80 nm. An equivalent circuit model $(R_1Q_1)(R_2Q_2)(R_3Q_3)$ was employed to explain three relaxation processes associated with bulk and grain boundaries in $ZnCr_2O_4$ nanoparticles, and electrodes. Conductivity of the nanoparticles increased with frequency, and dielectric constant of the material showed dispersion at comparatively lower frequencies. At higher frequencies, the dielectric constant remained independent of frequency as attributable to the atomic and electronic polarizations.

1. Introduction

Zinc chromite ($ZnCr_2O_4$) crystallizes in the cubic system and has a normal spinel structure. In this mixed oxide $ZnCr_2O_4$ non-magnetic Zn^{2+} and magnetic Cr^{3+} ions have a strong preference for the tetrahedral A-sites and the octahedral B-sites, respectively. It is a geometrically frustrated antiferromagnet with a first order transition at 12.5 K from paramagnetic phase with cubic structure to antiferromagnetic phase with tetragonal structure [1–4]. The nanocrystalline $ZnCr_2O_4$ spinel has many applications, e.g., as catalysts [5,6], sensors for toxic gases [7,8] and semiconductors [9]. $ZnCr_2O_4$ is also very attractive as air depollution catalytic material, for a variety of reactions like oxidation of hydrocarbons, oxidative dehydrogenation of hydrocarbons, synthesis of methanol [10–13], as gas sensing [8], humidity sensing [12,14–15] and photocatalyst [16,17]. For the synthesis of homogenous and sinterable chromite materials different methods are being used, and a great attention has been given to the improvement of these fabrication techniques. In solid state route [18–20], the spinel powder with low surface area can be produced by mixing oxides, carbonates, the mixture being calcined, and followed by grinding. However, the spinel oxides with high surface area can be achieved in wet chemical method, by processing the precursors by means of wet commixing [21,22], coprecipitation [23,24], cocrystallization [25], sol-gel [26,27], sol-spray process [28], sonochemical [29], thermolysis of polymer-metal complex [30], microemulsion [31], gel combustion [32–35], microwave [36] and hydrothermal methods [37–41]. Among all these synthesis methods, the hydrothermal method shows promising potential for synthesizing of nanosized chromite and ferrite spinel oxides, due to its good chemical homogeneity, high purity, and controlled nanostructure. In the present work the nanocrystalline zinc chromite spinel oxide materials have been synthesized by hydrothermal technique by optimizing the temperature, time and pH conditions and heat treatment of resultant powder specimens in order to achieve nanocrystallite with different sizes. The synthesized materials have been characterized for phase analysis, thermal decomposition behavior and microstructural analysis by XRD, TG/DTA and SEM, respectively. Optical and impedance properties of $ZnCr_2O_4$ spinel specimens are also investigated.

2. Experimental

2.1. Materials

Starting materials used in the present study were zinc nitrate ($Zn(NO_3)_2.6H_2O$, Merck, 99.9%), chromium nitrate ($Cr(NO_3)_3.9H_2O$, Merck, 99.9%) and sodium hydroxide pellets (NaOH, Merck). All chemicals were of analytical reagent grade and used without further purification. Double distilled water (DDW) with conductivity less than 5 μS/cm was used in all experiments (Metrohm 712 Conductometer).

2.2. Method

Zinc chromite ($ZnCr_2O_4$) oxide powder was prepared by simple hydrothermal process. In this method, aqueous solutions containing the respective zinc nitrate 6-hydrate and chromium nitrate 9-hydrate as precursors in a specified mole ratio of 1:2 were combined and dissolved in a 250 ml evaporator flask. The NaOH aqueous solution (10 M) was added drop wise and pH of the solution was maintained at 11 with pH-regulator (Selecta pH-2006). The evaporator flask was fitted in rotary evaporator (Heidolph Laborota 4001) maintained at 70–80 °C for 4 h until a homogeneous solution was obtained. The evaporator flask was first thoroughly degassed in order to minimize the contamination of the product from the atmospheric CO_2. The resultant solution was shifted in PTFE-lined

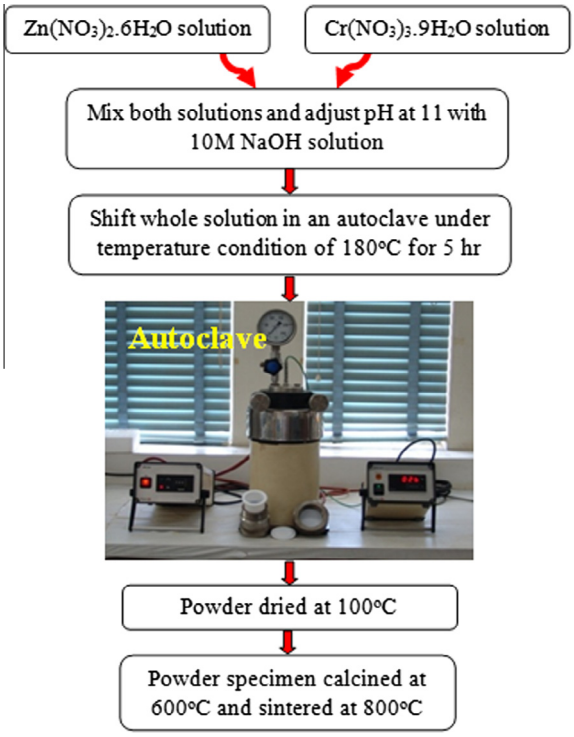

Figure 1 Schematic layout diagram for the hydrothermal synthesis of $ZnCr_2O_4$.