Materials Research Bulletin 76 (2016) 431–435

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Radio frequency abnormal dielectric response of manganese chromite ($MnCr_2O_4$) nanoparticles synthesized by coprecipitation method

Muhammad Gul

Nanoscience, Nanotechnology and Tribology Research Lab, National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar 25120, Pakistan

ARTICLE INFO

Article history:
Received 3 April 2015
Received in revised form 27 November 2015
Accepted 3 January 2016
Available online 6 January 2016

Keywords:
A. Nanostructures
B. Chemical synthesis
C. X-ray diffraction
D. Crystal structure
D. Dielectric properties

ABSTRACT

Radio frequency dielectric behavior of nanocrystalline $MnCr_2O_4$ synthesized via surfactant-free controlled coprecipitation route has been studied. Keeping in view the necessity of particle size uniformity and phase purity for genuine performance, experimental conditions were optimized accordingly. The scanning electron micrographs of the synthesized product revealed the formation of monodispersed particle system. X-ray diffraction analysis confirmed monophasic spinel structure formation with 65 nm crystallite size. Two characteristic peaks observed between 700 cm^{-1} and 400 cm^{-1} in the FTIR spectrum also supported the spinel phase purity of compound. The dielectric constant was found normal, but loss tangent of the sample showed abnormal behavior with frequency. The observed dielectric behavior of the synthesized product has been explained on the basis of space-charge polarization according to Maxwell–Wagner's model and mutual contribution of *n*-type & *p*-type charge carriers (Rezlescu model). The ac conductivity linearly increased with frequency highlighting the existence of polaron hopping.

1. Introduction

Metal chromites (MCr_2O_4) with spinel structure have been the focus of researchers due to their technological applications as catalysts, refractories, ceramic dyes, battery materials and electronic storage media [1,2]. $MnCr_2O_4$ is one of these compounds, of which magnetic properties has been extensively studied [3–5]. It is, however, difficult to find out its dielectric behavior in the existing literature. Only few studies have been conducted at high temperature like Song et al. [6] conducted impedance measurement on $MnCr_2O_4$, prepared by the solid-state method, in the frequency range of 1–10 MHz between 160 to 400 °C. Similarly, Lu et al. [7] measured electrical conductivity of Mn-doped $MnCr_2O_4$ both in an oxidizing and reducing environment while cooling from 1000 to 600 °C with intervals of 50 °C. Recently, Mufti et al. [8] investigated the magnetodielectric coupling in frustrated spin systems of some metal chromites. Electrical properties of $MnCr_2O_4$ has also been investigated, however, the sample contained secondary phases [9,10].

Furthermore, the properties of a material in nano-regime differ significantly from its bulk counterpart because each interface (grain boundary) act as a capacitor, thus changing the dielectric properties. Besides chemical composition, uniformity in particle size and phase purity is highly desirable for genuine electrical performance [11]. To address the latest issue, a suitable synthesis route must be devised.

The most commonly used method to prepare such materials is the conventional solid state ceramic route composed of a series of laborious heating/grinding cycles (>1200 °C) which results in an unavoidable compositional inhomogeneity. Improvement has been made in regard to homogeneity and control of stoichiometry by adopting chemical routes involving coprecipitation [12,13], sol–gel [7], hydrothermal synthesis [14], combustion method [2] and chemical vapor transport method [15]. Among these, coprecipitation seem better due to its simplicity, cost-effectiveness, product purity and good control over particle size. However, agglomeration of particles is usually accompanied with this method.

In the current study, a modified chemical coprecipitation route is followed. An attempt is made to optimize conditions such that monodispersed particles of $MnCr_2O_4$ in the nano-regime are obtained without using any sort of surfactant. The prepared product is characterized by SEM, XRD and FTIR spectroscopic techniques. The room temperature, frequency-dependent

E-mail addresses: mgul@upesh.edu.pk, mg46asim@gmail.com (M. Gul).

http://dx.doi.org/10.1016/j.materresbull.2016.01.007
0025-5408/

dielectric behavior of the end product, measured by an LCR-meter in the radio frequency range, are discussed in detail.

2. Experimental

2.1. Materials

The research grade chemicals used for the synthesis of $MnCr_2O_4$ nanoparticles were $MnSO_4$ [Scharlau], $Cr(NO_3)_3\,9H_2O$ [ACROS] and NH_4OH [BDH England]. All the stock and working solutions were prepared in de-ionized water. The glassware used for preparation of solution, storage and to carry out reactions were made of Pyrex glass.

2.2. Synthesis of $MnCr_2O_4$ precursors

Aqueous solutions containing equal concentrations of Mn^{2+} and Cr^{3+} species were mixed and heated to 80 °C in a double walled Pyrex glass vessel connected to a water bath (WiseCircu WCB-6) under constant stirring on a magnetic stirrer (WiseStir MSH-20D). The pH of heated mixture was adjusted to ~13 by the addition of 3 M NH_4OH. The stirring of the precipitates formed was continued for 3 h at room temperature and left overnight for aging. Next day the mother liquor was discarded, precipitates were washed with distilled water to pH 7 and then dried in an electric oven (BINDER FD53) at 100 °C (±2 K) for 20 h. The virgin precipitated precursors, $Mn(OH)_2$ and $Cr(OH)_3$, were obtained according to the ionic reaction below.

$$Mn^{2+} + 2Cr^{3+} + 8\overline{O}H \rightarrow Mn(OH)_2 \downarrow + Cr(OH)_3 \downarrow$$

2.3. Thermal treatment

A part of the synthesized product was calcined at 1000 °C for 2 h in an electric furnace (Nabertherm, L5/11) in air atmosphere. Heat treatment is considered to transform the precipitated precursors into the end product as:

$$Mn(OH)_2 + 2Cr(OH)_3 \rightarrow MnCr_2O_4 + 4H_2O$$

The virgin precipitates obtained is designated as MC and heat treated particles as MC-1000 in the rest of this document.

2.4. Characterization techniques

The crystalline nature and phase identification of MC and MC-1000 samples were carried out using X'pert PRO, PANalytical X-ray Diffractometer with CuKα (λ = 1.5406 Å) radiation at step angle 0.02°. The heat induced morphological variations, if any, were studied through JEOL, JSM-5910 scanning electron microscope. The FTIR spectroscopic technique was employed to characterize bond vibrations in the range 4000–400 cm^{-1}.

2.5. Dielectric measurement

For dielectric measurements, a suitable amount of MC-1000 powder was pressed into disc-shaped pellet of 10 mm diameter by applying uniaxial pressure using polyvinyl alcohol (PVA) as a binder. The pellet was calcined in two consecutive steps, i.e., with a slow heating rate at 650 °C for 4 h to remove the binder and then at 1100 °C for 2 h for densification of the material. The opposite surfaces of pellet were coated with highly conducting silver paint to make parallel plate capacitor geometry and manganese chromite as the dielectric material. The frequency dependent dielectric and ac conductance measurements were simultaneously performed on silver coated pellet using Agilent 4287A RF LCR meter in the frequency range 1–2000 MHz at room temperature.

3. Results and discussion

3.1. Scanning electron microscopic studies

Fig. 1 shows the scanning electron micrographs (SEM) of MC and MC-1000 samples. It is clear from the micrographs that MC particles are very small and uniform in size and shape, however, agglomeration up to some extent is observed due to high surface/volume ratio. The high temperature treatment lead to increase in particle size similar to spinel ferrite reported elsewhere [16]. It is assumed that at high temperatures, the grain boundaries move and several particles in close vicinity get merged to form a single large particle.

3.2. X-ray diffraction studies

The structure and phase purity of the MC and MC-1000 particles is confirmed by analysing X-ray diffraction patterns, displayed in Fig. 2. The XRD data was recorded in the range $10 < 2\theta < 80°$. It is found that MC particles are amorphous in nature, as expected for metal hydroxides. Heat treatment transforms hydroxides into oxides by removal of water. In the XRD pattern of MC-1000, all the diffraction peaks related to Brag's reflections from (1 1 1), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1), (4 4 0) and (5 3 3) planes correspond to pure $MnCr_2O_4$ phase with cubic spinel structure belonging to space group $Fd-\overline{3}m$. These peaks matched well with the standard PDF # 75-1614 of manganese chromite ($MnCr_2O_4$) stored in the database of NIST software CMPR-LOGIC. The signal noise for the pattern in Fig. 2 appears to be about 1/2–1% of the largest peak. No extra peak above this signal noise level is observed

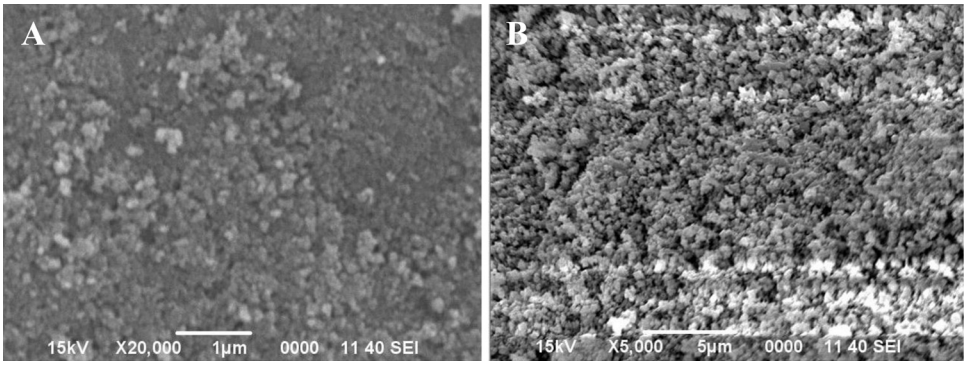

Fig. 1. Scanning electron micrographs (SEM) of (A) MC and (B) MC-1000 particles.