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ScienceDirect

Ceramics International 40 (2014) 15515–15521

CERAMICS INTERNATIONAL

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Structural, electrical and magnetic properties of nickel manganite obtained by a complex polymerization method

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Received 15 May 2014; received in revised form 4 June 2014; accepted 4 July 2014
Available online 10 July 2014

Abstract

Structural, electrical and magnetic properties of nickel manganite ceramics obtained by sintering fine powders prepared by a complex polymerization method are given in this work. The phase composition of the synthesized material was examined by x-ray powder diffraction (XRPD). Field-emission scanning electron microscopy (FE-SEM) was used to analyze the obtained powder morphology. Scanning electron microscopy (SEM) was used to analyze the microstructure of sintered ceramics. The activation energy of conduction E_a and the coefficient of temperature sensitivity $B_{25/100}$ were calculated from direct current (DC) resistivity measurements. The magnetization dependence of temperature $M(T)$ and alternating current (AC) susceptibility data obtained from SQUID measurements clearly demonstrate that quadruple magnetic phase transitions can be readily detected at $T_{M1} \sim 115$ K, $T_{M2} \sim 105$ K, $T_{M3} \sim 38$ K and $T_{M4} \sim 7$ K. These findings suggest a novel magnetic transition for nickel manganite at low temperature T_{M4}.

Keywords: A. Powders: chemical preparation; B. Electron microscopy; C. Electrical properties; C. Magnetic properties

1. Introduction

Spinel materials based on Mn and Ni have been intensively studied over the past years due to their excellent semiconductor properties [1]. Nickel manganite as a negative temperature coefficient (NTC) thermistor is widely used today in different industrial sectors. Up to now, $NiMn_2O_4$ has been synthesized in the form of powders, thin or thick films, and single crystals. Solid state processing of oxides [2] or corresponding organic precursors [3–10], as well as auto-combustion [11] were usually used for powder synthesis. A slight variation of cation compositions along with the introduction of dopants significantly affects structural, electrical and thermistor sensing properties [12]. Although $NiMn_2O_4$ belongs to the group of cubic spinels with a seemingly simple chemical formula, it has a partially inverse spinel structure and variable Ni to Mn ratio at certain cation positions. Merging of the mixed-valence manganese (Mn^{2+}, Mn^{3+}, Mn^{4+}) with Ni^{2+} ions and adjoining oxygen anions could result in different magnetic interactions, such as antiferromagnetic (AF) super-exchange in Mn^{3+}–O^{2-}–Mn^{3+} bonds, ferromagnetic (FM) double exchange in Mn^{3+}– O^{2-}–Mn^{4+} pairs, antiferromagnetic interaction between Mn^{2+}– O^{2-}–Mn^{3+}, surface spins canted structures, etc [13]. It was recently shown that the broad magnetic feature conditioned by the complex cationic distribution over octahedral and tetrahedral positions is additionally dependent on the particle structure, morphology, particle size and spinel stoichiometry [14–18]. Change of these parameters through control of the oxygen partial pressure during $NiMn_2O_{4-\delta}$ polycrystalline calcination in different atmospheres [19] leads to the appearance of three magnetic transitions in this material, at ~40 K (long-range antiferromagnetic transition), ~105 K (antiferromagnetic-type transition) and ~120 K

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http://dx.doi.org/10.1016/j.ceramint.2014.07.024
0272-8842/

(ferromagnetic-like transition). Interesting magnetic behavior was also found in pulse laser deposited thin films of stoichiometric nickel manganite [20]. Bulk powder and annealed films exhibited two magnetic transitions at $T_1=70$ K and $T_2=110$ K whereas the as-grown $NiMn_2O_4$ films exhibited only one magnetic transition. The same authors reported on new magnetic behavior of the spinel to Fe_2O_3 interface where a thin inter-diffused region of $(Fe, Mn, Ni)_3O_4$ was formed [21]. Recently, Menaka et al. [22] confirmed the morphology related dependence of the magnetic properties of nickel manganite. The ferrimagnetic transition temperature and magnetization decrease gradually with the change of the shape of nanoparticles towards elongated nanorods from 126 to 72 K. All these results corroborate the interesting and peculiar magnetic properties of the nickel manganite spinel structure.

In this work we report on a complex polymerization method (CPM) for producing nickel manganite fine particles with a homogeneous distribution of constituent cations in the crystal lattice that ensures formation of a dense monophased ceramic with novel magnetic properties after sintering in oxygen atmosphere.

2. Materials and methods

The starting point of the synthesis procedure was formation of a citrate-based precursor from nickel acetate tetrahydrate ($(CH_3COO)_2Ni\cdot 4H_2O$, Fluka, $\geq 99\%$) and manganese acetate tetrahydrate ($(CH_3COO)_2Mn\cdot 4H_2O$, Aldrich, $\geq 98\%$). The reagents were diluted in water taking into account the stoichiometric ratio between metal ions Mn/Ni = 2. Citric acid (CA) was added into the solution until the molar ratio between the metal ions (Me = Ni, Mn) and citric acid was 1:10. The solution was agitated at room temperature for 1 h, and then neutralized with ammonia. Ethylene glycol was used as a polymerization agent in the molar ratio defined to be Me: EG = 1:16. The obtained mixture was stirred first at 60 °C to evaporate water and increase viscosity, and then at 120 °C, to create a gel which slowly turned into a dark resin. The resin was dried at around 200 °C and calcined under the following regime: 250 °C /1 h, 400 °C /2 h (2 °C /min) and finally at 800 °C /2 h (5 °C /min) in oxygen atmosphere. The calcined powder was pressed into disc shape pellets and later sintered under oxygen gas flow for 2 h at 1200 °C.

The morphology of the powder prepared by CPM was monitored using a MIRA 3 TESCAN field emission scanning electron microscope (FE-SEM). The microstructure of the sintered ceramic was investigated using a TESCAN Vega TS 5130 MM scanning electron microscope equipped with a back-scatter electrons (BSE) detector and an energy dispersive X-Ray spectroscopy (EDXS) system (INCAPentaFETx-3 detector, Oxford Instruments, UK). The phase composition of the powder was analyzed by X-ray powder diffraction (XRPD) using a Seifert ID 3000 X-ray diffractometer with CuKα radiation. Data acquisition was done in the angular range $2\theta=10°–80°$ with a step scan of 0.02 and a counting time of 10 s per step. Structural refinement was performed through Rietveld analyses using the Topas Academic 4.1 software [23]. The Fundamental Parameter Approach was used to determine microstructural parameters. The FWHM based LVol (volume weighted mean column height) calculation was used to determine intermediate crystallite size broadening, modeled by a Voigt function, and the Gaussian based strain calculation was used for strain broadening. Peak shapes, lattice parameters and scale were refined simultaneously. After convergence, atomic positions and isotropic temperature factors were included in the refinement.

Electrical characteristics were measured on a Keithley 237 high voltage source unit analyzer. Electrical contacts for these measurements were prepared by spreading a silver paste on the sample surface. The resistance–temperature (R–T) and dc current–voltage (I–U) characteristics were measured in the temperature range from room temperature (22 °C) to 120 °C. The sample was immersed in a silicon oil bath to improve the accuracy of the temperature measurements.

Magnetic measurements of nickel manganite (powder and ceramic) were performed with a SQUID magnetometer (Quantum Design model MPMS XL5) in the temperature range from 2 to 300 K under a magnetic field of 100 Oe, in both, field cooled (FC) and zero-field-cooled (ZFC) modes. The AC susceptibility measurements were performed under an excitation field of 6.5 Oe at four different frequencies (1, 10, 100, and 1000 Hz) in the temperature range from 2 to 120 K.

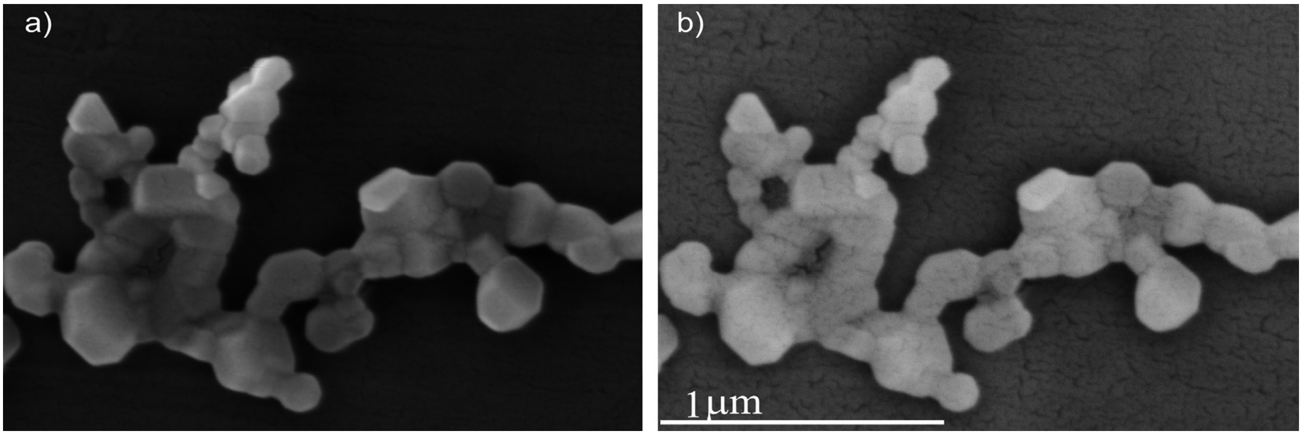

Fig. 1. Field emission scanning electron micrographs: SE (a) and BSE (b) mode of NMO-O_2 powder synthesized by CPM and calcined at 800 °C.