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Nanoindentation study of nickel manganite ceramics obtained by a complex polymerization method

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ABSTRACT

The chemical synthesis of nickel manganite powder was performed by a complex polymerization method (CPM). The obtained fine nanoscaled powders were uniaxially pressed and sintered at different temperatures: 1000–1200 °C for 2 h, and different atmospheres: air and oxygen. The highest density was obtained for the sample sintered at 1200 °C in oxygen atmosphere. The energy for direct band gap transition (*Eg*) calculated from the Tauc plot decreases from 1.51 to 1.40 eV with the increase of the sintering temperature. Indentation experiments were carried out using a three-sided pyramidal (Berkovich) diamond tip, and Young's modulus of elasticity and hardness of NTC (negative temperature coefficient) ceramics at various indentation depths were calculated. The highest hardness (0.754 GPa) and elastic modulus (16.888 GPa) are exhibited by the ceramics sintered at highest temperature in oxygen atmosphere.

1. Introduction

Negative temperature coefficient (NTC) thermistors, as the main part of many electronical devices, have been in use for long time owing to their excellent semiconductor properties [1]. Materials for NTC thermistors are usually composed of transition metal spinel and are

widely used in different industrial applications today [2–5]. Nickel manganite (NMO) material has been the subject of considerable practical interest as a potential candidate for NTC applications due to its interesting optical, electron transport, electronic and magnetic properties [6–10].

Nowadays, meeting growing environmental demands, this material has found its great use as a catalyst for volatile organic compounds [11], in electrochemistry as a electrochemical capacitor and in lithium ion battery applications [12,13]. In processing of the NTC devices, it is very important to optimize the synthesis conditions, for the quality of NTC powders reflects on the device's performance. Our previous results were based on obtaining the NMO by the solid state reaction or mechanochemically assisted solid state reaction method [6,8,14]. Recently, we have produced the NMO powder by the complex polymerization method and obtained a sample with fine particles and more homogeneous distribution of constituent cations in the crystal lattice, which ensured the formation of a dense monophased ceramic [15,16]. It is generally known that several changes of structure and microstructure may occur in a material during the synthesis and affect its properties.

In previous years we have dealt with the investigations of optical, electrical and magnetic properties of the NMO ceramics. Also, it was challenging to examine its mechanical properties considering its importance in the electronics industry. Apart from the most common mechanical properties of materials, such as hardness and Young's modulus of elasticity, the nanoindentation technique developed in the mid-seventies has become a powerful tool for investigating mechanical properties of miscellaneous materials at small length scales [17–19]. Recently, it has been applied as a method to measure residual stress in ceramics used in dental crowns [20]. Rapid development of sensors and actuators and their miniaturization allowed the indentation to be routinely performed on materials of the submicron and nanoscale dimensions. Beside the Young modulus, hardness [21–23], hardening exponents [24], creep parameters and residual stresses measurements, for which the indentation was commonly used, there has also been significant progress in utilization of this technique for

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the experimental studies of different processes in materials including the phase transformations [25–28].

In literature there has been almost no data about mechanical properties of nickel manganite. However, Guillemet Fritsch et al. [29] discussed the flexural strength of nickel manganite ceramics as a function of structural and microstructural parameters. The authors showed that variation in flexural strength strongly depended on the Ni/Mn content in the $Ni_xMn_{3-x}O_4$ ceramics and amount of NiO and Mn_2O_3 as secondary phases.

The aim of this work was to study the mechanical properties of the nickel manganite obtained by a complex polymerization method using a Berkovich nanoindenter, and to elucidate relationship between synthesis conditions and microstructure with its mechanical properties.

2. Experimental

2.1. Powder synthesis

Nickel manganite was synthesized by the complex polymerization method (CPM) starting from nickel (II) acetate tetrahydrate ($(CH_3COO)_2Ni \cdot 4\,H_2O$, Fluka, p.a. $\geq$99%) and manganese (II) acetate tetrahydrate ($(CH_3COO)_2Mn{\cdot}4H_2O$, Aldrich, p.a. $\geq$98%). The reagents were diluted in distilled water taking into account the stoichiometric ratio between metal ions Mn/Ni=2. Citric acid (CA) was added into solution considering the following molar ratio between metal ions (Me=Ni, Mn) and citric acid, Me: CA=1:10. The flowchart of the synthesis of the nickel manganite (NMO) powder is shown in Fig. 1. Additional details on the experimental procedure can be found elsewhere [15,16].

2.2. Characterization of powders and sintered samples

The morphology changes of the powder prepared by CPM were tracked using a MIRA 3 TESCAN field emission scanning electron microscope (FESEM). A few drops of sample solution (small amount of powder dissolved in ethanol) were placed onto a silicon substrate and then dried in air. The powder XRD analysis was done on a Rigaku RINT 2000 X-ray powder diffractometer using Fe$K\alpha$ radiation (λ=1.93604 nm). The as-prepared powders were uniaxially pressed into pellets and later sintered in air atmosphere at 1000, 1100 and 1200 °C, while one sample was sintered at 1200 °C under oxygen flow. The XRD analysis of the sintered samples was performed on an Ital Structure APD 2000 X-ray powder diffractometer using Cu$K\alpha$ radiation (λ=1.5418 Å) in the 2θ range of 20–70°, with a step-width of 0.02° and a counting time of 1.0 s per step. The ICSD database was used for the phase identification [30]. The unit cell parameters were calculated by the least squares methods using the LSUCRIPC software [31]. The UV–vis diffuse reflectance spectra were recorded in the wavelength range of 200–900 nm using a Shimadzu UV-2600 spectrophotometer equipped with an integrated sphere. $BaSO_4$ was used as the reference material. The microstructure of the NMO ceramics was examined by a TESCAN Vega TS 5130 MM scanning electron microscope. The nanoindentation measurements were performed using an Agilent Nanoindenter G200. Load and indenter displacement was continuously and simultaneously recorded during indenter loading and unloading. The unloading data were analyzed to determine the hardness and the Young's modulus of elasticity at various indentation depths. A Berkovich indenter, a three-sided pyramid, was used in all experiments. The surface approach velocity of the indenter was 10 nm s^{-1} and Poisson ratio was set to 0.25. Microstructure of the indents was followed by a Hitachi Tabletop Microscope TM3030 and NTEGRA NT-MDT Atomic Force Microscope.

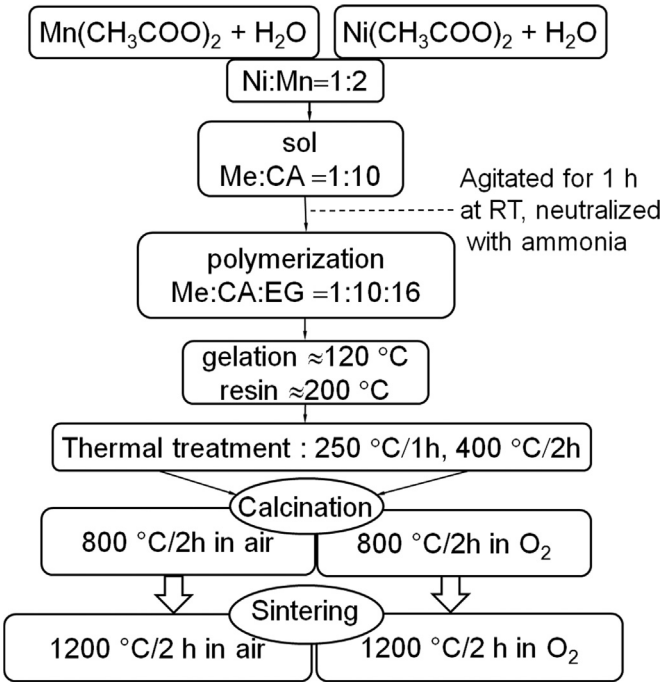

Fig. 1. Flowchart of the synthesis route for NMO powder.

3. Results and discussion

The XRD pattern of the NMO powder calcined at 800 °C (Fig. 2) shows main reflections that correspond to the cubic spinel phase ($Fd\bar{3}m$ space group, ICSD card # 185294). An enlarged part of the XRD pattern between 28° and 36° 2θ, shown as an inset (Fig. 2, to the left), reveals the presence of a small peak at 32.89°, which does not belong to the spinel $NiMn_2O_4$. The phase identification confirmed that the observed peak originated from the most intense (222) reflection of the cubic Mn_2O_3 phase (s.g. $Ia\bar{3}$, ICDD-JCPDS PDF 89–4836). Since the presence of the other reflections indicative for the Mn_2O_3 phase was not detected in the pattern, it should be concluded that only the traces of unreacted Mn_2O_3 phase existed in the calcined NMO powder. FESE micrograph of the same powder is presented in Fig. 2 (as an inset to the right). Smoothly rounded particles, whose size varies from 100 nm to a

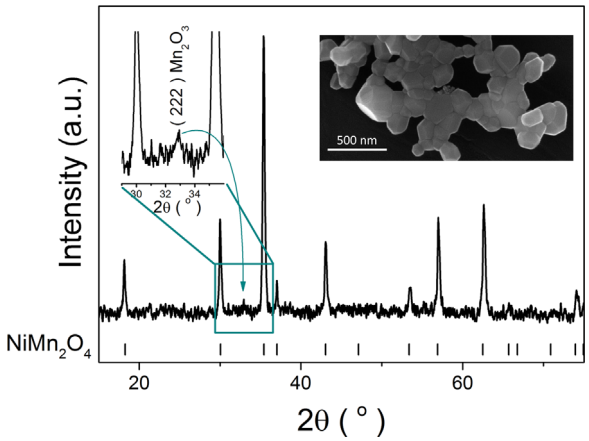

Fig. 2. XRD pattern of nickel manganite powder calcined at 800 °C. Inset on the left side reveals the presence of the most intense (222) reflection of the cubic Mn_2O_3 phase observed in the region 28–36° 2θ, while the inset on the right side shows the FESE micrograph (SE mode) of the same powder. Note that the Bragg reflections of the NMO phase (ICSD #185294) are collected as tick bars below the pattern.