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Structural characterization and activation energy of $NiTiO_3$ nanopowders prepared by the co-precipitation and impregnation with calcinations

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ABSTRACT

In this paper, we report on the formation of novel hexagonal $NiTiO_3$ nanopowders synthesized by the impregnation or co-precipitation methods through the thermal decomposition reaction of the precursors. The decomposition course was followed using differential thermal analysis (DTA) and thermogravimetric analysis (TGA) techniques. The intermediate decomposition products as well as the formed titanate were characterized using X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy. XRD patterns of the precursors calcined at 1000 °C showed the formation of the single ilmenite-type rhombohedral structure only with the impregnated precursor, while with the precipitated $NiTiO_3$ powders one it indicates the presence of some NiO and TiO_2 impurities. Transmission electron microscopy (TEM) exhibited loosely agglomerated hexagonal particles with uniform morphology having a size around 61 nm. The Brunauer-Emmett-Teller (BET) surface area measurements showed a type III isotherm with calculated surface area of 152 m^2/g. The plot of ln σ_{ac} vs. temperature as a function of frequency indicates a semiconducting behavior with ferroelectric phase transition at 605 K. The calculated activation in the ferroelectric region is 0.93 eV suggests the predominance of hopping conduction mechanism. Kinetic analysis of TG data according to different integral methods showed that in the $NiC_2O_4{\cdot}2H_2O$–TiO_2 precursor, the water molecules are coordinately bounded and the presence of TiO_2 reduces the activation energy needed to the oxalate decomposition reaction.

1. Introduction

The industrial materials titanium based ilmenite-type perovskites with general formula $MTiO_3$ (M = transition metal) have attracted great interest over the past decades because of their utilization in the field of pigments, photoactive catalysts, sensors, and so forth, due to the specially electronic and optical properties as well as the highly chemical stability, large surface areas and non-toxicity [1–4].

Nickel titanate ($NiTiO_3$), being one member of this well-known binary oxides family, has a broad range of the above-mentioned properties and is applicable for industries, such as semiconductor rectifiers [5], electrodes of solid oxide fuel cell [6], metal-air barrier [7], hydrocarbonate catalyzers [8] and gas sensors [9]. $NiTiO_3$ has been also investigated as a tribological coating to reduce friction and wear in high temperature applications without using liquid lubricants [10,11].

The electronic properties of ceramics are greatly affected by the characteristics of the powder, such as

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particle size, morphology, purity and chemical composition. Many efforts have been aimed to improve these properties by controlling their microstructure.

It is still a great challenge to search for a simple and cost-effective route to prepare nano-structured $NiTiO_3$ with a high yield. The traditional solid-state method used in preparing $NiTiO_3$ powder leads to poor homogeneity and high sintering temperatures. At the same time, many methods, such as sol-gel, the flux method, co-precipitations, solid-state reactions, electrospinning and the Pechini process, have been reported for the synthesis of crystalline $NiTiO_3$ powders [12–15].

Phani and Santucci [16] prepared $NiTiO_3$ thin films by sol-gel method using titanium isopropoxide and nickel acetate. Structural, morphological and elemental evolution were characterized by X-ray diffraction (XRD), tapping mode atomic force microscopy and X-ray photoelectron spectroscopy.

$NiTiO_3$ powders were prepared by a simple co-precipitation technique using ammonium carbonate and stoichiometric amounts of $Ni(NO_3)_2$ and $TiOCl_2$ [11]. The phase evolution was investigated by XRD patterns. Particle size and morphology was studied by transmission electron microscopy (TEM).

Nanocrystalline $NiTiO_3$ powders were produced at low temperature of 500 °C by sol-gel route [14]. XRD patterns and Fourier transform infrared (FT-IR) spectroscopy revealed that the powders contained $NiTiO_3$ besides impurities of NiO, as well as anatase and rutile-TiO_2 depending on the annealing temperature and Ni:Ti molar ratio. Based on Brunauer-Emmett-Taylor (BET) analysis, the synthesized powders showed a mesoporous structure containing pores with needle and plate-like shapes.

$NiTiO_3$ microtubes was constructed successfully via a simple solution-combusting method employing a mixture of ethanol and ethyleneglycol, nickel acetate, tetra-*n*-butyl titanate and oxygen gas [12]. The as-obtained product was characterized by XRD patterns, TEM, scanning electron microscopy (SEM), and energy dispersive X-ray spectrometry (EDS). The BET surface area of the product was 14.06 m^2/g and the pore size distribution mainly located from 20 to 30 nm.

Pure $NiTiO_3$ nanopowders were prepared by wet-chemistry method, using nickel stearate, tetra-*n*-butyl titanate and stearic acid [17]. The synthesis process was followed using thermal analysis techniques. FT-IR, XRD and TEM were used to characterize the crystallization process, the particle size and morphology of the calcined powders.

Therefore, in this paper, we communicate two simple processes for preparing nanocrystalline nickel titanate powder. These processes involve the formation of entire titanate through the thermal decomposition reaction of stoichiometric coprecipitated or impregnated mixture of nickel oxalate-dihydrate and titanium dioxide (anatase). The formation process and structural characterization of $NiTiO_3$ will be investigated by DTA-TG, FT-IR, XRD, and TEM. Furthermore, the specific surface area and electrical properties will be also evaluated. In addition, a mechanism for the thermal decomposition process and the kinetic parameters will be achieved using non-isothermal TG curves.

2. Experimental details

2.1. Materials

Nickel nitrate hexahydrate; $Ni(NO_3)_2{\cdot}6H_2O$, basic nickel carbonate; $NiCO_3.2Ni(OH)_2{\cdot}4H_2O$, oxalic acid; $H_2C_2O_4$ and titanium dioxide (anatase); TiO_2 were employed as the starting reagents. All chemicals are of analytical grade (BDH) and used without any further purification.

2.2. Synthesis of $NiTiO_3$ powders

Nickel titanate ($NiTiO_3$) powder were synthesized through the thermal decomposition reaction of $NiC_2O_4{\cdot}2H_2O$–TiO_2 precursor prepared through the impregnation technique or the coprecipitation route.

In the impregnation technique [18], pure $NiC_2O_4{\cdot}2H_2O$ was prepared by direct precipitation, using oxalic acid added dropwise to a solution containing the calculated amounts of nickel nitrate. The obtained fine precipitate was filtered, washed with distilled water and dried. Few drops of bi-distilled water were then added to weighed mixture of both $NiC_2O_4{\cdot}2H_2O$ and TiO_2 (1:1 mole ratio) with vigorous stirring to assure complete homogeneity. The wetted mixture was then dried at 80 °C.

In the co-precipitation method [19], TiO_2 was added to an aqueous solution containing a stoichiometric amount of $NiCO_3{\cdot}2Ni(OH)_2{\cdot}4H_2O$ under vigorous stirring. A stoichiometric amount of oxalic acid solution was then added dropwise into the suspension under constant stirring. During this process, the formed nickel oxalate will be precipitated on the surface of TiO_2 particles by heterogeneous nucleation. The resulting solution was then evaporated until dryness.

Samples of the prepared precursors were then calcined at different temperatures to characterize the decomposition reaction and follow titanate formation. The calcination temperatures and calcination times were 400 °C for 30 min, 600, 800 or 1000 °C for 2 h.

2.3. Characterizations

The decomposition course of the precursors and titanate formation were followed using simultaneous differential thermal analysis-thermogravimetry techniques (DTA-TG). The measurements were carried out using a Perkin–Elmer, STA 6000 thermal analyzer up to 1000 °C at a heating rate of 5 °C/min in air atmosphere. For kinetic measurements, other heating rates of 1, 2 and 3 °C/min were used.

The structure of the powders is examined by X-ray diffraction technique (XRD) using a Bruker D8 high-resolution diffractometer with nickel filtered Cu Kα radiation.

The Fourier transform infrared (FT-IR) spectra of the samples were recorded in the range 4000–200 cm^{-1} on JASCO FT-IR 310 spectrometer using the KBr pellet method.

The transmission electron microscopy (TEMJ) image of the $NiTiO_3$ nanopowders was obtained using an electron microscope (JEOL-2010) operating at 100 kV. The samples were prepared by ultrasonically dispersing the powder in