



Structural characterization of NiTiO₃ nanopowders prepared by stearic acid gel method

M.S. Sadjadi^a, K. Zare^{a,b}, S. Khanahmadzadeh^{a,c,*}, M. Enhessari^{a,d}

^a Department of Chemistry, Science and Research Campus, Islamic Azad University, Hesarak, Tehran, Iran

^b Department of Chemistry, Shahid Beheshti University, Tehran, Iran

^c Department of Chemistry, faculty of science, Islamic Azad University, Mahabad Branch, Mahabad, Iran

^d Department of Chemistry, Islamic Azad University, Naragh Branch, Naragh, Iran

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ABSTRACT

Pure nickel titanate nanopowders were successfully prepared in wet-chemistry synthesis method, using nickel stearate and tetra-*n*-butyl titanate as Ni, Ti sources and stearic acid as complexing reagent. The gel was calcined at different temperatures in air ranging from 500 to 750 °C. Results of thermal analysis are given, including both DTG and TG. Fourier transform infrared spectrometry (FTIR), X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the crystallization process, the particle size and morphology of the calcined powders. The results indicated that nickel titanate nanopowders with particle size between 30 and 65 nm could be obtained after calcinations of the dried gel at 750 °C for 2 h.

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1. Introduction

Titanium based oxides containing metals such as MTiO₃ (M: Ni, Pb, Fe, Co, Cu and Zn) are universally known as inorganic functional materials with wide applications. For example, they are applicable for industries, such as electrodes of solid oxide fuel cells, metal–air barriers, gas sensors and high performance catalysts [1–9]. Nickel titanate has been investigated as a tribological coating to reduce friction and wear at high temperature applications without using liquid lubricants [10–15].

The traditional preparation methods of NiTiO₃ can produce large NiTiO₃ particles with uncontrolled and morphologies due to their inherent problems such as high reaction temperature, heterogeneous solid phase reaction, etc. By contrast with the traditional methods, the wet-chemistry synthesis techniques, including sol–gel, sol–precipitation, combustion synthesis, chemical coprecipitation, and hydrothermal synthesis, offer many distinctive advantages over traditional methods in the production of powders. There are few reports regarding chemical synthesis of NiTiO₃ powders by citrate, maleate and propionic acid methods [13–18]. Thus, it is a meaningful work to investigate some routes at a low temperature to prepare ultra-fine particles of NiTiO₃ with a controlled morphology, a narrow size distribution, and a high purity.

In this study, we chose one typical wet-chemistry synthesis method, stearic acid gel, to try to prepare pure NiTiO₃ nanopowders. In this route, the carboxylic acid group and long carbon chain in stearic acid endow it with strong ability to disperse metal precursors. Moreover, this synthetic process is easily controlled and convenient in comparison with other methods.

2. Experimental

NiTiO₃ powders were prepared along a synthetic procedure as summarized in Fig. 1. Nickel stearate, tetrabutyl titanate, and stearic acid used in experiments were all of analytical grade reagents. An appropriate amount of stearic acid was first melted in a beaker at 73 °C, and then a fixed amount of nickel stearate was added to the melted stearic acid and dissolved to form a green transparent solution. Next, stoichiometric tetrabutyl titanate was added to the solution, stirring to form a homogeneous light green sol, naturally cooling down to room temperature, and drying in an oven for 12 h to obtain dried gel. Finally, the gel was calcined at different temperatures in air to obtain nano-crystallites of NiTiO₃.

The formation of process and structural characterization of NiTiO₃ phases have been investigated by TG/DTA, FTIR, XRD, and TEM. Thermogravimetric/differential thermal analysis experiments were performed by TG/DTA (METTLER TA4000) in air to investigate the calcinations temperature and possible phase transformation from 25 to 900 °C with a heating rate of 5 °C/min. The FTIR spectrum was recorded with an MB100 (BOMEM) spectrometer by using KBr pellet.

* Corresponding author. Department of Chemistry, faculty of science, Islamic Azad University, Mahabad Branch, Mahabad, Iran. Tel.: +98 442 2446534.

E-mail address: Khanahmad_s@yahoo.com (S. Khanahmadzadeh).

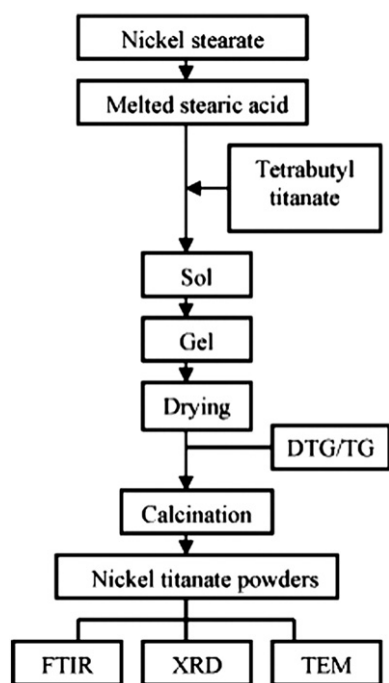


Fig. 1. Flowchart for the preparation of NiTiO_3 nanopowders.

The XRD patterns of the powders were recorded on a Model PTS 3003 of SEIFERT diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) in the range from 20° to 70° (2θ) to examine the crystallization and structural development of NiTiO_3 powders. The TEM pictures were recorded with Philips Model EM 208 instrument at the accelerating voltage of 100 kV. The fine powders were dispersed in amyl acetate on a carbon coated TEM copper grid.

3. Results and discussion

3.1. Thermal analysis

In order to investigate the synthesis process for NiTiO_3 , TG/DTG analysis was performed for the dried gel sample and the results are shown in Fig. 2. The first step, corresponding to 3.1% weight loss, was due to the evaporation of water and the melting of the gel at temperatures between 25 and 135.5°C . There are three peaks in the second step with larger weight loss (69.72%) that occur in the temperature range 135.5 – 509°C , the first peak at 280°C and the second sharp peak at 335.3°C in the DTG curve, respectively, were assigned to the combustion of the organic substance in the gel and

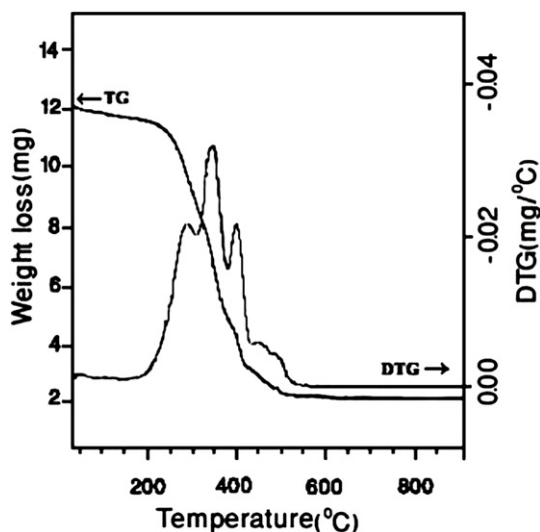


Fig. 2. TG/DTG curves of uncalcined NiTiO_3 dried gel.

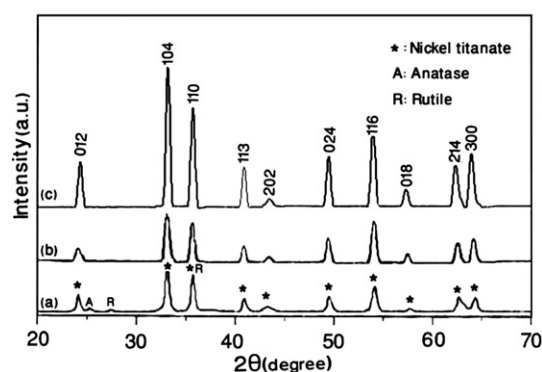


Fig. 3. X-ray diffraction patterns of NiTiO_3 Powders calcined at (a) 500°C ; (b) 600°C and (c) 750°C .

the formation of NiCO_3 and Ti-complex (the boiling point of stearic acid is 383°C). The last small and fairly broad peak, corresponding to 8.36% weight loss, was observed from 430 to 509°C which was assigned to the formation of NiTiO_3 phase. No apparent peak and significant weight loss was observed at the temperature range of over 509°C , which indicated the minimum crystalline temperature to get NiTiO_3 powders by stearic acid gel method was about 509°C .

3.2. X-ray diffraction patterns and IR spectra

Fig. 3. shows the XRD patterns of the NiTiO_3 powders after heat-treatment from 500 to 750°C in air for 2 h. At 500°C , the crystallization of rhombohedral nickel titanate phase began along with traces of rutile phase (R marked peaks) and anatase (A marked peaks) phase (Fig. 3a). Further, by increasing the calcination temperature to 600°C , the anatase and rutile phase was decreased with an increase in the intensity of NiTiO_3 phase (Fig. 3b). The nanopowders were obtained after calcination at 750°C (Fig. 3c). However, at this temperature, the nanopowders displayed sharp and intense peaks indicating fine crystalline rhombohedral NiTiO_3 phase. All the peaks corresponding to rhombohedral phase were well matched with database in JCPDS (file number: 33-960).

The formation of NiTiO_3 is further supported by the FTIR spectra as shown in Fig. 4. In this spectrum the NiTiO_3 powders calcined at 750°C showed peaks below 800 cm^{-1} which are assigned to the Ti–O stretching vibration, and corresponding to the formation of nickel titanate.

3.3. Morphology of samples

The particle size of powders can be determined from the TEM picture and calculated by Scherrer's formula [19] ($t = k \lambda / \beta \cos \theta$) where t is the average size of the particles, assuming particles are spherical, $k = 0.9$, λ is the wavelength of radiation, β is the full width at half maximum of the diffracted peak and θ is the angle of diffraction. Fig. 5 is the TEM micrograph of NiTiO_3 powders calcined at 750°C for 2 h. The particle size was estimated in the range of 30 – 65 nm . This grain size is consistent with the XRD results calculated by Scherrer formula (about 33 nm at 750°C). Conventional solid state

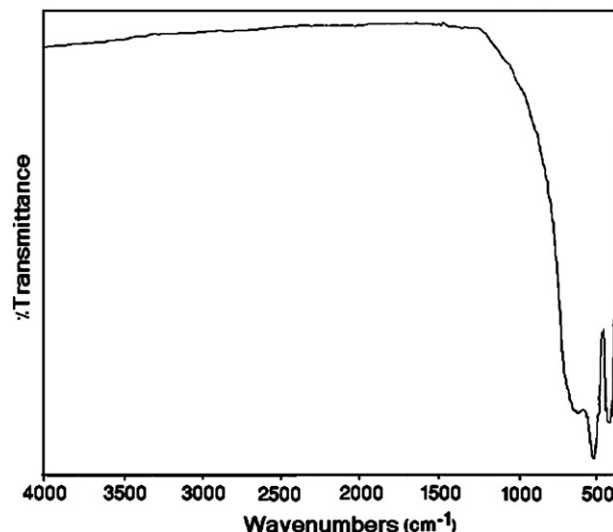


Fig. 4. FTIR spectra of the powders calcined at 750°C .

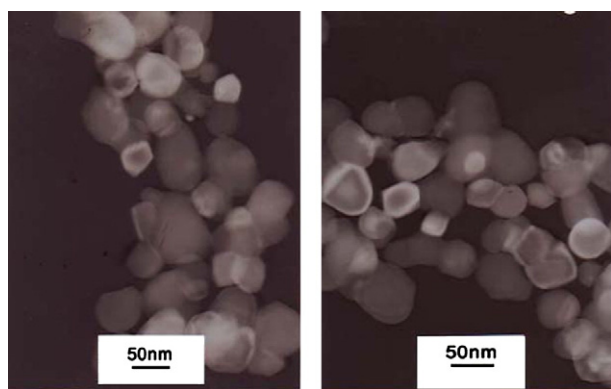


Fig. 5. TEM images of NiTiO_3 powders calcined at 750°C for 2 h.

method also forms NiTiO_3 phase at 1000°C [2] after prolonged heating (12 h) with comparatively larger particle size of $\sim 1\ \mu\text{m}$.

4. Conclusions

This study has demonstrated the feasibility of synthesis of pure NiTiO_3 powders using wet-chemistry synthesis route, stearic acid gel. Well crystallized NiTiO_3 nanopowders could be synthesized at 750°C for 2 h. In addition, the microstructures of NiTiO_3 powders have been evaluated using TEM and the grain sizes are shown to vary between 30 and 65 nm.

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