NiTiO₃ powders obtained by polymeric precursor method: Synthesis and characterization

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Abstract

Nickel titanate (NiTiO₃) powders were synthesized by the polymeric precursor method after thermal treatment at different temperatures for 2 h in air atmosphere. The decomposition of the precursors was monitored by differential scanning calorimetry and thermogravimetric analysis. The NiTiO₃ powders presented a reduction in the specific surface area and increase of the average particle size with the evolution of the temperature. The structural evolution of NiTiO₃ phase was accompanied by X-ray diffraction and Fourier transform Raman spectroscopy. By scanning electron microscopy was revealed the agglomerated nature of very fine particles of NiTiO₃ powders annealed from 600 to 1000 °C.

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1. Introduction

Perovskite oxides with general formula ATiO₃ containing metals such as: (A = Pb, Ni, Fe, Co, Zn and Cu) are well known as functional inorganic materials with wide applications in electrodes of solid oxide fuels cells [1], gas sensors [2], metal air barriers [3] and as high performance catalysts [4] for the complete oxidation of hydrocarbons or CO and NO reduction. It is known that metal acetates as well as metal alkoxides are easily dissolved in mixed solvents such as ethanol, ethylene glycol and 2-methoxy ethanol [5]. Several preparation methods have been reported in literature to synthesize nanocrystalline pyrochlore-type powders, such as: solid-state reaction [6], propionic acid routes [7], malate [8] coprecipitation [9], sol–gel [10], modified Pechini [11] and citrate [12].

Traditional solid-state reaction method for the preparation of NiTiO₃ leads to poor compositional homogeneity and high sintering temperatures. Average particle size, purity, chemical composition and morphology [9] are some of the powder characteristics that can affect the ceramic properties. In this way, the preparation of fine NiTiO₃ powders with good distribution in average particle size is possible by using the chemical method. It is also believed that fine powders or nanopowders reveal particular optical and electrical properties in comparison with bulk materials [13,14]. In literature, this perovskite is extensively employed as ceramic pigment [15] and solid lubricants [16].

However, in this paper we report the synthesis of NiTiO₃ powders prepared by the polymeric precursor method and their characterization by thermogravimetric analysis, specific surface area measurements using the BET method, X-ray diffraction, Fourier transform Raman spectroscopy and scanning electron microscopy analysis.

2. Experimental details

2.1. Synthesis of NiTiO₃ powders

NiTiO₃ nanoparticles were synthesized by the polymeric precursor method [17], which has been used to synthesize polycationic powders. The process is based on the metallic citrate polymerization using ethylene glycol. A hydrocarboxylic acid, such as citric acid, is used to chelate cations in an aqueous solution.
The addition of a glycol such as ethylene glycol leads to the formation of an ester. Polymerization, promoted by heating the mixture, result in a homogeneous resin in which metal ions are uniformly distributed throughout the organic matrix. Precursors used in this synthesis were nickel acetate [Ni(CH₃COO)₂] (98% Aldrich), titanium (IV) isopropoxide [Ti(OC₃H₇)₄] (99% Aldrich), ethylene glycol (C₆H₄O₂) (99% J.T. Baker) and citric acid (C₆H₈O₇) (99.5% Mallinckrodt). Titanium citrate was first formed by dissolution of titanium (IV) isopropoxide in citric acid aqueous solution under constant stirring. Soon after, nickel acetate was mixed to the titanium citrate solution. The molar ratio used was 3:1 of citric acid/metallic cations. After homogenization by 1 h of the solution containing Ni²⁺ cations, ethylene glycol was added to the mixture in the citric acid/ethylene glycol ratio of 60:40 wt.%. The resulting solution was stirred and heated at a temperature between 70 and 90 °C to promote the citrate polymerization by the polyesterification reaction [18]. The obtained polymeric resin was then placed in a conventional furnace in air atmosphere and the thermal decomposition was carried out in two stages: pre-heating at 300 °C for 2 h; after desaglomeration, the inorganic amorphous or disordered powders were passed through a 100-mesh sieve and heated at different temperatures for 2 h, resulting in the required NiTiO₃ powders.

2.2. Characterizations

Thermal effect was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in the apparatus STA 409, Netzsch, Germany. Synthetic air flow (30 cm³ min⁻¹) with a constant heating rate of 5 °C min⁻¹ from room temperature up to 1000 °C was employed. Nitrogen adsorption isotherms allow determining the specific surface area by means of the BET method (Brunauer, Emmett and Teller). The specific surface area of the powders was recorded on an ASAP 2000, USA. The crystalline phase of the NiTiO₃ powders was analyzed by X-ray diffraction (XRD) patterns recorded on a Rigaku-DMax 2500PC, Japan, with Cu Kα radiation in the 2θ range from 5 to 75° with 0.03° min⁻¹. FT-Raman spectroscopy was performed on a Bruker-RFS 100, Germany. A 1064 nm Nd:YAG laser was used to obtain the Raman spectra as excitation source with its power kept at 70 mW. Microstructural characterization was performed by scanning electron microscopy (SEM) in a Zeiss DSM940A, Germany apparatus.

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows the thermal decomposition behavior of the polymeric resin precursor of NiTiO₃ powders analyzed by TGA and DSC.

In these experiments, the decomposition process of the polymeric resin was monitored by TGA and DSC. The TGA curve shows two main regions, the first one is mostly due to dehydration and evaporation of organic matters from 70 to 230 °C. The other large one between 230 and 500 °C seems to be associated with the decomposition and burnout of the organic components. The DSC curve presents a small exothermic peak at 374 °C related to decomposition of residual organic compounds, recurrent of polymeric precursor such as: citric acid and ethylene glycol. A small shoulder at about 420 °C is due to the formation of NiO phase. The intense exothermic peak at around 460 °C may be ascribed as the major process of decomposition of the residual organic compounds to the beginning of the structural order of NiTiO₃ phase. Finally, a small exothermic peak at about 607 °C evidence the formation of ordered or crystalline NiTiO₃ phase in agreement with X-ray diffraction.

3.2. X-ray diffraction analysis

Fig. 2(a–g) shows the XRD patterns of NiTiO₃ powders heat treated in the temperature range of 400–1000 °C for 2 h in air atmosphere.

The diffractions peaks are used to evaluate structural order at long range. Fig. 2(a and b) presents a small peak of NiO phase which is formed at about 420 °C in agreement with DSC analysis (see Fig. 1). These powders heat treated from 400 to 500 °C for 2 h in air atmosphere present a structural disorder at long range in relation to NiTiO₃ phase, so no diffraction peak for NiTiO₃ phase is observed in this temperature range. The powders heat treated at 600 °C (see Fig. 2(c)) present characteristic diffraction peaks of crystalline structure suggesting the beginning of structural order at long range for NiTiO₃ phase. From 600 °C up to 1000 °C it is observed a great thermal stability of the NiTiO₃ powders and a progressive increase of structural
order with the increase of the temperature. All NiTiO$_3$ powders presented rhombohedral phase, with space group $R\overline{3}$, in concordance with literature [19–21] and the respective “JCPDS” (Joint Committee on Powder Diffraction Standards) card no. 33-0960 [22].

### 3.3. Lattice parameter analysis

The NiTiO$_3$ phase is confirmed by XRD patterns with the JCPDS card no. 33-0960 and the evolution of average lattice parameter with the increase of temperature can be observed in Fig. 3.

Experimental lattice parameters were calculated using the least square refinement from the UNITCELL-97 program [23] with the respective error bars. Lattice parameters of rhombohedral structure related in JCPDS card are $a = b = 5.03$ Å and $c = 13.79$ Å. NiTiO$_3$ powders heat treated at 600 °C presented large deviations of JCPDS card, due the low crystallinity degree of the phase. Increasing of the temperature leads to reduction in these deviations as observed by error bars. NiTiO$_3$ powders heat treated at 1000 °C presented less deviation due the high crystallinity.

### 3.4. Fourier transform Raman analysis

Fig. 4(a–g) shows the Raman spectra in 150–825 cm$^{-1}$ range to the NiTiO$_3$ powders heat treated in the temperature range of 400–1000 °C for 2 h in air atmosphere.

In the 150–825 cm$^{-1}$ range ten Raman modes or peaks are observed and assignments were analyzed using the $C_3$ symmetry and $R\overline{3}$ space group. The ten Raman active modes are characteristics of NiTiO$_3$ powders confirming the rhombohedral structure in agreement with the literature [24,25], with the following peaks positions: 184, 226, 238, 284, 338, 389, 458, 608, 705 and 760 cm$^{-1}$. Fig. 4(a and b) shows Raman spectra of the powders heat treated from 400 to 500 °C and, due the high structural disorder degree at short range, no Raman active modes were noted. In Fig. 4(c) appears a wide Raman active modes of
Fig. 7. SEM micrographs with (×20,000) of NiTiO₃ powders heat treated at: (a) 600 °C, (b) 700 °C, (c) 800 °C, (d) 900 °C and 1000 °C for 2 h in air atmosphere.
lower intensity to the NiTiO₃ powders heat treated at 600 °C, confirming that these powders it is not organized at long range, but present structural order to short range. The increase of the temperature promotes increase to structural order which can be observed by the appearance of the more defined Raman peaks (see Fig. 4(d–g)). The evolution of structural order degree can be verified by P₈ and P₁₀ Raman modes (see Fig. 4(g)). The P₈ and P₁₀ Raman in 613.9 and 760.5 cm⁻¹ are stretching vibrations of TiO₆, octahedra in the region 500–830 cm⁻¹ according to Busca et al. [25]. The changes in Raman peaks position are due to differences in preparation method, average crystal size and structural order degree of crystal. Literature reports XRD analysis to explain the formation of NiTiO₃ phase. However, this technique is not enough to prove the formation of pure NiTiO₃ phase at temperature up to 700 °C [8–11].

Several works reported in literature presents only structural evolution of NiTiO₃ phase at long or short range. However, in this work the structural evolution was analyzed by XRD and Raman analysis. We employed investigations at long and short range to inhibit the structural order–disorder degree of the main phase. In other way, Jacob et al. [26] evidenced that this phase present an order–disorder transition.

3.5. Specific surface area analysis

Specific surface area values of mean particle diameter were determined by the equation:

$$d_{\text{BET}} = \frac{6}{\rho \cdot S_{\text{BET}}}$$

where $\rho$ is the theoretical density of NiTiO₃ powders, $d_{\text{BET}}$ is the particle diameter size and $S_{\text{BET}}$ is the specific surface area measured by BET method (Brunauer, Emmett and Teller) [27].

Fig. 5 shows the specific surface area and mean particle diameter as a function of thermal treatment. Increasing of the temperature leads to a raise of mean diameter particle and reduction of specific surface area. NiTiO₃ powders heat treated at 600 °C present lower mean particle diameter and larger specific surface area as a result of the agglomerate prepared by Pechini method. This behavior is in agreement with Lin et al. [11].

3.6. Mean particle diameter analysis

The average particle size was determined from XRD powder pattern according to Debye–Scherrer’s equation [28].

$$D_{\text{XRD}} = \frac{k \cdot \lambda}{\beta \cdot \cos \theta}$$

where $D_{\text{XRD}}$ is the average particle size, $k$ is a constant equal to 0.9, $\lambda$ is the X-ray wave-length equal to 0.15406 nm and $\beta$ is the half-peak width.

Fig. 6 shows the average particle size as a function of the heat treatment to NiTiO₃ powders annealed in air atmosphere. The increase of the temperature promotes a raise in the average particle size. The Debye–Scherrer’s method presents difference in relation to BET method. The difference between $D_{\text{XRD}}$ and $D_{\text{BET}}$ could be confirmed by the presence of necks among particles observed by scanning electron microscopy analysis.

3.7. Scanning electron microscopy analysis

The morphologies of NiTiO₃ powders were evaluated by scanning electron microscopy (SEM) illustrated in Fig. 7. The agglomerate nature is observed for NiTiO₃ powders heat treated at 600 °C (see Fig. 7(a)). After thermal treatment at 700 °C the particles present homogeneous morphology with spherical form, as observed in Fig. 7(b). The increase of the temperature promotes the coalescence between the particles, as observed in Fig. 7(c–e). In these powders, we observe the formation of necks and blocks. The polymeric precursor method contains a large amount of organic substance that must be eliminated to synthesize pure oxides. In general, the powders treated in range of 300–600 °C presents as morphologies agglomerating [29–31].

Fig. 8 illustrate that the bigger deviations in the average particle size is caused by inhomogeneous distribution of particles due to the coalescence process (see Fig. 7(c–e)).

The three methods employed BET, XRD and SEM analysis allow obtaining the average particle size. All of them show a similar behavior: the increase in the particle size with evolution of the temperature of thermal treatment. However, we believe that SEM analysis is much accurate revealing that the NiTiO₃ powders, heat treated between 600 and 1000 °C, present a mean distribution of the particle in the range of 94–306 nm. The vertical bars (mean standard error) present in Fig. 8 shows that morphology of particle of NiTiO₃ prepared by PPM is not well homogeneous.

4. Conclusion

NiTiO₃ powders free of secondary phases and with rhombohedral structure were obtained from the polymeric precursor.
method. Less variation in the lattice parameters were observed in crystalline NiTiO₃ powders heat treated at 1000 °C for 2 h. XRD analysis suggests the start of crystallization of NiTiO₃ powders at 600 °C, but Raman analysis reveals the beginning of the structural order to short range at 700 °C. We believe that the difference obtained in the average particle size by BET, XRD and SEM analysis are due agglomerate nature of the NiTiO₃ powders prepared by the method employed.

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References