Effect of Reaction Temperature on Size and Optical Properties of NiTiO₃ Nanoparticles

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Abstract: Nickel titanate (NiTiO₃) nanoparticles were successfully prepared by wet-chemical method, using nickel acetate and titanium(IV) isopropoxide as Ni, Ti sources and citric acid as complexing reagent. The gel was calcined at different temperatures from 500-700 °C. Results of thermogravimetric analysis (TGA) are given. Fourier transform infrared spectrometry (FTIR), X-ray diffraction (XRD), Scanning electron microscopy (SEM), transmission electron microscopy (TEM), ultraviolet (UV) spectroscopy, vibrating sample magnetometer (VSM) were used to characterize the crystallization process, particle size, morphology, optical and magnetic properties of the calcined nanoparticles. TEM result reveals that the NiTiO₃ was homogeneous and hexagon morphology with the grain size of 30-70 nm. The band gap values of the NiTiO₃ nanoparticles were calculated to be 3.43, 3.39 and 3.31 eV. The magnetic property was confirmed that the NiTiO₃ nanoparticles of super paramagnetic behavior in nature. Our results suggested that the temperature plays an important role in the particle size effect of nanocrystalline NiTiO₃.

Keywords: Nanoparticle, X-ray diffraction, Optical properties, Morphology,

Introduction

The metal titanates based oxides including metals, such as nickel, cobalt, ferrite, zinc, copper and lead are universally known as inorganic functional materials with wide applications. For example, they are applicable for industries, such as semiconductor rectifiers, electrodes of solid oxide fuel cell, metal-air barrier, hydro carbonate catalyzers, color mixtures of surface coating and gas sensing devices, *etc.*¹⁻⁵.

NiTiO₃ belong to the ilmenite structure. Ni and Ti atoms prefer octahedral coordination with alternating cation layers occupied by Ni and Ti alone⁶. On conventional solid state reaction, the preparation of NiTiO₃ nanoparticles requires high-temperature treatment over 1000 °C for an extended period until intermediate phases disappear. The traditional preparation

methods of NiTiO_3 can produce large NiTiO_3 nanoparticles with uncontrolled morphologies due to their inherent problems such as high reaction temperature, heterogeneous solid phase reaction *etc.* By contrast with the traditional methods, the wet-chemical synthesis techniques, including sol-gel, sol-precipitation, combustion synthesis, chemical co-precipitation and hydrothermal synthesis, offer many distinctive advantages over traditional methods in the production of powders. There are few reports available regarding chemical synthesis of NiTiO_3 nanoparticles by citrate, maleate and propionic acid methods⁷⁻¹². Thus, it is a meaningful work some routes at a low temperature to prepare ultra-fine particles of NiTiO_3 with a controlled morphology, narrow size distribution and high purity.

As a matter of fact, metal alkoxides and metal acetates are both easily dissolved in certain solvents such as methanol, ethanol, iso-propanol, ethylene and 2-methoxy ethanol¹⁰. In this study, we chose one typical wet-chemical synthesis method, citric acid complex, to try to prepare pure NiTiO_3 nanoparticles from titanium(IV) isopropoxide and nickel acetate. Citric acid and methanol (CH_3OH) are used as the chelating agent and a solvent. Moreover, this synthesis process is easily controlled and convenient in comparison with other methods. The formation of process and structural characterization of NiTiO_3 phase have been investigated by thermogravimetric analysis (TGA), X-ray diffraction (XRD), fourier transform infrared (FTIR), scanning electron microscope (SEM), transmission electron microscope (TEM), ultra-violet vis absorption (UV) and vibrating sample magnetometer (VSM).

Experimental

NiTiO_3 nanoparticles were prepared along a synthetic procedure as summarized in Figure 1. A stoichiometric amount of nickel acetate and titanium(IV) isopropoxide with the cationic ratio of Ni: Ti = 1:1 were separately dissolved in methanol. Citric acid was then put into the Ti^{4+} solution, and it kept in transparency. While the Ni^{2+} solution was also mixed with the above-mentioned glassy solution, the precipitates came out. They were further heated at 90 °C in an oven for 12 h to remove the excess solvent and the agglomerate precursors in light green color were formed. After the organic precursor was calcined at 500-700 °C for 3 h, the phase-pure yellow NiTiO_3 nanoparticles were finally obtained after furnace cooling to room temperature.

Figure 1. Flow chart of the synthesis of NiTiO_3 nanoparticles by the wet chemical method

The size and crystalline phase of NiTiO_3 was determined using X-ray diffractometer Shimadzu model: XRD 6000 with $\text{CuK}\alpha$ radiation in the range $20\text{--}70^\circ$ ($\lambda=0.154\text{nm}$). Thermogravimetric analysis (TGA) was carried out with a Shimadzu 50-TG-DTA at a heating rate of $20^\circ\text{C}/\text{min}$. The FT-IR spectrum of the samples was taken using a FTIR model Bruker IFS 66W spectrometer. UV-Vis absorption spectra of NiTiO_3 were recorded using a Varian Cary 5E spectrophotometer at room temperature in the range of $200\text{--}1000\text{ nm}$. The surface morphologies of as-prepared NiTiO_3 the products were studied using the Hitachi S-4500 Scanning Electron Microscope. Transmission Electron Microscope (TEM) studies was taken using a model JEOL-2010 microscope with an accelerating voltage of 100 kV . The magnetic measurement was carried out in a Vibrating Sample Magnetometer (VSM: BHV-55, Riken Japan) at room temperature.

Results and Discussion

Figure 2 shows the TG curve of the citrate complex dried at 90°C for 12 h. The weight loss below 100°C was assigned to desorption of water. The weight loss between ~ 200 and $\sim 450^\circ\text{C}$ was due to desorption of organic components in the precursor. At temperature above 450°C no further weight loss was observed, which indicates complete removal of organic residues and the formation of crystalline NiTiO_3 . Thus, the minimum firing temperature to obtain organic-free precursor can be determined above 450°C . Since the decomposition seems to have several steps such as:

Figure 2. TGA Curve of the citrate complex dried at 90°C for 12 h

Figure 3(a-c) shows the XRD patterns of the NiTiO_3 nanoparticles calcined at different temperatures (500 , 600 and 700°C). At 500°C , the crystallization of rhombohedral nickel titanate phase began along with traces of rutile (R marked peaks) and anatase phase (A marked peaks; Figure 2a). Further, by increasing the calcination temperature to 600°C , both anatase and rutile phase was decreased with an increase in the intensity of NiTiO_3 phase (Figure 2b). The NiTiO_3 nanoparticles were further calcined at 700°C (Figure 2c). However, at this temperature, the nanoparticles displayed sharp and intense peaks indicating crystalline rhombohedral NiTiO_3 phase. All the peaks corresponding to rhombohedral phase were well matched with database in JCPDS (File No. 33-960). According to the Debye Scherrer's formula, $D=k\lambda/\beta\cos\theta$ where D is the average size of the particles, $k=0.9$, λ is the X-ray wavelength (0.154 nm for $\text{CuK}\alpha$), β is the full width at half maximum of the diffracted peak (FWHM) and θ is the Bragg diffraction angle¹³. The crystalline sizes of

NiTiO₃ were calculated to be 30, 45 and 65 nm for the samples prepared at temperatures 500, 600 and 700 °C respectively. The crystalline sizes were reveals that clearly with decreasing calcination temperature, the crystalline size also decrease.

Figure 3(a-c). XRD patterns of the NiTiO₃ nanoparticles calcined at different temperatures 500, 600 and 700 °C

Figure 4 shows the FT-IR spectra of as-synthesized NiTiO₃ nanoparticles calcined at 500 and 700 °C. It is clear from Figure 4a that the weak bands at 3391 and 1615 cm⁻¹ were assigned to the stretching vibrations of surface hydroxyl (–OH) groups and another band around 1280 cm⁻¹ was due to the bending vibration of the H–O–H bonds. However, as the temperature increased (Figure 4b), the stretching vibration of –OH and H–O–H bands were completely disappeared, which is consistent with the TGA results. The very strong bands appeared at 617 and 690 cm⁻¹ are due to the stretching of Ti–O bond and bending of O–Ti–O bond meanwhile the absorption at 547 cm⁻¹ is result from Ni–O bond, which indicating¹⁴ the formation of NiTiO₃.

Figure 4. (a-b) FT-IR spectra of as-synthesized NiTiO₃ nanoparticles calcined at 500 and 700 °C

Figure 5(ab) represents the SEM morphologies of the as-synthesized NiTiO_3 nanoparticles calcined at 500 and 700 °C. The SEM images clearly shows homogeneous, uniform crystal size and remarkably different morphologies for the NiTiO_3 nanoparticles. Spheroid-like morphology was observed for the sample calcined at 500 °C (Figure 5a). Whereas (Figure 5b) an ellipsoid-like morphology was obtained when the temperature increased to 700 °C, which is well accord with the XRD results. And also it is smaller than those prepared by co-precipitation method¹⁵ (about 90 nm) and solid state reaction method (sintered at above 1000 °C with comparatively larger particle size about 1 μm)¹⁶.

Figure 5(a-b). SEM morphologies of the as-synthesized NiTiO_3 nanoparticles calcined at 500 and 700 °C

The morphologies and particle sizes were further investigated by TEM. Figure 6a shows the TEM image of the as-prepared NiTiO_3 nanoparticles calcined at 500 °C. The obvious rings of selective area electron diffraction (SAED) in the inset of Figure 6a indicate that all the products are polycrystalline. Figure 6a shows NiTiO_3 nanoparticle with hexagon morphology of size about ~30-40 nm. Most of the nanoparticles were well separated although some of them partially aggregated. Figure 6b reveals TEM pattern of sample calcined at 700 °C. Comparing to that of 500 °C, crystalline size of the products were increased to 60-70 nm. Moreover, the particle size of the samples obtained from TEM patterns are quite similar to those calculated from Scherrer's equation.

Figure 6a. TEM image of the as-prepared NiTiO_3 nanoparticles calcined at 500 °C.

Figure 6b. TEM image of the as-prepared NiTiO_3 nanoparticles calcined at 700 °C

The room temperature UV-Visible spectrum (Figure 7a) of the as-prepared NiTiO_3 nanoparticles calcined at 500 °C has the absorption edge is at 364 nm, which is smaller than the band edge observed at 370 and 376 nm for calcined at 600 and 700 °C as shown in Figure 7b & c. In all the cases, blue shifts were observed. Considering the blue shifts of the absorption positions from the bulk NiTiO_3 , the absorption onsets of the present samples can be assigned to the direct transition of electron in the NiTiO_3 crystal¹⁷. The corresponding bandgap energies

can be calculated to be 3.43, 3.39 and 3.31 eV and are larger than the bulk NiTiO_3 (3.2 eV). The increasing trends of the band gap energy upon the decreasing particle size are well presented for the quantum confinement effect¹⁸.

Figure 7. UV-Vis absorption spectra of the as-prepared NiTiO_3 nanoparticles calcined at 500 °C.

Figure 8 shows the hysteresis loops of NiTiO_3 nanoparticles at 500 °C. From the result, it was found that the saturated magnetization (M_s) of the fabricated NiTiO_3 nanoparticles was 15 emu/g and its saturated magnetic strength was 2760 Oe. In addition, the experiment show that is residual magnetism and coercive force (H_c) was close to 31.85, confirming that the magnetic particle was super paramagnetic particle. In other words, when the particle is small enough, and the anisotropy energy is too small to be identical with the heat motion, the direction of magnetization would no longer be fixed and the direction of easy magnetization would change irregularly, causing the phenomenon of super para magnetism.

Figure 8. Magnetic property of the as-prepared NiTiO_3 nanoparticles calcined at 500 °C

Conclusion

This study has demonstrated the feasibility of synthesis of pure NiTiO_3 nanoparticles using wet-chemical synthesis route, metal-citrate complex at different temperatures (500, 600 and 700 °C). The TGA analysis indicates that the crystallization temperature of NiTiO_3 was above 450 °C. The chemical structure information of the products was studied by Fourier Transform Infrared (FT-IR) spectroscopy. Well crystallized NiTiO_3 nanoparticles could be synthesized at 700 °C for 3 h. The microstructures of NiTiO_3 nanoparticles have been evaluated using SEM and TEM and the grain sizes are shown to vary between ~30-70 nm. The significant optical properties of this material may be very interesting for further application on photo catalyst. The temperature can affect the particle size; the decreasing trends of temperature upon the decreasing particle size are well presented for the as-synthesized NiTiO_3 nanoparticles. The magnetic property was studied using a vibrating sample magnetometer. We hope that the procedure mentioned in the experimental section can be a suitable route for the high-yield synthesis of NiTiO_3 nanoparticles.

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References

1. Harris Q J, *Phys Rev Lett.*, 1997, **78**, 346.
2. Fisch R, *Phys Rev B.*, 1995, **51**, 11507.
3. Phani A R and Santucki S, *Mater Lett.*, 2001, **396**, 1.
4. Ming Chiang Y, Dumbar Birnie III, David Kingery W, Physical Ceramics, John Wiley & Sons Inc., New York, 1996, 34.
5. Taguchi H, Matsuda D, Nagou M, Tanihara K and Miyamota Y, *J Am Ceram Soc.*, 1992, **75**, 201.
6. Lerch M, Boysen H, Nerde R, Frey F and Laqua W, *J Phys Chem Solids.*, 1992, **53**, 1153.
7. Chu F, Liu X Q, Wang G Z and Mong G Y, *Mater Res Bull.*, 1999, **34**, 1789.
8. Vadivel Murugan A, Violet Samuel Y, Navale Sc and Ravi V, *Mater Lett.* 2006, **60**, 1791.
9. Marcilly C, Courty P and Delmon B J, *J Am Ceram Soc.*, 1970, **53**, 56.
10. Gaikwas S P, Dhesphande S B, Kholam Y, Samuel Y and Ravi V, *Mater Lett.*, 2004, **58**, 3474.
11. Taylor D J, Fleig P E and Page R A, *Thin Solid Films*, 2002, **408**, 104.
12. Dharmaraj N, Park H C, Kim C K, Kin H Y and Lee D R, *Mater Chem Phys.*, 2004, **87**, 5.
13. Sharma Y K, Kharkwal M, Uma S and Nagarajan R, *Polyhedron*, 2009, **28**, 579.
14. Docuff S, Henry M, Sanchez C and Livage J, *J Non-Cryst Solids*, 1987, **89**, 206.
15. Dharmaraj N, Park H C, Kim C K, Kim H Y and Lee D R, *Mater Chem Phys.*, 2004, **87**, 5.
16. Tietz F, Dias F J, Dubiel B and Penkalla H J, *Mater Sci Eng B*, 1999, **68**, 35.
17. Zhou G W, Chen D R and Xu G Y, *Acta Chimico Sinica*, 2005, **20**, 1971.
18. Zhou L, Liu X J, Zhang S Y, Wang J C and Zhang L D, *J Nanjing University Natural Science*, 1997, **33**, 32.