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Magnetic properties and heat capacity of CoTiO_3 nanopowders prepared by stearic acid gel method

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Pure cobalt titanate nanopowders were successfully prepared in wet-chemistry synthesis method, using cobalt acetate and tetra-n-butyl titanate as Co and Ti sources and stearic acid as complexing reagent. The gel was calcined at different temperatures in air ranging from 500°C to 650°C. Results of thermal analysis are given; including both differential thermal gravimetry (DTG) and thermogravimetric. X-ray diffraction was used to characterise the crystallisation process, the particle size and morphology of the calcined powders. The results indicated that cobalt nanopowders with a particle size of about 35 nm could be obtained after calcinations of the dried gel at 600°C for 2 h. In the temperature range between 80°C and 500°C, the empirical equation (C_P ($\text{JK}^{-1}\text{mol}^{-1}$) = $-136.311 + 0.141 T - 3.551 \times 10^7/T^2$) for the C_P of CoTiO_3 was determined from differential scanning calorimetry. The synthesised CoTiO_3 indicate a superparamagnetic behaviour, as evidenced by using vibrating sample magnetometer at room temperature.

Keywords: nanostructures; sol-gel synthesis; X-ray diffraction; magnetic measurements; heat capacity

1. Introduction

Titanium-based oxides containing metals, such as MTiO_3 (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, high performance catalysts and ferroelectric random access memories [1–12].

During the past decades the interest of the researchers in CoTiO_3 has increased due to a series of its physiochemical properties permitting its application as pigment [13], magnetic recording media, and gas sensor for alcohol indication, humidity sensor [14] and catalyst [15].

The oxide-based magnetic nanoparticles have been investigated by many researchers because of the interesting particular magnetic properties, such as superparamagnetic

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relaxation phenomena, surface effect by spin-canted structure, magneto-electrical transport and so on [16,17]. They also have immense potential for applications in the areas of high-density data storage, ferrofluids, magnetic resonance imaging, colour processing and magnetic refrigeration [18]. The superparamagnetic behaviour has often appeared in the magnetic nanoparticles with few nanometres [19]. In some cases the critical size was estimated to be about 30 nm in diameter for a spherical sample of the common ferromagnetic materials [20].

The wet-chemistry synthesis technique used in this study, including sol-gel, sol-precipitation, combustion synthesis, chemical coprecipitation and hydrothermal synthesis, offers many distinctive advantages over solid-state method in the production of powders, such as a controlled morphology, a narrow size distribution and high purity [21].

The sol-gel process appears attractive because it offers in principle several obvious advantages:

- (1) lower processing temperature,
- (2) high homogeneity and purity of resulting materials,
- (3) Possibility of various forming process [22].

In this study, we chose one typical wet-chemistry synthesis method, stearic acid gel, to prepare pure CoTiO_3 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. Magnetic properties and heat capacity of CoTiO_3 were studied.

2. Experimental

CoTiO_3 powders were prepared along a synthetic procedure as summarised in Figure 1. Cobalt acetate, tetrabutyl titanate and stearic acid used in experiments were all of analytical grade reagents. First, a 0.4 mol of stearic acid was melted in a beaker at 73°C , and then a 0.1 mol of cobalt acetate was added to the melted stearic acid and dissolved to form a dark blue transparent solution. Next, stoichiometric tetrabutyl titanate (0.1 mol) was added to the solution, stirring to form a homogeneous light red-brown 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 four stages. In the first stage, dried gel was heated at a rate of 3°C min^{-1} up to 400°C . In the second stage, heating was continued at 400°C for 40 min constantly. Then the temperature was increased up to 500°C , 550°C , 600°C and 650°C , for each sample, respectively. In the last stage, the temperature was held constant for 2 h in air. The process and structural characterisation of CoTiO_3 phases have been investigated by thermogravimetric/differential thermal analysis (TG/DTA) and X-ray diffraction (XRD). To obtain nanocrystallites of CoTiO_3 , TG/DTA experiments were performed by TG/DTA (METTLER TA4000) in air for dried gel sample to investigate the calcinations temperature and possible phase transformation from 25°C to 900°C with a heating rate of 5°C min^{-1} . The XRD patterns of the powders were recorded on a Model PTS 3003 of SEIFERT diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) in the range from 10° to 80° (2θ) to examine the crystallisation and structural development of CoTiO_3 powders.

The specific heat capacity was measured by scanning method and using a differential scanning calorimeter, and differential scanning calorimetry (DSC; METTLER TA4000) in

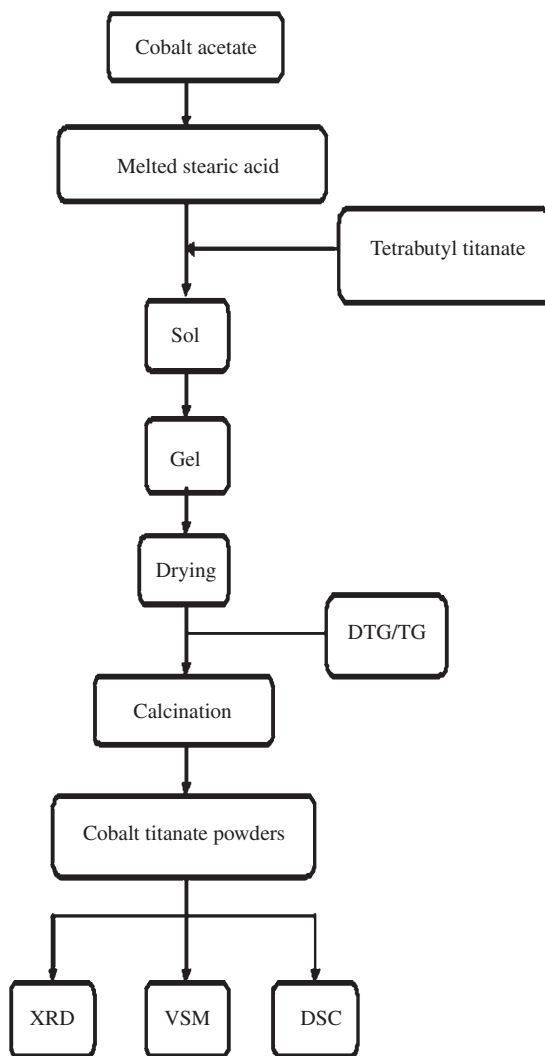


Figure 1. Flowchart for the preparation of CoTiO_3 nanopowders.

a pure nitrogen atmosphere. The sample (calcined at 600°C) was heated from 80°C to 500°C with a heating rate of 5°C min^{-1} . Magnetisation measurements for CoTiO_3 calcined at 500°C and 600°C are carried out using vibrating sample magnetometer (VSM; BHV-55, Riken, Japan) at room temperature.

3. Results and discussion

3.1. Thermal analysis

In order to investigate the synthesis process for CoTiO_3 , TG/DTG analysis was performed for the dried gel sample and the results are shown in Figure 2. The DTG curve, at the first

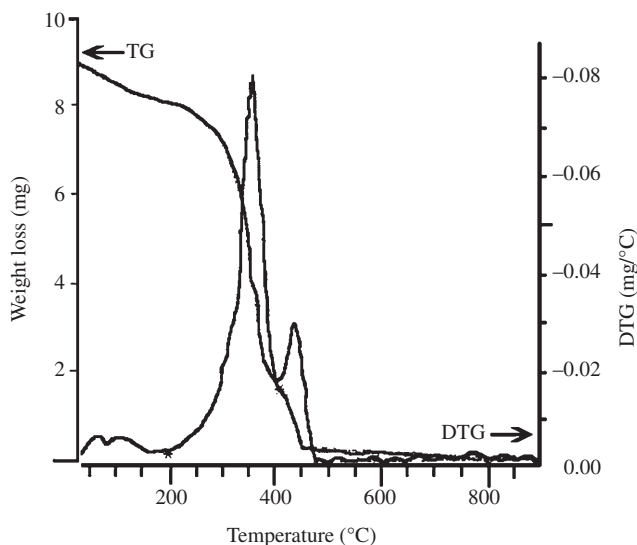


Figure 2. TG/DTG curves of uncalcined CoTiO_3 dried gel.

step, reveals a weight loss between 29.3°C and 165.3°C (7.41%), due to the evaporation of acetic acid, water and the melting of gel.

In the second step, a drastic weight loss (68.26%) at the temperatures between 165.3°C and 399.0°C can be assigned to the combustion of the organic derivatives in the gel and formation of cobalt carbonate and cobalt complex (the boiling point of stearic acid is 383°C). The next moderate peak corresponding to the 15.87% weight loss starting from 399°C to 471°C was assigned to the formation of CoTiO_3 phase. No apparent peak and significant weight loss was observed at the temperature range of over 471°C , which indicated the minimum crystalline temperature to get CoTiO_3 powders by stearic acid gel method was about 471°C .

3.2. XRD patterns

Figure 3 shows the XRD patterns of the CoTiO_3 powders after heat-treatment from 500°C to 650°C in air for 2 h. At 500°C , the crystallisation of rhombohedral cobalt titanate phase (* marked peaks) began along with the traces of Co_3O_4 phase (C marked peaks) (Figure 3a). Further, by increasing the calcination temperature to 600°C , the Co_3O_4 phase was decreased with an increase in the intensity of CoTiO_3 phase (Figure 3b). The nanopowders were obtained after calcination at 600°C (Figure 3c). However, at this temperature, the nanopowders displayed sharp and intense peaks indicating fine crystalline rhombohedral CoTiO_3 phase. All the peaks corresponding to the rhombohedral phase matched well with the database in JCPDS (file number: 77-1373).

3.3. Morphology of samples

The particle size of powders can be calculated by Scherrer's formula ($t = k\lambda/\beta \cos \theta$) [23] where t is the average size of the particles, assuming particles are spherical, $k = 0.9$, λ is the

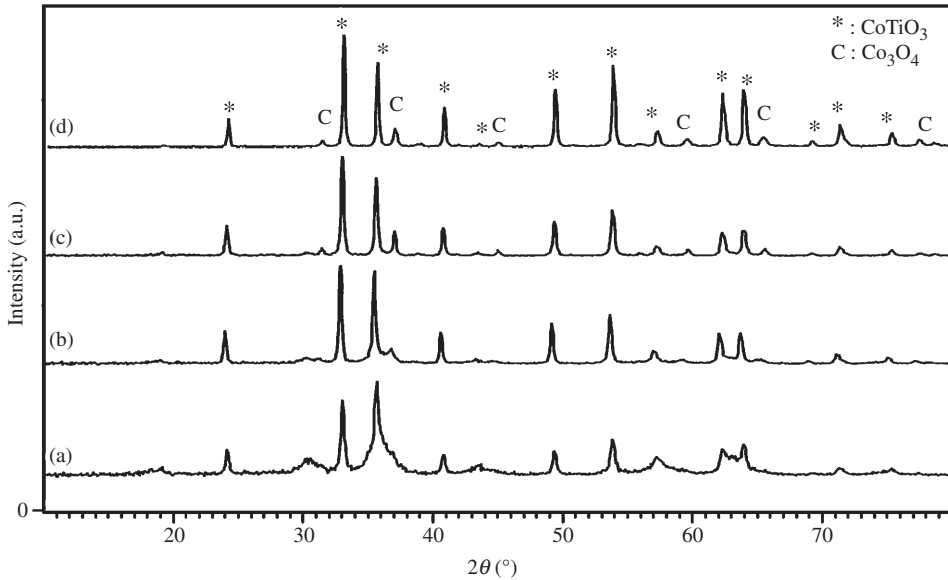


Figure 3. XRD patterns of CoTiO_3 powders calcined at (a) 500°C ; (b) 550°C ; (c) 600°C and (d) 650°C .

wavelength of radiation, β is the full width at half maximum of the diffracted peak and θ is the angle of diffraction. The particle size was calculated by Scherrer's formula for different calcination temperatures. The crystallite size of the powders calcined at 500°C , 550°C , 600°C and 650°C were about 28, 35, 35 and 47 nm, respectively.

3.4. Heat capacity

Piezoelectric and pyroelectric phenomena coexist in ferroelectric materials [24] whereas pyroelectric and piezoelectric properties are related to heat capacity [25]. The temperature dependence of the heat capacity of CoTiO_3 determined by the scanning method is shown in Figure 4. In the temperature range between 80°C and 500°C , the empirical equation for the C_P of CoTiO_3 is determined from the experimental values as follows:

$$C_P(\text{JK}^{-1}\text{mol}^{-1}) = -136.311 + 0.141T - 3.551 \times 10^7/T^2. \quad (1)$$

3.5. Magnetic properties

There are few reports regarding magnetic properties of CoTiO_3 . An antiferromagnetic transition was detected at the Néel temperature, $T_N = 38\text{ K}$, as reported for single crystals [26]. In the hexagonal crystallographic structure, the magnetic interactions of neighbouring Co^{2+} spins are ferromagnetic within the a - b planes and antiferromagnetic between adjacent a - b planes [27,28]. The sample exhibits a fully reversible transition, representative

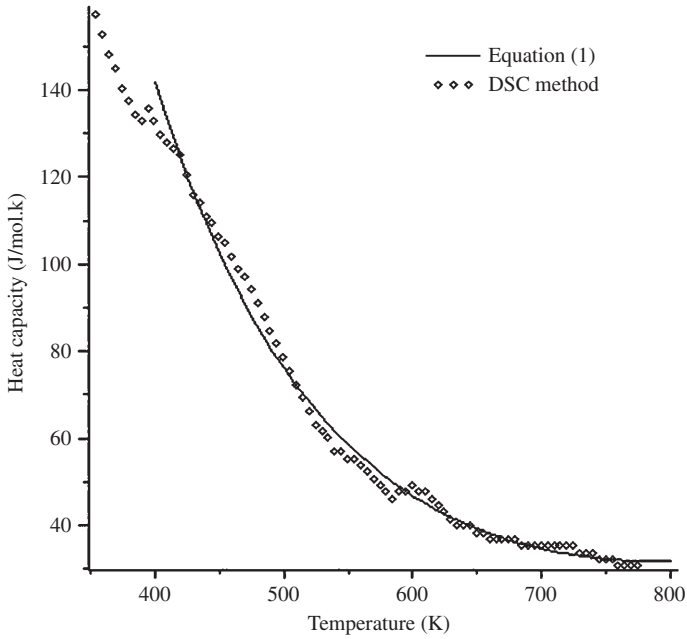


Figure 4. Heat capacities of CoTiO_3 by DSC.

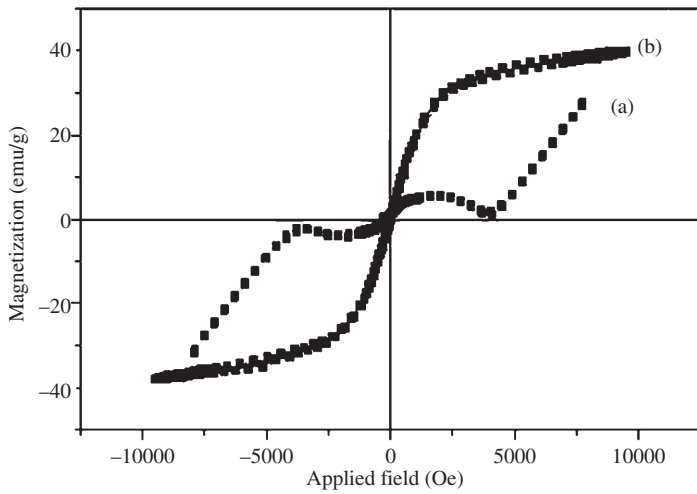


Figure 5. VSM curves of CoTiO_3 powders calcined at (a) 500°C and (b) 600°C .

of a genuine antiferromagnet. This fact reflects the good sample quality, since magnetic irreversibilities are often present in magnetic ceramic samples [29].

The VSM magnetic measurements for the cobalt titanate (Figure 5) show the magnetic properties of nanoparticles calcined at 500°C and 600°C . A comparison of VSM results of nanoparticles calcined at 500°C (Figure 5a) and 600°C (Figure 5b) shows

superparamagnetic behaviour in second sample which is more pure. The reduced M_r (room temperature remnant magnetisation) and H_c (magnetic coercivity) values is close to one of the characteristics of superparamagnetism response. The synthesised CoTiO_3 indicates a superparamagnetic behaviour, as evidenced by zero coercivity and remanance on the magnetisation loop. In a superparamagnetic system, particles do not show hysteresis in the $M-H$ curves; hence H_c and M_r are near zero [17]. A saturation magnetisation of $\sim 40 \text{ emu g}^{-1}$ was determined for the CoTiO_3 which is relatively higher than that of the bulk value of CoTiO_3 ($\sim 3 \text{ emu g}^{-1}$ in 60 kOe applied field [30]).

4. Conclusion

This study has demonstrated the feasibility of the synthesis of pure CoTiO_3 powders using a wet-chemistry synthesis method using stearic acid gel. Well-crystallised CoTiO_3 nanopowders could be synthesised at 600°C for 2 h. In addition, the empirical equation for the C_p of CoTiO_3 has been determined from DSC. Moreover, the synthesised CoTiO_3 has indicated a superparamagnetic behaviour, as evidenced by using VSM at room temperature.

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