JOURNAL OF MATERIALS SCIENCE **38** (2003) 2353–2356

Synthesis of cadmium titanate powders by a sol-gel-hydrothermal method

XIAOXUE ZHANG, HAO WANG,* ANPING HUANG, HAIYAN XU, YONGCAI ZHANG, DUNBO YU, BO WANG, HUI YAN
The Key Laboratory of Advanced Functional Materials of China Education Ministry, Beijing Polytechnic University, Beijing 100022, People's Republic of China
E-mail: haowang@bjut.edu.cn

Cadmium titanate ($CdTiO_3$) powders have been synthesized by a sol-gel-hydrothermal method at 200°C. The as-synthesized powders were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), Raman spectroscopy, and thermo-gravimetric and differential thermal analysis (TG-DTA). The results indicate that the as-obtained powders are ilmenite phase $CdTiO_3$ with rhombohedral structure. This phase changes to orthorhombic perovskite phase upon annealing at about 1050°C.

1. Introduction

The titanium-based oxides can be referred to as a 'smart' family owing to their excellent dielectric, piezoelectric, pyroelectric and photostrictive properties. Cadmium titanate $CdTiO_3$, as one member of this well-known family, has a broad range of such properties, which make it eligible to be used as the sensor material for the detection of NO_2 gas [1, 2], a possible new material for optical fiber [3–5] and so forth. It is known that $CdTiO_3$ crystallizes into a rhombohedral ilmenite phase when it is sintered above 800°C, and into an orthorhombic distorted perovskite phase above 1000°C [6, 7]. However, it cannot be denied that $CdTiO_3$ has been taken less notice in contrast with the other species of this family, as the ilmenite phase is not ferroelectric and the ferroelectric properties of the perovskite phase at low temperature (<50 K) are not well understood yet [6, 7]. From a fundamental point of view, $CdTiO_3$ represents an amusing system to study the nature of the ferroelectric and structural phase transition. Furthermore, like the other titanium-based systems, it may have unexplored potential for applications in non-linear optics.

As far as we know, one of the two conventional processes to create $CdTiO_3$ is solid-state reaction of the corresponding single oxides, CdO and TiO_2, at high temperatures. Unfortunately, CdO has severe toxicity, and the two starting oxides are subject to remaining in the final product, which mainly leads to the less study of $CdTiO_3$. Meanwhile, it's difficult to control the reactive sintering, particularly when a homogeneous and single phase is desired. The powders obtained are coarse and widely distributed. The other conventional preparation method is sol-gel technique which could bring about non-toxic starting materials and evenly mixed gelatin. But a little amount of CdO is still apt to be yielded during the post-heating so that pure $CdTiO_3$ cannot be prepared easily [8].

Hydrothermal process provides an inexpensive, low temperature, and environmentally friendly route for the preparation of advanced ceramic materials [9, 10]. Because the crystalline powders are directly formed in the hydrothermal treatment, the need for high temperature calcination and, in turn, the resulting aggregation and the subsequent milling process are eliminated. In this study, we make use of a sol-gel-hydrothermal technique to synthesize cadmium titanate powders. To the authors' knowledge, it is an initial work to achieve $CdTiO_3$ by a hydrothermal method so far and it is the lowest temperature ever reported to prepare phase-pure $CdTiO_3$.

2. Experimental

The raw materials were analytical grade cadmium acetate ($Cd(CH_3COO)_2$), tetrabutyl titanate ($Ti(C_4H_9O)_4$), and acetic acid (CH_3COOH). Fig. 1 illustrates a typical flowchart of our sol-gel-hydrothermal route for synthesizing $CdTiO_3$ powders. First, cadmium acetate was dissolved in CO_2-free distilled water. Then it was introduced into a prepared solution of stoichiometric amounts of tetrabutyl titanate which was dissolved in ethanol. Meanwhile, CH_3COOH was added to the mixture to control the hydrolysis of tetrabutyl titanate. The mixture was stirred at room temperature for 5 hrs, followed by being heated at 40°C constantly, keeping stirred as well. With the evaporation of water and CH_3COOH, a light yellow transparent gelatin, as the unique starting source of this hydrothermal preparation, was prepared. Then an

*Author to whom all correspondence should be addressed.

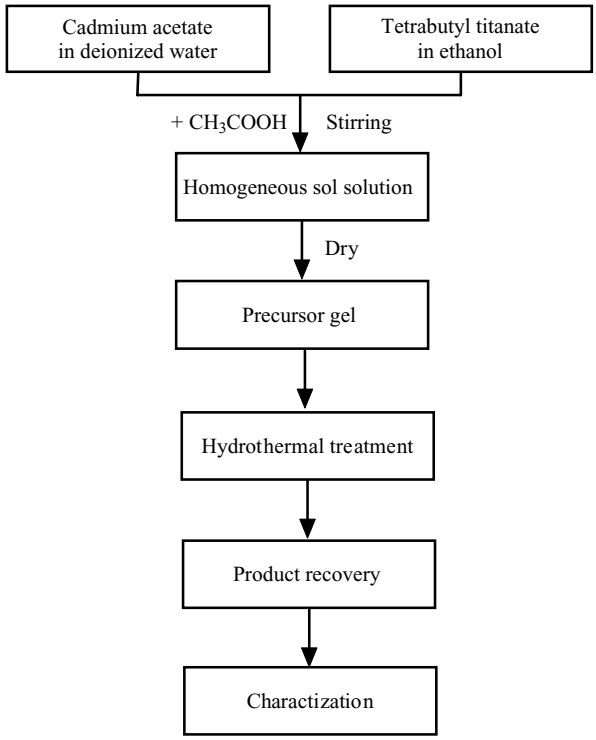

Figure 1 The flow chart of the synthesis of $CdTiO_3$ powders by hydrothermal method.

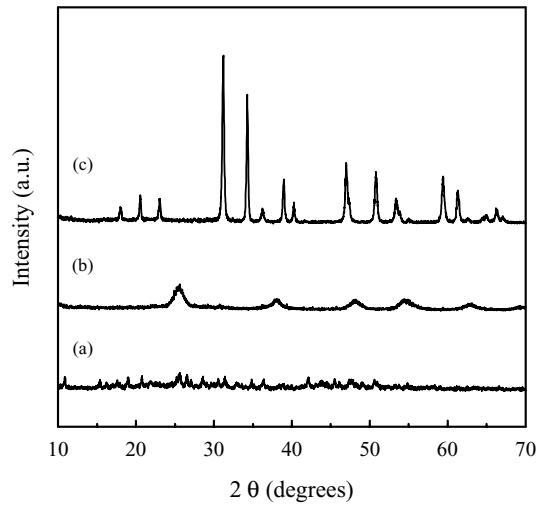

Figure 2 The comparison of the XRD pattern of (a) gelatin, (b) powders synthesized hydrothermally with pure water, and (c) 5 m/l KOH at 200°C for 12 hrs.

appropriate amount of the gelatin was put into a 40 ml Teflon-lined stainless autoclave. The autoclave was filled with pure water or KOH solution up to 80% of its total volume. After the autoclave was heated at 200°C for 12 h under autogeneous pressure, it was allowed to cool to room temperature naturally. The as-prepared products were filtered, washed with distilled water, and dried at ambient temperature.

The structure of the products was examined by X-ray diffractometry (XRD, Japan Rigaku D/Max-3C) using Cu K_α radiation. The morphology was investigated by scanning electron microscopy (SEM, Japan Hitachi S-3500N). Raman spectroscopy measurements were carried out on a Spex 1403 Raman spectrometer under backscattering geometry. Excitation was taken as the 488 nm line of Ar^+ laser with 100 mW output power. Thermogravimetric and differential thermal analysis (TG-DTA) were carried out using a Model STA 449C (Germany, NETZSCH-Gerätebau GmbH Thermal Analysis).

3. Results and discussion

Fig. 2 shows the XRD patterns of the gelatin (Fig. 2a) and the resulting products after hydrothermally treatment in pure water (Fig. 2b) and 5 M KOH (Fig. 2c) at 200°C for 12 h. From Fig. 2, it is obvious that there is no

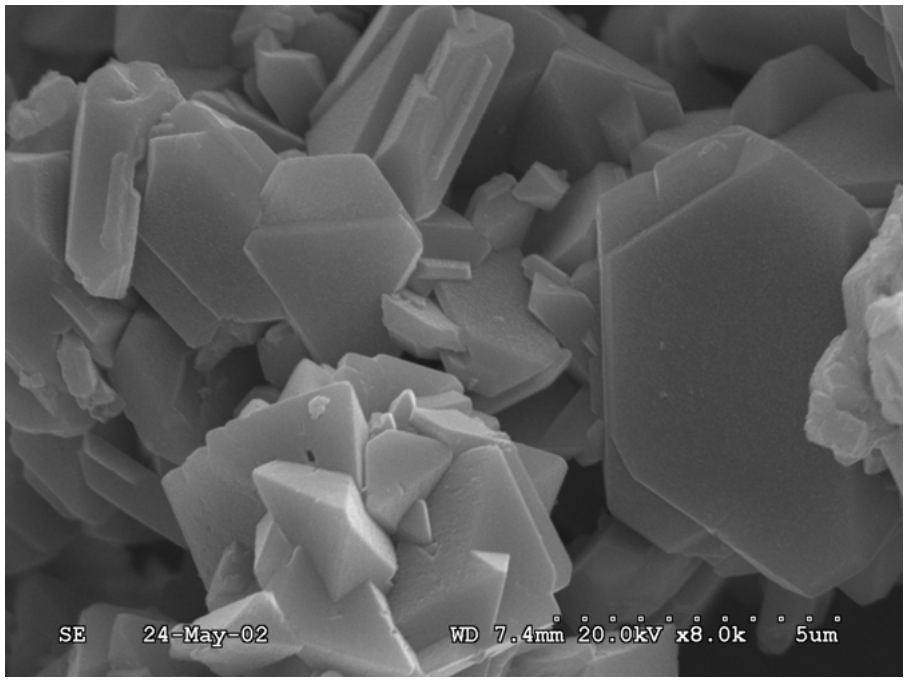

Figure 3 SEM image of the powders hydrothermally as-obtained.

peak in the XRD pattern of gelatin at all, indicating the gelatin is amorphous. When the gelatin was hydrothermally treated with pure water, several wide lumps appear which don't agree with any standard XRD pattern of $CdTiO_3$. On the other hand, when 5 M of KOH solution was used as the hydrothermal medium, the resulting product is highly crystallized as witnessed by the sharp and intense peaks of the XRD pattern shown in Fig. 1c. All the diffraction peaks of the resulting product can be attributed to the ilmenite phase $CdTiO_3$ (JCPDS, Card No: 29-277). The lattice parameters are calculated to be $a = 5.2302$ Å and $c = 14.8211$ Å, which agrees well with the literature values.

Fig. 3 shows the SEM image of the as-synthesized $CdTiO_3$ powders in 5 M KOH aqueous solution at 200°C for 12 h. It can be seen that the as-synthesized $CdTiO_3$ consists of well-defined hexagonal crystals with the size ranging from 2.5 to 5 μm.

The TG-DTA curves of the as-synthesized ilmenite phase $CdTiO_3$ in the range of 200–1100°C at a heating rate of 10°C min^{-1} are demonstrated in Fig. 4. There is only one endothermic peak centered at about 1040°C in DTA curve, while the TG curve keeps almost constant all the way, showing that no weight loss has occurred between 200°C and 1100°C. It is suggested that the endothermic peak at about 1040°C may be due to the phase transition of $CdTiO_3$ from ilmenite to perovskite phase. To confirm this, the as-synthesized ilmenite phase $CdTiO_3$ has been annealed at 900°C, 1000°C and 1050°C, respectively. The XRD patterns of the annealed samples are given in Fig. 5. From the XRD pattern, it can be seen that the ilmenite phase remains unchanged upon annealing at 900°C. With the annealing temperature increasing to 1000°C, most of the ilmenite phase of $CdTiO_3$ transforms to the perovskite phase. Till 1050°C, the ilmenite phase completely transforms to the perovskite phase with orthorhombic structure (JCPDS Card No. 78-1015), which are in agreement with the above TG-DTA results.

Fig. 6 shows the Raman spectra of the hydrothermally-synthesized ilmenite phase $CdTiO_3$ (Fig. 6a) and perovskite phase $CdTiO_3$ (Fig. 6b) obtained by annealing the ilmenite phase $CdTiO_3$ at 1050°C. In the Raman spectra of the ilmenite phase,

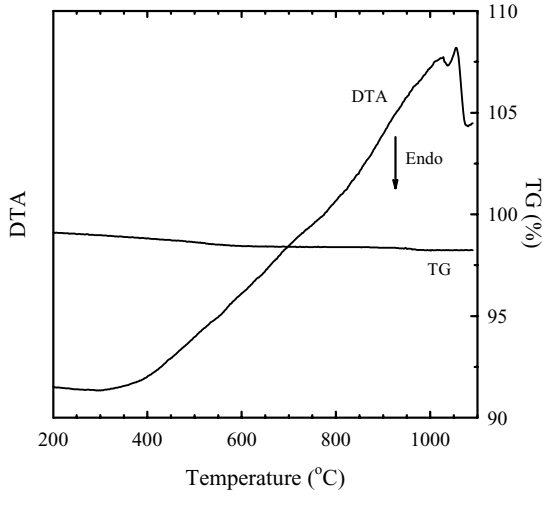

Figure 4 The TG-DTA curves of as-obtained powders.

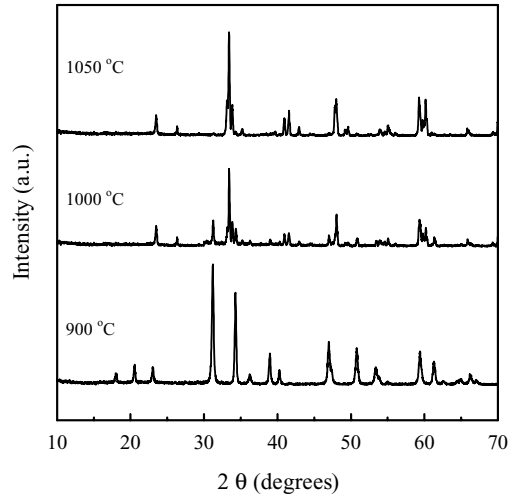

Figure 5 The XRD pattern of as-obtained powders post-annealed at 900°C, 1000°C and 1050°C.

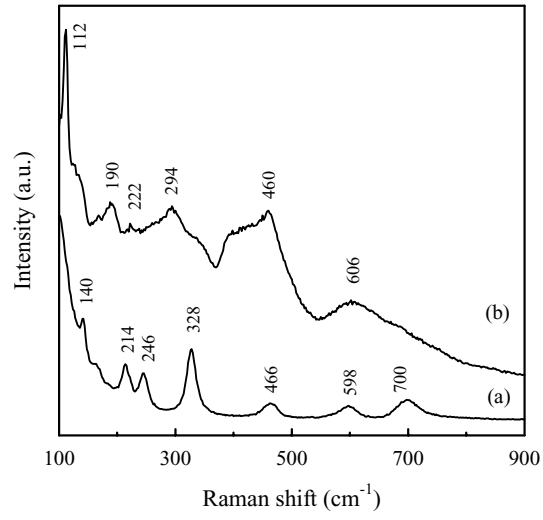

Figure 6 The Raman spectra of the (a) as-obtained powders and (b) the powders post-annealed at 1050°C.

there are seven peaks which appear at 140, 214, 246, 328, 466, 598 and 700 cm^{-1}, in ascending order. The last three peaks are wide lumps and the peak at 328 cm^{-1} is the sharpest. At the same time, it is interesting to note that one peak spilt at 214 cm^{-1} and 246 cm^{-1} which reproduces that reported in a previous literature [11]. On the other hand, one sharp peak and five broad peaks appear in the Raman spectra of perovskite phase. It is a fact that most perovskites show strong second-order scattering [12], therefore, these broad peaks may be interpreted as second-order two-phonon processes. So far no detailed interpretation about the Raman spectra of perovskite phase of $CdTiO_3$ was found in the literatures.

4. Conclusions

A sol-gel-hydrothermal method has been carried out to synthesize cadmium titanate powders. Well crystallized, phase pure ilmenite $CdTiO_3$ have been obtained at a low temperature of 200°C when 5 M KOH was used as mineralizer. This phase changes to perovskite phase upon annealing at about 1050°C.

References

1. T. BEIN, K. BROWN, G. C. FYE and C. J. BRILER, *J. Amer. Ceram. Soc.* **111** (1989) 7640.
2. Y. YAN and T. EEIN, in "Interfacial Design and Chemical Sensing," edited by T. E. Mallouk and D. J. Harrison (American Chemical Society, Wangington D. C., 1994) p. 16.
3. B. D. FADES, B.J. ZELINAKI and D. R. UHLMANN, in "Ceramic, Films and Coatings," edited by J. Wachtmann and JR. A. Haber (Noycs Publications, Park Ridgc, NJ, 1993) p. 224.
4. H. DISLICH, in "Sol.Gel Technology for Films, Fibers, Preforms, Electronics and Speciality Shapes," edited by L. C. Klein (Noycs Publications, Park Ridgc, NJ, 1993) p. 50.
5. R. B. PETTIT, C. S. ASHLEY, S. T. REEDAND and C. J. BRINKER, in "Sol.Gel Technology for Films, Fibers, Performs, Electronics and Speciality Shapes," edited by L. C. Klein (Noycs Publications, Park Ridgc, NJ, 1993) p. 224.
6. G. L. CATCHEN, S. J. WUKICH, D. M. SPAAR and M. BLASZKIEWIEZ, *Phys. Rev.* B **1885** (1990) 42.
7. I. N. GEIFMAN, M. L. SHOLOKHOVICH, V. I. MOLOCHAEVA and V. E. DUGIN, *Sov. Phys. Solid State* **1440** (1986) 25.
8. D. BERSANI, P. P. LOTTICI, M. CANALI, A. MONTENERO and G. GNAPPI, *J. Sol-Gel Sci. Tech.* **8** (1997) 337.
9. M. YOSHIMURA, *J. Mater. Res.* **13** (1998) 796.
10. W. J. DAWSON, *Amer. Ceram. Soc. Bull.* **67** (1988) 1673.
11. E. J. BARAN and I. L. BOTTO, *Z. Anorg. Allg. Chem.* **448** (1979) 188.
12. W. G. NILSEN and J. G. SLINNER, *J. Chem. Phys.* **48** (1968) 2440.

Received 29 July 2002
and accepted 21 January 2003