

HYDROTHERMAL SYNTHESIS OF MONODISPERSED LANTHANUM TITANATE PARTICLES

Zhili Ding, Mingfu Zhang and Jiecai Han

Center for Composite Materials, Harbin Institute of Technology, Harbin 150001, China

Received: June 20, 2001

Abstract. An isothermal hydrothermal reaction scheme has been developed to produce pure, ultrafine crystalline lanthanum titanate from lanthanum nitrate-titanium tetrabutylxide-water-alcohol. It was found that the pH of the hydrothermal reaction medium and the initial [La]/[Ti] (molar ratio) were critical factors in forming stoichiometric $\text{La}_{2/3}\text{TiO}_3$. By varying the pH of the reaction medium, different end products could be obtained. With [La]/[Ti]=0.5, the as-prepared $\text{La}_{2/3}\text{TiO}_3$ was in the cubic perovskite phase, and the structure did not change when the temperature was increased from room temperature to as high as 1000 °C. The optimum synthesis conditions including the ratio of [La]/[Ti], the concentration of NaOH and the lowest synthesis temperature were investigated. Under hydrothermal conditions, the La_2O_3 - 3TiO_2 system can tolerate the solid solubility of TiO_2 .

1. INTRODUCTION

Because of their interesting dielectric and ferroelectric properties, perovskite-type compounds of the system La_2O_3 - TiO_2 have been investigated by several workers. Among the lanthanum titanates, $\text{La}_{2/3}\text{TiO}_3$ was examined as solid solution with other perovskites, such as PbTiO_3 , BaTiO_3 , SrTiO_3 . This compound was said to have the perovskite structure but with one third of the A-sites vacant. Kestigian [1] described the preparation and properties of the $\text{La}_{(2/3+x)}\text{TiO}_3$ ($0 < x < 1/3$). Abe [2] synthesized the slightly oxygen deficient compound $\text{La}_{2/3}\text{TiO}_{3-y}$ under reduced oxygen pressure at 1300 °C and investigated its crystallographic properties with the powder X-ray diffraction. Yokoyama [3] grew the monocystals of $\text{La}_{2/3}\text{TiO}_{3-y}$ in an air atmosphere from a flux of the $\text{KF-Na}_2\text{B}_4\text{O}_7$ system at 950-1000 °C and measured their dielectric properties. The cubic compound $\text{La}_{2/3}\text{TiO}_3$ [4] has also been synthesized by calcining coprecipitated hydroxides at 400-800 °C. Recently it is generally accepted that the $\text{La}_{2/3}\text{TiO}_3$ structure may be stabilized by the presence of minute amounts of Ti^{3+} ions [5] and by partial fill-

ing of A-site vacancies with M^+ ($\text{M}=\text{Li}, \text{Na}, \text{K}$) [6]. It was also stabilized in the form of a solid solution with other dielectric compounds such as PbTiO_3 , SrTiO_3 , BaTiO_3 , CaTiO_3 , and LaAlO_3 [6,7].

In this paper, we investigated the growth of hydrothermal cubic $\text{La}_{2/3}\text{TiO}_3$ powder by systematically varying the alkali concentration in solution, the [La]/[Ti] ratio, and the reaction temperature.

2. EXPERIMENTAL PROCEDURE

Reagents of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ti}(\text{OC}_4\text{H}_9)_4$ and NaOH with 99 % purity were used as starting chemicals. The alcohol was chosen as the most favorable alcohol system to dilute $\text{Ti}(\text{OC}_4\text{H}_9)_4$ and CH_3COOH was used to slow the hydrolysis reaction. The synthesis were conducted by first preparing a clear aqueous precursor including stoichiometric amounts of lanthanum nitrate and titanium tetrabutylxide. Then a small amount of NaOH solution was slowly added to precursor to coprecipitate metal hydroxides. The resulting suspension was hydrothermally treated in a Teflon-lined stainless steel vessels. After the designated reaction time

Corresponding author: Zhili Ding, e-mail: dingnao@263.net

Table 1. Characteristics of nanocrystallines as a function of NaOH concentration.

Sample	Concentration of NaOH, (mol·l ⁻¹)	Resulting powders
LTD71	0	TiO ₂ (anatase)
LTD57	0.1	TiO ₂ (anatase)
LTD69	1	TiO ₂ (anatase)
LTD70	2	Amorphous phase
LTD33	4	Amorphous phase
LTD56	5	Multiple phase
LTD32	6	La _{2/3} TiO ₃
LTD31	8	La _{2/3} TiO ₃
LTD38	12	La _{2/3} TiO ₃

and reaction temperature, the slurry was poured into a beaker and diluted with hot acetic acid. This rinse of acetic acid eliminated any residual, unreacted lanthanum hydroxide and carbonate phases. The diluted slurries were filtered under ambient condition. The resulting powders were repeatedly washed with distilled water and were dried at 90 °C overnight.

Synthesis conditions for powders including the pH of the reaction medium, the reaction temperature and the [La]/[Ti] ratio were investigated. The pH of the initial feedstock solution was controlled by varying NaOH (or KOH) concentration. The phase composition of the products was determined by X-ray diffractometry (XRD, Rigaku D/max-rB, Japan). The Scherrer equation was used to estimate the La_{2/3}TiO₃ particle size. The lattice parameters were

determined by linear regression with diffraction peaks in the range 10°-90° of 2θ. The resulting powders were analyzed for lanthanum, titanium and sodium (or potassium) using an inductively coupled plasma spectrometer (ICP, Plasma 1000PE). Morphology of the product particles was determined using transmission electron microscope (TEM, JEM1200EX).

3. RESULTS AND DISCUSSION

Solution pH was one of the most critical reaction factors for the reproducible production of the perovskite ceramics, since solution pH mainly controlled the chemical nature of the aqueous solution species and determined phase composition and even morphology of the particles [8]. The pH condition for La_{2/3}TiO₃ formation under hydrothermal conditions was investigated. The data presented in this section were obtained from powders reacted for 72 h at 200 °C in solution with [La]=0.12 mol·l⁻¹ [Ti]=0.24 mol·l⁻¹, and NaOH concentrations ranging from 0 to 12 mol·l⁻¹. Table 1 shows the characteristics of the nanocrystallines as a function of NaOH concentration. When the concentration of NaOH was below mol·l⁻¹, the reaction product was anatase. When 2 mol·l⁻¹ ≤ [NaOH] ≤ 4 mol·l⁻¹, the product was an amorphous phase. La_{2/3}TiO₃ began to form at [NaOH] ≥ 6 mol·l⁻¹, but still was contaminated with the amorphous phase, whereas well-crystallized phase-pure La_{2/3}TiO₃ was produced at [NaOH] ≥ 8 mol·l⁻¹. It was determined that a highly alkaline condition was necessary for the production of the pure phase La_{2/3}TiO₃. This implies that the hydroxyl species (OH⁻) has an important kinetic role in the crystallization of powders under hydrothermal condition [9,10].

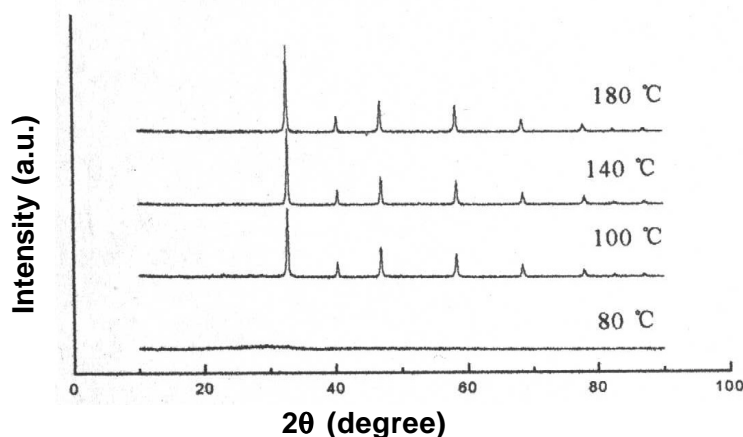


Fig. 1. XRD patterns for the hydrothermal reaction products as a function of synthesis temperature as the solution reacted for 72 h at [NaOH]=12 mol·l⁻¹.

Table 2. Characteristics of nanocrystallines prepared by hydrothermal method.

Sample	[La]/[Ti]	Hydrothermal product	Lattice parameters(Å)	Particle sizes(nm)
LTD1	1	La(OH) ₃ , La _{2/3} TiO ₃	3.8969	34.53
LTD37	0.67	La(OH) ₃ , La _{2/3} TiO ₃	3.8775	44.16
LTD36	0.6	La(OH) ₃ , La _{2/3} TiO ₃	3.8760	31.21
LTD35	0.55	La(OH) ₃ , La _{2/3} TiO ₃	3.8761	31.21
LTD38	0.5	La _{2/3} TiO ₃	3.8744	63.66
LTD34	0.45	La _{2/3} TiO ₃	3.8739	31.21
LTD39	0.4	La _{2/3} TiO ₃	3.8726	51.63

The lowest reaction temperatures in the hydrothermal synthesis of cubic La_{2/3}TiO₃ were also investigated. Precursors were reacted for 72 h in solutions containing [La]=0.12 mol·l⁻¹, [Ti]=0.24 mol·l⁻¹ and the NaOH concentration fixed at 12 mol·l⁻¹. The reaction were performed at 80 °C, 100 °C, 120 °C, 140 °C, 160 °C, 180 °C, 200 °C. It was determined that the lowest synthesis temperature for cubic La_{2/3}TiO₃ was 100 °C. X-ray diffraction patterns in Fig. 1 show the transition temperature of La_{2/3}TiO₃ from the X-ray amorphous phase to the perovskite phase under hydrothermal conditions. Higher reaction temperatures accelerate the crystallization process.

The effect of the initial ratio of [La]/[Ti] in solution on the end products were examined at a temperature of 200 °C for 72 h in solution that contained [NaOH]=12 mol·l⁻¹. The initial ratio of [La]/[Ti] in solution was varied from 0.4 to 1 (see Table 2).

Kestigian [1] has investigated the cubic perovskite phase La_(2/3+x)TiO₃ (0<x<1/3) and suggested that the lower limit of composition of the cubic phase is near La_{0.7}TiO₃. But our experiments found that the La₂O₃-3TiO₂ system could tolerate extensive solid solubility of TiO₂ in it, as in observations for the La₂O₃-2TiO₂ system [5]. Powders having [La]/[Ti] ratio values between 0.4 and 1.0 obtained from hydrothermal synthesis had the cubic perovskite structure. The lattice constant was found to vary from 3.8726 to 3.8969 (±0.002Å) with increasing lanthanum content. It was interesting to note that the calcined powder with [La]/[Ti]=0.5 also exhibited the cubic perovskite structure after calcination at 1000 °C.

ICP analysis of several resulting powders showed traces of sodium. These results agreed well with that of Skapin and Kolar [6]. Therefore it may be concluded that the stability of La_{2/3}TiO₃ was due to Na⁺ ions filling the A-site vacancies under hydrothermal condition.

Morphological observations by TEM are presented in Fig 2. The morphology of the sample LTD38 ([La]/[Ti]=2:4, 72 h sample) showed that the resulting powder had a snowflake-like fractal morphology. For the fractal morphology, further investigations of the morphology of hydrothermal product are being carried out.

4. CONCLUSIONS

The preparation of perovskite-type cubic La_{2/3}TiO₃ by the hydrothermal method was demonstrated. For the formation of pure La_{2/3}TiO₃, the conditions are that the [La]/[Ti] ratio was 0.4-0.5, the concentration of NaOH was greater than 8 mol·l⁻¹ and the synthesis temperature was above 100 °C were required. When the ratio of [La]/[Ti] varied from 0.4 to 1, the hydrothermal product had the cubic perovskite phase. The lattice constant increased from 3.8726 to 3.8969 (±0.002Å) with increasing lanthanum content.

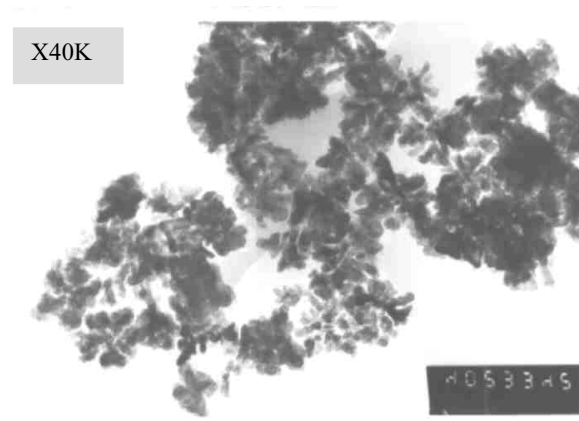


Fig. 2. TEM photograph of the hydrothermal cubic La_{2/3}TiO₃ crystallites.

REFERENCES

- [1] M.Kestigian and R. Ward // *Journ. of the Amer. Ceram. Soc.* **77** (1955) 6199.
- [2] M.Abe and K.Uchino // *Mater. Res. Bull.* **9** (1974) 147.
- [3] M.Yokoyama and T.Ota // *Journ. of Crystal Growth* **96** (1989) 490.
- [4] A.M. Sych // *Zh. Neorgan. Himii* **1** (1976) 3225.
- [5] J.B.Mac Chesney and H.A.Sauer // *Journ. of the Amer. Ceram. Soc.* **45** (1962) 416.
- [6] S. D. Skapin and D. Kolar // *Journ. of the European Ceram. Soc.* **20** (2000) 1179.
- [7] I.S.Kim and W.H.Jung // *Mater. Res. Bull.* **30** (1995).
- [8] J.Moon and J.A.Kerchner // *Journ. of Mater. Res.* **14** (1999) 425.
- [9] M.M. Lencka and R.E. Riman // *Chemistry of Materials* **5** (1993) 61.
- [10] J.Moon and T.Li // *Journ. of Mater. Res.* **12** (1997) 189.