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Effect of Calcination Temperatures on Phase Formation and Microstructure of Lead Titanate Powders Synthesized via Combustion Technique

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ABSTRACT

Lead titanate ($PbTiO_3$; PT) powders were sucessfully prepared by a combustion technique. PT powders were heated at various calcination temperatures, ranging from 500 to 900 ºC, for 2 h at a heating/cooling rate of 5 ºC/min. Powder samples were characterized using thermogravimetric (TGA), differential thermal analysis (DTA), X-ray diffractrometer (XRD) and scanning electron microscopy (SEM). The second phases such as PbO, PbO_2 and TiO_2 were detected in the powders calcined below 800 ºC. A single perovskite of the PT powders was found with calcination temperatures above 800 ºC. A lattice parameter c and c/a ratio increased while, the lattice parameter a decreased with increasing calcination temperature. The TGA-DTA results corresponded to the XRD investigation. The particle size tended to increase with increasing calcining temperature.

Key words: combustion technique, lead titanate, phase formation, microstructure, tetragonality

INTRODUCTION

Ferroelectric ceramics are important electronic materials that have a wide range of industrial and commercial applications, such as high-dielectric constant capacitors, transducers, sensors and ultrasonic motors (Kong *et al*., 2007). Among perovskite ferroelectric materials, lead titanate ($PbTiO_3$ or PT) ceramics have been investigated extensively. PT has a high Curie temperature (T_c) of about 490 ºC; a high pyroelectric coefficient and spontaneous polarization, make it useful for high frequency and high temperature applications, such as non-volatile memories, infrared sensors and capacitors (Ananta and Udomporn, 2004). It is difficult to prepare pure-phase PT ceramics with high density, because of a high c/a ratio of about 1.06 which gives rise to stresses in these ceramics, so they can be easily broken and are difficult to prepare in shape and size suitable for device applications (Shirane *et al*., 1970; Shirane *et al*., 1956). The most widely used approach is the formation of solid solution with additives, such as rare earth elements and alkaline earth elements and this is a promising technique for producing crack-free high-density materials (Ueda and Ikegami, 1968).

There are a lot of processing techniques for preparing PT powders, such as the solid state reaction technique (Ananta *et al.*, 2004), the sol-gel method (Liu *et al.*, 2002) molten salt synthesis (Idrissi *et al.*, 1999) and the hydrothermal technique (Moon *et al.*, 1997). Idrissi *et al.* (1999) prepared PT powders by a reaction in molten salt method: the tetragonality of the lattice is decreased by about 1% while the sinterability is improved. PT powders prepared by a sol-gel method; the tetragonal perovskite structure PT was prepared at 550 ºC. The dimension of particles is about 50 nm (Liu *et al.*, 2002). The conventional solid-state reaction method is the most widely used route. However, the ceramics which are synthesized by a solid state reaction require high temperature and the resulting powders exhibit many undesirable characteristics: large particle size and wide particle size distribution. Wet chemical synthesises can provide homogenous nanosized oxides of high purity at lower reaction temperatures but they have a high cost for starting materials, and are intricate and complicated. The combustion method has much interest; at present it helps to decrease the temperature in the preparation and has a small particle size. The combustion reaction method also has interesting characteristics such as its simplicity, its relatively low cost and the fact that it usually results in products with the desired structure and composition (Patil *et al.*, 1997). Thus, in this work, $PbTiO_3$ (PT) powders were prepared via the combustion method and we investigated the effect of firing temperatures on its phase formation and microstructure.

EXPERIMENTAL

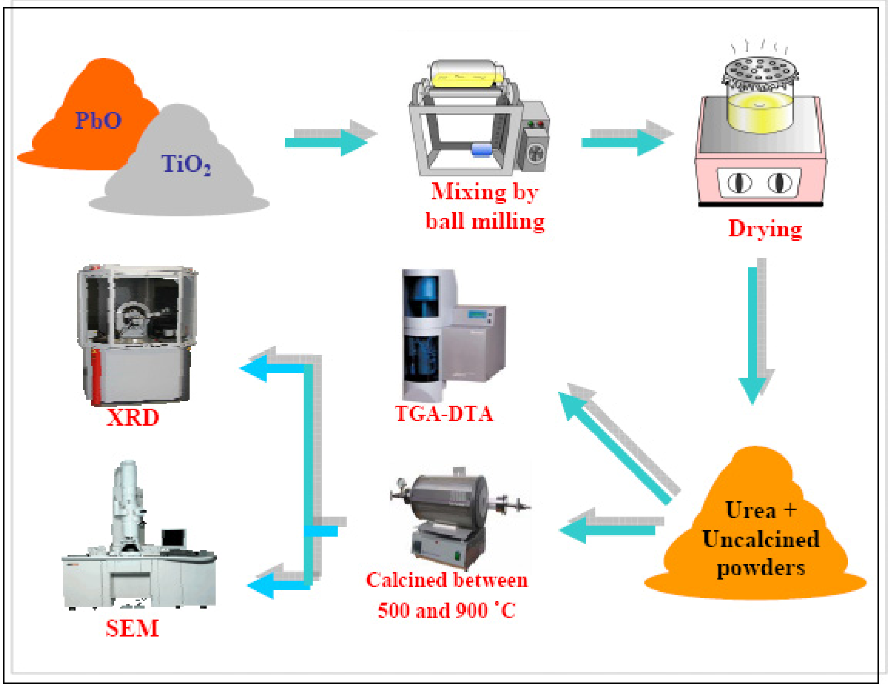

Figure 1 Preparation route for PT powders.

The raw materials used were commercially available lead oxide and titanium oxide. The $PbTiO_3$ powders were synthesized by the combustion route as shown in Figure 1. The powders were mixed by ball milling for 24 h with ethanol using zirconia balls. After drying and sieving, the powders and urea were mixed and ground in an agate motor. Then, the mixtured powders were calcined using various calcination temperatures, ranging from 500 to 900 ºC, for 2 h at a heating/cooling rate of 5 ºC /min. The reaction of uncalcined PT powders and urea fuel taking place during heat treatment was investigated by thermogravimetric analysis (TGA), differential thermal analysis (DTA). X-ray diffraction (XRD) was employed to identify the phase formed. The particle morphology and size were directly imaged, using scanning electron microscopy (SEM) and the average particle size was determined by using a mean linear intercept method.

RESULTS & DISCUSSION

Figure 2 shows the TGA and DTA curves of PT powders prepared via the combustion route. The PT powders demonstrated a three-stage weight loss; the first one was in the temperature range of 150 to 240 ºC, the second one from 311 to 520 ºC, and the last one began around 550 ºC. The first weight loss is believed to be caused by the melting of the urea. It was related with the endothermic peaks in the DTA curves at 166, 186 and 236 ºC. The second step was caused by the evaporation of water and gas. This was associated with the endothermic peak at 336, 412 and 473 ºC. The last curve corresponded to a small endothermic peak at 670 ºC, and represented the reaction of PbO and TiO_2.

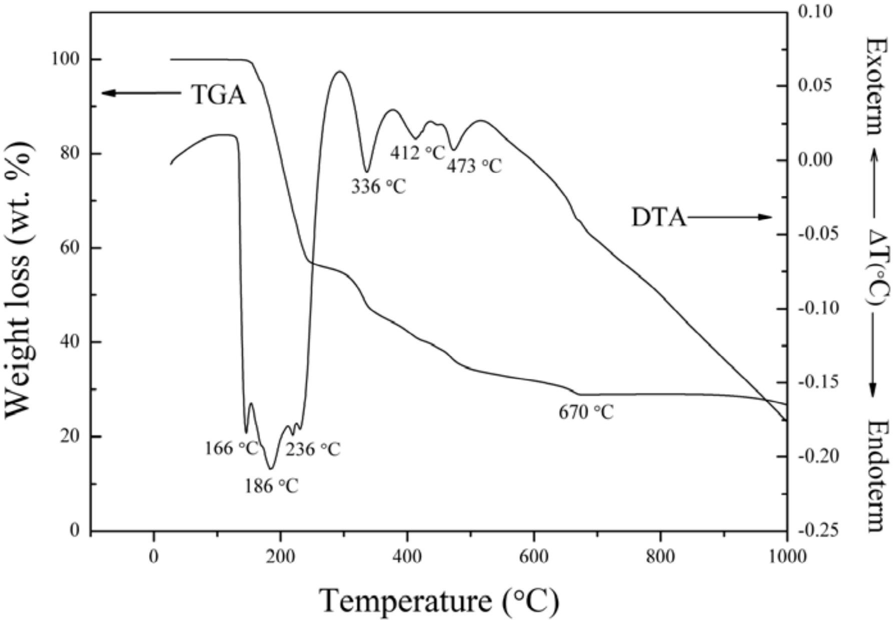

Figure 2 DTA-TG curves of uncalcined PT powders.

Based on the results of DTA and TGA, a series of calcinations were carried out from 500 to 900 ºC for 2 h, at a heating/cooling rate of 5 ºC /min for the uncalcined PT powders. The XRD patterns of the PT powders, formed with different calcination temperatures, are given in Figure 3. After calcination from 500 to 700 ºC, the precursor of PbO, PbO_2, TiO_2 and an unknown phase were detected. When the temperature went above 750 ºC, the minor phase of PbO remained. A high purity of the tetargonal perovskite phase was discovered in powders calcined above 800 ºC, which could be matched with JCPDS file number 06-0452.

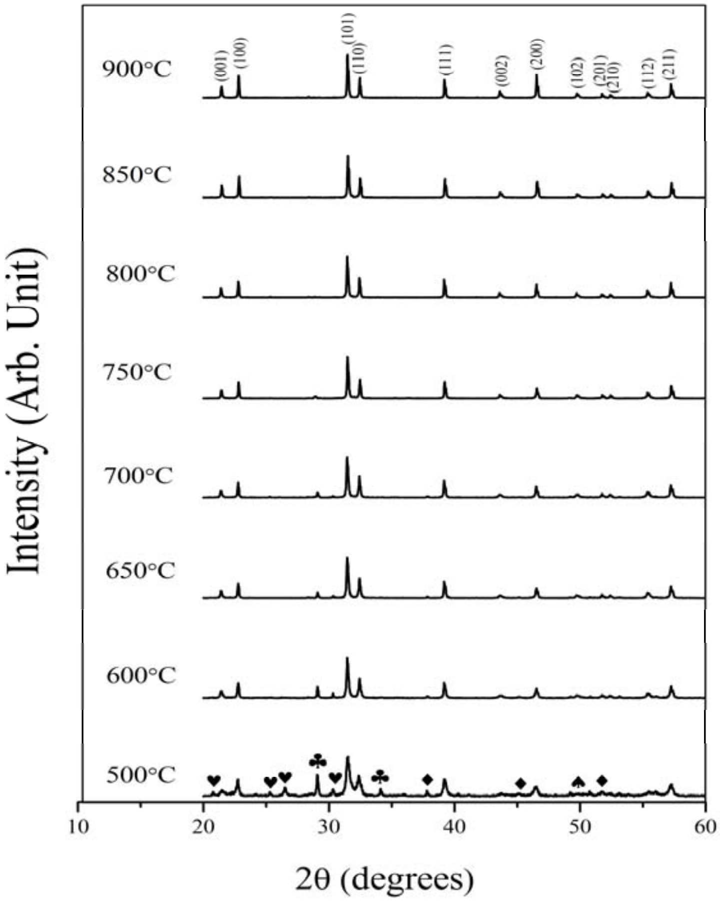

Figure 3 XRD patterns of PT powders with various calcination temperatures; (♣) PbO, (♠) PbO_2 , (♥) TiO_2 and (♦) unknown.

The relative percentage in the perovskite and impurity phases were determined by measuring the major XRD peak intensities of the perovskite and impurity phases. The percentage of the perovskite phase was estimated by the following equation:

$$(1)\quad \%perovskite\ \ phase = \left(\frac{I_{perov}}{I_{perov} + I_{PbO} + I_{PbO_2} + I_{TiO_2} + I_{unknown}} \right) \times 100$$

This equation is a well-known equation which is widely employed in the preparation of complex perovskite structure materials (Vittayakorn *et al.*, 2004; Vittayakorn *et al.*, 2003). Here $I_{perov}, I_{PbO}, I_{PbO_2}, I_{TiO_2}\ and\ I_{unknown}$ refer to the intensity of the (101) perovskite peak, intensities of the highest PbO, PbO_2, TiO_2 and the unknown. The percent perovskite phase increased with an increase in the calcining temperature as seen in Table 1. A handred percent of the perovskite phase was obtained from the samples calcined at temperatures higher than 800 ºC. The lattice parameter *c* tended to increase while, the lattice parameter *a* tended to decrease with an increase in the calcining as shown in Figure 4. The *c/a* ratio increased with increased calcination temperatures as seen in Figure 5. The average particle size was calculate using the Scherrer formula:

$$(2)\qquad D = k\lambda/(B\cos\theta)$$

Where; D is the size of powder
λ is the X-ray wavelength
B is the FWHM of diffraction peak
θ is the diffraction angle and the constant
$k \approx 0.9$

and based on the half-width of (101) reflection of the observed X-ray data. The average particle size tended to increase with increasing calcining temperatures, were between 217 and 417 nm and are demonstrate in Table 1.

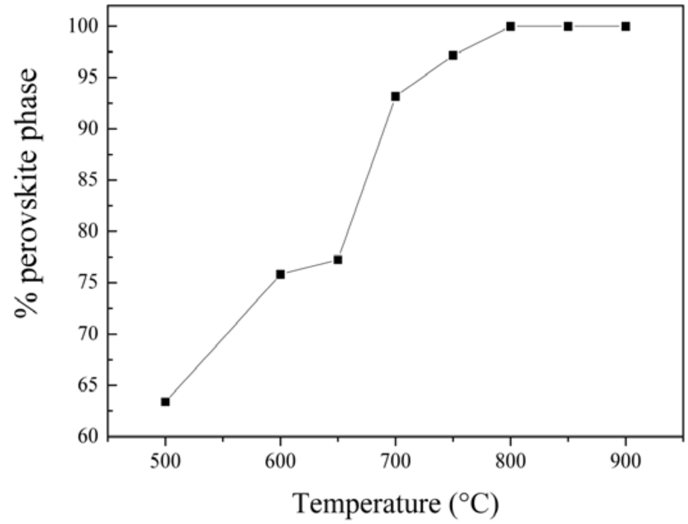

Figure 4 The percent perovskite phase of PT powders with various calcination temperatures.

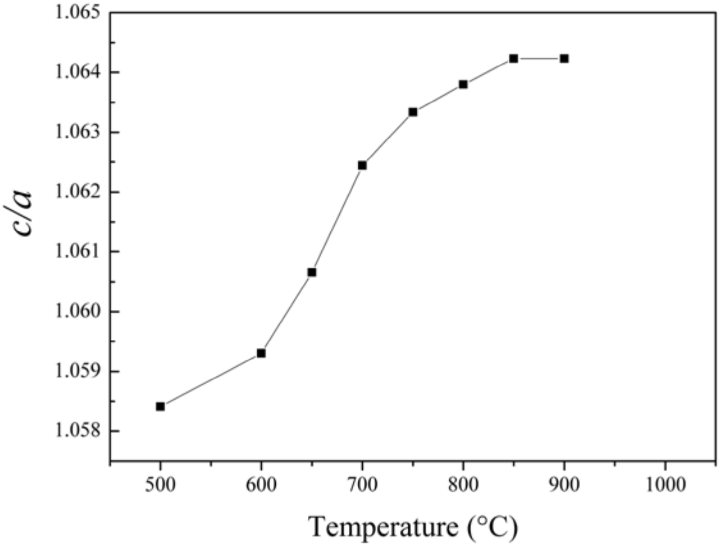

Figure 5 The *c/a* ratio of PT powders with various calcination temperatures.

The SEM photomicrographs of PT calcined powders between 600 and 900 ºC are illustrated in Figure 6. These powders exhibited an almost spherical morphology and have a porous agglomerate. The average particle size obtained from a linear intercept method tended to increase with the increasing of calcination temperatures (Table 1). The average particle size estimated from SEM is similar with the average particle size computed by XRD data.

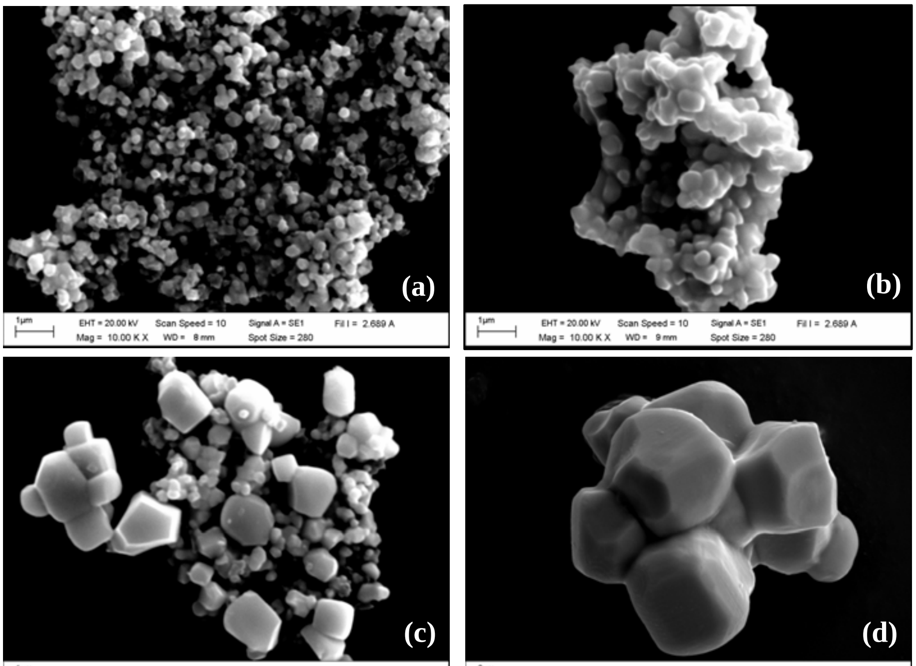

Figure 6 SEM morphology of PT powders calcined at (a) 600 ºC, (b) 700 ºC, (c) 800 ºC and (d) 900 ºC.

Table 1 Lattice parameter *a*, *c* and average particle size of PT powders

Calcination temperatures (ºC)	Lattice parameter *a* (Å)	Lattice parameter *c* (Å)	Average particle size (nm)	
			FWHM	SEM
500	3.9104	4.1388	217	250
600	3.9088	4.1406	312	270
650	3.9072	4.1442	331	340
700	3.9040	4.1478	359	400
750	3.9024	4.1496	377	470
800	3.9024	4.1514	389	500
850	3.9009	4.1514	392	480
900	3.9009	4.1514	417	660

CONCLUSIONS

Perovskite ($PbTiO_3$; PT) powders can be successfully obtained by the combustion technique. The pure perovskite tetragonal phase was discovered above 800 ºC. The calcination temperatures have a strong influence on the crystal structure, percent perovskite phase, lattice parameter and particle size of the PT powders.

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