

Synthesis and characterization of strontium titanate powder via a simple polymer solution route

Sang-Jin Lee^a, Pradheep Thiyagarajan^b and Man-Jong Lee^{b,*}

^aDepartment of Advanced Materials Science and Engineering, Mokpo National University, Muan 534-729, South Korea

^bDepartment of Advanced Technology Fusion, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, South Korea

A simple chemical route has been used to synthesize highly sinterable strontium titanate (SrTiO₃) powders using titanium isopropoxide, strontium nitrate and ethylene glycol. This method utilizes complexation-polymerization using ethylene glycol as an organic carrier, which leads to compositional homogeneity and fine particle sizes. The calcined SrTiO₃ powder showing a porous nature was fully crystallized to a cubic phase at 1,300 °C for 1 hour. Through ball-milling the porous SrTiO₃ powders with particle sizes of 200-300 nm were easily obtained, which was sintered to a bulk density of 4.8 g/cm³ at 1,400 °C for 1 h with a grain size of approximately 6.0 μm. The relative dielectric constant and loss tangent of SrTiO₃ sintered at 1,400 °C for 1 hour were 2078 and 0.022, respectively.

Key words: Strontium titanate; Titanium isopropoxide; Strontium nitrate; Ethylene glycol; Powder synthesis; Complexation-polymerization.

Introduction

Owing to a large polarization and a high dielectric constant, strontium titanate (SrTiO₃) has been used in a variety of applications. A typical preparation route for the strontium titanate powder is a solid-state reaction method [1] using TiO₂ and SrCO₃ as starting materials and calcination at high temperatures. Although this process is simple and cheap, the powders obtained are generally coarse, chemically inhomogeneous and usually contain some other phases, all of which prevent the powder's use for advanced electronic materials [2]. Meanwhile, in a chemical synthesis, several techniques are available to obtain fine strontium titanate powders. These include a chemical solution process [3], sol-gel methods [4], thermal decomposition of mixed citrate or oxalate complexes [5], hydrothermal methods [6], and freeze drying of nitrate solutions [7]. However, the main drawback of these solution techniques is that they are generally complex and expensive.

Recently, an organic-inorganic solution technique using PVA (polyvinyl alcohol), PEG (polyethylene glycol) or EG (ethylene glycol) as a polymer carrier has been developed to make an easier and highly-productive soft-solution processing method [8-11]. Using the organic-inorganic solution route, Lee et al. reported the successful synthesis of barium titanate (BaTiO₃) powders [12]. This method is based on complexation-polymerization with ethylene glycol (HOCH₂CH₂OH, EG) as an organic carrier. Unlike

the Pechini [13] method that only works with systems that are water-soluble, this process can be extended to chemicals that decompose in water, such as titanium isopropoxide by using the only polymerizing agent.

In this study, strontium titanate powders were synthesized by a polymer solution method employing EG as a polymeric carrier. The powder characteristics, its sintering behavior, and the dielectric properties were also examined.

Experimental Procedure

Strontium nitrate (Sr(NO₃)₂, reagent grade, Alfa Aesar Chem. Co., Ward Hill, MA) and titanium (IV) isopropoxide (Ti(OC₃H₇)₄, reagent grade, Alfa Aesar Chem. Co., Ward Hill, MA) were dissolved in stoichiometric proportions in liquid-type ethylene glycol (Fisher Chemical, FW:62.07, Fair Lawn, NJ). The amount of ethylene glycol was calculated using a ratio of total weight of metal ions from cation sources to weight of ethylene glycol. In this experiment, only a ratio of 1 : 3 is discussed because this composition showed optimum powder characteristics with no precipitation during the dissolution and lower crystallization temperatures. The strontium nitrate was first added to the ethylene glycol and the solution was stirred until the strontium nitrate was fully dissolved. Then, the titanium (IV) isopropoxide was slowly added while stirring. The solution was then allowed to gel for 24 h in a drying oven at 80 °C. The dried gel was then calcined for 1 h at various temperatures in an air atmosphere. The calcined powder was ball-milled with a zirconia ball media for 12 h. Isopropyl alcohol was used as a solvent for milling. The ball-milled powders were uni-axially

*Corresponding author:
Tel : +82-2-2049-6021
Fax: +82-2-452-3410
E-mail: leemtx@konkuk.ac.kr

pressed at 20 MPa and the pellet-shaped green compacts were sintered at various temperatures for 1 h in an air atmosphere.

The crystallization behavior of the gel-type precursors was examined as a function of calcining temperature using a X-ray diffractometer (Rigaku/USA, Dmax, automated powder diffractometer, Danvers, MA) with CuK α radiation (40 kV, 40 mA). The morphologies of the crystallized powders and grains after sintering were examined by scanning electron microscopy, (SEM, S-3500N, Hitachi, Japan). The pyrolysis and decomposition behavior of the organic/inorganic precursor were monitored by simultaneous differential scanning calorimetry and thermogravimetric analysis (DSC/TGA, Model STA 409, Netzsch GmbH, Selb, Germany) up to 1,200 °C, at a heating rate of 10 °Kmin⁻¹, in an air atmosphere. The relative dielectric constant and the loss tangent were measured at room temperature with a HP LCR meter 4284 A after the formation of silver electrodes at both sides of the sample.

Results and Discussion

After all the chemicals were dissolved in ethylene glycol, the solution was pale yellow and transparent. During the drying process at 80 °C, the transparent gel turned to a yellow-colored solid gel. Fig. 1 presents the XRD results at each processing temperature. At 600 °C SrCO₃ was formed by a reaction of strontium cations from the nitrate salt and residual carbon. TiO₂, Sr₂TiO₄ and SrTiO₃ were observed at 800 °C after decomposition of SrCO₃, and SrTiO₃ was gradually developed as the processing temperature increased. The powder was fully crystallized to cubic SrTiO₃ at a temperature of 1,300 °C.

The polymerization agent, EG in this method, acts to capture the metal ions through a polymerization-

complexation mechanism [14], which serves to decrease the mobility of metal ions and constrain the system to prevent precipitation of cation species and agglomeration. With the optimum amount of polymer, the metal ions are dispersed in solution and a homogeneous polymeric network is formed. By complex polymerizations with ethylene glycol it was possible to synthesize target compounds using common chemicals such as cation nitrite and titanium isopropoxide [12].

The thermal analysis plots for the strontium titanate precursor powder are shown in Fig. 2. In the TGA curve, the mass loss occurred in three stages (i) 250-350 °C, (ii) 500-550 °C and (iii) 600-650 °C. The DSC spectrum showed two exothermic peaks at 330 °C and 520 °C, and one endothermic peak at 640 °C. In general, polymer decomposition occurs by two steps [15]. The first step is degradation of the polymeric structure by pyrolysis, which is then followed by oxidation of the residual carbon. In the EG method, the first mass loss was due to the pyrolysis of EG, resulting in breaking of bonds, removal of free organics from metal-ion sources, and release of N_xO_y gases. An exotherm at 520 °C in the second weight loss was due to the burn out of the residual carbon by oxidation with CO, and CO₂ gases form. The endothermic peak appearing at 640 °C was due to the decomposition of SrCO₃.

SEM micrographs of the powder morphologies and the sintered surface of SrTiO₃ are shown in Fig. 3. The SrTiO₃ powders calcined at 1,000 °C for 1 h revealed soft, porous and large agglomerated particles as shown in Fig. 3(a). In the ball-milled powders shown in Fig. 3(b), significantly reduced particles of about 200-300 nm in size were observed. In the ethylene glycol method, both the pyrolysis/oxidation of the polymer carriers and the removal of free organics from metal-ion source made release of various gases such as CO, and CO₂ during calcinations occurred. It resulted in a soft and porous powder structure, which was easily ground to fine particles by a simple ball

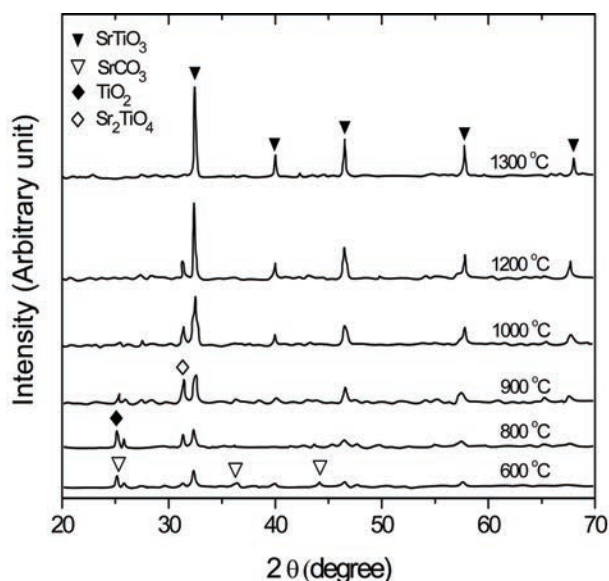


Fig. 1. Crystalline development of strontium titanate precursor synthesized by the ethylene glycol method.

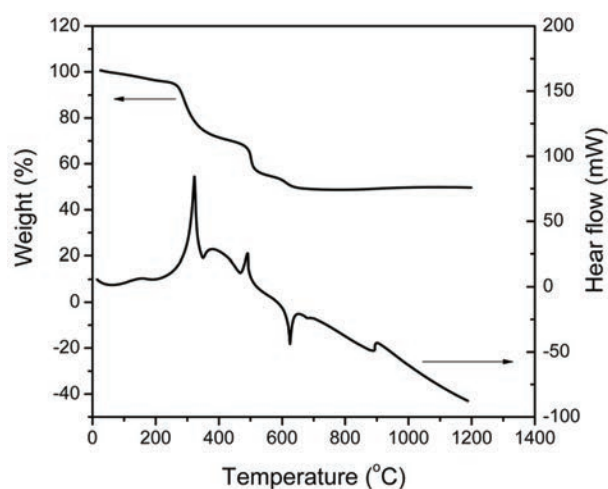


Fig. 2. TGA/DSC curves for the strontium titanate precursor made by the ethylene glycol method.

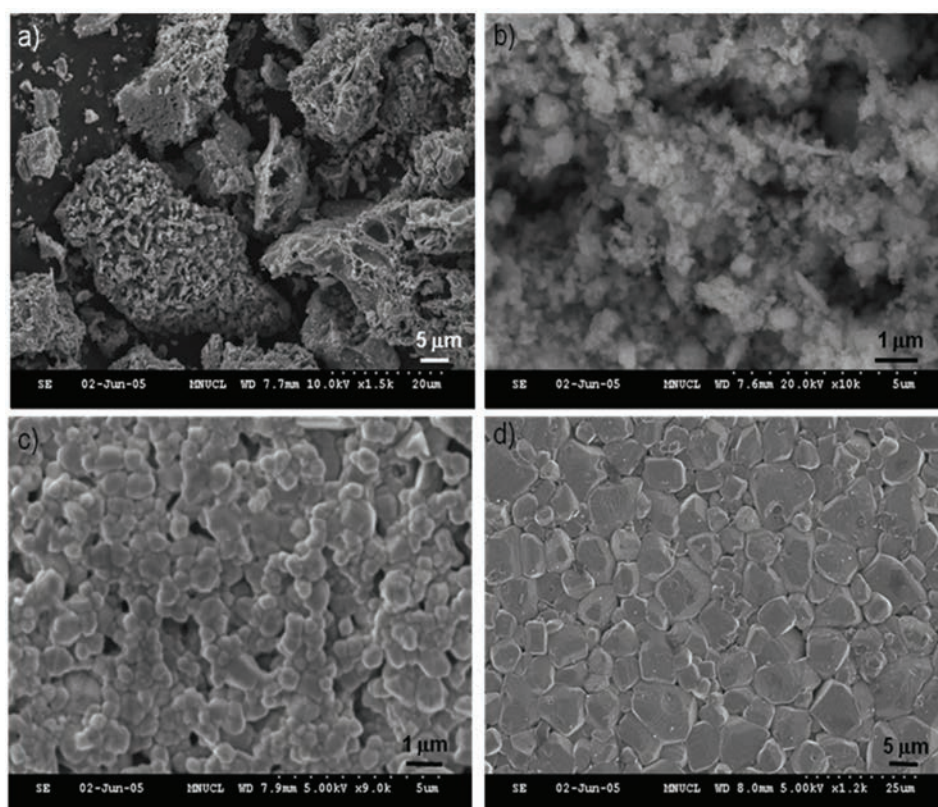


Fig. 3. SEM micrographs of powders (a) calcined at 1,000 °C for 1 h, (b) ball-milled for 12 h, and surfaces sintered (c) at 1,300 °C for 1 h, (d) at 1,400 °C for 1 h.

milling process. The surfaces of SrTiO₃ pellet sintered at 1,300 °C for 1 h (Fig. 3(c)) had a grain size of about 500 nm. The grain size was, however, abruptly increased up to an average grain size of 6.0 μm for the samples sintered at 1,400 °C for 1 h.

The density changes and the relative dielectric constants measured at 1 kHz of SrTiO₃ samples sintered at various temperatures are shown in Fig. 4. The densification occurred

gradually and the pellet sintered at 1,400 °C for 1 h had a bulk density of 4.8 g/cm³ with nearly 0% porosity. Due to the full densification, the relative dielectric constant of samples sintered at 1,400 °C showed higher values compared to those sintered at lower temperatures. Considering the pure SrTiO₃ nature synthesized by the polymer solution route, the relative dielectric constant showed high values. The loss tangent of samples in all frequency ranges remained below 0.03.

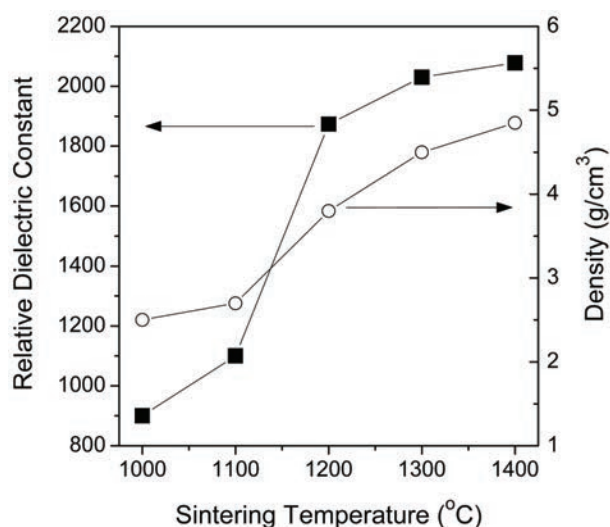


Fig. 4. Density and relative dielectric constant of SrTiO₃ pellets synthesized by the polymer solution route.

Conclusions

Strontium titanate powders have been successfully synthesized by the ethylene glycol, polymerization-complexation route, employing water-insoluble chemicals as a source of titanium ions. This method showed a distinctive advantage over other sol-gel methods in that it is easier and cheaper because direct dissolution of chemicals in ethylene glycol simplified the process. Also, this process leads to compositional homogeneity and fine particle sizes with a porous structure of the powder. The porous, calcined powders were easily ground to highly sinterable powders with average particle sizes of 200–300 nm by the simple ball milling process. Thus, the ethylene glycol method can be useful in the titanate ceramic powder synthesis process because of its merits such as being a simple process and easy control of the particle size.

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