



## The Preparation and Electrical Properties of SrTiO<sub>3</sub>-Based Capacitor-Varistor Double-Function Ceramics

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**Abstract.** SrTiO<sub>3</sub> powders were prepared using a sol–gel process. The electrical properties and the microstructure of doped SrTiO<sub>3</sub>-based capacitor-varistor double functions ceramics prepared by the sol–gel process were compared with those of ceramics prepared via the solid-state reaction method using X-ray diffraction, scanning electron microscopy, and measurements of dielectric constants and current-voltage characteristics. The sol–gel based materials exhibited enhanced capacitor-varistor properties compared to those prepared by a conventional solid-state method. These enhanced properties are attributed to the smaller, more uniform grain structure obtained in the sol–gel-derived material, which promotes the formation of an effective core-shell structure in which an acceptor-doped layer encapsulate the donor-doped SrTiO<sub>3</sub> grains. The effect of such microstructures on electrical properties is discussed.

**Keywords:** strontium titanate, double-functional ceramics, electrical property, capacitor, varistor

### 1. Introduction

Due to their high-frequency noise absorption, surge absorption, steep-fronted pulse absorption function and auto-comeback function, SrTiO<sub>3</sub>-based multi-functional ceramics are promising materials for applications in electronic circuitry [1, 2]. SrTiO<sub>3</sub>-based multi-functional ceramics are expected to act as a capacitor below a threshold voltage, and as a varistor above the threshold. These composite properties are generally attributed to the core-shell structure of grains in the SrTiO<sub>3</sub>-based ceramics, according to the boundary-layer model proposed for such materials [3, 4]. In this model, semi-conducting SrTiO<sub>3</sub> grains are separated by an insulating layer. For good electrical properties, controlling the grain size, the semi-conducting properties of grains and the insulating characteristics of the grain boundary are very important in the preparation of SrTiO<sub>3</sub> double-function devices. It is well known that the properties of materials depend

on their synthesis processes. To date, several methods have been reported for preparing SrTiO<sub>3</sub> powders, such as the conventional solid-state reaction route [5], co-precipitation [6, 7], sol–gel methods [8], etc. Homogenous compositions and uniform grain size are of great benefit to the electrical properties of electronic ceramics. Therefore, compared with the conventional solid-state method, the sol–gel process, which provides enhanced control of stoichiometry and homogeneity, should enable superior electrical properties to be obtained.

Although there have been many reports of the preparation of SrTiO<sub>3</sub> powders and films by the sol–gel process [8, 9], there are few studies of the fabrication and characterization of the SrTiO<sub>3</sub>-based double-function ceramics made by this method. In the present work, we have synthesized SrTiO<sub>3</sub> powders and the SrTiO<sub>3</sub>-based capacitor-varistor double-function ceramics by the sol–gel technique and compare the electrical properties of the corresponding ceramics with that made by the conventional solid-state reaction route.

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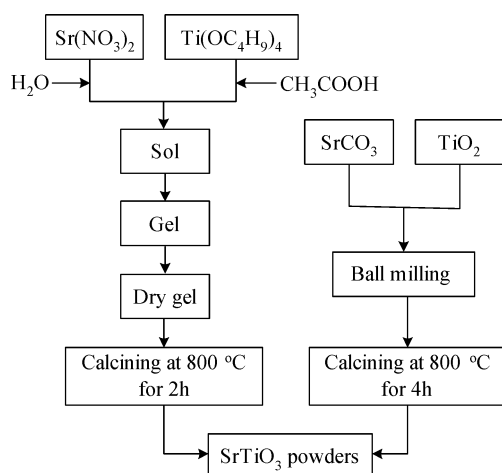


Figure 1. Flow chart for the preparation of SrTiO<sub>3</sub> powders via two processing routes.

## 2. Experimental Procedures

### 2.1. Preparation

Analytical grade Sr(NO<sub>3</sub>)<sub>2</sub>, Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>, SrCO<sub>3</sub> and TiO<sub>2</sub> were used as the main starting materials to prepare the SrTiO<sub>3</sub> powders, and analytical grade Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> were used as sintering aids in the production of ceramic test pieces. Spectroscopic-grade Nb<sub>2</sub>O<sub>5</sub>, La<sub>2</sub>O<sub>3</sub>, and Li<sub>2</sub>CO<sub>3</sub> were used as additives to prepare the capacitor-varistor multi-function ceramics. The typical procedures used to prepare SrTiO<sub>3</sub> powders via sol-gel processing and a conventional solid-state reaction route are shown in Fig. 1 (in each case, 0.1 mol of the corresponding SrTiO<sub>3</sub> powders were synthesized). In the sol-gel method, a mixture of CH<sub>3</sub>COOH and Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> (CH<sub>3</sub>COOH:Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> volume ratio = 1) was added to an aqueous solution of Sr(NO<sub>3</sub>)<sub>2</sub> ([Sr(NO<sub>3</sub>)<sub>2</sub>] = 3.4 M; H<sub>2</sub>O:Ti mole ratio = 40) with stirring. A transparent sol was obtained, which formed a gel over a ~2 h period. The resulting sol-gel precursor powders were calcined at 700–900°C, to identify the optimum temperature for producing crystalline SrTiO<sub>3</sub>.

To investigate the effect of different preparation method (sol-gel and solid-state) on the microstructure and electrical properties, SrTiO<sub>3</sub>-based capacitor-varistor ceramics were prepared from the powders as follows. The SrTiO<sub>3</sub> powders made by the two routes and electrical-property additives (0.3 mol% Nb<sub>2</sub>O<sub>5</sub>; 0.5 mol% La<sub>2</sub>O<sub>3</sub>; 0.5 mol% Li<sub>2</sub>CO<sub>3</sub>) were mixed via ball-mill in de-ionized water, together with small quan-

ties of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and TiO<sub>2</sub> (0.2, 0.7, and 0.5 mol%, respectively) as sintering aids. The resulting powders were uniaxially dry pressed at 100 MPa to form cylindrical bodies, which were sintered at 1400°C for 2 h in a 90Vol% N<sub>2</sub>/10Vol% H<sub>2</sub> atmosphere and cooled to room temperature. The sintered specimens were then annealed at 1000°C for 1 h in air to obtain the final ceramics. For measuring the electrical properties, electrodes were deposited on both faces of the ceramics using a thin layer of In-Ga alloy.

### 2.2. Measurement and Characterization

Dielectric constants were measured using an LCR Databridge (2810A, Tianjin Radio Factory No. 6,

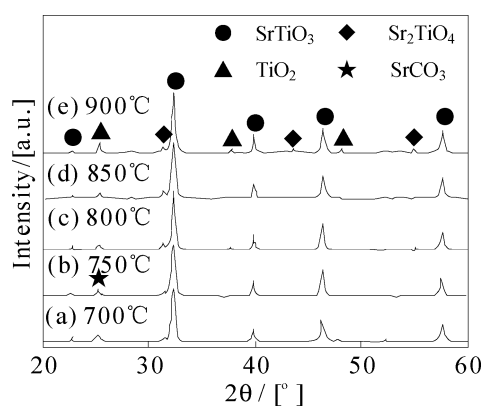


Figure 2. The XRD patterns of SrTiO<sub>3</sub> powders calcined at different temperature.

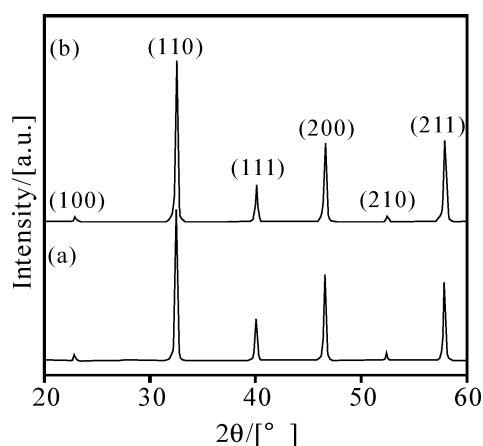


Figure 3. The XRD patterns of ceramic powders prepared by the different methods. (a) the sol-gel method; (b) the solid-state reaction method.

China) at 1 kHz. Current versus voltage electrical characteristics, varistor voltage ( $U_{1mA}$  and  $U_{10mA}$ ) and the non-linear coefficient value ( $\alpha$ ) were measured using the Voltage Sensitive Parameters instrumentation (JN2712, Changzhou Second Radio Factory, China).

The phase structure of SrTiO<sub>3</sub> powders and ceramics was determined by X-ray diffraction (XRD, Dmax-3c, Rigaku, Japan) using the Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) and a graphite monochromator with a  $2\theta$  range from 20 to 60°. The microstructures of as-fired samples were characterised by scanning electron microscopy (SEM, Hitachi S-570, Japan).

### 3. Results and Discussion

#### 3.1. Effect of Calcining Temperature on Powders

The XRD patterns of powders calcined at different temperature are shown in the Fig. 2. A semi-quantitative analysis indicated that the apparent strontium titanate content was 78% (700°C), 80% (750°C), 87% (800°C), 79% (850°C) and 75% (900°C), and hence, an intermediate temperature of 800°C was chosen to obtain sol-gel SrTiO<sub>3</sub> powders for subsequent investigations. The average crystallite size of SrTiO<sub>3</sub> powders calcined at 800°C, calculated using the Scherrer formula, was ca. 40 nm. In addition, the XRD data clearly reveal the presence of small quantities of process impurities, such as TiO<sub>2</sub>, SrCO<sub>3</sub> and Sr<sub>2</sub>TiO<sub>4</sub> in the powders. However, these impurities further react at the sintering temperature to yield the “pure” SrTiO<sub>3</sub> perovskite phase, as revealed by the XRD patterns in Fig. 3.

Table 1. The electrical properties of specimens prepared by the sol-gel and solid-state methods.

Samples	$\alpha$	$U_{1mA}/$ V·mm <sup>-1</sup>	$U_{10mA}/$ V·mm <sup>-1</sup>	$\epsilon_r/10^4$	C/nF
Solid-state reaction method	6.14	55	83	2.7	5
Sol-Gel method	6.45	28	40	6.28	14

#### 3.2. Effect of Different Preparation Method on the Electrical Properties

Table 1 shows the electrical properties of specimens prepared by the sol-gel and conventional solid-state methods. The varistor voltage of ceramics made by the sol-gel method was lower than that of materials prepared via the conventional route. At the same time, the non-linear coefficient, relative dielectric constant and the capacity of the ceramics ( $C$ ) were higher than that made by the conventional method. These superior electric properties are attributed to a core-shell structure in the ceramic grains obtained by sol-gel processing.

Core-shell structures play a key role in multi-function electronic ceramics such as those investigated in this work. Generally, at low voltages, the electrical properties of SrTiO<sub>3</sub>-based ceramics are determined by the insulating properties of the acceptor-doped (Li<sup>+</sup>) grain boundary material, with the ceramic acting as an internal-boundary-layer (IBL) capacitor with high resistivity. At voltages exceeding a characteristic breakdown threshold, the grain boundary

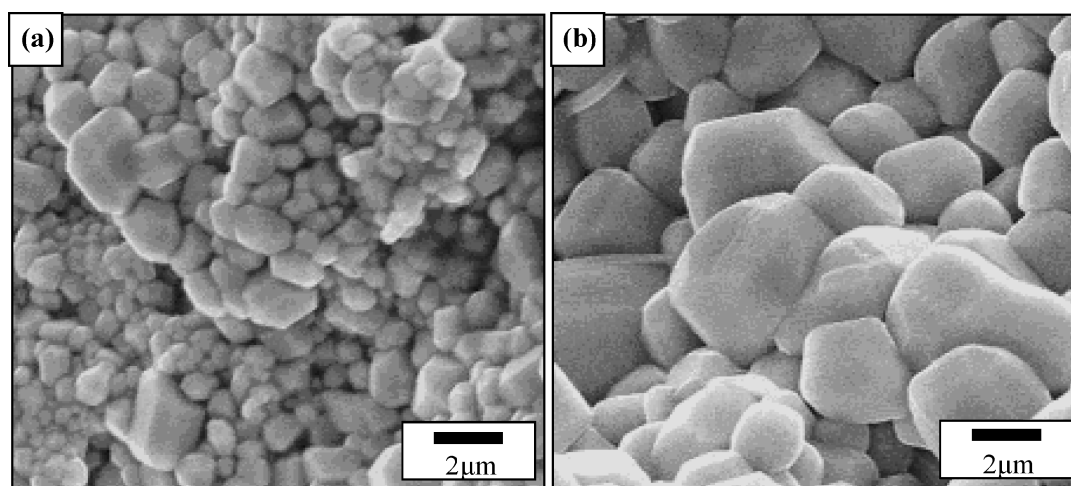


Figure 4. SEM micrographs of multi-function ceramics made by: (a) the sol-gel method; (b) the conventional solid-state reaction method.

material acts as a conductor, and the electrical properties are determined by the semi-conducting nature of the donor-doped ( $\text{La}^{3+}$ ,  $\text{Nb}^{5+}$ ) core, which exhibits predominantly varistor characteristics. Figure 4 compares the SEM micrographs of multifunction ceramics made by the sol-gel (Fig. 4(a)) and conventional solid-state method (Fig. 4(b)). It is clear that the grains in the sol-gel-derived material have a more uniform grain structure, with smaller grains than those prepared by the conventional solid-state method, thus yielding a more effective core-shell structure. In particular, due to the fine grains and relatively short diffusion distance in the sol-gel materials, better semi-conducting properties can be obtained. In addition, because both materials have the same acceptor content, the finer grains lead to more effective insulating layer, which encapsulates the semi-conducting core. Therefore, a more effective core-shell structure is obtained, resulting in better capacitor-varistor properties.

#### 4. Conclusions

$\text{SrTiO}_3$  powders were prepared by a sol-gel method. Compared with the properties of ceramics made by a

conventional solid-state method, the  $\text{SrTiO}_3$ -based ceramics prepared by sol-gel processing show enhanced capacitor-varistor properties. These enhanced properties are attributed to the smaller, more uniform grain structure obtained in the sol-gel-derived material, which promotes the formation of an effective core-shell structure.

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