

Dielectric properties of strontium titanate synthesized by means of solid state reactions activated mechanically

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In this work, strontium titanate samples were prepared starting from SrCO₃ and TiO₂ powders mixture. Raw materials were activated mechanically in a planetary mill and then calcined at different temperatures (900 to 1300 °C). Powders after grinding were analyzed by differential thermal analysis in order to follow the carbonate decomposition. On the other hand, samples resulting from heat treatment were characterized by XRD, SEM and electrical measurements. XRD analysis determines that SrTiO₃ synthesized presents the cubic structure of perovskite. Complete reaction for SrTiO₃ compound formation occurs at 1200 °C. SEM observations indicate the presence of a microstructure with very small grain size and consequently a large number of grain boundaries. Electrical measurements suggest the formation of a material with high insulating capacity. With this evidence, it can be concluded that solid state reactions activated mechanically, proved to be an effective way to fabricate strontium titanate compound with very fine microstructure and high insulating behavior.

Key words: SrTiO₃ compound, Dielectric constant, Solid state reactions, Mechanical activation.

Introduction

Strontium titanate (SrTiO₃) is an advanced ceramic material that has attracted great interest in the field of electroceramics due to their unique physico-chemical properties. At room temperature SrTiO₃ exists in the cubic perovskite structure. It is considered a ferroelectric oxide because it has an excellent high nonlinear optical properties, high dielectric constant, and presents photocatalysis [1]. In addition, it presents good mechanical strength, low coefficient of thermal expansion, high melting temperature and also has extraordinary thermal and chemical stability [2-3]. Due to all these unique properties this ceramic compound has been proposed to use for a wide array variety of applications such as: thermistors, multilayer capacitors, electro-optical appliances, electromechanical devices, dynamic random-access memory and field-effect transistors [4-9]. It is well knowing, that their properties are strongly affected by its microstructure and consequently by the method of synthesis.

Usually, the SrTiO₃ compound is synthesized by solid state reactions from solid precursors (SrCO₃ y TiO₂), at high temperatures and extensive sintering times; conditions that can affect considerably the microstructure and therefore electrical properties of the final compound

[10-11]. There are other methods to prepare the SrTiO₃, among which are; sol-gel technique [12-14], hydrothermal process [15-16], precipitation routes [17-18], microwave plasma [19] and combustion methods [20-22]. Nevertheless, these methods are very expensive, owing to the high costs of precursor agents, together with the complexity of the experimental methods, which makes them fewer productive procedures.

The aim of this study is to manufacture the SrTiO₃ compound, using techniques such as; mechanical activation and heat treatment of the precursor powders at different temperatures and short times that result in compounds with fine and homogeneous microstructures, which will be correlated with their electrical properties.

Methodology

Strontium titanate compound were prepared from SrCO₃ and TiO₂ (both from Sigma-Aldrich, 99.9% of purity and 1 mm particle size) by solid state reaction under different conditions. A stoichiometric amount of the two precursors in agreement with reaction 1 were weighed and transfer to a stainless steel container and was activated mechanically with the help of a ball mill planetary type (Retsch PM 100, Germany). Mechanical activation conditions were: 3 hrs at 300 rpm, the weight ratio between powder and spherical zirconia, grinding elements of 0.3 cm diameter was of 1 : 12. The particle size distribution and specific superficial area of the obtained powders were determined by using a Mastersizer 2000, England equipment. The microstructure

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of sintered samples was analyzed by scanning electron microscopy (JEOL, JSM 6300, Japan). The powders mixtures resulting from the mechanical activation step were subjected to heat treatment at different temperatures 1000, 1100, 1200 and 1300 °C during 2 hours. This heating was looking for the occurrence of chemical reaction 1. Heat treatment was carried out in an electric resistances furnace (Carbolite RHF17/3E, England). Chemical reaction advance was followed by differential thermal analysis and thermogravimetric analysis (TA Instrument SDT Q600 V20.9, USA). In addition to, X-ray diffraction analysis (Siemens, D-5000, Germany). Furthermore, the obtained compound was characterized by electrical measurements.



Results and Discussion

Powder size

The results of the particle size distribution are reported in Fig. 1. This figure shows two y axes, the first one (right) correspond to the percentage of cumulative volume for the SrCO₃-TiO₂ powder blend after the milling period, in where it is observed that approximately 41% of the powders have particle sizes under 10 micron; about 30% of particles present 10 to 50 microns in size and the remaining 29% of powders have sizes larger than 50 microns; these big sizes probable are due to the agglomeration of very small powders. In order to observe better the size distribution of the powders, in the same figure are presented in bars form the percentage of volume concentration per size range. The specific surface area measured in the powder blend was 17.6 m² · g⁻¹ with this value, it is expected to have sufficient area of contact between the reactants (SrCO₃ and TiO₂) to be effective the formation of SrTiO₃ in agreement with Reaction 1.

Thermal analysis

Fig. 2 shows the DTA and TGA curves for reaction (1). In the TGA curve a small loss in weight is

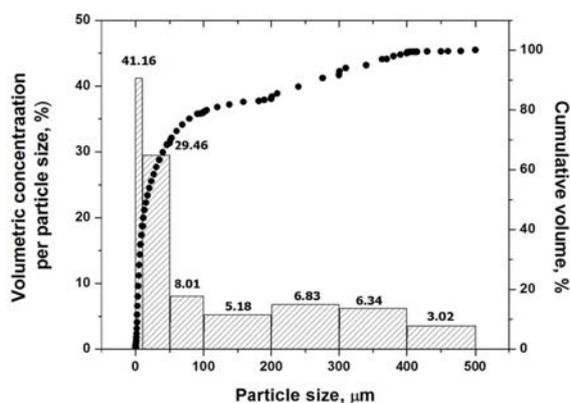


Fig. 1. Particle size distribution after mechanical activation stage

observed from room temperature to about 600 °C which is associated with the evaporation of humidity, subsequently from 600 °C the loss in weight converts considerable, finished the weight loss of the sample up to 900 °C, this loss in weight is associated with SrCO₃ decomposition in SrO and CO₂ with the consequent release of CO₂.

The total weight loss for a temperature range of 25-900 °C in the TGA curve is about 20% this weight loss can be due to the evaporation of adsorbed moisture by the sample and the CO₂ release thru SrCO₃ decomposition. In the DTA curve it is observed a phenomenon between 550 and 950 °C, this behavior can be associated with the formation of strontium oxide and a phase transformation of the TiO₂ rutile to another metastable phase of TiO₂ such as has been discussed in the literature [23].

According to thermodynamic data the formation of SrTiO₃ must occur at 1150°C, this temperature of SrTiO₃ formation is determined using Equations 2 and 3. The value of E employed in equation 2 was obtained from the reference [24].

$$K = e^{-E/RT} \quad (2)$$

$$\Delta G_{\text{reaction}} = -RTL \ln K \quad (3)$$

Where: K is the reaction constant (1), E is the activation energy of Reaction 1 (222 KJ·mol⁻¹, in this case), T is the temperature in Kelvin, R is the universal constant of gases (8.3143 J·K⁻¹·mol⁻¹) and ΔG is the free energy of Gibbs of reaction 1 (KJ·mol⁻¹).

Due the DTA and TGA analysis were done until 1100 °C it is not possible to observe it in this type of analysis the formation of SrTiO₃. However, at 900 °C, both SrO and TiO₂ compounds are already existing and will react at higher temperatures to form the desired SrTiO₃ ceramic.

X-ray diffraction

Fig. 3 shows the XRD pattern of the as prepared material treated at different temperatures. The diffraction

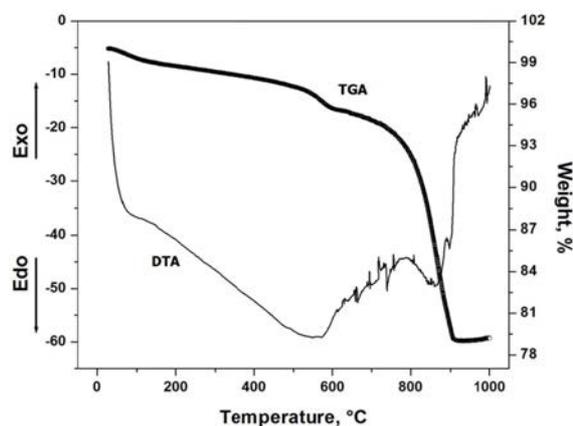


Fig. 2. DTA-TGA curves of as-prepared SrTiO₃ powder.

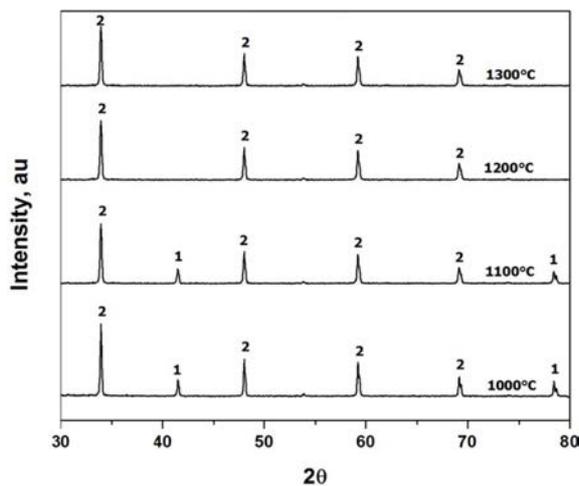


Fig. 3. DRX patterns of activated powders heat treated at different temperatures. 1: SrCO₃, 2: SrTiO₃.

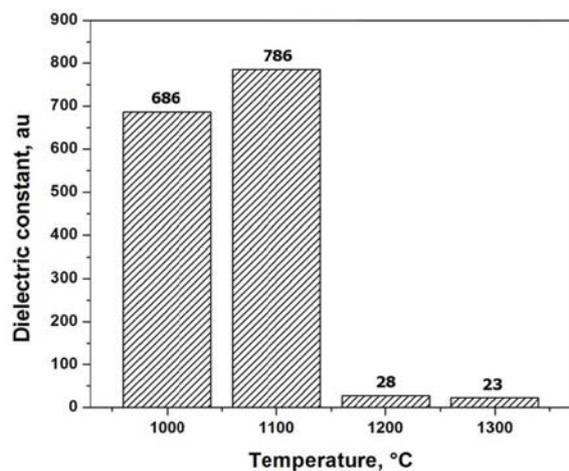


Fig. 4. Microstructure and EDS analysis realized in the SrTiO₃ obtained.

peaks nearly to 2θ of 41° and 78° is associated with the (220) and (420) plane of orthorhombic structure of stromianite compound (JCPDS 84-1778) [25-26]. Meanwhile, the other four diffraction peaks are characteristic of cubic crystalline SrTiO₃, with planes (110) (200) (211) (220) that were well indexed with the standard JCPDS 35-0734 data. The lattice constant calculated from the XRD data for SrTiO₃ has been 3.901 \AA . In the figure it is observed that as the temperature increases, the corresponding peaks to SrCO₃ decrease in intensity, while the intensity of SrTiO₃ perovskite peaks increases. The original SrCO₃ and TiO₂ reactants are not observed above 1200 °C. From these results and in agreement with thermodynamically calculus, Reaction 1 for the formation of SrCO₃ perovskite has been complete at 1200 °C.

Microstructure

Fig. 4 shows a micrograph of the sample thermal treated at 1200 °C during 2 hrs. In this figure there is

Table 1. Estimated conductivity, resistivity and dielectric constant in synthesized SrTiO₃ perovskite.

Synthesis temperature	Electric conductivity	Electric resistivity	Dielectric constant
1000 °C	$3.18 \times 10^{-11} \text{ Sm}^{-1}$	$3.14 \times 10^{10} \text{ } \Omega\text{m}$	686
1100 °C	$4.23 \times 10^{-11} \text{ Sm}^{-1}$	$2.36 \times 10^{10} \text{ } \Omega\text{m}$	786
1200 °C	$3.17 \times 10^{-11} \text{ Sm}^{-1}$	$3.15 \times 10^{10} \text{ } \Omega\text{m}$	28
1300 °C	$3.16 \times 10^{-11} \text{ Sm}^{-1}$	$3.16 \times 10^{10} \text{ } \Omega\text{m}$	23

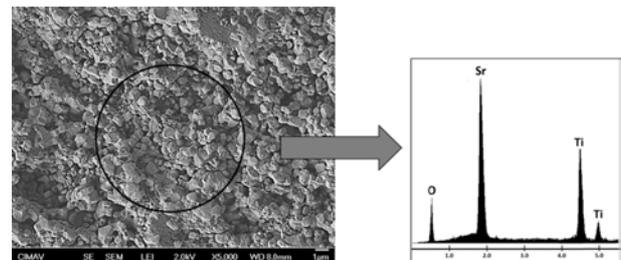


Fig. 5. Dielectric constant of the synthesized compounds.

observed small grains size distribution with polymorphic shapes. As can be seen (Fig. 4) the grain size is less than 1 micron, that causes the formation of a large number of grain boundaries, situation that may favor the obtaining of low values of resistivity in this compound. In this figure there is marked a zone with a circle in which it was performed an analysis by energy dispersive spectroscopy (EDS) with the aim to determine the elements present in the sample. In the EDS spectrum it is observed the presence of Sr, Ti and O chemical elements corresponding to the SrTiO₃ perovskite.

Electrical properties

Electrical properties such as; resistivity, conductivity and dielectric constant of the thermal treated samples are listed in Table 1. In all cases the values of resistivity are higher than $1 \times 10^{10} \text{ } \Omega\text{m}$; this means that the respective obtained compound is within what it is considered as an insulating material. On the other hand, with respect to the measurements of the dielectric constant, in Table 1 and in Fig. 5, it is observed a very interesting behavior, because the samples treated at 1100 and 1200 °C present a very high dielectric constant. However, samples treated at 1200 and 1300 °C present a very small dielectric constant. This situation can be explained as follows: in samples treated at 1000 and 1100 °C there is no complete reaction for the formation of the desired SrTiO₃ compound, existing secondary phases such as SrO and TiO₂ that make it very difficult for the electricity to pass through them. In contrast, in agreement with thermodynamic calculus and X-ray results at 1200 and 1300 °C Reaction 1 was completed, in this sense the final compounds have the chemical composition of the SrTiO₃ perovskite, presenting the characteristics of a semiconductor, for this reason the dielectric constant of the latter compounds own very low values.

Conclusions

After promoting solid state reactions by means of mechanical activation and treating at different temperatures mixtures of SrCO₃ y TiO₂, they were obtained two compounds with different electrical characteristics. The first of which was obtained by heating at 1000 or 1100 °C the original powder mixture, presents the characteristics of a strongly insulating material which is constituted by SrTiO₃ and traces of secondary phases of SrO and TiO₂. The other material with the chemical composition and cubic crystalline structure of the SrTiO₃ perovskite was obtained by heating the original powder mixture at 1200 or 1300 °C, these materials have semi conductive characteristics due to their very low dielectric constants. In all cases the action of the external forces during the mechanical activation of the powders, generate large volumes of particles smaller than 1 micron, responsible situation together with the treatment temperature of the electrical behavior presented by the materials manufactured here.

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