

# Scandium doped Strontium Titanate Ceramics: Structure, Microstructure, and Dielectric Properties

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Sc-doped strontium titanate (ST) ceramics were synthesised by solid state reaction, according to the composition  $\text{Sr}_{1-1.5x}\text{Sc}_x\text{TiO}_3$  with  $x = 0-0.01$ . Structural properties and microstructure development was examined by XRD and SEM. The dielectric properties were evaluated as a function of the temperature and frequency in the radio frequency range. Lattice parameter, density and grain size, were found to decrease slightly with increasing Sc content. The dielectric permittivity and losses decrease also. Sc-doping has only a weak effect on the quantum paraelectric behaviour of ST and no dielectric anomaly was observed, what is probably related to the limited solubility of Sc on the Sr site of the perovskite lattice of ST.

**Keywords:** Dopants, Microstructure, Electric/Dielectric properties, Insulators, Strontium Titanate, Ceramics.

## Materiales de titanato de estroncio dopados con escandio: estructura, microestructura y propiedades dieléctricas

Se sintetizaron materiales cerámicos de titanato de estroncio dopado con escandio mediante reacción en estado sólido De acuerdo a la composición  $\text{Sr}_{1-1.5x}\text{Sc}_x\text{TiO}_3$  con  $x = 0-0.1$ . Las propiedades estructurales y el desarrollo microestructural se estudiaron mediante XRD y SEM. La propiedades dieléctricas se estudiaron como función de la temperatura y de la frecuencia en el rango de la frecuencias de radio. Se observó que los parámetros de red, la densidad y el tamaño del grano disminuyen ligeramente con el contenido en Sc. La permitividad dieléctrica y las perdidas también disminuyen. El dopado con Sc tiene un efecto muy ligero sobre el comportamiento paraeléctrico cuántico del titanato de estroncio y no se observó anomalías dioeléctricas, lo que está probablemente relacionado con la baja solubilidad del Sc en posiciones del Sr en la estructura tipo perovskita del titanato de estroncio.

**Palabras clave:** dopantes, microestructura, propiedades eléctricas-dieléctricas, aislantes, titanato de estroncio, cerámica.

## 1. INTRODUCTION

Strontium titanate, as a material with a high dielectric constant  $\epsilon'$  and low loss tangent  $\tan\delta$ , is of interest for a wide range of applications, particularly in electronic devices.  $\text{SrTiO}_3$  (ST) is a incipient ferroelectric in which the ferroelectricity is suppressed by the quantum fluctuations and due to that the dielectric constant of ST increases continuously at cooling towards 0 K (1). Trivalent rare-earth ions, such as  $\text{La}^{3+}$  substituting divalent Sr in the perovskite lattice of ST are well known to induce a non-polar dielectric relaxation around room temperature (2). This relaxation seems to be related to oxygen vacancies and therefore might be suppressed by heat treatments in  $\text{O}_2$  flow (3). However, substitution of  $\text{Sr}^{2+}$  by  $\text{Bi}^{3+}$  can induce a low-temperature polar anomaly of relaxor type (4), related to the off-central displacements of  $\text{Bi}^{3+}$  lone-pair ions on Sr sites. Off-central displacements of  $\text{Sc}^{3+}$  ions on Sr sites and related polar dielectric relaxation are also possible, being caused not by the lone-pair nature of the dopant ions but by the its small ionic size. Such type of relaxation was also observed when small  $\text{Ca}^{2+}$  and  $\text{Mn}^{2+}$  ions substituted for  $\text{Sr}^{2+}$  in ST lattice (5, 6). Though, to the authors' best knowledge there are no studies reporting the role of  $\text{Sc}^{3+}$  on Sr sites on the dielectric response as well as on the microstructure of ST ceramics.

In this work, the systematic study of the effect of scandium on the crystallographic structure, microstructure and dielectric behaviour of ST ceramics with different Sc content is presented. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis are used for the crystallographic and microstructure characterisation. Dielectric properties of nonstoichiometric ST ceramics are evaluated as a function of temperature and frequency in the radio frequency range.

## 2. EXPERIMENTAL PROCEDURE

Ceramic samples were prepared by conventional mixed oxide method. Reagent grade  $\text{SrCO}_3$  (Merck),  $\text{TiO}_2$  (Merck), and  $\text{Sc}_2\text{O}_3$  (Aldrich) were weighed according to the compositions  $\text{Sr}_{0.9925}\text{Sc}_{0.005}\text{TiO}_3$  and  $\text{Sr}_{0.9850}\text{Sc}_{0.010}\text{TiO}_3$ . In this case, strontium vacancies are introduced as charge compensation. After ball milling in alcohol for 5 h using teflon pots and zirconia balls in a planetary mill, the powders were dried, and then calcined at 1150 °C for 2 h. The calcined powders were milled again for 5 h to obtain powders with particle size lower than 5  $\mu\text{m}$ . Pellets of 10 mm in diameter were uniaxially pressed at 100

MPa and then isostatically pressed at 200 MPa. Sintering was performed in air at 1500 °C for 5 h.

Densities of the sintered samples were measured by the Archimedes' method using diethylphthalat as the immersion liquid. Room temperature x-ray diffraction (XRD) analysis (Rigaku D/Max-B, Cu K $\alpha$ ) was conducted on grounded sintered samples, between 20 and 108 ° (2 $\theta$ ) and the scanning rate was 1 °/min with a sampling step of 0.02 °. The lattice parameter was calculated by a least-square-approach fitting of the XRD data using Rietveld refinement WinPLOTR software. The microstructure of the ceramics was observed on polished and thermally etched sections using SEM/EDS (Hitachi S-4100). For the dielectric measurements, sintered samples were polished and gold electrodes were sputtered on both sides. The dielectric permittivity and losses were measured at different frequencies between 100 Hz and 1 MHz, using Precision LCR Meter HP 4284A and a Displex APD-Cryogenics cryostat of He closed cycle during heating at a rate of 0.75 K/min in the temperature range of 10 to 300 K.

### 3. RESULTS AND DISCUSSION

XRD profiles of the sintered  $\text{Sr}_{1-1.5x}\text{Sc}_x\text{TiO}_3$  samples, shown in Figure 1, are consistent with the cubic crystallographic structure of undoped ST. Traces of the  $\text{TiO}_2$  phase are detectable for the  $x = 0.01$  composition. The appearance or segregation of  $\text{TiO}_2$  as a second phase might be caused by the partial occupation of Ti sites by  $\text{Sc}^{3+}$  ions. However, as obtained from

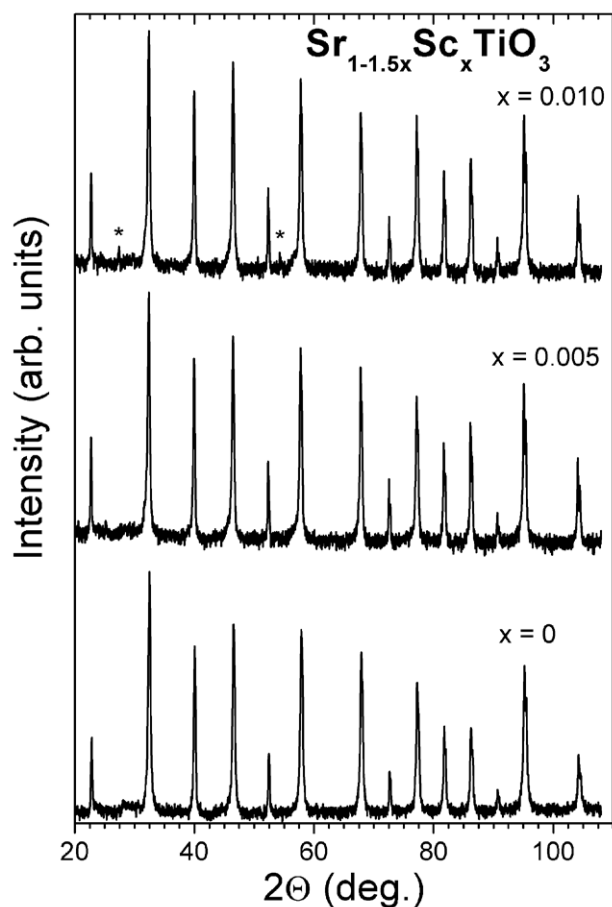


Fig. 1- XRD patterns of sintered  $\text{SrTiO}_3$ ,  $\text{Sr}_{0.9925}\text{Sc}_{0.005}\text{TiO}_3$ , and  $\text{Sr}_{0.9850}\text{Sc}_{0.010}\text{TiO}_3$ .  $\text{TiO}_2$  second phase is marked by \*.

TABLE I. RELATIVE DENSITY, LATTICE PARAMETER AND AVERAGE GRAIN SIZE OF  $\text{SrTiO}_3$ ,  $\text{Sr}_{0.9925}\text{Sc}_{0.005}\text{TiO}_3$ , AND  $\text{Sr}_{0.9850}\text{Sc}_{0.010}\text{TiO}_3$  CERAMICS SINTERED AT 1500 °C FOR 5 H.

Composition	Lattice parameter, Å	Average grain size, $\mu\text{m}$	Density, %
$\text{SrTiO}_3$	3.9063(1)	~29.0	~97
$\text{Sr}_{0.9925}\text{Sc}_{0.005}\text{TiO}_3$	3.9056(1)	~28.8	~96
$\text{Sr}_{0.9850}\text{Sc}_{0.010}\text{TiO}_3$	3.9051(1)	~22.2	~95

the Rietveld refinement of XRD profiles and depicted in Table 1, the lattice parameter decreases slightly with increasing Sc content what can be related to the partial occupation by  $\text{Sc}^{3+}$  ions of Sr sites, taking into account the ionic size considerations. For the coordination number 6, characteristic for Ti site of ST, the ionic radius of  $\text{Sc}^{3+}$  is 0.745 Å, higher than 0.605 Å of  $\text{Ti}^{4+}$  (7) and their ratio is  $0.745/0.605 = 1.23$ . On the other hand, for the coordination number 12, characteristic for Sr site of ST, the ratio between the ionic radii of  $\text{Sr}^{2+}$  and  $\text{Sc}^{3+}$  is estimated as  $1.44/1.12 = 1.29$  (7). Thus, both ratios are quite far from the unity, pointing to the difficult incorporation of Sc on either Sr or Ti sites of the ST lattice. So it is very probable that both sites will be occupied by  $\text{Sc}^{3+}$  ions in order to compensate the stresses induced in the ST lattice by doping, if the atomic substitution occurs.

The SEM micrographs of Sc-doped ST ceramics sintered

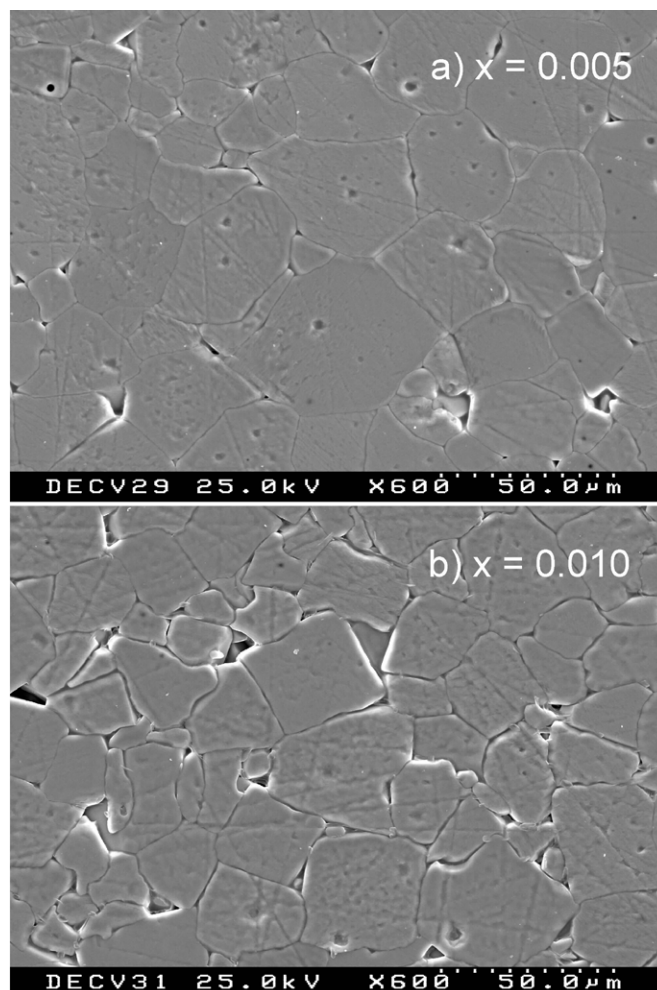


Fig. 2- SEM micrographs of a)  $\text{Sr}_{0.9925}\text{Sc}_{0.005}\text{TiO}_3$  and b)  $\text{Sr}_{0.9850}\text{Sc}_{0.010}\text{TiO}_3$  ceramics.

at 1500 °C for 5 h, shown in Figure 2, reveal larger grain size and denser microstructure for  $x = 0.005$ , compared to those of  $x = 0.01$  composition. The values of the average grain size and sample densities are also shown in Table 1. A slight decrease in the grain size and density with increasing Sc content might be related with the segregation of  $\text{TiO}_2$ .

The dielectric response of  $\text{Sr}_{1-1.5x}\text{Sc}_x\text{TiO}_3$  ceramics with  $x = 0-0.01$  is shown in Figure 3 (a,b). The temperature dependence of dielectric constant in the frequency range of  $10^2 - 10^6$  Hz is present in Figure 3a. The steep increase of the dielectric permittivity and its levelling-off at high values as the temperature approaches 0 K without any dielectric permittivity anomaly observed for undoped ST are typical for quantum paraelectrics (1). No considerable frequency dispersion was found. The dielectric constant at low temperatures decreases continuously with increasing Sc concentration. Figure 3b shows the temperature dependence of the dielectric loss at 10 kHz for undoped and Sc-doped ST ceramics. The loss of all the samples under study are characterised by a strong peak at 70 - 105 K in the frequency range  $10^2 - 10^6$  Hz. A similar peak was observed in nominally pure ST single crystals and was attributed to the slowing down of polar modes of unavoidable defects within ferroelastic domain walls (8,9). Sc doping induces only a small additional peak at low temperatures. Its temperature increases with Sc content and its origin can be related with the off-centre displacement of  $\text{Sc}^{3+}$  ions on the Sr sites by analogy with  $\text{Bi}^{3+}$ . However, the very small value of the loss peak and absence of the corresponding peak in the temperature dependence of the dielectric constant questioned this hypothesis. On the other hand,  $\tan\delta$  is progressively

decreasing with increasing Sc content.

The observed dielectric behaviour is similar to that of  $\text{Sr}_{1-x}\text{Mg}_x\text{TiO}_3$  system in which the solubility of Mg in ST, when occupying the large Sr sites with twelve fold coordination, was observed to be very limited ( $x < 0.01$ ), due to the small size of Mg ions (10,11). Hence the expected polar dielectric relaxation, due to the off-centre displacement of ions smaller than  $\text{Sr}^{2+}$  in a multi-well local potential, could not be observed. The dopant ionic size, smaller than that of  $\text{Sr}^{2+}$ , is a theoretical requirement for the aforementioned dielectric relaxation mechanism. However, as seen from this work and from Refs. 10,11, there is also a practical structural requirement that should be taken into account and that limits the number of doped ST systems in which polar dielectric relaxation takes place: the dopant ions have to be sufficiently large in order to keep the stability of the perovskite structure of the host ST lattice. Thus,  $\text{Sr}_{1-1.5x}\text{Sc}_x\text{TiO}_3$  as well as  $\text{Sr}_{1-x}\text{Mg}_x\text{TiO}_3$  systems do not fill this last requirement, whereas polar dielectric relaxations were found for dopants with larger ionic size than the previously mentioned, e.g., in  $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$  (5) and  $\text{Sr}_{1-x}\text{Mn}_x\text{TiO}_3$  systems for small  $x$  values (6).

#### 4. CONCLUSIONS

The structure, microstructure and dielectric response of  $\text{Sr}_{1-1.5x}\text{Sc}_x\text{TiO}_3$  ( $x = 0-0.01$ ) ceramics prepared by conventional mixed oxide method was studied. A slight decrease of the lattice parameter confirms the occupation of Sr sites by part of  $\text{Sc}^{3+}$  ions, whereas  $\text{TiO}_2$  second phase, detected for  $x = 0.01$ , suggests the partial occupation of Ti sites by  $\text{Sc}^{3+}$  ions. Accordingly, the ceramic density, grain size, dielectric permittivity and loss were found to decrease continuously with increasing Sc content. Thus, Sc doping induces no dielectric anomaly in ST and has only a weak effect on its quantum paraelectric behaviour due to low solubility limit on Sr site of  $\sim 0.005$ , caused by the very small ionic size of  $\text{Sc}^{3+}$  compared with  $\text{Sr}^{2+}$ .

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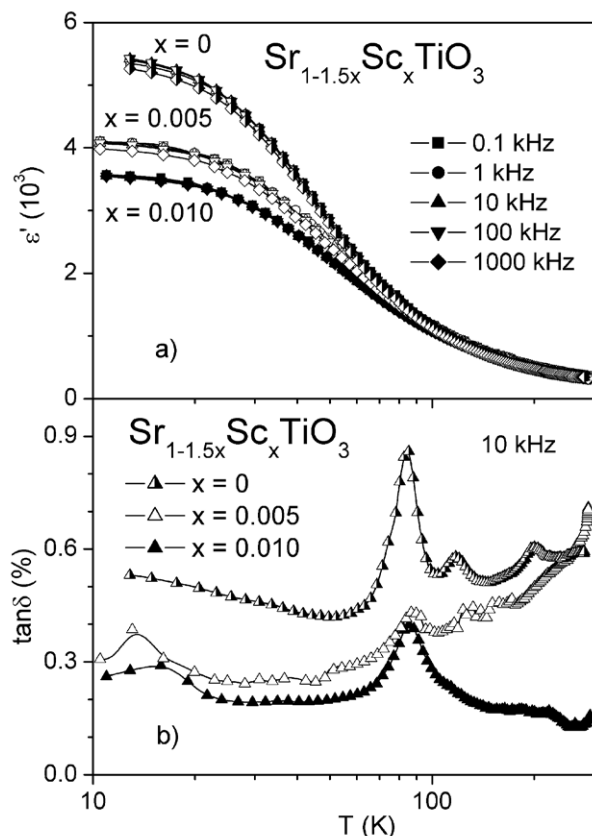


Fig. 3- Temperature dependence of a) the dielectric constant  $\epsilon'$  at different frequencies and b) the loss  $\tan\delta$  at 10 kHz of  $\text{SrTiO}_3$  (semi-open symbols),  $\text{Sr}_{0.9925}\text{Sc}_{0.005}\text{TiO}_3$  (open symbols), and  $\text{Sr}_{0.9850}\text{Sc}_{0.010}\text{TiO}_3$  (solid symbols) ceramics.

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