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Effect of nonstoichiometry on the microstructure and dielectric properties of strontium titanate ceramics

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Abstract

Nonstoichiometric strontium titanate (ST) ceramics with precisely controlled Sr/Ti ratio of 0.997–1.02 were synthesised by solid state reaction. Structural properties and microstructure development was examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The dielectric properties were evaluated as a function of the temperature and frequency in the radio frequency range. The grain size was found to decrease dramatically with increasing Sr/Ti ratio > 1. The variation of Sr/Ti ratio has only weak effect on the quantum paraelectric behaviour of ST without any dielectric anomaly observed. The TiO_2 excess promotes the increase of the dielectric permittivity values with loss factor similar to stoichiometric ST. $Sr_{1.01}TiO_{3.01}$ composition exhibits much lower loss, while the dielectric permittivity is somewhat below the values for stoichiometric ST ceramics.

Keywords: Electron microscopy; Dielectric properties; $SrTiO_3$; Capacitors

1. Introduction

With the increasing demand of oxide ferroelectrics, paraelectric $SrTiO_3$ (ST) and $(Ba,Sr)TiO_3$ are most promising capacitor materials, because of their high dielectric constant and thermal stability. ST is a quantum paraelectric, where the ferroelectric fluctuations are suppressed by the quantum fluctuations of the atomic positions.[1] It is known that the polar state in ST can be induced via: electric field,[2] uniaxial stress,[3] cation[4] or oxygen isotope substitutions in the lattice.[5] However the role of Sr/Ti ratio on the dielectric response as well as on the grain growth of undoped ST is not definite. Moreover, the dependence of the quantum behaviour on the grain size of undoped ST materials is not clearly established, too. The optimisation of the dielectric response is closely related to the precise control of the composition (stoichiometry). While there are several studies on the defect chemistry of BT, to the best our knowledge, not so systematic studies have been dedicated to the nonstoichiometry of ST.

In the case of ST bulk materials, the research studies have been performed on the relationship between nonstoichiometry and electrical conductivity largely by Eror and co-workers[6] and Smyth and co-workers.[7] In spite of some contradictions on the effect of TiO_2 excess on the conductivity, tentatively related to processing procedure and impurities in raw materials, it was reported that ST with TiO_2 excess down to 0.5 mol% shows the presence of Ti-rich second phase.[7] On the other hand, SrO excess is fully accommodated in the epitaxial perovskite lattice as a three-dimensional mosaic of single-layered rock-salt blocks, forming the so-called Ruddlesden–Popper (RP) structure, without forming secondary phases related to the SrO excess.[7]

The relationship between nonstoichiometry and dielectric properties is poorly characterized in ST ceramics. However, there are several reports on the study of stoichiometric effects on ST thin films fabricated by different deposition methods,[8–10] showing ambiguous results. ST film with slightly Ti-rich composition prepared by metal organic chemical vapour deposition (MOCVD) was reported to have a higher dielectric permittivity then stoichiometric film.[8] Maximum permittivity was also obtained for epitaxial ST film with Sr/Ti = 0.91 grown by an ArF excimer laser ablation

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(PLD) method.[9] On the other hand, Tsuzuki et al.[10] reported that the maximum dielectric constant occurs at the composition of Sr/Ti = 1.04 in polycrystalline strontium titanate films fabricated by the sol–gel method.

The raised questions justify the interest in the studies on nonstoichiometry of ST ceramics. In this work, preliminary results on the effect of nonstoichiometry on the crystallographic structure, microstructure and dielectric behaviour of ST ceramics with different Sr/Ti ratio are 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 grades $SrCO_3$ and TiO_2 were weighed according to the compositions $Sr_{0.997}TiO_{2.997}$, $Sr_{0.999}TiO_{2.999}$, $SrTiO_3$, $Sr_{1.01}TiO_{3.01}$, and $Sr_{1.02}TiO_{3.02}$. After ball milling in alcohol for 8 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 8 h to obtain powders with particle size lower than 5 μm. 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.

Room temperature XRD analysis (Rigaku D/Max-B, Cu Kα) was conducted on some of the grounded sintered samples with a scanning speed of 1°/min and a step of 0.02°. Lattice parameters were refined by the least square fitting to the observed XRD data, between $2\Theta = 20°$ and 106°. The microstructure of 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 density measured by Archimedes's method for all of the samples was about of 97%. 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 10–300 K.

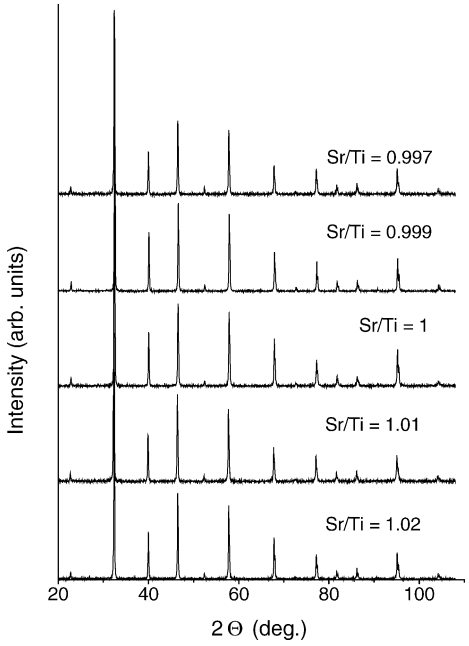

Fig. 1. XRD patterns of sintered nonstoichiometric ST ceramics.

3. Results and discussion

XRD patterns of the sintered samples are shown in Fig. 1. A cubic symmetry and absence of second phases were detected by XRD analysis for all compositions under study. No systematic variation of the lattice parameter was observed.

The SEM micrographs of nonstoichiometric ST ceramics sintered at 1500 °C for 5 h, shown in Fig. 2, reveal rather dense microstructures for all the samples, and huge difference in the grain size for Ti-rich and Sr-rich composition. The average grain size of ST ceramics with $Sr/Ti \leq 1$ was found to be in the range of tens of microns, whereas $Sr/Ti > 1$ yields ceramics with the grain size in the micron range (Table 1).

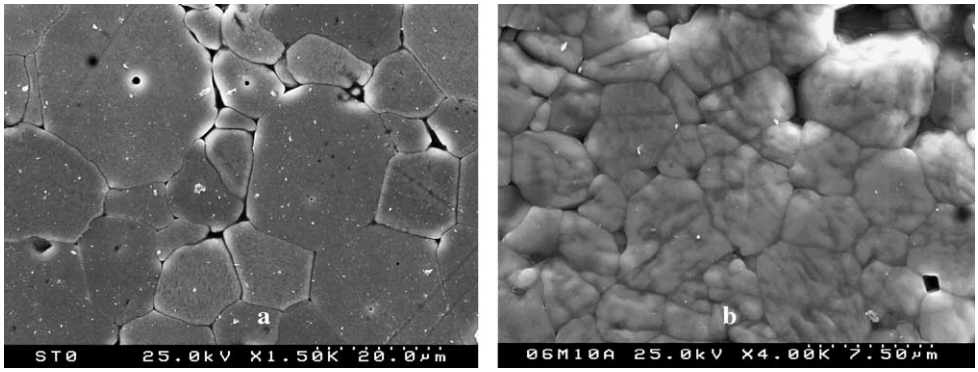

Fig. 2. SEM micrograph of: (a) $Sr_{0.997}TiO_{2.997}$ and (b) $Sr_{1.02}TiO_{3.02}$ ceramics, sintered at 1500 °C for 5 h.

Table 1
Parameters of ST samples with different Sr/Ti ratio, sintered at 1500 °C for 5 h.

Sr/Ti ratio	Average grain size (μm)	Barrett relation parameters		
		T_0 (K)	T_1 (K)	$C/10^3$ (K)
0.997	20	34	98	112
0.999	14	36	103	95
1	20	35	99	92
1.01	5	34	102	97
1.02	6	32	110	87

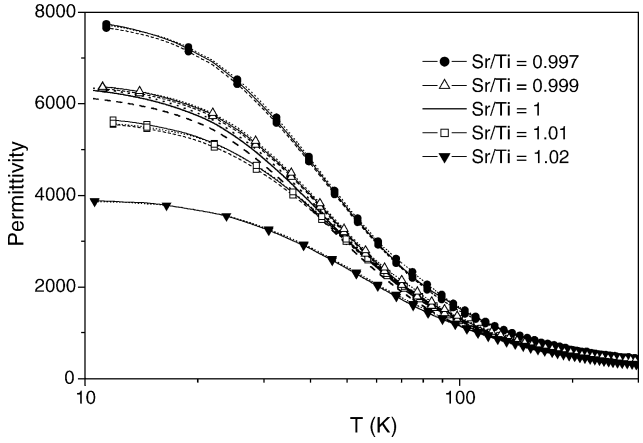

Fig. 3. Temperature dependence of the dielectric permittivity of $Sr_{0.997}TiO_{2.997}$, $Sr_{0.999}TiO_{2.999}$, $SrTiO_3$, $Sr_{1.01}TiO_{3.01}$ and $Sr_{1.02}TiO_{3.02}$ ceramics at 10^2, 10^4 and 10^6 Hz (dot, solid and dash lines, respectively).

The low-frequency dielectric measurements data are summarised in Figs. 3 and 4. The temperature dependence of dielectric permittivity for stoichiometric and nonstoichiometric ST in the frequency range 10^2–10^6 Hz is shown in Fig. 3. 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. A similar behaviour without dielectric anomalies is seen for nonstoichiometric compositions. SrO excess lowers the dielectric permittivity values at low temperatures, while TiO_2 excess raises it monotonously in range of Sr/Ti ratio under study. Thus, our results confirm the results reported for the films, obtained by MOCVD[8] and PLD,[9] but contradict to those for the films, deposited by sol–gel method.[10]

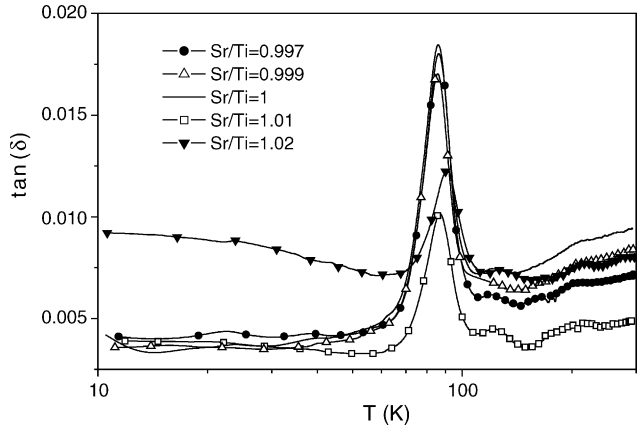

Fig. 4. Temperature dependence of tan δ of $Sr_{0.997}TiO_{2.997}$, $Sr_{0.999}TiO_{2.999}$, $SrTiO_3$, $Sr_{1.01}TiO_{3.01}$ and $Sr_{1.02}TiO_{3.02}$ ceramics at 10^4 Hz.

It is well known that the paraelectric state of pure $SrTiO_3$ can be described by Barrett's relation,[11] which is based on the mean-field theory taking quantum fluctuations into account: $\varepsilon_r = C/[(T_1/2)\coth(T_1/2T) - T_0]$, where C is the Curie–Weiss constant, T_1 is the temperature of the crossover between classical and quantum behaviour, and T_0 is the transition temperature at which the lattice instability would occur in the absence of quantum fluctuations. The fitted parameters of the experimental data to the Barrett's relation are indicated in Table 1. The series of parameters C and T_1 agree well with those reported for a nominally pure ST single crystal.[1] Nonstoichiometry does not tend to change the transition temperature T_0.

Fig. 4 shows the temperature dependence of the dielectric loss at 10 kHz for stoichiometric and nonstoichiometric ST ceramics. The loss of stoichiometric ST, which almost coincides with $Sr_{0.999}TiO_{2.999}$, are characterised by a strong peak at 70–105 K for 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 at unavoidable defects within ferroelastic domain walls.[12,13] TiO_2 excess has very weak effect on dielectric loss behaviour of ST. On the other hand, composition with Sr/Ti = 1.01 shows lower dielectric loss at all temperatures with the concomitant suppression of loss peak.

As previously mentioned, the excess of Sr in the ST lattice fully accommodates in the perovskite lattice forming the Ruddlesden–Popper structure and allowing the SrO excess in the ST lattice in the form of interlayers. The presence of such interlayers, which are expected to be less polarisable than the perovskite lattice, seems to contribute to the decrease of the dielectric permittivity and dielectric loss of Sr-rich ST samples observed in the present work. This is in line with the work on RP phases in ST.[14] The reduction of the grain size in these compositions is another factor that can also contribute to such a decrease.

The increase of polarisability of Ti-rich ST samples can be related to the formation of charged strontium and oxygen vacancies, which could result in the appearance of dipole pairs, however further studies are required to clarify this question.

4. Conclusions

The effect of Sr/Ti ratio (1.02–0.997) on the grain size and dielectric response was analysed in ST ceramics and preliminary results were reported. No second phases were detected for the studied samples. SrO excess impedes the grain growth and thus decreases the dielectric permittivity. On the contrary, TiO_2 excess promotes the increase of the

dielectric permittivity values. The variation of Sr/Ti ratio has only weak effect on the quantum paraelectric behaviour of ST and no dielectric anomaly was observed. More detailed analysis show that $Sr_{0.997}TiO_{2.997}$ can be used to increase the dielectric permittivity and $Sr_{1.01}TiO_{3.01}$ to suppress the loss.

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