

Nonstoichiometry Effects in SrTiO₃ Ceramics Assessed by Transmission Electron Microscopy

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Strontium titanate (SrTiO₃, ST) has a perovskite type structure that is cubic at room temperature, but transforms into a tetragonal one at 105K [1]. At very low temperatures, ST exhibits an extremely large dielectric permittivity and piezoelectric and superconducting characteristics. ST finds applications in tunable microwave devices, due to a dependence of its dielectric response on the electric field and low microwave losses [2]. ST electrical properties are strongly dependent on grain boundaries features and directly influenced by grain size distribution. It was found in our previous studies that a small variation in the stoichiometry of ST has a significant effect on the grain size of the sintered ceramic and related electrical properties: increased grain size and dielectric permittivity values have been reported for Ti excess compositions whereas Sr excess caused a decrease of grain size and of the dielectric permittivity [3]. The tailoring of the dielectric properties by small non-stoichiometric variations in ST needs, however, a full understanding of its effects on the microstructure, phases structure and on the structure / composition of the grain boundaries.

In this work, the effect of nonstoichiometry on the microstructure of ST ceramics was systematically addressed. Compositions with Sr/Ti ratios from 0.997 to 1.02 were prepared by the conventional mixed oxide method, isostatically pressed and sintered in air at 5 °C/min up to 1500 °C. X-ray diffraction (XRD) was used for the crystallographic characterization and the microstructural development of nonstoichiometric ST was studied by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)/ Energy Dispersive Spectroscopy (EDS).

Under the detection limits of the XRD no second phases were detected either before or after the sintering cycle for the three compositions. According to the SEM micrographs of the sintered samples, depicted in Fig. 1, Ti excess composition (ST0.997) presents a coarse microstructure with a significantly larger average grain size (Fig. 1d) than the ones of the stoichiometric (ST) and Sr rich (ST1.02) compositions. On the other hand, the Ti rich and the stoichiometric compositions present enlarged grain size distributions, while a narrow one was observed for the Sr rich sample. Confirming the XRD results, no second phases were detected by SEM.

TEM observations of samples of the three compositions are shown in Fig. 2. Rough grain boundaries are commonly observed, but some of the largest grains of Ti rich and stoichiometric compositions show faceting of the grain boundaries, as observed in Fig. 2a. In the Ti excess sample (ST0.997), dark spots, probably Ti precipitates or dislocations due to the accommodation in the lattice of Ti excess, are often observed in and near the grain boundary region (Fig. 2b). In the stoichiometric sample no dark spots were observed. Scarce second phases were detected by TEM/EDS analysis in triple points of Ti rich and stoichiometric samples (Fig. 2c). The EDS analysis of those second phases showed that they are rich in Sr. Regarding the Sr rich sample (Fig. 2d), instead of dark spots in the boundaries, a pattern of planar defects inside the grains is observed,

characteristic of the so-called Ruddlesden-Popper (RP) structure, a three-dimensional mosaic of single-layered rock-salt blocks, allowing SrO excess in ST lattice in the form of interlayers [5]. No second phases in the triple points were observed in this composition.

The microstructural (SEM and TEM) and structural analysis (XRD) observations are coherent with prevalent solid solution effects for all compositions, that can be inferred from (i) very small amount of second phases, only detectable by TEM in Ti rich and stoichiometric samples; (ii) the second

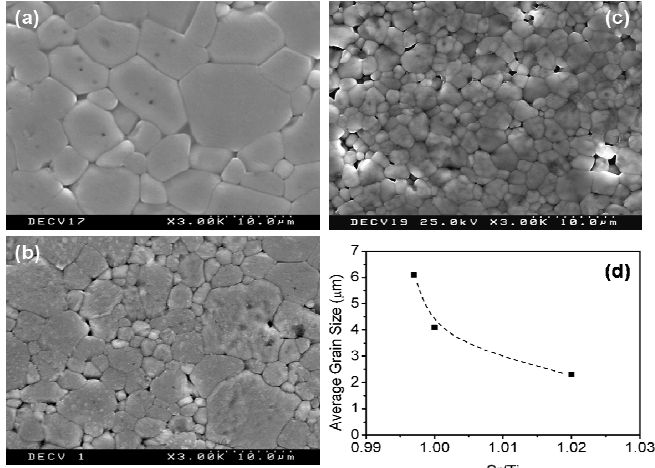


Fig. 1. SEM micrographs of SrTiO₃ ceramics with Sr/Ti ratios of (a) 0.997, (b) 1.00 and (c) 1.02, (d) average grain size as a function of Sr/Ti ratio.

phases are not rich in the excess element (Ti in ST0.997) but, instead, are Sr rich phases, probably related with the formation of Sr vacancies inside the grains in order to compensate the Ti accommodation in the lattice; (iii) formation of planar defects inside the grains of the Sr rich sample, characteristic of the RP structure; (iv) additionally, it was also detected a systematic variation of the lattice parameter with the Sr/Ti ratio, slightly increasing with increasing Ti content. The small excess of both TiO₂ and SrO must, therefore, be mostly incorporated into the perovskite lattice, either in bulk or in grain boundaries, changing the characteristics of species transport both for sintering and electrical transport.

Forthcoming studies will be directed to a more detailed analysis of the structure of the grain boundaries using high resolution TEM and to the determination of the profile of each element (Sr, Ti and O) along grains and grain boundaries by Electron Energy Loss Spectroscopy (EELS).

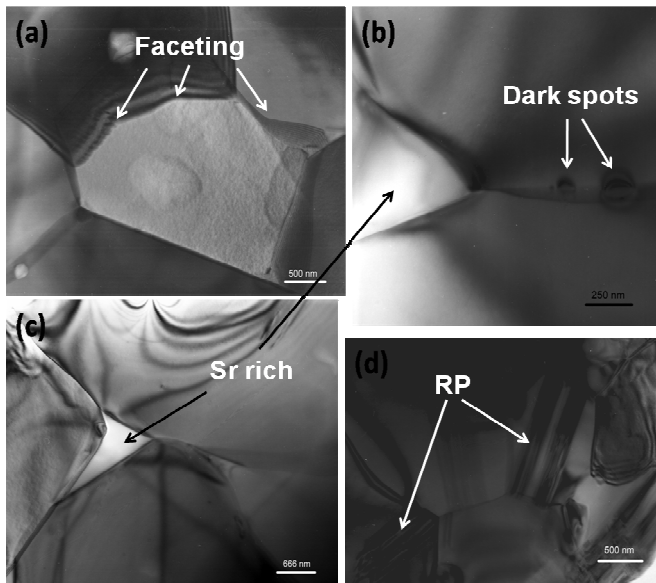


Fig. 2. TEM images of SrTiO₃ ceramics with Sr/Ti ratios of (a) and (b) 0.997, (c) 1.00 and (d) 1.02.

References

- [1] K.A. Müller, H. Burkard, Phys. Rev. B 19 (1979) 3593.
- [2] A. K. Tagantsev, V. O. Sherman, K. F. Astafiev, J. Venkatesh, N. Setter, J. Electroceram. 11 (2003) 5.
- [3] A. Tkach, P.M. Vilarinho, A.M.R. Senos, A.L. Kholkin, J. Eur. Ceram. Soc. 25 (2005) 2769.
- [4] Y.H. Han, M.P. Harmer, Y.H. Hu, D.M. Smyth, A²⁺/Ti nonstoichiometry in alkaline earth titanates, ATiO₃. In *Transport in Nonstoichiometric Compounds*, ed. G. Simkovich and V. S. Stubican. Plenum Press, New York, 1985, 73-85.