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Impedance Spectroscopy of n-doped $(Ba,Sr)TiO_3$ Ceramics Prepared by Modified Low Temperature Aqueous Synthesis

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Abstract

Low temperature aqueous synthesis (LTAS) has been applied to the preparation of La or Nb-doped (Ba,Sr)TiO₃ powders. Doping elements have been mixed to precursors, in order to directly obtain crystalline powders with modified composition. Similar powders, doped by conventional wet ball-milling process, have been also prepared for comparison. Ceramic samples have been obtained by isothermal sintering in air at different temperatures. Microstructural characterisation showed the presence of a secondary phase, identified as a Ti-rich barium titanate compound. Impedance spectroscopy (IS) has been used to study the PTCR behaviour of such materials. IS results are analysed, taking into account effect of the secondary phase, to discuss bulk and grain boundary characteristics. © 1999 Elsevier Science Limited. All rights reserved

1 Introduction

Barium titanate-based materials are widely used and extensively studied for the large number of possible applications in ferroelectric, dielectric and semiconducting devices.[1] Among these, the realisation of thermistors based on the PTCR (positive temperature coefficient of resistance) effect is one of the most important.[2]

In donor doped polycrystalline $BaTiO_3$ the effect is represented by a several order increase of electrical resistivity within a temperature interval of 100°C above the Curie point of the ferroelectric structure (about 120°C). As the substitution of Ba^{2+} with Sr^{2+} atoms lowers the ferroelectric-paraelectric transition temperature,[3] the onset of the PTCR effect can be shifted through the formation of solid solutions of the type $Ba_{(1\text{-}x)}Sr_xTiO_3$.

Several works have demonstrated the dependence of the PTCR effect on the donor doping level,[4] the oxygen partial pressure during high-temperature treatments[5] and the co-doping with acceptors.[6] Most of these effects can be explained within the model proposed by Heywang[7] and Jonker,[8] based on the existence at grain boundaries of a layer of acceptor states acting as traps for electrons. Many investigators have focused the role of charge compensating defects, like Ba^{2+} vacancies,[4] in the formation of such states, normally produced during thermal treatments and successive cooling stages.

In order to clarify the different phenomena related to the PTCR effect, several experimental techniques have been employed, like usual microstructural analyses, simple resistance measurements on bulk specimens, spectroscopic investigations by EPR[9] and single grain boundaries electrical characterisations.[10,11]

Among these techniques, the spectroscopic characterisation of a.c. electrical impedance (IS) has revealed a valuable tool in the description of PTCR ceramics,[12] for its sensibility to different elements of composite materials.[13]

In this work IS has been adopted to study the electrical behaviour of $(Ba,Sr)TiO_3$ ceramics prepared by a non-conventional route, the low-temperature aqueous synthesis (LTAS), which is a method suited for the preparation of various oxides with Perovskite structure,[14] like $BaTiO_3$ and $SrTiO_3$.

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2 Samples Preparation

Powders with nominal composition $Ba_{0\cdot9}Sr_{0\cdot1}TiO_3$ (BST) were obtained via the reaction:

$$0{\cdot}9Ba(OH)_2 + 0{\cdot}1Sr(OH)_2 + TiCl_4 + 4NaOH \rightarrow \\ \rightarrow Ba_{0\cdot9}Sr_{0\cdot1}TiO_3 + 4NaCl + 3H_2O$$

performed at 80°C and at atmospheric pressure under inert gas. In order to overcome the very low solubility of dopants into $TiCl_4$, the normal LTAS procedure[15] was modified and pure titanium chloride was replaced by a 3·4 M aqueous solution of $TiCl_4$, added with $LaCl_3$ or $NbCl_5$. After the synthesis, powders were washed with distilled water, dried and calcined in air at 950°C for 2 h. As reported in Table 1, one La-doped sample was also prepared by the normal LTAS reaction and doped by wet ball milling with an aqueous solution of $La(NO_3)_3$.

Forming was realised by cold isostatic pressing at 150 MPa, without the addition of binders, while isothermal sintering experiments were carried out at temperatures ranging from 1170 to 1350°C, for 2 h, in air. Cooling from sintering temperature to 700°C was performed at 10°C/min.

As-prepared and sintered powders were analysed by X-ray diffraction (Philips, PW 1710, Co K_α radiation), while 2 mm thick disks, sliced from sintered bodies, were used to prepare polished samples for SEM (Philips, 515) observations and electrical characterisation. Apparent densities (Table 1) were measured by the immersion method in water. The total concentration of major cations (Ba,Sr,Ti) and effective incorporation of dopants into the lattice were measured by plasma spectrometry analyses (ICP, Jobin Yvon JY24) on sintered samples.

Electrodes deposition for electrical measurements was carried out by sputtering of a 120 nm thick Au layer and successive annealing in air at 700°C for 5 h. The impedance data acquisition system used, ranging between 10^{-3} to 10^6 Hz and from 20 to 270°C, was composed by an impedance analyser (Solartron, SI 1260, 0.5 V excitation voltage) and an oven with digital controller and temperature sensor (Pt100), controlled by PC-based custom applications developed in the LabVIEW environment (National Instruments). Direct current measurements were also performed by a digital electrometer (Keithley, 617, 1 V excitation voltage).

3 Results and Discussion

From XRD analysis, as-prepared powders showed the presence of the major titanate phase with cubic or pseudo-cubic symmetry and some wt% of orthorhombic $BaCO_3$. After sintering, ceramics fired at 1300–1350°C contained a secondary phase with molar ratio $(Ba+Sr)/Ti<1$, detected both by XRD and SEM observations (Fig. 1), while BSTL2 showed no evidence of it. The formation of a Ti-rich phase in sintered ceramics prepared by the modified LTAS process can be related to the presence of polymeric chains of titanium hydroxo-complexes into titanium chloride aqueous solutions, as indicated by raman spectroscopy analyses on pure and diluted $TiCl_4$.[16]

Chemical analyses gave indications about the cationic ratio A/B of powders, that was in the typical range of the LTAS process (1·00 ± 0·01), and about the effective concentration of donors (Table 1). The actual stoichiometry of powders prepared by LTAS is known to be affected by the washing step, mostly through the dissolution into water of some amount of Ba from the surface of particles.[15] Moreover, a 25% reduction of the nominal amount of dopants has been registered after the

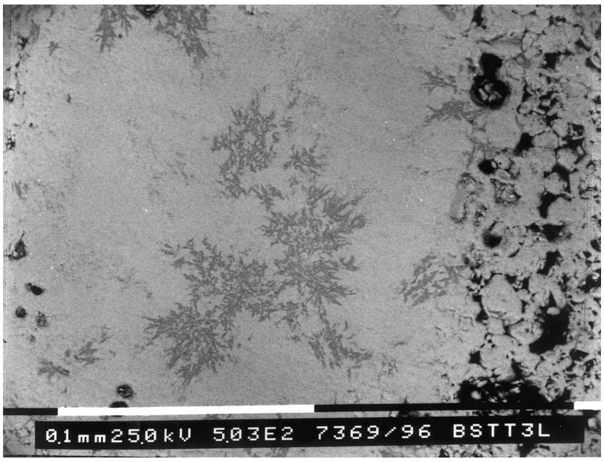

Fig. 1. SEM image of BSTL1 sample (back scattering). Darker region corresponds to the Ti-rich phase.

Table 1. Viviani, M. *et al.* Impedance spectroscopy of n-doped $(Ba,Sr)TiO_3$ ceramics prepared by modified low temperature aqueous synthesis

Sample	*Dopant (at %) nominal/ICP*	*Synthesis*	*T sintering (°C)*	*Additives (ppm)*	*Relative Density (%)*
BSTN1	Nb (0·70/0·57)	m-LTAS	1350	—	86
BSTN2	Nb (0·70/0·57)	m-LTAS	1300	—	85
BSTL1	La (0·30/0·22)	m-LTAS	1300	—	85
BSTL2	La (0·30/0·29)	LTAS	1170	SiO_2 (1000)	92

washing treatment in La, Pr, Gd, Er and Co, Ni doped $BaTiO_3$ powders prepared by the modified LTAS route. In the present work, as usual, Ba and Sr depletion was balanced by the addition of small excess (2·5 at%) of alkaline-earths at the beginning of reaction, in order to maintain cationic ratio close to 1. The reduction of 25% of the nominal amount of doping elements was also confirmed.

Resistivity measurements gave evidence of semiconducting behaviour at room temperature (Fig. 4) both in La and Nb-doped samples, in good agreement with previous investigations on similar compositions[17] and on $Ba_{0.3}Sr_{0.7}TiO_3$ ceramics doped with 1 at% of Nb.[18]

In particular, d.c. resistance and 1 kHz capacitance measurements suggested the formation of a core-shell structure of the grains, with effective dielectric constant around 10^5 and resistivity between 10^5 and 10^6 Ω cm at room temperature.

Impedance data relative to BSTN1 sample are reported in the complex plane representation (Fig. 2) and in the spectroscopic form (Fig. 3), together with electric modulus values calculated with the relation $M = j\omega C_0 Z$, where C_0 is the empty cell capacitance and ω the angular frequency. From complex representation curves is possible to note a continuous raising of total resistance with temperature, indicated by the low-frequency intersections with real axis and corresponding to a PTCR effect with ratio $R_{PTC} = R_{max}/R_{min} \sim 10^2$. The shape of such curves reveals the presence of two partially overlapping arcs, characterised by temperature dependent height and position: in particular, the arc at higher frequencies can be considered a relaxation in the grain core region, while the other one can be assigned to the grain boundary zone. Fitting of these curves with equivalent circuits of ideal resistive and capacitive elements is a commonly adopted procedure which enables a characterisation of different regions in the material. Here a division in two homogeneous zones, grain core and grain boundary, was assumed and a series model of two parallel RC elements was used to fit data at various temperatures.

The spectroscopic representation (Fig. 3) clarifies such division and, through modulus data, gives further information about dielectric properties of each region. In fact, while resistance determines the height of imaginary impedance peaks, modulus peaks depend on inverse capacitance and both parameters fix the frequency of maxima through the relation $f_{max} = 1/RC$, valid for Debye-like relaxations. On the basis of these results a few considerations are possible. The resistance of both regions grows rapidly with temperature and, in spite of a correspondent decrease in capacitance, maxima move towards lower frequencies on heating. Exceptions are represented by the low temperature behaviour of grain core capacitance that raises between 25 and 70°C and by the decreasing of grain boundary resistance between 150 and 200°C. Overall parameters trend gives evidence of a ferroelectric transition between 70 and 90°C, which can be recognised in both regions, and of PTCR behaviour, more pronounced in the core.

These aspects remain valid in all analysed samples regardless the dopant nature and the doping technique. For instance, resistive components of BSTN1, BSTN2 and BSTL1 samples, reported in

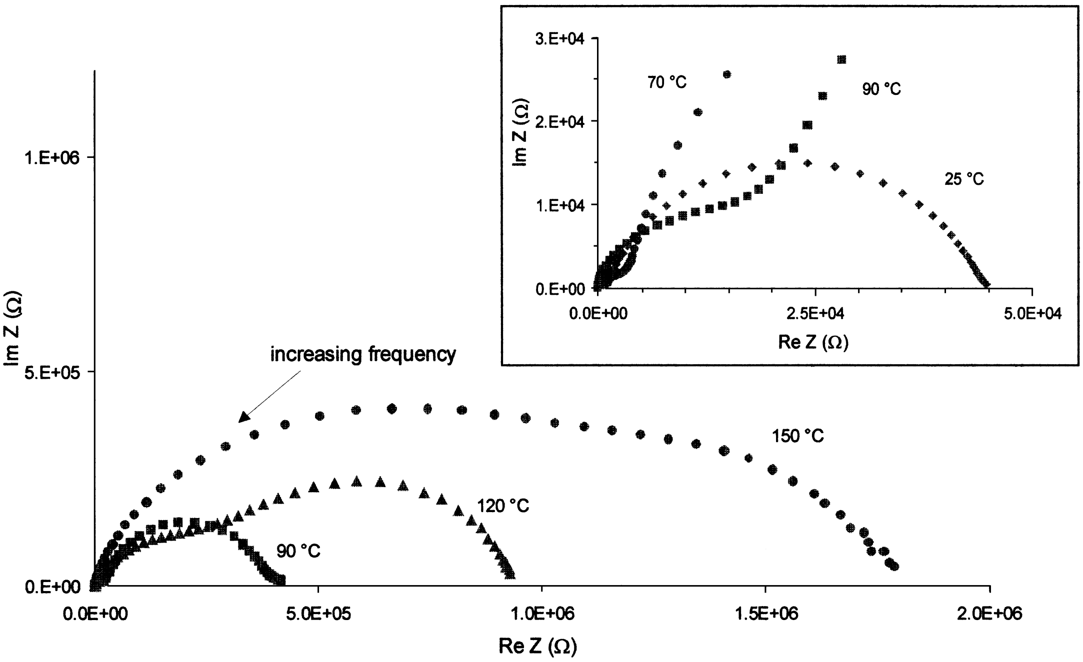

Fig. 2. Impedance curves at different temperatures represented in the complex plane (BSTN1).

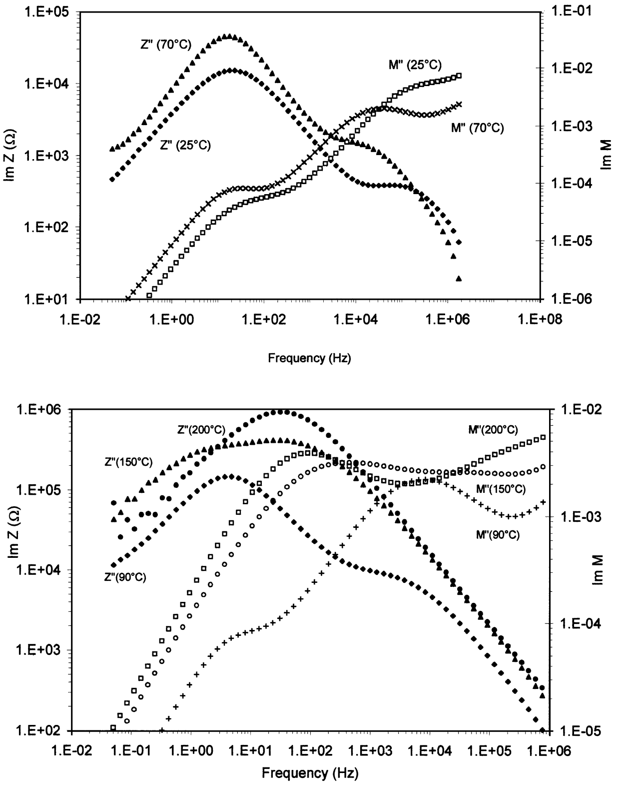

Fig. 3. Imaginary impedance and modulus data in the spectroscopic representation (BSTN1). Empty cell capacitance C_0 was 3 10^{-11} F.

Fig. 4, reproduce the PTC effect with onset temperatures close to the ferroelectric transition of these compounds and with R_{PTC} between 10^2 and 10^3.

This value appears to be principally limited by high resistivity levels at low temperature, mostly in the boundary region, that can be explained either as an effect of the grain size or of the secondary phase. In fact, sintered bodies showed average grain sizes around 1 μm, which are one order less than those normally reported for PTCR ceramics prepared by solid state route, and that make the volume ratio between boundary and core regions bigger than usual. Moreover the quite high resistivity measured for the inner zone could be explained by the existence of another, less resistive and capacitive, region at the very centre of grains, in accordance with Sinclair *et al.*[12] Even if our measurements do not show a third relaxation, its existence at near radio frequencies could be suggested by the shape of high-temperature spectroscopic modulus plots (Fig. 3).

On the contrary, no evident effect on conductivity can be ascribed to the presence of the Ti-rich phase, due both to the complete similarity among BSTL2 and other samples and to its distribution, non uniform but locally arranged in dendritic aggregates (Fig. 1).

These considerations indicate that PTCR effect was mostly limited by microstructure-related factors, largely independent from synthesis and doping techniques, that can be overcome by more favourable sintering conditions.

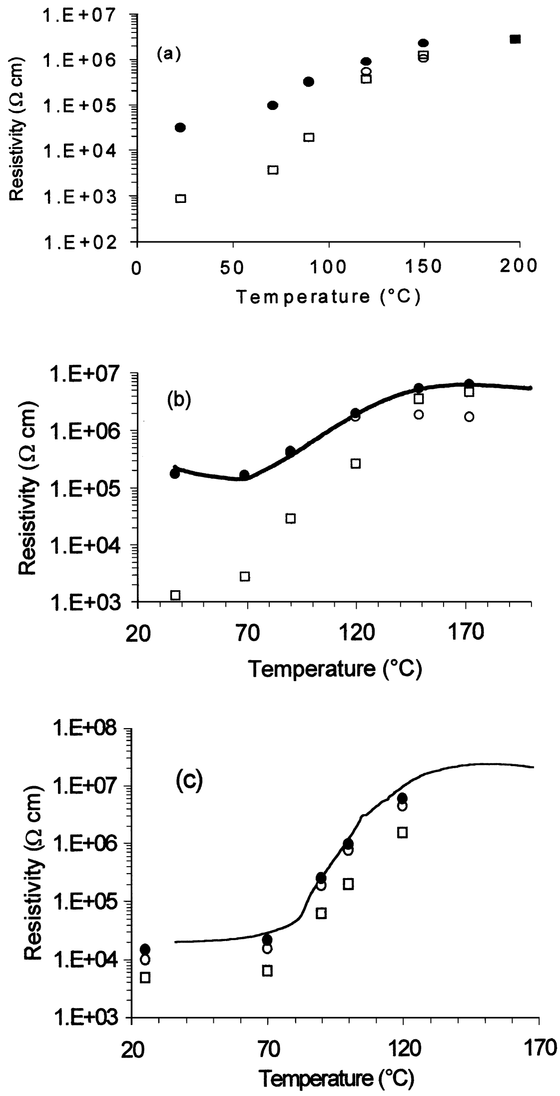

Fig. 4. Temperature dependence of resistive elements, calculated by impedance data fitting with equivalent circuits, relative to (a) BSTN1, (b) BSTN2 and (c) BSTL1. ○, boundary; □, core; ●, total. Curves in (b) and (c) are resistivity data measured at zero frequency.

4 Conclusions

Donor doped (Ba,Sr)TiO_3 solid solutions have been prepared by LTAS. A modified procedure has been experimented in order to obtain final composition directly during precipitation, without further treatments. The formation of a Ti-rich secondary phase, non uniformly distributed into the fine grained (1 μm) perovskite matrix, has been detected. Electrical characterisation by impedance spectroscopy has pointed out the presence of two regions with ferroelectric and PTCR behaviour which have been assigned to grain core and grain boundary zone. PTC ratio values have been discussed on the basis of grain size, while resistive effects from the secondary phase have been excluded. The results show that the doping by the modified LTAS process is a promising technique for the preparation of PTCR ceramics.

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