Journal of the European Ceramic Society **19** (1999) 1077–1080
© 1999 Elsevier Science Limited
Printed in Great Britain. All rights reserved
PII: S0955-2219(98)00377-X
0955-2219/99/$ - see front matter

Dielectric Properties of Porous $Ba_{0\cdot997}La_{0\cdot003}Ti_{1\cdot0045}O_3$ Ceramics

M. E. V. Costa* and P. Q. Mantas

Department of Ceramics and Glass Engineering, UIMC, University of Aveiro, 3810 Aveiro, Portugal

Abstract

An oxalate method was used in this work to produce La–$BaTiO_3$ materials. The obtained powders had small particle size and were disaggregated. However, the sintering process is difficult due to the presence of large pores uniformly distributed in the matrix. Grain size is not uniform, and the type of microstructure obtained suggests that clusters of particles readily sinter and densify, while leaving between them large pores. Impedance spectroscopy was done up 230°C. The variation of the permittivity with temperature showed that lanthanum changes the transition temperature of $BaTiO_3$, to T_o ~115°C. One of the resistances of the proposed equivalent circuit was related to grain boundary conductance, since its associated activation energy, 0·72 eV, is too high to be assigned to a donor species. It is proposed that La substituting Ba is compensated by Ba vacancies, which turns the material highly resistive, not showing the PTC effect. © 1999 Elsevier Science Limited. All rights reserved

Keywords: powders-chemical preparation, dielectric properties, $BaTiO_3$ and titanates, PTC devices.

1 Introduction

Barium titanate is a dielectric material, with a perovskite structure, that finds many applications in electronic devices, such as capacitors and positive temperature coefficient resistance (PTC), which are used for temperature control. When pure, this material is highly resistive at room temperature, but its electrical resistivity can be dramatically lowered by some dopants, like rare earth elements. Donor doped polycrystalline $BaTiO_3$ can exhibit PTC characteristics. The optimisation of the material performance, for these technological applications, demands a controlled preparation of the compounds. Among the several preparation routes that can be used, the coprecipitation method has the advantage of assuring chemical purity of the final product, this being a critical feature that must be considered for electrical characteristics purposes.

The addition of lanthanum to $BaTiO_3$ turns the material into a semiconductor in a narrow composition range, from 0·2 to 0·4 mol% La.[1] In this work, an oxalate based coprecipitation method was used to produce the precursor powders for the synthesis of La doped-$BaTiO_3$, with 0·3 mol% La. This is a simple chemical precipitation procedure to obtain fine powders with good physical characteristics for an easy sintering process. A Ti excess was used in order to assure that lanthanum occupies the A sites of the perovskite structure. Electrical measurements were performed in the sintered samples to study the effect of the preparation in PTC behaviour.

2 Experimental

The La doped-$BaTiO_3$ used in this work was prepared by the oxalate method. Solutions of barium, titanium, and lanthanum chlorides, and oxalic acid, all reagent grade, were used as precursors. The amounts of the precursors were calculated according to the desired molar ratio for the cations, to give the composition $Ba_{0\cdot997}$ $La_{0\cdot003}$ $Ti_{1\cdot0045}$ O_3. The precipitation immediately occurred when an aqueous solution of barium and lanthanum chloride was added to a stable solution of titanium chloride and oxalic acid. The acidic pH of the precipitating medium (pH = 1) was increased by ammonia addition, up to pH = 9, in order to maximize the precipitation yield. The only crystalline phase detected by XRD analysis in the final solid product of this process was barium oxalate.

The precipitated powders were converted into cubic $BaTiO_3$, upon calcination at 950°C, 2 h, in

---

*To whom correspondence should be addressed. Fax: +351-34-25-300; e-mail: elisabete@cv.ua.pt air. Disk-shaped samples were prepared by uniaxially pressing the calcined powders, at 750 MPa. Sintering of these samples was performed in air, at 1250, 1300 and 1350°C, for 2 h, with heating and cooling rates of 10°C min^{-1}. XRD analyses of sintered materials showed that they were composed by tetragonal $BaTiO_3$. Microstructures were observed on fracture surfaces by SEM.

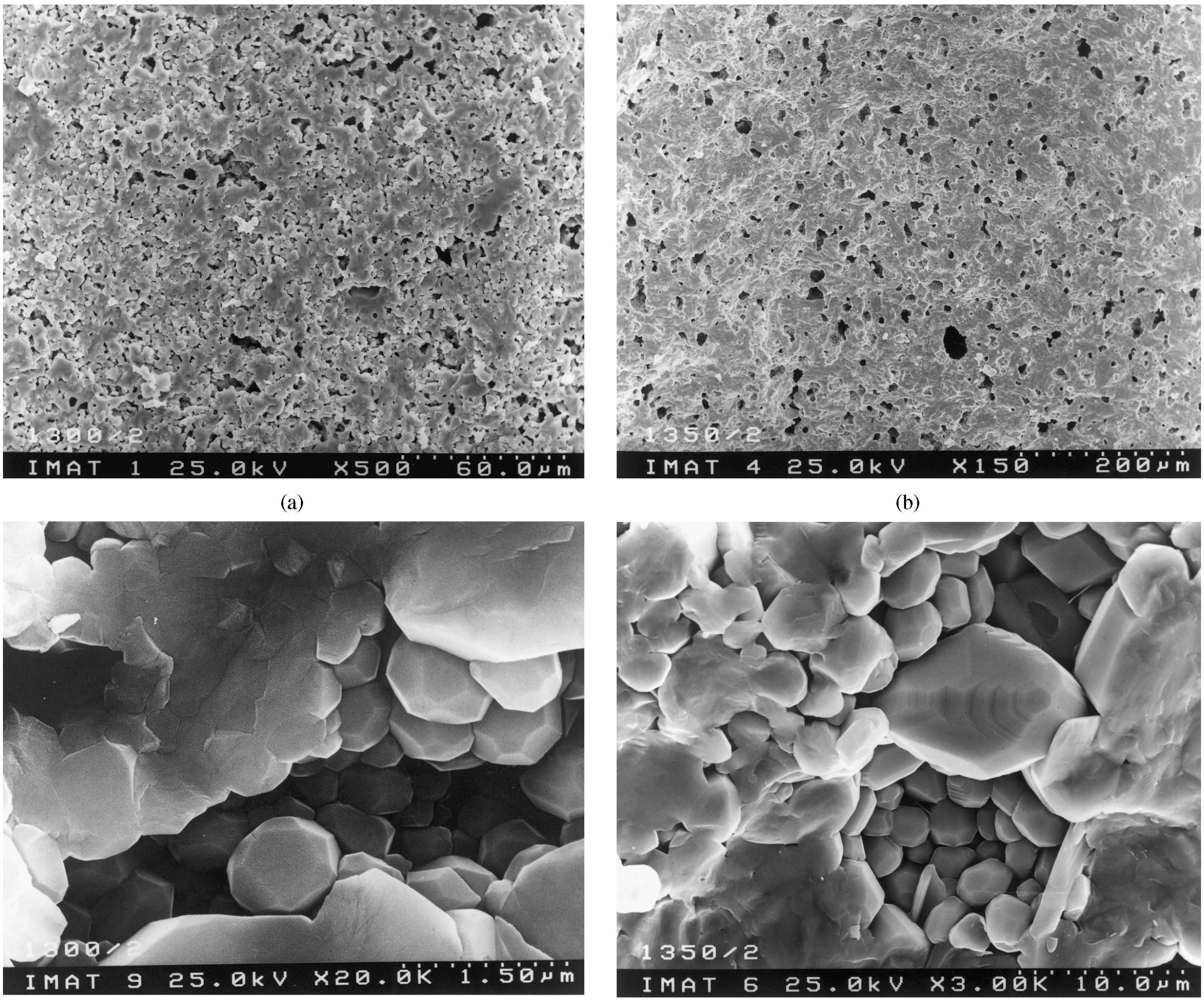
For electrical measurements, gold electrodes were sputtered on the opposite surfaces of the ceramic disks. ac measurements were done with a gain-phase analyzer (Solartron 1260), in the range of 1 Hz–1 MHz, from room temperature up to 230°C.

3 Results and Discussion

The oxalate method used in this work is a very simple one and allows to control carefully the desired chemical composition. After calcination, one obtains $BaTiO_3$ as the only phase, with cubic crystal structure, a common feature in $BaTiO_3$ produced by chemical methods.[2] The powders have small particle size and are disaggregated, suitable for pressing. In spite of these physical characteristics, the sintering process is difficult, since the relative density achieved by the samples were 0·70, 0·73, and 0·80, after sintering at 1250, 1300, and 1350°C, respectively. SEM micrographs show that the microstructure is composed by large pores uniformly distributed in the matrix [Fig. 1(a) and (b)]. The grain size is not uniform, with small grains near the large pores and larger grains in a densified matrix [Fig. 1(c) and (d)]. This type of microstructure suggests that clusters of particles readily sinter and densify, promoting later the grain growth, while leaving between them large pores. These large pores will be difficult to eliminate for longer times or higher sintering temperatures. This situation could be overcome by introducing a milling step after the calcination in order to obtain densified materials. In spite of these problems, we could observe that these porous samples change their colour after sintering, from pale yellow, at 1250°C, to light blue, at 1350°C, and this is an indication that the material is being reduced and turning to a *n*-type semiconductor.[3] Therefore, our next step was to analyse the electrical properties of the material and see if the PTC effect was present.

Impedance spectroscopy was done up to ~230°C, far above the phase transition temperature of pure $BaTiO_3$ (~125°C). To analyse the spectra, we used the formalism of complex impedance, $Z^* = Z' - Z''j$, and complex modulus, $M^* = M + M''j$, presented by Sinclair and West[4] for a commercial PTC material. Figure 2 shows the M'' spectrum for different temperatures, for the case of the sample sintered at 1350°C. It can be seen that two peaks are present, the strongest one at intermediate frequencies, being shifted to higher frequencies as temperature increases. The spectrum can be represented by a series of two parallel RC circuits. Taking the M'' peak values of the intermediate frequencies and calculating the capacitance associated with them, here denoted by C_2, it can be seen that it follows a Curie–Weiss law (Fig. 3), with a Curie temperature of $T_c = 113$°C. The capacitance associated with the M$''$ peak at low frequencies, C_1, does not change much with temperature. These results are quite in agreement with those reported by Sinclair and West.[4] However, the resistance, R_2, associated to the RC element of the intermediate frequencies decreases with temperature, from 140 to 230°C (Fig. 4), a temperature range where it should be increasing if a PTC effect was present. Its activation energy is $E_2 = 0{\cdot}72$ eV, far below the one found by the authors, 0·99 eV[4]. Figure 5 shows the variation of the relative permittivity, ε_R, with temperature, at 1 kHz, which is similar to the behaviour of pure $BaTiO_3$, with a transition temperature of T_o. For the samples sintered at 1250 and 1300°C, similar graphs gave the same transition temperature. The analyses of impedance and modulus spectra for these cases render difficult due to the scattering of the data (impedance values are very high).

The variation of the permittivity with temperature shows that lanthanum changes the transition temperature of $BaTiO_3$, to $T_o \sim 115$°C, for the composition under study. La is substituting Ba, and so it must behave as a donor species. In our impedance spectrum, the RC element of intermediate frequencies can be related to the grain characteristics. In fact, due to the porosity, and to the type of the used electrodes, sputtered gold electrodes in this work, it is quite reasonable to accept that both will introduce very high impedance features at low frequencies. Therefore, the R_2 resistance is related to grain conductance. However, its associated activation energy, $E_2 = 0{\cdot}72$ eV, is too high to be assigned to a donor species, and too low to be assigned to the band gap.[5] If the concentration of donor species is very low, in such a way that in the 140–230°C temperature range, the Fermi level in the material is situated around 0·72 eV, this would confirm that the material is donor doped. However, the La content used in this work should turn the material very conductive, i.e. the donor concentration should be high, and so that energy can not be assigned neither to the donor level nor to the Fermi level. Another possibility is that it is related to the depth of surfaces states at grain boundaries or to the grain boundary barrier height.[1] We do not have enough experimental evidence to test both possibilities, but it is worthy of mention that the activation energy must be related to the grain boundaries, i.e. the grain boundary behaves as a ferroelectric material (Fig. 3), contrary to the assumption of Sinclair and West[4] and in agreement with the Jonker model.[1]



(a) (b) (c) (d)

Fig. 1. SEM micrographs of fracture surface of sintered La-$BaTiO_3$ powders at 1300°C (a) and (c), and 1350°C (b) and (d).

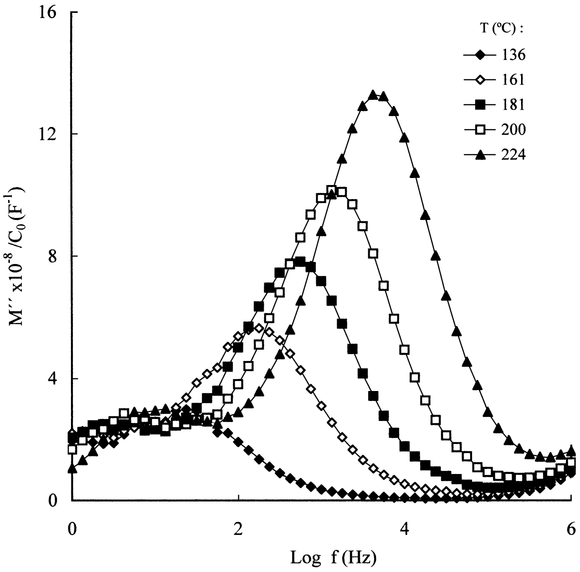


Fig. 2. M'' spectrum for the sample sintered at 1350°C, at several temperatures. C_O is the vacuum sample capacitance.

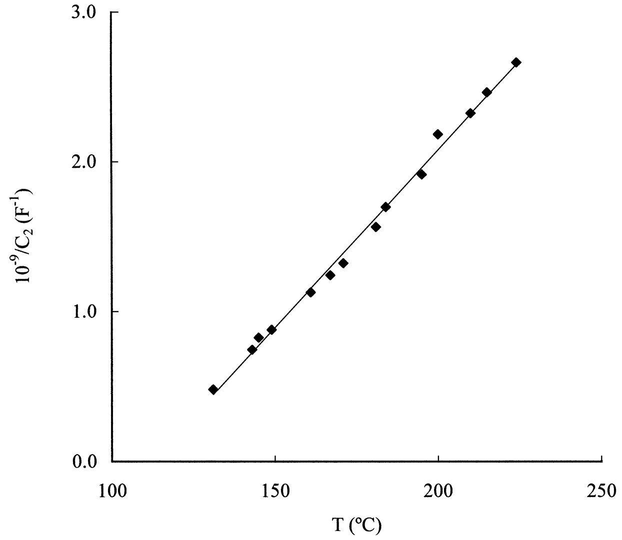


Fig. 3. Temperature dependence of the capacitance C_2, for the sample sintered at 1350°C.

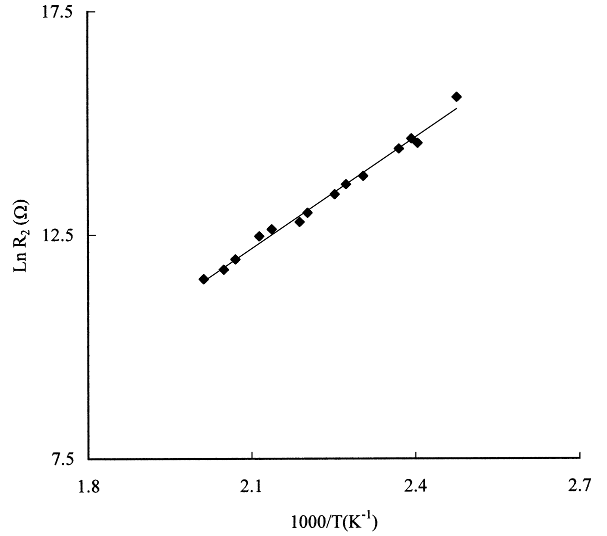


Fig. 4. Temperature dependence of the resistance R_2, in the same temperature range as in Fig. 3

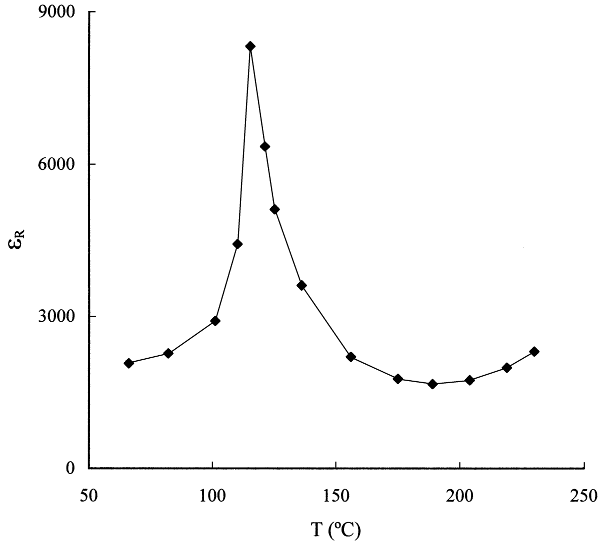


Fig. 5. Temperature dependence of the relative permittivity (ε_R) for La-BaTiO$_3$, at 1 kHz.

The second important point is to analyse the behaviour of La when substituting Ba, which is the case in the present work. As it is apparent, the $La_{Ba}^{\cdot}$ defect does not behave as a donor species and it must be compensated in the matrix for electroneutrality condition. For this charge compensation three possible candidates are present: the two cation vacancies, V_{Ba}'' or V_{Ti}'''', or the interstitial oxygen, O_i''. The perovskite is a close packed dense structure, and so a compensation by O_i'', if present, should only be observed at surfaces and grain boundaries. Titanium vacancies are not expected to occur in our system, because we have an excess of titanium in the starting composition. Therefore, barium vacancies are the best candidates to compensate the $La_{Ba}^{\cdot}$ defect. This compensation mechanism means that the material will be highly resistive, and will not show the PTC effect. Our experimental electrical results seem to agree with this picture. We would like to emphasize here that donor doping in BaTiO$_3$, like La doping, does not necessary creates extrinsic donor defects, and this is perhaps the reason why different chemical species change the room temperature resistivity of BaTiO$_3$ in the same way.[1]

4 Conclusions

The oxalate method used in this work is a very simple one to produce La–BaTiO$_3$ materials. The obtained powders had small particle size and were disaggregated. However, the sintering process is difficult due to the presence of large pores uniformly distributed in the matrix. Grain size is not uniform, with small grains near the large pores and larger grains in a densified matrix. This type of microstructure suggests that clusters of particles readily sinter and density, while leaving between them large pores.

Impedance spectroscopy was done up ~230°C. The variation of the permittivity with temperature showed that lanthanum changes the transition temperature of BaTiO$_3$, to T_o ~115°C. One of the resistances of the proposed equivalent circuit was related to grain boundary conductance, since its associated activation energy, 0·72 eV, is too high to be assigned to a donor species. It is proposed that La substituting Ba is compensated by Ba vacancies, which turns the material highly resistive, not showing the PTC effect.

Acknowledgements

Thanks are due to the Portuguese Foundation for Science and Technology, FCT, for supporting this work under the project PBIC/C/CTM/1934/95.

References

1. Nowotny, J. and Rekas, M., Positive temperature coefficient of resistivity for BaTiO$_3$ based materials. *Ceram. Int.*, 1991, **17**, 227–241.
2. Chaput, F, Boilot, J.-P. and Beauger, A., Alkoxide-hydroxide route to synthesize BaTiO$_3$-based powders. *J. Am. Ceram. Soc.*, 1990, **73**, 942–948.
3. Saburi, O., Properties of semiconductive barium titanates. *J. Phys. Soc. Jpn.*, 1959, **14**, 1159–1174.
4. Sinclair, D. C. and West, A. R., Impedance and modulus spectroscopy of semiconducting BaTiO$_3$ showing positive temperature coefficient of resistance. *J. Appl. Phys.*, 1989, **66**, 3850–3856.
5. Nowotny, J. and Rekas, M., Defect structure, electrical properties and transport in barium titanate. III. Electrical conductivity, thermopower and transport in single crystalline BaTiO$_3$. *Ceram. Int.*, 1994, **20**, 225–235.