



Título artículo / Títol article: Non-ohmic phenomena in Mn-doped BaTiO₃

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Revista: Phys. Status Solidi A 209, No. 11, 2267–2272 (2012)

Versión / Versió: Pre-print

Cita bibliográfica / Cita bibliogràfica (ISO 690): PRADES, Marta, BELTRÁN, Héctor, CORDONCILLO, Eloisa, ALONSO, Pablo J., MASÓ, Nahum, WEST, Anthony R. Non-ohmic phenomena in Mn-doped BaTiO₃. *Pharmacology Biochemistry and Behavior*, November 2012, Issue 11.

url Repositori UJI: <http://hdl.handle.net/10234/67863>

Non-Ohmic Phenomena in Mn-doped BaTiO₃

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Keywords: Non-Ohmic Phenomena, Barium Titanate, Ceramics, Electrical Conductivity.

We report here a novel effect in which the resistance of a semiconducting oxide ceramic increases on application of a small *dc* bias. The ceramic conducts at high temperatures by an *n*-type hopping mechanism. On application of a *dc* bias, conduction electrons are trapped at surface states and the resistance increases. On removal of the *dc* bias, the trapped electrons are released and the sample regains its original state. This effect is the mirror image of that seen with similar ceramics that conduct by a *p*-type mechanism whose resistance decreases reversibly on application of a small *dc* bias. These two phenomena together offer the possibility of novel switching devices and memristive applications, especially if the switching times can be reduced.

In the absence of interfacial effects, non-metallic materials such as oxide ceramics show linear voltage/current, V/I , behaviour at small applied voltages and their resistance, R , is therefore constant, as given by Ohm's law. This is because parameters that control conductivity, ie the number of mobile carriers and their mobility or hopping rate, are uninfluenced by small applied voltages.

Non-linear low-field behaviour has been observed recently^[1-3] in *p*-type, acceptor-doped BaTiO₃ ceramics in which the resistance decreased by 1–2 orders of magnitude on application of a small bias voltage, typically in the range 1–10V, across pellets of thickness 1–2mm; the resistance decrease was fully reversible on removal of the *dc* bias and was not associated with interfacial effects such as Schottky barriers. The rate of change of resistance with time was very temperature-dependent. It took several hours to achieve a bias-dependent steady state at 200–300 °C whereas the changes were complete in a few minutes at 600–800 °C. The enhanced conductivity was attributed to the presence of underbonded oxygen atoms surrounding acceptor dopants in the BaTiO₃ crystal lattice; facile ionisation of these underbonded oxygens generated holes, or O⁻ ions, and the increase in hole concentration was responsible for the enhanced conductivity. The driving force for ionisation was provided by the *dc* bias which caused the activation of electron trap states at the sample surface^[4].

The effect reported here is the mirror image of the behaviour of acceptor-doped systems and is observed in Mn-doped BaTiO₃ which, when lightly reduced, is an *n*-type semiconductor. The effect of a small *dc* bias is also to trap some of the conduction electrons which in this case, leads directly to a resistance increase. On removal of the *dc* bias, the trapped electrons are released and the conductivity regains its original value.

A key to understanding this, and the earlier phenomenon with acceptor-doped materials, is the observation that the conductivity of both *p*-type and *n*-type doped BaTiO₃ can be modified in a similar way by two independent methods, either by changing the oxygen partial pressure, P_{O₂}, in the atmosphere surrounding the sample during conductivity measurements^[5,6] or by application of a *dc* bias in an atmosphere of constant P_{O₂}.^[1-4] When O₂ molecules absorb on a ceramic surface, the molecules ionise by trapping electrons; dissociation of the molecules may also occur. Consequently, electrons are depleted from a region of the ceramic close to

traps at the sample surface. If the conductivity increases, the sample is *p*-type and vice versa, it is *n*-type if the conductivity decreases.

It thus appears that application of a *dc* bias provides a second mechanism to increase the trapping of conduction electrons at surface states. The sample of Mn-doped BaTiO₃ used here was an *n*-type conductor. Its resistance increased as conduction electrons were withdrawn from the sample, either by applying a *dc* bias or by increasing P_{O₂} in the atmosphere surrounding the sample.

These results are of possible significance for several reasons. First, they demonstrate that the partially ionised oxygens which must exist in many standard ceramic samples, especially at sample surfaces^[7], can readily act as either electron traps or electron sources. Second, if the sample is an *n*-type conductor, the trapping of electrons under the action of a small *dc* bias leads to an increase in sample resistance. Third, if the material is a *p*-type semiconductor then, under certain circumstances, as with acceptor-doped BaTiO₃, ionisation of underbonded oxide ions associated with the acceptor dopants may occur, providing electrons that are subsequently trapped at the surface states; this then leads to an increase in hole concentration and therefore a decrease in sample resistance. Fourth, novel non-linear phenomena are observed in which, depending on the particular system and conductivity mechanism, the sample resistance may either increase or decrease on application of a small *dc* bias voltage. Fifth, given the sensitivity of sample resistance to voltage, novel sensor and switching applications may be possible, especially if the switching speed can be increased, and at lower temperatures.

The samples used were sintered pellets of BaTiO₃ in which 0.5% of Ti was replaced by Mn to give the nominal composition BaTi_{0.995}Mn_{0.005}O_{3-δ}. Samples were prepared by sol-gel

synthesis of alkoxide precursors using methods described previously.^[8] Resulting powders were pelleted and fired in steps with final heating at 1400 °C for 12 h in air after which samples were slowly cooled to room temperature in the furnace. For electrical property measurements, electrodes were fabricated from organo Pt paste which was applied to opposite pellet faces, dried and hardened by heating to 900 °C. Samples with electrodes attached were returned to the furnace at 1400 °C for 2 h in air and then quenched in liquid N₂. Pellet densities were ~90 %. Samples were placed into the conductivity jig and electrical property data recorded using an Agilent 4294A impedance analyser over the frequency range, 40 Hz to 13 MHz and over the temperature range, room temperature to 900°C. Impedance data were corrected for the overall pellet geometry and for the blank capacitance of the jig. Resistance and capacitance data are, therefore, reported in units of Ωcm and Fcm⁻¹, respectively.

The oxidation state of Mn was studied by Electron Paramagnetic Resonance (EPR) at room temperature using an Elexys E580 spectrometer from Bruker, working in the X- band. The magnetic field was measured with a Bruker ER035M gaussmeter. Powdered samples were packed in fused quartz tubes (707-SQ from Wilmad-LabGlass).

Impedance data are shown at one temperature, 488 °C, for a sample quenched from 1400 °C, in Fig 1. A single arc was observed in the Z* complex plane (a) and single peaks in the Z''/M'' spectroscopic plots (b) which showed that the sample bulk dominated the impedance data without significant grain boundary or electrode contact effects. The permittivity as a function of temperature (c) showed a maximum at the Curie temperature and Curie-Weiss behaviour at temperatures above T_c (d). Bulk conductivity data presented in Arrhenius format in (e), showed that the quenched sample had higher conductivity and lower activation energy than the same sample which had been slow-cooled from 1400 °C. The conductivity increase was

attributed to a small amount of intrinsic oxygen loss from the sample at 1400 °C which was not regained during rapid quench, unlike reoxidation that occurred during slow cool.

The sample quenched from 1400°C was effectively in a frozen-in state and susceptible to reoxidation in air, at a rate that was dependent on temperature, leading to a decrease in conductivity (not shown) as a consequence of withdrawal of electrons from the sample according to the reaction: $O_2 + 2V_O^{\bullet\bullet} + 4e' \rightarrow 2O_O^x$. This indicated that electrons were the main charge carriers and, therefore, the conduction mechanism was predominantly *n*-type. Consequently, to avoid sample oxidation during impedance measurements, data on the quenched sample were recorded in an atmosphere of N₂. Impedance data for the quenched sample at 488°C in flowing N₂ are shown in Fig 1(f). Over a period of 24h, the resistance showed a gradual increase of ~9% attributed to presence of residual O₂ in the N₂ atmosphere. This gradual oxidation was on a much longer timescale than the other changes reported here.

The effect of a 10 V *dc* bias on the total conductivity of the quenched sample is shown in Fig 2(a) as function of time. It decreased rapidly at first, followed by a much more gradual decrease over longer times. On removal of the *dc* bias, the conductivity increased rapidly, although did not fully attain its original state, indicating that the changes induced by the *dc* bias were essentially reversible. The difference between initial and final conductivities in Fig 2(a) (ie before and after application/removal of the *dc* bias) is attributed to a partial reoxidation which was superposed on the reversible decrease in conductivity on application of the *dc* bias. Similar results to those shown in Fig 2(a) were obtained at other temperatures above ~200 °C but the rate of change was very temperature-dependent; for instance, the resistance continued to increase over a period of several days at 400 °C. The resistance changes shown in Fig 2(a) for *n*-type BaTiO₃, are the mirror image of those seen with acceptor-doped, *p*-type BaTiO₃, as shown for one example in Fig 2(b). These differences in

behaviour were independent of ceramic microstructure: as shown in Fig 3, grain sizes were comparable, ~5–30 μm for (a) and ~20–60 μm for (b).

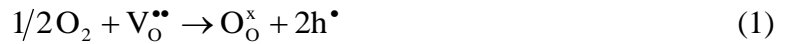
Further confirmation that the conduction mechanism in the quenched sample was *n-type* was obtained by conductivity measurements made in different atmospheres in a sample that was partially oxidised, Fig 4a. The conductivity increased reversibly with decreasing P_{O_2} in the measuring atmosphere and, therefore, electrons were the principal charge carriers.

EPR spectra for Mn centres ($g \approx 2$) over the magnetic field range 300–400 mT are shown for slow-cooled and quenched samples in Fig 4b and c, respectively. In the slow-cooled sample, a broad resonance and a singlet at $g = 1.97$ were observed, Fig 4b. No signals associated with Mn centres could be identified although the broad resonance could be related to aggregation of Mn centres. The signal at $g = 1.97$ was attributed to an unavoidable trace (ppm's) of Cr^{3+} (Ref. 9) in the starting materials.

By contrast, in the spectrum of the quenched sample, two sextets (marked as * and + in Fig 4c) and a singlet at $g = 1.97$ related to Cr^{3+} were identified. Both sextets were associated with ^{55}Mn centres (nuclear spin $I = 5/2$ and 100 % natural abundance) with g -factors and hyperfine coupling constants (A): $g = 2.05(1)$ and $A = 200(6)$ MHz (signals labelled as *) and $g = 2.00(1)$ and $A = 240(6)$ MHz (signals labelled as +). The Mn-sextets were assigned to *:Mn²⁺ and +:Mn⁴⁺ (Refs 10, 11) although alternatively, both sextets may be associated with Mn²⁺, as reported in SrTiO₃ (Ref. 12). In addition, samples could also contain Mn³⁺ since this cannot usually be detected by EPR.^[10,11] Therefore, the oxidation state of Mn in BaTiO₃ could be some combination of 2+, 3+ and 4+, depending on processing conditions. In the quenched sample, both Mn²⁺ and Mn⁴⁺ are present. If the Mn⁴⁺ was indeed present at 1400°C, and did

not form during reoxidation, then Mn^{3+} would also probably be present, giving $\text{Mn}^{2+,3+,4+}$ mixtures.

Ceramic samples, such as pure and doped BaTiO_3 , under equilibrium conditions at high temperature, generally show a p -type to n -type change in behaviour on reducing oxygen partial pressure^[13,14]. In the p -type region, holes are generated by the idealised reaction:



The location of the holes in ‘pure’ BaTiO_3 is often not clear but is frequently attributed to unspecified and unavoidable acceptor impurities such as Fe^{3+} . In the n -type region, the reverse reaction occurs,



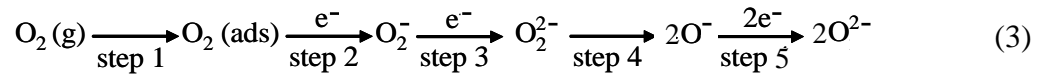
and the liberated electrons are presumed to be associated with cations, ie Ti or eg Mn.

In Mn-doped BaTiO_3 , several studies on the P_{O_2} dependence of conductivity have been reported^[13,15,16]. These show a p -type to n -type crossover with decreasing P_{O_2} and a displacement of the crossover region to higher P_{O_2} with increasing temperature. Neither studies reported data at 1400°C but, by approximate extrapolation, n -type behaviour could be expected at 1400°C . This is consistent with our experimental conductivity data in different atmospheres which show n -type behaviour and also by EPR measurements, Fig 4(b), which show the presence of Mn^{2+} species in the quenched samples.

The effect of a dc bias, leading to a decrease in conductivity, Fig 2, was similar to that of exposure of the quenched sample to an oxygen-rich atmosphere, Fig 4a. In both cases, n -type carriers were removed from the sample bulk leading to an increase in resistance. Variations in conductivity of this nature as a consequence of changing atmosphere are very well

established and, if they occur, are used as a strong indicator as to whether the carriers are principally *n*-type or *p*-type. However, we believe that this is the first time that a similar effect has been recognised on application of a small *dc* bias leading to depletion of *n*-type carriers from the sample bulk.

The trap states are not necessarily the same for the two cases of oxygen absorption and application of a *dc* bias: several possibilities are indicated in the following sequence of successive steps, three of which, steps 2, 3 and 5, involve a reduction process:



In the oxygen absorption case, the traps may be freshly adsorbed oxygen molecules from the surrounding atmosphere which pick up electrons from the sample to form superoxide ions, O_2^- , step 2. The first step involves adsorption of oxygen molecules on the ceramic surface but this would not be detected by impedance measurements since no reduction of the O_2 molecules is involved. These adsorbed O_2 molecules may act as electron traps, step 2, by picking up electrons from the sample to form superoxide ions, O_2^- . The superoxide ions may then pick up a second electron to form peroxide ions, O_2^{2-} , step 3, which may or may not be stable to dissociation, step 4. The O^- ions formed on dissociation may have some stability in an underbonded environment at sample surfaces or may pick up an extra electron, step 5, to form O^{2-} ions, which are then able to diffuse into the sample interior. At present, we cannot comment on the relative likelihood of these possibilities during changes to P_{O_2} in the atmosphere and on application of a *dc* bias but note that, in the case of acceptor-doped materials, *dc* bias effects were observed even when the sample was evacuated. This therefore indicates that pre-existing traps are present, spontaneously, at any time, on the surface of such oxide ceramics.

The results presented here show an increase in resistance of donor-doped materials on application of a *dc* bias and complement earlier results on acceptor-doped materials that showed a reduction in resistance. The behaviour of the present materials is simpler because there is only one electronic species to be considered, namely, the majority carriers which are electrons. These carriers are created by loss of oxygen at high temperatures, are retained in the sample quenched to room temperature, and may be trapped and subsequently released under the action of a *dc* bias. The driving force for the conductivity changes is activation of trap states at the sample surface through some combination of steps 2, 3 and 5.

In the case of acceptor-doped materials, the driving force is also activation of the trap states but this leads, by a more complex process, to an increase in concentration of holes that are the principal current carriers: holes are created by ionisation of underbonded oxygens surrounding the acceptor dopants and the resulting ionised electrons are trapped at surface states.^[1-4]

These various phenomena are associated with the existence of oxygen, especially at the ceramic surface, in a range of anionic states. Although the O^{2-} state is commonly regarded as the usual state in oxides, the electron affinity of oxygen in the gas phase, whilst negative for formation of O^- from O , is positive for addition of a second electron to form O^{2-} . Thus, the O^{2-} ion is unstable in the gas phase and is stabilised in the solid state only by the increased lattice energy of oxides based on the O^{2-} ion compared with that of (hypothetical) structures containing the O^- ion. We believe that partially-reduced oxygen species arise in structures where the oxygens are somewhat underbonded and there is insufficient lattice energy to fully stabilise them as O^{2-} species. Thus, acceptor-dopants in $BaTiO_3$, such as Mg^{2+} , Zn^{2+} and Ca^{2+} substituted for Ti^{4+} , cause the surrounding oxygens in the octahedral complex to be significantly underbonded. Oxygens at sample surfaces are also likely to be in various charge

states since they are not surrounded fully by a cationic coordination sphere and under appropriate conditions may act as either electron traps or electron donors. Recent studies on oxygen surface exchange kinetics of erbia-stabilised bismuth oxide^[17] have shown the existence of oxygen species with intermediate oxidation states at sample surfaces. It seems likely, therefore, that the occurrence of oxygen species in various states of reduction is widespread in both bulk materials and at surfaces.

Considering cation valencies alone, the Mn dopant should be regarded as either an acceptor ($\text{Mn}^{2+,3+}$) or an isovalent (Mn^{4+}) dopant. However, the loss of oxygen in air at 1400°C is an additional process that can occur in both undoped and doped BaTiO_3 leading to electron injection and *n*-type behaviour. There is no inconsistency therefore, between doping BaTiO_3 with lower valence (acceptor) Mn and achieving *n*-type behaviour by means of the O_2 loss mechanism.

Acknowledgements

We thank EPSRC for financial support. MP, HB, EC thank the “Bancaja-Universitat Jaume I”- project No. P1 1B2010-22 for financial support. MP thanks Universitat Jaume I for a fellowship (CONT/2011/08).

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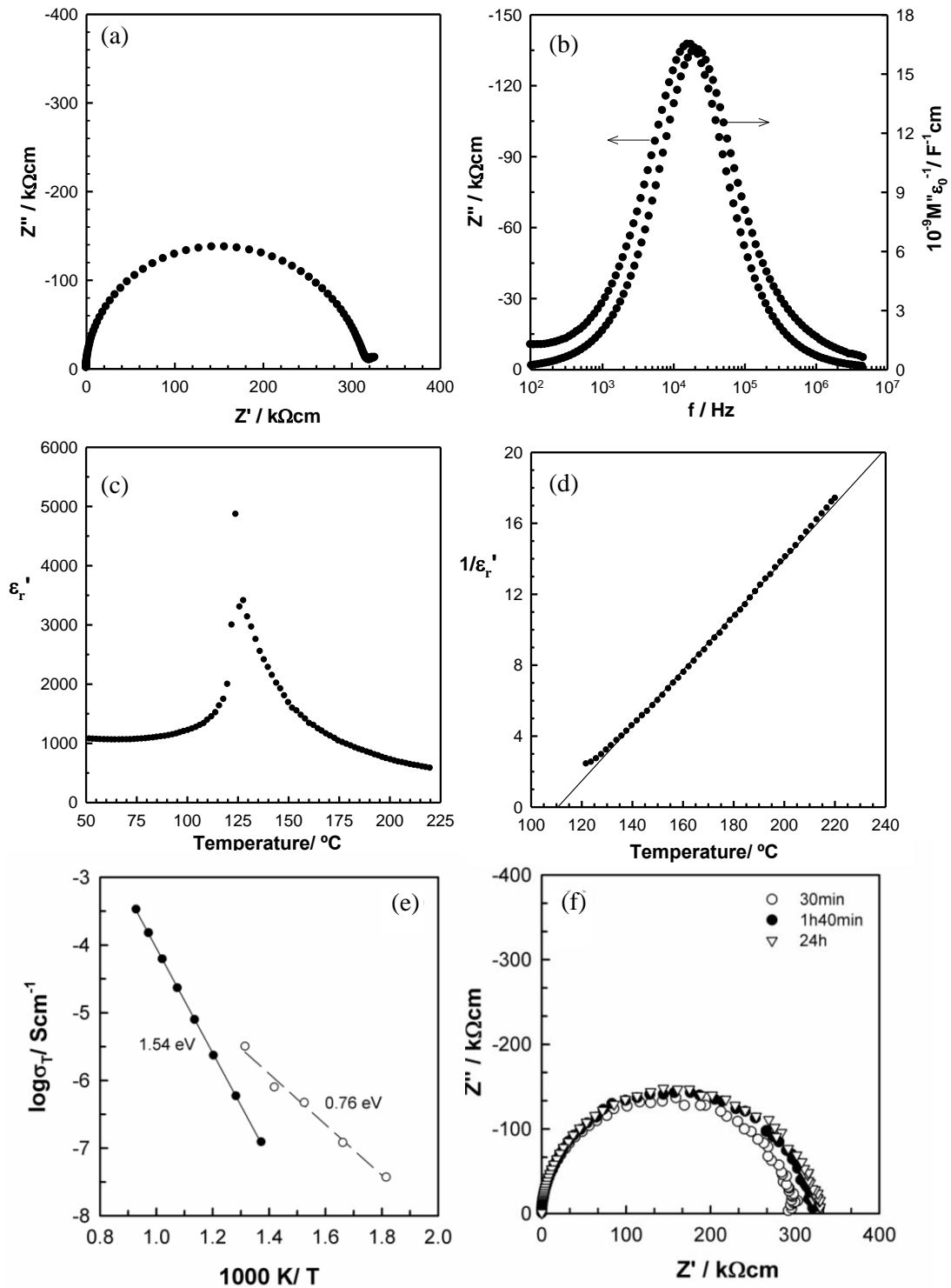


Fig 1. (a) Impedance complex plane plot, Z^* , (b) Z''/M'' spectroscopic plots at 488 °C, (c) relative permittivity, ϵ_r' , data as a function of temperature, (d) Curie-Weiss plot for the sample sintered at 1400°C and quenched in liquid nitrogen; (e) Arrhenius plots for the slow cooled (●) and quenched sample measured in N_2 (○), activation energy is shown beside each data set; (f) Impedance complex plane plot, Z^* at 488°C, for the sample sintered at 1400°C, quenched in liquid nitrogen and measured after different time lapses. Note: measurements (a,b,f) were done in N_2 .

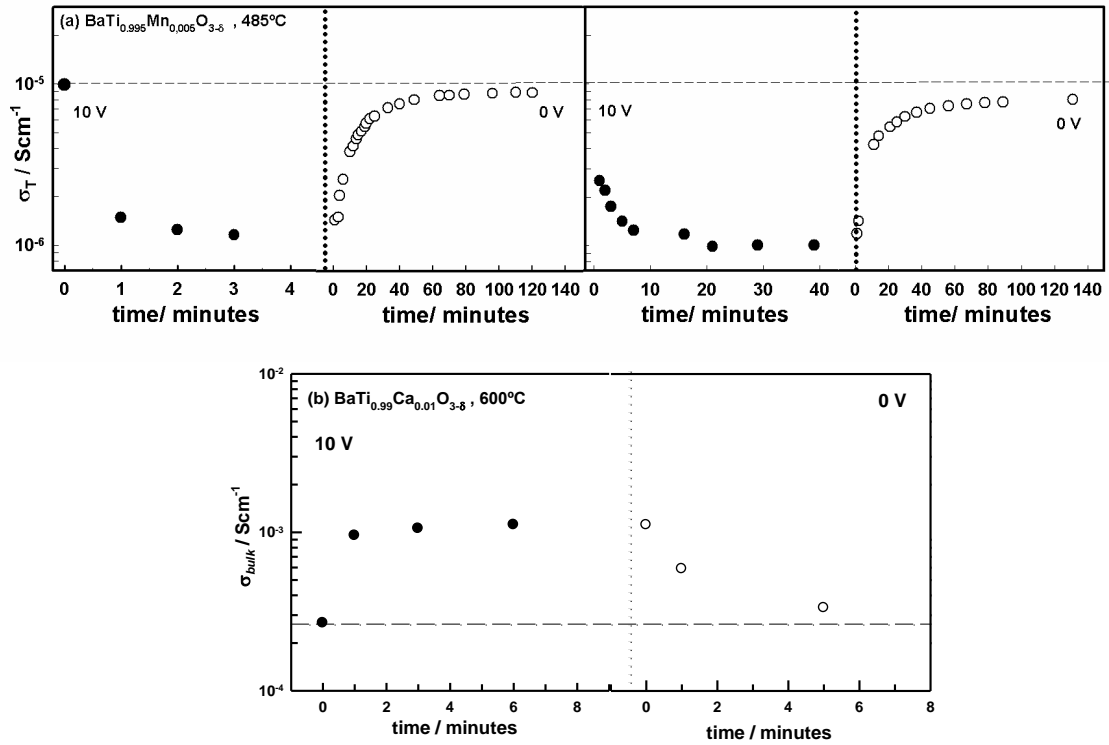


Fig 2. (a) Total conductivity at 485°C for BTM005 and (b) *bulk* conductivity at 600°C for $\text{BaTi}_{0.99}\text{Ca}_{0.01}\text{O}_{2.99}$ ^[3] after applying and removing a *dc* bias of 10V at different times in N_2 .

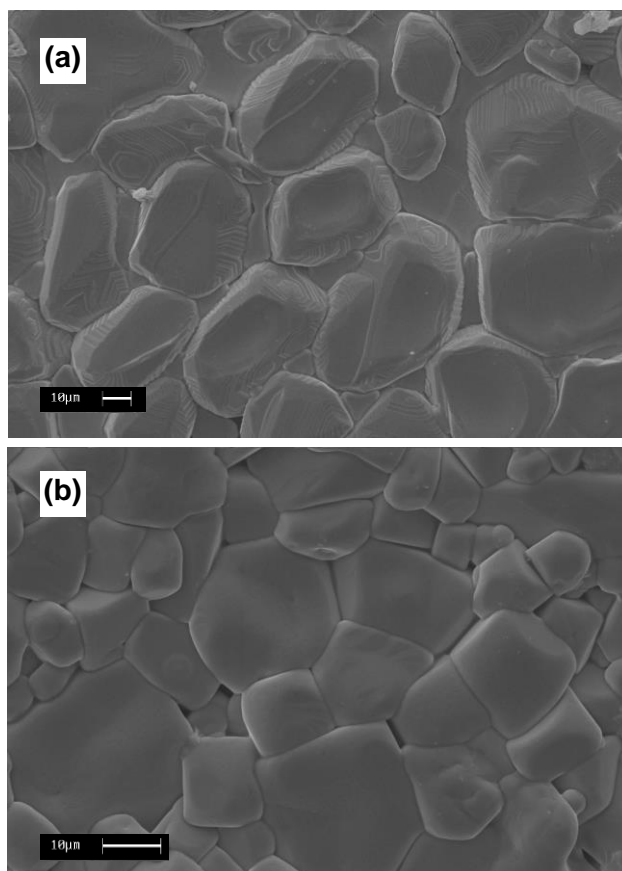


Fig 3. SEM of the pellet surface of (a) $\text{BaTi}_{0.995}\text{Mn}_{0.005}\text{O}_{3-\delta}$ and (b) $\text{BaTi}_{0.99}\text{Ca}_{0.01}\text{O}_{2.99}$.

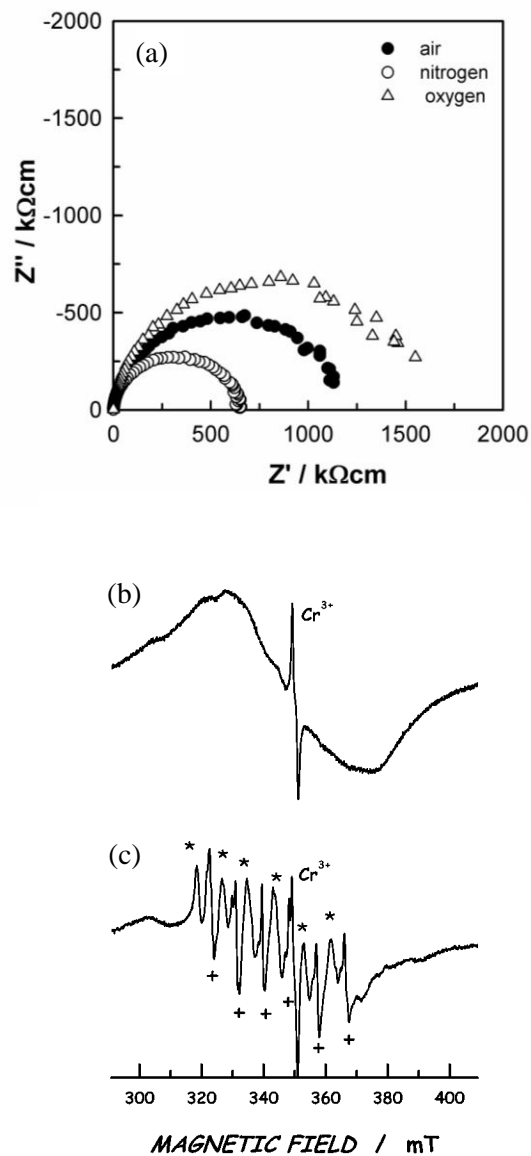


Fig 4. (a) Impedance complex plane plot, Z^* at 490°C, for the partial reoxidised sample (steady state), measured in different atmospheres; EPR spectra for the slow cooled (b) and quenched sample (c) at room temperature.