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Sintering and properties of highly donor-doped barium titanate ceramics

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The electrical properties of donor (La^{3+}) doped $BaTiO_3$ samples with a donor concentration in the range from 0.3 to 1.5 mol.% of La were studied. Samples were sintered at a low partial pressure of oxygen in order to facilitate anomalous grain growth and donor incorporation. In order to optimise the PTCR anomaly, the samples were annealed in air at 1100 °C. Results show that with the use of a specific sintering profile PTCR ceramics containing an amount of donor dopant >0.3 mol.%, can be prepared. Heavily doped samples which do not exhibit anomalous grain growth show a core shell structure.

1. Introduction

Donor-doped $BaTiO_3$ can be obtained through the solid state reaction of intimately mixed oxides. In this way, donor-doped ceramics can be obtained with a dopant content dependent on its solubility in the $BaTiO_3$ lattice. In such a solid solution the electron compensation of dopants is favoured at low partial pressures of oxygen. That is to say, the solid-state reaction or the already formed solid solution will result in the formation of semiconducting $BaTiO_3$ during treatment under low oxygen partial pressures. During this process a semiconducting donor-doped $BaTiO_3$ is formed which contains a dopant amount equal to the solubility limit of the corresponding dopant in $BaTiO_3$. These samples, when treated at high oxygen partial pressures, can be reoxidized and the insulating form of donor-doped $BaTiO_3$ is obtained [1]. According to defect chemistry based on electrical measurements it was shown that at lower temperatures and high oxygen partial pressures the insulating form is stable (vacancy compensation of dopants), while at higher temperatures and low oxygen partial pressures the semiconducting form, where electron compensation of dopants occurs, is stable (electron compensation of dopants). The transition temperature between the two phases is at roughly 1340 °C in an oxygen atmosphere and 1220 °C in air, and is donor dopant concentration dependent [2].

A consequence of these results is the fact that the synthesis of a semiconducting solid solution of donor-doped $BaTiO_3$ cannot be performed below 1220 °C in air by solid state reaction. However, it can be performed via anomalous grain growth. Thus, via anomalous grain growth the reduced form of donor-doped $BaTiO_3$ can be formed under thermodynamic conditions where it is otherwise not stable in air below 1200 °C [3, 4]. On the other hand, pure $BaTiO_3$ can be made semiconducting by heating it in a strongly reducing atmosphere.

It should be noted that, due to the large number of oxygen vacancies present in the $BaTiO_3$ lattice after reduction, it can be very easily reoxidised, and that, the presence of oxygen vacancies enhances the lattice diffusion of any oxygen absorbed at the interface, which would otherwise create the surface states required for the PTCR affect. In addition, when complete reoxidation of the grains during cooling is prevented and a thin layer containing acceptor states is formed, the PTCR effect could also be induced in the undoped reduced samples of $BaTiO_3$. Reduced semiconducting $BaTiO_3$ samples heated and cooled in the presence of a fluorine containing atmosphere meet these conditions. Fluorine adsorbed at the interface forms acceptor sates and prevents the reoxidation of reduced $BaTiO_3$ when cooled in air after being reduced in a reducing atmosphere [5]. During anomalous grain growth in the presence of liquid phase a semiconducting reduced form of donor-doped $BaTiO_3$ can be obtained. The semiconducting $BaTiO_3$ growing out from the liquid phase contains relatively small amounts of oxygen vacancies and can therefore adsorb oxygen during cooling forming acceptor states and/or creating cation vacancies. Foreign ions (donors) in doped $BaTiO_3$ are partially compensated for by cation vacancies and strongly suppress oxygen ion diffusion because of the absence of oxygen vacancies. The ambipolar diffusion coefficient of oxygen is a function of the concentration of the donor and the concentration and ambipolar diffusion coefficients of the charged defects. This has a consequence that the oxygen diffusion can be in some instances completely blocked [6]. Thus, in this case the oxygen atoms might be adsorbed at the grain surfaces and create the surface acceptor states needed for the PTCR anomaly.

It appears therefore, justifiable in asserting that the primary reason for donor dopant incorporation in $BaTiO_3$ is not to achieve a semiconducting phase but primarily to obtain a phase which is also highly resistant to reoxidation, making it possible to engineer the surface acceptor states and/or the PTCR effect. Taking into account the above discussion, it can be supposed that there is no reasonable objection to preparing PTCR ceramics over the whole donor concentration range where anomalous grain growth occcurs. Donor-doped $BaTiO_3$ growing out from the liquid phase during anomalous grain growth is semiconducting, resistant to the global reoxidation, and is therefore suitable for engineering the density of the acceptor surface states. At a lower oxygen pressure during sintering, the anomalous grain growth associated with donor dopant incorporation in the presence of the liquid phase takes place even if the samples contain a dopant amount which is above the critical concentration of samples usually sintered in air [3].

Once highly donor-doped semiconducting samples >0.3 mol.% are formed via anomalous grain growth, the surface acceptor state density must be optimised in order to tailor the PTCR effect. The purpose of the present paper is to study the effect of a high donor concentrations on the PTCR anomaly in $BaTiO_3$.

2. Experimental procedure

2.1. Powder preparation

Donor (La) doped $BaTiO_3$ was prepared by using $BaTiO_3$ (TRANSELCO, lot 219-9, lot 950097) with the addition of 1.74 wt. % excess of TiO_2 (TRANSELCO, lot 77295) and 0.3, 0.4, 0.5, 0.8, 1.0 and 1.5 mol. % of La respectively (Johnson Matthey, lot 530433). Weighed amounts of the starting oxides were homogenised in an agate planetary ball mill with alcohol for 3 hours.

2.2. Sintering and reoxidation conditions

Pellets with dimension $\phi = 12$ mm, $h = 3$ mm were prepared, placed on platinum supports in an alumina boat and sintered in a tube furnace at 1380 °C for 2 hours in nitrogen (99.9% pure). The samples were sintered with the same heating and cooling rate of about 20 °C/min. Reoxidation was carried out at 1150 °C in air with a flow rate of 300 cm^3/min. The duration of the reoxidation (1, 3 and 24 hours) was varied to change the surface acceptor state density. The reoxidation of some heavily doped and reduced samples was investigated by TGA analysis.

2.3. Electrical testing

For electrical measurements, the surfaces of sintered specimens were painted with In-Ga paste to provide ohmic contact. The temperature dependence of resistance and of capacitance at 100 kHz was measured with a multimeter (HEAWLETT-PACKARD 3457A) in a temperature-programmable furnace at a heating rate of 3 °C/min from 25 °C to 300 °C.

Impedance as a function of frequency in the range from 5 Hz to 13 MHz at 250 °C, was measured using an impedance analyser (HEWLETT-PACKARD 4092A) to obtain the sample grain resistivity.

The key parameters characterising the PTCR effect including the height of the potential barrier ($e\phi$) and the surface acceptor states density (N_s) were estimated according references [7].

3. Results and discussion

Fig. 1 shows the DC resistivity vs. the temperature characteristics of donor-doped $BaTiO_3$ sintered in air (Fig. 1a) and nitrogen (Fig. 1b). It can be seen that of all the tested samples only the 0.3 mol.sintering in air. On the other hand, when the samples were sintered in nitrogen and the partial pressure of oxygen was strongly decreased, the PTCR anomaly was also exhibited by the more highly donor-doped samples, i.e. 0.4 and 0.5 mol. % doped samples, while 0.6, 0.8, 1.0 and 1.5 mol. % doped samples showed NTCR characteristics.

In general the PTCR anomaly in donor-doped $BaTiO_3$ was exhibited by samples which developed anomalous grain growth during sintering, i.e. a microstructure which consists of semiconducting and reoxidation resistant grains.

Such semiconducting grains are appropriate for engineering the potential barrier by forming acceptor states at the grain boundaries: i) by adsorbing atoms which exhibit sufficient electron affinity and attract delocalized electrons, such as for example oxygen and/or halogen atoms [8], ii) by the creation of cation vacancies [2] or iii) by the segregation of transition elements, as for example Mn^{3+}, Cr^{3+} and Fe^{3+} at the grain boundary [9].

These various acceptors can function as acceptors individually or in combination, if present simultaneously, leading to a PTCR effect.

The thermodynamic conditions under which anomalous grain growth in donor-doped $BaTiO_3$ occurs, associated with oxygen release, are given by the relation $\ln P = A/C_0 + B$ [3]. Where $A = S_0\gamma$ ($S_0 =$ critical surface area, $\gamma =$ specific surface energy) and $B = G_{ox}$ ($G_{ox} =$ free energy associated with oxygen release during anomalous grain growth and donor dopant incorporation) and C_0 is the critical donor dopant concentration which blocks anomalous grain growth.

Thus the critical donor dopand concentration which blocks anomalous grain growth, at a constant critical specific surface S_0, can be increased when the partial pressure of oxygen during anomalous grain growth is decreased.

The anomalous grain growth, taking place at lower oxygen partial pressures will therefore proceed at a higher critical donor concentration (C_0), Fig. 1b. Samples sintered at a lower oxygen partial pressure and subjected to anomalous grain growth show a PTCR effect, also demonstrating that a relatively low concentration of oxygen during heat treatment, i.e. 0.01 vol. %., is enough to develop the necessary surface acceptor states.

Samples with an amount of donor dopant ≥ 0.6 mol. % proved to be exceptional, with the anomalous grain growth being blocked. These samples contain an amount of dopant within the concentration range where anomalous grain growth does not occur. Therefore in these samples anomalous grain growth cannot be expected in spite of the low oxygen partial pressure applied during heating, and normal grain growth via solid state diffusion occurs [10].

The increase in the average grain size after sintering in these heavily doped samples via normal grain growth

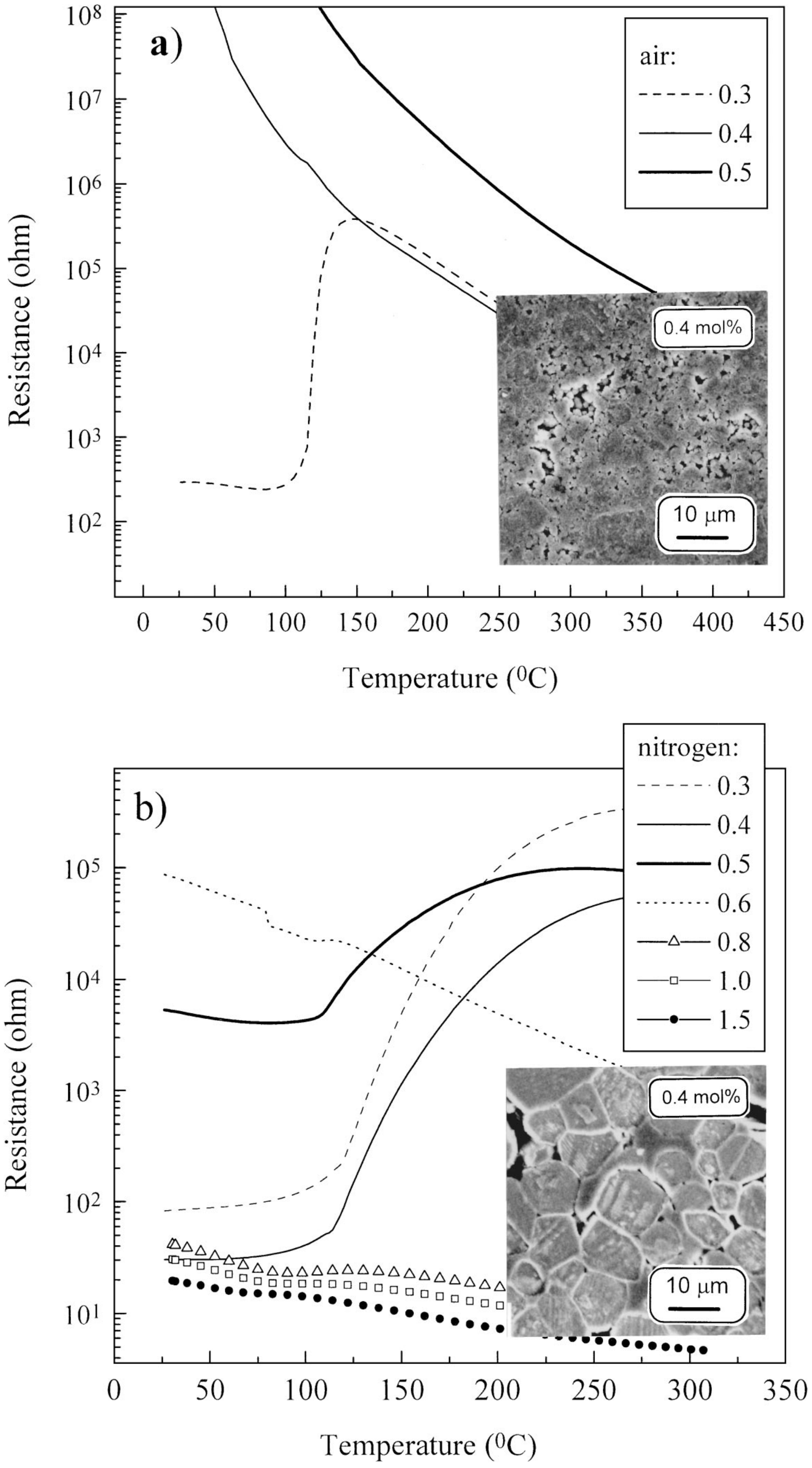


Figure 1 (a) Resistance vs. temperature for 0.3, 0.4, 0.5 mol.% doped samples sintered in air, (b) resistance vs. temperature for 0.3, 0.4, 0.5, 0.6, 0.8, 1.0 and 1.5 mol.% doped samples sintered in nitrogen (99.9% pure).

was limited to less than about 2 μm, Fig. 2. These samples, however, after sintering at 1400 °C in nitrogen were grey/blue in colour and exhibited a low electrical resistivity of about 20 Ω cm and showed NTCR behaviour over the whole measured temperature range, Fig. 1b.

Detailed TEM analysis of such fine-grained, highly La-doped $BaTiO_3$ samples revealed, that all the La added was incorporated into the $BaTiO_3$ matrix grains. Microstructures of these samples were composed of doped $BaTiO_3$ matrix grains and a Ti-rich phase, mainly $Ba_6Ti_{17}O_{40}$, which was crystallized from liquid phase during cooling of the samples. Any "free" La_2O_3 or La-rich phases have never been observed, suggesting complete dissolution of added La in the matrix grains. However, the doped $BaTiO_3$ matrix grains show a typical "core-shell" structure, indicating nonhomogeneous distribution of the dopant [11–13]. Because of very

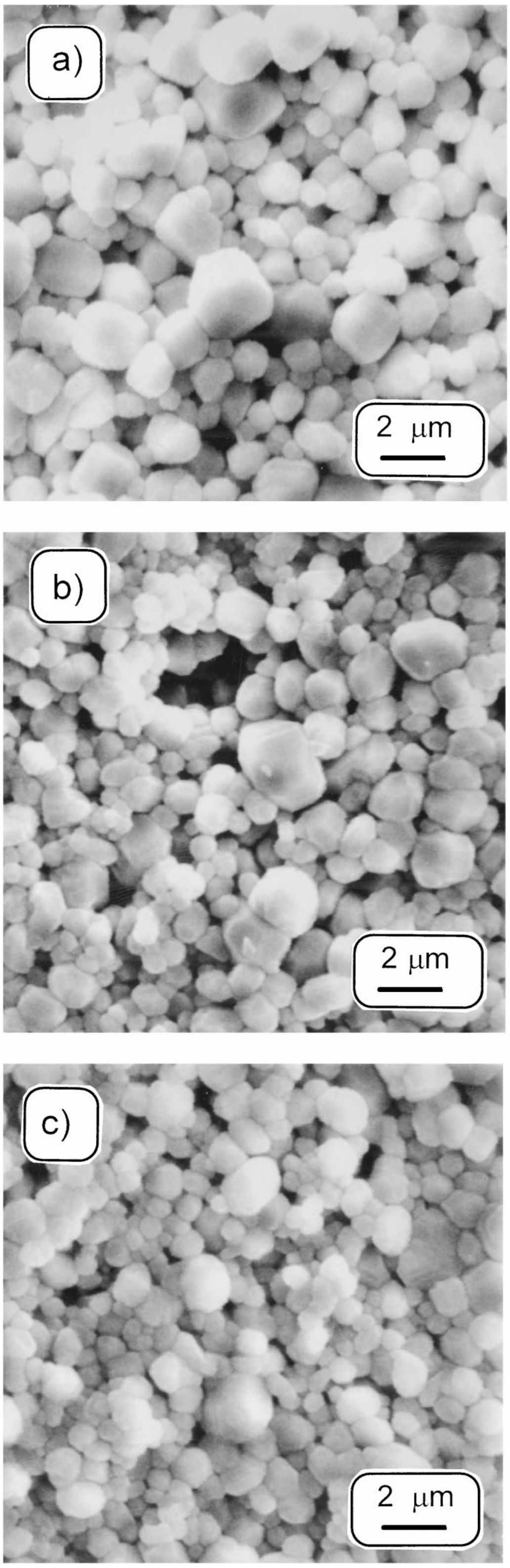


Figure 2 (a) Microstructure of 0.6 mol. % doped samples sintered in air, (b) microstructure of 0.8 mol. % doped samples sintered in nitrogen, (c) microstructure of 1.0 mol. % doped samples sintered in nitrogen.

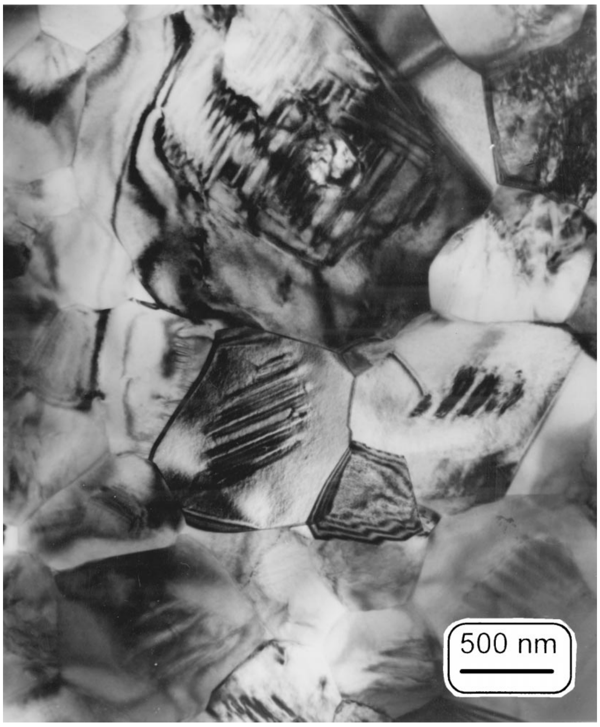


Figure 3 TEM image of sample doped with 1.5 mol. % La sintered in air at 1380 °C, showing a typical core shell structure. Image was taken at a temperature of approximately 90 °C.

low diffusivity of donor dopants in the $BaTiO_3$ lattice [11], the dopant is incorporated into the matrix grains preferentially during grain growth in the presence of the reactive liquid phase with the "dissolution-precipitation" mechanism [12]. Thus, the grain core is nearly free of any dopant, while the grain shell, obtained by grain growth, is highly doped. Due to different dopant concentrations, different parts of the grain (grain core-grain shell) display different Curie temperatures. It is known that with incorporation of La into the $BaTiO_3$ structure, the Curie temperature is decreased by more than 20 °C per mol. % La [14]. The undoped grain core will have the T_C of pure $BaTiO_3$ (~128 °C), while the doped grain shell will have a much lower T_C. If the sample's temperature was between the T_C of the core and the T_C of the shell, the "core-shell" structured grain would be characterized with a tetragonal core and a cubic shell. Fig. 3 shows a TEM micrograph of the microstructure of the 1.5 mol. % La-doped $BaTiO_3$ sample which was heated in a TEM to approximately 90 °C. Ferroelectric domain boundaries are visible in the cores of the matrix grains, while grain shells are absent from the ferroelectric domain boundaries, showing tetragonal grain cores and cubic grain shells.

The room temperature resistivity of the highly La-doped samples after sintering at low oxygen partial pressures were of the order of about 20 Ω cm indicating a free-electron concentration (n) of about 10^{18} /cm^3. The defect structure of the grains is different in the undoped grain core than in the highly La-doped grain shell. In the grain core, free electrons appear mainly as a consequence of oxygen deficiency, according to $n = [V_{\mathrm{O}}^{\bullet}] + 2[V_{\mathrm{O}}^{\bullet\bullet}]$, where $[V_{\mathrm{O}}^{\bullet}]$ is the concentration of singly ionized oxygen vacancies and $[V_{\mathrm{O}}^{\bullet\bullet}]$ is the concentration of doubly ionized oxygen vacancies. In the grain shell, the appearance of free electrons is additionally increased due to partial electronic compensation of the donor charge of La^{3+} incorporated in the $BaTiO_3$ structure at the Ba^{2+} sites. However, the majority of donors are compensated for by the formation of ionized cation vacancies. It is known [15–17] that equilibrium cation vacancies in donor-doped $BaTiO_3$ are Ti vacancies (V_{Ti}''''). Thus, the electroneutrality condition for the doped grain shell would be:

$$n + 4[V_{Ti}''''] = [La_{Ba}^{\bullet}] + [V_{O}^{\bullet}] + 2[V_{O}^{\bullet\bullet}]$$

Because of the relatively high concentration of oxygen vacancies present in the reduced $BaTiO_3$ grains, any O_2 adsorbed at the interface needed to form surface states for the PTCR effect, is eliminated via lattice diffusion, resulting in the NTCR character of these semiconducting grains after cooling in nitrogen at a very low oxygen partial pressure, Fig. 1b.

When the reduced, i.e. sintered in nitrogen, highly doped samples were treated in air complete reoxidation of the sample takes place. A relatively high anion and cation vacancy concentration enhances the reoxidation of doped $BaTiO_3$. After heat treatment in air the samples were yellow and highly resistant. Fig. 4 shows a typical TG analysis of oxygen uptake during the heat treatment in air of heavily doped samples. The weight gain of oxygen during reoxidation is higher for the more heavily doped samples, in agreement with general observations [1]. If no dopants were incorporated in the $BaTiO_3$, the weight gain would be the same for all samples.

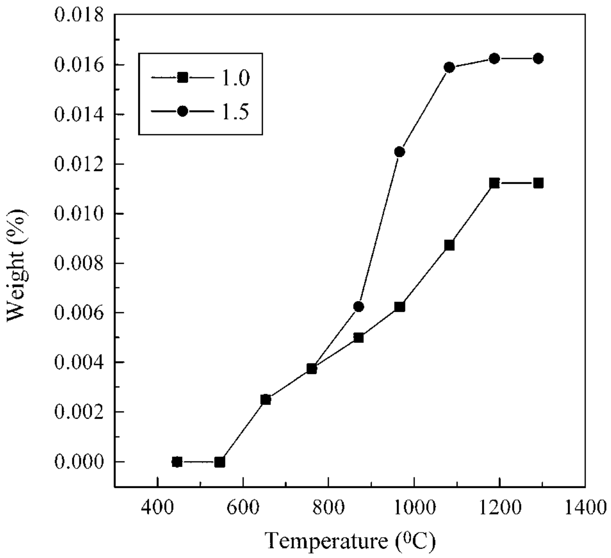


Figure 4 TGA analyses of reduced $BaTiO_3$ samples doped with 1.0 and 1.5 mol. % La.

In contrast, the grains which develop anomalous grain growth are very resistant to reoxidation. No changes can be detected when TG analysis was performed, however, in spite of this a strong resistivity increase in the samples can be noted after annealing at 1100 °C in air, Fig. 5.

During oxidation, cation vacancies are initially formed at the grain boundaries and the surfaces exposed to air. Their relative distribution is determined by the doping level, temperature and oxygen activity. As the temperature is lowered or the oxygen activity increased, the concentration of cation vacancies increases. These defects diffuse inwards to establish a new defect equilibrium. The reoxidation of reduced forms of donor-doped $BaTiO_3$ can be extremely slow for kinetic reasons [2, 6].

The more the samples are prone to anomalous grain growth and the more anomalous grains are developed, which is accompanied by donor incorporation, a small oxygen vacancy concentration and a small grain boundary surface, the less are they prone to reoxidation. Samples doped with 0.3 and 0.4 mol. % developed anomalous grain growth to the greatest extent. These grains are resistant to reoxidation and during sintering and/or cooling in a nitrogen atmosphere (0.01 vol. % O_2) develop surface acceptor states via oxygen adsorption and/or the formation of cation vacancies, as required for the PTCR anomaly.

In order to optimise the PTCR effect the surface acceptor state density must be optimised. To increase the number of surface acceptor states, the samples must be treated under thermodynamic conditions where surface acceptor states will be created. We believe that

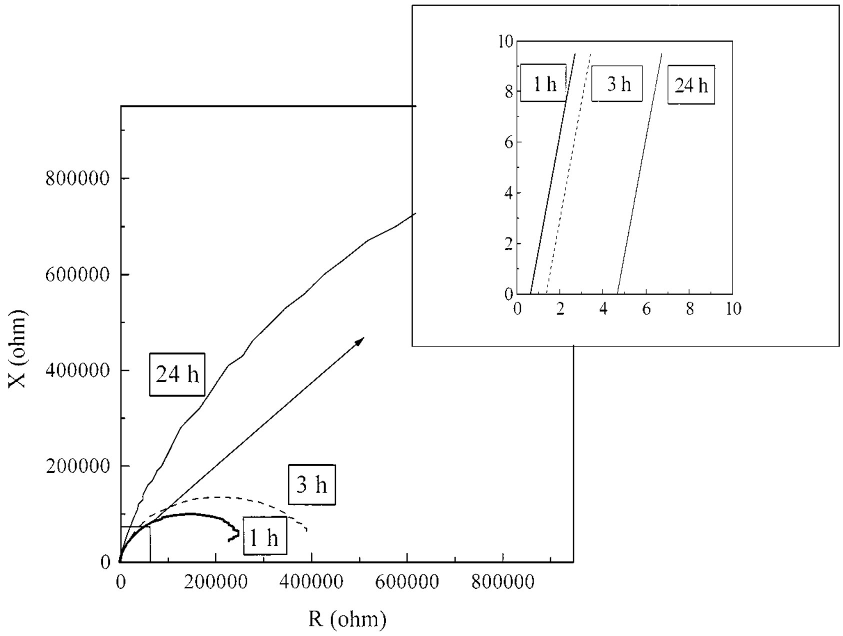


Figure 5 Complex impedance spectra of 0.4 mol. % doped samples measured at 250 °C.

TABLE I Calculated parameters of reoxidized 0.3 and 0.4 mol.% La-doped samples with dependence on the reoxidation time

Content of La (mol.%)	Reox. time (h)	$D(\mu\text{m})$	A/h (cm)	$R_{\max}$ (Ω cm)	R_G (Ω cm)	N_s (1/cm^2)	N_d (1/cm^3)	$e\phi$ (eV)
0.3	1	11	0.044	8.8×10^6	10.2	2.4×10^{13}	6.1×10^{18}	0.43
0.3	3	11	0.047	1.3×10^7	13.2	5×10^{13}	5×10^{18}	0.90
0.3	24	11	0.043	1.4×10^7	17.2	6×10^{13}	3.8×10^{18}	0.97
0.4	1	7	0.039	3.5×10^6	8.3	7.4×10^{13}	7.5×10^{18}	0.90
0.4	3	7	0.049	4.9×10^6	10.4	8.3×10^{13}	6×10^{18}	0.92
0.4	24	7	0.038	1.8×10^7	16.2	9.6×10^{13}	4×10^{18}	0.94

besides the adsorption of oxygen atoms, the cation vacancies formed during treatment of the samples under the appropriate thermodynamic conditions (in air below 1220 °C) are also important for optimisation of the surface acceptor state density [2].

After the reoxidation of, for example, 0.4 mol. % samples in which anomalous growth of donor-doped grains developed, the grain resistance after 24 hours of reoxidation changes by an order of magnitude, while the grain boundary resistance drastically increases, Fig. 5, due to the increase of the depletion layer thickness (δ), Table I. The diffusion of cation vacancies initially formed at the interfaces in these grains is extremely slow, as is the increase in the depletion layer thickness.

In general the optimisation of the PTCR anomaly in donor-doped $BaTiO_3$ is associated with the correlation between engineering the surface acceptor state density and the spontaneous polarisation of $BaTiO_3$.

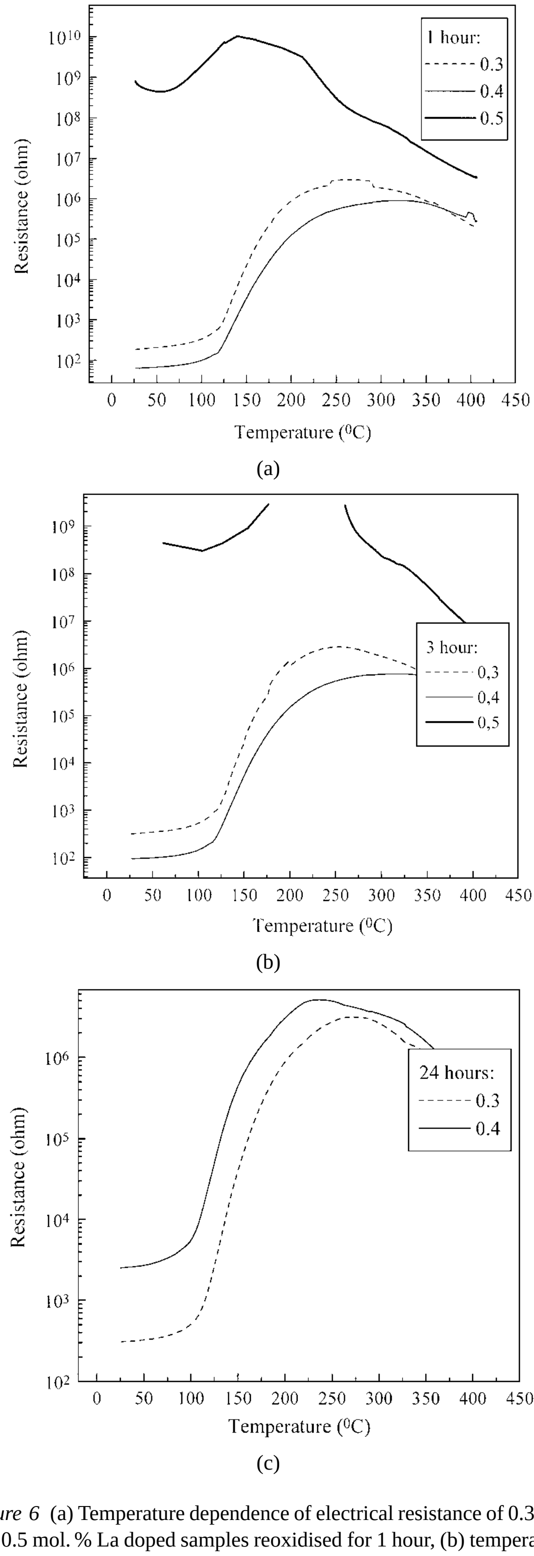
According to Jonker [18], in $BaTiO_3$ the difference in polarisation direction and consequently the net polarisation perpendicular to the grain boundaries associated with surface changes at the grain boundary, fills up the depletion layer either completely or partially.

However, since the surface charges at the grain boundary created by spontaneous polarisation P_s of $BaTiO_3$ is limited, the optimisation of the PTCR anomaly will be the highest when the induced acceptor state density is close to this limiting value, otherwise the cold resistivity, i.e. $\rho_{\min}$ will deviate significantly from that of the donor-doped grains and will increase very quickly with increasing N_s [19] .

Fig. 6 shows the temperature dependence of electrical resistivity of the reoxidized samples. The 0.3 and 0.4 doped samples after reoxidation for 1, 3 and 24 hours show some changes. Particularly for longer times of reoxidation the cold resistivity increases. However, drastic changes were noted for more highly doped samples where anomalous grain growth was not developed during sintering. In these samples, which are prone to reoxidation, the resistivity drastically increases.

So the samples doped with 0.6, 0.8, 1.0 and 1.5 mol. % of dopant after 1 h of heating in air were highly resistive (>107 Ω cm) while the other 0.3, 0.4 and 0.5 mol. % La doped samples showed remarkable changes. The cold resistance increased and the temperature of the PTCR effect increased as well; particularly with 0.5 mol. % La doped samples, where anomalous grain growth was not well developed, after 24 h of reoxidation in air they exhibited resistivity $>10^7$ Ω.

The temperature dependence of relative permitivity ε_r for the samples sintered in nitrogen and then reoxidized is shown in Fig. 7. After reoxidation the



(a)

(b)

(c)

Figure 6 (a) Temperature dependence of electrical resistance of 0.3, 0.4 and 0.5 mol. % La doped samples reoxidised for 1 hour, (b) temperature dependence of electrical resistance of 0.3, 0.4 and 0.5 mol. % La doped samples reoxidised for 3 hours, (c) temperature dependence of electrical resistance of 0.3 and 0.4 mol. % La doped samples reoxidised for 24 hours.

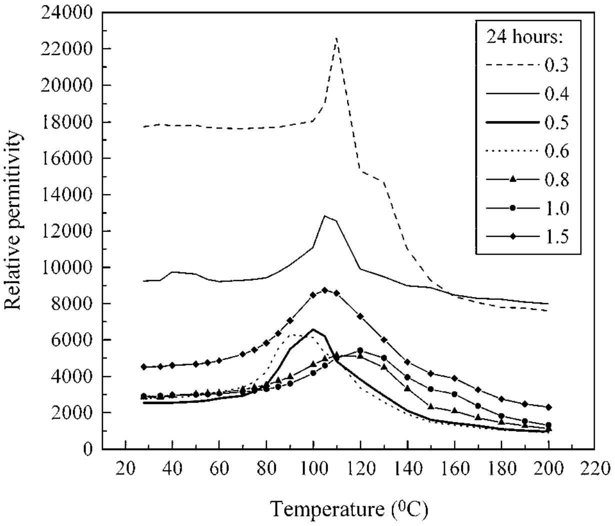


Figure 7 The temperature dependence of relative permitivity as a function of donor concentration in reoxidised samples.

0.5, 0.6, 1.0 and 1.5 mol. % La doped samples became isolators with $R_{\mathrm{DC}} > 10^7\ \Omega$ and exhibited a room temperature relative permeability close to that of pure BaTiO$_3$. On the other hand, the 0.3 and 0.4 mol. % La donor-doped samples, which exhibited the PTCR effect, showed considerably higher relative permeability, which is due to the presence of the depletion layer. From elementary dielectric theory and by assuming the brick wall model for the ceramic microstructure, the measured relative permitivity of the specimen ε_{r} is given by $\varepsilon_{\mathrm{r}} = 4\varepsilon_{\mathrm{a}} N_{\mathrm{s}}/DN_{\mathrm{d}}$, where ε_{a} is the dielectric constant of the material, D the average grain size, N_{s} the surface acceptor state density, N_{d} the concentration of charge carriers and $\delta = N_{\mathrm{s}}/2N_{\mathrm{d}}$ is the thickness of the depletion layer.

In Table I. the charge carrier concentration N_{d} and surface acceptor state density N_{s} are shown for 0.3 and 0.4 mol. % doped samples.

The acceptor state density increases during the reoxidation of the samples, however the charge carrier density decreases, Table I. Thus, during longer times of reoxidation the cation vacancy concentration in semiconducting donor-doped grains increases forming a new defect structure equilibrium. As a consequence of that the free charge carrier concentration decreases. After reoxidation for 1 h the $\delta = N_{\mathrm{s}}/2N_{\mathrm{d}}$ is relatively short $\approx 0.01\ \mu$m, i.e. below the thickness of the depletion layer of 0.1 μm usually observed in PTCR ceramics. Since these samples were previously sintered in nitrogen at a low oxygen partial pressure, it takes a relatively long time to increase the thickness of the depletion layer via the formation of cation vacancies in air during reoxidation of donor-doped BaTiO$_3$ with donor concentrations in the range where the diffusion of oxygen vacancies is strongly inhibited.

After a longer reoxidation time the acceptor state density increases and can be not completely compensated for by the spontaneous polarisation below T_{C}. In that case ρ_{min} is governed by the grain boundary resistivity.

4. Conclusions

This study has confirmed that BaTiO$_3$-based PTCR ceramics can be prepared with sintering in the atmosphere containing low concentration of oxygen (0.01 vol. % O$_2$) across the whole concentration range of donor-doped samples where the anomalous grain growth is found to occur.

Samples where the anomalous grain growth was blocked and normal grain growth takes place are very prone to reoxidation and exhibit a core-shell microstructure.

A oxygen concentration as low as 0.01 vol. % is sufficient for creating enough surface acceptor states in donor-doped BaTiO$_3$ for the PTCR anomaly to occur.

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