Journal of the European Ceramic Society 21 (2001) 1899–1903
www.elsevier.com/locate/jeurceramsoc

Electrical properties of undoped $BaTiO_3$ ceramics annealed in a fluorine containing atmosphere

Nina Ule *, Darko Makovec, Miha Drofenik

Department of Ceramics, Jožef Stefan Institute, Jamova 39, Ljubljana, Slovenia

Received 4 September 2000; received in revised form 23 October 2000; accepted 30 October 2000

Abstract

Air-sintered and atmospherically reduced $BaTiO_3$ ceramics were fluorinated by the introduction of a CF_3CH_2OH fluorination agent into a hot furnace using a supporting gas: either pure nitrogen or nitrogen containing a low concentration of oxygen. The nitrogen-supported fluorination resulted in a decrease in the resistivity of the insulating air-sintered samples to semiconducting values, primarily due to atmospheric reduction. When air-sintered samples were fluorinated using oxygen-containing nitrogen as the supporting gas, their resistivity remained very high. The exposure of fluorinated samples to air at high temperatures (1200°C) resulted in a decrease of their resistivity and a remarkable PTCR effect. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: $BaTiO_3$ and titanates; Grain boundaries; Thermistors

1. Introduction

The PTCR effect in $BaTiO_3$ ceramics originates in the temperature-dependent potential barriers at grain boundaries, which are formed by the creation of acceptor states at the surfaces of *n*-type semiconducting, ferroelectric grains.[1] Normally, semiconducting $BaTiO_3$ is formed by donor doping. By liquid-phase sintering $BaTiO_3$ with the addition of a low concentration of donor dopant (for example below ~ 0.3 mol% La^{3+}) in air, the semiconducting form of donor-doped $BaTiO_3$ ($Ba_{1-x}La_xTi^{4+}_{1-x}Ti^{3+}_xO_3$) results via a process of exaggerated (anomal) grain growth.[2] Exaggeratedly grown grains of such ceramics are resistant towards re-oxidation, allowing preferential re-oxidation of the grain boundaries.[3] Thus, acceptor states, adsorbed oxygen[4] and/or intrinsic cation vacancies[5] are formed at the grain boundaries with controlled reoxidation resulting in the formation of the potential barriers.

Undoped $BaTiO_3$ can also be prepared in a semiconducting form with atmospheric reduction ($BaTi^{4+}_{1-y}Ti^{3+}_yO_{3-y/2}(V_O^{\bullet\bullet})_{y/2}$). However, atmospherically reduced $BaTiO_3$ is very prone to re-oxidation due to the presence of oxygen vacancies in its structure. Consequently, preferential re-oxidation of grain boundaries is very difficult. The PTCR effect in atmospherically reduced $BaTiO_3$ is practically impossible to obtain by controlled re-oxidation. Nevertheless, Alles et al.[6] have reported that the PTCR effect can be provoked in such undoped, atmospherically reduced $BaTiO_3$, when it is exposed to a fluorine-containing atmosphere. The phenomenon was explained by the adsorption of fluorine acceptors at grain boundaries. The fluorine (F^{1-}) incorporated into the $BaTiO_3$ perovskite structure in the oxygen (O^{2-}) sub-lattice would act as the donor dopant.[7] Substitution of O^{2-} ions with F^{1-} ions is to be expected since both ions have similar ionic radii.

In the present work, the electrical conductivity of $BaTiO_3$ ceramics exposed to a fluorine-containing atmosphere has been studied. The experimental conditions were different to those used by Alles et al.,[6] leading to a change in the influence of the fluorination on the electrical properties of $BaTiO_3$ ceramics.

2. Experimental

Pellets of $BaTiO_3$ ceramics (~8 mm in diameter and ~ 2 mm high) were prepared by sintering at 1360°C for 6 h in air (samples denoted as "air-sintered"). Excess TiO_2 (2 mol%) and SiO_2 (0.8 mol%) were used as liquid-phase-forming sintering additives. Subsequently,

---

* Corresponding author. Tel.: +386-061-177-3836; fax: +386-061-126-3126.

E-mail address: nina.ule@ijs.si (N. Ule).

0955-2219/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0955-2219(01)00139-X

some of the samples were atmospherically reduced by annealing at 1150°C for 1 h in nitrogen containing 1% of hydrogen (samples denoted as "reduced"). The pellets were exposed to a fluorine-containing atmosphere for 2 h at high temperatures ranging from 500 to 1100°C. A flow of supporting gas, bubbling through a fluorination agent (2,2,2-trifluoroethanol = CF_3CH_2OH), was introduced into a hot alumina-tube furnace. Pure nitrogen (experiments referred to as "N_2-fluorinated") or nitrogen containing a low concentration of oxygen (~2%) (experiments referred to as "N_2/O_2-fluorinated") were used as the supporting gas for the fluorination. The concentration of the fluorination agent in the inlet atmosphere was determined with mass spectrometry to be approximately 0.5%. The fluorination agent decomposes at high temperatures forming free fluorine, which reacts with the $BaTiO_3$ pellets. Some of the fluorinated samples were additionally reoxidized by cooling in air from 1200°C at a cooling rate of 5°C/min.

As a result of a surface reaction of the $BaTiO_3$ pellets with the atmosphere, a dense surface- reaction layer was formed[8] during fluorination at temperatures above ~ 600°C. For electrical measurements and re-oxidation, the surface-reaction layers were removed by grinding. The pellets were then electroded with a gallium/indium eutectic to provide ohmic contacts. Resistivity versus temperature was measured with a computerized instrument (Model 3457A, Hewlett-Packard, Mountain View, CA). Impedance analyses were performed using an impedance/gain-phase analyzer (Model SI 1260, Solatron, Farnborough, UK) in the frequency range from 0.1 Hz to 8 MHz.

3. Results and discussion

3.1. Fluorination with the nitrogen-supported fluorine-containing atmosphere (N_2-fluorination)

Fig. 1 shows the electrical resistivity versus temperature for the $BaTiO_3$ samples which were exposed to the nitrogen-supported fluorine-containing atmosphere (N_2-fluorination) at various temperatures for 2 h. After fluorination, all the samples showed common NTCR behaviour. Therefore, under the applied experimental conditions fluorine did not provide the grain boundary acceptors[6,9] necessary for the appearance of the PTCR effect in atmospherically reduced samples as observed by Alles et al.[6] The differences in the influence of fluorination on the electrical properties of $BaTiO_3$ ceramics in the two studies may be due to the different experimental conditions.

Before fluorination, the air-sintered samples were white and exhibited high values of resistance. However, when the samples were fluorinated the resistivity of the samples decreased to the semiconducting region (Fig. 2, curve 1, solid line), while their colour gradually changed from white to dark grey.

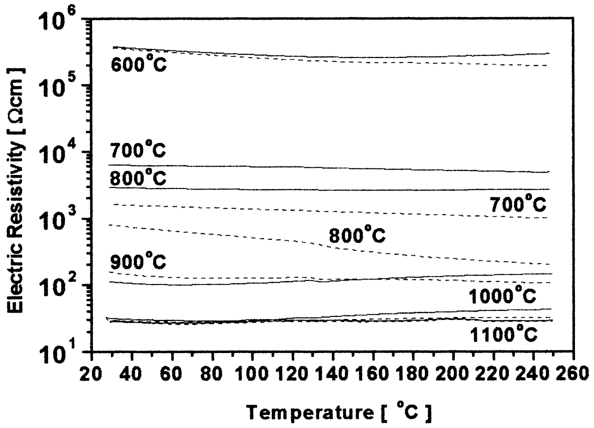

Fig. 1. Temperature dependence of resistivity for air-sintered (solid lines) and subsequently reduced (dashed lines) samples, N_2- fluorinated for 2 h at different temperatures.

A critical evaluation of the experimental procedure under which these results were obtained leads to the conclusion that such a decrease in the resistivity of pure $BaTiO_3$ after fluorination could be the result of fluorine incorporation in the $BaTiO_3$ grains as donors at the oxygen lattice sites. This would definitely increase the number of charge carriers and decrease the bulk resistivity. However, this could also be a consequence of the atmospheric reduction during fluorination when the oxygen partial pressure was very low due the de-integration of the organic fluorination agent at high temperatures. To evaluate this possibility, the $BaTiO_3$ samples were heat treated in ethanol vapour by bubbling nitrogen through the ethanol and introducing it to the hot

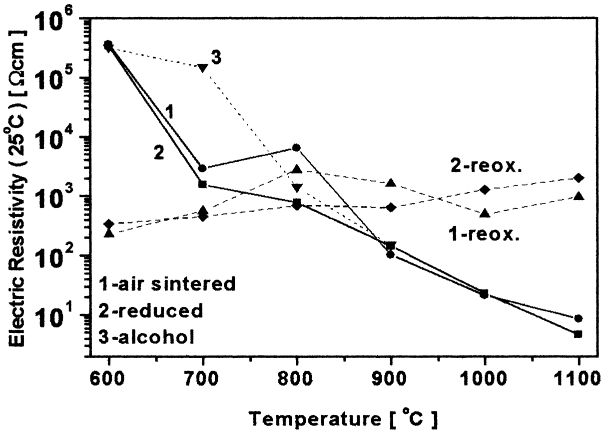

Fig. 2. The room-temperature resistivity of air-sintered samples and those subsequently reduced as a function of the temperature of fluorination using nitrogen as a supporting gas (N_2-fluorination) before "re-oxidation" (solid lines) and after "re-oxidation" (dashed lines). Dotted line 3 illustrates changes in the resistivity of the air-sintered samples by atmospheric reduction when the fluorination agent (CF_3CH_2OH) was replaced by ethanol (CH_3CH_2OH).

furnace. The resistivity of air-sintered samples heated under these conditions showed a similar behaviour to the fluorinated samples (compare curve 1-solid line and 3-dotted line in Fig. 2).

3.2. Fluorination with the nitrogen-supported fluorine-containing atmosphere with a low concentration of oxygen (N_2/O_2-fluorination)

When the air-sintered samples were treated in a fluorine-containing atmosphere using oxygen-containing nitrogen as the supporting gas (N_2/O_2-fluorination) their colour remained white and their resistivity remained very high (above 10^9 Ω cm, not shown in Fig. 3). On the other hand, when the reduced samples were fluorinated with the same fluorine-containing atmosphere (N_2/O_2-fluorination) their colour gradually changed with temperature, from the original dark grey to white, at the same time their resistivity increased, strongly suggesting their reoxidation (Fig. 3, solid line, 2).

When the fluorination experiments were completed and the samples were examined, the following general observations were noted regarding the resistivity of the samples: (i) the decrease in resistivity of air-sintered and subsequently N_2-fluorinated samples could be primarily attributed to their atmospheric reduction (Fig. 2, dotted line, 3) and (ii) the resistivity of the air-sintered samples remained practically unchanged after N_2/O_2-fluorination, while the increase in the resistivity of the atmospherically reduced samples after N_2/O_2-fluorination could be ascribed to the bulk reoxidation (Fig. 3, solid line, 2).

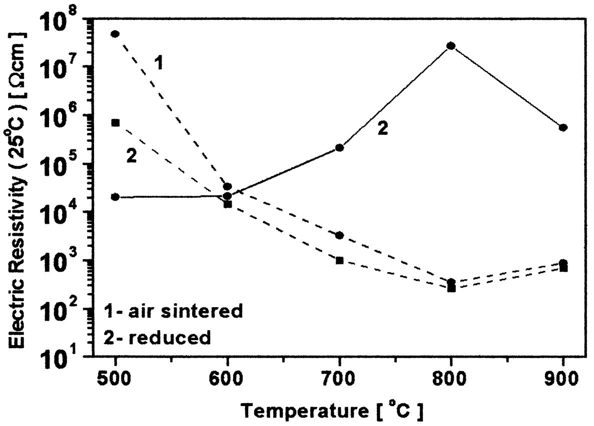

Fig. 3. The room-temperature resistivity of reduced samples as a function of the temperature of fluorination using oxygen-containing nitrogen as a supporting gas (N_2/O_2-fluorination, solid line, 2). The air-sintered samples remained insulating after N_2/O_2-fluorination with a resistivity above 10^9 Ωcm (not shown in Fig. 3). The dashed lines show the room-temperature resistivity of the N_2/O_2-fluorinated samples (air-sintered — dashed line, 1 and reduced — dashed line, 2) after "reoxidation" with cooling in air from 1200°C.

3.3. Re-oxidation of the fluorinated samples

Here we must stress that in spite of the fact that after the fluorination experiments no exaggerated changes regarding the electrical properties were noted [see the comments under (i) and (ii)], drastic changes were noted when the samples were re-oxidized by cooling from 1200°C in air.

Samples which were atmospherically reduced by introducing ethanol with nitrogen supporting gas into the hot furnace (Fig. 2, dotted line, 3), had, after "reoxidation", a high resistivity above 10^9 Ωcm (not shown in the figure) and their colour changed to white. The oxygen vacancies formed during the atmospheric reduction were neutralised. In contrast to these atmospherically reduced samples, the resistivity of N_2-fluorinated air-sintered samples and those subsequently reduced, were relatively low after reoxidation (few kΩcm, Fig. 2, dashed lines, 1 and 2). However, most surprising was the finding that these samples exhibit a pronounced PTCR effect (Fig. 4). The room-temperature resistivity of these samples increased with increasing fluorination temperature (Fig. 2, dashed lines). So the resistivity of samples fluorinated at 600°C decreased from a value of ~ 300 kΩcm (Fig. 2, solid lines) after re-oxidation to less than 1 kΩcm (Fig. 2, dashed lines).

The room-temperature resistivity of the white, air-sintered samples, which were insulating after N_2/O_2-fluorination, decreased after "re-oxidation" with the temperature of fluorination to semiconducting values (Fig. 3, dashed line, 1), while their colour changed to dark grey.

All these "re-oxidized" samples showed a pronounced PTCR effect (Fig. 5). The complex-impedance analysis (Fig. 6) revealed that all the samples exhibiting the PTCR effect had a low grain resistence of a few ohms, while their grain-boundary resistivity changed, primarily as a result of the temperature of fluorination.

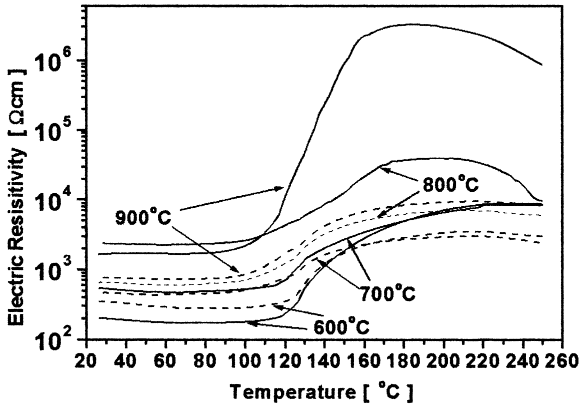

Fig. 4. Temperature dependence of resistivity for air-sintered samples (solid lines) and subsequently reduced samples (dashed lines), N_2-fluorinated for 2 h at different temperatures and subsequently re-oxidized by cooling from 1200°C in air.

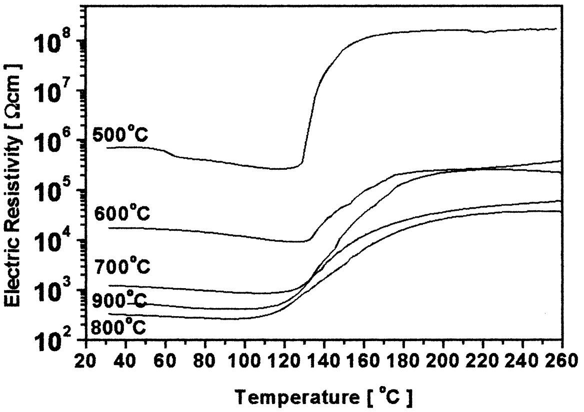

Fig. 5. Temperature dependence of resistivity for air-sintered samples, which were fluorinated using an oxygen-containing supporting gas (N_2/O_2-fluorinated) for 2 h at different temperatures and subsequently re-oxidized by cooling from 1200°C in air.

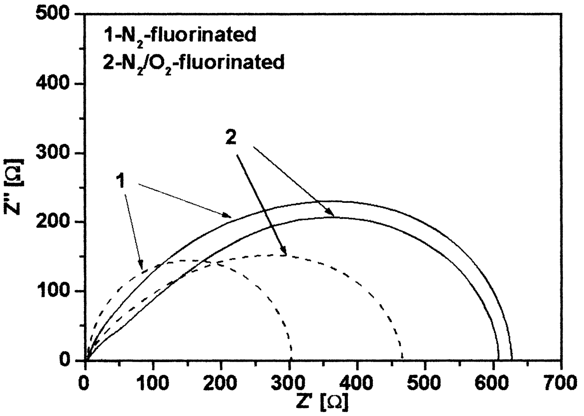

Fig. 6. Complex impedance spectra of samples fluorinated for 2 h at 900°C and subsequently re-oxidized by cooling in air from 1200°C. The air-sintered (solid line) and reduced (dashed line) samples were fluorinated using pure nitrogen or oxygen-containing nitrogen as the supporting gas.

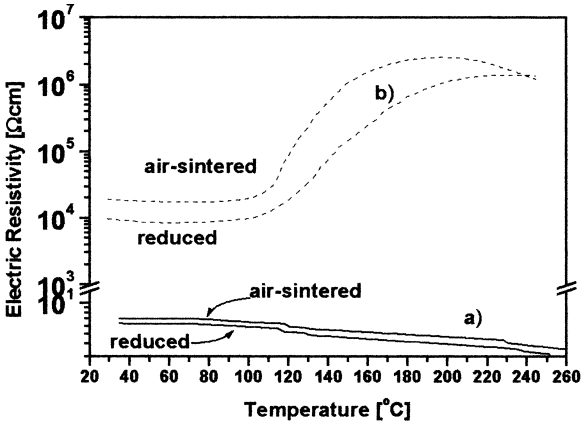

Fig. 7. Temperature dependence of resistivity for samples which were fluorinated at 900°C using an oxygen-containing supporting gas (N_2/O_2-fluorinated) and then heated to 1200°C in nitrogen (heating and cooling rate 5°C/min) before (solid line) and after (dashed line) re-oxidation by cooling from 1200°C in air.

According to the Heywang[1] and Jonker[4] model, three basic demands have to be fulfilled for the formation of the temperature-dependent potential barriers at the grain boundaries in $BaTiO_3$ ceramics: (i) ferroelectricity, (ii) *n*-type semiconductivity of the matrix grains, and (iii) the presence of acceptor surface states at the grain boundaries. The semiconductivity of $BaTiO_3$ could be achieved by donor doping, in the case of fluorination by the incorporation of fluorine donors into the $BaTiO_3$ structure, or by atmospheric reduction, as observed during nitrogen-supported fluorination. The high resistivity of air-sintered samples, fluorinated using oxygen-containing supporting gas proved that fluorine donors were not incorporated into the $BaTiO_3$ structure during fluorination. On the other hand, fluorination could provide acceptor states when fluorine is adsorbed at the grain boundaries.[6,9] Since the PTCR effect was never observed after the fluorination of reduced samples (before re-oxidation), this possibility is unlikely for the experimental conditions we used for fluorination. Using SEM and TEM, fluorine could not be detected anywhere inside the $BaTiO_3$ samples. However, the remarkable changes in the resistivity of the fluorinated samples after the "re-oxidation" step strongly suggest the presence of the fluorine somewhere inside the ceramics. We believe that fluorine is present at the grain boundaries. During the "re-oxidation" step the temperature is increased and fluorine can be incorporated as a donor into the $BaTiO_3$ grains, resulting in a drastic decrease in the resistivity of the $BaTiO_3$ grains. At the same time, the re-oxidation of the grain boundaries provides the required acceptor surface states, which can result in the appearance of the PTCR effect. When air-sintered samples, N_2/O_2-fluorinated at 900°C, were heated to 1200°C and then cooled in pure nitrogen, their resistivity was dramatically decreased from the insulating region to a few Ωcm. However, because of the absence of the acceptor surface states normally formed during reoxidation, these samples showed a common NTCR behaviour. After the reoxidation of these samples by cooling from 1200°C in air, a remarkable PTCR effect was induced (Fig. 7).

4. Conclusions

As reported by Alles et al.,[6] the fluorination of atmospherically reduced $BaTiO_3$ ceramics can provide the grain-boundary acceptor states necessary for the appearance of the PTCR effect. In the present study a different influence of the treatment in the fluorine-containing atmosphere on the $BaTiO_3$ ceramics' resistivity has been observed, most probably because of the different experimental conditions used.

The influence of the fluorination on the ceramics resistivity depended primarily on the supporting gas used. If pure nitrogen was used as the supporting gas for the fluorination agent CF_3CH_2OH, the resistivity of the insulating air-sintered samples was decreased primarily due to their atmospheric reduction. If an oxygen-containing supporting gas was used, the resistivity of the fluorinated air-sintered samples remained high. The influence of the fluorine on the resistivity of the samples was clearly visible only when fluorinated samples were exposed to air at high temperatures (reoxidation). In this case, the resistivity of fluorinated samples decreased and a remarkable PTCR effect appeared. The results suggest that at high temperatures the fluorine present after fluorination inside the $BaTiO_3$ ceramics is incorporated into the $BaTiO_3$ grain structure as a donor at the oxygen lattice sites.

Acknowledgements

The authors would like to thank the Ministry of Science and Technology, Republic of Slovenia, for financial support.

References

1. Heywang, W., Barium titanate as a semiconductor with blocking Layers. *Solid-State Electron.*, 1961, **3**, 51–58.
2. Drofenik, M., Oxygen partial pressure and grain growth in donor-doped $BaTiO_3$. *J. Am. Ceram. Soc.*, 1987, **70**(5), 311–314.
3. Seuter, A. M. J. H., Defect chemistry and electrical transport properties of barium titanate. *Philips Res. Rep. Suppl.*, 1974, **3**, 1–84.
4. Jonker, H. G., Some aspects of semiconducting barium titanate. *Solid-State Electron.*, 1961, **7**, 895–903.
5. Daniels, J., Hardtl, K. K. and Wernicke, R., The PTC effect of barium titanate. *Philips Technol. Rev.*, 1978/1979, **38**(3), 73–82.
6. Alles, A. B., Amarakoon, V. R. and Burdick, V. L., Positive temperature coefficient of resistivity effect in undoped, atmospherically reduced barium titanate. *J. Am. Ceram. Soc.*, 1989, **72**(1), 148.
7. Endo, T., Kobayashi, T., Sato, T. and Shimada, M., High pressure synthesis and electrical properties of $BaTiO_{3-x}F_x$. *J. Mater Sci.*, 1990, **25**(1B), 619–623.
8. Ule, N., Makovec, D. and Drofenik, M., SEM/EDS analysis of the surface reaction layer of $BaTiO_3$ ceramics exposed to a fluorine-containing atmosphere. In *Proceedings of the 12th European Congress on Electron Microscopy*, ed. L. Frank and F. Čiampor, Brno, 2000, pp. 397.
9. Jonker, G. H., Halogen treatment of barium titanate semiconductors. *Mater. Res. Bull.*, 1967, **2**, 401–407.