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PTCR Behaviour of Highly Donor Doped $BaTiO_3$

S. Urek and M. Drofenik*

'Jozef Stefan' Institute, Ceramics Department Jamova 39, 1111 Ljubljana, Slovenia

Abstract

The electrical properties of donor doped $BaTiO_3$ samples with a donor concentration >0·3 mol% were studied. Samples were sintered at a low partial pressure of oxygen in order to facilitate the anomalous grain growth and donor incorporation. In order to optimise the PTCR anomaly the samples were annealed in an oxidising atmosphere. The samples were characterised using impedance spectroscopy and SEM. Results show that by the use of a specific sintering profile PTCR ceramics containing a higher amount of donor dopant can be prepared. © 1999 Elsevier Science Limited. All rights reserved

Keywords: La doped $BaTiO_3$, grain boundary, defects, electrical properties, PTC devices,

1 Introduction

The donor-doped semiconducting $BaTiO_3$ formed via anomalous grain growth is resistant against the global reoxidation which makes it possible to engineer its surface acceptor state density and/or the PTCR effect during annealing in an oxidising atmosphere.

In general, it is not possible to provoke the anomalous grain growth of donor-doped $BaTiO_3$ and prepare the PTCR ceramics via conventional processing method when the concentration of donor-dopant, for example 0·3 mol% La, is surpassed. However, 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 also when the donor concentration is higher than that of the critical donor concentration in samples sintered in air.[1]

Once highly doped semiconducting ceramics is formed via anomalous grain growth at low oxygen concentration the grain boundary properties must be tailored in order to optimise the PTCR effect. The aim of this contribution is to consider the influence of high donor concentration on the PTCR anomaly in $BaTiO_3$.

2 Experimental Procedure

Donor- (La) doped $BaTiO_3$ was prepared by $BaTiO_3$ (Transelco) with 1·74 wt% excess of TiO_2 (Transelco) and various contents of 0·3, 0·4, 0·5, 0·6, 0·8, 1·0 and 1·5 mol% of La (Johnson Matthey). Weighed amounts of starting oxides were homogenised in an agate planetary ball mill in alcohol for 3 h. From the dried powders pellets of the dimension $\phi = 12$ mm and $h = 3$ mm were pressed. Pellets were sintered in a tube furnace at 1380°C in nitrogen (99.9% pure) for 2 h. Reoxidation of sintered samples was carried out at 1150°C in air for 24 h. The temperature dependence of resistance and capacitance at 100 kHz were measured in a temperature-programmable furnace with a heating rate of 3°C min^{-1} from 25°C to 300°C.

The impedance as a function of the frequency in a range from 5 Hz to 13 MHz at 250°C, was measured using an impedance analyser (Hewlett Packard 4092 A).

3 Results and Discussion

Figure 1 shows the DC resistance versus temperature characteristics of donor doped BaTiO3 sintered in air [Fig. 1(a)], and nitrogen, [Fig. 1(b)], respectively. Samples treated in air do not show a PTCR anomaly, [Fig. 1(c)], an exeption prove the sample with 0·3 mol% dopant.

When the samples were sintered in nitrogen and the partial pressure of oxygen was strongly

*To whom correspondence should be addressed. Fax: + 86-61-126-3126; e-mail:miha.drofenik@ijs.si

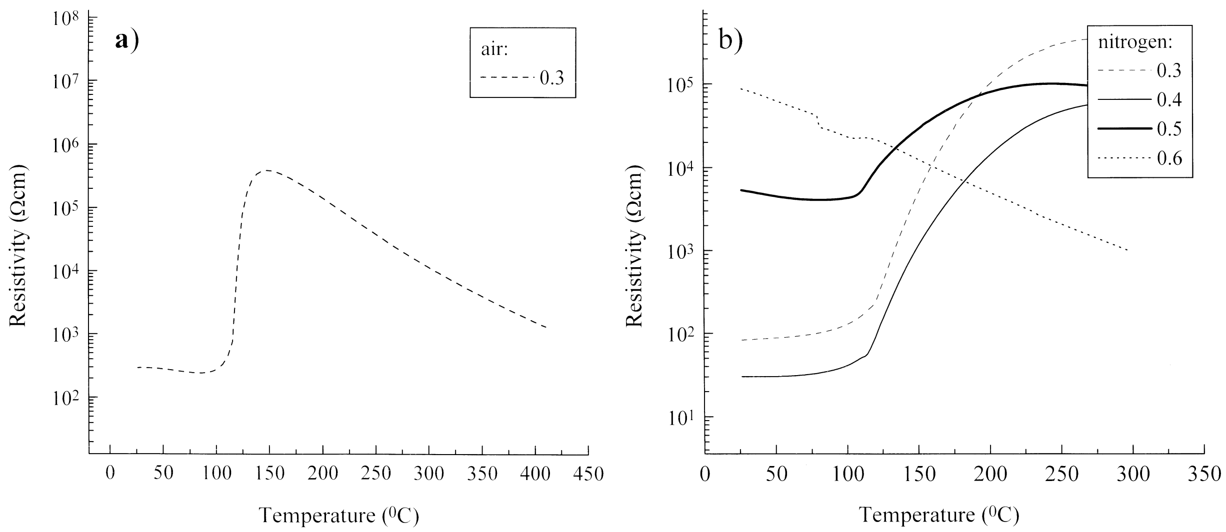

Fig. 1. (a) Resistance versus temperature for 0·3–0·5 mol% La doped sample sintered in air and (b) resistance versus temperature for 0·3 to 1·5 mol% La doped samples sintered in nitrogen (99·9% pure).

decreased (0·01 Vol% O_2), the PTCR anomaly appears also for higher donor-doped samples, i.e. 0·4 and 0·5 mol% doped samples, respectively, while 0·6 mol% and higher doped samples show a NTCR character [Fig. 1(b)]. Changes in PTCR anomaly are connected with microstructure of samples treated in air [Fig. 2(a)] or nitrogen [Fig. 2(b)]. At higher concentrations of dopant ($\geq$0·6 mol%) the anomalous grain growth is blocked in spite of relative low oxygen partial pressure applied during heating. However, the normal grain growth, which is kinetically hindered and relatively slow, proceeds.[2] The normal grain growth of highly donor doped samples leads to the formation of a core–shell structure.[3] Such a donor doped concentration profile divides the doped grains, after sintering at low oxygen partial pressure, in the highly donor doped outer part of the grain and an inner part of the grain, mostly free of the donor.

When the reduced highly doped samples with core–shell structure were treated in air the complete reoxidation of sample proceeds. On the other hand the samples, where the anomalous grain growth proceeds, i.e. 0·3 and 0·4 mol%, were relatively stable to the global reoxidation and their grain boundary properties can be optimised by applying the controlled reoxidation.[4] After the reoxidation of, for example, 0·4 mol% doped samples, where the anomalous grain growth proceeds, the grain resistance after 24 h of reoxidation changes within an order of magnitude while the grain boundary resistance drastically increases due to the increase of the depletion layer, (Fig. 3). So the samples doped with 0·3 and 0·4 mol% retain the PTCR anomaly in spite of being annealed in an oxidising atmosphere for 24 h, (Fig. 4).

During the reoxidation cation vacancies are initially formed at the grain boundaries and at surfaces exposed to the air. Their relative distribution is

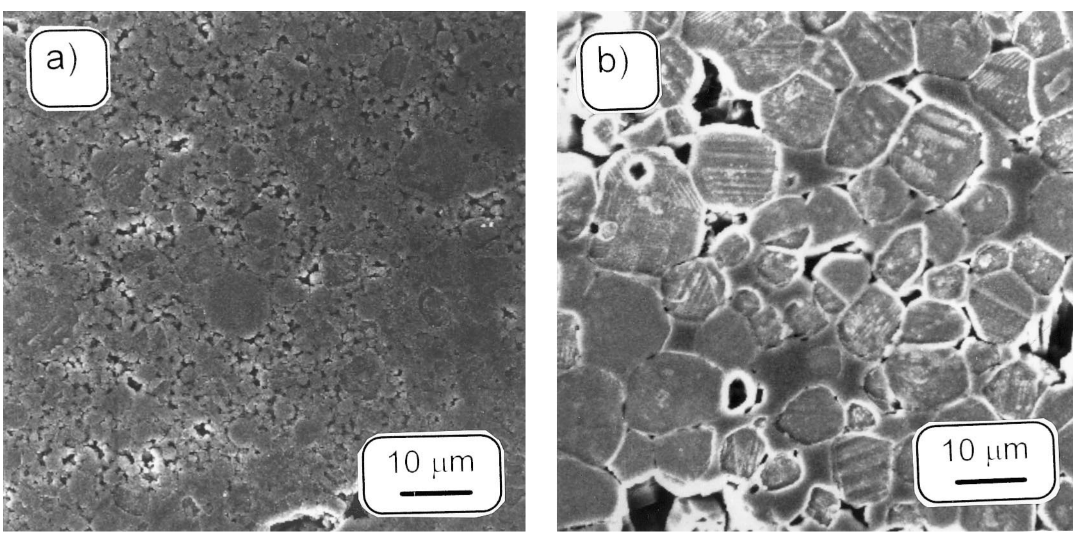

Fig. 2. Final microstructure of: (a) sample 0·4 mol% treated in air and (b) sample 0·4 mol% treated in nitrogen.

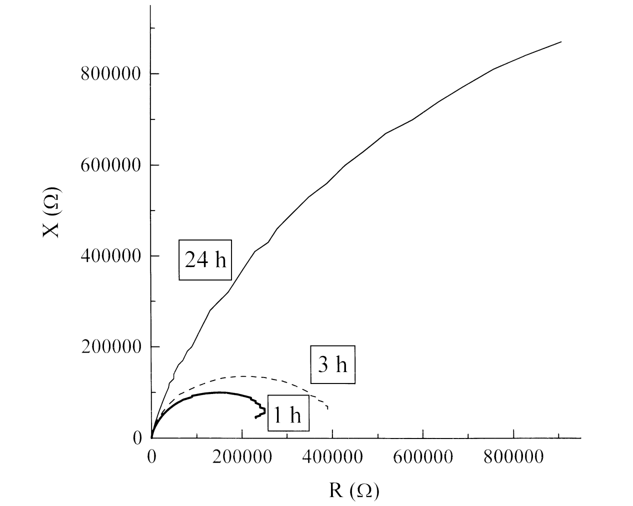

Fig. 3. Complex impedance spectra of 0·4 mol% doped samples.

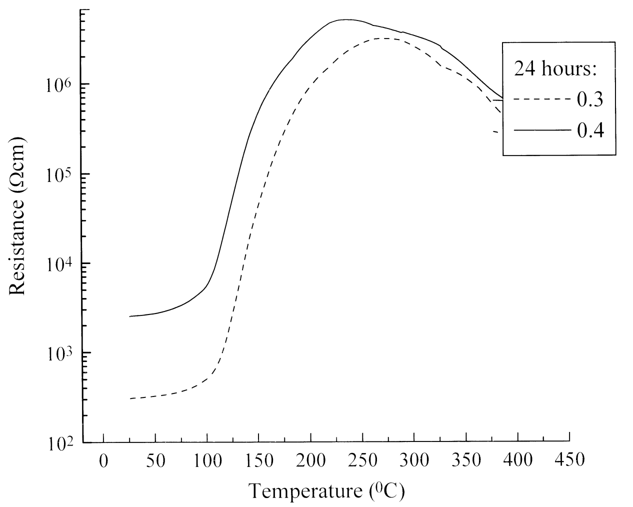

Fig. 4. Temperature dependence of electrical resistance of 0·3 and 0·4 mol% La doped samples sintered in air and after that 24 h reoxidised.

determined by the doping level, temperature and oxygen activity. It is believed that besides the adsorption of oxygen atoms also the cation vacancies formed during treating samples at appropriate thermodynamic condition (in air below 1220°C) are important for the optimisation of surface acceptor state density.[5,6] The less samples are subjected to the anomalous grain growth and the less the anomalous grains are developed the more they are prone to global reoxidation.

Drastic changes were noted for higher doped samples where the anomalous grain growth was not performed during sintering. In these samples, which are prone to the reoxidation, the resistance drastically increases. So the samples doped with 0·6, 0·8, 1·0 and 1·5 mol% of dopant were high resistive $>10^7 \Omega$ cm after 1 h of heating in air. The temperature dependence of relative permitivity ε_r for samples sintered in nitrogen and reoxidised in air is shown in Fig. 5. After the 24 h reoxidation

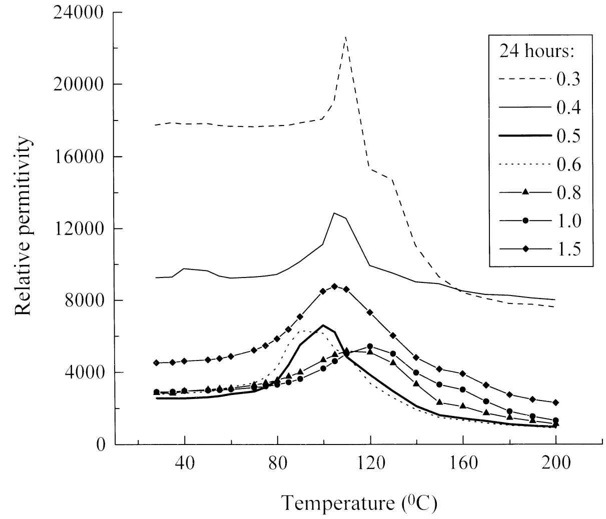

Fig. 5. The temperature dependence of relative permittivity ε_r as a function of donor concentration for N_2 sintered and 24 h reoxidised samples.

the 0·5, 0·6, 1·0 and 1·5 mol% La doped samples become insulators $R_{DC} > 10^7$ Ωcm and exhibit at room temperature relative permeability close to that of pure $BaTiO_3$. On the other hand, samples doped with 0·3 and 0·4 mol% La donor, which exhibit PTCR effect, show considerably higher relative permeability, which is caused due to the presence of the high resistive grain boundaries.

These samples exhibit a pronounced PTCR effect with its maximum shifted to higher temperatures.

4 Conclusion

This study has shown that the PTCR ceramics can be prepared in the whole concentration range of donor-doped $BaTiO_3$ where the anomalous grain growth occurs. A relatively low oxygen partial pressure during sintering of donor-doped $BaTiO_3$ is sufficient for creating enough surface acceptor states for the PTCR anomaly to occur.

Samples where the anomalous grain growth was blocked and the normal grain growth occurs are very prone to the reoxidation.

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