

Influence of High Oxygen Partial Pressure Annealing on the Positive Temperature Coefficient of Mn-doped $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$

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Abstract

A barium strontium titanate compound which exhibited positive temperature coefficient resistivity (PTCR) behavior was annealed in high oxygen partial pressures, in order to obtain a high acceptor density at the grain boundaries. The PTCR behavior changed significantly. Rises in maximum resistivity up to 200 times were obtained. The temperature of maximum resistivity decreased by 40–50°C. From the Heywang model the changes in PTCR behavior due to the high oxygen partial pressure annealing are explained by a rise in acceptor density possibly accompanied by an increase in acceptor energy.

Eine Barium–Strontium-Titanat-Verbindung mit positivem Temperaturkoeffizienten des Widerstandes (PTCR) wurde unter hohem Sauerstoffpartialdruck gegläht um eine hohe Akzeptorendichte an den Korngrenzen zu erhalten. Das Verhalten des PTCR änderte sich dabei signifikant. Ein Anstieg des Widerstandes bis zu einem Faktor 200 konnte erreicht werden. Die Temperatur des höchsten Widerstandes nahm um 40 bis 50° ab. Mit dem Heywang Modell konnte das veränderte Verhalten des PTCR infolge des Glühens in einem hohen Sauerstoffpartialdruck durch die Zunahme der Akzeptorendichte, möglicherweise verbunden einer Zunahme der Akzeptorenenergie, erklärt werden.

Un composé de titanate de strontium–baryum qui présente un coefficient positif de résistivité en fonction de la température (PTCR) a été recuit sous des pressions partielles d'oxygène élevées, afin d'obtenir une grande densité d'accepteurs aux joints de grains. Le comportement du PTCR a été modifié de façon significative. Des augmentations du maximum de résistivité jusque 200 fois ont été ainsi obtenues. La température du maximum de résistivité est diminuée

de 40 à 50°C. A partir du modèle de Heywang, ces changements dans le comportement du PTCR suite aux recuissons sous pression partielle d'oxygène élevée, s'expliquent par un accroissement de la densité en accepteurs, accompagnée, probablement, d'une augmentation de l'énergie des accepteurs.

1 Introduction

Due to its technical importance and the difficulty to explain certain experimental observations, the positive temperature coefficient resistivity (PTCR) of BaTiO_3 has always been a popular research subject since its discovery in 1955. The Heywang model^{1–3} attributed the abnormal rise in resistivity at the Curie point, T_C , to the presence of acceptors at the grain boundaries, resulting in a build-up of a potential barrier. The exact nature of these acceptors is still a subject of discussion. Some authors claim it is adsorbed oxygen or other gases (F, Cl, Br, etc.) when treated in a special atmosphere, which act as electron acceptor.^{2–7} Daniels and co-workers claimed that the acceptors are barium vacancies (V_{Ba}) which diffuse into the grains during cooling after sintering at high temperature.^{8–13} Still others say it can be segregated impurities.¹⁴

No matter what the exact nature of the acceptors really is, it is an experimental fact that small additions of some 3d elements like Fe, Cr and Mn improve the PTCR behavior considerably.^{15–19} It is, however, unlikely that the additions of 3d elements in the range of 0.01 to 0.1 at.% influence the adsorption of gases at the grain boundaries. Moreover, different acceptor energy levels are found for non-acceptor-doped and different 3d element-doped BaTiO_3 samples.^{15,17} This means that adsorbed gases cannot be the only acceptors in 3d element-doped BaTiO_3 PTCR material.

Daniels & Wernicke⁹ explained the influence of small additions of 3d elements as follows. Small additions of 3d elements with an energy level similar to or higher than the energy level of a double ionized barium vacancy, make the V_{Ba} -rich insulating layer thicker, resulting in a change of the PTCR behavior. This model does not explain the difference in acceptor level for different 3d elements and non-acceptor-doped PTCR material. Therefore, this model can be discarded as far as the explanation for the PTCR enhancement by 3d elements is concerned.

Ueoka¹⁶ proposed a model in the case of Mn additions, although it can also be applied to other acceptors, as will be explained further. He claimed that during sintering, the Mn present as Mn^{2+} on the Ti sites is compensated by double ionized oxygen vacancies (V_O^{++}). During cooling, the grain boundaries oxidize, and Mn^{2+} changes its oxidation state to Mn^{3+} or Mn^{4+} , which have deeper acceptor levels. Later Hagemann and co-workers^{20,21} confirmed this possibility. Hagemann and co-workers found by magnetic susceptibility and weight change measurements of non-donor-doped but acceptor-doped $BaTiO_3$ that Mn, Cr and Co reversibly change their oxidation state when annealed at different oxygen partial pressures, while other 3d elements do not. At low P_{O_2} the acceptors have low oxidation states, while after oxidation they have higher oxidation states. Because the oxidation states less than 4 are compensated by V_O^{++} , the oxidation state changes are inseparably connected with the V_O^{++} concentration. Nakahara & Murakami²²

found that Mn^{3+} has indeed a deep acceptor trap in Gd donor-doped $Ba_{0.97}Sr_{0.03}TiO_3$ single crystals.

From the previous discussion it is known that treatment in high oxygen partial pressures will increase the number of 3d elements with a high oxidation state, and create deep acceptor levels. Although Al-Allak *et al.*¹⁵ annealed acceptor-doped PTCR samples in air for several hours, by the authors' knowledge the influence of high oxygen partial pressure annealing on the PTCR behavior of acceptor-doped $BaTiO_3$ has not yet been a subject of study. Therefore a barium strontium titanate is annealed in an oxygen hot isostatic press (O_2 -HIP) in order to examine the influence on the PTCR behavior.

2 Experimental

The $Ba_{0.8}Sr_{0.2}TiO_3$ is produced by conventional solid-state reaction of a $BaCO_3$, $SrCO_3$ and TiO_2 mixture in a molar ratio of 80:20:101. The reactants were ball-milled in ethanol for 16 h, using ZrO_2 balls in a nylon vessel. The slurry was then dried, followed by presintering at 1100°C for 3 h in air. After crushing and sieving the reacted powder, dopants (0.15 mol% Sb_2O_3 and 0.04 mol% $MnCO_3$) and additives (1.5 mol% SiO_2 and 1 mol% Al_2O_3) were ball-milled (nylon vessel, ZrO_2 balls) in ethanol for 16 h. After spray-drying, the powder mixture was uniaxially pressed (100 MPa) into pellets of 20 mm in diameter. The pellets were sintered for 1 h at

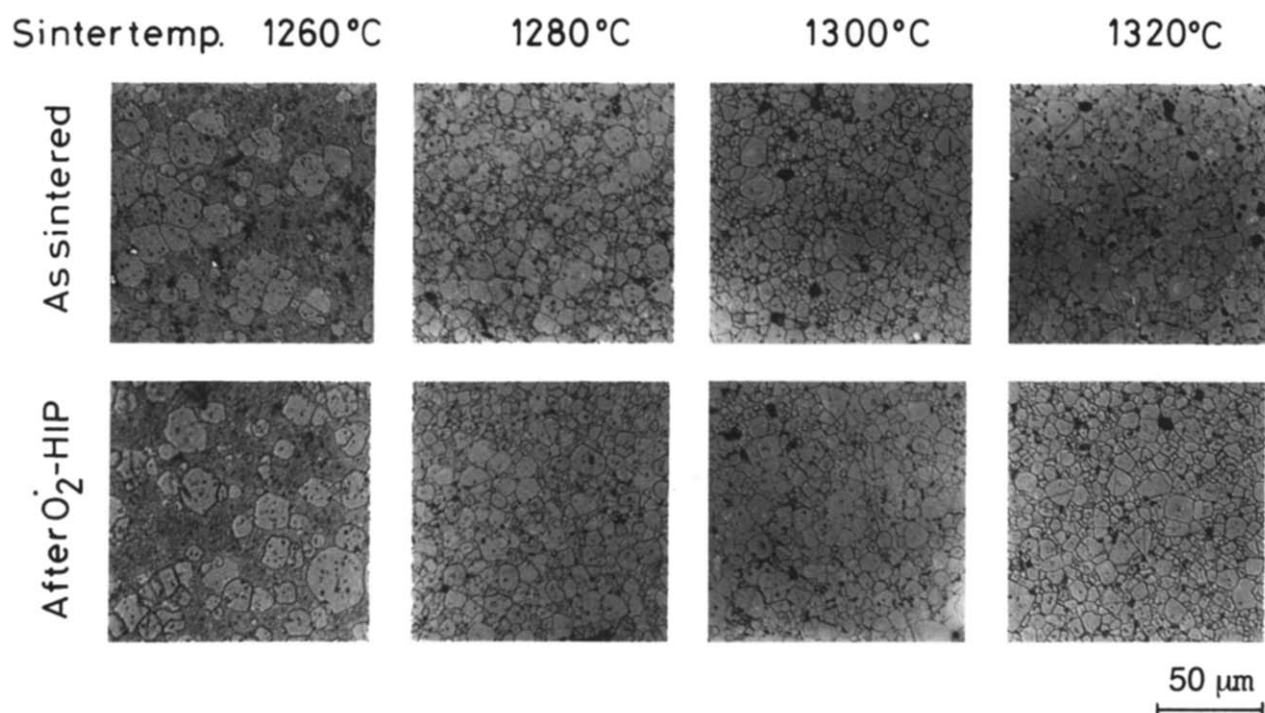


Fig. 1. Microstructures for the different sinter temperatures, before and after O_2 -HIPping. Note especially the difference between the samples sintered at 1260°C and the others. This difference is attributed to the low nucleation rate for abnormal grain growth at 1260°C. O_2 -HIPping has no detectable influence on the microstructure (sinter time 1 h).

temperatures ranging from 1260°C to 1320°C. The heating rate was 300°C/h. After soaking for 1 h, the samples were cooled from the sinter temperature to 1000°C at a rate of 60°C/h followed by normal furnace cooling. Some samples were post-treated in an O₂-HIP under $P_{tot} = 100$ MPa (90% Ar, 10% O₂) and $P_{O_2} = 10$ MPa at $T = 1200$ °C, for 1 h. The heating rate in this case was 400°C/h and also in this case the samples were cooled from 1200°C to 1000°C at a rate of 60°C/h.

The resistivity was measured after In-Ga electroding. The log ρ - T curves were obtained using a computer-controlled two-probe technique. Complex-impedance measurements in the 5 Hz–13 MHz range were used to determine the grain resistivity. Details are described elsewhere.^{2,3} Density was calculated by the Archimedes method after weighing in air and water. The grain size was obtained using an intercept technique.

3 Results

3.1 Microstructure

Figure 1 shows the microstructure for the sintered samples and O₂-HIPped samples. It is clear that O₂-

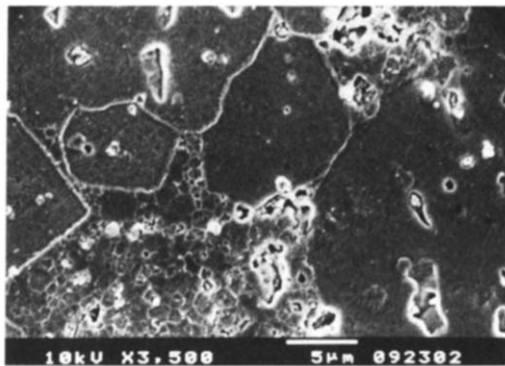


Fig. 2. SEM micrograph of a sample sintered at 1260°C. Note the small grains of about 1 μ m next to the large grains.

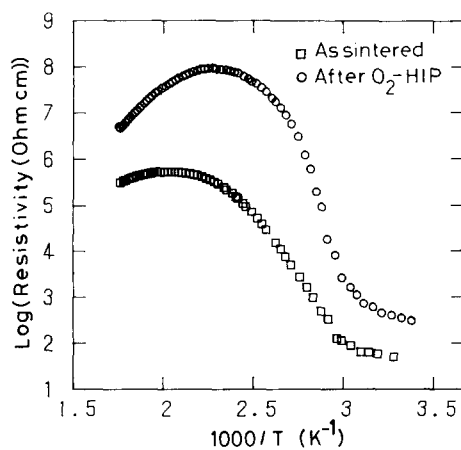
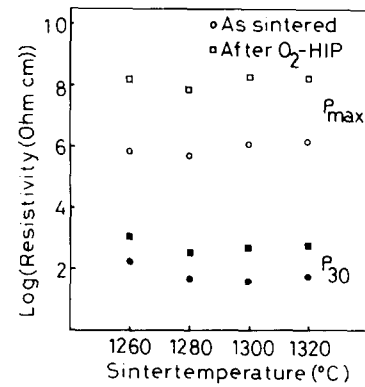
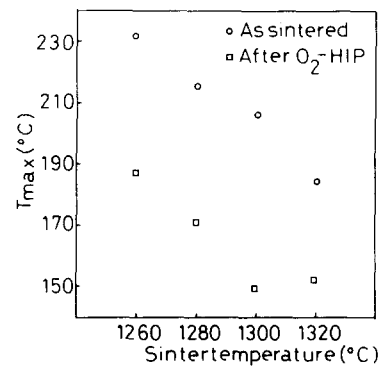


Fig. 3. Arrhenius plot of log ρ versus $1/T$. Note the increase in ρ_{max} and ρ_{30} . Also the slope in the transition region from low to high temperature decreased remarkably due to O₂-HIPping. This is ascribed to the increase in acceptor states. The decrease in T_{max} is also due to an increase in acceptor density.

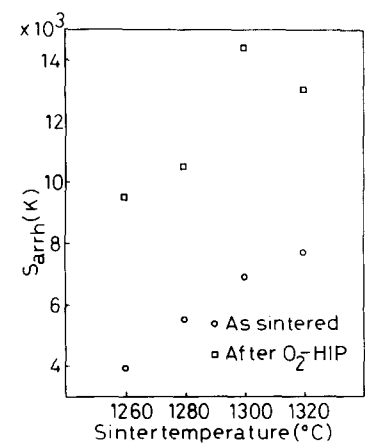
HIPping had no detectable influence on the microstructure. The average grain size (5–6 μ m) is the same for all the samples except for the ones sintered at 1260°C. Figure 2 shows a SEM micrograph of a sample sintered at 1260°C. These samples have a duplex microstructure of very big grains (20–30 μ m) and very small grains (about 1 μ m). Although the number of big grains ($d > 20$ μ m) decreased considerably for the samples sintered at temperatures above



(a)



(b)



(c)

Fig. 4. Different PTCR characteristics before and after O₂-HIPping versus the sinter temperature. (a) ρ_{30} and ρ_{max} versus sinter temperature. Both properties increased due to O₂-HIPping, but the increase in ρ_{max} is the largest, which results in a higher PTCR jump. (b) T_{max} versus sinter temperature. Although there is a decrease with increasing sinter temperature, the decrease due to O₂-HIPping is much larger. (c) S_{arrh} versus sinter temperature. S_{arrh} , the opposite sign in the plot log ρ versus $1/T$ of the transition region from low to high resistivity, increased with O₂-HIPping and sinter temperature, proving that the acceptor state density increases with increasing sinter temperature and O₂-HIPping.

1260°C, there are still a few big grains after sintering at higher temperatures. The density of all the samples was $5.65 \pm 0.03 \text{ g/cm}^3$.

3.2 Resistivity

Figure 3 shows the logarithm of the resistivity against the reciprocal of the absolute temperature for a sample sintered at 1280°C. It is clear that the maximum resistivity (ρ_{\max}) and the resistivity at 30°C (ρ_{30}) both increase with O₂-HIPping. The gradient of $\log \rho$ over $1/T$ in the transition region from low to high resistivity decreased remarkably. The opposite sign of this slope will be further referred to as S_{arrh} . Figure 4(a), (b) and (c) show the different PTCR characteristics as a function of the sintering temperature. Roughly it can be stated that due to O₂-HIPping ρ_{\max} increased by a factor of 10 to 200, ρ_{30} by a factor of 7 to 12 and S_{arrh} by a factor of 1.6 to 2.3. T_{\max} , the temperature of maximum resistivity, decreased by about 40–50°C after O₂-HIPping. In Fig. 4(b) and (c) it can also be seen that T_{\max} decreases and S_{arrh} increases with rising sintering temperature.

4 Discussion

4.1 Microstructure

When the eutectic point of the liquid phase is reached, abnormal grain growth in BaTiO₃ is found by many authors.^{24–28} Hennings *et al.*²⁵ and Cheng²⁹ proposed models for the mechanism of this abnormal grain growth. Cheng proposed that once the liquid phase is formed, the BaTiO₃ particles start to swim in the liquid phase. There they form clusters of several particles. The particles in the clusters grow rapidly, thereby creating big grains. Cheng attributed a grain size decrease after Al₂O₃ addition (0.3 mol%) to Al₂O₃ particles on the grain boundaries inhibiting grain growth in the clusters.

It is known that the eutectic point is decreased by Al₂O₃ addition,²⁶ therefore Cheng's idea that the Al₂O₃ is present in the form of particles and is not dissolved in the liquid phase is very unlikely. In addition Al-Allak *et al.*²⁶ found that Al₂O₃ addition increased the grain size rather than decreasing it. It is also questionable that the particles swim in the small amount of liquid phase (less than 1 vol%). Therefore the model of Cheng is very doubtful, and is not used to analyze the microstructures obtained in this work.

The model proposed by Hennings *et al.*²⁵ is more acceptable. This model is based on the dissolution of smaller particles in the liquid phase and segregation to the surface of nuclei, which grow bigger and form big grains. The exact character of these nuclei is unknown, but the number increases quickly with

rising temperature. Just above the eutectic point of the liquid phase, the nucleation is slow, which gives the few nuclei space to grow before they impinge on each other. At higher temperatures the nucleation rate is much higher and the nuclei can only have limited growth before impingement. This results in a finer average grain size and a narrower grain size distribution.

One might expect that the grain size therefore decreases with rising temperature. This is not the case for the samples sintered above 1260°C, as shown in Fig. 1. This means that the microstructure is determined by the grain growth and nucleation during the heating from the eutectic point to 1280°C. After the grains impinge on each other further grain growth is very slow,^{15,24} which results in a similar microstructure for the samples sintered above 1260°C.

The reason why a duplex structure is obtained for the samples sintered at 1260°C has not been explained completely. One would expect that the few nuclei grow during the soaking time until they impinge on each other. This does not happen for two reasons. Firstly, the temperature is relatively low and therefore so is the diffusion towards the big particles after dissolution. Secondly, when the big grains grow the liquid-phase layer between the particles gets thicker, because the surface area to be wetted decreases during the grain growth. This means that the diffusion path becomes longer and the grain growth rate decreases.

From this it must be concluded that a higher heating rate and sintering temperature result in a finer and more homogeneous grain size.

As the samples are O₂-HIPped below the eutectic point and normal grain growth in BaTiO₃ is very slow, as stated earlier, it is no surprise that the grain size and microstructure does not change detectably by O₂-HIPping.

4.2 Resistivity characteristics

Heywang^{1,3} described the resistivity of the samples in a qualitative way with the following equation:

$$\rho = \alpha \rho_b \exp\left(\frac{e\Phi_0}{kT}\right) \quad (1)$$

where α is a geometrical factor, ρ_b is the bulk resistivity, e is the electron charge, T is the absolute temperature and k is the Boltzmann constant. The potential barrier $e\Phi_0$, caused by a one-dimensional layer of acceptor states at the grain boundaries that attract electrons, can be derived as

$$\Phi_0 = \frac{eN_s^2}{8\epsilon_0\epsilon_r N_d} \quad (2)$$

where N_s is the concentration of acceptors, ϵ_0 is the

permittivity in free space, ϵ_r is the relative permittivity in the grain boundary region, and N_d is the bulk charge-carrier concentration. The relative permittivity, ϵ_r , obeys the Curie-Weiss law:

$$\epsilon_r = \frac{C}{T - \theta} \quad (3)$$

where C is the Curie constant and θ is the extrapolated Curie-Weiss temperature. This means that above the Curie point, T_C , ϵ_r drops very quickly, causing the abnormal resistivity behavior.

By derivation of eqn (1), S_{arrh} is found to be proportional to the ratio of N_s^2 over N_d .³⁰ Therefore, in order to come to some conclusions about N_s , N_d must be known. N_d can be derived from the high-frequency intercept in the complex-impedance plane,²³ see Fig. 5. If the mobility of the electrons, μ , is known N_d can be derived from eqn (4):

$$N_d = \frac{1}{\rho_b e \mu} \quad (4)$$

Unfortunately μ is unknown for the $Ba_{0.8}$

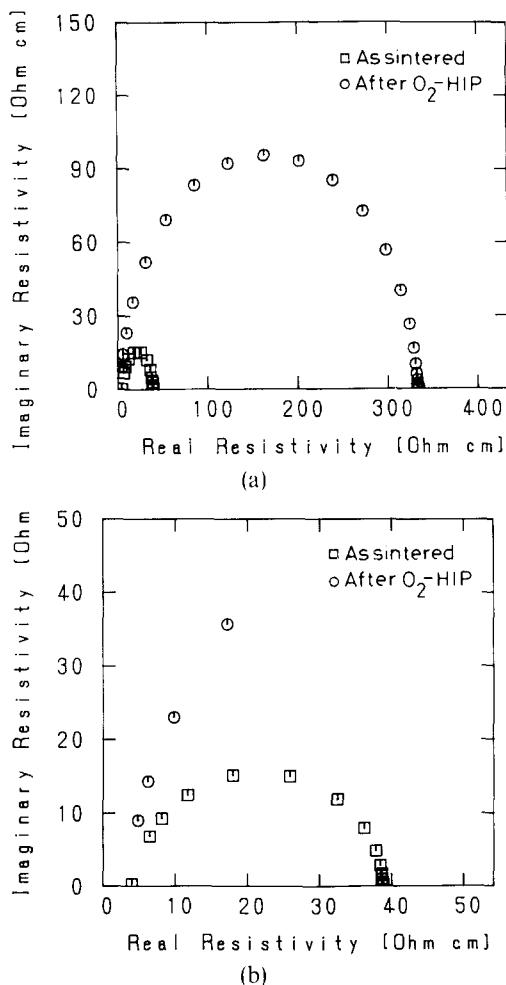


Fig. 5. Complex impedance plane for a sample sintered at 1280°C; (b) is an enlargement of (a). The high-frequency intercept with the x -axis indicates the bulk resistivity, ρ_b , while the low frequency intercept with the x -axis indicates the sum of the bulk resistivity and the grain boundary contribution to the sample resistivity. Note that, although the grain boundary resistance is quite different, the bulk resistivity is the same before and after O_2 -HIPping, a feature found for all the samples.

$Sr_{0.2}TiO_3$ used in this work. However, since ρ_b is constant (4–5 Ω cm) for all the samples in this study, N_d must also be the same for all the samples. Because the sintering temperatures for the different samples is quite different and the annealing temperature, is quite high, one might expect some influence of the sintering and annealing temperatures on the bulk resistivity, as different sintering temperatures result in different equilibria. This is, however, not the case, as ρ_b is independent of the sintering temperature and annealing conditions, a fact also found by other authors.^{15,31}

The drop in T_{max} and the rise in ρ_{max} and S_{arrh} can be explained with the Heywang model by a rise in N_s . As N_d is constant for all the samples, the rises in N_s due to O_2 -HIPping, which can be estimated from the S_{arrh} values, range between 30 and 50%, depending on the sample. The rise in ρ_{30} can be explained by the model proposed by Jonker.² Jonker said that at temperatures below T_C , a fixed number of acceptors is compensated by the polarization difference between two adjacent grains. Huybrechts *et al.*³⁰ later confirmed this experimentally. However, from the moment this number is exceeded, the minimum resistivity rises quickly with increasing acceptor density,³⁰ which is also the case in this work.

The acceptor-state density increase is compatible with the Ueoka model explained in the Introduction. The annealing took place under high oxygen partial pressure, high total pressures and at a temperature lower than the sintering temperature, three factors which decrease the V_o^{++} concentration at the grain boundaries. As explained before, these vacancies compensate the Mn^{2+} on the Ti sites. A lower concentration of V_o^{++} therefore causes a higher effective acceptor concentration, which results in an enhanced PTCR behavior.

5 Conclusions

- (1) Abnormal grain growth is mainly governed by the nucleation rate, and more homogeneous microstructures are obtained at higher sintering temperatures, due to a higher nucleation rate for abnormal grain growth.
- (2) The bulk resistivity was not influenced by O_2 -HIPping. The resistivity at 30°C and S_{arrh} increased due to O_2 -HIPping, while T_{max} decreased by 40–50°C. These changes in PTCR behavior are caused by an increase in N_s . The increase in acceptor density is estimated at 30–50%, depending on the sample.
- (3) Rises in acceptor energy caused by the high oxygen partial pressures are likely to happen, although could not be proven. These rises

might be partly responsible for the high maximum resistivity after O₂-HIPping.

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References

- Heywang, W., Barium Titanat als Sperrschichtbleiter. *Solid State Electronics*, **3** (1961) 51.
- Jonker, G. M., Some aspects of semiconducting barium titanate. *Solid State Electronics*, **7** (1964) 895.
- Heywang, W., Resistivity anomaly in doped barium titanate. *J. Am. Ceram. Soc.*, **47**(10) (1964) 484.
- Kuwabara, M., Determination of the potential barrier height in barium titanate ceramics. *Solid State Electronics*, **27**(11) (1984) 929.
- Jonker, G. M., Halogen treatment of barium titanate semiconductors. *Mater. Res. Bull.*, **2** (1967) 401.
- Takahashi, T., Nakano, Y. & Ichinose, N., Influence of reoxidation on the PTC-effect of porous BaTiO₃. *Nippon Seramikksu*, **98**(8) (1990) 879.
- Alles, A. B., Amarakoon, V. R. W. & Burdick, L., Positive temperature coefficient of resistivity in undoped atmospherically reduced barium titanate. *J. Am. Ceram. Soc.*, **72**(1) (1989) 148.
- Daniels, J., Hardtl, K. H. & Wernicke, R., The PTC effect of barium titanate. *Philips Tech. Rev.*, **38**(3) (1978) 73.
- Daniels, J. & Wernicke, R., Part V. New aspects of an improved PTC model. *Philips Res. Repts*, **31** (1976) 544.
- Daniels, J., Part I. Electrical conductivity at high temperatures of donor-doped barium titanate ceramics. *Philips Res. Repts*, **31** (1976) 489.
- Daniels, J., Part II. Defect equilibria in acceptor-doped barium titanate. *Philips Res. Repts*, **31** (1976) 505.
- Hennings, D., Part III. Thermogravimetric investigations. *Philips Res. Repts*, **31** (1976) 516.
- Wernicke, R., Part IV. The kinetics of equilibrium restoration in barium titanate ceramics. *Philips Res. Repts*, **31** (1976) 526.
- Heywang, W., Semiconducting barium titanate. *J. Mater. Sci.*, **6** (1971) 1214.
- Al-Allak, H. M., Brinkman, A. W., Russell, G. J. & Woods, J., The effect of Mn on the positive temperature coefficient of resistance characteristics of donor-doped BaTiO₃ ceramics. *J. Appl. Phys.*, **63**(9) (1988) 4530.
- Ueoka, H., The doping effects of transition elements on the PTC anomaly of semiconductive ferroelectric ceramics. *Ferroelectrics*, **7** (1974) 351.
- Ihrig, H., PTC effect in BaTiO₃ as a function of doping with 3d-elements. *J. Am. Ceram. Soc.*, **64**(16) (1981) 617.
- Illingsworth, J., Al-Allak, H. M., Brinkman, A. W. & Woods, J., The influence of Mn on the grain boundary potential barrier characteristics of donor-doped BaTiO₃ ceramics. *J. Appl. Phys.*, **67**(4) (1990) 2088.
- Matsuoka, T., Matsuo, Y., Sasaki, H. & Hayakawa, S., PTCR behavior of BaTiO₃ with Nb₂O₃ and MnO₂ additives. *J. Am. Ceram. Soc.*, **55**, 108.
- Hagemann, H. J. & Ihrig, H., Valence change and phase stability of 3d-doped BaTiO₃. *Phys. Rev. B*, **20**(9) (1979) 3871.
- Hagemann, H. J. & Hennings, D., Reversible weight change of acceptor-doped BaTiO₃. *J. Am. Ceram. Soc.*, **64**(10) (1981) 590.
- Nakahara, M. & Murakami, T., Electronic states of Mn-ions in Ba_{0.97}Sr_{0.03}Ti₃ single crystals. *J. Appl. Phys.*, **45**(9) (1974) 3795.
- Maiti, H. S. & Basu, R. N., Complex-plane impedance analysis for semiconductive barium titanate. *Mater. Res. Bull.*, **21** (1986) 1107.
- Tsai-Fa, L. & Chen-Ti, H., Influence of stoichiometry on the microstructure and positive temperature coefficient of resistivity of semiconducting barium titanate ceramics. *J. Am. Ceram. Soc.*, **73**(3) (1990) 531.
- Hennings, D., Janssen, R. & Reynen, P. J. L., Control of liquid phase enhanced discontinuous grain growth in barium titanate. *J. Am. Ceram. Soc.*, **70**(1) (1987) 23.
- Al-Allak, H. M., Parry, T. V., Russell, G. J. & Woods, J., Effects of aluminum on the electrical and mechanical properties of PTCR BaTiO₃ ceramics as a function of the sintering temperature. *J. Mater. Sci.*, **23** (1988) 1083.
- Drofenik, M., Popovic, A., Irmancnik, L., Kolar, D. & Krasevec, V., Release of oxygen during sintering of doped BaTiO₃ ceramics. *J. Am. Ceram. Soc.*, (1982) 203.
- Drofenik, M., Popovic, A. & Kolar, D., Grain growth and related effects in doped BaTiO₃. *Ceram. Bull.*, **63**(5) (1984) 703.
- Cheng, H. F., Effect of sintering aids on the electrical properties of positive temperature coefficient of resistivity BaTiO₃ ceramics. *J. Appl. Phys.*, **66**(3) (1989) 1382.
- Huybrechts, B., Ishizaki, K. & Takata, M., Experimental evaluation of the acceptor states compensation in PTC-type barium titanate. *J. Am. Ceram. Soc.*, **75**(3) (1992).
- Lin, T. F. & Hu, C. T., Defects restoration during cooling and annealing in PTC-type barium titanate ceramics. *J. Mater. Sci.*, **25** (1990) 3029.