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Preparation of PTCR Ceramics in the $BaO–Nb_2O_5–TiO_2$ System

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Abstract

The PTCR effect was investigated in the ferroelectric $BaNb_2O_6$ phase doped with TiO_2. Composite ceramics formed after sintering in a reducing atmosphere and subsequent reoxidation show the PTCR effect at around 70 and 300°C, respectively. Both PTCR anomalies are associated with the formation of high resistivity grain boundaries after controlled oxidation of reduced constituent phases. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: impedance, electrical properties, niobates, TiO_2, thermistors.

1 Introduction

Semiconducting $BaTiO_3$ ceramics are used as positive temperature coefficient resistors (PTCR). The anomaly in resistivity in donor doped $BaTiO_3$ can be well described by the model developed by Heywang[1] and Jonker.[2] Heywang assumed the formation of a two-dimensional layer of surface acceptor states at the grain boundaries. Acceptor states at the grain boundaries trap conduction electrons near the interface, creating a negatively charged grain boundary with a positively charged space charge region adjacent to the boundaries. On the basis of this model, Heywang found that the resistivity obeys the relation $\rho = \alpha\rho_0 \exp\ (e\Phi/kT)$, where Φ is the height of the potential barrier and α is a geometrical factor. To explain the low resistivity below Curie temperature (T_C) Jonker applied a model based upon the ferroelectric behaviour of tetragonal $BaTiO_3$. Below T_C $BaTiO_3$ is tetragonal with its polarisation along the tetragonal axis, which means that a net polarisation component perpendicular to the grain boundary causes positive and/or negative charging of the grain boundaries, and in the first case this annihilates the potential barrier. This makes the resistivity of this phase low below T_C.

Thus, T_C of such ceramics is crucial for the PTCR effect whose origin can be described by the Heywang-Jonker model. Thus, in order to increase the temperature of the PTCR effect of a ceramic its T_C must be increased. One can do this by modifying T_C of the solid solution $(Ba,Pb)TiO_3$, or by using a ferroelectric phase with a higher T_C. Previous investigators studied the PTCR effect in many other ferroelectric materials, such as for example $KNbO_3$, $KBiTi_2O_6$, $PbFeNbO_6$ and others.[3,4]

The purpose of our work was to study some compositions within the $BaO–Nb_2O_5–TiO_2$ system,[5,6] which is a promising material for preparing high T_C-PTCR ceramics.

2 Experimental

The compound $BaNb_2O_6$ was prepared by calcination of an equimolar mixture of $BaCO_3$ and Nb_2O_5 at 1100°C in air. Additions of 0·25, 0·5, 0·75, 1, 1·25, 1·5, 1·75 and 2 wt% TiO_2 were admixed to milled $BaNb_2O_6$ and homogenised in a planetary ball mill. From the dried powders samples of equal dimensions were pressed and sintered:

- at 1300°C for 2 h in air or
- at 1400°C for 2 h in pure hydrogen

Subsequent heating in pure hydrogen for 1 h at 1100 and/or 1200°C reduced the samples sintered in air. Reduced samples were reoxidized by heating in air at 500°C for 10 min at a heating rate of 3°C min^{-1}, which represents one cycle of reoxidation.

The dependence of electrical resistance and capacitance on temperature was measured in a programmable muffle oven during heating (heating rate 3°C min^{-1}). Electrical resistances were measured in the range from room temperature to 500°C using a Hewlett Packard HP-3457A multimeter (max.

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measured resistance $3\times10^9\,\Omega$). Some measurements were performed from lower temperature by cooling the oven with liquid nitrogen. For capacitance measurements an HP-4192A impedance analyser was used at a measuring frequency of 1 MHz in the temperature range from room temperature to around 400°C. Rubbing In–Ga alloy on planar surfaces provided electrodes on the samples. The electrical frequency characteristics of the samples were measured at room temperature by the HP-4192A in the frequency range from 5 Hz to 13 MHz. Complex impedance spectra were fitted by the NLLS-fit program. Using an equivalent circuit model consisting of two parallel R-CPE elements (where CPE represents the constant phase element), the best fit was achieved.

Samples were polished and chemically etched. The microstructure was observed by a JEOL JSM 5800 scanning electron microscope and the grains were analysed by the energy dispersive X-ray analysis (EDX).

3 Results and Discussion

Figure 1 shows the room temperature resistance of samples with various compositions based on the TiO_2 doped $BaNb_2O_6$ ceramic after reduction at different atmospheric conditions. It can be seen that the resistance of the reduced ceramics decreases remarkably with the increase in temperature and/or using pure hydrogen. Samples sintered in hydrogen show the highest conductivity. The resistance of samples in general decreases with the amount of TiO_2 present.

A typical microstructure of the samples sintered in hydrogen is shown in Fig. 2. The samples show a 2-phase microstructure, which consists of light grey grains (phase I) and white elongated grains (phase II). Microanalysis using EDXS shows that the reduced phase I has the composition $Ba_{1-x}Ti_xNb_2O_{6+x}$ where $x = 0{\cdot}12$ and that phase II has the composition $BaNb_{1{\cdot}66}O_{5{\cdot}2}$.

Semiconducting samples were reoxidised in order to form a depletion layer. The experimental work showed that the limiting temperature which induces the zone oxidation, i.e. total oxidation of the samples, is around 500°C in air. So the temperature interval up to 500°C was found to be useful for engineering the grain boundary properties. After every cycle of reoxidation below 500°C semiconducting samples were characterised by measuring their room temperature resistance and $R = f(T)$ characteristics. Figure 3 shows the room temperature resistance of samples reoxidised by various numbers of cycles. It can be seen that the addition of TiO_2 stabilises the composite samples against the influence of reoxidation. Samples with the highest amount of TiO_2 were found to be more resistant to reoxidation. Since the addition of TiO_2 induces the formation of phase I, one is justified in supposing that this phase is more resistant to reoxidation. A higher amount of TiO_2 and/or the formation of the large-grained phase I hinders the increase of resistance during controlled reoxidation.

The reoxidized samples were characterised by measuring their complex impedance spectra, in order to obtain some information regarding the status of the grain boundaries. In Fig. 4 some typical complex impedance spectra are shown for samples reoxidised in air. The semicircles representing the complex impedance spectra were found

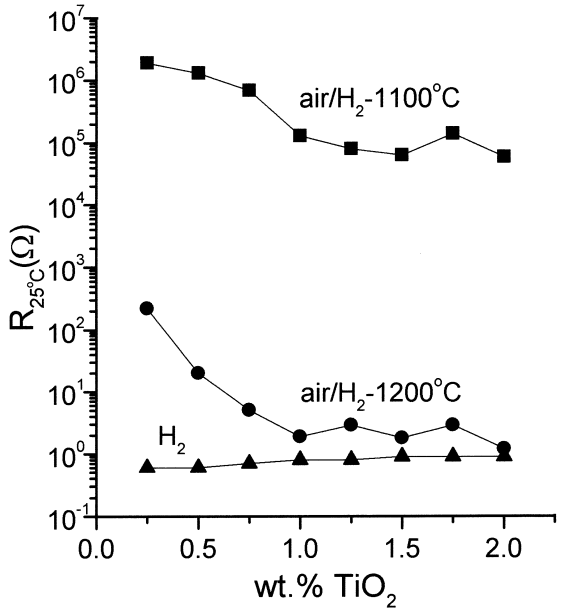

Fig. 1. Room temperature resistance of reduced two-phase ceramics composed of the constituent phases $BaNb_{1{\cdot}66}O_{5{\cdot}2}$ and $Ba_{1-x}Ti_xNb_2O_{6+x}$ against the amount of TiO_2; reduced at (a) 1100°C, (b) 1200°C and (c) treated in pure hydrogen.

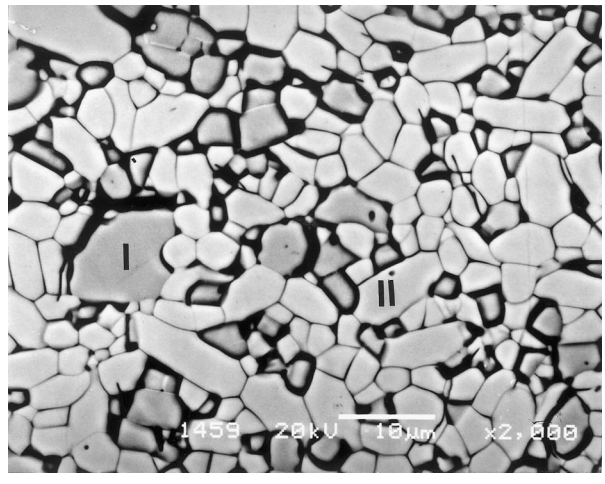

Fig. 2. Microstructure of samples with 2 wt% TiO_2 additions, sintered in hydrogen at 1400°C; round light grey grains phase I, white elongated grains phase II.

to be depressed. By applying the NLLS-fitting curve program it was observed that they consisted of two depressed semicircles, in accordance with the existence of two different phases in the composite and two types of grain boundaries, which represented the fit best to the complex impedance spectra. The grain boundary resistance increased with the number of reoxidation cycles, but the grain resistance was fairly constant. From the impedance analysis it can be concluded that high resistivity grain boundaries were formed after controlled reoxidation in these composite ceramics.

Figure 5(a) shows the temperature dependence of electrical resistance of samples sintered in air, reduced in hydrogen and then reoxidised. The composite shows a remarkable PTCR effect at around 70°C. After further heating an NTCR dependence of the composite can be noted. At around 300°C a second PTCR anomaly can be identified [Fig. 5(b)], which is accompanied by a maximum in the dielectric permittivity $\varepsilon/\varepsilon_{25°C} = f(T)$ at the same temperature.

The composite ceramic is composed of two constituent phases, which are the reduced form of $BaNb_2O_6$ and/or $BaTiNb_2O_8$, and exhibit two PTCR anomalies at 70 and 300°C, respectively. We believe that the first anomaly could be ascribed to $BaNb_{1.66}O_{5.2}$ since this phase in its oxidised form

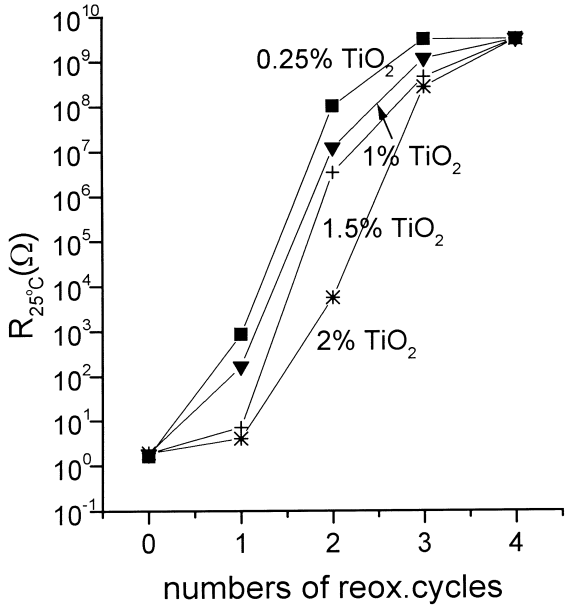

Fig. 3. Room temperature resistance of samples reoxidized below 500°C in air versus the number of reoxidation cycles and the amount of TiO_2.

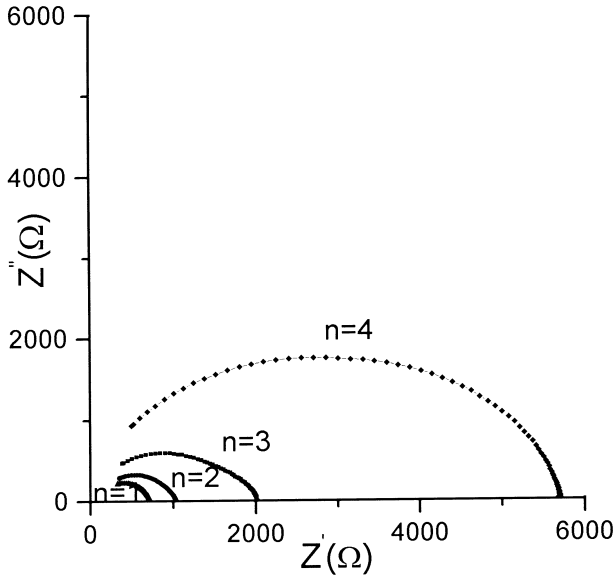

Fig. 4. Complex impedance spectra of samples doped with 0·75 wt% TiO_2, sintered in air at 1300°C, reduced at 1200°C and treated for various numbers of reoxidation cycles (n).

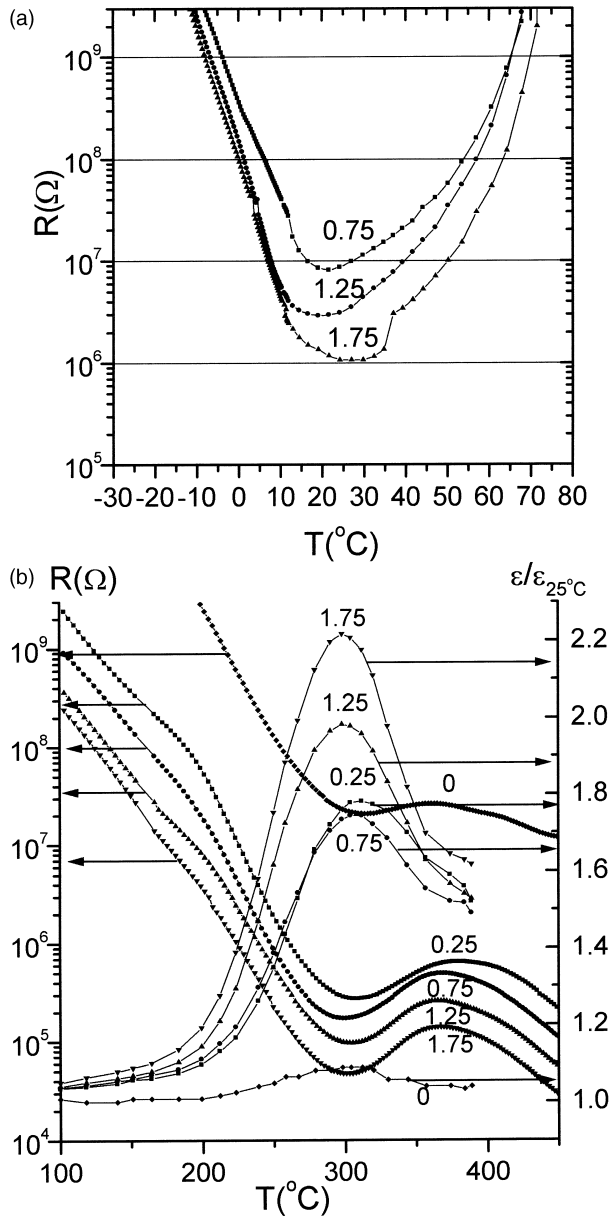

Fig. 5. (a) Temperature dependence of electrical resistance of reoxidised samples doped with various amounts of TiO_2 in the temperature range from −10 to 100°C. (b) Temperature dependence of electrical resistance of reoxidised samples doped with various amounts of TiO_2, from 100 to 500°C. In addition, the temperature dependence of $\varepsilon/\varepsilon_{25°C}$ is shown in the temperature range up to about 380°C.

$BaNb_2O_6$ exhibits a value of T_C at 75°C.[5] On the other hand, the second PTCR effect can be ascribed to the phase I being in its reduced semiconducting form $Ba_{1-x}Ti_xNb_2O_{6+x}$. However, after controlled reoxidation and the formation of the depletion layer, this phase also exhibits a PTCR anomaly. Since the PTCR anomaly in the composite studied is associated with the formation of a depletion layer and accompanied by a maximum in dielectric permittivity, we believe that the anomaly in the electrical resistivity can be interpreted by the Heywang–Jonker model. However, the origin and the type of surface acceptor states on the highly reduced and reoxidised grain boundaries are not well understood and will be the subject of further investigations.

4 Conclusions

- The reduction of $BaNb_2O_6$ doped with TiO_2 leads to a low resistive composite ceramic where the conductive network consists of two constituent phases $BaNb_{1.66}O_{5.2}$ and $Ba_{1-x}Ti_xNb_2O_{6+x}$ ($x = 0{\cdot}12$).
- Global oxidation of the samples occurs above 500°C in air. Below 500°C the reoxidation of the grain boundaries can be controlled.
- The concentration of TiO_2 has a noticeable influence on the phase composition and electrical properties of the composite ceramics.
- The peak of dielectric constant at 300°C coincides with the PTCR effect, indicating that the Heywang–Jonker model can explain the anomaly in electrical resistance.

References

1. Heywang, W., Barium titanate as a semiconductor with blocking layers. *Sol. State Electron.*, 1961, **3**, 51–58.
2. Jonker, G. H., Some aspects of semiconducting $BaTiO_3$. *Sol. State Electron.*, 1964, **7**, 895–903.
3. Raevskii, I. P., Bondarenko, E. I., Pavlov, A. N. and Prokopalo, O. I., PTCR effect in $KNbO_3$. *Ferroelectrics*, 1987, **76**, 55–60.
4. Raevskii, I. P., Pavlov, A. N., Prokopalo, O. I. and Bondarenko, E. I., The PTCR effect in oxides of the perovskite family. *Ferroelectrics*, 1988, **83**, 171–178.
5. Francombe, M. H., The relation between structure and ferroelectricity in lead barium and barium strontium niobates. *Acta Cryst.*, 1960, **13**, 131–140.
6. Millet, J. M., Roth, R. S., Ettlinger, L. D. and Parker, H. S., Phase equilibria and crystal chemistry in the ternary system $BaO–TiO_2–Nb_2O_5$. *J. Sol. State Chem.*, 1989, **67**, 259–270.