

The effect of B_2O_3 - Bi_2O_3 glass additions on exaggerated grain growth in donor-doped barium titanate

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Interactions between $BaTiO_3$ and the B_2O_3 - Bi_2O_3 system were studied by sintering $BaTiO_3$ with B_2O_3/Bi_2O_3 glass powder. In general, the microstructural development of $BaTiO_3$ depends very much on the amount and composition of glassy phase present in the samples during sintering. With large amounts of B_2O_3 - Bi_2O_3 glassy phase and, as a consequence, a high Bi^{3+} donor-dopant concentration, the grain growth is suppressed. On the other hand, when the amount of donor-dopant supplied by the glassy phase decreases, the grain growth occurs, leading to the formation of semiconducting ceramics. All prepared samples exhibited the Positive Temperature Coefficient Resistivity (PTCR) effect.

Key words: $BaTiO_3$, semiconducting ceramics, PTCR effect, glassy phase, grain growth.

Introduction

The donor ions La^{3+} , Nd^{3+} and Bi^{3+} on the Ba^{2+} lattice sites or Nb^{5+} , Sb^{5+} and Ta^{5+} on the Ti^{4+} lattice sites are the most common cations used to modify the electrical resistance of $BaTiO_3$. They may lead to two different phases, depending on the method of donor-dopant compensation. When the donor dopant is compensated with cation vacancies an insulating phase is obtained, however, when the donors are compensated with electrons a semiconducting phase results. In general, the number of donors that can be incorporated into the $BaTiO_3$ lattice via a solid-state reaction depends on the solubility limit, which in turn depends on the particular donor species [1].

According to the defect-chemistry model, which is based on electrical measurements [2] the vacancy compensation of ionised donors (D^+) in $BaTiO_3$ proceeds up to about 1220°C in air and 1300°C in oxygen. So, when a solid solution of donor-doped $BaTiO_3$ is prepared via a conventional ceramic route involving calcinations of the powder mixture below 1220°C in air, vacancy compensation occurs and an insulating donor-doped phase is always obtained where the donor concentration can be increased to the solubility limit. This phase can be transformed into a semiconducting phase when it is treated under reducing conditions that ensure the thermodynamic stability of the so-called "reduced" or semiconducting donor-doped $BaTiO_3$ phase.

On the other hand when the donor dopants are incor-

porated in $BaTiO_3$ grains under conditions which result in anomalous grain growth [3, 4] the concentration of the incorporated donor dopant is limited to the so-called critical donor-dopant concentration (C_0), which is usually much smaller than the donor solubility in the $BaTiO_3$ lattice and is more or less the same for all donors, provided that the donors are incorporated exclusively on one lattice site.

Usually, because donors tend to enter exclusively onto one lattice site, the preparation of PTCR thermistors based on $BaTiO_3$ is straightforward. One of the donors that needs a little more care is Bi^{3+} . The preparation of thermistors based on Bi^{3+} and/or studies which would explain the role of Bi^{3+} in $BaTiO_3$ -based PTCR ceramics are rare in the literature even though PTCR ceramics based on Bi^{3+} as a donor are known.

In order to understand all the above-mentioned features, a B_2O_3 - Bi_2O_3 glassy phase was formed in order that we could study the microstructural development and the formation of PTCR ceramics resulting from Bi^{3+} incorporation in $BaTiO_3$.

There are some reports of $BaTiO_3$ with additions of Bi_2O_3 -containing glassy phases. Mostly, the amount of the glassy-phase additions was higher than 1 mol%, which is used in order to lower the sintering temperature, optimise the microstructural development and the dielectric properties of the $BaTiO_3$ ceramics [5, 6]. In contrast, studies of the effect of bismuth on semiconducting $BaTiO_3$ are not common in the literature [7].

A Bi_2O_3 - B_2O_3 glassy phase can influence the preparation of $BaTiO_3$ -based PTCR materials in two ways: i) the glassy-phase may govern the kinetics of grain-growth due to the presence of a diffusion layer. A large amount of glassy-phase associated with a thick diffusion layer

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can substantially slow down the grain growth rate and decrease the final grain size and ii) on the other hand, when the concentration of the donor dopant (Bi_2O_3) is too high the anomalous grain growth (AGG) which causes the semiconductivity in donor-doped $BaTiO_3$ can be blocked in accordance with the so-called donor-dopant-induced grain size and conductivity anomaly [4].

The aim of this work was to study the microstructural development and electrical properties of samples with compositions lying in the system $BaTiO_3$ - B_2O_3 - Bi_2O_3 .

Experimental

Ceramic samples of the $BaTiO_3$ -containing glassy phase were prepared by using $BaTiO_3$ (CABOT BT-10, $Ba/Ti = 1.00$, $d = 0.12 \mu m$) with the addition of various amounts of glassy phase: 0.1 mol%, 0.2 mol%, 0.4 mol% and 0.8 mol%. Weighed amounts of the starting powder were homogenised in an agate planetary ball mill with alcohol for 2 hours. The binary glass system with various ratios of glass modifier (Bi_2O_3) to glass former (B_2O_3): 20 mol% Bi_2O_3 -80 mol% B_2O_3 glass (B), 50 mol% Bi_2O_3 -50 mol% B_2O_3 glass (C) and 80 mol% Bi_2O_3 -20 mol% B_2O_3 glass (D) were chosen to prepare the glass-containing samples. In addition to these three binary glass systems the compositions with only one of the constituent oxides were also investigated, i.e. B_2O_3 and Bi_2O_3 . The first tie-line, $BaTiO_3$ - B_2O_3 , is abbreviated as A and the last tie-line, $BaTiO_3$ - Bi_2O_3 , using only

Bi_2O_3 oxide, is labelled as E (Figure 1).

Calculated amounts of reagent-grade chemicals - Bi_2O_3 and/or H_3BO_3 for various glass compositions - were weighed, mixed and melted in platinum crucibles in air at $1000^\circ C$ for 3 hours. Pouring into cold water quenched the molten glass. The quenched glass was crushed and milled in a ball mill. Barium titanate and weighed amounts of glassy phase were thoroughly mixed. From these powders pellets were prepared with dimensions: diameter- $\phi = 6$ mm, height=5 mm. The pellets were placed on platinum supports in an alumina boat and sintered in a tube furnace at $1300^\circ C$ for two hours in air. The samples had a heating and cooling rate of about $5 K \text{ minute}^{-1}$. Some of the samples containing only Bi_2O_3 additions were analysed for Bi_2O_3 content.

The polished-and-etched samples were examined using an optical microscope and a scanning electron microscope.

For the electrical measurements the surfaces of the sintered samples were rubbed with an In-Ga alloy to provide ohmic contacts. The temperature dependence of the resistance was measured with a multimeter (Hewlett-Packard 3457A) and the temperature dependence of the capacitance at 10 kHz was measured with an impedance analyser (Hewlett-Packard 4192A) in a temperature-programmable furnace at a heating rate of $3 K \text{ minute}^{-1}$ from 25 to $300^\circ C$.

Complex-impedance spectra in the range from 5 Hz to 13 MHz at room temperature were measured using an impedance analyser (Hewlett-Packard 4192A).

Results and Discussion

In order to get some information regarding the microstructural development and electrical resistance for the compositions investigated, the dependence of the amount and composition of the Bi_2O_3 -containing glassy phase on the microstructure of $BaTiO_3$ was studied and the results were expressed in the form of a composition-properties diagram, Fig. 1.

Each point in this diagram represents the nominal composition of the sample studied, while the symbol of the points in the diagram match the samples' main characteristics - whether the samples are coarse or fine grained and semiconducting or isolators.

It should be emphasised that the data in the composition-properties diagram refer to the composition as indicated in the composition diagram. The possible change of the overall composition of samples due to the evaporation of the constituent oxides forming a glassy phase during heating was not considered, except in the case of the $BaTiO_3$ - Bi_2O_3 system. However, also in this case the starting composition is indicated in the composition diagram. Based on the microstructure of the sintered samples and the corresponding electrical measurements the composition diagram can be divided into two major regions. The larger part of the system

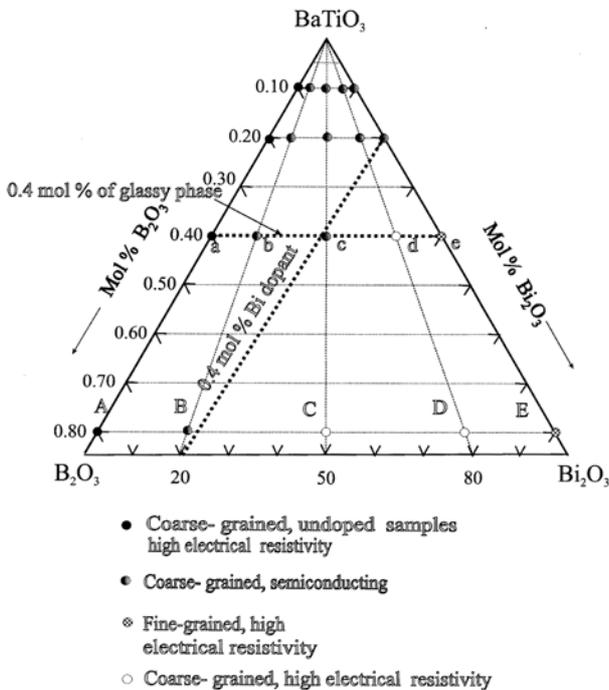


Fig. 1. Composition diagram showing the compositions studied, the region where the anomalous grain growth (AGG) occurs and the region where the AGG is blocked, their electrical resistivity and their grain size.

with an amount of glassy phase higher than 0.8 mol% is characterised by a fine-grained microstructure and was not considered here. This part of the diagram is well documented [4], and because of the relatively large amount of the donor-containing B_2O_3 - Bi_2O_3 glassy phase, the anomalous grain growth in this region is blocked. The composition in this part of the diagram is more or less suitable for the preparation of dielectric materials.

In this work the part of the composition diagram containing less than 0.8 mol% of glassy phase was considered.

Microstructural development of barium titanate at a constant amount of glassy phase with different compositions

How effectively the glassy-phase governs the microstructural development of donor-doped $BaTiO_3$ can be demonstrated when a tie-line connecting the compositions exhibiting a constant amount of 0.4 mol% glassy phase is considered, the dashed line in Fig. 1. The composition (a) contains no bismuth, the composition (b) contains 0.16 mol% Bi^{3+} , the composition (c) contains 0.4 mol% Bi^{3+} , the composition (d) contains 0.64

mol% and the composition (e) contains 0.8 mol% Bi^{3+} (nominal composition).

The amount of Bi^{3+} donors in the glassy phase increases from the left to the right. No Bi is present on the line $BaTiO_3$ - B_2O_3 (left), while incorporation of the total amount of Bi at the Ba sites on the line $BaTiO_3$ - Bi_2O_3 (right) would correspond to 0.8 mol% Bi^{3+}_{Ba} . Because the ratio between Ba and Ti in the system was constant at 1.00, the total incorporation of Bi at Ba

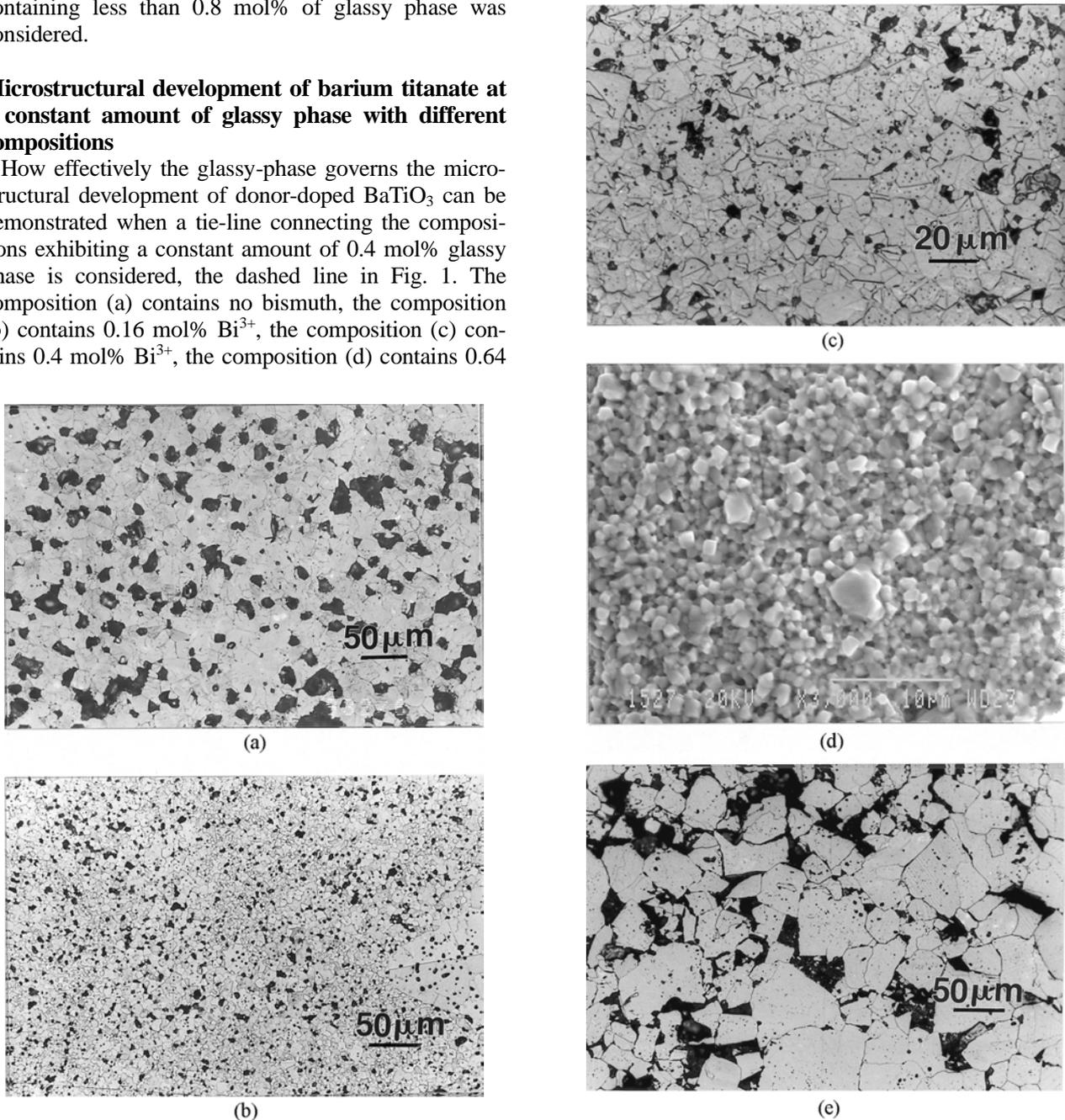


Fig. 2. Microstructures of samples a, b, c, d, e lying on the tie-line covering the compositions with a constant amount of 0.4 mol% glassy phase containing various amounts of donor dopant (Bi_2O_3); (a) sample containing 0.4 mol% of a glassy phase with the composition 100 mol% B_2O_3 , (b) sample containing 0.4 mol% of a glassy phase with the composition 80 mol% B_2O_3 -20 mol% Bi_2O_3 , (c) sample containing 0.4 mol% of a glassy phase with the composition 50 mol% B_2O_3 -50 mol% Bi_2O_3 , (d) sample containing 0.4 mol% of a glassy phase with the composition 20 mol% B_2O_3 -80 mol% Bi_2O_3 and (e) sample containing 0.4 mol% of a glassy phase with the composition 100 mol% Bi_2O_3 .

sites implies that some Ba should be expelled from the solid solution, entering into the liquid phase.

When we consider the properties of the samples lying on this tie-line, we can see that in spite of the constant amount, regardless of the different compositions of the glassy phase, there are four separate regions with respect to the microstructure and the corresponding electrical properties of samples.

The sample with composition (a), which lies on the first line $BaTiO_3$ - B_2O_3 , without any Bi^{3+} donors show surprisingly a PTCR effect. The room temperature resistance is relatively high but the samples show definitely a reproducible PTCR effect with a noticeable anomaly in electrical resistance, Fig. 4d. To our knowledge there were no published results that would support this finding. Regarding the boron valence 3+ it might in principle serve as a donor on the Ba lattice sites. In spite of this B_2O_3 shows some indication to serve as a donor and might in particular conditions function as a donor, its solid solubility must be very limited. We didn't include its concentration during considering the overall critical donor-dopant amount in samples.

The next two samples with compositions (b) and (c), lying on crossings with the tie-lines $BaTiO_3$ -B and $BaTiO_3$ -C, contain donor-doped $BaTiO_3$. Here the grain growth is subjected to the so-called donor-dopant induced grain size and electrical conductivity anomaly. In this case the grain growth must depend on the amount and composition of the glassy-phase and consequently on the amount of donor.

In Figs. 2a, 2b, 2c the microstructures of the compositions abbreviated as (a), (b) and (c) are shown, they contain 0.00, 0.16 and 0.4 mol% Bi^{3+} , respectively. All samples are semiconducting and they exhibit the PTCR anomaly, Figs. 4a, 4b, 4c.

When the amount of Bi_2O_3 present in the glassy phase increases further, to 80 mol%, i.e. to the point (d), which is located at the crossing with the tie-line $BaTiO_3$ -D, i.e. $BaTiO_3$ -(20 mol% B_2O_3 -80 mol% Bi_2O_3) the amount of donor in the samples increases to 0.64 mol% Bi^{3+} . In this case the grain growth is hindered and after sintering a fine-grained microstructure is obtained. In general, the AGG and the formation of semiconducting grains do not occur here, rather they occur at some discrete positions, which might be a consequence of the inhomogeneity of the samples, Fig. 2d.

The end of this tie-line connecting the constant molar amount of 0.4 mol% "glassy phase" represents the sample (e) containing pure Bi_2O_3 with a melting point of 820°C.

During sintering at 1300°C in samples with pure Bi_2O_3 a certain amount of Bi_2O_3 evaporated so that the final amount of Bi^{3+} was lower than that of the starting composition. This was not the case when the Bi_2O_3 was a part of B_2O_3 - Bi_2O_3 glassy phase. The chemical ana-

lyses indicated that after sintering about 0.1 mol% of Bi_2O_3 evaporates during sintering of the 0.4 mol% doped sample. These samples contain after sintering an amount of donor higher than the critical concentration. However, sample (e) shows large grains, Fig. 2e, with a faint PTCR effect at high resistance, close to the instrument detection limit, Fig. 4c.

The tie-line containing 0.4 mol% of glassy phase shows explicitly how the composition of the glassy phase governs the microstructure development associated with the electrical resistance. One can observe that close to the compositions (c) the boundary representing the composition of samples with 0.4 mol% of donor-dopant divides the tie-line into two different parts. In one part, below 0.4 mol% Bi^{3+} , where the microstructure consists of large semiconducting grains, and the other part, above 0.4 mol% Bi^{3+} , where a microstructure that consists of isolating, small grains prevails, Fig. 2d. So, this amount was adopted as the critical donor concentration C_0 for this system.

Exceptions prove samples (a) where the PTCR effect was identified in spite of the fact that the "true" donors were absent. The reason for this phenomenon is not known yet.

On the other hand in samples (e) grain growth occurs despite the overall composition of these samples is higher than 0.4 mol% Bi^{3+} .

Microstructural development of barium titanate at a constant glassy-phase composition with different amounts of glassy phase

The samples with the composition lying on the tie-line A, ($BaTiO_3$ - B_2O_3) contain no "proper" donors. Here the sintered samples show surprisingly a PTCR effect, Fig. 4d. The final grain size was more or less similar while the final grains show a relatively high resistance and a noticeable and a reproducible PTCR effect. One of the reasons might be the supposition that the amount of boron that dissolves in $BaTiO_3$ should be very small and independent of the glassy phase composition.

Tie-line B, i.e. $BaTiO_3$ - (80 mol% B_2O_3 -20 mol% Bi_2O_3): when the composition of the glassy phase changes to that of 80 mol% B_2O_3 -20 mol% Bi_2O_3 , which suggests a presence of donor dopant, the semiconductivity of donor-doped $BaTiO_3$ can be expected as well as the anomaly in the grain growth and the conductivity. On this tie-line the microstructure and the electrical properties are strongly related to the donor concentration in samples. The critical concentration and the formation of a fine-grained non-conducting microstructure of the composition lying on this tie-line is above 0.80 mol% of glassy phase, which is 0.32 mol% Bi^{3+} . All the investigated compositions on this tie-line are semiconducting and exhibit the PTCR effect, Fig. 4a, since they contain less donor dopant than the critical concentration C_0 0.4 mol% Bi^{3+} .

Tie-line C, $BaTiO_3$ -(50 mol% B_2O_3 -50 mol% Bi_2O_3):

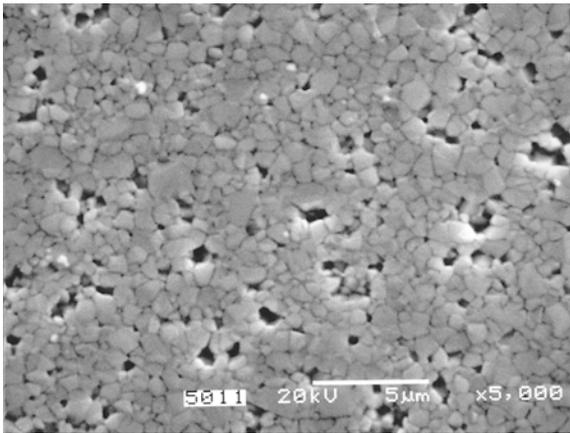


Fig. 3. Microstructure of a sample lying on the tie-line C, BaTiO_3 - $(50 \text{ mol}\% \text{ B}_2\text{O}_3$ - $50 \text{ mol}\% \text{ Bi}_2\text{O}_3)$ containing $0.8 \text{ mol}\%$ of glassy phase ($0.8 \text{ mol}\% \text{ Bi}^{3+}$).

on this tie-line the samples containing up to $0.4 \text{ mol}\%$ of glassy phase were found to be semiconducting, while those samples with $0.8 \text{ mol}\%$ of glassy phase and more, were fine grained. In samples containing $0.8 \text{ mol}\%$ of glassy phase, the amount of donor dopant was too high, i.e. $0.8 \text{ mol}\% \text{ Bi}^{3+}$, so that anomalous grain growth (AGG) was blocked, Fig. 3. On the other hand, all samples containing $0.4 \text{ mol}\%$ glassy phase and less which equates to $0.4 \text{ mol}\% \text{ Bi}^{3+}$ and less, were large grained and semiconducting and showed the PTCR effect, Fig. 4b.

Tie-line D, BaTiO_3 - $(20 \text{ mol}\% \text{ B}_2\text{O}_3$ - $80 \text{ mol}\% \text{ Bi}_2\text{O}_3)$: when the composition of the glassy phase changes to $20 \text{ mol}\% \text{ B}_2\text{O}_3$ - $80 \text{ mol}\% \text{ Bi}_2\text{O}_3$ we find the composition with $0.4 \text{ mol}\%$ glassy phase and/or $0.64 \text{ mol}\% \text{ Bi}^{3+}$ in the composition diagram, where the AGG is blocked, i.e. where the fine-grained and highly resistive samples

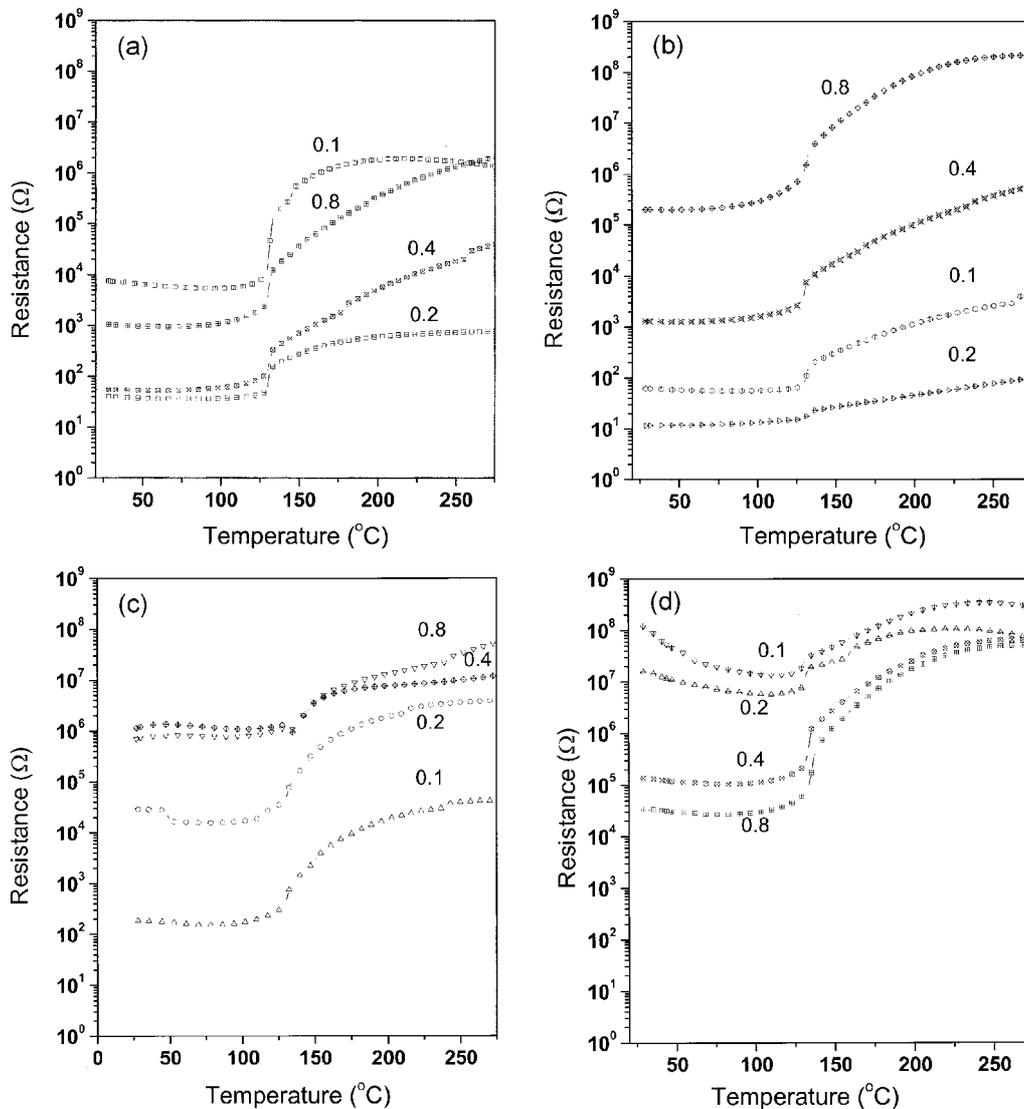


Fig. 4. (a) Resistance versus temperature for samples with their composition along the tie-line B, BaTiO_3 - $(80 \text{ mol}\% \text{ B}_2\text{O}_3$ - $20 \text{ mol}\% \text{ Bi}_2\text{O}_3)$. (b) Resistance versus temperature for samples with their composition along the tie-line C, BaTiO_3 - $(50 \text{ mol}\% \text{ B}_2\text{O}_3$ - $50 \text{ mol}\% \text{ Bi}_2\text{O}_3)$. (c) Resistance versus temperature for samples with their composition along the tie-line E, BaTiO_3 - Bi_2O_3 . (d) Resistance versus temperature for samples with their composition along the tie-line A, BaTiO_3 - B_2O_3 .

are located. In contrast, the microstructure of the samples with 0.2 mol% glassy phase, which is 0.32 mol% Bi^{3+} , exhibit AGG and were semiconducting.

Tie-line E, ($BaTiO_3$ - Bi_2O_3): on this tie-line four samples with 0.1, 0.2, 0.4 and 0.8 mol% Bi_2O_3 were investigated. Two of them doped with 0.1 and 0.2 mol% Bi_2O_3 containing less donor-dopant than the critical concentration (C_0) found for the system showed a remarkable PTCR effect and were semiconducting, Fig. 4c. The other two samples doped with 0.4 and 0.8 mol% Bi_2O_3 show a higher resistance and a small PTCR effect. Both samples contain more donor-dopant than the critical concentration (C_0) estimated for the system, Fig. 1.

The chemical analyses showed that in low-doped samples, up to 0.2 mol%, the evaporation of Bi_2O_3 from the samples was not significant and was not taken into the account. The identification of the PTCR anomaly in both samples (0.1 and 0.2 mol% Bi_2O_3) is in accordance with the grain-growth and conductivity anomaly in donor-doped $BaTiO_3$, where donor-dopants in the concentration range of around a few tenths of a mol percent cause the semiconductivity in $BaTiO_3$ and result in the PTCR effect.

The other two samples doped with 0.4 and 0.8 mol% Bi_2O_3 had a coarse-grained structure. Here, the grains grew to more than 50 μm but the samples showed a high resistance. Chemical analyses of the 0.8 mol% Bi_2O_3 -doped samples show, after sintering, only half of the nominal donor amount, i.e. 0.4 mol% Bi_2O_3 (0.8 mol% Bi^{3+}), which is substantially above the critical concentration observed in this system.

When the donor concentration gets too high in $BaTiO_3$ the mechanism of the donor incorporation usually changes and instead of grain growth of the reduced donor-doped phase the grain growth should be blocked. However, instead of that the insulating grains grew during sintering. One of the reasons for this could be the lack of ions with a high ionic strength during grain growth, for example Si^{4+} or B^{3+} , which stimulate AGG [8] and can influence the method of donor incorporation in the $BaTiO_3$ grains. However, the real reason is, at present, not known.

Electrical Properties

In parallel with the anomalous grain growth the Bi^{3+} and B^{3+} in small amounts, if at all, were incorporated, inducing the semiconductivity and the PTCR effect. Bi^{3+} was the only effective donor present in the studied composition diagram. It induces the semiconductivity when incorporated in grains during the anomalous grain growth (AGG). The anomalous grain growth in $BaTiO_3$ is expected and can be treated as an intrinsic property of $BaTiO_3$. So, whenever during anomalous grain growth in $BaTiO_3$ suitable donors are present in concentrations below the critical level the anomalous

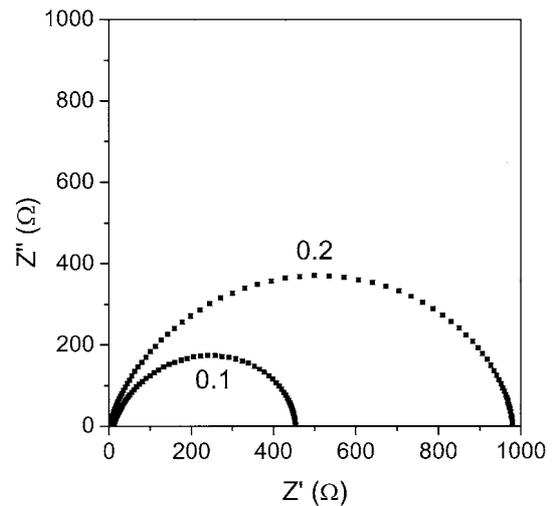


Fig. 5. Complex-impedance spectra of samples from the tie-line D, $BaTiO_3$ -(20 mol% B_2O_3 -80 mol% Bi_2O_3).

grain growth associated with donor-dopant incorporation will proceed and induce the semiconductivity. In the whole region characterized by the semiconducting anomalous grains the samples exhibit the PTCR anomaly. The resistivity anomaly in the samples is a few orders of magnitude. The anomaly in the electrical resistivity of the sintered samples was not optimized and was not very high but it was present in all the samples considered, Fig. 1. The room-temperature resistance is dependent on the amount of glassy phase present in the samples. A large amount of glassy phase decreases the average grain size and increases the number of grain boundaries per sample volume and their thickness. In Fig. 4a the temperature dependence of the resistance of the samples lying on the tie-line $BaTiO_3$ -B is shown, they contain a glassy phase with composition B. All samples lying on this tie-line exhibit the AGG, the PTCR anomaly and a low resistance.

The complex-impedance spectra complete these results of the $R(T)$ measurements, Fig. 5. The grain resistance stays more or less constant while the grain-boundary resistance of the samples is strongly dependent on the amount of the glassy phase. All the compositions studied on this tie-line show the PTCR anomaly, however, the room-temperature resistance increases with the amount of liquid phase.

A higher amount of liquid phase slows down the AGG, which has the consequence that the average grain size decreases. More grain boundary surface area per sample volume unit in samples changes the resistance and capacitance of the chemical make up. So, a larger amount of glassy phase strongly increases the ultimate grain-boundary resistance at a nearly constant grain resistance.

The temperature dependence of relative permittivity (ϵ_r) for the samples containing 0.8, 0.4, 0.2 and 0.1 mol% of glassy phase is shown in Fig. 6. Also, the relative permittivity decreases for samples with large

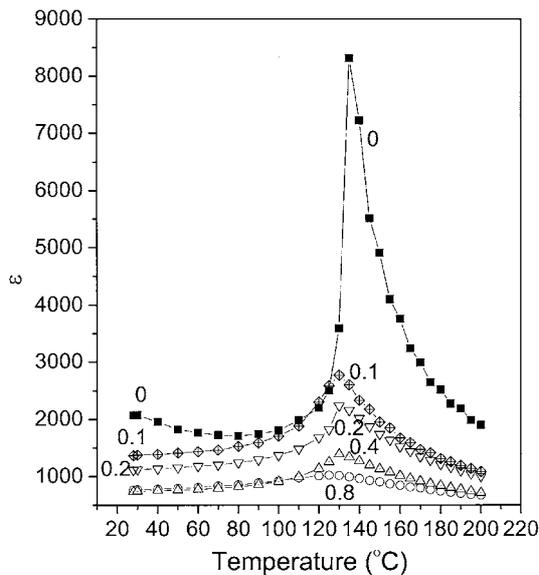


Fig. 6. Temperature dependence of relative permittivity as a function of BaTiO_3 samples with various amount of glassy phase (20 mol% B_2O_3 -80 mol% Bi_2O_3).

amounts of glassy phase, due to the dielectric dilution.

Conclusions

The samples within the composition diagram show

the donor-dopant-induced anomaly in grain size and electrical conductivity and the PTCR effect.

The samples containing less than 0.4 mol% of the donor-dopant Bi^{3+} were semiconducting and showed a PTCR anomaly of a few orders of magnitude. The PTCR effect in samples can be optimised by the modification of the microstructure and the potential barrier at the grain boundaries of samples. An exception was the highly doped samples on the tie-line E, (BaTiO_3 - Bi_2O_3).

Samples containing B_2O_3 were found to be semi-conducting exhibiting a PTCR effect. The effect is under the consideration.

References

1. L. Hanke and H. Schmelz, *Ceramic Forum International* 59[4] (1982) 1-7.
2. J. Daniels and R. Wernicke, *Philips Res. Repts.* 31 (1976) 544-552.
3. B. Huybrechts, K. Ishizaki, and M. Takata, *J. Mat. Sci.* 30 (1995) 2463-2474.
4. M. Drofenik, *J. Am. Cer. Soc.* 70[5] (1987) 311-314.
5. I. Burn, *J. Mat. Sci.* 17 (1982) 1398-1408.
6. Y. Kuromitsu, S.F. Wang, S. Yoshikawa, and R.E. Newnham, *J. Am. Cer. Soc.* 77[2] (1994) 493-498.
7. J. Qi, W. Chen, Y. Wu, and L. Li, *J. Am. Cer. Soc.* 81[2] (1998) 437-438.
8. T. Yamamoto and T. Sakuma, *Mat. Sci. Forum* 204/206 (1996) 491-496.