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Semiconducting Barium Titanate Doped with Oxygen-free Compounds

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Abstract

The physicochemical properties of semiconducting $BaTiO_3$ *doped with* TiB_2*, TiC, TiN, ZrN, BN, and AlN have been studied using thermogravimetry, XRD analysis and electron microscopy. When the above dopants are added, compounds are formed which influence redox reactions, which proceed during the synthesis of* $(Ba,Y)TiO_3$ *ceramics, and allow the temperature range of reduction to be extended. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: powders: solid state reactions, sintering, $BaTiO_3$ and titanates, borides, carbides, nitrides.

1 Introduction

Barium titanate-based semiconducting posistor ceramics with tailor-made properties is prepared by firing in an oxidizing atmosphere with aliovalent doping. In addition to dopants which act as donors, mineralizers are added to posistor ceramics, to form a homogeneous microstructure, decrease the sintering temperature, promote the reduction of ceramics in case of high-temperature sintering and improve the reproducibility of the properties. Oxygen-free compounds, which interact with oxygen during firing and accelerate the reduction process, can be used as mineralizers. When choosing mineralizer, the possibility of its interaction with $BaTiO_3$ or with the products of its reduction to form a low-melting liquid phase, which is able to slow down the grain oxidation, must be also taken into account. Si_3N_4,[1] boron[2] and titanium compounds[3] are used as oxygen-free mineralizers in the synthesis of semiconducting barium titanate. However, the effect of oxygen-free titanium compounds on the properties of semiconducting posistor ceramics is scantily studied in literature.

The aim of this study was to elucidate the character of the action of the dopants TiB_2, TiC, TiN, ZrN, BN and AlN on the synthesis and the electrophysical properties of barium titanate-based semiconducting ceramics.

2 Experimental

Extra pure $BaCO_3$, TiO_2, and Y_2O_3, chemically pure TiB_2, TiC, TiN, ZrN, BN and AlN were used as stating reagents for synthesis. Samples in the form of 3 mm thick disks of 10 mm in diameter with applied aluminium electrodes were investigated. Thermogravimetric investigations were carried out on a Q-1000 OD-102 device; X-ray phase analysis was carried out on a DRON-UM diffractometer (Cu K_α radiation). The electrophysical properties were measured over the wide temperature range as well as the electric field strength. Electronic reflection visible spectra (200–850 nm) were taken with a Pye Unicam PU 8800 UV/VIS spectrophotometer at $T = 20°C$.

3 Results and Discussion

At the first stage, the phase transformations that are observed during the oxidation of the individual compounds TiB_2, TiC, TiN, ZrN, BN, and AlN were studied. When titanium diboride TiB_2 is heated at temperatures ranging from 20 to 1000°C, an exothermic effect is observed at 550°C, which is caused by the formation of the anatase modification of titanium (IV) oxide and boron oxides (B_2O_3, B_2O_2); this agrees with the data reported in Ref. 4. Boron oxides are X-ray amorphous at this temperature. At 640°C, a mixture of the anatase and rutile modifications of TiO_2 is observed. The exothermic effect at 730°C is caused by the interaction between B_2O_2 and TiO_2 to form

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*To whom correspondence should be addressed. Fax: +38-044-444-3070; e-mail: belous@mail.kar.net titanium borate $TiBO_3$.[5] Above 850°C, anatase changes into rutile. At temperatures of over 1300°C, the Ti_3O_5 phase was detected, which was formed by the decomposition of titanium borate; this agrees with the results of Ref. 6.

When TiC is heated, an exothermic effect is observed at 450°C, which is caused by the formation of TiO_2 (anatase) followed by its change into rutile.

The compound TiN oxidizes at over 780°C, the rutile modification of titanium oxide being formed.

In the order ZrN–BN–AlN, zirconium nitride is the least thermodynamically stable compound. A peculiarity of the oxidation of ZrN, which occurs at over 730°C, is the formation of the tetragonal modification of zirconium oxide.

We observed the oxidation of boron nitride at over 950°C, which is different from the data reported in Ref. 7 (800°C), which may be due to the prehistory of BN synthesis.

The oxidation of aluminium nitride occurs at over 1000°C. To change completely AlN into Al_2O_3, a 2–4 h long heat treatment at temperature $T > 1200°C$ is needed, which agrees with the results of Ref. 8.

The investigation of the phase transformations which are observed on heating mixtures of doped barium titanate $(Ba,Y)TiO_3$ with oxygen-free compounds showed that $BaTi(BO_3)_2$ is formed in the $(Ba,Y)TiO_3$–TiB_2 system at over 1150°C, and only a small part of titanium diboride is oxidized.

In the $(Ba,Y)TiO_3$–TiC system, titanium carbide oxidizes at 490°C (Fig. 1.) to TiO_2 (anatase). When the temperature is raised, the amount of the rutile modification increases.

In the $(Ba,Y)TiO_3$–TiN system, titanium nitride oxidizes at high temperatures (780°C), the rutile modification of titanium oxide being formed.

When ZrN, BN, AlN (15 mol%) are added to semiconducting barium titanate, the decomposition temperature of the above nitrides decreases to 710, 880, 970°C, respectively.

Zirconium oxide (ZrO_2 tetr.) formed on heating in the $BaTiO_3$–ZrN system exists in the range 700–900°C and reacts with barium carbonate at its decomposition temperatures to form barium zirconates ($BaZrO_3$, Ba_2ZrO_4). At temperatures of over 1300°C, barium zirconates dissolve in barium titanate to form a solid solution.

In the $BaTiO_3$–BN system, an exothermic effect is observed at 950°C after the oxidation of boron nitride to boric anhydride: this effect is associated with the formation of barium borates, $Ba_nB_2O_{3+n}$, where $n \geq 3$. The significant decrease in the intensity of all diffraction peaks in the XRD patterns of the specimens after heat treatments at 1200°C indicates the formation of boron-containing glasses with barium titanate (Fig. 2). The formation of the low-melting boron-containing phase is corroborated by the intensification of the reflection band at $2{\cdot}6\times10^4$–$4\times10^4\,cm^{-1}$ in the electronic diffuse reflection spectrum of the $(Ba,Y)TiO_3$–BN system.

In the $(Ba,Y)TiO_3$–AlN system the endothermic effect at 970°C indicates the formation of barium aluminate $Ba_{10}Al_2O_{13}$.

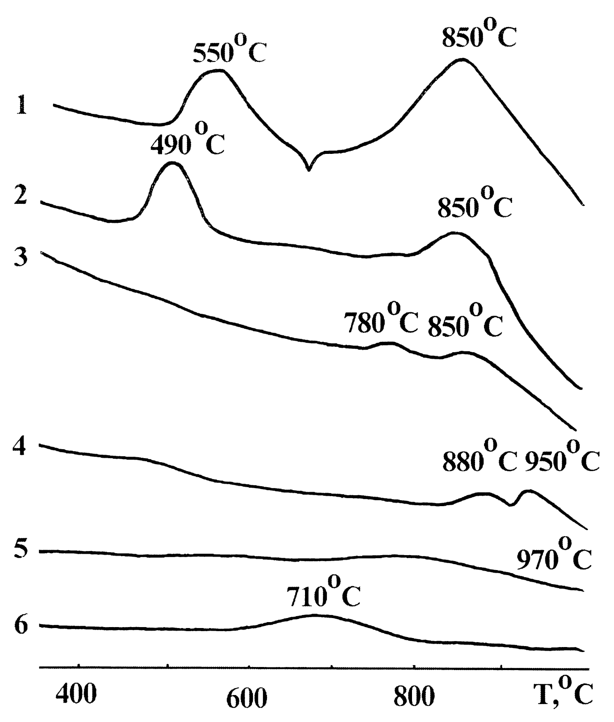

Fig. 1. DTA of $BaTiO_3$ with additives of TiB_2 (1), TiC (2), TiN (3), BN (4), AlN (5) and ZrN (6).

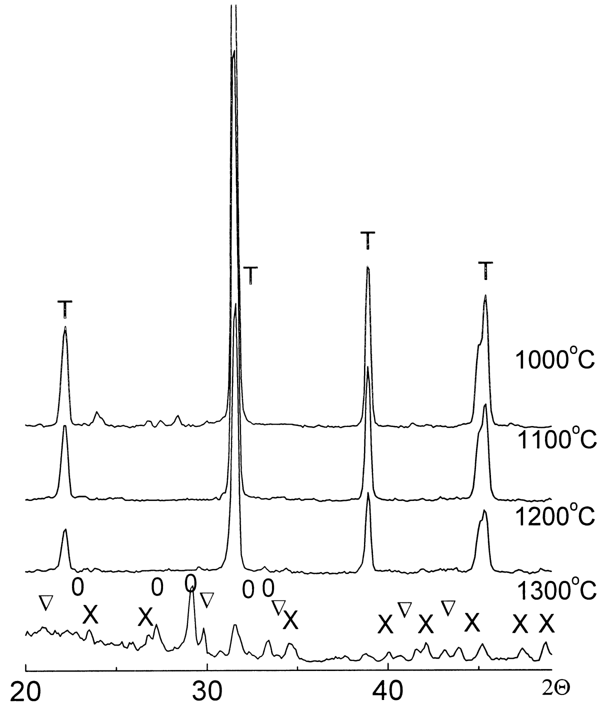

Fig. 2. XRD patterns of $BaTiO_3$–BN systems versus temperature of synthesize. T, $BaTiO_3$; O, $Ba_3B_2O_6$; ▽ $BaTi(BO_3)_2$; X, $Ba_nB_2O_{3+n}$, where $n \geq 3$.

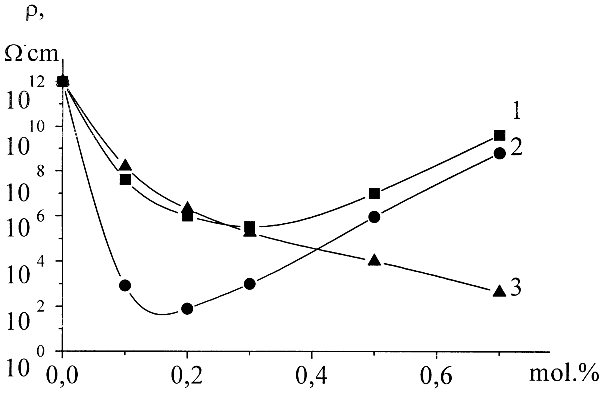

Fig. 3. Resistivity of $BaTiO_3$-based semiconducting ceramics at 20°C as a function of the amount of the dopants TiB_2 (1), TiC (2) and TiN (3) ($T_{sint} = 1360°C$).

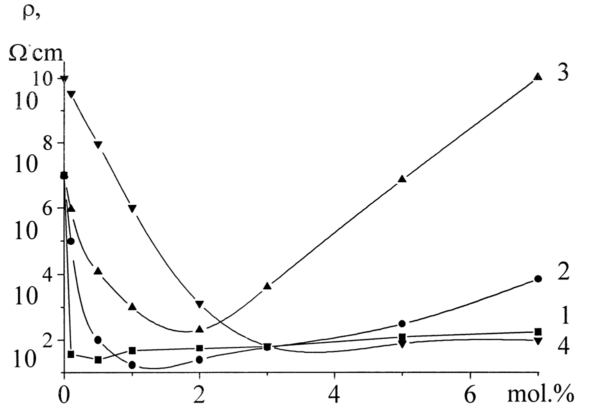

Fig. 4. Resistivity of $BaTiO_3$-based semiconducting ceramics at 20°C as a function of the amount of the dopants BN (1), AlN (2), ZrN (3) and 2 mol% SiO_2 (4) ($T_{sint} = 1360°C$).

As follows from the examination of electronic diffuse reflection spectra, a small amount of the $Ba_6Ti_{17}O_{40}$ phase and a small number of oxygen vacancies are present in all specimens of semiconducting barium titanate doped with oxygen-free compounds as evidenced by the absorption bands at 770, 840 and 650, 510 nm, respectively.

At low TiB_2, TiC and TiN concentrations, resistivity decreases (Fig. 3), which can be attributed to the formation of a weakly reducing atmosphere and a liquid phase, which hinders oxidation on cooling. The dopants ZrN, BN and AlN decrease the electrical resistance of posistor ceramic by 5–6 orders of magnitude at low concentration (0–2 mol%) (Fig. 4).

Addition of oxygen-free dopants leads to a widening of the temperature range of posistor ceramic sintering (Figs 5 and 6). The widest temperature range of posistor ceramic sintering is observed when boron nitride is added (Fig. 6).

Analysis of the dependence of normalized resistivity on electric field strength shows that the resistivity of TiB_2-, TiC-, and TiN-doped ceramic depends less strongly on electric field strength. Resistivity of BN-doped ceramic as a function of electric field strength pass through a maximum.

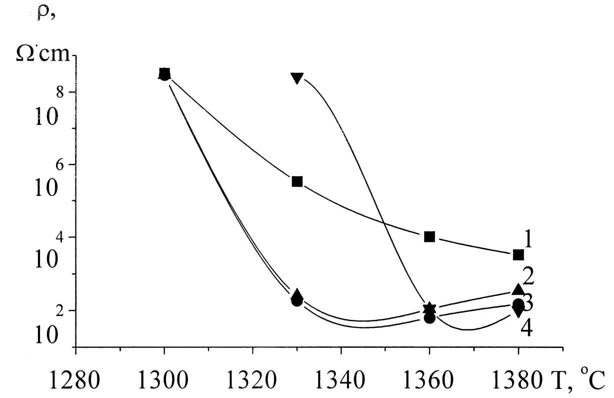

Fig. 5. Resistivity of $BaTiO_3$-based semiconducting ceramics containing 0·3 mol% TiB_2 (1), 0·1 mol% TiC (2), 0·7 mol% TiN (3) and 2 mol% SiO_2 (4) at 20°C as a function of sintering

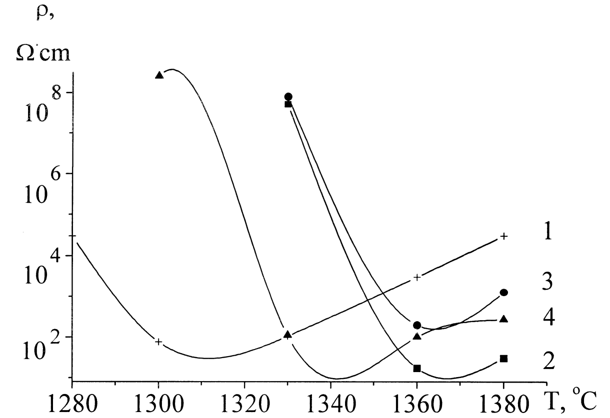

Fig. 6. Resistivity of $BaTiO_3$-based semiconducting ceramics containing 5 mol% BN (1), 1 mol% AlN (2), 2 mol% ZrN (3) and 2 mol% SiO_2 (4) at 20°C as a function of sintering temperature.

4 Conclusion

Thus, addition of the oxygen-free compounds TiB_2, TiC, TiN, ZrN, BN, and AlN to semiconducting barium titanate makes it possible to widen the temperature range of ceramic sintering, which may be accounted for by the formation of a weakly reducing atmosphere and a liquid phase, which hinders oxidation.

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