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THE INFLUENCE OF TiB_2, TiC AND TiN ON THE FORMATION AND PROPERTIES OF SEMICONDUCTIVE BARIUM TITANATE

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Semiconductive $BaTiO_3$-base ceramics doped with TiB_2, TiC and TiN are characterized by thermogravimetric measurements, X-ray diffraction analysis and electron microscopy data. The dopants promote the formation of the compounds which improve redox processes upon sintering of the $(BaY)TiO_3$ ceramics and widen the reduction temperature interval.

Semiconductive posistor ceramics on the basis of barium titanate possessing controlled electric properties are obtained by firing in oxidizing medium upon heterovalent doping. In addition to dopants acting as donors, mineralizers are also introduced into the ceramics. They ensure the forming of uniform microstructure, lower the sintering temperature, promote reduction of the ceramics upon high-temperature burning, prevent deep oxidation of the grains, and improve reproducibility of semiconductor properties. Several oxygenless compounds, which interact with oxygen upon firing and accelerate the reduction process, can be employed as the mineralizers. When choosing the mineralizers, one should also take into account that they can interact with $BaTiO_3$ or its reduction products to give a low-melting liquid phase which is capable of retarding the oxidation of the grains.

Silicon nitride Si_3N_4 [1–3], boron [1] and titanium [3–5] compounds were tested as oxygenless mineralizers in $(BaY)TiO_3$ ceramics. Silicon nitride creates a weakly reducting medium and induces the formation of low-melting compounds which decrease specific resistance of the semiconductive ceramics and widen the interval of its sintering temperature [2]. The boron compounds reduce the firing temperature, apparently due to the formation of a boron-containing low-melting eutectic mixture and the sintering in the presence of the liquid phase [1]. The material doped with titanium nitride exhibits a high reproducibility of the semiconductor properties [3]. The effects of other oxygenless titanium compounds on semiconductive posistor ceramics are poorly understood. The aim of the present study is to elucidate the influence of TiB_2, TiC and TiN additives on the synthesis and electrophysical properties of the $BaTiO_3$ based semiconductive ceramics.

The starting materials for the mixtures were extra-purity $BaCO_3$ (7–4), TiO_2 (9–2), and Y_2O_3. The temperature of the synthesis was chosen such as the concentration of free boron oxide after the first thermal treatment not to be higher than 1%. Before the second heat treatment, 0.1 to 0.7 mol.% of reagent-grade TiB_2, TiC, TiN or 2 mol.% SiO_2 was added to the mixture at the stage of wet grinding. The ceramics with the SiO_2 additive was used as the reference. The disk specimens, 3 mm thick and 10 mm in diameter, were prepared by semidry molding with an organic binder and

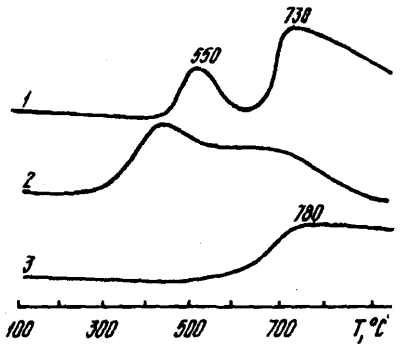

Fig. 1

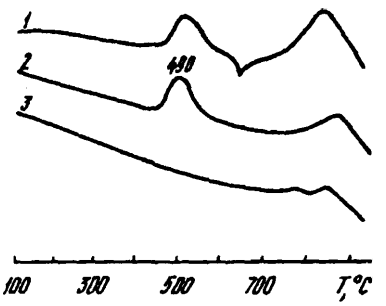

Fig. 2

Fig. 1. DTA curves for compounds TiB_2 (*1*), TiC (*2*), and TiN (*3*).

Fig. 2. DTA curves for systems $(BaY)TiO_3$–TiB_2 (*1*), $(BaY)TiO_3$–TiC (*2*), and $(BaY)TiO_3$–TiN (*3*).

sintered in air at 1300–1400 °C. The ohmic contact with the ceramics was realized through aluminum electrodes applied to the specimens. The phase transformations occurring upon heating TiB_2, TiC, TiN and on the synthesis of the semiconductive barium titanate were studied by thermogravimetric measurements on a derivatograph Q–1000 OD–102 at the heating rate of 10 °C/min. The samples calcined at a constant temperature for 2 h were identified by X-ray diffraction (XRD) analysis on a diffractometer DRON–UM (CuK_α radiation). Electrophysical characteristics were measured over a wide range of temperature and field strength.

The DTA and XRD data characterizing phase transformations upon oxidation of TiB_2, TiC, and TiN dopants are presented in Fig. 1 and Table 1. When heated from 20 to 1000 °C, titanium diboride showed an exothermic effect at 550 °C associated with the formation of titanium dioxide (anatase modification) and boron oxides (B_2O_3, B_2O_2). The reaction proceeds by the following scheme [6,7]:

$$3\ TiB_2 + 7\ O_2 \xrightarrow{550\ ^\circ C} 3\ TiO_2\ (anatase) + 2\ B_2O_3 + B_2O_2.$$

The boron oxide phases are not detected by XRD analysis because at the indicated temperature they are in a liquid state [8]. At 640 °C a mixture of the anatase and rutile modifications of TiO_2 is observed. A second exothermic effect appears at 730 °C due to the interaction of the lower boron oxide B_2O_2 with TiO_2 to give titanium borate [9]:

$$2\ TiO_2\ (anatase) + B_2O_2 \xrightarrow{730\ ^\circ C} 2\ TiBO_3.$$

Anatase is completely converted into rutile above 850 °C:

$$TiO_2\ (anatase) \xrightarrow{850\ ^\circ C} TiO_2\ (rutile).$$

At the temperature above 1300 °C, a new phase, Ti_3O_5, is formed due to decomposition of titanium borate via a series of intermediate products [9,10].

The phase transformations in the system $(BaY)TiO_3$–TiB_2 are characterized in Fig. 2 and Table 2. Titanium diboride in this system reacts with BaO to form $BaTi(BO_3)_2$, and only a small portion of the added TiB_2 is oxidized [8]:

$$2\ BaO + 2\ TiB_2 + 5\ O_2 \xrightarrow{1150\ ^\circ C} 2\ BaTi(BO_3)_2.$$

Titanium carbide exhibits an exothermic effect at 450 °C (Fig. 1) caused by the formation of TiO_2 (anatase) and its subsequent transition into rutile [11]:

$$TiC + 2\ O_2 \xrightarrow{450\ ^\circ C} TiO_2\ (anatase) + CO_2\uparrow.$$

Table 1

Phase Transformations of TiB_2, TiC, and TiN on Heating in Air (τ = 2 h)

T, °C	Phase composition		
	TiB_2	TiC	TiN
300	TiB_2	TiC	TiN
500	TiB_2	TiC, TiO_2 (anatase), TiO_2 (rutile) traces	TiN
640	TiB_2, TiO_2 (anatase), TiO_2 (rutile) traces	TiO_2 (anatase), TiO_2 (rutile) traces	TiN
800	TiO_2 (anatase) traces, TiB_2, TiO_2 (rutile)	TiO_2 (anatase) traces, TiO_2 (rutile), TiO, Ti_2O_3	TiO_2 (rutile), TiO, Ti_2O_3
1300	TiB_2, TiO_2 (rutile), $TiBO_3$	TiO_2 (rutile)	TiO_2 (rutile)
1360	TiB_2, TiO_2 (rutile), Ti_3O_5	TiO_2 (rutile)	TiO_2 (rutile)

Table 2

Phase Transformations in the Systems $(BaY)TiO_3$–TiB_2, $(BaY)TiO_3$–TiC, and $(BaY)TiO_3$–TiN on Heating in Air (τ = 2 h)

T, °C	Phase composition*		
	$(BaY)TiO_3$–TiB_2	$(BaY)TiO_3$–TiC	$(BaY)TiO_3$–TiN
20	TiB_2, $BaTiO_3$	TiC, $BaTiO_3$	TiN, $BaTiO_3$
350	TiB_2, $BaTiO_3$	TiC, $BaTiO_3$	TiN, $BaTiO_3$
500	TiB_2, $BaTiO_3$, TiO_2 (anatase) traces, TiO_2 (rutile)	TiC, $BaTiO_3$, TiO_2 (anatase) traces, TiO_2 (rutile)	TiN, $BaTiO_3$
800	TiB_2 traces, $BaTiO_3$, TiO_2 (anatase), TiO_2 (rutile)	$BaTiO_3$, TiO_2 (anatase), TiO_2 (rutile)	TiN traces, $BaTiO_3$, TiO_2 (rutile)
1150	$BaTiO_3$, TiO_2 (rutile), $BaTi(BO_3)_2$	$BaTiO_3$, TiO_2 (rutile)	$BaTiO_3$, TiO_2 (rutile)
1360	$BaTiO_3$	$BaTiO_3$	$BaTiO_3$

* No yttrium was observed by XRD analysis.

Examination of the phase transformations in the system $(BaY)TiO_3$–TiC has shown that titanium carbide is oxidized at 480 °C to TiO_2 (anatase) which is transformed into rutile at higher temperature (Table 2).

$$TiO_2 \text{ (anatase)} \xrightarrow{640\ ^\circ C} TiO_2 \text{ (rutile)}.$$

Titanium nitride is oxidized at a relatively high temperature (780 °C) to give titanium dioxide in the rutile modification [10]:

$$2\ TiN + 3\ O_2 \xrightarrow{780\ ^\circ C} 2\ TiO_2 \text{ (rutile)} + N_2\uparrow.$$

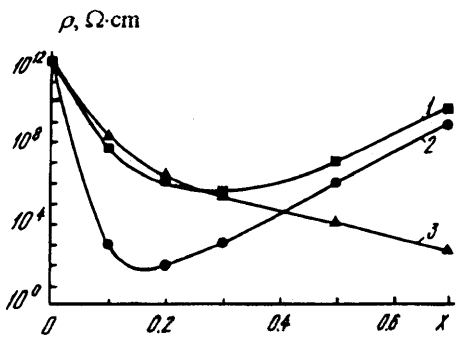

Fig. 3

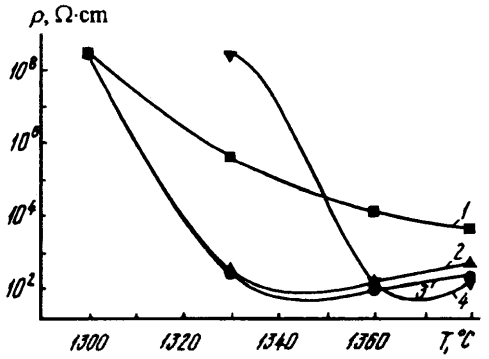

Fig. 4

Fig. 3. The concentration dependence of specific resistance for semiconductive ceramics $BaTiO_3$ doped with TiB_2 (*1*), TiC (*2*), and TiN (*3*) (T_{sint} = 1330 °C).

Fig. 4. Specific resistance ρ (20 °C) of semiconductive ceramics $BaTiO_3$ doped with 0.3 mol.% TiB_2 (*1*), 0.1 mol.% TiC (*2*), 0.7 mol.% TiN (*3*), or 2 mol.% SiO_2 (*4*) as a function of sintering temperature.

Owing to the high oxidation temperature of TiN [8,10], the anatase phase is not formed. The samples after heating contain only the rutile modification of TiO_2, the content of which increases with temperature (Table 1). The same is observed in the system $(BaY)TiO_3$–TiN where TiO_2 (rutile) appears at > 800 °C (Table 2).

In all the cases studied, a weakly reducing medium is produced within the specimens upon sintering of the $(BaY)TiO_3$ ceramics with the TiB_2, TiC, and TiN additives in the ambient atmosphere. In addition, an excess of TiO_2 is formed and a liquid phase appears between the grains. This improves the sintering process and widens the temperature range of the reduction.

As shown in Fig. 3, specific resistance ρ of the $BaTiO_3$ based semiconductive ceramics essentially depends on concentration of the additives TiB_2, TiC, and TiN. At small dopant concentrations, the value of ρ decreases that can be explained by the creation of a weakly reducing atmosphere and the appearance of a liquid phase which prevents oxidation upon cooling. At 0.3, 0.1 and 0.7 mol.% content of TiB_2, TiC and TiN, respectively, the specific resistance passes through the minimum. On a further increase in concentration of the additives, the superstoichiometric content of TiO_2 rises together with the resistance [12]. The difference in dopant concentration corresponding to the minimum value of ρ can be explained by different mechanisms of oxidation of the additives and, in the case of TiB_2, also by the formation of low-melting compound $BaTi(BO_3)_2$.

The oxygenless titanium additives in the ceramics widen the temperature interval in which the material exhibits semiconductor properties. Similar results were obtained with carbon additives which produce a weakly reducing atmosphere [13]. The SiO_2-doped ceramics, which is often used in manufacturing posistors, has optimum properties when sintered at 1360 °C (Fig. 4). Compounds TiB_2, TiC, and TiN decrease the sintering temperature to 1330 °C, the specific resistance of the materials with TiC and TiN additives being close to that of the reference SiO_2-doped ceramics (Fig. 4). The higher resistance of the composition with TiB_2 can be accounted for by the formation of boron compounds.

Figure 5 represents the temperature variations of specific resistance for the ceramic materials modified by TiB_2, TiC, TiN (sintered at 1330 °C), or SiO_2 (sintered at 1360 °C). Compounds TiC and TiN increase the ratio of the maximum and minimum resistance (ρ_{max}/ρ_{min}). The analysis of the semi-log plots of normalized specific resistance ρ/ρ_0 versus electric field strength $E^{1/2}$ for the samples with concentration of the additives corresponding to ρ_{min} shows that TiB_2, TiC, and TiN make the specific resistance less sensitive to temperature compared to SiO_2 (Fig. 6).

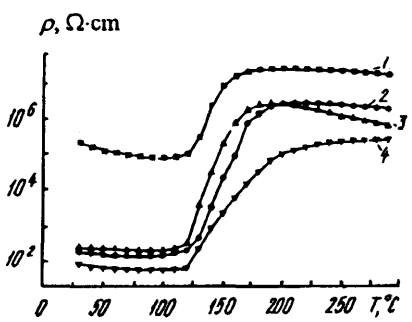

Fig. 5

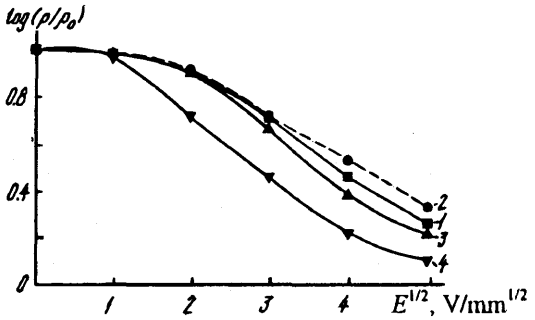

Fig. 6

Fig. 5. Temperature dependence of specific resistance for semiconductive $BaTiO_3$-base ceramics doped with 0.3 mol.% TiB_2 (*1*), 0.1 mol.% TiC (*2*), 0.7 mol.% TiN (*3*), or 2 mol.% SiO_2 (*4*) (T_{sint} = 1330 °C for *1–3* and 1360 °C for *4*).

Fig. 6. The plots of $\log(\rho/\rho_0)$ *vs.* $E^{1/2}$ for semiconductive $BaTiO_3$-base ceramics doped with 0.3 mol.% TiB_2 (*1*), 0.1 mol.% TiC (*2*), 0.7 mol.% TiN (*3*), or 2 mol.% SiO_2 (*4*). For T_{sint} see Fig. 5.

In summary, the introduction of TiB_2 into composition of the $BaTiO_3$ based ceramics results in the creation of a weakly reducing atmosphere within the samples and the formation of TiO_2 and $BaTi(BO_3)_2$ phases. At the same time the interval of the reduction temperature becomes wider, the varistor effect is weakened and the resistance of the samples increases. The TiC and TiN additives promote the formation of the TiO_2 phase upon sintering and produce a weakly reducing atmosphere in the ceramics. This widens the reduction temperature interval, increases the ratio ρ_{max}/ρ_{min} and decreases the varistor effect.

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