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THE INFLUENCE OF BN, AlN AND ZrN ADDITIVES ON PROPERTIES OF SEMICONDUCTING BARIUM TITANATE

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Physicochemical properties of semiconducting Y-containing $BaTiO_3$ ceramics doped with BN, AlN and ZrN were investigated by using thermogravimetry, X-ray diffraction analysis and electron microscopy. The additives were shown to form compounds which affect the redox reactions during the synthesis of $BaTiO_3$ and extend thereby the temperature interval of the ceramics reduction.

Ceramics on the basis of semiconducting barium titanate ($BaTiO_3$) is widely used in resistors with a positive temperature coefficient of resistance (PTCR). The semiconductor properties appear on doping $BaTiO_3$ with heterovalent donor additives. Mineralizers are also introduced in the ceramics together with the dopants. Though not inducing semiconductance, they substantially affect behavior of the dopants, the forming of microstructure, and redox reactions occurring on synthesis of the ceramics. It is very important in production of posistors to attain reproducibility of tlieir properties and for this reason the variations in the cooling rate should have minimum effect on oxidation of the ceramic grains. Oxygenless compounds used as mineralizers stabilize the reduced semiconductor phase owing to oxidation of the additives during sintering. The oxidation products of the mineralizers, in turn, may change die sintering temperature and microstructure of the ceramics. Several oxygenless compounds, e.g., Si_3N_4 [1,2], BN [3,4], TiB_2, TiC, TiN [5,6] were tested as mineralizers. Among titanium compounds, TiN was shown to be the best [6]. In this connection it seems worthwhile to extend the range of mineralizers for synthesis of semiconducting barium titanate ceramics by testing new nitrides.

The aim of the present work is to clarify the effect of boron, aluminum and zirconium nitrides on the formation and electrophysical properties of the BaTiO3-based semiconducting ceramics.

The starting materials for synthesis of semiconducting $BaTiO_3$ by ceramic process were $BaCO_3$, TiO_2 and Y_2O_3, all of the special purity grade. The yttrium, substituting ions Ba^{2+} imparts semiconductor properties to the samples. Before the second heat treatment, reagent-grade BN, ZrN or AlN were introduced in the blend at the stage of wet grinding (the grinding with AlN was conducted in benzene to prevent hydrolysis). The SiO_2-modified ceramics was used as the reference. Disk specimens, 3 mm thick and 10 mm in diameter, were molded, under the pressure of 0.1 MPa, by semidry method with an organic binder and sintered at 1300-1380 °C. Aluminum electrodes were applied to the specimens to provide ohmic contact with the ceramics. The phase transformations were studied through thermal analysis (derivatograph Q-1000 OD-102, heating rate 10°C/min) and X-ray diffraction analysis (diffractometer DRON-3M, CuK_α radiation). Electrophysical measurements were performed over a wide range of temperature and electric field strength.

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Table 1

Phase Composition of BN, AlN and ZrN after Heating in Air for 2 h

T,°C	Phase composition		
	BN	AlN	ZrN
20	BN	AlN	ZrN, ZrO_2(tetr.) (traces), ZrO_2(mncl.) (traces)
600	BN	AlN	ZrN, ZrO_2 (telr.), ZrO_2 (mncl.) (traces)
750	BN	AlN	ZrO_2 (tetr.), ZrO_2 (mncl.)
900	BN, B_2O_3 (traces)	AlN, Al_2O_3 (traces)	ZrO_2 (tetr.), ZrO_2 (mncl.)
1000	B_2O_3	AlN,Al_2O_3	ZrO_2 (tetr.), ZrO_2 (mncl.)
1200	B_2O_3	Al_2O_3	ZrO_2 (tetr.), ZrO_2 (mncl.)

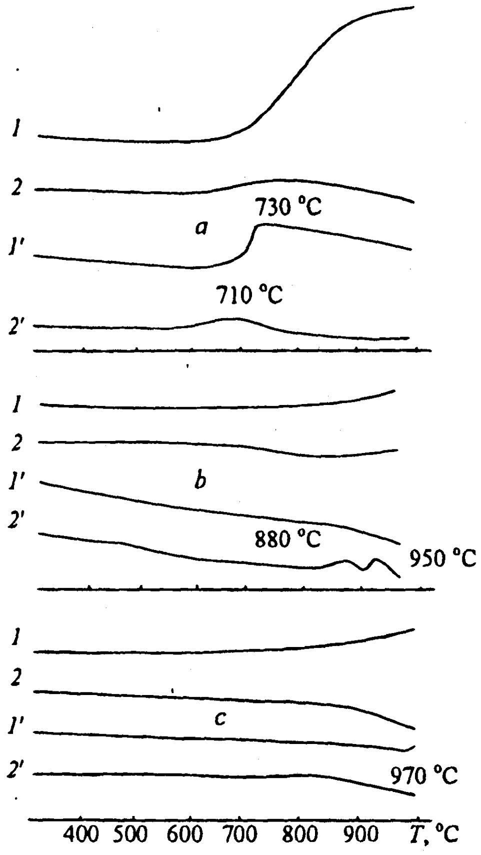

Fig. 1. TG (1,2) and DTA (1',2') curves: *a* - ZrN (1,1'), (BaY)TiO_3-ZrN (2.2'); *b* - BN (1,1'), (BaY)TiO_3-BN (2,2'); c - AlN (1,1'), (BaY)TiO_3-AlN (2,2').

According to Table 1 and Fig. 1, zirconium nitride is the least stable in the series BN, AlN, ZrN. The exotherm at 730 °C points to oxidation of ZrN by the scheme

$$2\,ZrN + 2\,O_2 \xrightarrow{730\,°C} 2\,ZrO_2\,(tetr.) + N_2 \qquad (1)$$

which is consistent with the data reported in [10]. The oxidation should lead to 17.1% gain in weight (found 16.5%). The oxidation product is tetragonal zirconium oxide.

Table 2

Phase Composition of Semiconducting Barium Titanate
with Nitride Additives (15 mol.%) after Heating in Air for 2 h

T, °C	Phase composition*		
	$BaTiO_3$-$BaCO_3$-BN	$BaTiO_3$-$BaCO_3$-AlN	$BaTiO_3$- $BaCO_3$-ZrN
20	$BaTiO_3$, $BaCO_3$, BN	$BaTiO_3$, $BaCO_3$, AlN	$BaTiO_3$, $BaCO_3$, ZrN
600	$BaTiO_3$, $BaCO_3$, BN	$BaTiO_3$, $BaCO_3$, AlN	$BaTiO_3$, $BaCO_3$, ZrN
750	$BaTiO_3$, $BaCO_3$, BN	$BaTiO_3$, $BaCO_3$, AlN	$BaTiO_3$, $BaCO_3$, ZrN (traces), ZrO_2 (tetr.)
900	$BaTiO_3$, $BaCO_3$, сліди BN, B_2O_3	$BaTiO_3$, $BaCO_3$, AlN	$BaTiO_3$, $BaCO_3$, ZrO_2 (tetr.), $BaZrO_3$ (traces)
1100	$BaTiO_3$, $Ba_3B_2O_6$, $Ba_nB_2O_{3+n}$	$BaTiO_3$, $Ba_{10}Al_2O_{13}$	$BaTiO_3$, $BaZrO_3$, Ba_2ZrO_4
1300	$BaTiO_3$, $Ba_3B_2O_6$, $Ba_nB_2O_{3+n}$	$BaTiO_3$, $Ba_{10}Al_2O_{13}$	$Ba(Zr,Ti)O_3$

* ≤ 5 mol.% $BaCO_3$ was found by chemical analysis.

The absence of exothermic effects in DTA curves for BN and AlN up to 950 °C indicates that the compounds are oxidized at higher temperatures than ZrN. Judging by the data of thermal and XRD analysis, the oxidation of boron nitride by the scheme

$$4BN + 3O_2 \xrightarrow{900^o C} 2B_2O_3 + 2N_2\uparrow \tag{2}$$

occurs above 900 °C while in [7,8] the oxidation temperature of BN was reported to be 800 °C.

The most thermally stable aluminum nitride is oxidized to corundum at > 950 °C with the gain in weight:

$$4AlN + 3O_2 \xrightarrow{950^o C} 2Al_2O_3 + 2N_2\uparrow \tag{3}$$

The reaction is complete in 2-4 h at a temperature of no less than 1200 °C, in agreement with [8,9].

When ZrN, BN or AlN (15 mol.%) are introduced in the blend, the oxidation temperature of the additives decreases to 700, 880, and 970 °C, respectively (Fig. 1, Table 2) owing to reactions with the components of the mixtures.

Zirconium dioxide, ZrO2(tetr.), formed in the system BaTiO3-ZrN exists in the temperature range of 700-900 °C. According to the data of thermal and XRD analysis, the decomposition of $BaCO_3$ and its interaction with ZrO_2 occurs at > 820 °C:

$$BaCO_3 + ZrO_2 \xrightarrow{820\text{-}1000^o C} BaZrO_3 + CO_2\uparrow, \tag{4}$$

$$2BaCO_3 + ZrO_2 \xrightarrow{820\text{-}1000^o C} Ba_2ZrO_4 + 2CO_2\uparrow. \tag{5}$$

At temperatures close to the sintering temperature of the ceramics (1300 °C), barium zirconates and barium titanate give solid solution of the type $Ba(Ti_{1-x}Zr_x)O_3$.

In the system $BaTiO_3$-BN, after oxidation of BN to B_2O_3, barium borates are formed with the exothermic effect at 950 °C:

$$3BaCO_3 + B_2O_3 \xrightarrow{950^o C} Ba_3B_2O_6 + 3CO_2\uparrow, \tag{6}$$

$$nBaCO_3 + B_2O_3 \xrightarrow{950^o C} Ban_2O_{3+n} + nCO_2\uparrow \text{ (n>3).} \tag{7}$$

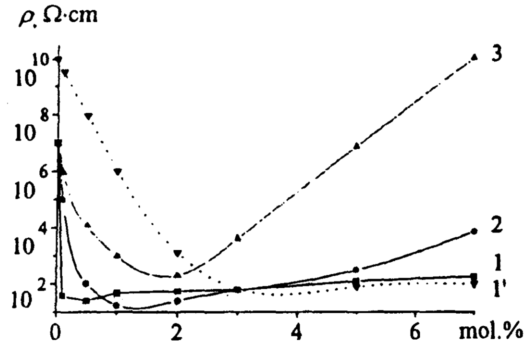

Fig. 2

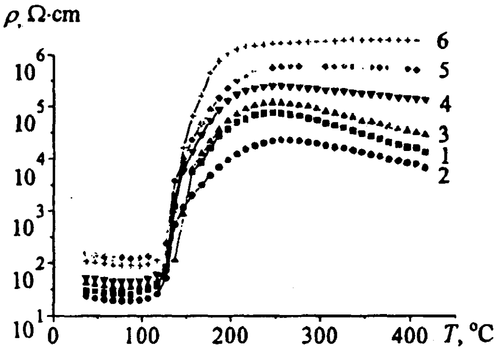

Fig. 3

Fig. 2. Specific resistance ($\rho_{20^{\circ}C}$) of the $BaTiO_3$-based semiconducting ceramics as a function of nitride concentration: 1 - BN, 2 - AlN, 3 - ZrN (T = 1360 °C); 1' - BN (T=1300°C).

Fig. 3. Temperature variations in specific resistance of $BaTiO_3$-based semiconducting ceramics with BN additives: 1 - 0.1, 2 - 0.5, 3 - 1.0, 4 - 3.0, 5 - 5.0, 6 - 7.0 mol.%.

The significant decrease in intensity of all the reflections in diffractograms of the samples after thermal treatment at 1200 °C points to the formation of boron-containing glasses with barium titanate.

The exotherm at 970 °C observed in the system $BaTiO_3$-AlN suggests that AlN is oxidized under these conditions into barium aluminate, rather than to corundum as happens in the individual state:

$$20BaCO_3 + 4AlN + 3O_2 \xrightarrow{970^{\circ}C} 2Ba_{10}Al_2O_{13} + 20CO_2\uparrow + 2\,N_2\uparrow \qquad (8)$$

Therefore, AlN can be considered as the most reactive reducing additive at high temperatures.

Figure 2 illustrates the variation of specific resistance of the semiconducting ceramics with concentration of BN, AlN and ZrN additives. At low concentration (0-2 mol.%), all the additives reduce significantly, by 5 to 6 orders of magnitude, the electric resistance of the posistor ceramics. Boron and aluminum nitrides stabilize the reduced semiconductor phase most effectively.

With BN, the ceramics exhibit semiconductance over the widest concentration range. This mineralizer is the most suitable in cases where it is necessary to reduce the sintering temperature. Thus, with 3 mol.% BN, the sintering temperature decreases from 1360 to 1300°C with retention of semiconductivity. It is felt that at such BN concentration a liquid phase is formed at grain boundaries in quantities sufficient to wet them and to reduce the rate of oxygen diffusion into the grains. Therefore, a further increase in BN concentration will not affect the specific resistance of the polycrystalline samples. This inference is confirmed by the temperature dependence of ρ for the boron-containing ceramics (Fig. 3): beginning with 3 mol. % BN, the electric resistance of the samples at 200—400° C remains constant which is in complete agreement with the conclusions made in [11] about the influence of the glass phase on temperature variations in the resistance of posistor ceramics. At the same time, the PTCR of the ceramics continuously rises with increasing BN concentration.

With other nitrides, i.e. AlN or ZrN, in contrast to BN, the concentration range of semiconductance is shortened to 0.5-5 and 1.5-2.5 mol.%, respectively. This is obviously due to migration of Al^{3+} and Zr^{4+} ions, at sintering temperatures, from the boundary deep into the grain and incorporation in the crystal lattice. In so doing, aluminum acts as an acceptor decreasing effective concentration of donor yttrium atoms, while the formation of barium titanate-zirconate disturbs the Ba/Ti stoichiometry and substantially affects thereby the properties of the ceramics [12]. The

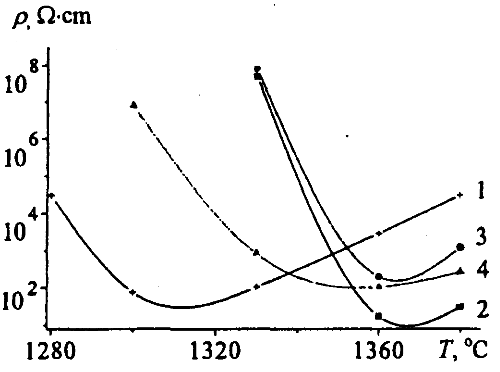

Fig. 4

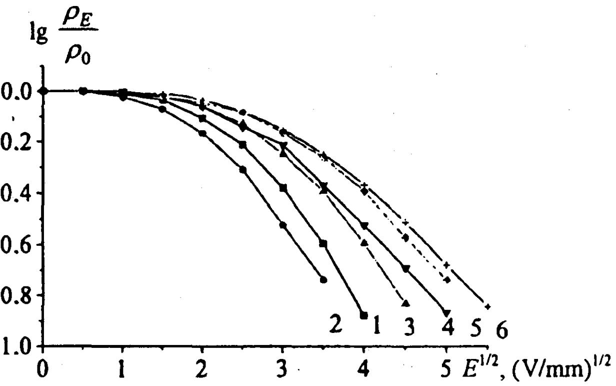

Fig. 5

Fig. 4. The influence of sintering temperature on specific resistance ($\rho_{20^\circ C}$) of $BaTiO_3$-based semiconducting ceramics with 5 mol.% BN (1), 1 mol.% AlN (2), 2 mol.% ZrN (3), or 2 mol.% SiO_2 (4).

Fig. 5. The influence of electric field strength on normalized specific resistance of $BaTiO_3$-based semiconducting ceramics with BN additives: 1 - 0.1, 2 - 0.5, 3 - 1.0, 4 - 3.0, 5 - 5.0, 6 - 7.0 mol.% (T_{sint} = 1360 °C).

lower efficiency of ZrN, compared to BN and AlN, as a resistance-lowering additive can be explained by the lower temperatures at which ZrN exhibits reducing properties.

The widely used SiO_2-modified posistor ceramics has maximum conductivity if sintered at 1360 ± 10 °C (Fig. 4). The use of oxygenless additives such as nitrides makes it possible either to reduce the sintering temperature of the ceramics by 50-60 °C, as in the case of BN, or to increase the conductivity, as with AlN. From the viewpoint of widening the temperature interval of reduction, ZrN has no significant advantages over BN and AlN.

An important technical characteristic of posistor ceramics is its stability in an electric field. Figure 5 shows the variation in the normalized specific resistance (ρ_E/ρ_0) of the $BaTiO_3$-based BN-modified semiconducting ceramics with the electric field strength. As may be seen, the varistor effect is rather appreciable at 0.1-0.5 mol.% BN but it decreases with a further increase in concentration of the additive. The investigation of the samples by electron microscopy shows that with ≥ 3 mol.% BN the size of crystallites is diminished which weakens the varistor effect.

In summary, (i) the resistance of the nitrides to oxidation on heating increases in the order ZrN < BN < AlN; (ii) the ability of the nitrides to stabilize the reduced semiconductor phase of the posistor ceramics is proportional to their thermal stability and increases in the order ZrN < BN < AlN; (iii) only the glass-forming BN additive is capable of significant widening and lowering the temperature interval of the sintering-reduction process in the semiconducting ceramics as compared to SiO_2.

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