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THE EFFECT OF GeO_2 AND Si_3N_4 DOPANTS ON PHASE COMPOSITION AND ELECTROPHYSICAL PROPERTIES OF SEMICONDUCTIVE $BaTiO_3$*

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Physicochemical properties of semiconductive $BaTiO_3$ were studied by XRD, TG, and SEM techniques. The GeO_2 and Si_3N_4 dopants were shown to form compounds affecting redox reactions during synthesis of the ceramics. Electrophysical properties of the $BaTiO_3$ ceramics were found to depend on the phase composition.

Semiconductor ferroelectric $BaTiO_3$ ceramics are used for preparation of posistors, i.e., thermosensitive positive temperature coefficient resistors [1]. Above the ferroelectric transition temperature, the resistance of the posistor materials rises by several orders of magnitude. The rise is characterized by the ratio of the maximum (ρ_{max}) to the minimum (ρ_{min}) value of the resistance. The resistor anomaly is reduced with increase in the external electric field strength (the varistor effect). Germanium and silicon dopants have a substantial effect on basic properties of the posistor materials such as multiplicity of the resistance change, minimum specific resistance, and varistor effect [2–5].

According to [2], germanium and silicon dopants reduce mean grain size of semiconductor $BaTiO_3$ ceramics and thereby, as believed, lower the varistor effect. With 7 mol.% GeO_2 added, the temperature of the ceramics synthesis decreases from 1380 to 1300 °C [3]. Using GeO_2 dopant, one can obtain semiconductor ceramics with low resistance at room temperature [4]. For $BaYTiO_3$ ceramics, the temperature of synthesis is reduced by 100 °C in the presence of 0.5 wt.% Si_3N_4 [5]. The effects of GeO_2 and Si_3N_4 on resistance of the posistor ceramics were not explained in the literature. For this reason we undertook the present research to elucidate the effect of GeO_2 and Si_3N_4 on synthesis and electrophysical properties of barium titanate semiconductor ceramics.

The starting materials for synthesis were high purity metal salts and oxides. The temperature of the synthesis was set with regard to the content of free barium oxide in the blend: after the first thermal treatment its concentration must be no more than 1%. After the addition of dopants (0.1–10 mol.%) and organic binder, the blend was molded to discs 10 mm in diameter and 3 mm in thickness and sintered at different temperatures (1250–1380 °C).

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Table 1

Phase Composition of Calcined $BaTiO_3$–GeO_2 and $BaTiO_3$–Si_3N_4 Systems

T, °C	$BaTiO_3$–GeO_2	$BaTiO_3$–Si_3N_4
800	$BaTiO_3$	$BaTiO_3$
900	$BaTiO_3$, $Ba_2Ge_2TiO_8$ (traces)	$BaTiO_3$, $Ba_2TiSi_2O_8$ (traces)
1000	$BaTiO_3$, $Ba_6Ti_{17}O_{40}$ (traces), $Ba_2Ge_2TiO_8$	$BaTiO_3$, $Ba_6Ti_{17}O_{40}$ (traces), $Ba_2TiSi_2O_8$
1100	$BaTiO_3$, $Ba_6Ti_{17}O_{40}$, $Ba_2Ge_2TiO_8$	$BaTiO_3$, $Ba_6Ti_{17}O_{40}$, $Ba_2TiSi_2O_8$
1200	$BaTiO_3$, $Ba_6Ti_{17}O_{40}$ (traces), $Ba_2Ge_2TiO_8$ (traces)	$BaTiO_3$, $Ba_6Ti_{17}O_{40}$, $Ba_2TiSi_2O_8$
1300	$BaTiO_3$	$BaTiO_3$, $Ba_6Ti_{17}O_{40}$ (traces), $Ba_2TiSi_2O_8$ (traces)
1360	$BaTiO_3$	$BaTiO_3$

Phase transitions were studied thermogravimetrically on a derivatograph Q–1000 Model OD–102 at the heating rate of 10 deg/min. The products were identified by powder XRD analysis on a diffractometer DRON–3M (CuK_α radiation). Electrophysical characteristics were measured over a wide range of temperature and electric field strength. The electrodes were made by chemical deposition of nickel. The size of crystals in ceramics was determined with a microanalyzer JXCA Superprobe 733 (JEOL, Japan) using samples subjected to thermochemical etching as described in ref. [6].

DTA curves for the system $(BaLn)TiO_3$–GeO_2 (Ln is a rare-earth element) show an exothermal effect at 960 °C. Reflections of $Ba_6Ti_{17}O_{40}$ and $Ba_2Ge_2TiO_8$ formed in the reaction of $(BaLn)TiO_3$ with GeO_2 were found in XRD patterns of the $(BaLn)TiO_3$–GeO_2 system calcined at 900–1300 °C (Table 1). According to [7], the system $BaTiO_3$–$Ba_6Ti_{17}O_{40}$ undergoes eutectic melting at 1312 °C, the phase $Ba_2Ge_2TiO_8$ melts at 1200 °C [8]. This explains the absence of peaks due to compounds $Ba_6Ti_{17}O_{40}$ and $Ba_2Ge_2TiO_8$ in diffractograms of samples calcined at the temperature above 1300 °C.

In the system $(BaLn)TiO_3$–Si_3N_4, the exothermal effect is observed at ~900 °C. Above 800 °C, the sample gains in weight due to oxidation of Si_3N_4 to SiO_2. In the temperature range of 900–1300 °C barium titanate reacts with silica to give $Ba_6Ti_{17}O_{40}$ and $Ba_2TiSi_2O_8$ (Table 1). As the $Ba_2TiSi_2O_8$ phase melts at 1300 °C [9] and the system $BaTiO_3$–$Ba_6Ti_{17}O_{40}$ gives eutectics melting at 1312 °C, no peaks corresponding to $Ba_6Ti_{17}O_{40}$ and $Ba_2TiSi_2O_8$ were detected in samples calcined at the temperature above 1300 °C.

Thus, the GeO_2 and Si_3N_4 dopants favor formation of the $Ba_6Ti_{17}O_{40}$ phase in barium titanate. The phase is easily reduced above 1300 °C and rapidly oxidized on cooling in air [7,10,11]. The low-melting compounds $Ba_2Ge_2TiO_8$, $Ba_2TiSi_2O_8$ are likely to hamper oxidation processes in the systems $(BaLn)TiO_3$–GeO_2 and $(BaLn)TiO_3$–Si_3N_4 in the cooling stage by stabilizing titanium in the trivalent state. Owing to this, the degree of reduction increases in the ceramics doped with GeO_2 and Si_3N_4 as indicated by the decrease in specific resistance.

Electrophysical characteristics are summarized in Table 2. With the increase in content of GeO_2 and Si_3N_4 to 1 mol.%, the multiplicity of the change in resistance, ρ_{max}/ρ_{min}, rises by three orders of magnitude. The high value of the parameter remains almost unchanged up to 5 mol.% of GeO_2, in full agreement with the reported data [5], or Si_3N_4. The increase in the ρ_{max}/ρ_{min} ratio is determined, for the most part, by the decrease in the low-temperature resistance ρ_{min}.

The varistor effect was evaluated by the formula [12]

$$K = -\frac{\ln(\rho_{E_1}/\rho_{E_2})}{E_1 - E_2} \cdot 100\,\% ,$$

where ρ_{E_1} and ρ_{E_2} are specific resistances at electric field strength E_1 and E_2 (V/mm).

Table 2

Electrophysical Properties of $BaTiO_3$ Samples Doped with GeO_2 and Si_3N_4

Dopant	Dopant concn., mol.%	Multiplicity of change in resistance	Resistance at 20 °C, $\Omega \cdot cm$	Varistor effect, %	Mean grain size, μm
—	—	1	10^6	5.0	10
GeO_2	0.1	2	$8 \cdot 10^5$	6.7	10
	0.5	3	$1 \cdot 10^5$	7.6	15
	1.0	$3 \cdot 10^3$	$2 \cdot 10^3$	8.1	—
	3.0	$2.4 \cdot 10^4$	$2.5 \cdot 10^2$	8.6	—
	5.0	$2.5 \cdot 10^4$	$3 \cdot 10^2$	8.8	40
Si_3N_4	0.1	4	$3 \cdot 10^4$	6.2	10
	0.5	$3 \cdot 10^3$	$5 \cdot 10^3$	7.0	16
	1.0	$1.6 \cdot 10^4$	$8 \cdot 10^2$	7.7	—
	3.0	$3.1 \cdot 10^4$	$3 \cdot 10^2$	8.0	—
	5.0	$3 \cdot 10^4$	$4 \cdot 10^2$	8.1	45

The varistor effect increases in the doped samples (Table 2). One of the factors determining the intensity of the effect is the ceramics grain size. The latter was determined by electron microscopy. The surface of the posistor samples was preliminarily subjected to thermochemical etching that considerably improved discernibility of the grain boundaries. The relationship between the varistor effect and the mean grain size is nonlinear. The deviation from linearity can be explained by the change in potential barrier at the $(BaLn)TiO_3$ grain boundaries [1] and the effect of resistance of the grain interior [13].

Thus, GeO_2 and Si_3N_3 dopants induce the following changes in semiconductor barium titanate. Germanium dioxide forms compounds $Ba_6Ti_{17}O_{40}$ and $Ba_2Ge_2TiO_8$. The $Ba_6Ti_{17}O_{40}$ phase promotes reduction of titanium while $Ba_2Ge_2TiO_8$ melting at 1200 °C hinders oxidation of the ceramics on cooling. Owing to these effects, the resistance of semiconductor $BaTiO_3$ in the low-temperature region decreases. Silicon nitride oxidizes to SiO_2 at high temperature and creates weekly reductive conditions in the ceramics. When reacting with $BaTiO_3$, silica produces $Ba_6Ti_{17}O_{40}$ and $Ba_2TiSi_2O_8$ (mp 1300 °C) which decrease resistance of the posistor ceramics at low temperature.

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