THE EFFECT OF Al_2O_3–TiO_2–SiO_2 ADDITIVES ON PROPERTIES OF SEMICONDUCTIVE $BaTiO_3$

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Ukrainskii Khimicheskii Zhurnal,
Vol. 61, No. 1, pp. 15–18, 1995

UDC 621.315.592

The introduction of mixed additives composed of Al_2O_3, TiO_2, and SiO_2 into semiconductive $BaTiO_3$ enhances the varistor effect and extends the temperature range of reduction of the posistor ceramics. An explanation for the effects observed was proposed.

A small additive of rare-earth elements is known to reduce resistivity of barium titanate to 10^{-1} to 10^4 $\Omega \cdot m$, the range characteristic of common semiconductors [1]. Such doped materials exhibit a high positive temperature resistance coefficient above the transformation point (posistor effect). Preparation of $BaTiO_3$-base posistor ceramics is a complicated scientific and engineering problem. The basic chemical reactions responsible for their semiconductor and posistor properties are reduction on high-temperature synthesis and oxidation upon cooling. The temperature region of forming semiconductor properties is determined by occurrence of a liquid phase, the temperature of its formation, the presence and composition of titanium-containing dope phases, and the temperature at which rare-earth metal (donor) titanates $LnTiO_3$ are formed [2].

It should be also noted that at the ratio $Ti^{4+}/Ba^{2+} < 1$ a segregation of barium orthotitanate (Ba_2TiO_4) occurs at the grain surface in the blend that drastically changes kinetics of the process [2]. The surface Ba_2TiO_4 phase can form also at $Ti^{4+}/Ba^{2+} = 1$ [3]. The barium orthotitanate is not reduced under the experimental conditions and hinders sintering of the material.

At $Ti^{4+}/Ba^{2+} > 1$, hexabarium heptadecatitanate $Ba_6Ti_{17}O_{40}$ arises at the grain surface [4]. It is readily reducted at temperatures lower than those required for reduction of barium metatitanate $BaTiO_3$ [5]. Therefore, this phase determines the degree of reduction of the ceramics at low temperatures.

Earlier, the effect of mixed Al_2O_3–SiO_2–TiO_2 additives (AST) was studied [6]. The AST was shown to improve conductivity of commercial $BaTiO_3$ that could not be achieved by using known donor additives, e.g., La_2O_3 and Bi_2O_3. This was accounted for by that the mixed AST additive adsorbs detrimental impurities occurring in the raw materials and thereby promotes the appearance of semiconductor properties with $BaTiO_3$. The choice of a proper ratio $Al_2O_3 : SiO_2 : TiO_2$ and concentration of the additive relied upon providing stability of properties that, in its turn, is connected with microstructure of the ceramics. When samples had similar in size, small grains, the spread in resistivity was minimal. At AST concentration in the range 1.6–2.8 mol.%, a considerable increase in grain size was observed in the ceramics (up to 50–100 μm) while at a 3–7 mol.% content of AST the grain growth slowed down, and at higher concentrations (above 8 mol.%) the grains started to grow again [6]. It was also established that AST is ineffective in oxalate synthesis of $BaTiO_3$ [6]. At the same time, nothing was said in the cited report [6] about the presence and content of donor dopants and the effect of AST on properties of semiconductive $BaTiO_3$ synthesized from chemically pure reagents. There are no data also on the influence of AST on performance of the posistor ceramics in strong electric fields.

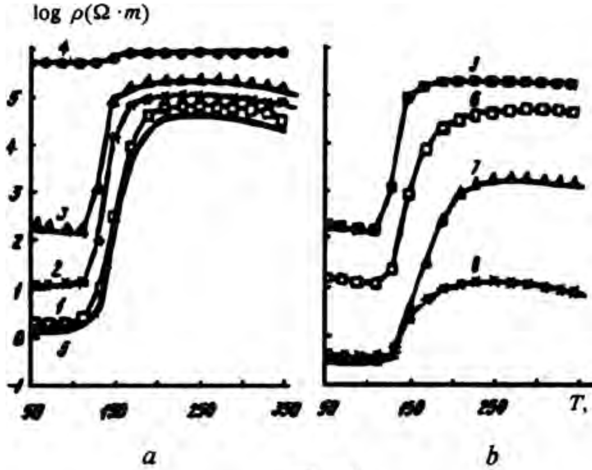

Fig. 1

Fig. 2

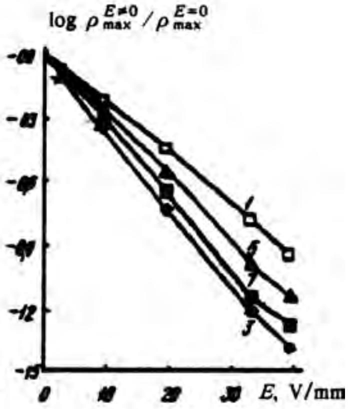

Fig. 3

Fig. 1. The temperature–resistivity plots for semiconductive materials: 1) $Ba_{0.998}Ln_{0.002}Ti_1O_3$; 2) $Ba_{0.998}Ln_{0.002}Ti_1O_3$ + 3% AST; 3) $Ba_{0.998}Ln_{0.002}Ti_1O_3$ + 7% AST; 4) $Ba_{0.998}Ln_{0.002}Ti_1O_3$ + 11% AST; 5) $Ba_{0.998}Ln_{0.002}Ti_{1.04}O_3$ + 0% AST; 6) $Ba_{0.998}Ln_{0.002}Ti_{1.04}O_3$ + 7% AST; 7) $Ba_{0.998}Ln_{0.004}Ti_{1.04}O_3$ + 7% AST; 8) $Ba_{0.998}Ln_{0.012}Ti_{1.04}O_3$ + 7% AST.

Fig. 2. The temperature dependence of minimal resistivity in the *ρ–T* curves for materials: *5* – $Ba_{0.998}Ln_{0.002}Ti_{1.04}O_3$; *7* – $Ba_{0.998}Ln_{0.002}Ti_{1.04}O_3$ + 7% AST.

Fig. 3. A decrease in resistivity at the maximum point of the *ρ–T* curves as a function of electric field strength for materials: *1* – $Ba_{0.998}Ln_{0.002}Ti_1O_3$; *3* – $Ba_{0.998}Ln_{0.002}Ti_1O_3$ + 7% AST; *5* – $Ba_{0.998}Ln_{0.002}Ti_{1.04}O_3$ + 0% AST; *7* – $Ba_{0.998}Ln_{0.004}Ti_{1.04}O_3$ + 7% AST.

Because of this, we decided to study in detail the effect of mixed additives containing Al_2O_3, SiO_2, and TiO_2 on electrophysical properties of semiconductive barium titanate prepared from chemically pure materials.

The starting reagents for synthesis were metal salts and oxides of ultrahigh purity. The temperature of synthesis was set with allowance for the barium oxide content in the blend: after the first thermal treatment it should not be higher than 1%. The $BaTiO_3$ obtained was mixed with an organic binder, pressed to prepare discs 10 mm in diameter and 3 mm in thickness, and then sintered at a high temperature. The active reduction of titanium was a criterion for choice of the sintering temperature. The oxidation only at the boundaries was attained by proper control of the cooling rate. The products were identified by powder X-ray analysis on a DRON–3M instrument (CuK_α radiation). Chemically applied nickel films served as electrodes. Electrophysical measurements were performed in a wide range of temperatures and electric field strengths. The size of crystallites in ceramics was determined with an X-ray microanalyzer "JCXA Super probe–733" (JEOL, Japan).

The posistor materials studied can be classified into two groups: the first of them includes materials based on solid solutions of barium titanate and rare-earth metal titanates with equimolar ratio of ions in the cation sublattices (Ti/(Ba + Ln) = 1, where Ln is Y or a rare-earth element) and different content of the mixed additive AST (3, 7, or 11 mol.%); the second group consists of materials with equal concentration of AST (7 mol.%), small excess of TiO_2 (Ti/(Ba + Ln) = 1.04), and varying content of rare-earth elements.

In parallel, we studied AST-free semiconductive barium titanate samples with (Ti/(Ba + Ln) = 1.04) or without (Ti/(Ba + Ln) = 1) excess of titanium dioxide (compositions 1 and 5). In this case the temperature dependence of resistance was almost identical (Fig. 1*a*). This fact indicates that the resistance of the ceramics is determined mainly by the degree of reduction of the $BaTiO_3$ phase, the oxidation at the grain boundaries being only slightly dependent on the ratio Ti/(Ba + Ln).

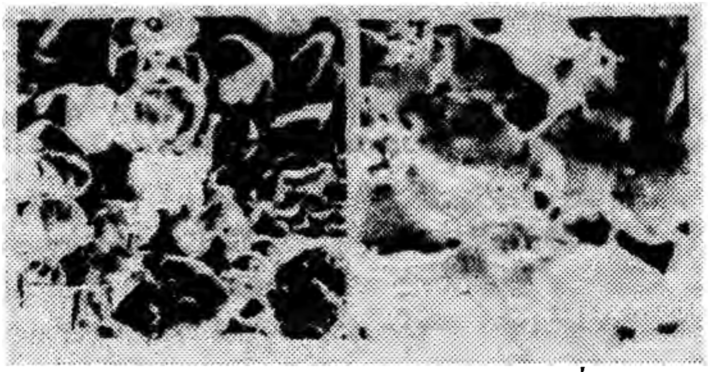

Fig. 4. Micrographs (×400) of ceramics spalls: *a* – $Ba_{0.998}Ln_{0.002}Ti_1O_3$; *b* – $Ba_{0.998}Ln_{0.002}Ti_1O_3$ + 7% AST.

Figure 1*a* illustrates the temperature dependence of resistivity for ceramic materials with a fixed concentration of the donor dopant, $Ti^{4+}/Ba^{2+} = 1$, and a varying quantity of the AST added. The increase in concentration of AST leads to a rise in resistance of the samples and a decrease in the ratio ρ_{max}/ρ_{min}, where ρ_{max} and ρ_{min} are the resistivity at the maximum and minimum point of the ρ–T curve, respectively. This can be accounted for by that the liquid phase formed in the presence of AST [6] interferes with reduction of barium metatitanate upon high-temperature burning.

When comparing properties of the ceramics with different concentration of the donor dopant and the constant content of AST, 7 mol.% (Fig. 1*b*), one can note a considerable drop in resistance in the range of 0.2 to 0.4 mol.% Ln (compositions 6 and 7) due to an increase in concentration of charge carriers. A further buildup of the Ln content results in a sharp reduction of the resistivity in the paraelectric temperature region apparently because of retardation of the oxidation process on cooling.

The properties of the AST-modified $BaTiO_3$ are essentially dependent on the ratio Ti^{4+}/Ba^{2+}. At equal concentrations of the dopant and AST, the samples have a lower resistivity at a small excess of titanium dioxide, $Ti^{4+}/Ba^{2+} = 1.04$ (Fig. 1*a*, compositions 3 and 6), providing formation of the $Ba_6Ti_{17}O_{40}$ phase. The hexabarium heptadecatitanate favors reduction of the ceramics at milder conditions.

The liquid phase formed in the presence of AST promotes widening of the reduction range (Fig. 2) and allows lowering the sintering temperature by 50 to 70 °C. High concentrations of AST accelerate the grain growth (Fig. 4) and enhance the varistor effect (Fig. 3).

Thus the addition of AST to doped $BaTiO_3$ synthesized from ultrahigh purity materials produces the following effects. Provided that $Ti^{4+}/Ba^{2+} = 1$, AST added in the second synthetic stage impedes the reduction of barium titanate and thereby causes the resistance to increase considerably. At a small excess of titanium dioxide ($Ti^{4+}/Ba^{2+} = 1.04$), AST facilitates reduction of barium titanate. High concentrations of the donor and AST retard oxidation on cooling thus providing only small changes in resistivity near the Curie point. This effect is accounted for by the growth of crystallite grains and appearance of a glassy phase in large quantities. The addition of AST induces a considerable varistor effect due to a growth of crystallites.

The temperature range of reduction is extended in the presence of AST because of the appearance of the low-temperature liquid phase.

REFERENCES

1. Semiconductors on the Basis of Barium Titanate [Russian translation], Energoizdat, Moscow, 1982.
2. B. B. Leikina, Yu. P. Kostikov, and A. O. Oleks, Izv. AN SSSR. Neorgan. Materialy, vol. 25, no. 2, pp. 325–327, 1989.

3. M. A. Kvantov and G. A. Tarabanov, Ibid., vol. 27, no. 11, pp. 2402–2405, 1991.

4. H. Inrig, Phys. Status Solidy (a), vol. 47, no. 2, pp. 437–444, 1978.

5. N. P. Velikaya, M. A. Kvantov, G. D. Rubal'skii, and V. I. Yarmarkin, Izv. AN SSSR. Neorgan. Materialy, vol. 22, no. 3, p. 519, 1986.

6. Y. Matsuo, M. Fujimura, H. Sasaci, K. Nagase, and S. Hayakawa, Amer. Ceram. Soc. Bull., vol. 47, no. 3, pp. 292–297, 1968.

June 11, 1993

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