Ukrainian Chemistry Journal
Vol. 64, No. 11, pp. 1–5, 1998

Ukrainskii Khimicheskii Zhurnal
Vol. 64, No. 11, pp. 3–7, 1998
UDC 621.315.592

INORGANIC AND PHYSICAL CHEMISTRY

SYNTHESIS AND PROPERTIES OF FERROELECTRIC SEMICONDUCTORS IN THE SYSTEM $(Ba_{1-x-y}Sr_yY_x)TiO_3$*

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Semiconductor properties and microstructure of the ferroelectric system $(Ba_{1-x-y}Sr_yY_x)TiO_3$ were investigated. The strontium (y) and yttrium (x) concentration ranges, where the $BaTiO_3$-based solid solutions exhibit semiconductor behavior, were estimated. The dependence of the unit cell parameters, grain size, varistor effect and temperature resistance coefficient on the degree of iso- and heterovalent substitution in the barium sublattice was established.

Barium titanate doped with heterovalent additives, $(Ba_{1-x}Ln_x)TiO_3$, has found wide application in engineering as a semiconductor material with positive temperature resistance coefficient (PTRC) [1,2]. It is important in practice to control the temperature range of anomalous growth of the specific electrical resistance. It is known that, depending on composition of the material, the temperature at which the anomalies occur is shifted together with Curie point (T_C). Barium-strontium titanate based solid solutions are used to shift T_C to lower temperatures [3,4]. The literature data on the solid solutions $(Ba_{1-x-y}Sr_yY_x)TiO_3$ are incomplete. The aim of the present work is to amplify and systematize information concerning the effect of substitution of barium with strontium ions in barium metatitanate on semiconductor properties and microstructure of the posistor ceramics.

The starting reagents were extra-pure $BaCO_3$, TiO_2, Y_2O_3, SiO_2 and reagent grade $SrCO_3$. The complex oxides were synthesized by the ceramic technology at 1100–1150 °C. The polycrystalline samples were prepared by adding 2 mol.% SiO_2 to the complex oxides and sintering the blends at 1340–1380 °C under the ambient atmosphere at controlled rates of heating and cooling.

The phase transformations were studied by thermal analysis (a derivatograph Q–1000 OD–102, heating rate 10 °C/min). The phases were identified by XRD data (a diffractometer DRON–3M, CuK_α radiation). The crystal lattice parameters of the solid solutions were determined at 2θ in the range of 137–145° (peaks 224 and 422) with the accuracy of no less than $5 \cdot 10^{-2}$ pm. The ohmic contacts were obtained by burning-in of the aluminum paste. The size of crystallites in the samples was determined with an X-ray microanalyzer JCXA Superprobe 733 (JEOL, Japan). The formation and properties of the semiconductor phases were investigated in the system $(Ba_{1-x-y}Sr_yLn_x)TiO_3$, where Ln = Y, $0 < x < 0.01$, $0 < y < 0.35$.

* This research was financially supported by the Ministry for Science and Technologies of Ukraine.

Table 1

Phase Composition of the Mixtures $(1-x-y)\,BaCO_3 - xY_2O_3 - y\,SrCO_3 - TiO_2$ after Thermal Treatment for 2 h

T, °C	Phase composition*
600	$BaCO_3$, TiO_2, $SrCO_3$
700	$BaCO_3$, TiO_2, $SrCO_3$, $Ba_{1-y}Sr_yTiO_3$
800	$BaCO_3$, TiO_2, $SrCO_3$, $Ba_{1-y}Sr_yTiO_3$
900	$Ba_{1-y}Sr_yTiO_3$
1000	$Ba_{1-y}Sr_yTiO_3$
1300	$Ba_{1-y}Sr_yTiO_3$

* In the range of x used the Y-containing phases are beyond the responsivity limits of the X-ray analysis.

The formation of $(Ba_{1-x}Y_x)TiO_3$ in the system $(1-x)\,BaCO_3-xY_2O_3-TiO_2$ was shown to proceed via a series of phase transformations,

$$\gamma\text{-}BaCO_3 \xrightarrow{830-850\ ^\circ C} \beta\text{-}BaCO_3,$$

$$BaCO_3 \xrightarrow{800-1100\ ^\circ C} |BaO| + CO_2\uparrow,$$

$$|BaO| + TiO_2 \xrightarrow{700-900\ ^\circ C} BaTiO_3,$$

$$2\,|BaO| + TiO_2 \xrightarrow{800-950\ ^\circ C} Ba_2TiO_4,$$

$$|BaO| + 4\,TiO_2 \xrightarrow{900-1000\ ^\circ C} BaTi_4O_9,$$

$$Ba_2TiO_4 + TiO_2 \xrightarrow{950-1050\ ^\circ C} 2\,BaTiO_3,$$

$$BaTi_4O_9 + 3\,|BaO| \xrightarrow{950-1100\ ^\circ C} 4\,BaTiO_3.$$

As can be seen, the synthesis of barium metatitanate is limited by the processes represented by the last two reactions which, in turn, are possible owing to interaction of labile barium oxide |BaO| with TiO_2 to give barium ortho- and tetratitanate.

The thermal analysis of the system $(1-x-y)\,BaCO_3 - xY_2O_3 - y\,SrCO_3 - TiO_2$ ($x = 0.01$, $y = 0.20$) has revealed the sole endothermal effect at 845–850 °C which is accompanied by weight loss. The XRD data (Table 1) point to the presence of free oxides (BaO and SrO) and intermediate phases among the products of the thermal treatment. Therefore, one can assume that the sequence of the chemical reactions leading to the barium-strontium metatitanate based solid solution occurs in a narrow temperature range and can be represented by the following overall scheme (without taking into consideration the heterovalent additive Y_2O_3):

$$(1-y)\,BaCO_3 + y\,SrCO_3 + TiO_2 \xrightarrow{800-900\ ^\circ C} (Ba_{1-y}Sr_y)TiO_3 + CO_2\uparrow.$$

Thus, the synthesis of $(Ba_{1-x-y}Sr_yY_x)TiO_3$ proceeds under milder conditions, as compared to $(Ba_{1-x}Y_x)TiO_3$, evidently because of the reduction of decomposition temperature of the individual carbonates in the order $BaCO_3 > SrCO_3 > CaCO_3$ which excludes the intermediacy of ortho- and tetratitanates.

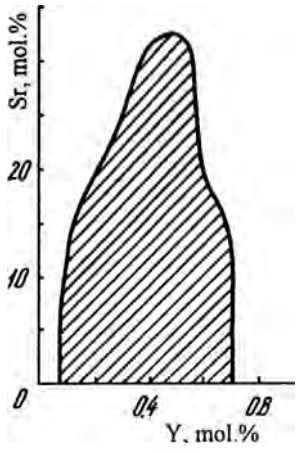

Fig. 1

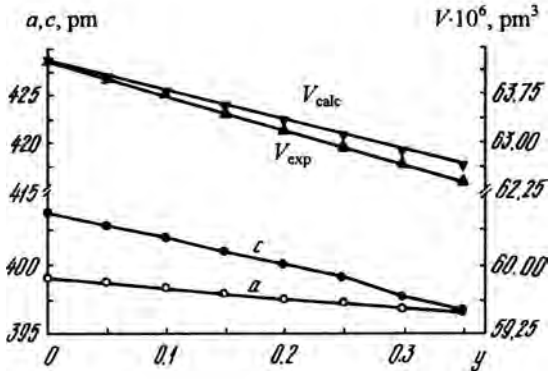

Fig. 2

Fig. 1. The additive effect of the iso- and heterovalent substitution on semiconductor properties of the system $(Ba_{1-x-y}Sr_yY_x)TiO_3$. The semiconductor region is cross-hatched.

Fig. 2. Unit cell dimensions and volume for the ceramics $(Ba_{0.996-y}Sr_yY_{0.004})TiO_3$ at different degrees of isovalent substitution y.

Table 2

Crystallographic Parameters of $BaTiO_3$ in the Trigonal Modification

Composition	*a*	*b*	*c/a*	$V \cdot 10^6$, pm³	Ref.
	pm				
$BaTiO_3$	399.4	403.8	1.011	64.41	[6]
$BaTiO_3$	398.9	402.9	1.010	64.11	[7]
$BaTiO_3$	399.2	403.6	1.011	64.32	[8]
$BaTiO_3$	399.45	403.30	1.0096	64.35	[9]
$Ba_{0.996}Y_{0.004}TiO_3$	399.09	403.73	1.0116	64.30	—*

* This work.

Electrophysical measurements on the solid solutions $(Ba_{1-x-y}Sr_yY_x)TiO_3$ have shown that the appearance of semiconductor properties depends both on the heterovalent (x) and isovalent (y) substitution (Fig. 1). As the content of strontium is raised, the yttrium concentration region (x), in which the semiconductor behavior is observed, is narrowed down. The narrowing is particularly noticeable at high ($y > 0.15$) strontium concentrations. The limiting degree of barium substitution with strontium ($y = 0.30$–0.32), at which the solid solution still exhibits semiconductor properties, is possible only at $0.0040 < x < 0.0055$. At $y < 0.25$ the low-ohmic ceramics can be obtained at the yttrium concentration $x = 0.006$, but at a higher content of strontium ($y > 0.25$) the necessary amount of yttrium is reduced to $x = 0.004$.

The comparison of the literature data for $BaTiO_3$ with those obtained in the present work indicates that the heterovalent substitution in the barium sublattice at the chosen values of x does not appreciably affect the crystallographic parameters (Table 2).

The increase in the degree of isovalent substitution (y) in the solid solutions $(Ba_{1-x-y}Sr_yY_x)TiO_3$ leads to the decrease in the volume and dimensions of the unit cell (Fig. 2) which is in agreement with the data reported in [10]

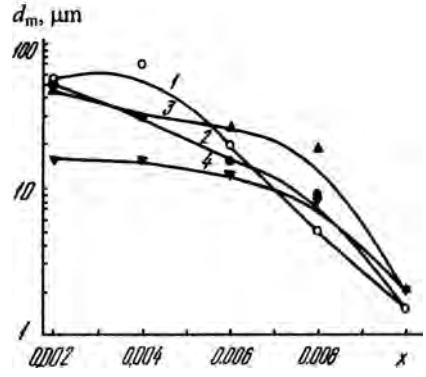

Fig. 3. Mean grain size (d_m) of the ceramics $(Ba_{1-x-y}Sr_yY_x)TiO_3$: $y = 0$ (*1*), 0.05 (*2*), 0.15 (*3*), 0.25 (*4*).

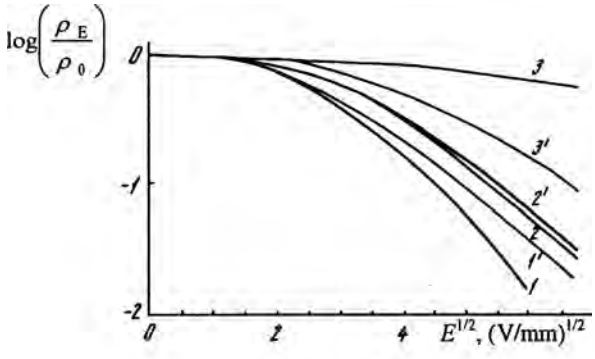

Fig. 4

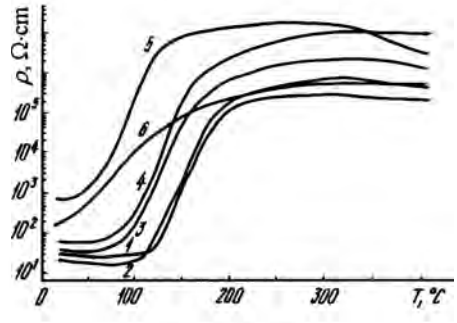

Fig. 5

Fig. 4. The semi-log plots of the normalized specific resistance versus electric field strength at 300 °C for ceramics $(Ba_{0.85-x}Sr_{0.15}Y_x)TiO_3$: $x = 0.004$ (*1*), 0.006 (*2*), 0.007 (*3*); $(Ba_{0.994-y}Sr_yY_{0.006})TiO_3$: $y = 0.05$ (*1'*), 0.15 (*2'*), 0.25 (*3'*).

Fig. 5. Temperature dependence of specific resistance for the ceramics $(Ba_{0.996-y}Sr_yT_{0.004})TiO_3$: $y = 0$ (*1*), 0.05 (*2*), 0.10 (*3*), 0.15 (*4*), 0.20 (*5*), 0.25 (*6*).

where, however, the effect of heterovalent substitution in the barium sublattice on crystallographic param barium-strontium metatitanate based solid solutions was not considered.

The microstructural investigation of the ceramics (Fig. 3) shows that the iso- and heterovalent a substantially affect the grain size of barium titanate, causing its diminution. At $x > 0.008$ the grain size decreases and this coincides with the transition of the ceramics to the dielectric region. One of the reasons appearance of dielectric properties may be the complete oxidation of the doped barium titanate grains during t temperature treatment.

Since the iso- and heterovalent substitution in the barium cationic sublattice reduces the grain size of Ba varistor effect of the materials must decrease, what is observed in the experiments (Fig. 4). The strontium additi especially strong influence on the varistor effect. The lowest susceptibility to the electric field strength is obse the solid solution with the composition $(Ba_{0.744}Sr_{0.25}Y_{0.006})TiO_3$.

The temperature dependence of the specific resistance for the solid solutions $(Ba_{1-x-y}Sr_yY_x)TiO_3$ is illus Fig. 5. The shift of the Curie point to lower temperatures is 2.5 K per mol.% Sr which is in agreement with the

value [11]. At constant y the high values of PTRC are observed at small degrees of heterovalent substitution ($x = 0.004$). In addition, at $y > 0.25$ there is a trend to the decrease in ρ_{max}/ρ_{min} and PTRC.

Thus, the formation of $(Ba_{1-x-y}Sr_yY_x)TiO_3$ occurs under milder conditions and in the narrower temperature range as compared to $(Ba_{1-x}Y_x)TiO_3$; the maximum degree of isovalent substitution of barium with strontium, at which the solid solutions $(Ba_{1-x-y}Sr_yY_x)TiO_3$ preserve semiconductor properties, is $y = 0.32$–0.33 at the yttrium content $0.004 < x < 0.0055$; the unit cell dimensions and volume linearly decrease as the degree of isovalent substitution is raised; the introduction of strontium ions in the semiconducting barium titanate leads to the decrease in the size of ceramic grains; the varistor effect in the solid solutions $(Ba_{1-x-y}Sr_yY_x)TiO_3$ decreases as the degree of isovalent substitution of barium with strontium increases; the temperature shift of the posistor effect for the solid solutions is –2.5 K/mol.%Sr; at high degrees of isovalent substitution ($y > 0.25$) the ratio ρ_{max}/ρ_{min} and the value of PTRC decrease.

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February 25, 1998