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Synthesis and Electrophysical Properties of Ba(Ti, Sn)TiO$_3$ and (Ba, Nd)TiO$_3$ Solid Solutions

L.L. Kovalenko, O.I. V'yunov*, T.O. Plutenko,
O.Z. Yanchevskii, O.P. Fedorchuk,
A.G. Bilous and Yu.D. Stupin

*V.I. Vernadsky Institute of General and Inorganic Chemistry of NAS of Ukraine,
32/34 Palladina Ave., 03142 Kyiv, Ukraine*

Doi: 10.12693/APhysPolA.141.410 *e-mail: vyunov@ionc.kiev.ua

Ba(Ti, Sn)TiO$_3$ and (Ba, Nd)TiO$_3$-based solid solutions were synthesized using the solid-state reaction technique. The sequence of phase transformations during synthesis was established. Crystallographic parameters and microscopy were studied. Changes in crystallographic parameters and average grain size with substitution degree were determined. It was found that the introduction of 0.5 wt% manganese oxide (IV) and 2 wt% of low-melting glass AST (Al$_2$O$_3$–SiO$_2$–TiO$_2$) reduces the sintering temperature and improves the dielectric parameters (ε and tan(δ)). It has been shown that the obtained materials are promising for the development of ceramic capacitors.

topics: barium titanate, high dielectric constant, complex impedance, solid-state reaction technique

1. Introduction

Barium metatitanate (BaTiO$_3$) with a high dielectric constant at room temperature ($\varepsilon \approx 1000$–1500) is of great potential for use as a basis for high-capacity ceramic materials [1, 2]. Materials with high dielectric constant values ($\varepsilon \geq 10^4$) and low dielectric losses (tan(δ) < 0.10) are important for practical application in modern electronics. High dielectric constant values in barium metatitanate at room temperature are determined by the presence of ferroelectric properties and phase transition to the paraelectric state at 120°C (Curie temperature — T_C). The characteristics of polycrystalline BaTiO$_3$ solid solutions can be changed with partial substitution in the cationic sublattices. Partial substitution in the titanium sublattice by zirconium or tin in Ba(Ti, Sn)TiO$_3$, Ba(Ti, Zr)TiO$_3$ solid solutions shifts the Curie temperature to room temperature and increases dielectric constant ($\varepsilon \approx 5000$–8000 for Ba(Ti, Sn)TiO$_3$ [3, 4]). However, unlike the solid solution of Ba(Ti, Zr)TiO$_3$, the Ba(Ti, Sn)TiO$_3$ system has several advantages [2]. The Sn^{4+} ion (r = 0.71 Å) is smaller than the Zr^{4+} ion (r = 0.79 Å) and is easily replaced by the Ti^{4+} ion (r = 0.68 Å) [5], leads to the formation of finer ceramic grains, and the shift of the phase transition to room temperature occurs in a smaller amount 10–15 wt% of tin against 20–25 wt% of zirconium. However, the sintering temperature of Ba(Ti, Sn)TiO$_3$ ceramics is very high (> 1400°C), which can lead to a negative change in tin stoichiometry due to the evaporation of tin. In addition, high sintering temperatures of BaTiO$_3$ solid solutions contribute to the partial reduction of titanium ion Ti^{4+} to Ti^{3+}. As a result, the conductivity of the material increases, which leads to a decrease in the dielectric constant ε and an increase in the dielectric loss tangent tan(δ) [6]. In [7, 8] it was shown that with partial substitution of barium by lanthanum in BaTiO$_3$, when vacancies are formed in the titanium lattice (Ba$_{1-x}$La$_x$Ti$_{1-x/4}$O$_3$, where $0.01 \leq x \leq 0.1$), it is possible to increase the dielectric constant at room temperature. These solid solutions with high dielectric constant values are, however, formed only during sintering at high temperatures (> 1450°C) for a long time (days) [8]. It can be expected that under these conditions, the values of tan(δ) will increase due to the Ti^{3+} formation. From the above study, it can be assumed that the Nd^{3+} as an alloying addition can also change the structure and dielectric properties of BaTiO$_3$ ceramics [9, 10]. Additional introduction into polycrystalline materials of transition oxides of 3d-elements (Fe$_2$O$_3$ and MnO$_2$) can prevent the partial formation of Ti^{3+} at the grain boundaries. These dopants segregate on the grain surface [11] and form a "core/shell" structure [12] that leads to a decrease in dielectric losses [13]. It should be noted that the main dielectric parameters (ε and tan(δ))

TABLE I

Phase composition during the synthesis of Ba(Ti, Sn)O_3 and (Ba, Nd)TiO_3 solid solutions respectively.

Heat treatment temp. [°C]	Phase composition	
	Mixture $BaCO_3$–TiO_2-SnO_2	Mixture $BaCO_3$–Nd_2O_3–TiO_2
20–600	γ-$BaCO_3$, SnO_2, TiO_2	γ-$BaCO_3$, Nd_2O_3, TiO_2
700	γ-$BaCO_3$, SnO_2, TiO_2	γ-$BaCO_3$, Nd_2O_3, TiO_2
800	γ-$BaCO_3$, SnO_2, TiO_2, $BaTiO_3$	γ-$BaCO_3$, Nd_2O_3, TiO_2, $BaTiO_3$
900	β-$BaCO_3$, SnO_2 (traces), Ba_2TiO_4, TiO_2, $BaTi_4O_9BaTiO_3$	γ-$BaCO_3$(traces), β-$BaCO_3$, Nd_2O_3 (traces), Ba_2TiO_4, TiO_2, $BaTi_4O_9$, $BaTiO_3$
1000	β-$BaCO_3$ (traces), SnO_2 (traces), $BaTiO_3$, Ba_2TiO_4, TiO_2, $BaTi_4O_9$, $BaSnO_3$	β-$BaCO_3$ (traces), Nd_2O_3 (traces), Ba_2TiO_4, TiO_2, $BaTi_4O_9$, $BaTiO_3$, Nd_2TiO_5
1100	Ba(Ti, Sn)O_3	$BaTi_4O_9$ (traces), (Ba, Nd)TiO_3
1200	Ba(Ti, Sn)O_3	(Ba, Nd)TiO_3
1300	Ba(Ti, Sn)O_3	(Ba, Nd)TiO_3

are influenced not only by the chemical composition of the solid solution but also by the grain size. Usually, in fine-grained ceramics, the values of dielectric constant are higher, and the values of tan(δ) are lower compared to ceramics with large grains. At high temperatures ($>$ 1400°C), ceramics with mainly large grains are formed, which is undesirable. The introduction of low-melting glass-forming compounds [14] reduces the sintering temperature of polycrystalline solid solutions, which leads to the formation of fine-grained ceramics. For example, the admixture of AST (Al_2O_3–SiO_2–TiO_2) in the molar ratio of 1:1:0.5 reduced the sintering temperature of semiconductor (posistor) $BaTiO_3$-based ceramics [3, 15]. The introduction of additives that simultaneously affect the processes of partial reduction of titanium ion and the formation of the fine-grained microstructure of ceramics at low temperatures can improve the dielectric parameters (increase the dielectric constant and reduce the dielectric loss) of polycrystalline $BaTiO_3$-based solid solutions, which is necessary for practical use.

However, the question of partial substitution degree (of barium or titanium) in $BaTiO_3$ solid solutions, which is optimal for improving the basic dielectric parameters (ε and tan(δ)), remains open.

From the practical point of view, solving this problem will optimize the chemical composition of the material in order to obtain large values of ε, lower values of tan(δ), and a weak dependence of these parameters on temperature.

Therefore, this work aimes to study the formation conditions of Ba(Ti, Sn)O_3 and (Ba, Nd)TiO_3 solid solutions during the solid-state reaction technique and the effect of MnO_2 and AST additives on the electrophysical properties.

2. Methodology

Ba(Ti, Sn)O_3 and (Ba, Nd)TiO_3 solid solutions were synthesized by the solid-state reaction technique. Barium carbonate, oxides of tin, neodymium, and titanium (grade 99.9% purity) were used as initial reagents for the synthesis. To lower the sintering temperature and to form a fine-grained "core/shell" structure, 2 wt% of low-melting AST additive and 0.5 wt% of manganese oxide MnO_2 were added. The reagents were mixed and ground in a planetary ball mill (Fritsch Pulverisette). Obtained powders were pressed into pellets. The pellets were sintered at temperatures of 1000–1450°C for 2 h in a high-temperature furnace KSL1700X. The phases were characterized by X-ray powder diffractometry (XRPD) using the DRON-4-07 diffractometer (Cu K_α radiation; 40 kV, 20 mA). Certified SiO_2 (standard 2Θ) and Al_2O_3 (intensity standard) were used as external standards. The PDF-2 (ICDD) database was used to decrypt the data.

Dielectric parameters were studied using impedance spectroscopy in a wide frequency (1–10^7 Hz) and temperature (20–200°C) ranges using 1260 Frequency Response Analyzer and 1296 Dielectric Interface (Solartron). Data were analyzed using Zview software (Solartron). Obtained frequency dependences of the complex impedance $Z'' = f(Z')$ were used to calculate the dielectric constant and dielectric losses, i.e., $\tan(\delta) = Z'/Z''$, $Y'' = Z''/(Z'^2 + Z''^2)$, $\varepsilon' = Y''/(2\pi f \varepsilon_0)$, where $\omega = 2\pi f$, f is the frequency [Hz], and ε_0 is the dielectric constant of vacuum ($\varepsilon_0 = 8.854 \times 10^{-12}$ F/m).

3. Experimental part

The sequence of phase transformations during the synthesis of Ba(Ti, Sn)O_3 and (Ba, Nd)TiO_3 solid solutions was studied by the methods of differential thermal and X-ray phase analyses. Intermediate and final transformations during the synthesis of solid solutions are presented in Table I.

During the synthesis of Ba(Ti, Sn)O_3 and (Ba, Nd)TiO_3 solid solutions from the corresponding mixtures, some noteworthy features were revealed. During the interaction of barium carbonate with titanium oxide, the decomposition of

TABLE II

Parameters of Ba(Ti, Sn)O_3 and (Ba, Nd)TiO_3 solid solutions: a is the unit cell parameter, V is unit cell volume, R_b and R_f are the indicators of quality of refined structure model, Bragg and structure factor respectively.

Solid solution	Ba(Ti, Sn)O_3		(Ba, Nd)TiO_3	
	Without additives	With MnO_2 and AST	Without additives	With MnO_2 and AST
Elementary cell parameters				
a [Å]	4.02251(4)	4.02254(4)	3.99664(9)	3.99667(9)
V [Å^3]	65.086(1)	65.088(1)	63.839(3)	63.840(3)
Coherence factors				
R_b [%]	3.85	4.01	4.78	5.33
R_f [%]	2.12	2.87	2.61	3.01

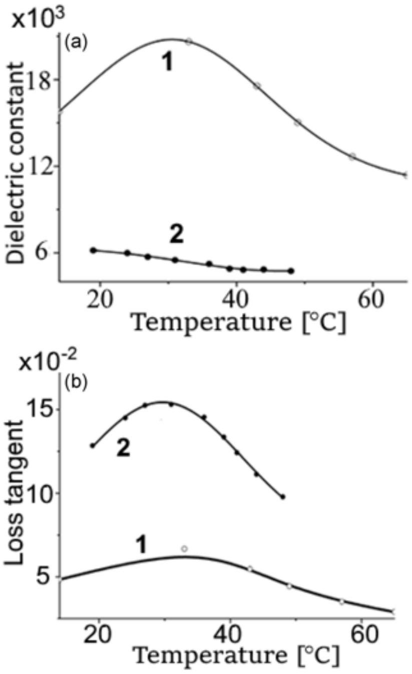

Fig. 1. Temperature dependences of ε (a) and tan(δ) (b) at 1 MHz for Ba(Ti, Sn)O_3 ceramics without (1) and with manganese oxide and AST additives (2).

gamma polymorphic modification of barium carbonate (γ-BaCO_3) occurs at 1450°C [16, 17]. In the presence of tin and neodymium oxides, there is a decrease in the temperature of the decomposition of barium carbonate from 1450 to 820°C [18, 19]. Regardless of the metal replacing ions nature, the synthesis of barium titanate takes place with the formation of intermediate phases Ba_2TiO_4 and $BaTi_4O_9$ in the temperature range 900–1100°C. The formation of these intermediate phases is explained by the long process of barium carbonate decomposition in the mixture during the solid-state route. The corresponding solid solutions are formed at 1100°C, as indicated by the shift in the X-ray peak position of barium titanate. With a further increase in temperature, only the phases of the corresponding single-phase solid solutions are observed. On the X-ray diffraction patterns of samples sintered at 1400°C, there are no X-ray reflexes of additional crystalline phases. There is a transition from the tetragonal to the cubic phase at room temperature for the Ba(Ti, Sn)O_3 system with a tin content of 12 mol%. An increase in the tin content in a solid solution of barium titanate–stannate leads to an increase in the volume of the unit cell. An increase in neodymium concentration in a (Ba, Nd)TiO_3 solid solution, on the contrary, leads to a decrease in the unit cell volume. This happens due to the smaller size of neodymium ions (Nd^{3+} = 0.983 Å) compared to barium ions (Ba^{2+} = 1.35 Å) [5], as well as the formation of vacancies in the titanium sublattice. In addition, the replacement of barium with neodymium leads to a significant reduction in the tetragonality degree of the barium titanate unit cell. In all studied (Ba, Nd)TiO_3 solid solutions (with neodymium content of 5–7 mol%) at $2\Theta = 10$–$90°$, X-ray reflexes almost coincide with similar reflexes of cubic BaTiO_3, shifted by $\sim 0.5°$ on a 2Θ scale in the direction of higher angles.

Unit cell parameters for Ba(Ti, Sn)O_3 and (Ba, Nd)TiO_3 solid solutions with the MnO_2 and AST additions are shown in Table II. Manganese oxide and AST are not included in the crystal cell of solid solutions, as seen in Table II, but AST significantly reduces the sintering temperature, and manganese oxide affects the dielectric parameters ε and tan(δ) (see Fig. 1).

It was found that in the Ba(Ti, Sn)O_3 system when the titanium substitution degree by tin increases, the grain size of ceramics increases from 20 μm (BaTiO_3) to 130 μm (with 15 mol% of Sn). There are two reasons for this increase. The first reason is the formation of the eutectic liquid phase between the grains during the solid-state reaction route of ceramics [20]. The second reason is the replacement of smaller titanium ions with tin ions, which leads to mechanical stresses and deformations in crystals, accelerating diffusion processes and leading to grain growth [21, 22].

A decrease in the average ceramic grain size to 8 μm in (Ba, Nd)TiO_3 with neodymium content of 5–7 mol% is associated with the size of replacement ions, as well as the formation of vacancies in the titanium substrate.

The main dielectric characteristics (ε and tan(δ)) of Ba(Ti, Sn)O_3 solid solution without and with additives of MnO_2 and AST at a frequency of 1 MHz in a wide temperature range are shown in Fig. 1.

Ba(Ti, Sn)O_3 ceramic materials without additives are formed at temperatures above 1400°C. At 20°C, the value of ε reaches 4700, but the value of tan(δ) is also high (equals 0.15). On the temperature dependence of ε in the temperature range 20–60°C, the maximum is observed at 33°C

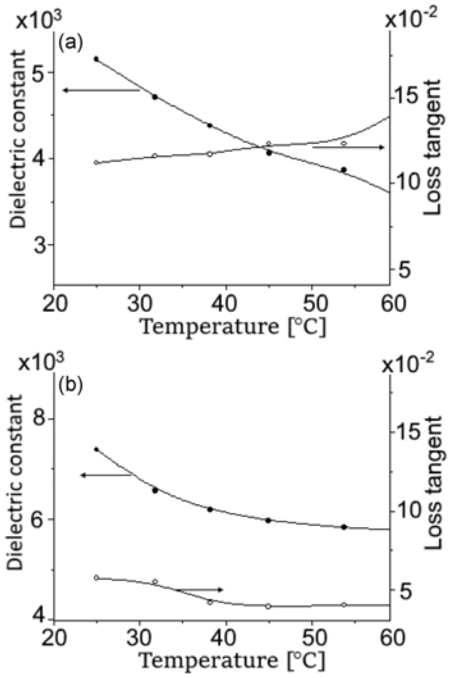

Fig. 2. Temperature dependences ε and $\tan(\delta)$ at 1 MHz for (Ba, Nd)TiO_3 ceramics without (a) and with manganese oxide and AST (b).

($\varepsilon_{\max} = 6600$). The values of $\tan(\delta)$ also change with the transition through the maximum at the same temperature ($\tan(\delta_{\max}) = 0.15$). With the introduction of a low-melting AST additive, the sintering temperature of Ba(Ti, Sn)O_3 ceramics decreases to 1100°C. The addition of manganese oxide affects the values of dielectric parameters (ε and $\tan(\delta)$, i.e., the value of the dielectric constant at 20°C increases to 12900 and to $\varepsilon_{\max} = 15800$ at 40°C. Loss tangent $\tan(\delta)$ also changed, i.e., at 20°C, the value is 0.06, and with subsequent heating, it decreases linearly to 0.05 at 40°C. It should be noted that the introduction of manganese oxide not only increases the value of $\varepsilon_{\max}$ but also narrows the peak on the temperature curve of the dielectric constant.

Figure 2 shows the temperature dependences of the dielectric characteristics (ε and $\tan(\delta)$) for (Ba, Nd)TiO_3 solid solution without and with manganese oxide and AST additives at 1 MHz.

(Ba, Nd)TiO_3 ceramic samples without additives are sintered at 1400°C and characterized by low values of ε (5000) and high values of $\tan(\delta)$ (0.11) at room temperature. In the temperature range of 20–60°C, the values of ε and $\tan(\delta)$ change linearly — the dielectric constant decreases and $\tan(\delta)$ increase. With the introduction of low-melting AST additive, the sintering temperature of ceramics decreases to 1200°C, and the manganese oxide addition affects the dielectric parameters ε and $\tan(\delta)$. At room temperature, the dielectric constant increases to 7500, and $\tan(\delta)$ decreases to 0.057. When heated from 20 to 60°C, a slow change in the parameters ε and $\tan(\delta)$ is observed. Thus, at 60°C, $\varepsilon = 6000$ and $\tan(\delta) = 0.04$. These results indicate a weak dependence of dielectric parameters on temperature.

Analysis of crystallographic, microstructural, and electrophysical data indicates that in the production of Ba(Ti, Sn)O_3 and (Ba, Nd)TiO_3 ceramic materials with high dielectric parameters (high ε and low $\tan(\delta)$) using the manganese oxide and low-melting AST additive simultaneously is promising. The ceramics of both compositions are characterized by low dielectric losses. At the same time, high values of $\varepsilon_{\max} = 15800$ are achieved in the Ba(Ti, Sn)O_3 system. In contrast, a weak dependence of the dielectric constant on the temperature in the (Ba, Nd)TiO_3 system is observed.

Based on the data [23], we calculated the electrophysical parameters of the capacitor block, which consists of ceramic plates set. Thus, when using plates with a dielectric constant of 10000, the following parameters of the capacitor unit are obtained: capacity 5–8 F, power 9–12 kW, weight = 70 kg. Such energy storages are useful from a practical point of view.

The obtained experimental data indicate a significant potential of Ba(Ti, Sn)O_3 and (Ba, Nd)TiO_3 solid solutions in terms of their use in the development of new materials with high dielectric constant and low dielectric loss. Such materials will be determined by the low cost of starting reagents, simplicity of production technology (low sintering temperatures, low exposure time in the air), high values of ε, and low values of $\tan(\delta)$, which will effectively solve the problem of microminiaturization of energy storage of modern electronic equipment.

4. Conclusions

Ceramic samples of Ba(Ti, Sn)TiO_3 and (Ba, Nd)TiO_3 solid solutions with MnO_2 and AST additives, synthesized by solid-state reactions technique, were studied. AST addition lowered the synthesis temperature for Ba(Ti, Sn)TiO_3 and (Ba, Nd)TiO_3 systems from 1400 to 1100 and 1200°C, respectively. Introduction of MnO_2 allowed to increase the dielectric constant of the samples from 4700 to 12900 at room temperature for the Ba(Ti, Sn)TiO_3 system and from 5000 to 7500 for the Ba(Ti, Nd)TiO_3 system. Used additives also decrease values of the loss tangent in ceramics. Obtained data allows us to say that such materials are useful for energy storage units and microelectronics.

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