Composite ceramics based on $(Ca_{1/4}Cu_{3/4})TiO_3$

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Presented are the main results of the obtaining of the composite ceramic material based on $(Ca_{1/4}Cu_{3/4})TiO_3$. It was investigated the influence of isovalent and non-isovalent substitution in $(Ca_{1/4}Cu_{3/4})TiO_3$ on the dielectric permittivity and temperature stability of the ceramics is investigated.

Представлены основные результаты исследований диэлектрических параметров в системе твёрдых растворов на основе $(Ca_{1/4}Cu_{3/4})TiO_3$. Исследовано влияние изовалентного и неизовалентного замещения в $(Ca_{1/4}Cu_{3/4})TiO_3$ на диэлектрическую проницаемость и температурную стабильность керамики.

During recent few years $(Ca_{1/4}Cu_{3/4})TiO_3$ (CCTO) composite ceramic compound with perovskite crystal lattice has evoked keen interest due to its high value of dielectric permittivity $\varepsilon \sim 10000$ which remains stable at temperatures up to 500 К [1–5].

For the development of condenser materials based on CCTO it is necessary to achieve diffusion of the maximum of the dependence $\varepsilon(T)$ and its shift towards room temperatures. There are known the methods for changing the Curie point of the compounds with perovskite structure, in particular, of $BaTiO_3$ [6]. First of all, this is modification of the structure by varying the substituting components and their composition. Such substitutions may be realized in the site A and/or B by both isovalent and non-isovalent ions.

Considerable quantities of isovalent ions may be incorporated into the perovskite lattice and gradually change its properties. Non-isovalent substitution favors more noticeable changes in the dielectric properties. In the case when the valences of the substituted and substituting ions differ, the region of the existence of the solid solutions becomes narrower.

The goal of the present paper was to investigate the possibility of the obtaining of a condenser material based on $(Ca_{1/4}Cu_{3/4})TiO_3$ with high temperature stability and high value of dielectric permittivity (exceeding 10 000).

For this purpose there were obtained and investigated ceramic $(Ca_{1/4}Cu_{3/4})TiO_3$ samples doped with isovalent ions (Sn and Hf) in the site B and with non-isovalent ions (Bi and La) in the site A. The influence of special fusible technological additions on the dielectric properties and temperature stability of the dielectric properties of ceramics was studied, too.

The regimes of the synthesis of the ceramic samples were chosen on the base of the results of investigations performed by the methods of derivatography (DTA), thermogravimetry (TG), dilatometry (DLA) and X-ray diffraction analysis (XRDA). Sintering of the ceramic samples was realized within (950–1050)°C temperature interval, the sintering duration being from 4 to 25 hours.

The value of the real part of dielectric permittivity ε' was determined by measuring the electric capacity by means of L,C,R E7-8 meter at a frequency of 1 kHz. The maximum AC voltage amplitude on the sample was 0.25±0.05 V. The temperature was controlled by chromel-alumel thermocouple. The temperature dependence $\varepsilon'(T)$ was fixed under the conditions of continuous tempera-
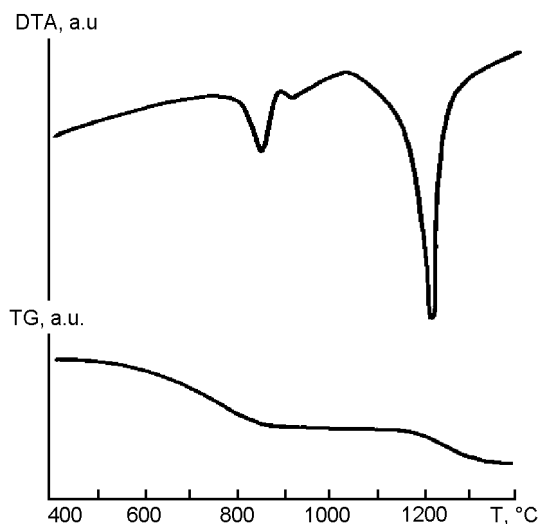
Fig. 1. DTA and TG curves for the stoichiometric mixture of $CaCO_3$, CuO and TiO_2 components.

ture variation. The aim of the first stage of our research was to obtain the one-phase ceramic material CCTO. Presented in Fig. 1 are the DTA and TG curves for the stoichiometric mixture of the components $CaCO_3$, CuO and TiO_2.

The endoeffect at 845°C accompanied with the loss of the mass on TG curve corresponds to $CaCO_3$ decomposition; the experimental amount of the loss of CO_2 coincides with the calculated one. The endothermal peak at 920°C characterized by a low heat efficiency, corresponds to the solid-phase interaction and the formation of $(Ca_{1/4}Cu_{3/4})TiO_3$. Further rise of the temperature (an intense endoeffect at 1220°C) leads to the reduction of Cu^{2+} according to the reaction: $4CuO \rightarrow 2Cu_2O + O_2$ and then to melting of the mixture.

The loss of the mass observed on the TG curve in this temperature interval is caused by the loss of oxygen as a result of the process of copper oxide (II) reduction. As established by XRDA, after carrying out the process of solid-phase synthesis at 1050°C during 2 hours, practically one-phase product CCTO was formed. It contained (1.0 ± 0.1) % of admixtures and crystallized as cubic perovskite-like structure (Im3 structure group) with the lattice parameter $a = 7.391$ Å.

The value of dielectric permittivity of the one-phase $(Ca_{1/4}Cu_{3/4})TiO_3$ samples reached 22 000 and had a strongly pronounced maximum at 80°C (Fig. 2a, curve 5). It should be noted that the introduction of
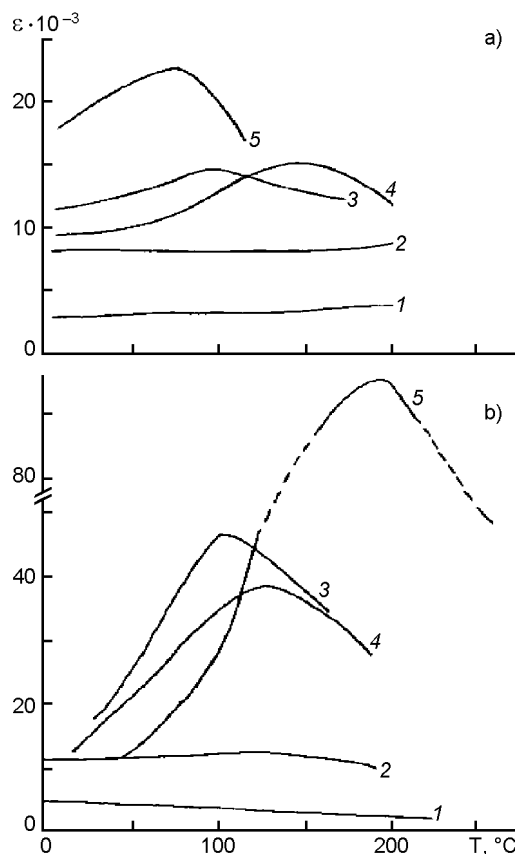

Fig. 2. Influence of different substitutions in $(Ca_{1/4}Cu_{3/4})TiO_3$ on the temperature dependence of dielectric permittivity in the absence of a fusible addition (a) and in the presence of it (b). The substituting elements: 1 — Hf, 2 — Sn, 3 — La, 4 — Bi, 5 — without substitution.

an easily fusible addition into $(Ca_{1/4}Cu_{3/4})TiO_3$ samples which contain 95 % and 97 % of the main phase leads to the appearance of a strongly pronounced maximum on the curve of the dependence $\varepsilon-T$ with extreme values of ε in the maximum point: 99900 (Fig. 2b, curve 5) and 17800, respectively.

The doping cations were introduced into $(Ca_{1/4}Cu_{3/4})TiO_3$ as SnO_2, HfO_2, Bi_2O_3, La_2O_3 oxides in amounts of 1–40 mol % in the process of synthesis.

As shown while studying the dielectric properties, the growth of the degree of isovalent substitution in the titanium sublattice by tin ions in quantities from 10 to 40 mol % resulted in the decrease of the value of dielectric permittivity from 10 000 to 4 000. The value of ε equal to 9600, remained unchanged within (10–100)°C
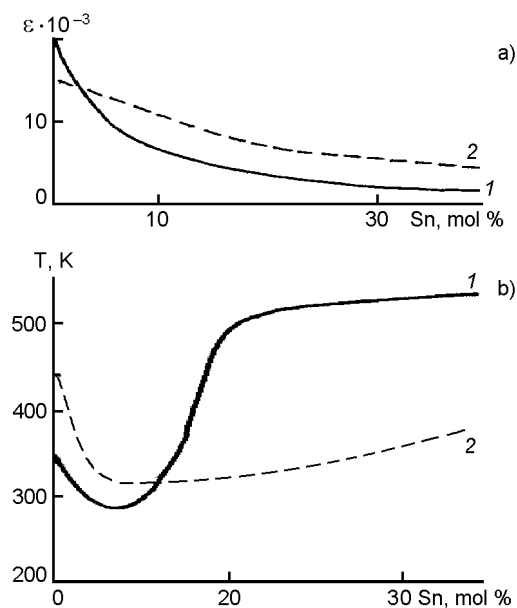
Fig. 3. Concentration dependence of dielectric permittivity (a) and the Curie point (b) at room temperature for $(Ca_{1/4}Cu_{3/4})TiO_3$ substituted by tin, with a modifying addition (curve *1*) and without it (curve *2*).

temperature interval only for the samples $(Ca_{1/4}Cu_{3/4})Ti_{0.9}Sn_{0.1}O_3$ (Fig. 2a, curve *2*).

In the process of successive substitution of titanium by hafnium ions the value of dielectric permittivity was changing monotonously in the investigated temperature interval (Fig. 2a, curve *1*). At the substitution of calcium and copper ions in the sub-lattice A by La or Bi ions (10 mol %), there were observed pronounced maxima of dielectric permittivity −14700 and 15300 — at 100°C and 145°C, respectively (Fig. 2a,curves *3,4*). Further increase of the concentrations of the doping ions led to the decrease of the value of ε, and its maximum was shifted towards higher temperatures.

Presented in Fig. 2b are the temperature dependences of dielectric permittivity for the samples $(Ca_{1/4}Cu_{3/4})_{0.85}Bi_{0.1}TiO_3$ and $(Ca_{1/4}Cu_{3/4})_{0.85}La_{0.1}TiO_3$, which contain a fusible addition. The value of ε for La- and Bi-containing samples increased approximately by 3 times (curves *3, 4*), with $\varepsilon(T)$ maxima at 110°C and 125°C, respectively. $(Ca_{1/4}Cu_{3/4})Ti_{0.9}Sn_{0.1}O_3$ samples obtaining a fusible addition turned out to have the highest stability. The value of ε equal to 11000 remained practically unchanged; its deviation from the average magnitude in the interval $(10-120)°C$ was less than 1 % (Fig. 2b, curve *2*).

Presented in Fig. 3a and 3b are the concentration dependences of ε at room temperature and the Curie points for $(Ca_{1/4}Cu_{3/4})Ti_{1-x}Sn_xO_3$ samples with a fusible addition (curve *1*) and without it (curve *2*).

Thus, in the system of solid solutions based on $(Ca_{1/4}Cu_{3/4})TiO_3$ there are found the compounds which have extremely high values of dielectric permittivity, and established are the conditions under which a high degree of temperature stability of dielectric parameters is achieved.

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Композиційна кераміка на основі $(Ca_{1/4}Cu_{3/4})TiO_3$

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Наведено основні результати досліджень діелектричних параметрів у системі твердих розчинів на основі $(Ca_{1/4}Cu_{3/4})TiO_3$. Досліджено вплив ізовалентного заміщення в $(Ca_{1/4}Cu_{3/4})TiO_3$ на діелектричну проникність та температурну стабільність кераміки.