

Synthesis of $(\text{Ca,Cu})_{(1-3x/2)}\text{N}_x\text{TiO}_3$ solid solutions (N = Bi, La)

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Solid solutions $(\text{Ca,Cu})_{(1-3x/2)}\text{N}_x\text{TiO}_3$ (N = Bi, La; $x \leq 0.116$) have been synthesized. The effect of bismuth and lanthanum content on the crystal structure parameters and dielectric properties of sintered polycrystal samples has been studied. The heterovalent cationic substitution by trivalent dopants for calcium results in increasing lattice parameters accompanying the rising x and reduction of the maximum intensity in the temperature dependence of dielectric constant.

Синтезированы твердые растворы $(\text{Ca,Cu})_{(1-3x/2)}\text{N}_x\text{TiO}_3$ (N = Bi, La; $x \leq 0.116$), исследовано влияние содержания висмута и лантана на параметры кристаллической структуры и диэлектрические свойства спеченных поликристаллических образцов. Результатом гетеровалентного катионного замещения кальция трехвалентными допантами является увеличение параметров кристаллической решетки с ростом x , снижение максимума температурной зависимости диэлектрической проницаемости.

Calcium-copper titanate $(\text{Ca}_{0.25}\text{Cu}_{0.75})\text{TiO}_3$ (CCTO) is characterized by high dielectric constant values (of the order of 10^4 at 1 kHz frequency for ceramic samples [1] and thin films [2] and up to 10^5 for single crystals [3]) and is of interest in the field of materials for capacitors. The CCTO crystal structure is characterized by a centrally symmetrical cubic unit cell (the space group $Im\bar{3}$, $a = 7.391(1) \text{ \AA}$) containing four formula units ABO_3 (A = Ca and Cu, B = Ti) [4, 5]. The Ti^{4+} cations are located within oxygen octahedrons attached together by vertices and Ca^{2+} and Cu^{2+} , between the octahedrons inside of icosahedrons. The perovskite-like structure of calcium-copper titanate allows both isovalent and heterovalent substitutions in the positions of calcium, copper (A) and titanium (B) with formation of a wide variety of solid solutions.

There are few publications related to preparation on the basis of calcium-copper titanate. In particular, syntheses of com-

pounds isostructural to CCTO have been reported [4, 6] where the A sites of the perovskite crystal lattice are occupied by bivalent cations ($\text{M}_{0.25}\text{Cu}_{0.75}\text{TiO}_3$, M = Cd, Sr), trivalent ones ($\text{M}_{2/3}\text{Cu}_{0.75}\text{TiO}_3$, M = rare-earth cations) or univalent ones with simultaneous titanium substitution in the B site with pentavalent cations ($\text{NaCu}_{0.75}\text{Ti}_{0.75}\text{M}_{0.25}\text{O}_3$, M = Ta, Nb, Sb). Later, new compounds on the basis of CCTO were obtained using substitution for Ti. In particular, the effect of $(\text{Ca}_{0.25}\text{Cu}_{0.75})\text{TiO}_3$ doping with niobium, iron (0 to 4 mol. %) [7, 8] as well as with nickel and cobalt [9] on the dielectric properties has been studied. The introduction of niobium and especially of iron into the titanium position results in reduced dielectric constant values of CCTO. The doping with cobalt increases the dielectric constant up to 150000. The observed dependence of dielectric properties on the doping element nature offers a possibility to develop novel ceramic materials on the basis of calcium-cop-

per titanate solid solutions having improved electrophysical characteristics. This work is aimed at synthesis of $(\text{Ca}_{0.25}\text{Cu}_{0.75})_{(1-3x/2)}\text{N}_x\text{TiO}_3$ ($\text{N} = \text{Bi}, \text{La}$) system solid solutions and at the study of the dopant content on the phase composition and dielectric properties of the synthesized substances.

The stoichiometric ratios of initial compounds required to form the CCTO based solid solutions with trivalent substituents (N^{3+}) (which are bismuth and lanthanum cations) were calculated according to the formula $(\text{Ca}_{0.25}\text{Cu}_{0.75})_{(1-3x/2)}\text{N}_x\text{TiO}_3$ assuming that the doping cations occupy the A position in the ABO_3 perovskite, calcium and copper cations being substituted simultaneously. The polycrystal samples of $(\text{Ca}_{0.25}\text{Cu}_{0.75})_{(1-3x/2)}\text{N}_x\text{TiO}_3$ ($x = 0.01, 0.05, 0.1$ for Bi and $x = 0.01, 0.02, 0.04$ for La) were prepared by solid phase synthesis starting from calcium carbonate CaCO_3 and $\text{CuO}, \text{TiO}_2, \text{La}_2\text{O}_3, \text{Bi}_2\text{O}_3$ oxides. All the initial materials were of special purity grade. The blends were annealed in air at $1050 \pm 5^\circ\text{C}$ for 2 h. Repeated grinding/annealing cycles were carried out if necessary. The optimum synthesis conditions were determined basing on thermal analysis and X-ray phase examination. The differential thermal analysis (DTA) and thermogravimetric analysis (TG) were carried out using an OD-103 derivatograph (MOM) in air within the temperature interval of 20 to 1200°C at the heating rate of 5 deg/min. The X-ray phase studies were carried out using a SIEMENS D500 diffractometer (the Bragg-Brentano geometry, $\text{Cu K}\alpha$ emission, $\lambda = 1.5418 \text{ \AA}$, graphite monochromator in the diffracted beam, the angular range $15^\circ \leq 2\theta \leq 140^\circ$, the scan step 0.02° , accumulation time 10 s in each point). The phases were identified by means of PDF-4 library and the EVA search system included in the diffractometer software. The phases were analyzed quantitatively according to the Rietveld method using the FullProf program. For electrical measurements, silver electrodes were applied onto 1.5 mm thick ceramic tablets of 10 mm in diameter. The dielectric constant was measured using an E7-8 universal bridge at 1 kHz frequency.

The CCTO preparation conditions have been determined previously basing on the differential thermal analysis and X-ray phase examination results [11]. The DTA and TG curves are similar to each other for blends of CCTO and those of CCTO based solid solutions. At 850°C , calcium carbonate decomposition occurs and above 920°C , a

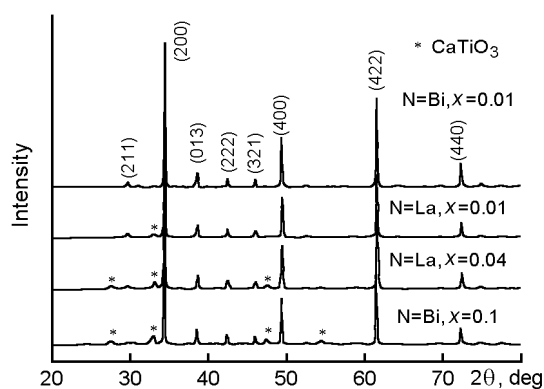


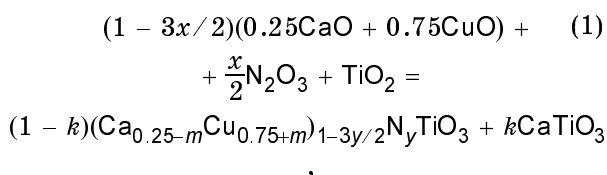
Fig. 1. X-ray diffraction patterns of $(\text{Ca}_{0.25}\text{Cu}_{0.75})_{(1-3x/2)}\text{N}_x\text{TiO}_3$ solid solutions.

compound isostructural to the calcium-copper titanate is formed. The temperature increase above 1100°C results in reduction of divalent copper into univalent one according to the reaction $4\text{CuO} \rightarrow 2\text{Cu}_2\text{O} + \text{O}_2$ and in the mixture melting at 1220°C .

The X-ray analysis of the synthesized solid solutions $(\text{Ca}_{0.25}\text{Cu}_{0.75})_{(1-3x/2)}\text{Bi}_x\text{TiO}_3$ ($x = 0.01, 0.05, 0.1$) (CCBTO) and $(\text{Ca}_{0.25}\text{Cu}_{0.75})_{(1-3x/2)}\text{La}_x\text{TiO}_3$ ($x = 0.01, 0.05, 0.1$) (CCLTO) confirms the formation of compounds having the cubic crystal lattice of calcium-copper titanate. The diffraction peaks correspond to the b.c.c. structure of the $Im\bar{3}$ space group according to [4]. A small amount of CaTiO_3 impurity has been revealed in the studied samples along with the primary phase CCBTO/CCLTO (see Table 1 and Fig. 1). The calcium titanate amount increases in parallel with the dopant concentration.

The CaTiO_3 presence in the reaction products evidences that the solid solutions formed contain a lower calcium concentration than the initial raw blend, thus, their composition does not answer to the formula $(\text{Ca}_{0.25}\text{Cu}_{0.75})_{(1-3x/2)}\text{N}_x\text{TiO}_3$ assumed initially. Basing on the quantitative X-ray phase analysis data, the true compositions were determined for the formed solid solutions of calcium-copper titanate doped with bismuth and lanthanum (CCNTO) (see Table 2).

Proceeding from the solid phase reaction equation



the true compositions of the formed solid solutions were determined basing on the material balance equation with parameters x , a and unknown y , k , m :

$$\begin{cases} y(1-k) = x \\ (1-k)(0.75+m)(1-3y/2) = 0.75(1-3x/2) \\ \frac{\alpha_{\text{CCNTO}}}{(1-k)M_{\text{CCNTO}}} = \frac{\alpha_{\text{CaTiO}_3}}{kM_{\text{CaTiO}_3}} \end{cases}, \quad (2)$$

where x is the N (N = Bi, La) mole fraction in the initial raw blend; y , the N mole fraction that in the formed solid solution; k , the CaTiO_3 mole fraction; m , the mole fraction of Cu and Ca content deviation between the solid solution and initial blend; α – the content of the substance in products of reaction, M – the molecular mass of the substance in consideration. The composition of the formed solid solutions corresponds to formulas presented in the right-hand column of Table 2. The molar fraction of calcium in the formed solid solutions of calcium-copper titanate doped with bismuth and lanthanum is seen to decrease as compared to that in the raw blend, while the copper molar fraction increases up to 0.75, those of bismuth and lanthanum increase, too.

The changes in Ca^{2+} , Cu^{2+} , and cationic vacancies as functions of bismuth (0 to 4.3 mol.%) and lanthanum (0 to 11.6 mol.%) are plotted in Fig. 2. The points for $\text{La}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ with containing 17 mol.% of lanthanum [1] are shown in the plots, too. As the trivalent dopant concentration rises from 0 to 17 mol.%, the calcium content decreases linearly from 25 mol.% to 0, that of copper remains constant (75 ± 1 mol.%) and that of vacancies increases from 0.5 to 8.5 mol.%. The triva-

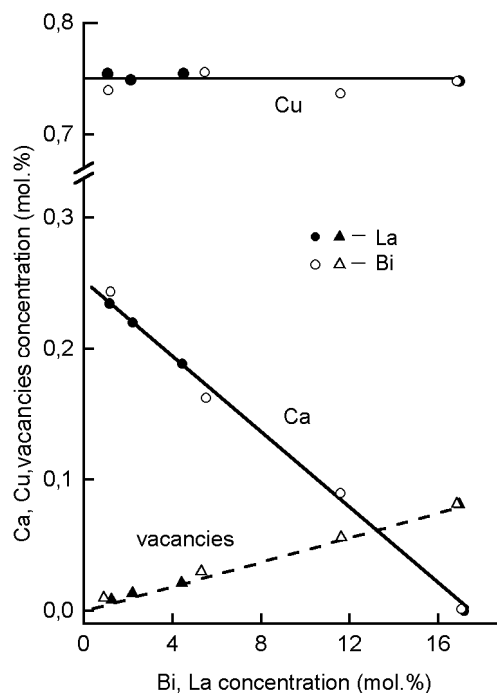


Fig. 2. Dependences of Ca^{2+} , Cu^{2+} , and cationic vacancies contents in Bi and La doped CCTO solid solutions versus the dopant concentration.

alent bismuth and lanthanum cations displace the calcium ones out of the A position of the $\text{Ca}_{0.25}\text{Cu}_{0.75}\text{TiO}_3$ perovskite structure. The introduction of trivalent cations into the divalent calcium position is a heterovalent substitution and results in formation of cationic vacancies according to the electrical neutrality equation $3\text{Ca}^{2+} = 2\text{N}^{3+} + \square$, \square being the cationic vacancy. The composition of solid solutions being formed in this case does not correspond to the initially supposed formula $(\text{Ca}_{0.25}\text{Cu}_{0.75})_{(1-3x/2)}\text{N}_x\square_{x/2}\text{TiO}_3$ but to $\text{Ca}_{0.25-3x/2}\text{Cu}_{0.75}\text{N}_x\square_{x/2}\text{TiO}_3$ where N = Bi, La. The predominant substitution of bismuth and lanthanum for calcium in the A

Table 1. Phase composition of reaction products of $(\text{Ca}_{0.25}\text{Cu}_{0.75})_{(1-3x/2)}\text{N}_x\text{TiO}_3$ (CCNTO) formation

Dopant	Dopant content (x)	Calculated composition (basing on raw blend)	Phase composition of reaction products (X-ray analysis), % by mass	
			CCNTO	CaTiO_3
Bi	0.01	$\text{Ca}_{0.246}\text{Cu}_{0.739}\text{Bi}_{0.01}\text{TiO}_3$	100	–
	0.05	$\text{Ca}_{0.231}\text{Cu}_{0.694}\text{Bi}_{0.05}\text{TiO}_3$	92.7	7.2
	0.10	$\text{Ca}_{0.213}\text{Cu}_{0.638}\text{Bi}_{0.1}\text{TiO}_3$	88.8	10.9
La	0.01	$\text{Ca}_{0.246}\text{Cu}_{0.739}\text{La}_{0.01}\text{TiO}_3$	98.4	1.6
	0.02	$\text{Ca}_{0.243}\text{Cu}_{0.728}\text{La}_{0.02}\text{TiO}_3$	97.6	2.3
	0.04	$\text{Ca}_{0.235}\text{Cu}_{0.705}\text{La}_{0.04}\text{TiO}_3$	92.6	5.5

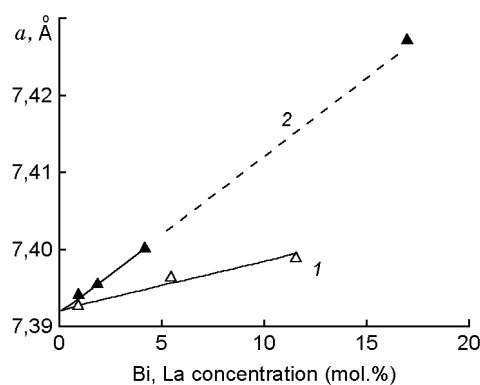


Fig. 3. Concentration dependence of the unit cell parameter a for calcium-copper titanate solid solutions: $\text{Ca}_{0.25-3x/2}\text{Cu}_{0.75}\text{Bi}_x\text{TiO}_3$ (1) and $\text{Ca}_{0.25-3x/2}\text{Cu}_{0.75}\text{La}_x\text{TiO}_3$ (2).

position of the CCTO structure is due to similar values of ionic radii of said elements.

The parameter a of the cubic unit cell has been calculated for all the CCNTO composition using the Rittveld method. Fig. 3 shows the dependence of parameter a for CCBTO (line 1) and CCLTO (line 2) on the bismuth and lanthanum concentration, respectively. The linear dependence of the unit cell parameters on the composition answers to the Vegard rule, thus confirming additionally the formation of the substitution solid solutions and the correctness of the composition determination thereof. The parameter a of the cubic unit cell increases slightly as the dopant content rises; this is explained by the small size difference between the cations $\text{Ca}_{(\text{XII})}^{2+}$ (1.34 Å), $\text{La}_{(\text{XII})}^{3+}$ (1.36 Å) and Bi^{3+} (1.40 Å when being extrapolated to the coordination number 12) [12]. The a value for lanthanum concentration 17 mol.% ($\text{La}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$) [1] is shown also in the Figure. The dielectric constant was measured for tablets sintered at 1050°C

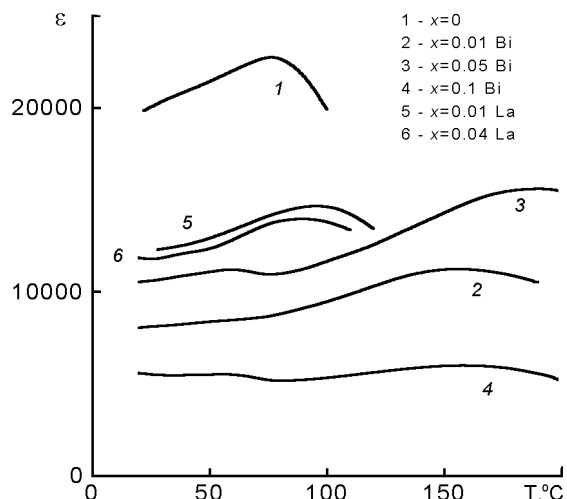


Fig. 4. Temperature dependences of dielectric constant for ceramic $\text{Ca}_{0.25-3x/2}\text{Cu}_{0.75}\text{Bi}_x\text{TiO}_3$ and $\text{Ca}_{0.25-3x/2}\text{Cu}_{0.75}\text{La}_x\text{TiO}_3$ solid solutions.

for 25 h. These measurements have shown that as the Bi^{3+} and La^{3+} cations are dissolved in the A sublattice, the temperature dependence of the dielectric constant becomes smoothened, its maximum value is reduced and shifted towards higher temperatures (Fig. 4). These changes are more pronounced at the doping with bismuth than with lanthanum.

Thus, $\text{Ca}_{0.25-3x/2}\text{Cu}_{0.75}\text{Bi}_x\text{TiO}_3$ ($x \leq 0.043$) and $\text{Ca}_{0.25-3x/2}\text{Cu}_{0.75}\text{La}_x\text{TiO}_3$ ($x \leq 0.116$) solid solutions have been obtained by solid phase synthesis, the structure and properties thereof have been studied. As the dopant content increases, the parameter a of the cubic unit cell rises due to the fact that lanthanum and bismuth cations are larger than calcium ones. The dielectric measurements have shown that as the Bi^{3+} and La^{3+} cations are dissolved in the calcium sublattice, the maximum of temperature depend-

Table 2. CCNTO solid solutions: comparison of calculated and experimental compositions

Dopant	Calculated composition (basing on raw blend)		Experimental composition (X-ray data)	
	x	Composition	x'	Composition
Bi	0.01	$\text{Ca}_{0.246}\text{Cu}_{0.739}\text{Bi}_{0.01}\text{TiO}_3$	0.010	$\text{Ca}_{0.246}\text{Cu}_{0.739}\text{a}_{0.005}\text{Bi}_{0.010}\text{TiO}_3$
	0.05	$\text{Ca}_{0.231}\text{Cu}_{0.694}\text{Bi}_{0.05}\text{TiO}_3$	0.055	$\text{Ca}_{0.161}\text{Cu}_{0.758}\text{a}_{0.027}\text{Bi}_{0.055}\text{TiO}_3$
	0.10	$\text{Ca}_{0.213}\text{Cu}_{0.638}\text{Bi}_{0.1}\text{TiO}_3$	0.116	$\text{Ca}_{0.089}\text{Cu}_{0.737}\text{a}_{0.056}\text{Bi}_{0.116}\text{TiO}_3$
La	0.01	$\text{Ca}_{0.246}\text{Cu}_{0.739}\text{La}_{0.01}\text{TiO}_3$	0.010	$\text{Ca}_{0.232}\text{Cu}_{0.752}\text{a}_{0.006}\text{La}_{0.010}\text{TiO}_3$
	0.02	$\text{Ca}_{0.243}\text{Cu}_{0.728}\text{La}_{0.02}\text{TiO}_3$	0.021	$\text{Ca}_{0.221}\text{Cu}_{0.748}\text{a}_{0.010}\text{La}_{0.021}\text{TiO}_3$
	0.04	$\text{Ca}_{0.235}\text{Cu}_{0.705}\text{La}_{0.04}\text{TiO}_3$	0.043	$\text{Ca}_{0.183}\text{Cu}_{0.753}\text{a}_{0.021}\text{La}_{0.043}\text{TiO}_3$

ence of the dielectric constant becomes reduced and its temperature dependence becomes smoothened.

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Синтез твердих розчинів (Ca,Cu)_(1-3x/2)N_xTiO₃ (N = Bi, La)

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Синтезовано тверді розчини (Ca,Cu)_(1-3x/2)N_xTiO₃ (N = Bi, La) (x≤0.116), досліджено вплив вмісту вісмуту та лантану на параметри кристалічної структури та діелектричні властивості спечених полікристалічних зразків. Результатом гетеровалентного катіонного заміщення кальцію трьохвалентними допантами є збільшення параметрів кристалічної ґратки зі зростанням x, зниження максимуму температурної залежності діелектричної проникності.