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CARBONATE PRECURSOR ROUTE FOR PREPARATION OF $CaCu_3Ti_4O_{12}$

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A simple $CaCu_3Ti_4O_{12}$ synthesis method by carbonate precipitation has been developed, which is not inferior to the known methods of precipitation from solutions. The optimum temperatures for the synthesis of powder (850 °C) and sintering of ceramics (1080 °C) have been found. The CCTO ceramic prepared has stable and fine electrical properties. In the frequency range of 1 kHz to 1 MHz, the ε' value always is higher 10^4 with the dielectric losses, $\tan\delta \sim 0.05–0.08$. Such CCTO ceramic prepared by the carbonate co-precipitation method with good electric properties should find applications in electric devices.

Keywords: calcium-copper titanate, high dielectric constant, co-precipitation, carbonate precursor.

INTRODUCTION. In recent decades, calcium-copper titanate, $CaCu_3Ti_4O_{12}$ (CCTO) has attracted the attention of researchers as a material with a high dielectric constant ($\varepsilon' \sim 10^4–10^5$), low dielectric losses ($\tan\delta \leq 0.15$), photocatalytic and sensory activity in a wide temperature range (100–600 K). These facts make it possible to consider CCTO as a material with a wide potential for practical application as supercapacitors, dielectric resonators, chemical and photocatalytic sensors [1–5]. CCTO has a pseudocubic ABO_3 perovskite structure with space group Im3 [6]. The Cu^{2+} and Ca^{2+} ions are located in A sublattice of the crystal lattice, but occupy the positions with different coordination numbers (4 for Cu^{2+} and 12 for Ca^{2+}) due to the inclination of TiO_6 oxygen octahedra.

Various CCTO preparation methods with their advantages and disadvantages are known. The method of solid-phase reactions has been widely used industrially [6–8]. The disadvantages of this method are the contamination during grinding, several stages of grinding, and prolonged high-temperature heat treatments. Wet (or soft) chemistry methods are of interest because of greater purity, better granulometric characteristics, higher reactivity of synthesized powders, and as a result, significantly lower temperatures of ceramic sintering. Among wet methods, namely hydrothermal mehod [9, 10], combustion synthesis techniques [11, 12], sol-gel [13–16], and co-precipitation [17–21], the last one is the most economical and effective method.

The characteristics of CCTO ceramics synthesized by co-precipitation methods (Table 1) show the mainly used precipitants (oxalate and hydroxide ions); significant differences in the conditions of heat treatment, dielectric losses, and dielectric constants. So, the particularity of carbonates impact on properties of such ceramics has a great interest and formed the purpose of these studies – to develop a method for the synthesis of CCTO by precipitation using carbonates.

Table 1

Heat-treatment conditions and dielectric characteristics at room temperature for $CaCu_3Ti_4O_{12}$ ceramics sintered from powders deposited by various methods.

Precursor-precipitant	Temperature/ duration of synthesis,°C/h	Temperature/ duration of sintering, °C/h	ε′ (1 kHz)	tan δ (1 kHz)	Year and reference
$H_2C_2O_4$	900/10	1050/24	23000	0.12	2006 [17]
$H_2C_2O_4$	700/-	1000/- (spark plasma)	20000	0.20	2009 [18]
$H_2C_2O_4$	950/10	1100/24	115000	0.20	2009 [19]
NaOH	850/2	1050/4	10700	0.15	2011 [20]
NH_4OH	850/2	1050/2	3100	0.05	2015 [21]

*EXPERIMENT AND DISCUSSION OF THE RESULTS***.** Pure $Cu_2(OH)_2CO_3$ and analytical grade $CaCO_3$, K_2CO_3, KOH, $TiCl_4$, and HNO_3 were used as starting reagents. The aqueous solution of titanium tetrachloride ($TiCl_4$) was prepared. $Cu_2(OH)_2CO_3$ and $CaCO_3$ were dissolved in dilute HNO_3 to form solutions of $Cu(NO_3)_2$ and $Ca(NO_3)_2$, respectively. Solutions of $Ca(NO_3)_2$, $Cu(NO_3)_2$ and $TiCi_4$ were mixed in the stoichiometric ratio Ca : Cu : Ti = 1 : 3 : 4. Aqueous solutions of K_2CO_3 and KOH were used as precipitants. Precipitation was carried out in a reactor with a magnetic stirrer. Solution of precipitant and Ca^{2+}, Cu^{2+}, Ti^{4+}-cations-containing solutions were added at a constant rate. The flow rate of KOH solution was controlled to maintain pH = 10, and prevent the formation of partially soluble calcium bicarbonate. After precipitation, the precipitate was heated with stirring to 60–70 °C and left for 24 hours for stabilization. The suspension was filtered, and the precipitate was washed free of K^+, Cl^-, NO_3^- ions by double distilled water with an amount of water 5 l for 0.04 mol $CaCu_3Ti_4O_{12}$. The content of K^+ ions in the washed water was controlled by a photoelectric flame photometer and did not exceed $1{\cdot}10^{-5}$ g/l. The precipitate was a green paste of the general composition $CaCO_3{\cdot}1.5Cu_2(OH)_2CO_3{\cdot}4Ti(OH)_4{\cdot}nH_2O$. This paste was dried at 110 °C to form a dispersed powder. Powder of CCTO precursor was synthesized at 750–900 °C for 4 h. The synthesized powders were ground in an agate mortar with a pestle, mixed with a 5 % aqueous solution of polyvinyl alcohol and passed through a 150 mesh nylon sieve. Disc-shaped specimens with a diameter of 8.5 mm and a thickness of 2 mm were pressed under a pressure of 120 MPa.

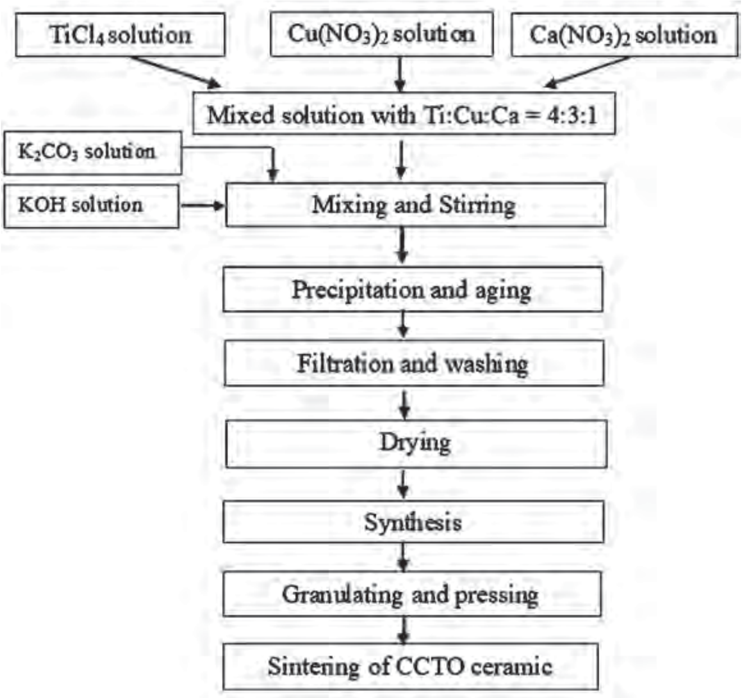


Fig. 1. The process of CCTO preparation.

Ceramics were sintered at 1080–1100 °C for 10 h. Fig. 1 shows a schematic diagram of the process for CCTO fabrication. The phase composition of the products was determined by X-ray diffractometry (XRD) on a DRON-4-07 diffractometer (40 kV, 20 mA) using Cu*K*α radiation and Ni filter. Certified standards, NIST SRM640e-SiO_2 (2Θ standard) and NIST SRM1976-Al_2O_3 (intensity standard) were used. The relative X-ray impulse counting error did not exceed 0.5 %. The unit cell parameters of the samples were determined using FullProf software by the whole-pattern profile-matching Le Bail procedure [22]. The crystallite sizes of etched ceramic samples were studied using a scanning electron microscope JEM 10CX II (JEOL). The average grain diameters were measured by at least 50 grains from 3 different areas using ImageJ software [23]. The density of ceramics was determined by Archimedes principle. To deposit the silver electrodes on polished ceramic samples, Ag-containing paste was burned at 600 °C for 0.5 h. The complex impedance of the samples with a diameter of 7.3 mm and a thickness of 1.6 mm was investigated using a 1260 Impedance/Gain-Phase Analyzer (SolartronAnalytical). The measurements were carried out in a dry atmosphere to avoid the contribution of water vapour [30]. The equivalent circuit and the value of its components were determined using the ZView® software (Scribner Associates Inc., USA). Measurement error for ε and tan δ in the frequency range 10^3–10^5 Hz does not exceed 2 %.

Fig. 2 shows the diffraction patterns of the precipitated CCTO precursor after drying at 100 °C and after heat treatment at 750–1100 °C.

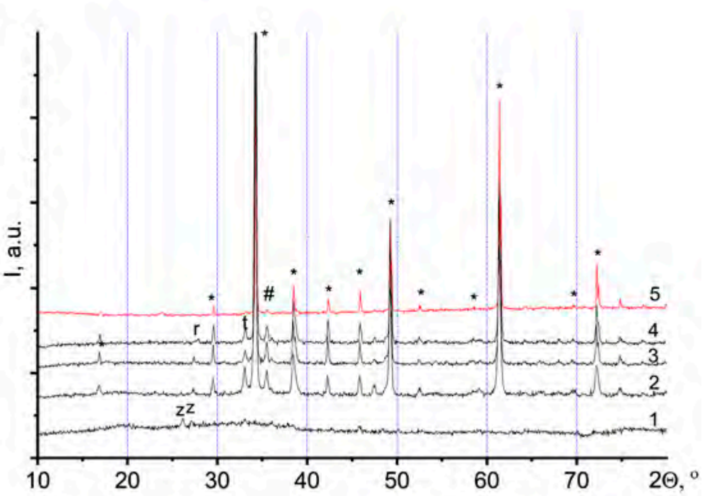


Fig. 2. Powder diffraction patterns of CCTO precursor dried at 100 °C (1) and synthesized at temperatures of 750 (2), 800 (3), 850 °C (4) and CCTO ceramic sintered at 1100 °C (5). Second phases: * = $CaCu_3Ti_4O_{12}$, z = $CaCO_3$, r = TiO_2, t = $CaTiO_3$, # = CuO.

Fig. 2 shows that in the precipitate dried at 100 °C, copper and titanium compounds are in an X-ray amorphous state and only weak reflections of $CaCO_3$ (ICDD PDF-2, card № 76–0606) are observed. At 750 °C, perovskite phase, $CaCu_3Ti_4O_{12}$ becomes the dominant phase (№ 75–2188), and a trace amount of intermediate phases $CaTiO_3$ (№ 78–1013), CuO (№ 89–5899) and TiO_2 (№ 21–1276) are observed. At 1100 °C, single-phase CCTO ceramics were sintered: all diffraction reflections indexed in Im3m space group with the parameter of the cubic unit cell a = 7.3939(1) Å; unit cell volume V = 404.23(1) Å^3 was determined.

To determine the optimal mode of heat treatment, the temperatures of powder synthesis and CCTO ceramic sintering were varied (Table 2). Table 2 shows that the relative density of ceramics depends on the synthesis temperature. The sample 800/1080 synthesized at 800 °C and sintered at 1080 °C has the maximum density (93%). The decrease in ceramic density with an increase in synthesis temperatures can be explained by the loss of powder activity and the improvement of the particles crystal lattice.

Table 2

Influence of temperature regime on the density of polycrystalline CCTO samples.

Sample designation	Synthesis, °C/h	Sintering, °C/h	Apparent density, g/cm^3	Relative density, %
750/1080	750/4	1080/10	4.46(3)	88(3)
800/1080	800/4	1080/10	4.71(8)	93(2)
850/1080	850/4	1080/10	4.43(8)	89(2)
900/1080	900/4	1080/10	4.30(5)	85(3)
800/1100	800/4	1100/10	4.62(8)	91(2)
900/1100	900/4	1100/10	4.15(9)	82(2)

SEM microstructure of ceramic samples 800/1080, 900/1080, 800/1100, and 900/1100 are shown in Fig. 3. Fig. 3 shows that the smallest grains (5 ± 3 μm) occur at the synthesis temperature of 800 °C. With an increase in the synthesis temperature to 900 C, the grain size increases to 7 ± 3 μm. Large grains have a smaller surface area, closed porosity remains at the sintering stage, which leads to a decrease in the apparent density of polycrystalline samples. Thus, the optimal synthesis and sintering temperatures of the CCTO ceramics should not exceed 850 and 1080 °C, respectively.

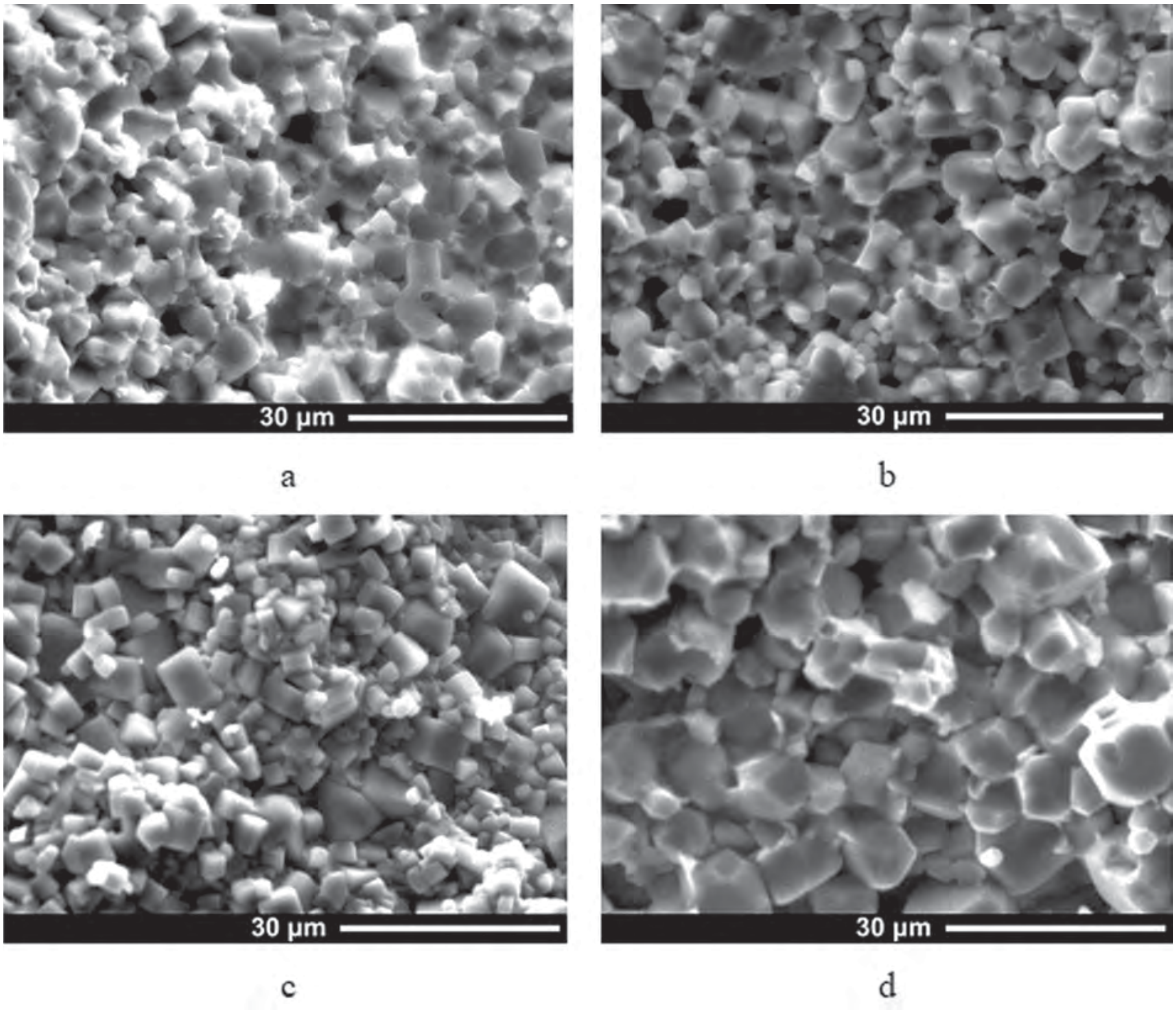
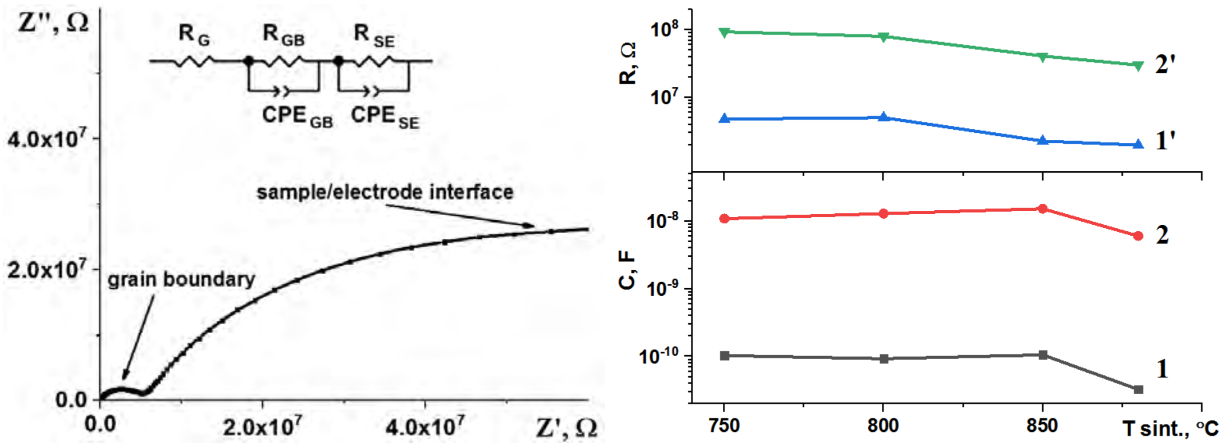


Fig. 3. SEM microstructure of the CCTO ceramics at different synthesis and sintering temperatures, °C: 800/1080 (a); 800/1100 (b); 900/1080 (c); 900/1100 (d).



a

b

Fig. 4. a – Complex impedance diagrams at room temperature and an equivalent circuit (insert) for $CaCu_3Ti_4O_{12}$ ceramic sample 850/1080 °C. R and CPE are resistance and constant phase element. Subscripts indicate grain (G), grain boundary (GB) and the interface between sample and electrode (SE).

b – Capacity and resistance of grain boundary (1, 1') and sample/electrode interface (2, 2') depending on synthesis temperature.

CCTO ceramics are electrically heterogeneous with low grain and high grain boundary resistance [24, 25]. Fig. 4a shows a room-temperature complex impedance diagram of CCTO ceramic synthesized at 850 °C and sintered 1080 °C. As can be seen from Fig. 4a, the dependence Z" = *f* (Z') is described by two semicircles, that indicates the presence of two relaxation mechanism in the structure. These two mechanisms are also observed on the dependencies ε′(*f*) and tan δ(*f*) (Fig. 5). The equivalent circuit for the complex impedance of CCTO ceramics (Fig. 4a, insert) is composed of R_G (resistance of grain), R_{GB} and CPE_{GB} (resistance and constant phase element of grain boundary), R_{SE} and CPE_{SE} (resistance and constant phase element of interface between sample and electrode) [26, 27]. As can be seen in Fig. 4b, with an increase in the synthesis temperature, the grain boundary resistance and the sample-electrode resistance of the samples almost does not change, while the capacitance at the grain boundary and the sample-electrode area passes through a maximum. The maximum value of capacity is observed for the sample synthesized at 850 °C and sintered 1080 °C.

Fig. 5 shows the results of frequency measurements ε′ (*f*) and tan δ (*f*) at room temperature of the $CaCu_3Ti_4O_{12}$ ceramics prepared by deposition methods in this work and the works of other authors. As can be seen from Fig. 5a, the ε′ (*f*) dependence of synthesized in this work ceramic (curve 1) demonstrates a decrease with frequency and is 11400 at 1 kHz. The sample synthesized in this work is characterized by a low dielectric loss tangent ($\tan\delta \leq 0.2$) in a frequency range 10^3–10^5 Hz and a high dielectric constant $\varepsilon > 10^4$ in a wide frequency range 10^2–10^6 Hz. These characteristics agreed well with the data of Ref. [20] (curve 4), exceed values shown in Ref. [21] (curve 5) and lower than that showed in Refs [17, 18] (curves 2 and 3). In a frequency range of 0.1–100 kHz, CCTO ceramics with the lowest dielectric losses, tan δ ~ 0.05–0.08, are demonstrated the lowest dielectric constant, 2500–3000 (curve 5). At frequencies above 10 kHz, the dielectric loss of the investigated ceramic (tan δ ~ 0.11 ÷ 0.14) exceeds the analogous (curves 2 and 4) and becomes close to the data in curves 3 and 5. Above 1 MHz, dielectric losses increase sharply.

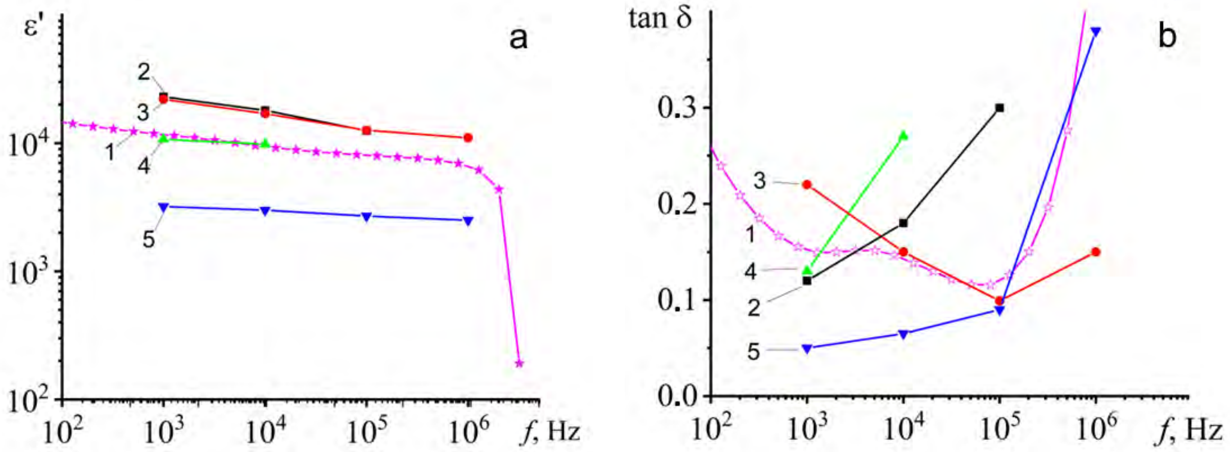


Fig. 5. Frequency dependences of ε′ (a) and tan δ (b) of CCTO ceramics at room temperature: this work, synthesized at 850 °C and sintered 1080 °C (1) and Refs [17] (2), [18] (3), [20] (4), [21] (5).

Dielectric parameters obtained are characteristic of the CCTO prepared by deposition methods (Table 1) and are mainly explained by the small size of the ceramics grains and consequently a larger number of interfaces between grains [15, 28]. Namely, according to the model of internal barrier layer capacitor (IBLC) structure, the effective dielectric constant (ε_{eff}) can be estimated by the following equation [29]:

$$\varepsilon_{eff} = \varepsilon_{gb}(d_g + d_{gb}) / d_{gb}$$

where ε_{gb} is the dielectric constant of the grain boundary, d_g is the average grain size, and d_{gb} is the thickness of the grain boundary layer. This equation shows that the value of ε_{eff} is determined by the ratio of $(d_g + d_{gb}) / d_{gb}$. Therefore, the increase in grain size and the thickness of the grain boundary layer increases the ε_{eff} value of CCTO ceramics.

CONCLUSIONS. Carbonate precursor can be successfully used to synthesize $CaCu_3Ti_4O_{12}$ powders by precipitation from solutions. The sample synthesized at 800 °C and sintered at 1080 °C for 10 h has the maximum density (93%). The smallest grains (5 ± 3 μm) occur at the synthesis temperature of 800 °C and increases to 7 ± 3 μm at 900 °C. The optimal synthesis and sintering temperatures of the CCTO ceramics should not exceed 850 and 1080 °C, respectively. The complex impedance diagrams of CCTO ceramic indicate the presence of two relaxation mechanisms in the structure. These two mechanisms appear due to the difference in electrical properties of grain boundaries and interfaces between ceramic sample and electrode. With an increase in the synthesis temperature, the resistances of grain boundaries and the sample-electrode interfaces almost do not change, while their capacitances pass through a maximum. The maximum value of capacity is observed for the sample synthesized at 850 °C and sintered 1080 °C. The sample synthesized is characterized by a low dielectric loss ($\tan \delta \leq 0.2$) and a high dielectric constant ($\varepsilon' > 10^4$) in a frequency range of 1–100 kHz.

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МЕТОД ОТРИМАННЯ $CaCu_3Ti_4O_{12}$ ІЗ КАРБОНАТНОГО ПРЕКУРСОРА

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Титанат кальцію-міді $CaCu_3Ti_4O_{12}$ (CCTO) має значний потенціал практичного застосування для створення суперконденсаторів, резонаторів, хімічних і фотокаталітичних сенсорів. Співосадження є одним із найбільш економічних і доступних методів «вологої хімії» отримання CCTO, який забезпечує високу чистоту, дисперсність і зниження як температур синтезу порошку, так і спікання кераміки. Для отримання CCTO методом співосадження як вихідні використовували $Cu(OH)_2 \cdot CuCO_3$, $CaCO_3$, K_2CO_3, KOH, $TiCl_4$ і HNO_3. Після розчинення $(CuOH)_2CO_3$, $CaCO_3$ в HNO_3 розчини $Ca(NO_3)_2$, $Cu(NO_3)_2$ і розчин $TiCl_4$ змішували в стехіометричному співвідношенні Ca:Cu:Ti = 1:3:4. Осадження проводили за постійного pH = 10 з одночасною подачею при перемішуванні в реактор нітратно-хлоридного розчину і розчинів осаджувачів – K_2CO_3 і KOH. Осад зеленого кольору, що відповідає загальній формулі $CaCO_3 \cdot Cu(OH)_2 \cdot CuCO_3 \cdot 4Ti(OH)_4 \cdot nH_2O$, ретельно промивали, сушили і синтезували за 750–900 °C упродовж 4 год. За 750 °C домінуючою фазою була $CaCu_3Ti_4O_{12}$ із мінімальною кількістю проміжних фаз $CaTiO_3$, CuO і TiO_2. Спечена за 1060–1100 °C / 10 год. кераміка CCTO була однофазною (пр. гр. Im3m). Відносна щільність кераміки суттєво залежала від температури синтезу. Максимальну щільність (93%) продемонстрував зразок, синтезований за 800 °C і спечений за 1080 °C. При цьому кераміка мала дрібні (5 ± 3 мкм) зерна. При підвищенні температури синтезу до 900 °C розмір зерен збільшується до 7 ± 3 мкм, а уявна густина кераміки знижується до 87 % відповідно. Залежність комплексного імпедансу $Z'' = f(Z')$ отриманої кераміки CCTO

можна описати двома напівколами, що вказує на наявність у структурі двох релаксаційних механізмів. Дослідження залежностей ε′ (*f*) і tan δ (*f*) за кімнатної температури показало, що ε′ знижується з частотою (11380 за 1 кГц та 8050 за 100 кГц), а tan δ становить 0,11–0,14 за частот $f \geq 10$ кГц; із підвищенням частоти до 1 MHz діелектричні втрати різко зростають. Отримані діелектричні параметри є характерними для CCTO кераміки, отриманої методами осадження і пояснюються, в першу чергу, малими розмірами її зерен і великою кількістю границь розділу зерен.

Ключові слова: титанат кальцію-міді, висока діелектрична проникність, спільне осадження, карбонатний попередник.

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