Synthesis of CaCu$_3$Ti$_4$O$_{12}$: How Heat Treatment Influences Morphology and Dielectric Properties

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Abstract—A ceramic powder, the precursor of CaCu$_3$Ti$_4$O$_{12}$, was prepared by liquid-phase synthesis in acetic acid. The synthesized samples were calcined at 200, 400, 600, 800, and 1100°С and then characterized by a set of physicochemical methods. An increase in annealing temperature induced changes in the particle size distribution and quantitative porosity parameters of the powder. Analysis of the dielectric spectra of suspensions of synthesized materials allowed us to conclude that high-temperature annealing of the powder leads to a decrease in relaxation time.

Keywords: CaCu$_3$Ti$_4$O$_{12}$, synthesis, dielectric spectra, morphology, heat treatment

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INTRODUCTION

In recent years, the attention of researchers has been directed to ceramic materials with the perovskite structure due to their potential for use in high-frequency electronics, for the production of capacitors, generators, and filters [1]. Barium, strontium, and calcium titanates are just such materials, but these perovskites exhibit an abrupt change in dielectric constant near the Curie temperature, and this largely limits their practical applicability.

Among the perovskite-like oxides, one can distinguish calcium copper titanate CaCu$_3$Ti$_4$O$_{12}$ (CCTO) and related materials. The dielectric constant of this compound changes little over a wide temperature range up to 600 K; so, CCTO is suitable for use in design of microelectronic elements, namely, capacitors, microwave devices, gas sensors, automotive electronic devices, random access memory devices, etc. [2, 3].

The development of new synthesis methods for preparing nanoscale CaCu$_3$Ti$_4$O$_{12}$ is of great interest with the view of reducing the size of electronic elements, increasing their efficiency and productivity. Solid-phase synthesis is the most common method for preparing CCTO, like for most perovskites, due to its facility [4–8]. Along with calcium copper titanate, however, this synthesis can also yield copper(II) oxide, which fills-in intergrain spaces of the ceramics and influences the functional properties of the material. In addition, the heat treatment of the initial components of the mixture takes more than 1 h, and leads to significant energy costs in the production of CCTO [9].

Other methods for preparing CaCu$_3$Ti$_4$O$_{12}$ are also described in the literature, among them, liquid-phase synthesis (including a sol–gel process), combustion synthesis, coprecipitation, and other processes [10–16]. The advantage of liquid-phase synthetic methods over solid-phase methods is a lower process temperature and the ability to provide the exact stoichiometry and uniform phase composition of the powders. Depending on the used liquid-phase synthesis technique, it is possible to control not only the particle size, but also the shape, specific surface, area and pore structure of the particles. Zhao et al. [17] employed the sol–gel process followed by annealing at 900°С for 2 h to produce CCTO powders with particle sizes less than 100 nm.

Ahmadipour et al. [10] in their survey provide data on the influence of the CaCu$_3$Ti$_4$O$_{12}$ preparation conditions (annealing temperature and process time) and impurities on the product dielectric properties; they also show the relevance of such studies for solving both fundamental and applied problems.

This work is a continuation of the earlier study [18] where the thermal evolution of the CCTO ceramic powder precursor and its photocatalytic activity were studied by X-ray phase analysis, mass spectroscopy, thermal analysis, UV and IR spectroscopy. The study showed that CaCu$_3$Ti$_4$O$_{12}$ phase formation is over by 1100°С.

In the article presented here, the CCTO precursor was synthesized by the liquid-phase method and stud-
SYNTHESIS OF CaCu$_3$Ti$_4$O$_{12}$

Particle size distribution diagrams for powders annealed at various temperatures.

The precursor of CCTO ceramic powder was prepared by a liquid-phase method in acetic acid. The initial reagents used were Ca(OH)$_2$, Cu(CH$_3$COO)$_2$H$_2$O, and Ti(C$_4$H$_9$O)$_4$ (Sigma-Aldrich) taken in the CaO : CuO : TiO$_2$ = 1 : 3 : 4 stoichiometry. The first synthesis step involved the preparation of a Cu(CH$_3$COO)$_2$H$_2$O solution in water and a Ca(OH)$_2$ solution in acetic acid. Then, the solutions were mixed together and then stirred for 1 h at 85°C. To the resulting homogeneous mixture, Ti(C$_4$H$_9$O)$_4$ was added dropwise and was also kept for 1 h at 85°C under continuous stirring. Then, the solution was concentrated to a constant weight in a drying cabinet at 100°C, and the thus-obtained sample was annealed in air at 200, 400, 600, 800, and 1100°C.

Heat-treated powder samples were studied by a set of physicochemical methods.

Particle size compositions in the range from 0.3 nm to 10 μm were determined on a Zetasizer Nano ZS (Malvern Instruments) laser diffraction analyzer. The powders were pretreated in an ultrasonic bath in isopropyl alcohol for 1 h in order to destroy agglomerates.

The specific surface areas and quantitative characteristics of the porous structure of annealed samples of the synthesized powder were estimated based on the analysis of low-temperature (77 K) nitrogen vapor adsorption—desorption isotherms. Isotherms were recorded using a QuantaChrome Nova 1200 high-speed gas sorption analyzer.

Dielectric properties were measured in 30% suspensions of prepared materials using an E7-20 RCL meter at frequencies in the range from 25 to 10$^6$ Hz in a capacitor cell. The required amounts of the solid phase and PMS-20 (PENTA) silicone oil were thoroughly triturated in an agate mortar for 2 h until a homogeneous stable suspension was obtained. What silicone oil is used in the work means the need to study its effect on the behavior of the CCTO precursor powder, while it is heat-treated to be converted to CaCu$_3$Ti$_4$O$_{12}$, on the dielectric characteristics in the liquid phase. In choosing silicon oil (PMS-20) we were guided by its high performance characteristics: a wide operating temperature range (−60 to +200°C) and a high breakdown voltage (>7 kV/mm).

RESULTS AND DISCUSSION

Particle Size Distribution

Figure 1 shows particle-size distribution diagrams for the tested powder depending on the annealing temperature. Clearly, the transverse sizes are in the range from 100 to 2000 nm for almost all particles. For the powder annealed at 100°C, the distribution curve is monomodal with a peak at 615 nm. The increasing annealing temperature leads to an increase in the proportion of smaller particles. In addition, the distributions for 600 and 800°C are bimodal.
**Pore Structure**

The porosity studies on annealed samples of CaCu$_3$Ti$_4$O$_{12}$ precursors involving low-temperature nitrogen adsorption–desorption measurements showed that, regardless of the annealing temperature, the resulting isotherms were type IV in terms of the IUPAC classification [19]. Wide hysteresis (Fig. 2) indicates micro- and mesopores in the material.

The Brunauer–Emmett–Teller (BET), Barrett–Joyner–Halenda (BJH), and Frankel–Halsey–Hill (FHH) models [20–25] were used to fit the experimental data for quantifying the porosity of the studied powders. In the calculations it was set that the cross-sectional area of the N$_2$ molecule is 0.162 nm$^2$, the N$_2$ monolayer thickness is 0.354 nm, and the density of liquid nitrogen is 0.808 g/cm$^3$.

The values of texture parameters derived from the isotherms for CaCu$_3$Ti$_4$O$_{12}$ precursor samples annealed at 200, 400, 600, 800, and 1100°C, appear in Table 1. These are the following parameters:

- $S_{\text{BET}}$ and $S_{\text{BJH}}$ are the total surface area calculated using the BET and BJH models, respectively;
- $V_T$ is the total pore volume determined as the liquid nitrogen volume corresponding to the amount of nitrogen adsorbed at the relative pressure $p/p_0 = 0.99$;
- $D_{\text{avg}}$ is the average pore diameter; and $D_{\text{prob}}$ is the most probable pore diameter corresponding to the particle-size distribution peak.

From Table 1, one may infer that for samples annealed at 400°C, the pore volume is more than 10 times the respective value for samples annealed at 200°C. This result is consistent with the thermal analysis and mass spectrometry data presented earlier [19]; from those data, it flows that water, acetate groups, and acetone are removed when the as-synthesized powder is heated to 320°C. Therefore, we may assume that a significant volume of pore space is freed up due to this removal, to become accessible to nitrogen.

The specific surface areas of annealed samples were determined using the BET and BJH models. $S_{\text{BET}}$ and $S_{\text{BJH}}$ decrease when the annealing temperature becomes higher than 400°C (Table 1). One can also see some difference between the values determined in terms of the two models. This difference is likely to arise from the different postulates of these models. The BJH model, for example, is based on Kelvin’s theory of filling-in cylindrical pores, while the BET theory has no this assumption.

Figure 3 shows pore-size distribution diagrams. The diagrams represent the proportions (in percent of the total pore space $V_1$ and $V_2$) corresponding to small (<11 nm in diameter) and large (>11 nm) pores. For almost all of the annealed samples (except for those annealed at 800°C), most nitrogen is adsorbed in pores with diameters less than 11 nm. The average pore sizes are in the range from 5.3 to 8.7 nm.

### Table 1. Porosity parameters of annealed CaCu$_3$Ti$_4$O$_{12}$ precursor samples

| Parameter | 200 | 400 | 600 | 800 | 1100 |
|-----------|-----|-----|-----|-----|------|
| $S_{\text{BET}}, \text{m}^2/\text{g}$ | 4.283 | 83.669 | 54.074 | 35.234 | 2.078 |
| $S_{\text{BJH}}, \text{m}^2/\text{g}$ | 3.628 | 70.903 | 61.914 | 20.746 | 2.266 |
| $V_T, \text{cm}^3/\text{g}$ | 0.008 | 0.110 | 0.090 | 0.077 | 0.003 |
| $D_{\text{avg}}, \text{nm}$ | 7.162 | 5.305 | 6.633 | 8.697 | 6.174 |
| $D_{\text{prob}}, \text{nm}$ | 3.984 | 3.571 | 4.016 | 3.144 | 4.012 |
The inhomogeneity of the materials was quantified in terms of the FHH fractal model [24, 25]; namely, low-temperature N₂ vapor adsorption–desorption was used to determine \( d_f \), the fractal dimension of the surface of a porous material.

According to Pomonis and Tsaous [24], the FHH method can calculate the fractal dimension of the adsorbent surface taking into account the effects of adsorbate surface tension, where the liquid/gas surface tension (capillary force) tends to decrease the interface area. The analytical expression for the FHH isotherm in this case is

\[
\frac{V_{\text{ads}}}{V_m} = \frac{RT \log \left( \frac{P_a}{p} \right)}{d_f - 3},
\]

where \( R \) is universal gas constant, \( T \) is absolute temperature, \( V_{\text{ads}} \) is adsorbed gas volume, and \( V_m \) is volume required for one monolayer to form. From relationship (1) it flows that \( d_f \) can be calculated from the slope of the \( \log(V_{\text{ads}}) \) versus \( \log \left( \log \left( \frac{P_a}{p} \right) \right) \) plot. The fractal dimensions found in this way for the adsorption and desorption branches of the isotherms appear in Table 2.

The fractal dimension decreases as the annealing temperature increases starting with 400°C. This trend indicates a reduction in surface profile and is consistent with the trends toward reductions in specific area and pore space elucidated by BET and BJH.

**Dielectric Measurements**

We studied how heat treatment influenced the frequency-dependent dielectric constant and dielectric loss tangent in suspensions of prepared powders in silicon oil. The results appear in Fig. 4. One can see that dielectric constant dispersion is observed in the range 25–10⁶ Hz. The \( \tan \delta \) values do not exceed 0.1 for the untreated powder (Fig. 4a). For a high annealing temperature (1100°C), the \( \tan \delta \) does not exceed 0.03 at frequencies in the range from 100 to 10⁶ Hz (Fig. 4b).

In terms of the Debye theory, the analytical relation for the dielectric constant as a function of AC cyclic frequency (\( \omega = 2\pi f \)) is

\[
\varepsilon = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + (\omega \tau)^2},
\]

where \( \varepsilon_s \) is static dielectric constant (when \( \omega \to 0 \)); \( \varepsilon_{\infty} \) is high-frequency dielectric constant (when \( \omega \to \infty \)); and \( \tau \) is relaxation time, i.e., the time required for the transition of the system from a nonequilibrium state to an equilibrium state.

Here, we used Eq. (2) for processing experimental frequency-dependent dielectric constant data, in order to calculate the relaxation times for the studied suspensions of synthesized powders. Annealing was found to decrease the relaxation time in powders: \( \tau \) is \( 3.1 \times 10^{-4} \) s for an untreated powder, while for a sample annealed at 1100°C, \( \tau = 3.5 \times 10^{-5} \) s.

**CONCLUSIONS**

Our study shows that the precursor of CCTO ceramic powders prepared by liquid-phase synthesis experiences significant changes upon heat treatment. In particular, the particle size composition of the powder, pore structure characteristics, and dielectric relaxation parameters change. The observed thermal evolution is likely to arise from the formation of a CaCu₃Ti₄O₁₂ phase, which is over by 1100°C as probed by X-ray powder diffraction.

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The authors declare that they have no conflict of interest.

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Fig. 4. Frequency-dependent dielectric constant and dielectric loss tangent for suspensions of as-synthesized powders: (a) without heat treatment and (b) after being annealed at 1100°С.
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