Investigation of the Thermal Expansion and Heat Capacity of the $CaCu_3Ti_4O_{12}$ Ceramics

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Abstract—The thermal expansion of the $CaCu_3Ti_4O_{12}$ ceramics has been measured over a wide temperature range 120−1200 K. The high quality of the samples under study has been confirmed by good agreement of the results of measurements of the heat capacity in the range 2−300 K and in the vicinity of the phase transition of magnetic nature at 25 K with the data for the single crystal. No anomalies in the thermal expansion that can be associated with the phase transition at 726−732 K assumed by other investigators have been found. The influence exerted on the thermal expansion by the heat treatment of the sample in a helium atmosphere and in air has been investigated.

1. INTRODUCTION

Anomalous dielectric behavior of perovskite-like oxide $CaCu_3Ti_4O_{12}$ (CCTO) was for the first time discovered by Subramanian et al. [1] more than ten years ago. Permittivity ε of this compound reaches $\sim 10^4$ at approximately 100 K and varies weakly in a broad temperature range up to 600 K. In addition, quantity ε has a substantial frequency dispersion and abruptly decreases to $\sim 10^2$ below 100 K with no structural variations. These results caused considerable interest in CCTO and similar compounds both from the fundamental and applied viewpoints.

The crystal structure of $CaCu_3Ti_4O_{12}$ was determined at room temperature as cubic with space group Im3 [2]. This structure suggests that large local dipole moments associated with TiO_6 are arranged oppositely, and the unit cell has a centrosymmetrical space group.

Numerous studies are devoted to the elucidation of the causes of the anomalous dielectric behavior of this compound. Ab initio calculations did not reveal the presence of any internal lattice or electronic mechanisms of this phenomenon [3]. As a consequence, large ε cannot be associated with the internal nature of the compound; it should be caused by external factors.

It was assumed in some experimental and theoretical studies that the microstructure or, more exactly, twinning at the nanolevel, is responsible for the giant permittivity of $CaCu_3Ti_4O_{12}$. Some models [4, 5], which explain this phenomenon, are based on the assumption of the electric nonuniformity of the material and the presence of nanotwins in the crystal or micrograins in ceramics. Their electrical properties and stoichiometry of the boundary layer (insulator) strongly differ from the properties of internal regions (*n*-type semiconductor), as it is observed for the $Ba_{1-x}Sr_xO_3$ ceramics. Such a microstructure leads to the formation of the potential barrier at the grain boundaries or domains; it is responsible for dielectric properties of the compound. At present, this model is considered to be most probable.

Despite the active studies of $CaCu_3Ti_4O_{12}$ by different methods, many aspects of phenomena that occur in them still remain incompletely clarified. Particularly, the question is still open as to the high-temperature structural phase transition, the presence of which at 726−732 K was assumed based on the analysis of the results of structural, dielectric, and calorimetric studies [6−9].

In this work, we represent the results of studies of thermal expansion and heat capacity of $CaCu_3Ti_4O_{12}$ ceramic samples in order to clarify the influence of experimental conditions and heat treatment in air and in a helium atmosphere on the structural variations observed in [6−9]. There are no direct measurements of thermal expansion of these compounds to our knowledge. Only the results of measurements of temperature dependences of the lattice parameter by the X-ray diffraction technique are presented.
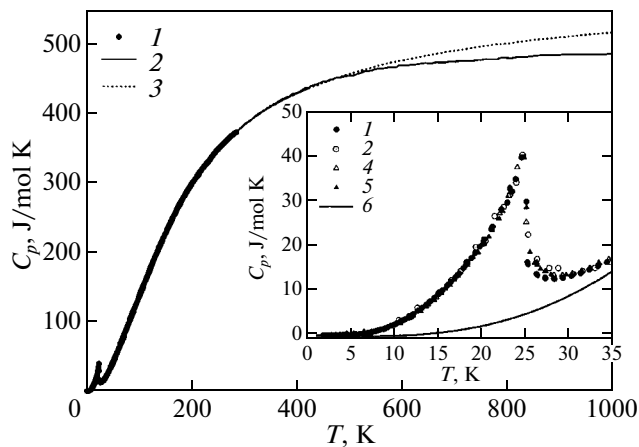
Fig. 1. Temperature dependence of the heat capacity of $CaCu_3Ti_4O_{12}$: (*1*) our data, (*2*) Levchenko et al. [13], (*3*) Jacob et al. [15], (*4*) Tsukada et al. [14], (*5*) Koitzsch et al. [12], and (*6*) lattice component of the heat capacity.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Ceramic samples were prepared by the procedure described in [10].

The synthesis of CCTO was performed by the method of joint precipitation of precursor oxalates with the use of $TiCl_3$, $CaCl_2$, and $CuCl_2 \cdot 2H_2O$. The starting compounds were dissolved in water in various ratios, while the precipitation was performed with the addition of the solution of the oxalic acid in ethanol. The $TiCl_3$ compound was selected from reasons of operation simplicity compared with $TiCl_4$. The complete transformation of Ti^{3+} into Ti^{4+} in the solution was provided by air passage during the reaction and controlled by the variation of the color from white to blue. The water volume was selected much smaller than the volume of ethanol for decreasing the dielectric constant of the precipitate. Since the nucleation is preferable compared with the growth, it is considerably easier to obtain small particles homogeneous in size and composition. The solution was evaporated for 2 h, and the obtained precipitate was dried in a centrifuge. Precursors were then calcined in air at 900°C for 10 h to obtain oxides. Microphotographs obtained using a JEOL JSM-6700 scanning electron microscope showed the homogeneity of the grains over the shape and size, which varied in a range of 0.2–1.0 μm. The obtained powder was pressed into the discs 6 mm in diameter and 5–6 mm thick at a pressure of 250 MPa. Green ceramics was obtained by sintering in air at 1050°C for 24 h. The X-ray diffraction analysis showed that the sample contains only an insignificant amount of impurities ($CaTiO_3$ and Cu_2O), no larger than 3%. The unit cell parameter $a_0 = 7.391$ Å determined at room temperature agrees well with the parameter known for the single crystal $a_0 = 7.3906$ Å [11].

In order to characterize the sample by the physical properties, the heat capacity of the ceramics was investigated in a temperature range of 2–300 K by the relaxation method using the PPMS calorimeter (Quantum Design Inc., San Diego, CA). To form good thermal contact of the sample weighing ~150 mg with the measuring system, we used the vacuum low-temperature grease Apiezon N. The heat capacity of the grease was measured in the separate experiment. The measurement error of the heat capacity was ≲1% below 60 K and ~0.25–0.50% above 100 K.

The thermal expansion measurements were performed using the DIL-402C induction dilatometer NETZSCH in a temperature range of 120–1200 K in the dynamic mode with heating and cooling rates of 3–5 K/min for ceramic samples with $L \approx 5$ mm. To calibrate and take into account the thermal expansion of the measuring system, we used reference samples from the fused quartz and corundum.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Heat Capacity

Results of measurements of the heat capacity of CCTO are shown in Fig. 1. The well-noticeable lambda-anomaly of $C_p(T)$ near 25 K is associated with the known antiferromagnetic phase transition in this compound [12]. Accordance of obtained results in a broad temperature range and near the phase transition with previously published data obtained both for crystals [12] and for ceramics [13–15] confirm good quality of our samples.

To describe lattice heat capacity $C_L(T)$ and determine the thermodynamic parameters of the antiferromagnetic transition, we used the combination of the Debye $C_D(\Theta_D/T)$ and Einstein $C_E(\Theta_E/T)$ functions during processing the experimental data above $T > 60$ K. The best result in the temperature range from 60 to 300 K was obtained at $\Theta_D = 365$ K and $\Theta_E = 671$ K. These quantities are somewhat lower than those determined in [13] (407 and 745–762 K) for the temperature range below 1000 K. However, our account for the difference in the isobaric C_p and isochoric C_v heat capacities described by two additional contribution AT and BT^2

$$C_L(T) = mC_D(\Theta_D/T) + nC_E(\Theta_E/T) + AT + BT^2, \quad (1)$$

leads to a decrease in the Debye and Einstein temperatures $\Theta_D = 352$ K, $\Theta_E = 648$ K, $A = -0.05$ J/mol K^2, $B = 0.00017$ J/mol K^3. Most likely, the divergence of the obtained parameters with data [13] is associated with different temperature ranges used for processing.

Excluding the lattice contribution of the heat capacity $C_L(T)$ from the experimental data $C_p(T)$ below 60 K, we found the entropy of the antiferromagnetic transition $\Delta S = 15.1$ J/mol K. This quantity is
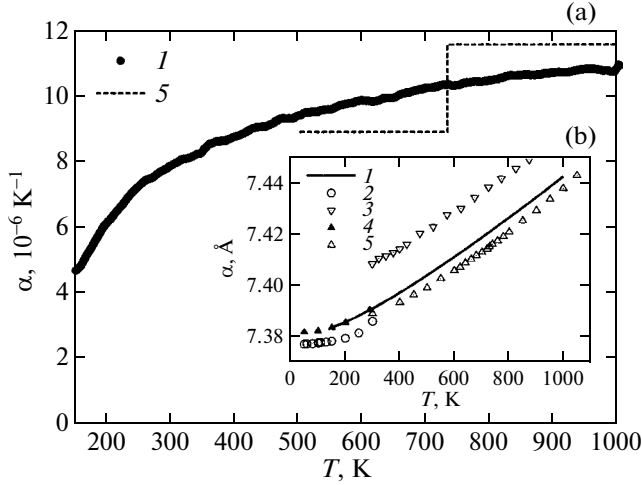
Fig. 2. Temperature dependences of (a) the thermal expansion coefficient and (b) the lattice parameter: (*1*) our data, (*2*) Ramirez et al. [17], (*3*) Moussa et al. [2], (*4*) Bažin et al. [11], and (*5*) Onodera et al. [6].

Fig. 3. Temperature dependence of the thermal expansion coefficient after series of annealings in helium.

sufficiently close to the maximally possible magnetic entropy $3R\ln(2S + 1) = 17.28$ J/mol K for three Cu^{2+} ions with spin $S = 1/2$ in $CaCu_3Ti_4O_{12}$.

The analysis of the low-temperature (0.6–5.0 K) heat capacity allowing for the extremely large number of various contributions, such as the Schottky anomaly, low-lying optical modes with $\Theta_E \approx 50$ K, phonon modes localized at the grain boundaries, etc., was recently fulfilled in [16]. We did not perform such an analysis since it requires the additional experimental information confirming the presence of such effects.

The results of measurements of the heat capacity found by us and in [13, 15] agree well in the temperature range below 300 K (1). At higher temperatures, the data found in [15] lie considerably higher, and the difference increases as the temperature increases. At 1050 K, the difference considerably exceeds the total measurement error in two experiments [15]. Along with other possible causes, this difference can be associated with various thermal prehistories of the studied samples. Before the measurements, the sample [15] was subjected to the heat treatment at 673 K in the argon flow. Levchenko et al. [13] studied the heat capacity for the sample without any preliminary treatment in the oxygen-free medium.

3.2. Thermal Expansion

The thermal expansion of the samples was measured in a helium atmosphere and in air.

Results of investigations of the thermal expansion coefficient $\alpha(T)$ below 1000 K in helium are presented in Fig. 2. The thermal expansion coefficient gradually increases from $\sim 5 \times 10^{-6}$ to $\sim 11 \times 10^{-6}$ K^{-1}. We did not found any noticeable anomalies at high temperatures,
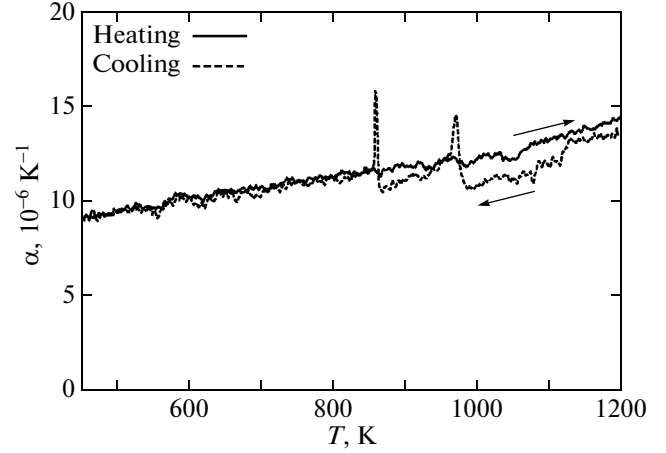
which could be attributed to the diffuse anomaly of $\varepsilon(T)$ at 630 K and the phase transition at 726–732 K, which was assumed on the basis of the anomalous behavior of the heat capacity and lattice parameter [6–9].

Thermal expansion coefficient $\alpha(T)$ computed in [6] from the temperature dependence of the unit cell parameter is shown in Fig. 2 by the dashed line. An essential jump in α at ~730 K is most likely the consequence of description of $a(T)$ data by linear dependences for temperatures above and below 730 K. The inset to Fig. 2 shows the temperature dependence of the lattice parameter calculated from the experimental data on $a(T)$:

$$a(T) = a(T_0)\left(1 + \int_{T_0}^{T}\alpha(x)dx\right), \quad (2)$$

where $a(T_0) = 7.391$ Å is the lattice parameter at $T_0 = 298$ K.

The temperature dependence $\alpha(T)$ in a temperature range of 120–300 K was described by the equation

$$\alpha(T) = KC_L(T) \quad (3)$$

with the use of the relation between the thermal expansion and heat capacity in the context of model (1).

The best result was obtained at $K = 2.06 \times 10^{-8}$ mol/J.

3.3. Influence of Heat Treatment

It was revealed in [18–21] that dielectric properties of CCTO are very sensitive to parameters of heat treatment, namely, temperature and atmosphere (thermal prehistory of the sample). A similar situation was also probably observed in the case of the heat capacity measurements [13, 15].

To investigate the influence of the annealing atmosphere on the thermal expansion of CCTO, the sam-
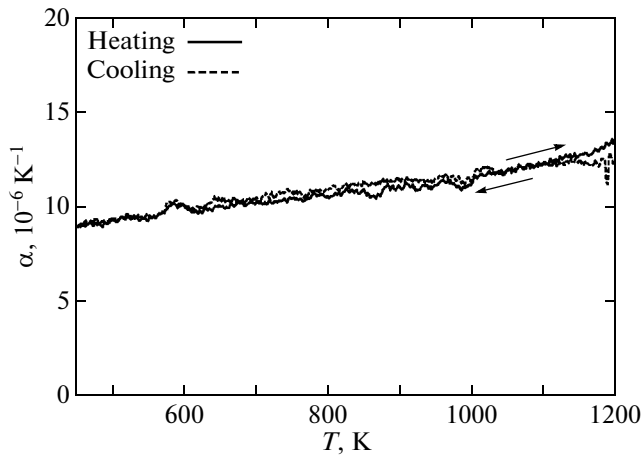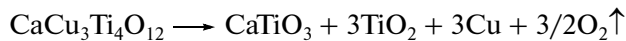
Fig. 4. Temperature dependence of the thermal expansion coefficient after series of annealings in air.

Fig. 5. Temperature dependence of the thermal expansion coefficient after the second series of annealings in helium.

ples were annealed in dilatometer at 773 K for 2 h in the helium and in air.

Annealing in the helium flow leads to a considerable increase in $\alpha(T)$ at $T > 800$ K in the case of measurements in the heating mode and to the anomalous behavior of $\alpha(T)$ at ~850 and ~950 K in the case of measurements in the cooling mode (Fig. 3). Magnitudes of anomalies, temperatures of the peaks, and even their number vary in various measurement series. Observed anomalies of $\alpha(T)$ are accompanied by an abrupt decrease in sample size $\Delta L/L$ in limits of 0.001−0.003%. With the subsequent heat treatment in air, the recovery of the magnitude and temperature dependence of thermal expansion is observed (Fig. 4). With the subsequent annealing in helium, the anomalous behavior of $\alpha(T)$ upon cooling in the region of ~850 K was observed (Fig. 5).

The observed phenomenon can be associated with several processes such as, for example, the decomposition of the compound and the formation of vacancies. The decomposition process in the oxygen-free medium

$$CaCu_3Ti_4O_{12} \longrightarrow CaTiO_3 + 3TiO_2 + 3Cu + 3/2O_2\uparrow$$

leads, as it was shown in [19], to the formation of porous "coral-like" outer layers of the grains. It is also well known that during the heat treatment in the oxygen-free medium such as helium, argon, and nitrogen in oxide perovskites at temperatures above 200°C, the oxygen vacancies are formed:

$$O_O \text{ (normal state of oxygen)}$$

$$\longrightarrow V_O^{2+} \text{ (oxygen vacancy)} + e^- + 1/2O_2.$$
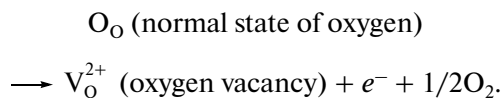
In addition to these reactions, the Cu(II) ion becomes unstable upon heating and transforms into Cu(I). This phenomenon in oxides can occur at ~440°C [22]. Oxygen vacancies forming at grain boundaries and decomposition of the compound can lead to an increase α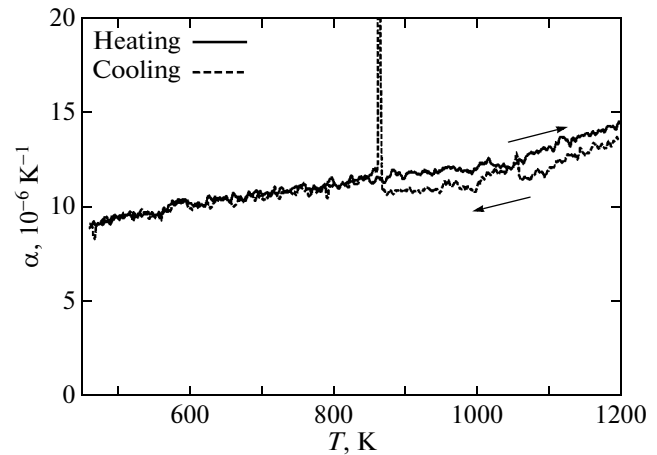 at high temperatures. On the other hand, these reactions are reversible during annealing in the oxygen atmosphere, which leads to the recovery of the magnitude and temperature behavior of thermal expansion.

Thus, we can assume that the found anomalies of the thermal expansion are associated with the variation in the stoichiometry of the surface layer of the grains and with mechanical variations in the system of grains in the ceramic samples rather than with the structural variations and phase transitions.

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Translated by N. Korovin