



# High-temperature heat capacity and heat content of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO)

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## ABSTRACT

The isobaric heat capacity of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) was measured from 300 to 1100 K using differential scanning calorimetry (DSC). The results were verified using drop calorimetric measurement of enthalpy increment ( $H_T - H_{298.15}$ ) at  $T = 973$  and 1073 K. The samples were dropped from room temperature into a calorimeter maintained at high temperature. The results show small negative deviation from Neumann–Kopp rule. The enthalpy and entropy increments are computed as a function of temperature and compared with values available in the literature. The results obtained in this study are consistent with available information on enthalpy and Gibbs energy of formation of CCTO.

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## 1. Introduction

Materials having high dielectric constant find important applications in microelectronic devices such as dynamic random access memory (DRAM) devices based on capacitive elements. Generally, materials with high dielectric constant are either ferroelectrics or relaxor ferroelectrics such as  $\text{BaTiO}_3$ ,  $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ , and  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ . The dielectric constant of these materials depends strongly on both temperature and frequency. From the application point of view such dependency is undesirable. Further, ceramic capacitors free from Ba and Pb are required to meet environmental concerns.

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) is a recently discovered centrosymmetric perovskite-like compound with high dielectric constant (typically  $10^4$ ) over a broad range of temperatures extending from 100 to 600 K and frequencies up to 10 kHz [1–4]. Besides high dielectric constant Zhao et al. [1] have found low dielectric loss in *c*-axis oriented CCTO thin films. Polycrystalline CCTO is an excellent candidate as a sensor material with high sensitivity because of its very non-linear *I*–*V* characteristics that are susceptible to interactions with reactive gases [5]. Many investigations have been carried out to explain the large dielectric constant of CCTO. Some workers have suggested that the origin of high dielectric constant of CCTO is intrinsic [3,4,6], while others support extrinsic causes such as defects and inhomogeneities [7,8]. Recently Hutagalung

et al. [9] showed that Zn-dopant reduced the dielectric loss of CCTO.

Thermodynamic stability of CCTO has been explored recently [10,11]. Levchenko et al. [10] measured heat capacity in the temperature range from 2 to 1100 K and formation enthalpy of CCTO using calorimetric methods. The standard molar enthalpy of formation from constituent binary oxides at 298.15 K is  $-122.1 (\pm 4.5) \text{ kJ mol}^{-1}$  [10]. The third-law entropy at 298.15 K was evaluated as  $368.4 (\pm 0.1) \text{ J mol}^{-1} \text{ K}^{-1}$  [10]. The uncertainty is underestimated and a more realistic assessment of uncertainty in entropy is  $(\pm 0.6) \text{ J mol}^{-1} \text{ K}^{-1}$ . Jacob et al. [11] determined the standard Gibbs energy of formation of CCTO from its component binary oxides, CaO, CuO and  $\text{TiO}_2$  in the temperature range from 925 to 1350 K using a solid-state electrochemical cell with yttria-stabilized zirconia as the solid electrolyte:

$$\Delta G_{f,\text{ox}}^{\circ}(\text{CaCu}_3\text{Ti}_4\text{O}_{12})/\text{J mol}^{-1}(\pm 600) = -125,231 + 6.57(T/\text{K}) \quad (1)$$

It is interesting to note that “second-law” enthalpy of formation evaluated from this expression at a mean temperature of 1138 K ( $-125.23 \pm 2.5 \text{ kJ mol}^{-1}$ ) appears to be in reasonable accord with the solution calorimetric value of  $-122.1 (\pm 4.5) \text{ kJ mol}^{-1}$  at 298.15 K [10], ignoring the effect of temperature at this juncture.

## 2. Experimental

### 2.1. CCTO powder preparation

Used for the preparation of CCTO powder were commercial-grade  $\text{CaCO}_3$  (Aldrich, 99%),  $\text{TiO}_2$  (Aldrich, 99%) and CuO (Aldrich, 99%). The materials were weighed accurately using a Sartorius single pan balance and mixed in the stoichio-

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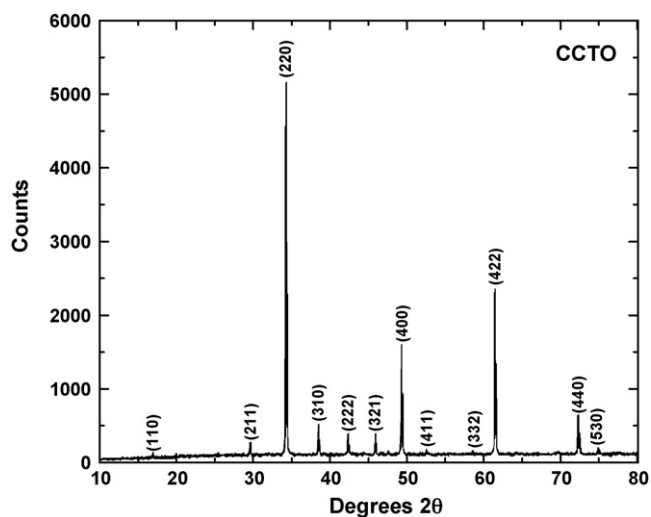
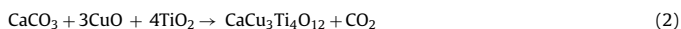


Fig. 1. Indexed XRD pattern of single phase CCTO powder.

metric molar ratio 1(CaCO<sub>3</sub>):3(CuO):4(TiO<sub>2</sub>). Powders were ball-milled in a sealed plastic bottle container with zirconium oxide beads having a diameter  $\leq 0.005$  m in ambient air under acetone. The resulting homogeneous powder was calcined at 1053 K for 7.2 ks and 1273 K for 21.6 ks in static air. CCTO was formed during calcinations according to the reaction:



The final product (CCTO) was ground into a fine powder. The formation of single phase CCTO powder was confirmed by the XRD pattern shown in Fig. 1. Philips APD 1700 powder diffractometer at ambient temperature and pressure and Cu K $\alpha$  radiation were used for XRD. SEM showed that the particle size was in the range from 20 to 30 nm (Fig. 2). Since particles in this range would be associated with significant surface enthalpy, they were compacted and heat treated to increase particle size.

## 2.2. Pellet preparation

The finely powdered CCTO sample was first compacted into discs by uniaxial die pressing at approximately 14 MPa pressure, and then pressed at 250 MPa pressure in a cold isostatic press for further compaction. The specimens were subsequently sintered at 1273 K for 14.4 ks, and annealed at 1073 K for another 14.4 ks in air during the cooling cycle. SEM image of the fractured surface of sintered CCTO pellet at a magnification of 10,000 $\times$ , shown in Fig. 3, revealed that the average grain size was 2.4  $\mu\text{m}$ . The sintered sample was used for calorimetry.

## 2.3. Calorimetric study of CCTO

A differential scanning calorimeter (DSC) was used to measure the heat capacity of CCTO in air from 300 to 1100 K. The DSC was operated in the step heating mode to increase accuracy with  $\alpha\text{-Al}_2\text{O}_3$  as the reference material. The alumina powder

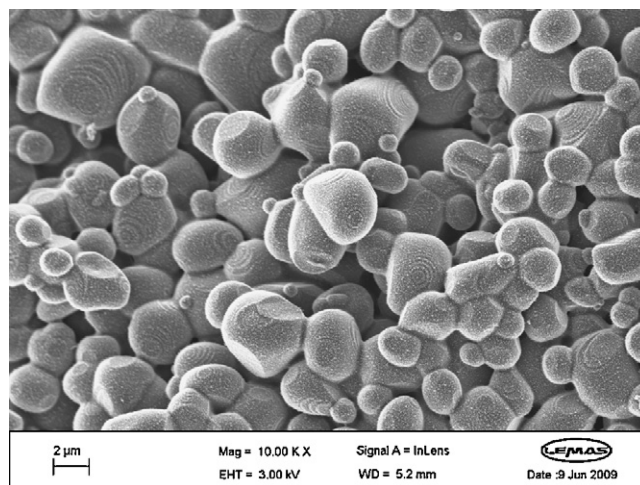


Fig. 3. SEM image of the fractured surface of sintered CCTO pellet.

was dehydrated by heat treatment at 1200 K and CCTO at 673 K in flowing high purity argon gas before use. The difference in the heat flux into the sample and the reference material was integrated during heating at a constant rate (0.0333 K s<sup>-1</sup>) over small temperature steps (25 K) with isothermal dwell time of 0.9 ks. The DSC measurements were conducted in dry air. Analysis of CCTO by XRD after the DSC experiment indicated no detectable change in its structure or lattice parameter.

A Setaram HT 1500 Calvet micro-calorimeter was used to determine the enthalpy increment of CCTO between 1073 K and room temperature (298.15 K). This instrument has been described elsewhere [12]. The measurement involved dropping a sample of known mass from room temperature into the calorimeter maintained at 1073 K. The heat required to raise the temperature of the sample from room temperature to that of the calorimeter was measured by the calorimetric detector, which determines heat flow between the reaction crucible (into which the sample is dropped) and a reference crucible. The heat flow was monitored as an emf of the thermopile in mV, which was recorded as a function of time on a computer using a Picolog analogue/digital converter. The integral of this curve with respect to time gave the heat change. By using an appropriate calibration, this area was converted to joules. The calibrant used was  $\alpha$ -alumina.

CCTO and  $\alpha$ -alumina pellets were broken into small pieces approximately 0.002 m in diameter and weighed accurately for the measurement. The masses of CCTO and  $\alpha\text{-Al}_2\text{O}_3$  samples used for the drop calorimetry experiment were 0.0214 and 0.0309 g, respectively. In order to determine the enthalpy increment ( $H_{1073} - H_{298.15}$ ) of CCTO,  $\alpha\text{-Al}_2\text{O}_3$  was first dropped into the reaction crucible as the reference sample. This was followed by the three CCTO specimens that were dropped sequentially, the heat effects being recorded for each sample separately. Finally, a second  $\alpha\text{-Al}_2\text{O}_3$  was dropped in order to check that the calibration had not changed during the experiment.

## 3. Results and discussion

### 3.1. Heat capacity measurement

The variation of isobaric heat capacity ( $C_p^0$ ) of CCTO as a function of temperature is displayed in Fig. 4. The uncertainty in the measured heat capacity is estimated as  $\pm 1.2\%$ . The heat capacity increases continuously with temperature, indicating the absence of phase transitions with significant heat effect in the temperature range from 300 to 1100 K. The value of  $C_p^0$  reaches Dulong–Petit limit for  $C_p^0$  at 767 K. The measured heat capacity can be represented by the empirical equation:

$$C_p^0/\text{J mol}^{-1} \text{K}^{-1} = 697.23 - 0.02109T - \left( \frac{1,642,275.8}{T^2} \right) - \left( \frac{4968.708}{T^{0.5}} \right) \quad (3)$$

Levchenko et al. [10] studied the heat capacity of CCTO from 2 to 1100 K using low-temperature adiabatic relaxation and differential scanning calorimetry. They expressed their results using the

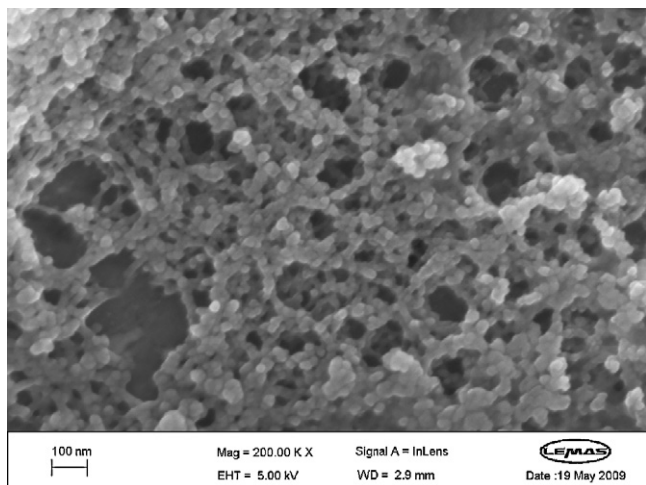


Fig. 2. SEM image of the as-prepared CCTO powder.

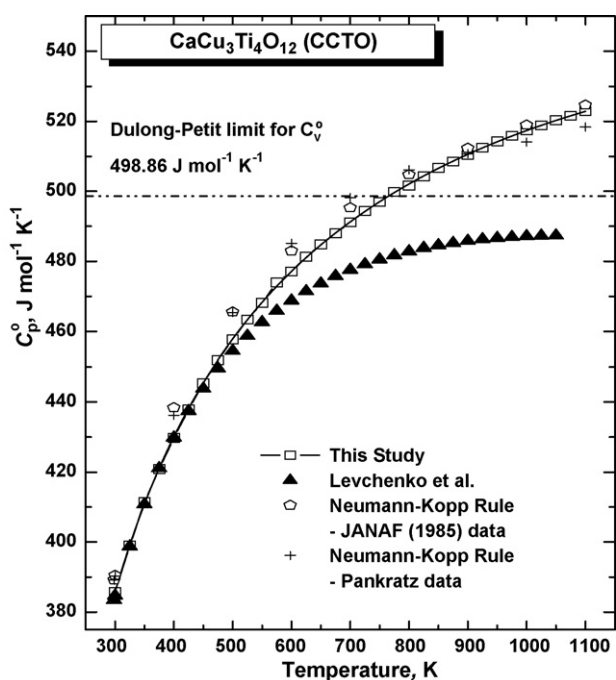


Fig. 4. Heat capacity of CCTO as a function of temperature.

expression:

$$C_p^{\circ} / \text{J mol}^{-1} \text{K}^{-1} = 3R \left[ mD \left( \frac{\theta_D}{T} \right) + nE \left( \frac{\theta_E}{T} \right) \right] + AT + BT^2 \quad (4)$$

The best fit to their data in the temperature range from 60 to 1050 K was obtained with  $m=10.4$ ,  $n=9.44$ , Debye temperature  $\theta_D=408.0$  K, Einstein temperature  $\theta_E=763.2$  K,  $A=0.030$  J mol<sup>-1</sup> K<sup>-2</sup> and  $B=-2.44 \times 10^{-5}$  J mol<sup>-1</sup> K<sup>-3</sup>. Values of the Debye specific-heat function  $D(\theta_D/T)$  and Einstein specific-heat function  $E(\theta_E/T)$  were taken from reference tables [13]. The sum ( $m+n$ ) should be approximately equal to the number of atoms in the formula unit. The results obtained by Levchenko et al. [10] are compared in Fig. 4 with the results obtained in this study. The results from the two studies are in good agreement up to 450 K. At higher temperatures the results obtained in this study are significantly higher; the divergence increases with temperature. At 1050 K the difference is well beyond the combined uncertainty of the two measurements. The value of  $C_p^{\circ}$  suggested by Levchenko et al. [10] asymptotically reaches a value slightly lower than the Dulong and Petit limit ( $3nR$ ) for  $C_V^{\circ}$  at temperatures close to 1100 K. The convergence of heat capacities from the two sets of measurements at low temperatures suggests that the standard entropy of CCTO at 298.15 K evaluated from low-temperature heat capacity [10] is probably in order.

Heat capacities calculated using the Neumann–Kopp rule are also shown in Fig. 4 for comparison. The heat capacities of the constituent binary oxides CaO, CuO and TiO<sub>2</sub> from two different thermodynamic compilations [14,15] are used to compute heat capacity of CCTO. The source of data does not significantly affect the calculated result. Heat capacities obtained in this study show only mild deviation from the Neumann–Kopp rule, whereas the results of Levchenko et al. [10] show large negative deviation. High-temperature heat capacities of other titanates follow the Neumann–Kopp rule to a first approximation. For example, heat capacity of CaTiO<sub>3</sub> agrees with Neumann–Kopp rule up to 800 K and shows mild positive deviation at higher temperatures until the onset phase transition [16]. In view of the disagreement in measured heat capacities of CCTO at high temperatures, drop

calorimetric measurements of enthalpy increment ( $H_T - H_{298.15}$ ) were conducted at 973 and 1073 K.

### 3.2. Heat content measurement

The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> drop measurement represents the enthalpy increment from room temperature to the calorimeter temperature (1073 K), i.e.  $H_{1073} - H_{298.15}$ . It is actually equal to the integral of the  $C_p^{\circ}$  as a function of temperature for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> between the two temperatures. The value was calculated using data from SGTE [17] as 87.150 kJ mol<sup>-1</sup>. Enthalpy data for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in other thermodynamic compilations [14,15] are very close to that in SGTE. Fig. 5 shows the thermograms produced by the alumina calibration sample superimposed on that for CCTO. The area under the curve is proportional to the heat effect caused by the drop. The average value of ( $H_{1073} - H_{298.15}$ ) for CCTO was 383.766 ( $\pm 9.04$ ) kJ mol<sup>-1</sup>. Similar measurements at 973 K gave ( $H_{973} - H_{298.15}$ ) = 325.59 kJ mol<sup>-1</sup>.

The enthalpy increments ( $H_T - H_{298.15}$ ) determined in this study are compared in Fig. 6 with values calculated from heat capacity data measured in this study and those reported by Levchenko et al. [10]. The measured enthalpy increments are slightly higher than that obtained by integrating the heat capacity equation (Eq. (3)) between 298.15 and  $T$  K. The heat capacity measurements of Levchenko et al. [10] give enthalpy increments that are lower than those obtained from heat capacity data measured in this study. The comparison suggests that the heat capacity data obtained in this study is the best compromise among the three sets of data. The measured enthalpy increments essentially serve as confirmation of heat capacity data, counterbalancing the input from Levchenko et al. [10].

### 3.3. Derived thermodynamic parameters

The thermodynamic parameters  $H_T - H_{298.15}$  and  $S_T - S_{298.15}$  were derived from  $C_p^{\circ}$  measured in this study (Eq. (3)). Compared in Table 1 are the numerical values of  $H_T - H_{298.15}$  and  $S_T - S_{298.15}$  at regular intervals of temperatures obtained in this study with those given by Levchenko et al. [10]. The two sets of data agree well up to 450 K and diverge gradually with increasing temperature. The “second-law” entropy of formation of CCTO derived from the temperature dependence of Gibbs energy of formation offers test of the correct value of  $S_T - S_{298.15}$ . Combining the value of  $S_{298.15}^{\circ} = 368.4$  ( $\pm 0.6$ ) J mol<sup>-1</sup> K<sup>-1</sup> [10] with  $S_{1100} - S_{298.15}$  evaluated in this study and auxiliary data for the binary oxides from JANAF tables [14] gives the entropy of formation of CCTO from component binary oxides at 1100 K as  $-5.58$  ( $\pm 2.6$ ) J mol<sup>-1</sup> K<sup>-1</sup>, which compares well with the “second-law” value of  $-6.57$  ( $\pm 2.3$ ) J mol<sup>-1</sup> K<sup>-1</sup>

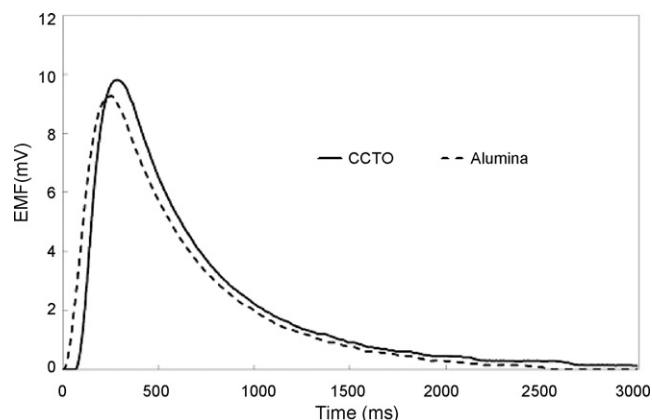
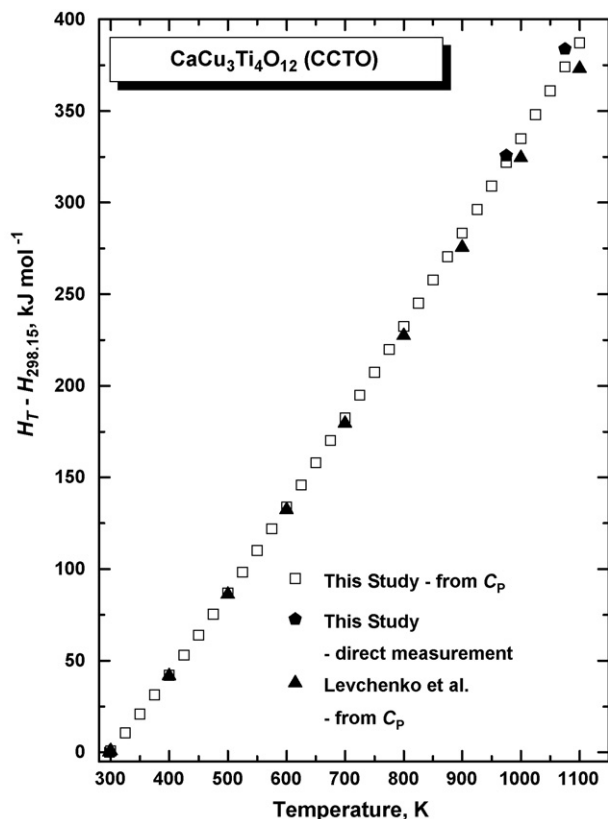


Fig. 5. Thermograms of  $\alpha$ -alumina (calibrant) and CCTO from drop calorimetry.

**Table 1**  
Comparison of entropy and enthalpy increments of CCTO from 298.15 to 1100 K based on the two sets of calorimetric measurements.

Temperature (K)	Levchenko et al. [10]			This study	
	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$S_T - S_{298.15}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$H_T - H_{298.15}$ (kJ mol <sup>-1</sup> )	$S_T - S_{298.15}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$H_T - H_{298.15}$ (kJ mol <sup>-1</sup> )
298.15	368.4	0	0	0	0
300	370.77	2.37	0.71	2.38	0.72
400	488.14	119.74	41.62	120	42.03
500	587.18	218.78	86.09	219.17	86.81
600	671.46	303.06	132.39	304.45	133.87
700	744.25	375.85	179.49	379.12	182.56
800	808.03	439.63	227.29	445.46	232.48
900	864.91	496.51	275.59	505.12	283.34
1000	916.17	547.77	324.39	559.28	334.94
1100	963.41	595.01	373.19	608.85	387.15



**Fig. 6.** Enthalpy increment of CCTO as a function of temperature.

[11]. If  $S_{1100} - S_{298.15}$  values of Levchenko et al. [10] are used for the same calculation, the entropy of formation of CCTO at 1100 K is  $-19.43 (\pm 2.6) \text{ J mol}^{-1} \text{ K}^{-1}$ . The comparison clearly favors the high-temperature heat capacity determined in this study. Similarly, the values of enthalpy of formation at 298.15 K from solution calorimetry and “second-law” enthalpy of formation at 1138 K from electrochemical measurements also align better using the high-temperature heat capacity obtained in this study. The calorimetric enthalpy of formation of CCTO at 298.15 K from component binary oxides ( $-122.1 (\pm 4.5) \text{ kJ mol}^{-1}$ ) [10] converts to  $-123.73 (\pm 4.8) \text{ kJ mol}^{-1}$  at 1100 K using the high-temperature heat capacity data obtained in this study along with auxiliary data for binary oxides from JANAF tables [14]. If the high-temperature heat capacity data for CCTO from Levchenko et al. [10] are used, the enthalpy of formation at 1100 K becomes  $-137.69 (\pm 4.8) \text{ kJ mol}^{-1}$ . The measured “second-law” enthalpy of formation is  $-125.23 (\pm 2.5) \text{ kJ mol}^{-1}$  at 1138 K [11].

#### 4. Conclusions

The heat capacity of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) as a function of temperature was measured in the temperature range from 300 to 1100 K using DSC. The measured values at the elevated temperatures are significantly higher than those reported by Levchenko et al. [10]. The heat capacity measured in this study showed mild negative deviation from Neumann–Kopp rule. The results were crosschecked by measuring enthalpy increments  $H_T - H_{298.15}$  at  $T = 973$  and  $1073$  K. The new heat capacity data obtained in this study connect well the calorimetric entropy and enthalpy of formation at 298.15 K with the “second-law” enthalpy and entropy of formation of CCTO obtained at a mean temperature of 1138 K from solid-state electrochemical measurements.

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