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# Heat capacity of mixed oxides in the $Bi_2O_3$–CaO system

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## Abstract

The low-temperature heat capacities of mixed oxides in the Bi–Ca–O system have been determined by the relaxation method at temperatures from 15 to about 225 K. The high-temperature heat capacities have been measured from 340 to about 1030 K using differential scanning calorimetry (DSC) in a stepwise mode. From the results, standard molar entropies and molar heat capacities at 298.15 K as well as their temperature dependencies were evaluated. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Calcium bismuth oxide; Heat capacity; Entropy; DSC; Relaxation time calorimetry

## 1. Introduction

The discovery of superconducting cuprates containing bismuth, calcium and strontium has led to an enhanced understanding of the synthesis and phase equilibria of compounds in the Bi–Sr–Ca–Cu–O system and the constituent binary and ternary subsystems. Conflant et al. [1] have identified four stable compounds of fixed composition ($Bi_{10}Ca_7O_{22}$, $Bi_2CaO_4$, $Bi_6Ca_7O_{16}$ and $Bi_{14}Ca_5O_{26}$) and three solid solutions ($\gamma$, $\delta$, $\beta_1/\beta_2$) by high temperature XRD and DTA measurements. All four compounds melt incongruently. Roth et al. [2] and Burton et al. [3] have investigated and revised the phase diagram of $Bi_2O_3$–CaO by using high temperature XRD on quenched samples. The stoichiometry of the phases $Bi_{10}Ca_7O_{22}$ and $Bi_6Ca_7O_{16}$ was corrected to $Bi_6Ca_4O_{13}$ and $Bi_2Ca_2O_5$, respectively. Vstavskaya et al. [4] have reported only three stable stoichiometric compounds ($Bi_6Ca_7O_{16}$, $Bi_2CaO_4$ and $Bi_{10}Ca_7O_{22}$). In contrast to previous studies $Bi_{14}Ca_5O_{26}$ does not appear in their phase diagram. Tsang et al. [5] have studied the $Bi_2O_3$–CaO–CuO system and have found $Bi_{14}Ca_5O_{26}$, $Bi_6Ca_4O_{13}$ and $Bi_2Ca_2O_5$ to be stable at temperature of 1023 K while only $Bi_2Ca_2O_5$ was stable at 1173 K. Isothermal section of the phase diagram of the Bi–Ca–O system at 1000 K has been studied by Jacob and Jayadevan [6]. Four ternary oxides ($Bi_{14}Ca_5O_{26}$, $Bi_2CaO_4$, $Bi_6Ca_4O_{13}$ and $Bi_2Ca_2O_5$) have been identified. In a recently published paper [7], Gökcen et al. have examined phase-equilibria relations in the $Bi_2O_3$–CaO system over the temperature range of 923–1323 K in an oxygen atmosphere at a pressure of 1 bar. Three solid solutions and four different stoichiometric phases ($Bi_2Ca_2O_5$, $Bi_2CaO_4$, $Bi_6Ca_4O_{13}$ and $Bi_{14}Ca_5O_{26}$) have been found to be stable.

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Thermodynamic properties of mixed oxides $Bi_{14}Ca_5O_{26}$, $Bi_2CaO_4$, $Bi_6Ca_4O_{13}$ and $Bi_2Ca_2O_5$ have been assessed by Hallstedt et al. [8] in the frame of the thermodynamic evaluation of the Bi–Ca–O system. Based on the solution calorimetry measurements carried out by Idemoto et al. [9] and thermogravimetric data from Shimpo and Nakamura [10] as well as the phase-diagram data from [1–3], the values of enthalpy ($\Delta H_{ox}$) and entropy ($\Delta S_{ox}$) of formation of mixed oxides from $Bi_2O_3$ and CaO have been optimized. The approximated values $\Delta S_{ox}$ of 20 and $10\ J\ K^{-1}\ mol^{-1}$ are published for $Bi_{14}Ca_5O_{26}$ and $Bi_6Ca_4O_{13}$, respectively, while zero for $Bi_2CaO_4$ and $Bi_2Ca_2O_5$ [8]. Jacob and Jayadevan [6] have measured the chemical potentials of $Bi_2O_3$ and CaO in phase fields involving the stoichiometric compounds by combined use of oxide and fluoride electrolytes. The temperature dependence of the standard Gibbs free energy of formation for all above-mentioned stoichiometric phases has been derived. The respective values of $\Delta S_{ox}$ resulting from these measurements: $-12.76$, $-2.31$, $-7.04$ and $-5.79\ J\ K^{-1}\ mol^{-1}$ for $Bi_{14}Ca_5O_{26}$, $Bi_2CaO_4$, $Bi_6Ca_4O_{13}$ and $Bi_2Ca_2O_5$ are different from those assessed by Hallstedt et al. [8].

As a part of systematic studies on phase equilibria and thermodynamic properties of the quaternary system Bi–Sr–Ca–Cu–O [11–14], measurements of heat capacities of mixed oxides in the ternary system Bi–Ca–O have been carried out and are presented in this paper.

## 2. Experimental

The $Bi_2Ca_2O_5$, $Bi_2CaO_4$, $Bi_6Ca_4O_{13}$ and $Bi_{14}Ca_5O_{26}$ oxides were prepared from of $Bi_2O_3$ (Aldrich, 99.99%) and $CaCO_3$ (Aldrich, purity >99.9%) in a tube furnace. Stoichiometric amounts of the constituent chemicals were weighed on an analytical balance with an accuracy 0.1 mg, mixed together in an agate mortar and pestled. The weighted specimens were calcined two times at various temperatures from 873 to 1093 K in air or oxygen atmosphere, with powdering and homogenizing before each heat treatment. The duration of each heat treatment was generally between 20 and 60 h (see Table 1). For the final step of each preparation the specimens were pressed into pellets.

The composition of prepared samples was checked by powder-XRD analysis. The diffraction patterns showed the samples consisted of single phase without any observable diffraction lines from other phases.

The atomic absorption spectroscopy was used in order to find the actual ratio of Bi and Ca in prepared samples. The values of 2.84, 1.97, 1.44 and 0.98 for $Bi_{14}Ca_5O_{26}$, $Bi_2CaO_4$, $Bi_6Ca_4O_{13}$ and $Bi_2Ca_2O_5$ show slight deviations from ideal stoichiometry (2.8, 2.0, 1.5 and 1.0).

The low-temperature heat capacity was measured in the range between 15 and 215 K by the relaxation method. A plate-shaped sample was attached to platinum resistance heater, which was connected by two tungsten wires to a heat sink equilibrated at desired temperature. When the sample is heated, a temperature difference $\Delta T$ occurs between the sample and the heat sink, which is stabilized at certain temperature value. The following thermal stabilization rate gives the characteristic value of relaxation time $\tau$. Then the heat capacity of the sample can be expressed as $C = P\tau/\Delta T$, where $P$ is the heating power. The obtained value must have been further corrected to an addenda dependent of the particular sample holder.

Table 1
Samples preparation

| Oxide | First calcination | | | Second calcination | | | Final step | | |
|---|---|---|---|---|---|---|---|---|---|
| | $T$ (K) | Duration (h) | Atmosphere | $T$ (K) | Duration (h) | Atmosphere | $T$ (K) | Duration (h) | Atmosphere |
| $Bi_2CaO_4$ | 973 | 53 | Air | 1023 | 90 | Air | 1043 | 20 | Air |
| $Bi_2Ca_2O_5$ | 1023 | 48 | Air | 1053 | 30 | Air | 1093 | 48 | Air |
| $Bi_6Ca_4O_{13}$ | 973 | 48 | Air | 1033 | 24 | Air | 1093 | 50 | Air |
| $Bi_{14}Ca_5O_{26}$ | 873 | 48 | Air | 93 | 24 | Oxygen | 983 | 60 | Oxygen |

The high-temperature heat capacities have been measured from 340 to about 1030 K on the multi-detector high temperature calorimeter SETARAM equipped with the heat flux DSC detector. The DSC method with reference in a stepwise mode with heating rate 1 K $\mathrm{min}^{-1}$, temperature step 20 K and isothermal delay 5500 s was employed. The calibration of the apparatus was performed by measuring the heat capacity of a synthetic sapphire, NIST standard reference material no. 720. The samples were preheated before each measurement. All measurements were carried out in air closed atmosphere.

## 3. Results and discussion

The obtained temperature dependencies of $C_{pm}$ are shown in Figs. 1–4. The high- and low-temperature data series of each stoichiometric compound (except the phase $Bi_{14}Ca_5O_{26}$) join smoothly and show no transitions in the measured temperature range. As the two subsequent runs have been performed with the same sample the observed discrepancies should be ascribed to lower reproducibility of the DSC measurements above 400 K. Since for $Bi_{14}Ca_5O_{26}$ phase the required reproducibility of low-temperature measurements was not achieved only the high-temperature values of heat capacity are presented in this case.

The low- and high-temperature heat capacities were correlated simultaneously by the least square method applying boundary conditions. The entire temperature interval of measured data was divided into four subintervals. The experimental data in the range of 0–$T_1$ were fitted to the function (1), while those between the temperature $T_1$ and $T_2$ are approximated by the Eq. (2), etc.

$$C_{pm,1} = A_1 + B_1T^3, \quad T \in \langle 0, T_1 \rangle \tag{1}$$

$$C_{pm,2} = A_2 + B_2T + C_2T^2 + D_2T^{-2}, \quad T \in \langle T_1, T_2 \rangle \tag{2}$$

$$C_{pm,3} = A_3 + B_3T + C_3T^2 + D_3T^{-2}, \quad T \in \langle T_2, T_3 \rangle \tag{3}$$

$$C_{pm,4} = A_4 + B_4T + C_4T^{-2}, \quad T \in \langle T_3, T_4 \rangle \tag{4}$$

At boundary temperatures $T_1$, $T_2$ and $T_3$ the equality of corresponding function values and the equality of corresponding first partial derivatives with respect to temperature are required. These requirements are included into subsequent boundary conditions (5) and (6):

$$C_{pm,i}(T_i) = C_{pm,j}(T_i), \quad i = 1,2,3; \quad j = 2,3,4 \tag{5}$$

$$\left(\frac{\partial C_{pm,i}}{\partial T}\right)_{T=T_i} = \left(\frac{\partial C_{pm,j}}{\partial T}\right)_{T=T_i}, \quad i = 1,2,3; \quad j = 2,3,4 \tag{6}$$

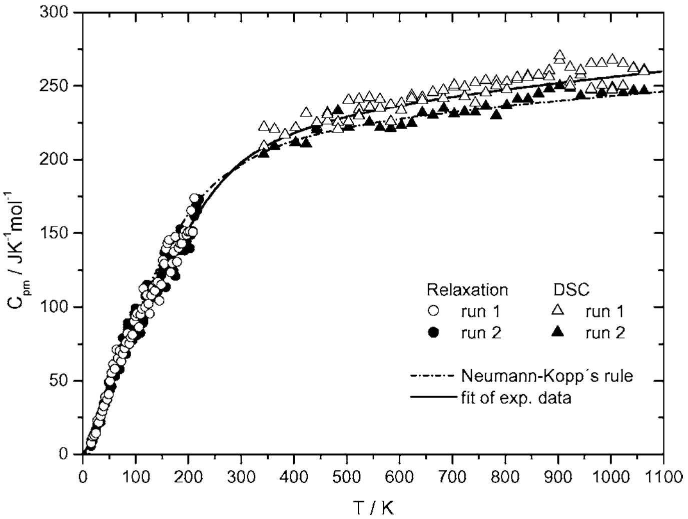

Fig. 1. Molar heat capacity of $Bi_2Ca_2O_5$ as a function of temperature.

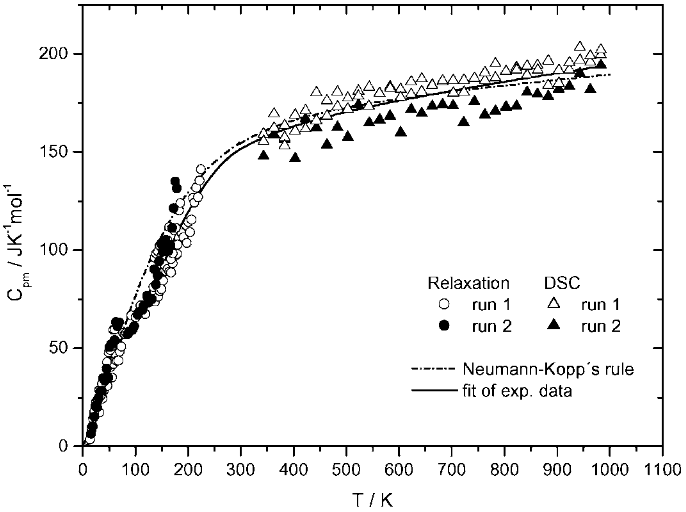

Fig. 2. Molar heat capacity of $Bi_2CaO_4$ as a function of temperature.

In order to acquire a set of unknown statistical parameters it is necessary to find a minimum of function $F$:

$$\begin{aligned}
&F(A_1, B_1, \ldots, C_4, \lambda_1, \ldots, \lambda_6) \\
&\quad = \sum_{i=1}^{N_1} [C_{p\mathrm{m},i} - A_1 T_i - B_1 T_i^3]^2 \\
&\quad + \sum_{j=1}^{N_2} \left[ C_{p\mathrm{m},j} - A_2 - B_2 T_j - C_2 T_j^2 - \frac{D_2}{T_j^2} \right]^2 \\
&\quad + \sum_{k=1}^{N_3} \left[ C_{p\mathrm{m},k} - A_3 - B_3 T_k - C_3 T_k^2 - \frac{D_3}{T_k^2} \right]^2 \\
&\quad + \sum_{l=1}^{N_4} \left[ C_{p\mathrm{m},l} - A_4 - B_4 T_l - \frac{C_4}{T_l^2} \right]^2 \\
&\quad + \lambda_1 [C_{p\mathrm{m},1}(T_1) - C_{p\mathrm{m},2}(T_1)] \\
&\quad + \lambda_2 \left[ \left( \frac{\partial C_{p\mathrm{m},1}}{\partial T} \right)_{T=T_1} - \left( \frac{\partial C_{p\mathrm{m},2}}{\partial T} \right)_{T=T_1} \right] \\
&\quad + \lambda_3 [C_{p\mathrm{m},2}(T_2) - C_{p\mathrm{m},3}(T_2)] \\
&\quad + \lambda_4 \left[ \left( \frac{\partial C_{p\mathrm{m},2}}{\partial T} \right)_{T=T_2} - \left( \frac{\partial C_{p\mathrm{m},3}}{\partial T} \right)_{T=T_2} \right] \\
&\quad + \lambda_5 [C_{p\mathrm{m},3}(T_3) - C_{p\mathrm{m},4}(T_3)] \\
&\quad + \lambda_6 \left[ \left( \frac{\partial C_{p\mathrm{m},3}}{\partial T} \right)_{T=T_3} - \left( \frac{\partial C_{p\mathrm{m},4}}{\partial T} \right)_{T=T_3} \right] \qquad (7)
\end{aligned}$$

Differentiation of the function $F$ with respect to its variables gives the system of normal equations. By solving it the required set of parameters is obtained. Statistical processing of measured data is accompanied by evaluation of covariance matrix and prediction bands. These values are presented in Table 2.

The optimized low- and high-temperature experimental data have been compared with those estimated by the Neumann–Kopp's additive rule. The significant deviations between the fitted curves and the Neumann–Kopp approximations in the temperature range of 80–200 K might be indicative of the coexistence of heavy (and highly polarizable) Bi-atoms and relatively light Ca and O atoms within one structure, giving strongly different Debye temperatures for the respective lattice vibration modes. The differences at 298.15 K are reaching the values 0.24, 2.12 and 0.40% for $Bi_2Ca_2O_5$, $Bi_2CaO_4$ and $Bi_6Ca_4O_{13}$, respectively. The described statistical procedure was used for $Bi_2Ca_2O_5$, $Bi_2CaO_4$ and $Bi_6Ca_4O_{13}$. The experimental data of $Bi_{14}Ca_5O_{26}$ were fitted to the function (4) applying $C_{pm}$ (298.15) as a boundary condition. This value was assessed by the Neumann–Kopp's additive rule since a good agreement between the measured and estimated values was found in case of the other phases.

The standard molar entropy at 298.15 K is calculated by the stepwise integration as expressed in

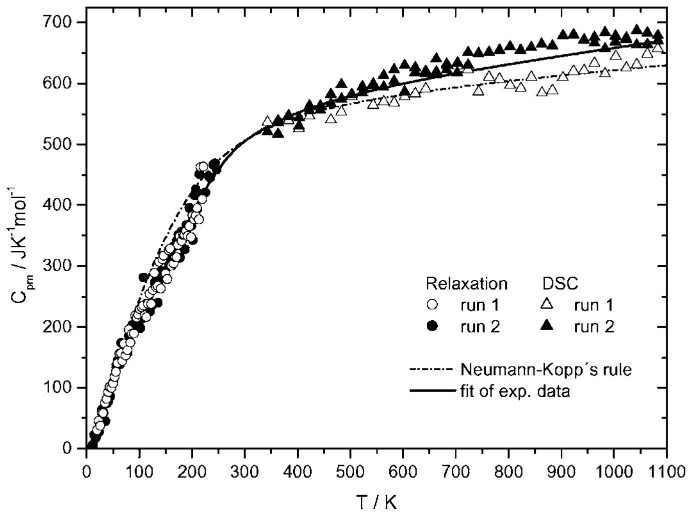

Fig. 3. Molar heat capacity of $Bi_6Ca_4O_{13}$ as a function of temperature.

Eq. (8):

$$S_m(298.15) = \int_0^{T_1} \frac{C_{pm,1}}{T}\,dT + \int_{T_1}^{T_2} \frac{C_{pm,2}}{T}\,dT + \int_{T_2}^{298.15} \frac{C_{pm,3}}{T}\,dT \tag{8}$$

This value is used for the determination of the temperature dependence (9):

$$S_m(T) = S_m(298.15) + \int_{298.15}^{T} \frac{C_{pm,4}}{T}\,dT \tag{9}$$

The standard molar entropies of formation of $Bi_2CaO_4$, $Bi_2Ca_2O_5$ and $Bi_6Ca_4O_{13}$ from the constituent binary oxides are calculated from the molar

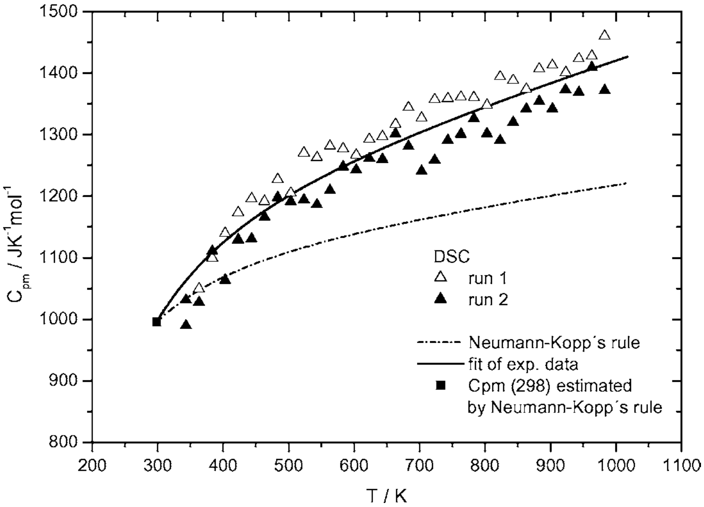

Fig. 4. Molar heat capacity of $Bi_{14}Ca_5O_{26}$ as a function of temperature.

Table 2
Evaluated parameters for the polynomial representation of the molar heat capacities

| Oxide | $Bi_2Ca_2O_5$ | | $Bi_2CaO_4$ | | $Bi_6Ca_4O_{13}$ | | $Bi_{14}Ca_5O_{26}$ | |
|---|---|---|---|---|---|---|---|---|
| | Parameter | Error | Parameter | Error | Parameter | Error | Parameter | Error |
| $C_{pm,1} = A_1T + B_1T^3$ | | | | | | | | |
| Temperature range (K) | 0–40 | 0–40 | 0–40 | 0–40 | 0–40 | 0–40 | – | – |
| $A_1$ | 0.5128 | 0.179 | 0.5688 | 0.201 | 1.3319 | 0.574 | – | – |
| $B_1 \times 10^3$ | 0.1985 | 0.102 | 0.1635 | 0.121 | 0.3997 | 0.337 | – | – |
| $C_{pm,2} = A_2 + B_2T + C_2T^2 + D_2/T^2$ | | | | | | | | |
| Temperature range (K) | 40–120 | 40–120 | 40–110 | 40–110 | 40–110 | 40–110 | – | – |
| $A_2$ | 7.9552 | 37.084 | 72.194 | 60.59 | −64.872 | 142.8 | – | – |
| $B_2$ | 1.0059 | 0.684 | −0.3979 | 1.20 | 4.2301 | 2.731 | – | – |
| $C_2 \times 10^3$ | −1.8068 | 3.232 | 3.7418 | 6.056 | −14.084 | 13.46 | – | – |
| $D_2 \times 10^{-3}$ | −19.338 | 22.90 | −46.474 | 33.88 | 4.703 | 8.39 | – | – |
| $C_{pm,3} = A_3 + B_3T + C_3T^2 + D_3/T^2$ | | | | | | | | |
| Temperature range (K) | 120–298.15 | 120–298.15 | 110–298.15 | 110–298.15 | 110–298.15 | 110–298.15 | – | – |
| $A_3$ | −65.770 | 72.88 | −72.762 | 68.79 | −312.901 | 134.85 | – | – |
| $B_3$ | 1.4232 | 0.499 | 1.3081 | 0.488 | 4.6156 | 0.933 | – | – |
| $C_3 \times 10^3$ | −1.8545 | 0.867 | −1.8997 | 0.864 | −6.4634 | 1.629 | – | – |
| $D_3 \times 10^{-3}$ | 331.245 | 357.29 | 262.860 | 315.14 | 1367.59 | 633.49 | – | – |
| $C_{pm,4} = A_4 + B_4T + C_4/T^2$ | | | | | | | | |
| Temperature range (K) | 298.15–1060 | 298.15–1060 | 298.15–990 | 298.15–990 | 298.15–1120 | 298.15–1120 | 298.15–985 | 298.15–985 |
| $A_4$ | 226.096 | 9.06 | 157.161 | 11.42 | 550.808 | 21.56 | 1115.90 | 57.84 |
| $B_4 \times 10^2$ | 3.3374 | 1.01 | 3.8750 | 1.33 | 11.489 | 2.42 | 32.391 | 6.91 |
| $C_4 \times 10^{-7}$ | −0.34323 | 0.073 | −0.15461 | 0.087 | −0.72005 | 0.155 | −1.92895 | 0.3355 |

Table 3
Molar heat capacity, molar entropy and entropy of formation from binary oxides

| Oxide | $Bi_2Ca_2O_5$ | $Bi_2CaO_4$ | $Bi_6Ca_4O_{13}$ |
|---|---|---|---|
| $C_{pm}$ (298.15) (J K$^{-1}$ mol$^{-1}$) | 197.44 ± 1.90 | 151.32 ± 2.02 | 504.06 ± 3.71 |
| $S_m$ (298.15) (J K$^{-1}$ mol$^{-1}$) | 231.28 ± 2.91 | 188.46 ± 3.29 | 574.13 ± 8.77 |
| $\Delta S_{ox}$ (298.15) (J K$^{-1}$ mol$^{-1}$) | 6.59 | 1.87 | −23.74 |
| $\Delta S_{ox}$ (1000) (J K$^{-1}$ mol$^{-1}$) | 15.56 | 0.70 | −5.19 |
| $\Delta S_{ox}$ (J K$^{-1}$ mol$^{-1}$) [8] | 0.00 | 0.00 | 10.00 |
| $\Delta S_{ox}$ (J K$^{-1}$ mol$^{-1}$) [6] | −5.79 | −2.31 | −7.04 |

entropies and the heat capacities obtained in this study and those of $Bi_2O_3$ and CaO reported in [15,16]. The results are compared in Table 3 with both the values optimized by Hallstedt et al. [8] and those derived from the linear temperature dependencies of standard Gibbs energies ($\Delta G_{ox}$) of formation, which were evaluated from the solid-state EMF measurements in the temperature range of 850–1100 K [6].

The standard molar entropy of formation of $Bi_2CaO_4$ at 298.15 K from this study corresponds very well to the value optimized by Hallstedt et al. [8]. At 1000 K the value is small positive while that reported by Jacob and Jayadevan [6] is small negative. $\Delta S_{ox}$ of $Bi_6Ca_4O_{13}$ at 298.15 K obtained in this study is not compatible with the value of Hallstedt et al. [8], while at 1000 K it is in a close agreement with the result of Jacob and Jayadevan [6]. In the case of $Bi_2Ca_2O_5$ we obtain, as distinct from [6], a positive value of $\Delta S_{ox}$ which increases with increasing temperature.

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