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Calibration of the Setaram high-temperature calorimeter for determination of heat capacity of phases in the Sr–Cu–O system

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Abstract

A high-temperature Setaram calorimeter was calibrated to measure the heat capacities of Sr–Cu–O phases. The indicated temperature was calibrated through the solidification points of pure metals (ITS-90). Powdered CuO having similar emissivity and heat conductivity to the measured materials was used as a standard for caloric calibration. Two different methods of measurement were examined. Working in continuous scanning mode, the 'classical' three-step method of heat flow rate calibration was used, while for the discontinuous method the respective peak areas were calibrated. The sensitivity calibration curve for the discontinuous method was evaluated from two successive runs carried out on the reference material. The calibrated calorimeter was used for determination of temperature dependences (473–1133 K) of heat capacity of the $SrCuO_2$, Sr_2CuO_3 and $Sr_{14}Cu_{24}O_{41}$ phases. Obtained $C^0_{p,m}$ data measured by the step-by-step procedure were evaluated by two different methods. In the first method, the mean value of $C^0_{p,m}$ was obtained by dividing the enthalpy change attributed to a given change of temperature by a corresponding ΔT. The second method consisted of summing the individual enthalpy contributions and subsequent differentiation of the resulting temperature dependence of enthalpy. Both these approaches yielded comparable results with relative standard deviations of 2–3% from the standard polynomial fit $C^0_{p,m} = a + bT + cT^{-2}$. The temperature dependences of heat capacity of measured phases were compared with the low-temperature data taken from the literature as well as with the estimated curves. Our results exhibit a systematic shift to lower $C^0_{p,m}$ values.

Keywords: DSC high-temperature calorimeter; Heat capacity; Heat flow rate calibration; Superconducting phases

1. Introduction

Numerous papers have been published on the superconducting, structural and physical properties of SrO(CaO)–CuO–Bi_2O_3 systems, but little is known about their thermodynamics. The knowledge of the heat capacity of a material as a function of temperature is the basis for determination of any thermodynamic quantity. The Neumann–Kopp rule was frequently used for the evaluation of the temperature dependence of molar heat capacities ($C^0_{p,m}$) of strontium cuprates. Nevertheless, experimentally determined values of $C^0_{p,m}$ (T) are usually required for accurate modeling of high-temperature thermodynamic properties of these compounds. Up to now only a few calorimetric measurements have been performed. Shaviv, et al. [1] presented the results of low-temperature heat

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capacity measurement for $SrCuO_2$, Sr_2CuO_3 and $Sr_{14}Cu_{24}O_{41}$ in the temperature range of 6–350 K, which were measured by the use of a low-temperature adiabatic calorimeter. Another value of $C^0_{p,m}$ at 350 K for Sr_2CuO_3 was obtained by Krüger, et al. [2] using a DSC. In this paper, the measurement of the heat capacities of the above-mentioned phases was extended to the high-temperature region (473–1133 K). For the measurement, a multidetector high-temperature calorimeter Setaram was used.

For reliable measurements and optimum evaluation, a precise calibration of the calorimeter and the correct analysis of the measurement curves are necessary. The entire DSC calibration factor depends on the instrument and sample parameters. There is not, as yet, an international agreement on procedures for the temperature calibration and caloric calibration of DSCs. Moreover, no complete theory of the DSCs exists, which takes full account of the systematic influences from the instrument and inherent sources of error. It is worth noting that it is overall uncertainty of the calibration, which yields the smallest possible systematic uncertainty of the measurements. Therefore, in this work, attention was also devoted to this problem.

2. Sample preparation

All the samples were prepared by a standard ceramic route, consisting of several preheating/regrinding steps followed by final heat treatment of the pelletized material. The starting powders, $SrCO_3$ and CuO (Fluka Chemie), were chemically analyzed before the solid-state reaction. The content of the main components was determined to be higher than 99.5% of the theoretical amount in both cases. Two calcinations at 800 and 850°C for 24 h and three firing steps at 900, 920 and 965°C (940°C for $Sr_{14}Cu_{24}O_{41}$) for 48 h, each followed by thorough homogenization and pelletization, were performed in order to achieve the equilibrium state. All experiments were carried out in platinum crucibles under ambient atmosphere. The detailed description of the experimental conditions is given elsewhere [3]. The phase purity of the prepared materials was checked by X-ray powder diffraction.

3. Temperature and caloric calibration

The temperature indicated by the instrument was calibrated using the fixed solidification points of pure metals of the International Temperature Scale of 1990 (ITS-90). The difference between the measured and reference temperature was fitted on a four-parameter function of measured absolute temperature and heating rate. The resulting error of temperature measurement ± 0.8 K was found.

Powdered CuO [4] of high purity (99.95%) having similar emissivity and heat conductivity to the measured materials was used as a standard for caloric calibration. Working in the continuous scanning mode the 'classical' three-step method of heat flow rate calibration was used. For the discontinuous (step-by-step) method the respective peak areas were calibrated.

As the particular sample masses used in DSC heat flux cylinder-type detector are relatively large (typically 1000–1300 mg) and the thermal conductivity of the measured materials is rather low, very long times of heat flux stabilization in isothermal regime were needed (ca. 5000 s). The typical heating rates were 1 and 5 K min^{-1} for the step-by-step and the continuous methods, respectively. The temperature difference between two isothermal delays in the former method was programmed to 20 K with the assumption of $C^0_{p,m}$ being constant within this temperature interval. Indeed, the resulting experimental error was found to be higher than the $C^0_{p,m}$ variation in the range of 20 K. All the measurements were performed in ambient atmosphere. The filling of the crucible was maintained at the same level for all the measured samples. All measured samples were preheated to final temperature with a heating rate 10 K min^{-1} before each measurement.

The recorded curves were first corrected to the temperature dependence of isothermal heat flow rates in order to set the offset of both isothermal levels (prior to, and after the ramp) to zero. For the continuous method, the polynomial fit of the isothermal zero line was used (see example in Fig. 1). In the case of discontinuous method, the approximation by a straight line seems to be reasonable because of the small temperature change (20 K). Also, the correction for the blank crucible line differs for the two methods. Whereas in the continuous method the heat flow line of the empty crucibles was directly subtracted from

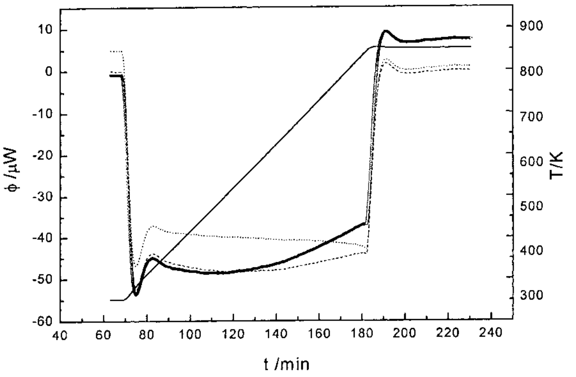

Fig. 1. Isothermal heat flow (ϕ^0) and blank crucible heat flow (ϕ^B) correction of the recorded ϕ vs. time curve for $SrCuO_2$ using continuous method; measured heat flux (—), corrected to ϕ^0 (- - -) corrected to ϕ^B (·····), temperature (—).

that of the sample (or the reference), in the step-by-step method the integrated peak areas of the respective effects were subtracted from each other.

The sensitivity calibration curve for discontinuous method was evaluated from two successive runs carried out on the reference material, as well as on the blank crucibles. The four-parameter polynomial fit was applied on the calculated sensitivity data with the confidence interval ranging from 0.7 to 2.5%, depending on temperature (see Fig. 2). Using two or more data sets for the evaluation of the calibration curve is appropriate in order to improve the reliability of the measured values. Unfortunately, this option is not available with the software delivered by Setaram. Therefore, our own evaluation program was developed for such data processing. This program also enables the user to enter into the evaluation procedure and to avoid some larger errors resulting from the irregularities in temperature and heat flux stabilization. The comparison, including the mean relative standard deviations of the Setaram and our evaluation procedure, is given on an example of Sr_2CuO_3 phase in Fig. 3. It is obvious that the use of fitted calibration curve suppresses the negative influence of occasional opposite deviations of the sample and reference peak area. The sensitivity calibration curve (precision of heat capacity measurement) was tested performing an independent measurement on the reference material, CuO [4]. The results given in Fig. 4 show quite good agreement with the tabulated data [4], which fall almost entirely into the confidence interval not exceeding 2.5% of the measured value (σ_r=1.9%). A similar measurement was performed on synthetic sapphire α-Al_2O_3 (NIST, reference material 720). The relative error was found to be dependent on temperature and sample mass. For a comparable sample mass, the relative error averaged over the temperature range 330–1120 K was 2%.

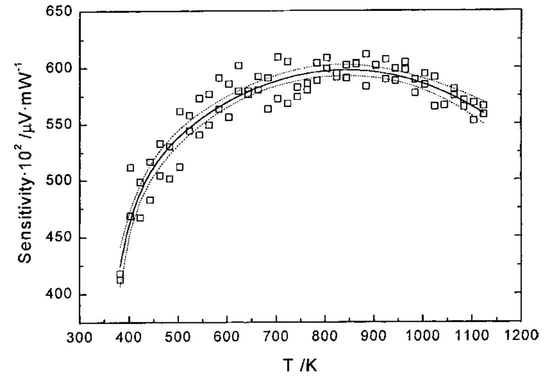

Fig. 2. Sensitivity curve used for $C_{p,m}$ evaluation by the discontinuous method. $C_{p,m}$ values of the CuO used as a reference were taken from JANAF tables [4]; Polynomial fit (—) $a+bT+cT^2+d/T^3$ (a=454±28, b=0.515±0.111, c=−4.59E-4±1.04E-4, d=−0.048±0.38E8, σ=14.1); measured data (□).

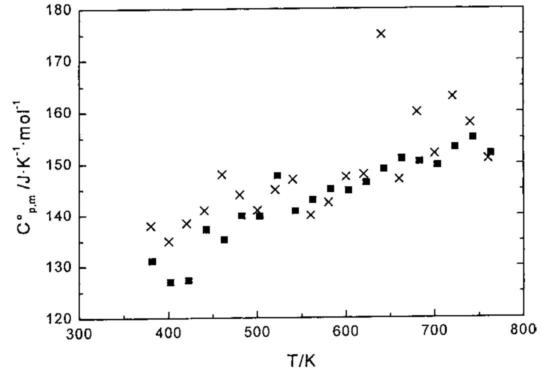

Fig. 3. Heat capacity $C_{p,m}$ of Sr_2CuO_3 evaluated by original Setaram procedure (×) and using the calibration curve from Fig. 2 (■).

4. Heat capacity determination

The heat capacity of samples measured by the continuous method was evaluated by substitution of the measured heat flows of sample (ϕ_S), reference

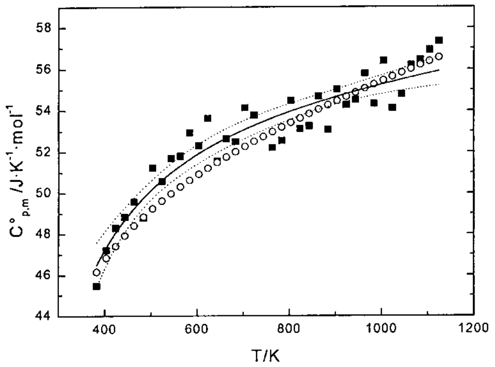

Fig. 4. Heat capacity of CuO calculated from an independent step-by-step experiment (■) compared to the original $C_{p,m}$ (T) dependence (○) used as a reference. Regression curve (—) with a confidence interval (·····).

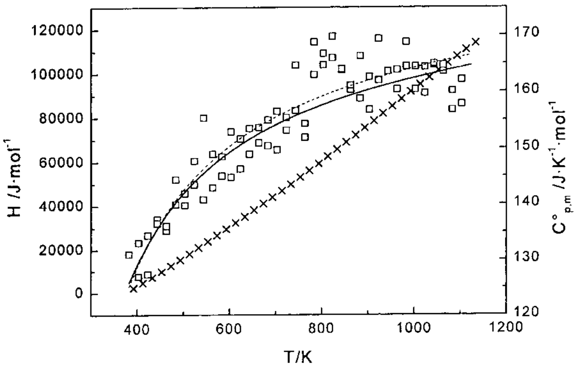

Fig. 5. Comparison of two methods for $C_{p,m}$ evaluation of data measured by the discontinuous method; measured enthalpy H (×), measured $C_{p,m}$ (□), regression curve of $C_{p,m}$ data (- - -), $C_{p,m}$ calculated from polynomial fit of H (—).

(ϕ_R) and blank crucibles (ϕ_B) into Eq. (1).

$$C_p^{0S}(T)=\frac{\phi_S-\phi_B}{\phi_R-\phi_B}\frac{m_R}{m_S}C_p^{0R}(T)\equiv\frac{\phi_S-\phi_B}{S(T)m_S}, \tag{1}$$

where m_S and m_R are sample and reference masses, and $S(T)=(\phi_R-\phi_B)/(C_m^R m_R)$ is the sensitivity.

For the step-by-step method two different procedures were used. In the first method, the mean value of $C_{p,m}^0$ was obtained by dividing the change in enthalpy

$$\Delta H_i=\int_{T_i}^{T_{i+1}}C_p^{0S}\mathrm{d}T\equiv\frac{I_S-I_B}{I_R-I_B}\frac{m_R}{m_S}\int_{T_i}^{T_{i+1}}C_p^{0R}\mathrm{d}T=\frac{I_S-I_B}{S_i m_S},\quad I=\int_{\tau_1}^{\tau_2}\phi\,\mathrm{d}\tau \tag{2}$$

attributed to a given change of temperature by a corresponding ΔT.

$$C_p^{0S}\left(\frac{T_i+T_{i+1}}{2}\right)=\frac{\Delta H_i}{(T_{i+1}-T_i)} \tag{3}$$

The second procedure consists of summing the individual enthalpy contributions and subsequent differentiation of the resulting temperature dependence of enthalpy.

$$H(T_j)=\sum_{i=1}^{j}\Delta H_i \quad C_p^{0S}(T_j)=\left(\frac{\partial H}{\partial T}\right)_{T_j} \tag{4}$$

Both these approaches yielded comparable results with the relative standard deviations not exceeding 4% from the standard polynomial fit $C_{p,m}^0=a+bT+cT^{-2}$ (see Fig. 5). Therefore, in the following paragraph only the data evaluated by the first mentioned procedure are presented.

5. Results and discussion

The temperature dependences of heat capacity measured for individual phases using both methods described above can be seen in the Fig. 6a–c. For comparison, the temperature dependences published by other authors in the literature, together with the values obtained using the Neumann–Kopp rule, were plotted into Fig. 7a–c. The literature values of $C_{p,m}^0$ at 350 K and the values obtained using the Neumann–Kopp rule are summarized in Table 1. Unfortunately, it follows from the comparison that our results systematically deviate to lower values in the low-temperature region. This might be due to a less accurate fit of the sensitivity data in this temperature interval. Moreover, the sensitivity is about 1.5 times lower in magnitude at 380 K as compared to that at 800 K, which results in a

Table 1
Molar heat capacities $C_{p,m}^0$/J K^{-1} mol^{-1} of strontium cuprates at 350 K

Compound	Shaviv [1]	Krüger [2]	Neumann–Kopp rule[a]
$SrCuO_2$	91.41	–	91.6
Sr_2CuO_3	141.85	131.92	138.1
$Sr_{14}Cu_{24}O_{41}$	1873.88	–	1776

[a] Calculated using $C_{p,m}^0$ (CuO)=44.98 J K^{-1} mol^{-1} (Ref. [4]) and $C_{p,m}^0$ (SrO)=46.58 J K^{-1} mol^{-1} (Ref. [6]).

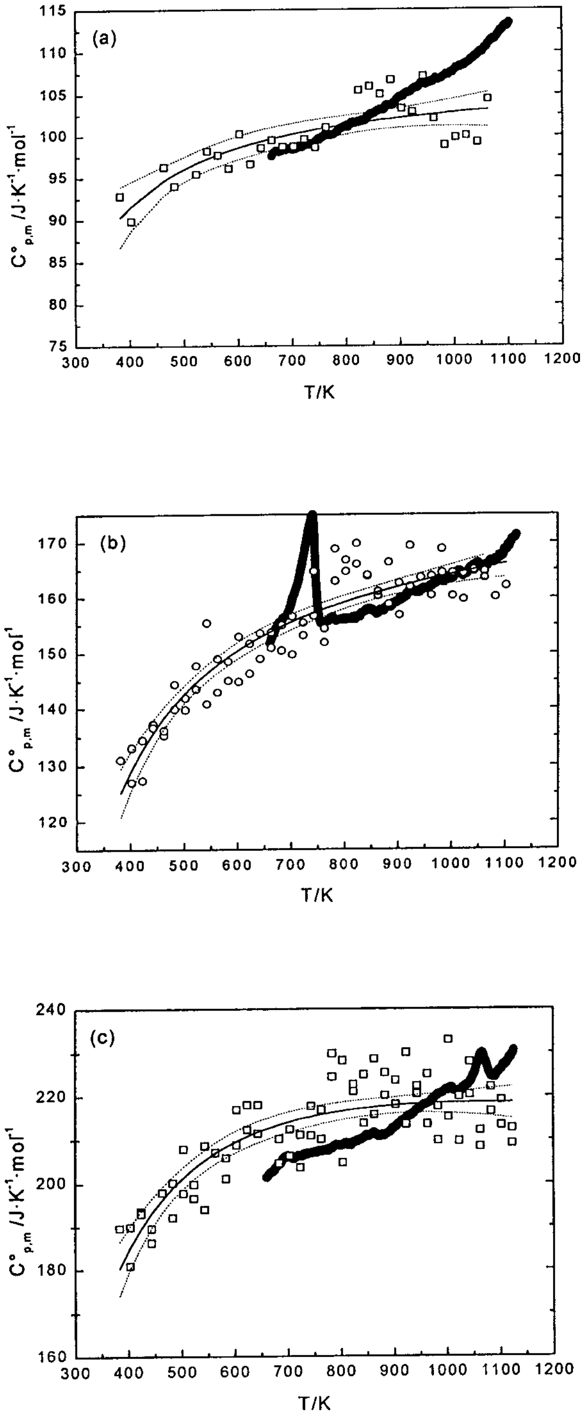

Fig. 6. Measured heat capacities $C_{p,m}$ of the compounds $SrCuO_2$ (a), Sr_2CuO_3 (b), and $Sr_{14}Cu_{24}O_{41}$ (c), using the continuous (●) and discontinuous (○) methods; fitted curve (—) with a confidence interval (·····).

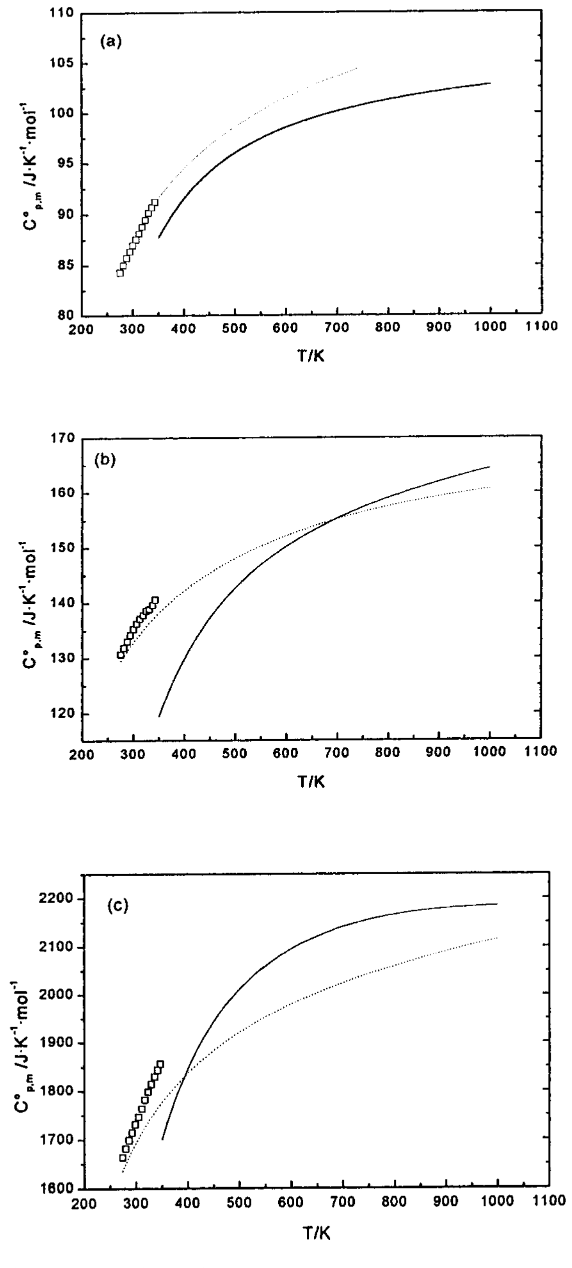

Fig. 7. Comparison of our data (—) with the low-temperature calorimetric data published by Shaviv, et al. [1] (□) and Neumann–Kopp rule (——) for the compounds $SrCuO_2$ (a), Sr_2CuO_3 (b), and $Sr_{14}Cu_{24}O_{41}$ (c).

lower accuracy. Another explanation of the observed discrepancy lies in the data for the reference material itself. It has been shown recently [5] that the $C^0_{p,m}(T)$ dependence for CuO differs slightly from the JANAF data [4], showing a broad maximum due to a magnetic contribution, which should be influenced, for example, by oxygen stoichiometry, disorder, etc. Apparently, the higher value of $C^0_{\mathrm{p,m}}$ would lead to an increase of the measured $C^{0\mathrm{S}}_{\mathrm{p,m}}$. Hence, the applicability of CuO as a reference material for the $C^0_{\mathrm{p,m}}$ measurement, especially in the temperature range where the magnetic contribution is significant, is a question of debate and must be further verified.

As it can be seen from temperature dependences, the $C^0_{\mathrm{p,m}}$ data measured using the continuous method (Fig. 6) are in good agreement with the data scanned by the step-by-step method with an exception of the $SrCuO_2$ phase, where a positive departure from step-by-step data is observed above 900 K. This result seems to be incorrect, because of the very unlikely convex shape of the curve. The main advantage of the continuous method is, apparently, its speed, which is >10 times higher than that of the discontinuous method. It is worth to note that the enthalpy change accompanying some phase transition within a measured temperature range can be only distinguished if the data are acquired by use of the continuous method (see observed peak on the corresponding temperature dependence of the Sr_2CuO_3phase shown in the Fig. 6a). On the contrary, this transition effect appears only as the enlarged data scattering at the corresponding temperatures on the temperature dependence plot determined by the step-by-step method. Nevertheless, the latter method is preferred since the sample is brought into equilibrium state prior to, and after each measuring step. Furthermore, the continuous method is presumably much more sensitive to preheating conditions, sample mass and other effects, and therefore less reproducible.

The relative standard deviation of our step-by-step measurements did not exceed 4%, while the mean value of σ_r ranges from 2 to 3%. This value is almost twice better then the discrepancy between two experimental values published for Sr_2CuO_3 [1] (see Table 1). The use of He atmosphere, recommended by the manufacturer, was not found to yield substantially better accuracy. Moreover, at higher temperatures it was excluded due to decomposition of the $Sr_{14}Cu_{24}O_{41}$ phase.

6. Conclusions

The calibration of high-temperature calorimeter Setaram for $C^0_{\mathrm{p,m}}$ measurement was performed using CuO as a reference material and the temperature dependeces of $C^0_{\mathrm{p,m}}$ of three strontium cuprates were measured. A program was developed which enables the evaluation of the sensitivity calibration curve from two or more successive runs and avoids some larger errors resulting from the irregularities in temperature and heat flux stabilization. The use of two or more data sets improves the reliability of the measured values. The sensitivity calibration curve was tested performing an independent measurement on the reference material CuO.

The heat capacities of the $SrCuO_2$, Sr_2CuO_3 and $Sr_{14}Cu_{24}O_{41}$ phases were determined applying both, the continuous and step-by-step methods. The results obtained by the latter method were found to be more reliable.

Acknowledgements

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References

[1] R. Shaviv, E.F. Westrum, T.L. Yang, C.B. Alcock, B. Li, J. Chem. Thermodyn. 22 (1990) 1025–1034.

[2] Ch. Krüger, W. Reichelt, A. Almes, U. König, H. Oppermann, H. Scheler, J. Sol. Stat. Chem. 96 (1992) 67–71.

[3] M. Nevřiva, H. Kraus, D. Sedmidubský, Thermochim. Acta 282/283 (1996) 205–224.

[4] M.W. Chase, Jr., C.A. Davies, J.R. Downey, Jr., D.J. Frurip, R.A. McDonald, A.N. Syverud (JANAF Thermochemical Tables, 3rd edition), J. Phys. Chem. Ref. Data (Suppl. No.1) 14 (1985) 1.

[5] E. Gmelin, Indian J. Pure Appl. Chem. 30 (1992) 596–608.

[6] E.H.P. Cordfunke, R.R. van der Laan, J.C. van Miltenburg, J. Phys. Chem. Sol, 55 (1994) 77–84.