Journal of Thermal Analysis and Calorimetry, Vol. 88 (2007) 2, 531–535

# PHASE TRANSITION OF $YBO_3$

*J. Plewa*[*] *and T. Jüstel*

University of Applied Sciences Münster, Department of Chemical Engineering, Stegerwaldstrasse 39, 48565 Steinfurt, Germany

Yttrium orthoborate crystallizes in the vaterite-type structure and has two polymorphous forms, viz. a low- und a high temperature one. DTA measurements of $YBO_3$ confirmed a reversible phase transition with a large thermal hysteresis. The phase transition has been accurately characterized by the application of different heating and cooling rates ($\beta$). Consequently, the extrapolation of the experimental data to zero $\beta$ yields the transition points at 986.9°C for the heating up and at 596.5°C for the cooling down cycle. These values correspond to samples just after treatment at 1350°C. For samples with a different 'thermal history' other phase transition temperatures are observed, (e.g. after having performed several heating and cooling cycles).

The linear relationship between the associated DTA signal $\Delta T = T_{\text{onset}} - T_{\text{offset}}$ and the square root of the heating rate $\beta$ was confirmed, but the relation between $T_{\text{onset}}$ and square root of $\beta$ is not found here.

From the empirical data a good linear fitting between $T_{\text{onset}}$ and $\ln(\beta+1)$ can be derived.

From the kinetic analysis (Kissinger method) of the phase transformation of $YBO_3$ an apparent activation energy of about 1386 kJ $\text{mol}^{-1}$ for heating and of about 568 kJ $\text{mol}^{-1}$ for cooling can be determined.

***Keywords:*** *orthoborate, phase transitions, thermal hysteresis*

## Introduction

Yttrium orthoborate $YBO_3$ has found manifold applications as a host for luminescent ions such as $Eu^{3+}$, $Ce^{3+}$, $Tb^{3+}$ and $Bi^{3+}$ to obtain efficient phosphors for fluorescent lamps and plasma display panels [1–3]. Some advantages of orthoborates are their high stability over a wide temperature range and their ability to form solid solutions, i.e. $Y^{3+}$ can be easily replaced by almost all of the trivalent rare earth ions.

According to the classification of Levin [4, 5], the orthoborates can be subdivided into three groups, which correspond to the crystal modifications of $CaCO_3$: while Ce-, Sm-, La-, Pr- and Nd-orthoborates crystallizes in the aragonite type structure [4, 6], In-, Sc- and Lu-orthoborates crystallizes in the calcite type structure [7, 8], and Y- and Gd-orthoborate are crystallographically related to vaterite [9, 10].

So far it has not been completely clarified to which crystal structure type yttrium orthoborate belongs [11]. Some authors report that $YBO_3$ has a hexagonal structure (($P6_3/mnc$) [12], while others came to the conclusion that it crystallizes in a monoclinic cell ($C2/c$) [13]. However, in both cases the trivalent yttrium ion is 8-fold coordinated by oxygen, i.e. the structure comprises $YO_8$ polyhedron, which are more or less distorted from the ideal $S_6$ point symmetry. In contrast to that, the boron atoms can be either 3- or 4-fold coordinated by oxygen: this results in the observation of polymorphic $YBO_3$ modifications, in which either isolated trigonal $[BO_3]^{3-}$-groups or tetrahedral $[BO_3]^{3-}$-groups condensed to $[B_3O_9]^{9-}$-rings occur.

Many investigations on orthoborates revealed that a phase transition between those two polymorphic forms takes place upon heating [4, 13–15], whereby a low-temperature (LT) and a high-temperature (HT) modification exists. The phase transition temperature of some orthoborates is different for heating up and cooling down [5, 14–16]. This temperature hysteresis is relatively large and was explained by the required re-arrangement of the borate units during the LT→HT and HT→LT phase transition [16].

This work deals with the LT→HT and HT→LT phase transition of $YBO_3$, which was investigated as function of the heating/cooling rate. Moreover, the thermodynamic and kinetic data of the phase transition of $YBO_3$ were determined.

## Experimental

All samples of $YBO_3$ were prepared by using conventional solid-state reaction starting from $Y_2O_3$ (Rhodia) and $H_3BO_3$ (Chempur), whereby an excess of $H_3BO_3$ (about 10%) was used. All components were thoroughly mixed in a ball mill and subsequently annealed at 1000 and 1350°C with an intermediate grinding step. The obtained products were

---

[*] Author for correspondence: plewa@fh-muenster.de

1388–6150/\$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

bright white powders and are highly crystalline and of single phase according to XRD measurements performed on a Philips APD 1700.

Thermal analysis experiments were performed by using a thermobalance (Netzsch STA 409). As a reference material purified α-$Al_2O_3$ was used. The heating and cooling rate was chosen between 1 and 20 K $min^{-1}$, whereby for each experiment about 100 mg of the material were weighed in. All measurements were done in the dynamic mode and in synthetic air (flow rate: 100 mL $min^{-1}$).

The samples were also characterized by infrared spectroscopy (PerkinElmer FT-IR Spectrum 100) and by taking SEM images (Zeiss LEO 982).

## Results and discussion

### *Thermal properties of $YBO_3$*

Thermogravimetry shows that heating $YBO_3$ up to 1300°C does not result in any mass loss, i.e. the material does not show any decomposition in this temperature range. The DTA experiment reveals an endothermic process at about 1014.4°C (Fig. 1a). This reversible process is attributed to the LT→HT phase transition of $YBO_3$ whereby the peak area corresponds to a reaction enthalpy of $12.1\pm1.3$ kJ $mol^{-1}$.

The peak related to the LT/HT phase transition shows a tremendous hysteresis between heating up and cooling down (Fig. 1b). From the difference of the onsets of both peaks (575.6 and 981.2°C) a hysteresis of 406 K can be calculated (heating/cooling rate $\beta=10$ K $min^{-1}$).

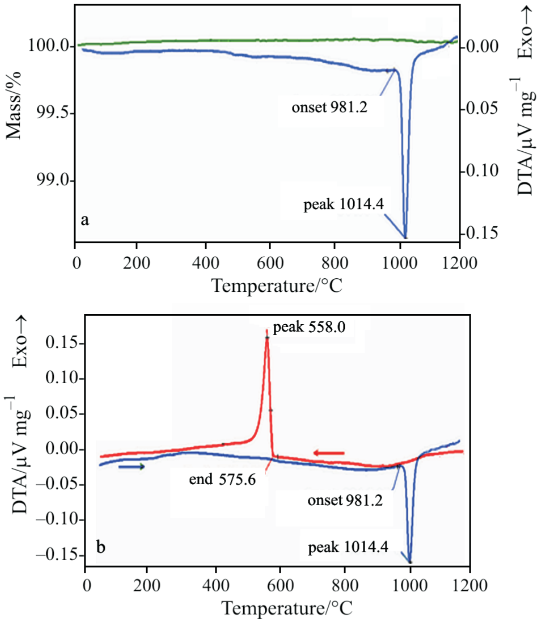

**Fig. 1** TG and DTA curves of $YBO_3$; a – heating rate $\beta=10$ K $min^{-1}$ and b – cooling rate $\beta=10$ K $min^{-1}$

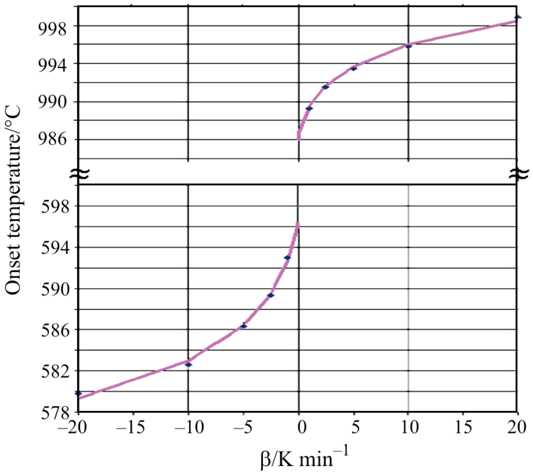

**Fig. 2** Dependence of the onset temperature of the LT/HT phase transition of $YBO_3$ on the heating and cooling rate. The data points are fitted by a curve according to the empirical equation $T_{onset}=a+b\ln(\beta+1)$

The true phase transition temperature can be derived from the investigation of the peak position as function of the heating/cooling rate β. To this end an extrapolation to $\beta=0$ K $min^{-1}$ has to be made according to Fig. 2. The transition temperature $T_{tr}$ is observed at 986.9°C for the heating up cycle and of 596.5°C for the cooling down cycle.

The temperature difference of the phase transition for heating up and cooling down, i.e. the true hysteresis, can be taken out of Fig. 2 for $\beta=0$, which corresponds to 390.3 K.

Former publications have already shown that the phase transition temperature of polymorphic compounds depends on the heating rate β [17–19]. Several authors showed that the phase transition temperature (onset temperature) has to be extrapolated linearly from the dependence on the heating/cooling rate [20]. Other authors showed that the dependence of the onset temperature on the heating rate is of the linear or square root type. The solid/liquid phase transition of Fe–Si alloys shows, for instance, a linear dependence for the solidus curve and a square-root dependence for the liquidus curve on the β parameter [18]. However, most types of phase transitions exhibit DTA peaks with a square-root type dependence on the heating rate β [17, 18].

These latter cases can be derived from the general dependence of the temperature difference $\Delta T=T_{onset}-T_{end}$ (associated DTA signal) on the square-root of the heating rate $\sqrt{\beta}$ [19].

Figure 3a shows that the characteristic temperatures of the DTA peaks of $YBO_3$ show no linear dependence on the heating rate β. For the temperature difference Δ*T* of the DTA peak corresponding to LT→HT phase transition one can derive a linear dependence on the square-root of β (Fig. 3b).

The best linear fit ($R^2$-value) is achieved if the onset temperature of the phase transition peak is plotted over the function ln(β+1) (Fig. 3c). This empirical determined dependence yields a significant better fitting than for a plot over β or the square-root of β.

### *Kinetic of the phase transition of $YBO_3$*

For the LT→HT and HT→LT phase transition of $YBO_3$ an energetic barrier has to be overcome, which can be calculated from experimental data by the Kissinger method [21].

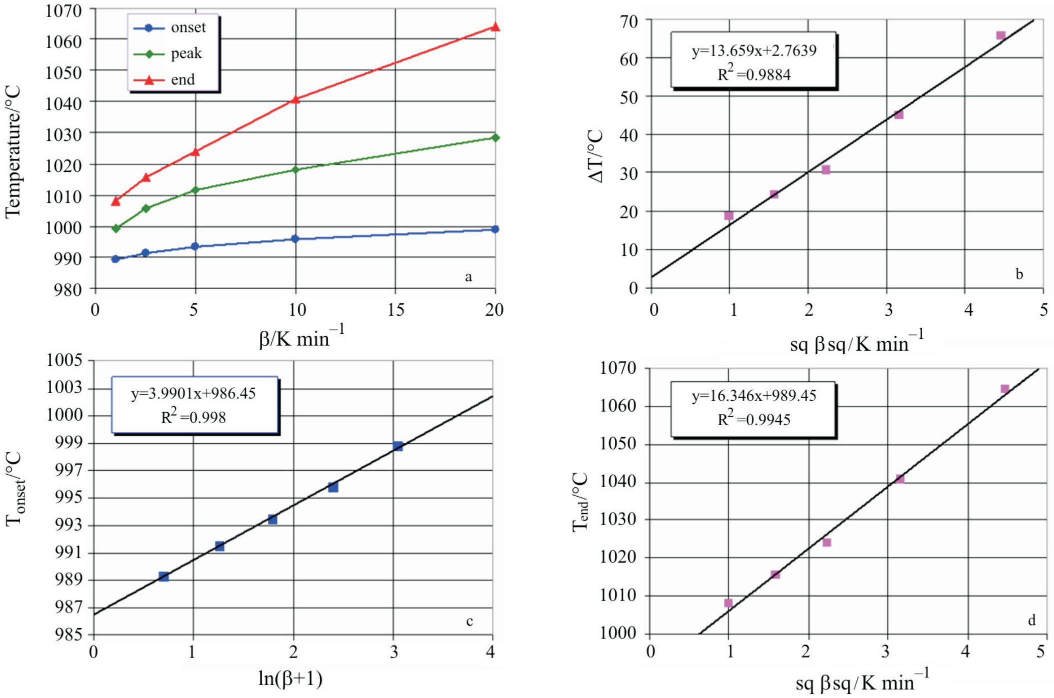

**Fig. 3** Experimental characteristic temperatures of the DTA phase transition peak recorded at different heating rates β; a – experimental data, b, c, d – square root-fittings of Δ$T$, $T_{onset}$ and $T_{end}$

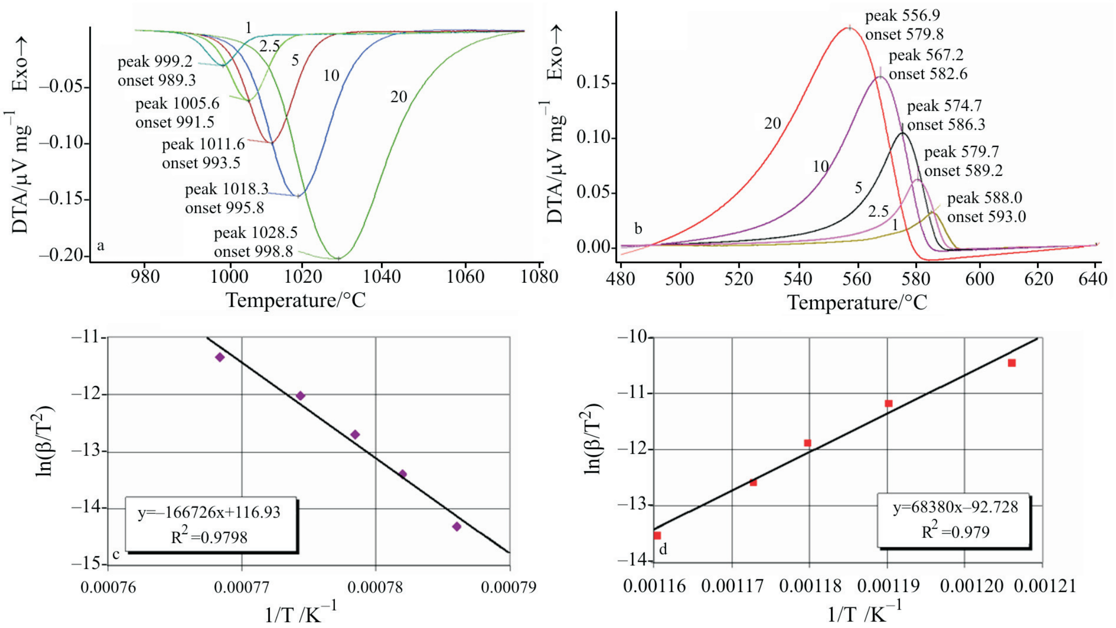

**Fig. 4** Dependence of the DTA peak position of the $YBO_3$ phase transition on the heating rate β for 1, 2,5, 5, 10 and 20 K min$^{-1}$; a – heating up, b – cooling down, c – Kissinger plot for heating up, d – Kissinger plot for cooling down

The obtained values for the apparent activation energy $E_a$ are 1386 kJ mol$^{-1}$ for the LT→HT phase transition and 568 kJ mol$^{-1}$ for the HT→LT phase transition. These high activation energy values are thus in the same order of magnitude than those of solid/liquid phase transitions of metals, e.g. shows Au an apparent activation barrier $E_a$ for the melting process of 5372 kJ mol$^{-1}$.

### *Cyclic thermal treatment*

The synthesized $YBO_3$ samples show a high purity according to the XRD pattern (Fig. 5), since no impurity phases can be detected. The FTIR spectrum does not show any bands around 1300 cm$^{-1}$, which are typical for isolated $[BO_3]^{3-}$-groups [16]. Therefore, the LT phase should comprise borate groups condensed to $[B_3O_9]^{9-}$-rings, whereby the rings are cleaved during the LT→HT phase transition and thus the HT form comprises isolated $[BO_3]^{3-}$-groups.

It is well known, that the LT→HT phase transition of $YBO_3$ results in a change in the cell parameters [13], i.e. the *a*-parameter increases and the *c*-parameter shrinks. This is caused by the increase in the yttrium oxygen distances and by the reduction of the boron oxygen distances [13].

It is obvious that HT→LT phase transition corresponds to the reversible process, viz. $[B_3O_9]^{9-}$-rings are formed by the reaction of isolated $[BO_3]^{3-}$-groups.

On the basis of the results of cyclic DTA experiments (several heating and cooling cycles) one can derive that the discussed phase transition is even more complicated. This results from by the shift of the phase transition with the number of performed heating and cooling cycles (Fig. 6).

The above depicted graphs clearly show that after 10 heating/cooling cycles the LT→HT phase transition is shifted from 1015.0°C to 1021.9°C (peak value), while the HT→LT phase transition is shifted from 560.3 to 550.5°C. At the same time the activation energy of the phase transition increases significantly. After 20 cycles (heating up to 1200°C and cooling down to 20°C, heating rate β=10 K min$^{-1}$), the $E_a$ values have been increased by 25% for the LT→HT phase transition and by 11% for the HT→LT phase transition.

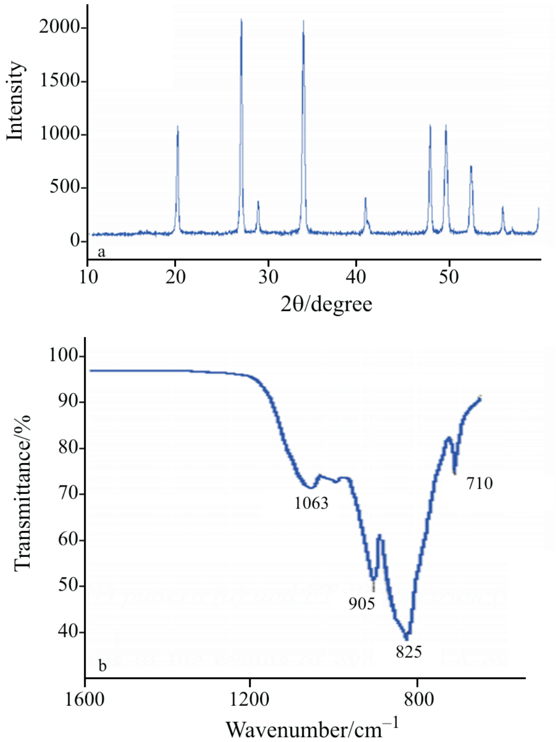

**Fig. 5** a – XRD pattern and b – FTIR spectrum of a typical $YBO_3$ sample

SEM images of an $YBO_3$ sample before and after the cyclic thermal treatment reveal that the particles coagulate and grow during the thermal treatment (Fig. 7b). Additionally, the sample density decreases due to the formation of more cavities. This morphology change reduces the thermal conductivity, whereby a decrease in the thermal conductivity results in a higher peak temperature for heating and in a lower peak temperature for cooling.

Summarizing, the shift in the peak positions of the phase transition is attributed to the morphology change of $YBO_3$, which is a function of its 'thermal history'.

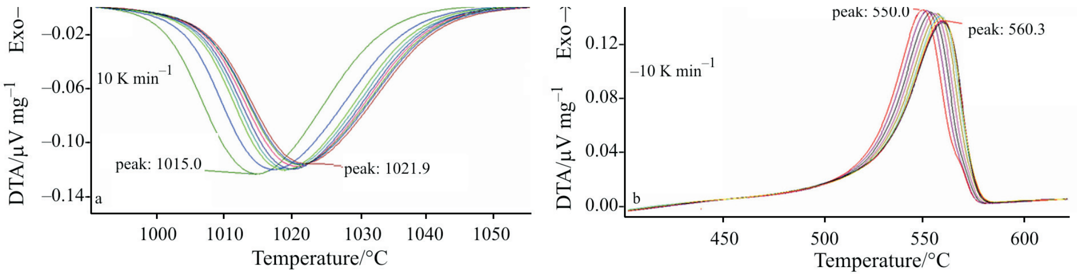

**Fig. 6** Shift of the DTA peak of the $YBO_3$ phase transition with the number of thermal treatment cycle a – heating up to 1200°C and b – cooling down to 200°C plotted for 10 cycles

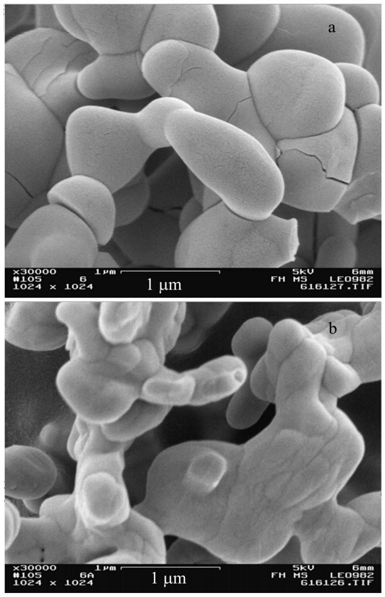

**Fig. 7** SEM pictures of $YBO_3$ samples; a – fresh powder, b – and after thermal cycling

## Conclusions

A series of TG and DTA experiments on a freshly prepared $YBO_3$ (made at 1300°C) sample were performed, from which the thermodynamic data of the phase transition of $YBO_3$ were determined. The true phase transition temperature of $YBO_3$ is $T_{tr}$=986.8°C, whereby the phase transition enthalpy is $\Delta_{tr}H^0$= 12.1 kJ mol$^{-1}$ and a thermal hysteresis of 390 K is observed. The apparent activation energy $E_a$ of the phase transition of $YBO_3$ for the LT→HT transition is 1386 kJ mol$^{-1}$, while it is 568 kJ mol$^{-1}$ for the HT→LT transition.

The identified kinetic parameters undergo a change with number of cyclic thermal treatments and therefore the history of the material must be regarded as an additional material parameter to completely describe the phase transition of $YBO_3$. Such a behavior is not new and known from many solid material, e.g. from carbonates [22].

## References

1 S. R. Chinn and H. Y. P. Hong, Opt. Commun., 18 (1976) 87.
2 Z. Wei, L. Sun, C. Liao, J. Yin, X. Jiang, C. Yan and S. Lii, J. Phys. Chem. B, 106 (2002) 10610.
3 K. N. Kim, H.-K. Jung, H. D. Park and D. Kim, J. Mater. Res., 17 (2002) 907.
4 E. M. Levin, C. R. Robbins and J. L. Waring, J. Am. Ceram. Soc., 44 (1961) 87.
5 E. M. Levin, R. S. Roth and J. B. Martin, Am. Mineral., 46 (1961) 1030.
6 E. Antic-Fidancev, J. Aride, J.-P. Chaminade, M. Lemaitre-Blaise and P. Porchev, J. Solid State Chem., 97 (1992) 74.
7 E. Tkachenko, P. Fedorov, S. Kuznetsov, V. Voronov, S. Lavrishchev, Y. Shukshin, I. Yarotskaya and N. Kononova, Inorg. Mater., 42 (2006) 171.
8 A. Wolfert, E. W. Oomen and G. Blasse, J. Solid State Chem., 59 (1985) 280.
9 G. Corbel, M. Leblanc, E. Antic-Fidancev, M. Lemaitre-Blaise and J. C. Krupa, J. Alloys Compd., 27 (1999) 71.
10 P. E. D. Morgan, P. J. Caroll and F. F. Lange, Mater. Res. Bull., 12 (1977) 251.
11 G. Chadeyron, R. Mahiou, M. El-Ghozzi, A. Arbus, D. Zambon and J. C. Cousseins, J. Luminescence, 72–74 (1997) 564.
12 R. E. Newnham, M. J. Redman and R. P. Santoro, J. Am. Ceram. Soc., 46 (1963) 253.
13 J. Lin, D. Sheptyakov, Y. Wang and P. Allenspach, Chem. Mater., 16 (2006) 2418.
14 J. Madarász, E. Beregi, J. Sztatisz, I. Földvari and G. Pokol, J. Therm. Anal. Cal., 64 (2001) 1059.
15 M. T. Cohen-Adad, O. Aloui-Lebbou, C. Goutaudier, G. Panczar, C. Dujardin, C. Pedrini, P. Florian, D. Massiot, F. Gerard and C. Kappenstein, J. Solid State Chem., 154 (2000) 204.
16 M. Ren. J. H. Lin, Y. Dong, L. Q. Yang and M. Z. Su, Chem. Mater., 11 (1999) 1576.
17 W. J. Illers, Eur. Polym. J., 10 (1974) 911.
18 H. Meco and R. E. Napolitano, Scripta Materialia, 52 (2005) 221.
19 S. M. Sarge, G. Höhne, H. K. Cammenga, W. Eysel and E. Gmelin, PTB-Mitteilungen, 109 (1999) 357.
20 G. W. H. Höhne, H. K. Cammenga, W. Eysel, E. Gmelin and W. Hemminger, Thermochim. Acta, 160 (1990) 1.
21 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
22 M. Maciejewski and H. R. Oswald, Thermochim. Acta, 86 (1985) 39.

DOI: 10.1007/s10973-006-8029-9