ELSEVIER

Thermochimica Acta 290 (1996) 115–121

thermochimica acta

Determination of Phase Diagrams by Heat Evaluation from DTA

U. Wiesner *, W. Bieger, G. Krabbes

Institut für Festkörper - und Werkstofforschung Dresden, D - 01171 Dresden, Germany

Received 2 January 1996; accepted 12 June 1996

Abstract

Basing on a quantitative analysis of DTA heat flow measurements the compositions of eutectic and peritectic reactions in complicated systems can be sensitively determined. In addition to the conventionally used DTA onset temperatures, the quantitative analysis of the corresponding heat flows provides important further information which significantly improve the determination of phase relations in complicated systems. The general concept is demonstrated for simple model systems. The sensitivity of detection and the separability of the DTA events will be discussed in detail. The applicability of the method is proved for two complicated examples from the Y–Ba–Cu–O system: (1) the quasibinary section $YBa_2Cu_3O_{7-\delta}$–$BaCuO_2$ and (2) the ternary eutectics $YBa_2Cu_3O_{7-\delta}$–$BaCuO_2$–CuO.

Keywords: Thermal analysis; Phase diagrams; Y–Ba–Cu–O high temperature superconductors

1. Introduction

The knowledge of phase diagrams and thermochemical reaction data is necessary for solid state research and for the development of new materials.

A favoured method for the investigation of phase equilibria is the differential thermal analysis (DTA). Usually the construction of phase diagrams has been performed using the onset temperatures from the DTA heat flow rate peaks.

Another well – known possibility to determine eutectic compositions is the use of the arrest periods of the heat flow rate events which are roughly proportional to the heat of the eutectic reaction or more exactly the evaluation of the eutectic heats by determination of the peak areas from the DTA events at the eutectic temperature.

The onset temperatures are very useful to determine exact reaction temperatures. However, the type of reaction as well as the corresponding compositions can only be derived for simple systems. In more complicated systems with several subsequent reactions the only analysis of onset temperatures is not sufficient to clarify the phase relations in dependence on the temperature.

Therefore, this paper deals with the extension of the more sensitive method of the determination of complicated phase diagrams by evaluating the heats of reaction measured by DTA investigations.

2. Methodical aspects

From a DTA curve one gets information about the temperature and the heat exchange for an observed reaction, expressed by the starting tempera-

---

* Corresponding author.

0040-6031/96/$15.00 Copyright © 1996– Elsevier Science B.V. All rights reserved

PII: S0040-6031(96)03040-7

ture and the area of the adequate DTA peak, respectively. The peak area A enclosed between the measured DTA curve and the base line is proportional to the heat of the considered reaction:

$$A = \int \Delta U(t)\mathrm{d}t \propto \int \Delta T(t)\mathrm{d}t \propto q = \int \Phi(t)\mathrm{d}t \qquad (1)$$

($\Delta U(t)$ measured voltage difference, which is proportional to the temperature difference $\Delta T(t)$ between the sample and the reference sample, Φ heat flow rate, q heat of reaction).

The quantitative analysis of the heat flow rate from DTA measurements has considerable advantages for the sensitive determination of the exact compositions of invariant or univariant mixtures in complicated systems. The principle will be demonstrated for a simple eutectic system, the pure substances A and B of which are assumed to be immiscible in the solid state and form a homogeneous melt L (Fig. 1a).

Considering a heating process of any mixture in this example, the total heat of reaction q_{tot} is divided into two parts, that of the eutectic reaction q_s at T_s and that of the proceeding melt process q_l, which proceeds until the liquidus temperature T_l is attained. Between T_s and T_l the mixture consists of a solid phase with the mole fraction y_S and a liquid phase with the mole fraction $y_L (y_S + y_L = 1)$. The change of the amount of the molten part y_L is connected with a heat flow rate $\Phi(t)$, and the $\mathrm{d}y_L(T)/(\mathrm{d}T)$ vs. T-curve represents the course of the DTA event $\Delta T(t)$:

$$\Delta T(t) \propto \frac{\mathrm{d}q(t)}{\mathrm{d}t} = \Phi(t) \propto \frac{\mathrm{d}y_L(t)}{\mathrm{d}t} = \frac{\mathrm{d}y_L(T)}{\mathrm{d}T}\cdot\frac{\mathrm{d}T}{\mathrm{d}t}$$

$$= \beta\cdot\frac{\mathrm{d}y_L(T)}{\mathrm{d}T} \qquad (2)$$

(heating rate $\beta = (\mathrm{d}T)/(\mathrm{d}t)$).

Considering the region $(0 \leq x_B \leq x_B^E)$ to the left in Fig. 1a, the part y_L of a mixture with the initial content $x_B^0 (x_B^0 < x_B^E)$, which is molten at the eutectic temperature T_s can be expressed by

$$y_L(T_s) = x_B^0 + \frac{x_A^E}{x_B^E}\cdot x_B^0 = \frac{x_B^0}{x_B^E} \qquad (3)$$

(x_A^E, x_B^E the mole fractions of A and B at the eutectics E, $x_A^E + x_B^E = 1$).

The molten part $y_L(T)$ is calculated by the lever principle for any temperature $T_s < T \leq T_l$:

$$y_L(T) = \frac{x_B^0}{l(T)} \qquad (4)$$

($l(T)$ is the value x_B of the liquidus l at the temperature T).

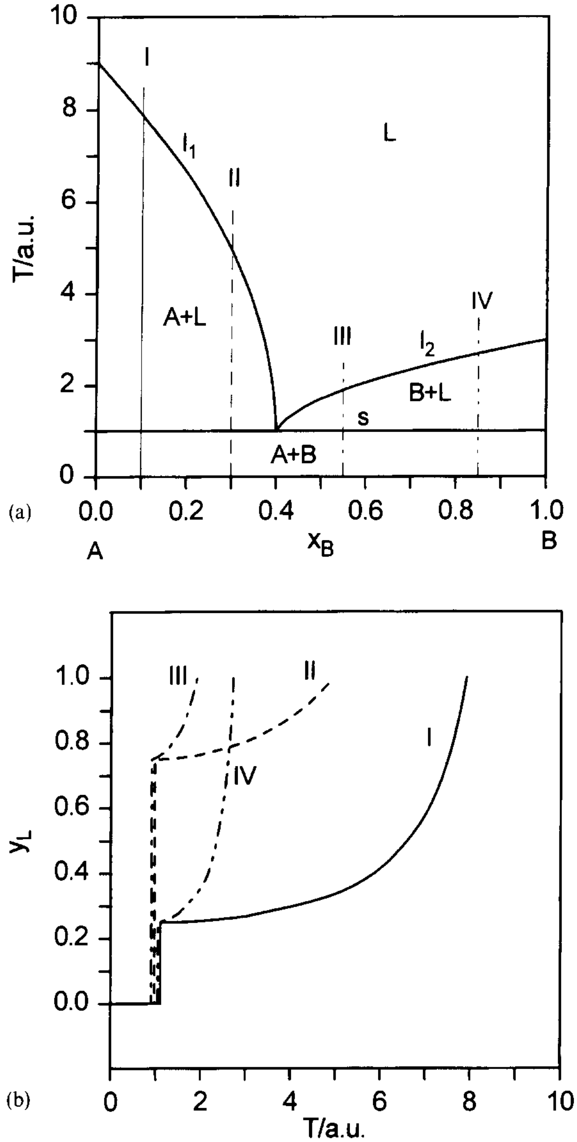


Fig. 1. a: Schematic simple binary phase diagram b: $y_L(T)$ vs. T-diagram for the mixtures I–IV (see Fig. 1a). c: $\mathrm{d}y_L(T)/(\mathrm{d}T)$ vs. T-diagram for the mixtures I–IV.

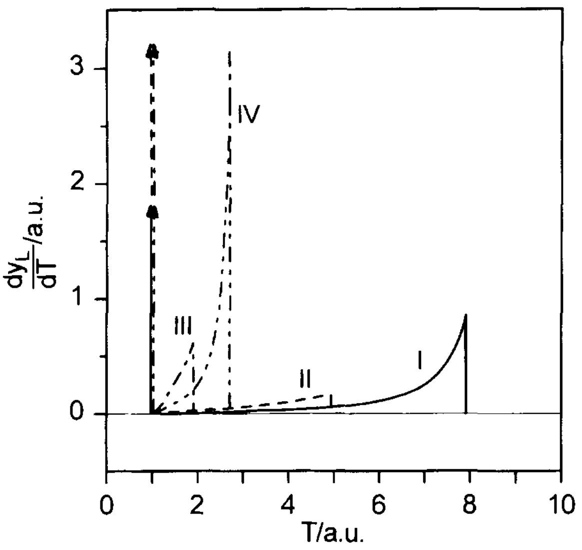


Fig. 1c

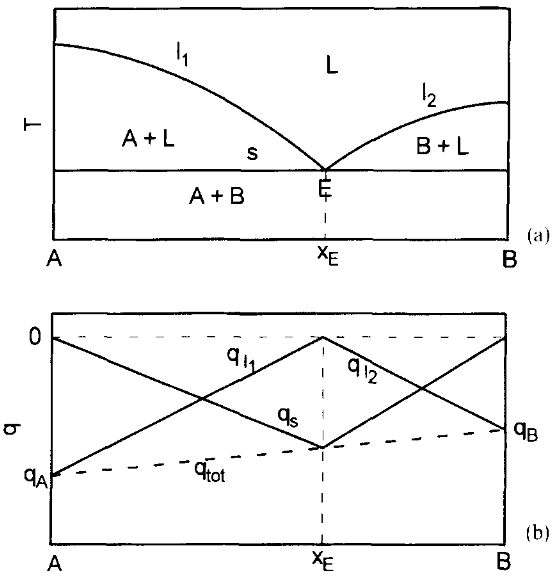


Fig. 2. a: Phase diagram of a simple binary system (schematic). b: Pertinent heats of reaction q_s and q_l, respectively (schematic). (A, B: pure phases; x_E: composition of the eutectics E).

The heat exchange between T and $T + \mathrm{d}T$ is obtained combining Eqs. (2) and (4):

$$\Delta T(t) \propto \beta \cdot \frac{\mathrm{d}y_L(T)}{\mathrm{d}T} = \beta \cdot x_B^0 \cdot \frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{1}{l(T)}\right) \quad (5)$$

(If $x_B^0 > x_B^E$, the equivalent equation $y_L(T_s) = x_A^0 + (x_B^E/x_A^E) \cdot x_A^0 = (x_A^0/x_A^E)$ and the exchange of A by B and vice versa has to be used for further calculations).

Figures 1b and 1c represent the shapes of $y_L(T)$ for four selected mixtures marked by I to IV in Fig. 1a and its derivatives $\mathrm{d}y_L(T)/(\mathrm{d}T)$, respectively. The latter are proportional to the DTA signals $\Delta T(t)$ (Eq. (2)).

As shown in Fig. 1c, the DTA signal in the liquidus region depends strongly on the composition of the mixture as well as on the shape of the liquidus l_1 or l_2. Heating the mixture I one yields a DTA signal with both, a good separability and identifiability of T_s and T_l, whereas for the mixture II a small part of the solid melts slowly within a large temperature region thus resulting in a weakly detectable DTA event. On the other hand, the rate of the melt formation is fast for the mixtures III and IV, which leads to a liquidus temperature close to T_s.

Consequently, it is sometimes difficult to determine the exact temperature of the DTA event of the liquidus and, therefore, to separate the temperatures in the surroundings of the invariant point E.

Equation (5) reveals that also the applied heating rate β may influence the detectability of the DTA events. Both the sensitivity of detection (for mixtures of type II) and the separability (for mixtures of type III) of the DTA signals are practically restricted by the finite heating rate β.

On the other hand, the change of the heat q in dependence on the composition of the initial mixture can be used for an exact analysis as proved in Fig. 2. The total heat of reaction q_{tot} is a continuous and monotonous function of the composition $x_B(x_A + x_B = 1$, sample weight $m = \mathrm{const})$. This quantity becomes a linear function if A and B are completely immiscible and if the melt behaves ideally ($\Delta_{mix}H = 0$), which is supposed in the present schematic study. As already mentioned, the total heat of reaction q_{tot} in this example can be divided for all compositions into the two parts q_s and q_l, that is $q_s + q_l = q_{tot}$. According to Eq. (3), $y_L(T_s) = 1$ is obtained for the eutectic composition $x_B^0 = x_B^E$. This mixture immediately melts at T_s and the total heat of reaction q_{tot} is completely consumed by the eutectic reaction. On the other hand, q_s becomes zero for

$x_B = 0$ and $x_B = 1$. Therefore, $q_s(x_B)$ has its maximum at $x_B = x_E$ and its minima at $x_B = 0$ and $x_B = 1$, respectively, as shown in Fig. 2. $q_s(x_B)$ is a straight line, if A and B are completely immiscible. On the other hand, $q_l(x_B)$ vanishes at the eutectic composition and becomes a maximum for the pure phases.

Consequently, an extrapolation of the heat values in dependence on the initial composition leads to a reliable estimation of the eutectic composition. This is even true in the discussed extremal cases II and III. Whereas the mixture II in Fig. 1a (slow melting rate) and the mixture III (complete melting close to T_s) may be sometimes not suitable for a quantitative DTA analysis, some mixtures in the regions near I and IV can be used to derive approximations for the $q_s(x_B)$ and $q_l(x_B)$ curves. The intersection of these lines leads to a sensitive estimation of the eutectic composition.

The extension of the described principle to more complicated systems is pointed out in Fig. 3. The compound A is assumed to be peritectically decomposed into the melt with the composition x_P and a phase C. The region $x_P - B$ in Fig. 3a leads to a dependence of the heat flow rate analogous to the simple eutectic case. Obviously, the q_p curve is broken at A because the initial phase relations are changing.

According to Eq. (1) the peak area A is proportional to the heat $q : q = K(T) \cdot A$. Therefore it is possible to use the normalized peak areas $Q = A/m$ (m = sample weight) for the quantitative analysis of heat flow rates, if $K(T)$ is constant.

In practice, the occurrence and the measuring accuracy of T_l as well as the magnitude of the area A of the DTA peak are depending moreover on the kinetic conditions of the DTA apparatus (e.g. thermal conductivity between the sample and the thermocouple) as well as the investigated chemical system (e.g. kinetic hindrances due to solid state reactions). Therefore it may be possible, that a coexistence line will be "passed", so that the pertinent DTA event does not occur, and a nonequilibrium reaction will be observed at another temperature.

3. Experiments and results

All experiments have been carried out using a thermal analyzer SETARAM TG/DTA 92 in a flowing argon – oxygen atmosphere (the oxygen content of which was controlled by a zirconia e.m.f. cell) with a flow rate of 2.5 l/h, a heating rate 10 K/min and Al_2O_3– crucibles, embedded in a Pt–crucible.

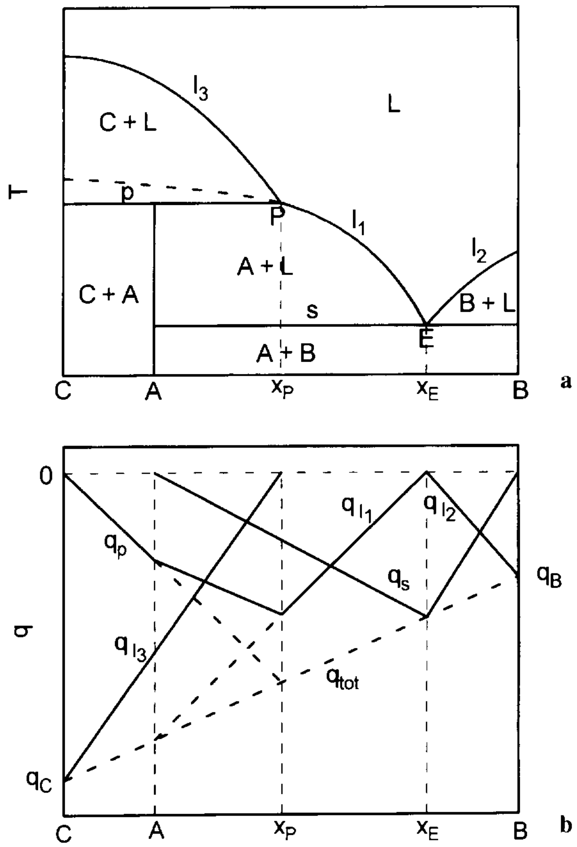


Fig. 3. a: Schematic complicated phase diagram containing an eutectics and peritectics, respectively. b: Representation of the pertinent heats of reaction q_i (schematic). (A, B, C: pure phases; x_E, x_P: compositions of the eutectics E and the peritectics P, respectively).

According to the ICTAC recommendation the extrapolated onset temperature T_e is used as the reaction temperature in this paper.

It was proved, that $K(T)$ is nearly independent of the temperature T within the investigated temperature ranges, so that the application of the normalized peak areas Q is permitted.

The applicability of the quantitative analysis of DTA heat flow rates is demonstrated for two special problems of the Y–Ba–Cu–O HTSC system, the

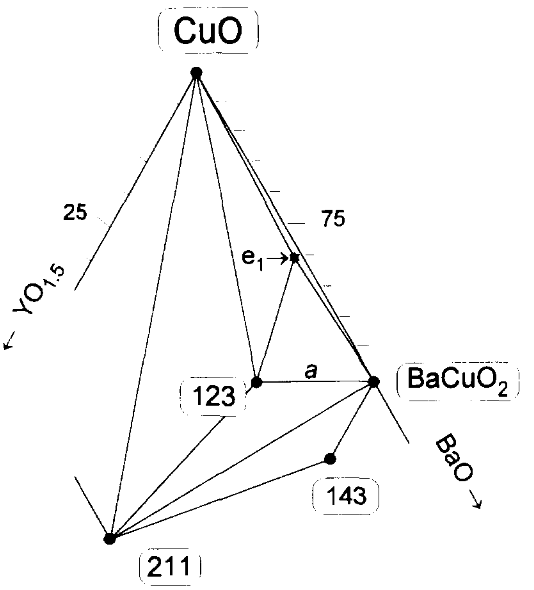


Fig. 4. Part of the Y–Ba–Cu–O phase diagram at the ternary eutectic temperature $T_e = 899°C$ and $p(O_2) = 0.21 \times 10^5$ Pa (e_1: composition of the ternary eutectics, *a*: considered section $YBa_2Cu_3O_{7-\delta}$– $BaCuO_2$).

phase diagram of which at $T = 899°C$ and $p(O_2) = 0.21 \times 10^5$ Pa is partially shown in Fig. 4 (for more detail see e.g. [1,2,3].

"The quasibinary section $YBa_2Cu_3O_{7-\delta}$–$BaCuO_2$ at $p(O_2) = 0.21 \times 10^5$ Pa." This section is an example of a complex reaction system, which has to be clarified by a combination of several methods. Within a large extent of mixtures of both phases DTA reveals three signals at almost constant temperatures (Fig. 5a). But, obviously, because of the small differences of the temperatures it is impossible to determine exactly the type and the compositions of the univariant reactions. Using the method described in section 2 the diagram Fig. 5b has been obtained and by combining Figs. 5a and 5b it became possible to develop a tentative phase diagram of the $YBa_2Cu_3O_{7-\delta}$–$BaCuO_2$ section (Fig. 5c), which had been supported by the determination of the reaction products by TG and soaking experiments.

As shown in Fig. 5b, the heat of the reaction (1) at 991°C is continuously increasing with increasing $BaCuO_2$ content up to at least 95 mol% of (1/2 $BaCuO_2$). Therefore, according to the considerations in [4] the reaction (1) is of the peritectic type and the corresponding composition (point P_a) is $x(P_a) > 95$ mol% of (1/2 $BaCuO_2$).

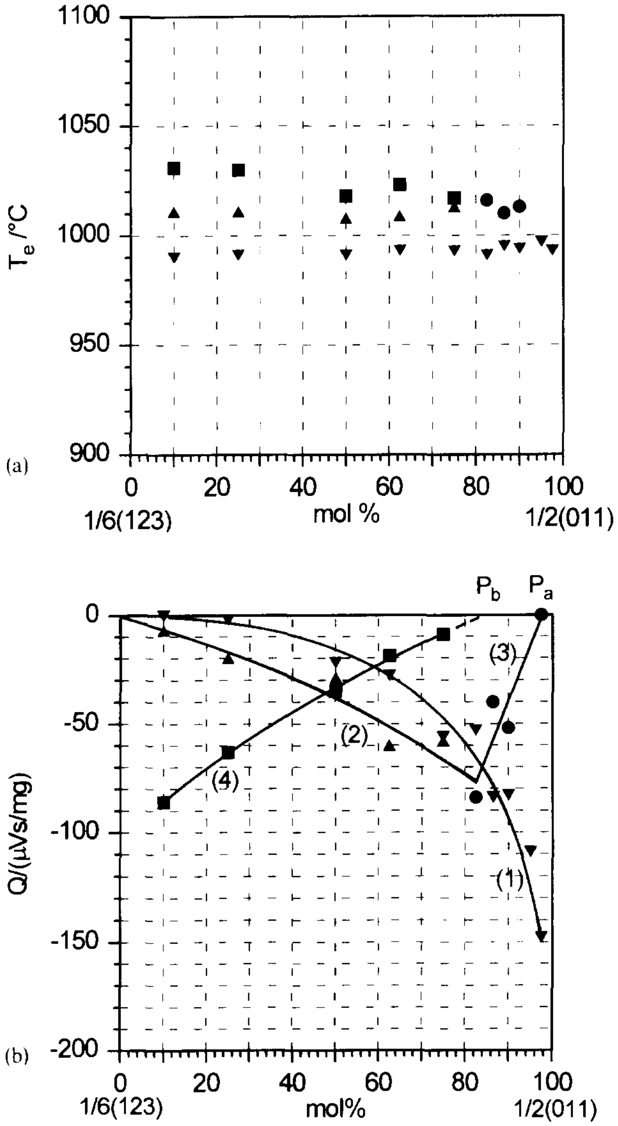
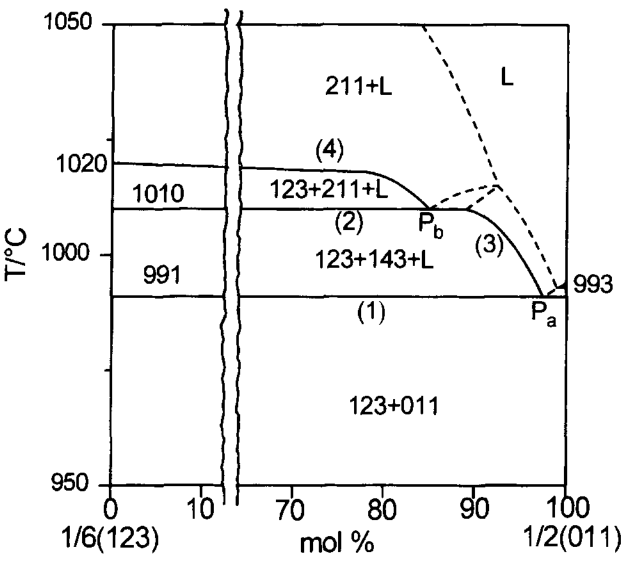


Fig. 5. Determination of the quasibinary section YBa $Cu_3O_{7-\delta}$–$BaCuO_2$ at $p(O_2) = 0.21 \times 10^5$ Pa. a: Onset temperatures T_e of the DTA heat flow rate peaks. b: Normalized DTA peak areas Q(▼: DTA events at ca. 991°C; ▲,●: DTA events at ca. 1010°C; ■: DTA events at 1010–1020°C) c: Tentative quasibinary phase diagram of the system $YBa_2Cu_3O_{7-\delta}$–$BaCuO_2$.



(c)

Fig. 5. (*Continued*).

The reactions (2) and (3) also start from zero heats at the pure $YBa_2Cu_3O_{7-\delta}$-phase and composition P_a, respectively, to have their maxima at P_b for a mixture consisting of about 85 mol% of (1/2 $BaCuO_2$) and 15 mol% of (1/6 $YBa_2Cu_3O_{7-\delta}$) as shown in Fig. 5c. Therefore, these reactions also have to be considered to be of the peritectic type. On the other hand, the heat of reaction (4) approaches to zero at the composition (P_b) but it increases with increasing $YBa_2Cu_3O_{7-\delta}$ content. Consequently, reaction (4) in Fig. 5b is based on the univariant reaction m_1 at 1020°C for pure $YBa_2Cu_3O_{7-\delta}$ [4]:

$$a\mathrm{YBa_2Cu_3O_{7-\delta}} = b\mathrm{Y_2BaCuO_5} + cL(m_1) + \mathrm{d}\mathrm{O_2}$$

However, the reaction does not remain univariant for a composition apart from the exact 1:2:3 ratio, but can be formally expressed by an equation

$$\alpha\mathrm{YBa_2Cu_3O_{7-\delta}} \rightarrow \beta\mathrm{Y_2BaCuO_5} + L(\gamma_{\mathrm{Y}}, \gamma_{\mathrm{Ba}}, \gamma_{\mathrm{Cu}}) + \delta\mathrm{O_2}$$

within the region 1010°C $< T \leq$ 1020°C and the reaction temperature of (4) must slightly decrease with decreasing $YBa_2Cu_3O_{7-\delta}$ content in the initial mixture.

"The ternary eutectics $YBa_2Cu_3O_{7-\delta}$–$BaCuO_2$–CuO at $p(O_2) = 0.21 \times 10^5$ Pa." Mixtures of these three phases melt eutectically at 899°C (see e.g. [4]):

$$a\mathrm{YBa_2Cu_3O_{7-\delta}} + b\mathrm{BaCuO_2} + c\mathrm{CuO} \rightarrow \mathrm{d}L + e\mathrm{O_2}$$

However, the composition of this ternary eutectics e_1 (Fig. 4) was known only approximately [2]. Therefore we considered the heat flow rates of several mixtures containing $YBa_2Cu_3O_{7-\delta}$, $BaCuO_2$ and CuO along two lines in the composition triangle shown in Fig. 6a. The first series of experiments (i) was performed for mixtures the overall composition of which was kept parallel to the $BaCuO_2$–CuO line with a constant concentration of the component $YO_{1.5}$ of 1.25 mol%. The heat of reaction of the eutectic peak at 899°C becomes a maximum at 28.75 mol% BaO (Fig. 6b). Exactly at the same composition the liquidus heat has its minimum which is nearly zero thus proving that the eutectic point is very close to this composition. Experiments along the line (ii) representing a constant CuO concentration and intersecting the line (i) at its extreme point prove that the above determined composition has really to be considered as the eutectic one (Fig. 6c). Consequently, the ternary eutectic composition consists of 1.25 mol $YBa_2Cu_3O_{7-\delta}$,

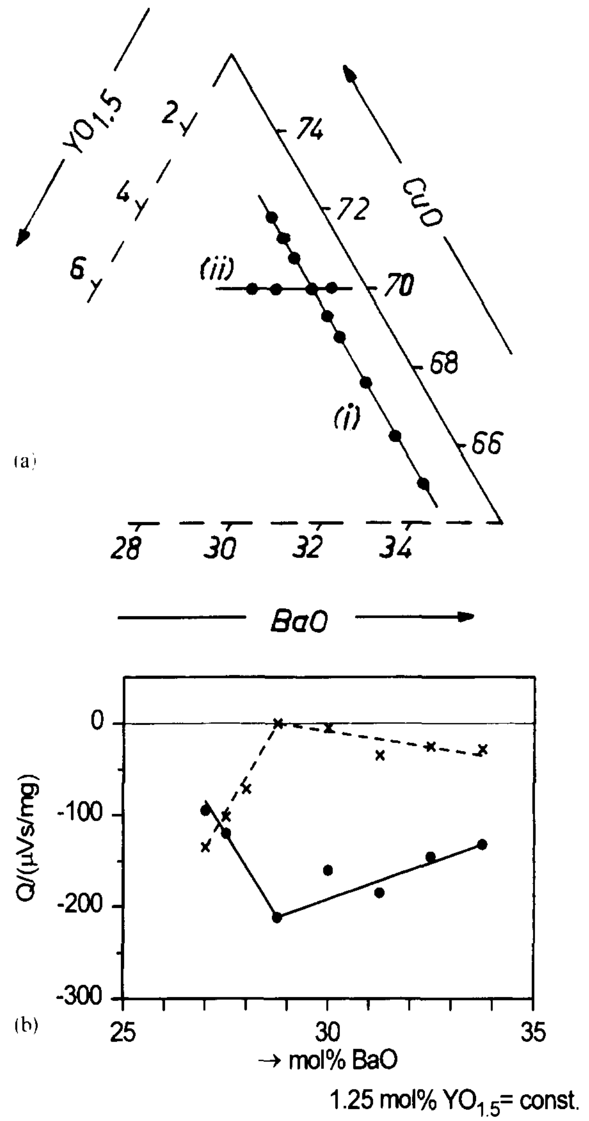


Fig. 6. Determination of the ternary eutectics in the system $YBa_2Cu_3O_{7-\delta}$–$BaCuO_2$–CuO at $p(O_2) = 0.21 \times 10^5$ Pa. a: Representation of the investigated $YBa_2Cu_3O_{7-\delta}$–$BaCuO_2$–CuO mixtures. b: Normalized DTA peak areas Q at the line containing 1.25 mol% $YO_{1.5}$ c: Normalized DTA peak areas Q at the line containing 70 mol% CuO_x (●: DTA events at ca. 899°C).

26.25 mol $BaCuO_2$ and 40 mol CuO, which corresponds to point e_1 at 1.25 mol% $YO_{1.5}$, 28.75 mol% BaO and 70 mol% CuO in the quasiternary representation of Fig. 6a.

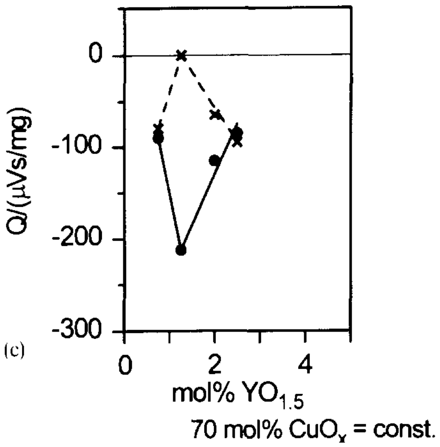


Fig. 6. (Continued)

4. Conclusions

The quantitative analysis of DTA heat flow rate measurements is an useful tool to support phase diagram investigations in complex systems. Especially in such cases where the sensitivity of determination or the separability of subsequent DTA events is too low, the proposed concept provides a clarification of the type of the considered reaction as well as a sensitive determination of the corresponding composition. Using this concept the quasibinary section $YBa_2Cu_3O_{7-\delta}$–$BaCuO_2$ and the ternary eutectics of $YBa_2Cu_3O_{7-\delta}$–$BaCuO_2$–CuO have been determined.

The authors wish to express their thanks to Mrs. B. Thaut for careful experimental work.

This paper results in part from a project granted by the Federal Minister of Education and Research (BMBF) under N° 13 N 5897 A. The support by the Fonds der Chemischen Industrie is also gratefully acknowledged.

References

[1] G. Krabbes, U. Wiesner, K. Fischer, W. Bieger and P. Schätzle, J. electronic mat., 23 (1994) 1135.

[2] T. Aselage and K. Keefer, J. Mater. Res., 3 (1988) 1279.

[3] G. Krabbes, W. Bieger, U. Wiesner, M. Ritschel and A. Teresiak, J. solid state chem., 103 (1993) 420.

[4] G. Krabbes, U. Wiesner, W. Bieger and M. Ritschel, Z. Metallkde 85 (1994) 70.