ESTIMATION OF AVERAGE HEAT CAPACITIES OF CONDENSED PHASE TRANSFORMATION PRODUCTS IN THE Y-Ba-Cu-O SYSTEM

G. Moiseev, N. Vatolin, B. Štěpánek[1] and J. Šesták[1]*

Institute of Metallurgy, Ural Division of Russian Academy of Sciences, 101 Amundsen, GSP – 812, Ekaterinburg 620219, Russian Federation
[1]Institute of Physics, Section of Solid State Physics, Academy of Sciences of the Czech Republic, 162 00 Prague 6, Czech Republic

Abstract

A method of calculation of average heat capacities of phase transformation products of complex oxides is suggested. The method takes into account the physical state of products and the increase in the heat capacities of products due to the change of entropy at a phase transformation.

Average heat capacities of products formed in a congruous melting of compounds ($YCuO_2$ and $Y_4Ba_3O_9$), in an incongruous melting of compounds ($Y_2Cu_2O_5$, $BaCuO_2$, $BaCu_2O_2$, Y_2BaCuO_5, $YBa_2Cu_3O_7$, $YBa_2Cu_3O_6$) and in a decomposition in a crystalline state of compounds (Y_2BaO_4, $Y_2Ba_2O_5$, $Y_2Ba_4O_7$, Ba_2CuO_3, $Ba_3Cu_5O_8$, $YBa_2Cu_{3.5}O_{7.5}$, $YBa_2Cu_4O_8$, $YBa_2Cu_5O_9$) was estimated by using three methods.

Keywords: heat capacity, phase transformation, Y-Ba-Cu-O system

Introduction

It is usually assumed that a heat capacity of a liquid phase bears a constant value which is equal approximately to the value of heat capacity of a crystal at the melting temperature. This simple method is widely used for an estimation of heat capacities of different melts, including oxides [1-3]. This is usually the first method which can be used for a congruous and an incongruous melting of compounds. For the second method, however, it is valid [4] that a heat capacity of a liquid phase has to include the part of the entropy change shown by the following equation:

$$C_p^{at}(1) = C_p^{at}(cr)_{T_{ph.tr.}} + \Delta S_{ph.tr.}^{at}/4, \quad J/K \cdot g\text{-atom} \tag{1}$$

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* Correspondence to: Prof. Dr. J. Šesták, Institute of Physics, Department of Semi-conductors, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 00 Prague 6, Czech Republic.

where $C_p^{at}(1)$ is a heat capacity of a liquid phase, $C_p^{at}(cr)_{T_{ph.tr.}}$ is a heat capacity of a crystal at the temperature of the phase transformation per 1 g-atom of an initial compound and $\Delta S_{ph.tr.}^{at}$ is the entropy change of a phase transformation per 1 g-atom of an initial compound.

We there suggest a third method to take into account the type of phase transformation: decomposition in a crystal state – *DCS*, congruous and incongruous melting – *CM* and *IM*, respectively, as well as compositions, properties of phase transformation products and also the increment of the average heat capacity of products assuming Eq. (1).

By the application of all three methods we can determine the average heat capacities of products of *DCS* (Y_2BaO_4, $Y_2Ba_2O_5$, $Y_2Ba_4O_7$, Ba_2CuO_3, $Ba_3Cu_5O_8$, $YBa_2Cu_{3.5}O_{7.5}$, $YBa_2Cu_4O_8$, $YBa_2Cu_5O_9$), *IM* ($Y_2Cu_2O_5$, $BaCuO_2$, $BaCu_2O_2$, Y_2BaCuO_5, $YBa_2Cu_3O_7$, $YBa_2Cu_3O_6$) and *CM* ($YCuO_2$ and $Y_4Ba_3O_9$). In this way the results and data obtained earlier [5] are discussed.

Methods of calculation

The first method does not need any detailed explanations. It is just necessary to use known dependencies $C_p(i)=f(T)$ [6] and $T_{ph.tr.}$ [7] of compounds and to calculate the values of C_p at $T=T_{ph.tr.}$. These values, as supposed, are equal to the centered values $C_p(1)$.

For the second method, besides of knowing $C_p(i)=f(T)$ and $T_{ph.tr.}$, it is necessary to get the values of $\Delta S_{ph.tr.}$, e.g. from Ref. [8].

We would like to explain in more details the third method:

Decomposition of a crystalline state

Hypothetical oxide $A_aB_bC_cO_y$ at $T=T_{DCS}$ can be decomposed accordingly to the schema:

$$A_aB_bC_cO_y \ (cr) = A_aB_bO_m \ (cr) + C_cO_{y-m} \ (cr) \qquad (2)$$
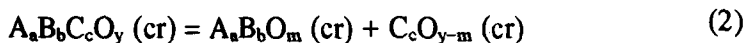
The average heat capacity of products per 1 g-atom ($\overline{C}_p^{at}$) can then be calculated by an equation valid for the dimension of J/K g-atom:

$$\overline{C}_p^{at} = C_p^{at} \ (A_aB_bO_m) \cdot N(A_aB_bO_m) + C_p^{at}(C_cO_{y-m}) \cdot N(C_cO_{y-m}) +$$

$$+ \tfrac{1}{4}\Delta S_{dcs}^{at} \ (A_aB_bC_cO_y). \qquad (3)$$

Here $C_p^{at}(i)$ is a heat capacity of i-th oxide at $T=T_{DCS}$, N(i) is a molar fraction of i-th oxide in a mixture of products, ΔS_{DCS}^{at} is the entropy change at $T=T_{DCS}$
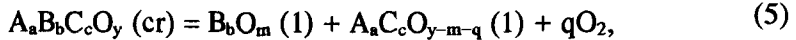
for an initial complex oxide. The molar average heat capacity of the phase transformation products can be calculated from the relation:

$$\overline{C}_p = \overline{C}_p^{at} \cdot n, \tag{4}$$

where n is a number of atoms in a molecule of an initial compounds.

Incongruous melting

There are two principal variants of phase transformation:

$$A_aB_bC_cO_y \ (cr) = B_bO_m \ (l) + A_aC_cO_{y-m-q} \ (l) + qO_2, \tag{5}$$

where i.e. a crystal, a liquid phase and oxygen can be formed and

$$A_aB_bC_cO_y \ (cr) = A_aO_m \ (l) + B_bC_cO_{y-m-q} \ (l) + qO_2, \tag{6}$$

where i.e. two unmixed liquids and oxygen can be formed.

For this variant we decided to use the next equations, J/K g-atom:

$$\overline{C}_p^{at} \cong C_p^{at} \ [B_bO_m(cr)] \cdot N[B_bO_m(cr)] +$$

$$+ C_p^{at}[A_aC_cO_{y-m-q}(l)] \cdot N[A_aC_cO_{y-m-q}(l)], \tag{7}$$

and

$$\overline{C}_p^{at} \cong C_p^{at} \ [A_aO_m(l)] \cdot N[A_aO_m(l)] +$$

$$+ C_p^{at}[B_bC_cO_{y-m-q}(l)] \cdot N[B_bC_cO_{y-m-q}(l)]. \tag{8}$$

The molar average heat capacity can be calculated from the Eq. (4).

The meaning of terms in the Eqs (5–8) was explained before. It is necessary to add that the determination of $C_p^{at}[i(l)]$ is carried out by the Eq. (1), for example using J/K g-atom dimension:

$$\overline{C}_p^{at} \ [A_aO_m(l)] = C_p^{at} \ [A_aO_m(cr)]_{T=T_{CM}} + \tfrac{1}{4}\Delta S_{CM}^{at} \ [A_aO_m(cr)] \tag{9}$$

Congruous melting

This phase transformation can be described by the reaction:

$$A_aB_bC_cO_y \ (cr) = A_aB_bC_cO_y \ (l) \cong A_aO_m \ (l) + B_bO_n \ (l) + C_cO_{y-m-n} \ (l), \tag{10}$$
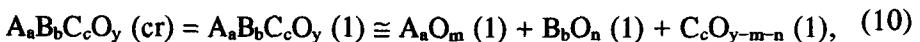
and the average heat capacity by:

$$\overline{C}_p^{at} = C_p^{at} [A_aO_m(1)] \cdot N[A_aO_m(1)] + C_p^{at} [B_bO_n(1)] \cdot N[B_bO_n(1)] +$$

$$+ C_p^{at}[C_cO_{y-m-n}(1)] \cdot N[C_cO_{y-m-n}(1)]. \tag{11}$$

For every constituent part of a liquid phase the $C_p^{at}[i(1)]$ must be calculated in analogy with Ref. [9]. The molar heat capacity can be found through the Eq. (4).
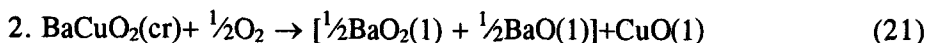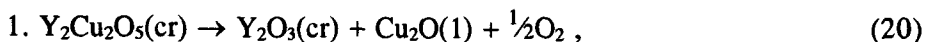
The above mentioned method takes into account the type of the phase transformation, composition, ratio, physical states and properties of phase transformation products as well as the increasing values of $\overline{C}_p^{at}(J)$ due to the entropy change at phase transformation.

For compounds of the Y–Ba–Cu–O system the information was taken from Refs [6–8] and for simple oxides from Refs [3, 9, 10]. Reactions of the phase transformations were taken accordingly to Ref. [8] and are described as follows:

Decomposition in a crystalline state

1. $Y_2BaO_4(cr) \rightarrow \frac{1}{3}Y_2O_3(cr) + \frac{1}{3}Y_4Ba_3O_9(cr)$ (12)

2. $Y_2Ba_2O_5(cr) \rightarrow \frac{2}{3}Y_2BaO_4(cr) + \frac{1}{3}Y_2Ba_4O_7(cr)$ (13)

3. $Y_2Ba_4O_7(cr) \rightarrow \frac{5}{2}BaO(cr) + \frac{1}{2}Y_4Ba_3O_9(cr)$ (14)

4. $Ba_2CuO_3(cr) \rightarrow BaCuO_2(cr) + BaO(cr)$ (15)

5. $Ba_3Cu_5O_8(cr) \rightarrow 3BaCuO_2(cr) + 2CuO(cr)$ (16)

6. $YBa_2Cu_{3.5}O_{7.5}(cr) \rightarrow YBa_2Cu_3O_7(cr) + \frac{1}{2}CuO(cr)$ (17)

7. $YBa_2Cu_4O_8(cr) \rightarrow YBa_2Cu_3O_7(cr) + CuO(cr)$ (18)

8. $YBa_2Cu_5O_9(cr) \rightarrow YBa_2Cu_3O_7(cr) + 2CuO(cr).$ (19)

Incongruous melting

1. $Y_2Cu_2O_5(cr) \rightarrow Y_2O_3(cr) + Cu_2O(1) + \frac{1}{2}O_2$, (20)

2. $BaCuO_2(cr) + \frac{1}{2}O_2 \rightarrow [\frac{1}{2}BaO_2(1) + \frac{1}{2}BaO(1)] + CuO(1)$ (21)
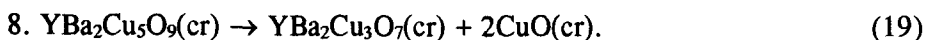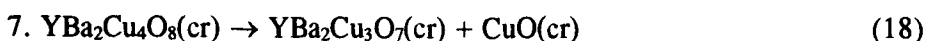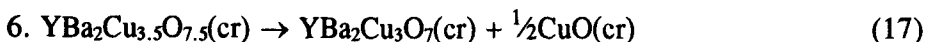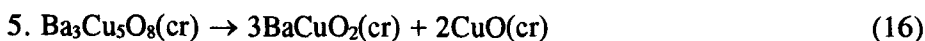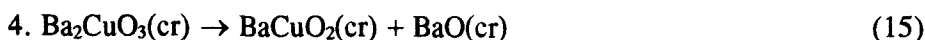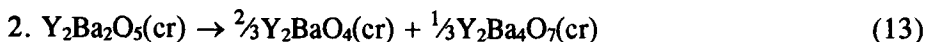
where it was supposed that two unmixed liquids can be found formed;

3. $BaCu_2O_2(cr) \rightarrow Cu(1) + BaCuO_2(1),$ (22)
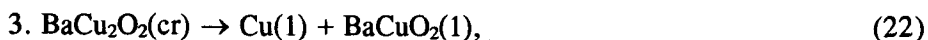
where two unmixed liquids can be also formed.

$$4.\ Y_2BaCu_4O_5(cr) \rightarrow Y_2O_3(cr) + BaCuO_2(l), \tag{23}$$

$$5.\ YBa_2Cu_3O_7(cr) \rightarrow \tfrac{1}{2}Y_2O_3(cr) + [2BaCuO_2(l)+CuO(l)]+\tfrac{1}{2}O_2, \tag{24}$$

$$6.\ YBa_2Cu_3O_7(cr) \rightarrow \tfrac{1}{2}Y_2O_3(cr)+ [2BaCuO_2(l)+CuO(l)]+\tfrac{1}{2}Cu_2O(l)] \tag{25}$$

Congruous melting

$$1.\ YCuO_2(cr) \rightarrow 1/2\ Y_2O_3(l) + \tfrac{1}{2}Cu_2O(l), \tag{26}$$

$$2.\ Y_4Ba_3O_9(cr) \rightarrow 2Y_2O_3(l)+3BaO(l). \tag{27}$$
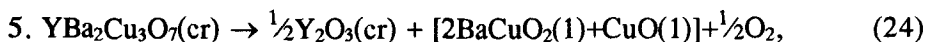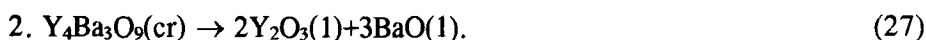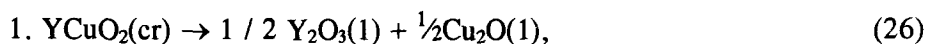
The results of calculation of the molar $\overline{C}_p(J)$ by three methods are given in Table 1.

Results and discussion

From Table 1 it is possible to see that there are differences between the values of $\overline{C}_p(J)$, calculated by these three methods applied to the same compounds. As we supposed the values of $\overline{C}_p(J)$ by the second method (II) are slightly higher than that calculated by the first one (I). We can presume that the values of $\overline{C}_p(J)$ (II) are more correct than $\overline{C}_p(J)$ (I). Although the comparison $\overline{C}_p(J)$ of (III) with $\overline{C}_p(J)$ (II) shows a different sign of deviations. The average maxim. deviation is not more than 4%. The deviation for $Ba_3Cu_5O_8$, $YBa_2Cu_4O_8$ and $YBa_2Cu_3O_6$ are rather considerable which is likely connected with the nature and properties of the phase transformation products and with an application of more correct way of the estimation. In general we can consider that the data of $\overline{C}_p(J)$ (III) are more correct than the other. Such data are needed for an experimental control, as we are not able to take into account all errors of the investigation of phase transformation characteristics (compositions, T and $\Delta H_{ph.tr.}$) and functions $C_p=f(T)$ [6–8]. The agreement of $\overline{C}_p(J)$ data calculated by different methods is a verification of data published in Refs [6–8]. For the apriori estimation the methods I–II can be conveniently used.

According to the empirical rule [3] at $T=T_{melting}$ the $\overline{C}_p^{at}(i)$ for crystalline compounds are equal 30.32 ± 2.1 J/K.g-atom. We employed all $\overline{C}_p^{at}$ values as calculated by I–III methods, and they averaged to $\overline{C}_p^{at} = 28.74\pm0.0602$ J/K g-atom for DSC-compounds and to $\overline{C}_p^{at}=31.166\pm0.166$ J/K g-atom for IM and *CM*-compounds. It follows that our data are in good agreement with the empiric law [3] although we have established certain differences in $\overline{C}_p^{at}$ value for *DCS*

Table 1 Average heat capacities of phase transformation products ($\overline{C}_p$) for some compounds in the Y–Ba–Cu–O system

N°	Compound	$T_{\text{ph. tr.}}/K$ and type of ph. tr.	$\overline{C}_p$ / $J \cdot K^{-1} \cdot mol^{-1}_{\text{initial compound}}$			Differences/ % between $\overline{C}_p(III)$ and $\overline{C}_p(II)$
			I. method	II. method	III. method	
1	2	3	4	5	6	7
1	Y_2BaO_4	1673, DCS	198.27	199.70	198.37	−0.67
2	$Y_2Ba_2O_5$	1313, DCS	254.70	256.65	249.28	−2.87
3	$Y_2Ba_4O_7$	1413, DCS	367.40	372.35	386.75	+3.87
4	Ba_2CuO_3	1123, DCS	176.30	177.32	176.00	−0.74
5	$Ba_3Cu_5O_8$	1073, DCS	473.72	474.48	445.05	−6.20
6	$YBa_2Cu_{3.5}O_{7.5}$	1190, DCS	404.16	409.08	416.60	+1.83
7	$YBa_2Cu_4O_8$	1110, DCS	404.05	406.17	445.80	+9.75
8	$YBa_2Cu_5O_9$	1023, DCS	478.50	480.55	498.20	+3.67
9	$Y_2Cu_2O_5$	1428, IM	260.50	260.80	265.14	+1.66
10	$BaCuO_2$	1318, IM	123.23	128.50	122.46	−4.70
11	$BaCu_2O_2$	1500, IM	158.60	165.65	163.76	−1.14
12	Y_2BaCuO_5	1543, IM	258.00	264.60	262.00	−0.98
13	$YBa_2Cu_3O_7$	1288, IM	382.90	404.37	418.10	+3.40
14	$YBa_2Cu_3O_6$	1470, IM	410.90	411.00	362.12	−11.90
15	$YCuO_2$	1843, CM	117.28	131.55	125.60	−4.52
16	$Y_4Ba_3O_9$	2433, CM	510.33	535.65	510.18	−4.75
						$|\overline{\delta}| = 3.92\%$

and *IM*, *CM*-compounds. It can be found useful for an estimation of $\overline{C}_p(i)$ of compounds at $T = T_{ph.tr.}$ when type of the phase transformation is known.

The molar values of $\overline{C}_p(i)$ at $T=T_{ph.tr.}$ for some substances of the Y–Ba–Cu–O system in the work [5] were given. This data were obtained by the supposition of only *CM*-type of phase transformation. Therefore values $\overline{C}_p(i)$ at $T=T_{ph.tr.}$ for compounds in the Y–Ba–Cu–O system, published in [5], are not completely correct.

Conclusion

A new method of the calculation of the average heat capacity of phase transformation products $[\overline{C}_p(i)]$ was suggested and it have been used for an analysis of the compounds of the Y–Ba–Cu–O system.

It was shown that suggested method of the calculation gives the values of $\overline{C}_p(i)$ in a good agreement with $\overline{C}_p(i)$, obtained by known methods the values calculated by this method are more precise. It was shown also that the data of $\overline{C}_p(1)$, obtained by the authors earlier [5, 13] must be corrected.

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Zusammenfassung — Es wird eine Methode zur Berechnung von mittleren Wärmekapazitäten der Phasenumwandlungsprodukte von Komplexoxiden vorgeschlagen. Diese Methode berücksichtigt den physikalischen Zustand der Produkte und das wegen der Entropieänderung während der Phasenumwandlung eintretende Ansteigen der Wärmekapazitäten der Produkte.

Mittels drei Methoden wurden die mittleren Wärmekapazitäten von Produkten geschätzt, die bei einem kongruenten Schmelzen der Verbindungen $YCuO_2$ und $Y_4Ba_3O_9$, bei einem inkongruenten Schmelzen der Verbindungen $Y_2Cu_2O_5$, $BaCuO_2$, $BaCu_2O_2$, Y_2BaCuO_5, $YBa_2Cu_3O_7$, $YBa_2Cu_3O_6$ und bei der Zersetzung im kristallinen Zustand der Verbindungen Y_2BaO_4, Y_2O_5, $Y_2Ba_4O_7$, Ba_2CuO_3, $Ba_3Cu_5O_8$, $YBa_2Cu_{3.5}O_{7.5}$, $YBa_2Cu_4O_8$, $YBa_2Cu_5O_9$ entstanden.