

THERMODYNAMIC CHARACTERIZATION OF MULLITE

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Giving advantage to the $2.762 \text{ Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ -formula and applying the phase equilibrium criterion, to the discrete points at the mullite liquidus curve, two sets of ΔG -values of mullite were calculated, by using two mathematical models, for the temperature interval 1860–2122 K as well as the composition range 5–50 mol% Al_2O_3 in the Al_2O_3 - SiO_2 - system. ΔG -values for $3 \text{ Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ - formula were presented too. The most probable set of ΔG -values was selected and a correlation between the Gibbs free energy of mullite and temperature was suggested, after adopting both referent state enthalpy and entropy. Also, the parameters in the specific heat function were obtained, as a result of the correlating procedure.

INTRODUCTION

Mullite is one of the compounds in the Al_2O_3 – SiO_2 - system, which is very important in variety of ceramic products. It can be regarded to as a solution of cristobalite in corundum, according to Howald and Eliezer [1]. As far as mullite composition is concerned, there is no unique formula. It has caused serious problems in determining its thermodynamic properties. They can be found in JANAF tables [2], widely used source of data. However, a basis for all there presented values is the $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ - formula of mullite, recently found questionable. Thermodynamic properties given in Babushkin's tables [3] are even less precise than the JANAF ones and rather out-of-date.

Many experimental investigations on the Al_2O_3 – SiO_2 - system were employed for presenting phase diagrams, which also are useful sources of thermodynamic properties. From great number of published references, here will be cited only two [4, 5]. Finally, appearance of immiscibility gap, in the mullite region of the phase diagram, far below the liquidus temperatures, was noticed by many authors [6–8]. Such metastable equilibria were investigated experimentally as well as by applying some thermodynamic methods. Also, number of thermodynamic models have been developed, for predicting and better understanding of the Al_2O_3 – SiO_2 - system behaviour [9, 10].

The aim of this paper is to suggest the Gibbs free energy of the $2.762 \text{ Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ -mullite as a function of temperature for the interval 1860–2122 K and the composition range 5–50 mol% Al_2O_3 . The function was obtained by processing the G - values, calculated from solid- liquid- equilibria. It has been assumed that the solid phase do not change its composition, while the liquid phase behaves as a non- ideal solution. Also, the specific heat function of the same mullite was defined.

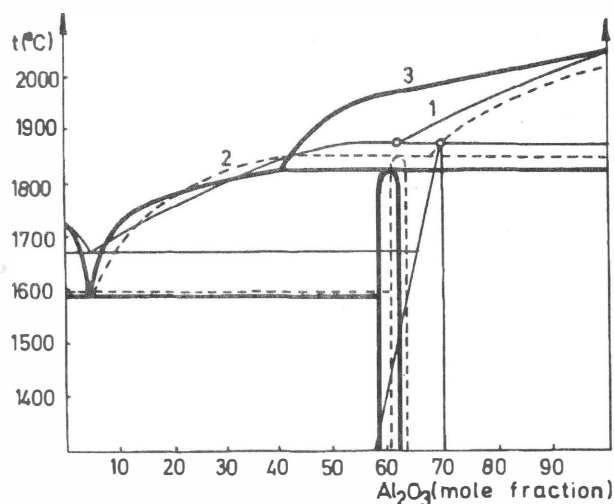
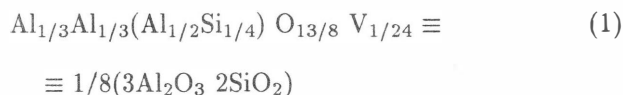


Fig. 1. Presentation of Various Mullite Liquidus Lines
References: line 1 [4], line 2 [5], line 3 [8]

About Mullite Formula

The ideal mullite crystal structure has one octahedral site and two different tetrahedral sites, all equally occupied with metal atoms. So, the idealized formula for a mullite would be:



where V- denotes necessary oxygen vacancies.

Howald and Eliezer [1] suggested incongruent melting point of mullite at 2123 K, very close to the composition of nominal 3:2-formula. Mullite from JANAF tables [2] is based on the same composition as well as mullite included in Babushkin's book [3]. Early result of Welch [4] (line 1 in Fig. 1.) suggests 3:2-type of

mullite, but when temperature rises the composition approximates to 2:1-formula rather than 3:2-formula. Welch's version was improved by many investigators; Aramaki and Roy [5] were probably the most cited authors, at that time. They decreased the eutectic temperature and improved slightly the mullite composition (line 2 in Fig. 1). However, some experimental evidences make theoretical formula questionable. These evidences have to be (and are) taken into account.

Since Haller et al. [6] have proposed the use of SiO₂ or B₂O₃ multimers to satisfy the shape of experimentally reported miscibility gaps, in the SiO₂-B₂O₃-system, the same idea has been accepted in researching on other systems as well. So, Aksay and Pask [7] considered a few stable and metastable binary phase relations in the Al₂O₃-SiO₂-system. Which formula of mullite should be accepted was answered by Risbud and Pask [8] who analyzed some alternative pseudo-binary systems (in the range 40–100 mol% Al₂O₃) and compared the calculated miscibility gaps with the experimental results showing that the 2.762 Al₂O₃ 2SiO₂-formula is the most likely to be accurate (line 3 in Fig. 1). We come to the same conclusion.

THERMODYNAMIC CHARACTERIZATION OF MULLITE

(A) Theoretical Background

When an oxide-compound melts, it dissociates giving a liquid solution with the constituent oxides as components:



Under the assumption that the solution is non-ideal one, its Gibbs free energy can be expressed as:

$$\begin{aligned} \Delta G_{z_1 \text{Al}_2\text{O}_3 \ z_2 \text{SiO}_2}^1 &= \\ &= z_1 (\Delta G_{\text{Al}_2\text{O}_3}^1 + RT \ln x_{\text{Al}_2\text{O}_3} + RT \ln \gamma_{\text{Al}_2\text{O}_3}) + \\ &+ z_2 (\Delta G_{\text{SiO}_2}^1 + RT \ln x_{\text{SiO}_2} + RT \ln \gamma_{\text{SiO}_2}) \end{aligned} \quad (3)$$

where the terms which take into account composition of the liquid phase are due to the entropy increase (during a mixing process) and the terms which take into account activities are due to the non-ideal behaviour of the solution.

Thermodynamics defines a necessary condition for the solid-melt equilibrium as an equality between the Gibbs free energy of each solid compound (in equilibrium with melt) and the Gibbs free energy of its melt. It is as follows:

$$\Delta G_{z_1 \text{Al}_2\text{O}_3 \ z_2 \text{SiO}_2}^s = \Delta G_{z_1 \text{Al}_2\text{O}_3 \ z_2 \text{SiO}_2}^l \quad (4)$$

where exponents s- and l- denote solid and liquid phase.

Gibbs free energy of any compound, at any specified temperature T , can also be expressed by the equation:

$$\begin{aligned} \Delta G^T &= \Delta H_{T_0}^0 + \int_{T_0}^T C(T) dT - TS^0 - \\ &- \int_{T_0}^T \frac{C(T) dT}{T} \end{aligned} \quad (5)$$

Mostly, three types of $C(T)$ -functions can be found:

$$C(T) = a + cT^{-2} + fT^{-0.5} + hT^{-1} \quad (6a)$$

$$C(T) = a + b(T - 1000) + c(T - 1000)^2 \quad (7a)$$

$$C(T) = a + bT + cT^{-2} \quad (8a)$$

whose integration, in accordance with the equation (5), gives following three $\Delta G(T)$ -functions:

$$\Delta G^T = \Delta H_{T_0}^0 - TS^0 + a[(T - T_0) - \quad (6b)$$

$$-T \ln(T/T_0)] + c[1/2T(1/T^2 - 1/T_0^2) -$$

$$-(1/T - 1/T_0)] + f[2(T^{0.5} - T_0^{0.5}) +$$

$$+ 2T(1/T^{0.5} - 1/T_0^{0.5})] +$$

$$+ h[\ln(T/T_0) + T(1/T - 1/T_0)]$$

$$\Delta G^T = \Delta H_{T_0}^0 - TS^0 + a[(T - T_0) - \quad (7b)$$

$$-T \ln(T/T_0)] + b[1/2(T^2 - T_0^2) - (T - T_0)(10^3 + T) +$$

$$+ 10^3 T \ln(T/T_0)] + c[1/3(T^3 - T_0^3) -$$

$$- 1/2(T^2 - T_0^2)(2 \times 10^3 + T) +$$

$$+ (T - T_0)(10^6 + 2 \times 10^3 T) - 10^6 T \ln(T/T_0)]$$

$$\Delta G^T = \Delta H_{T_0}^0 - TS^0 + a[(T - T_0) - \quad (8b)$$

$$-T \ln(T/T_0)] + b[1/2(T^2 - T_0^2) - T(T - T_0)] +$$

$$+ c[1/2T(1/T^2 - 1/T_0^2) - (1/T - 1/T_0)]$$

Deriving of the Gibbs free energy of mullite (as a function of x and T) is based on the equations (4) and (5).

(B) Numerical procedure

The aim of the calculations is to find ΔG_{MULL}^s -values from the data along the liquidus curve as well as to define a correlation between these values and

Table I
Data for ΔG - liquid Calculations

Comp.	Ref.	Thermodynamic Data		
		ΔH_{298}° (J/mol)	S_{298}° (J/mol K)	$C(T)$ (J/mol K)
Al_2O_3^1	9	$\Delta H_{298}^{\circ} = -1\,584\,090$	$S_{298}^{\circ} = 52$	$C(T) = 143.415$
	10	$\Delta H_{298}^{\circ} = -1\,648\,998$	$S_{298}^{\circ} = 52$	$C(T) = 189.392 + 39.632 \times 10^{-3}(T - 1000) - 24.77 \times 10^{-6}(T - 1000)^2$
SiO_2^1	9	$\Delta H_{298}^{\circ} = -906\,608$	$S_{298}^{\circ} = 45.535$	$C(T) = 117.432 - 1\,769\,104T^{-2} - 1200.86T^{-0.5}$
	10	$\Delta H_{298}^{\circ} = -902\,656$	$S_{298}^{\circ} = 45.535$	$C(T) = 69.4962 + 13.501 \times 10^{-3}(T - 1000) + 5.1815 \times 10^{-6}(T - 1000)^2$

the liquid phase temperatures. The procedure is as follows: Gibbs free energies of particular components (Al_2O_3 and SiO_2), in the liquid phase at discretely given liquidus temperatures, should be determined from eq. (6b) or (7b). The obtained values should be substituted in the condition (4), together with the terms which represent composition and activity influence.

Once evaluated values of the Gibbs free energy of mullite can serve to the regression analysis, whose result will be the correlation between the ΔG -values and temperatures.

(C) Results of the ΔG_{MULL}^s
Calculations

When applying equations (2)–(4) to mullite, which contains 2.762 moles of Al_2O_3 and 2 moles of SiO_2 , following expression for the ΔG_{MULL}^s -calculations appears:

$$\begin{aligned} \Delta G_{\text{MULL}}^s = & \quad (9) \\ & = 2.762(\Delta G_{\text{Al}_2\text{O}_3}^l + RT \ln x_{\text{Al}_2\text{O}_3} + RT \ln \gamma_{\text{Al}_2\text{O}_3}) + \\ & + 2(\Delta G_{\text{SiO}_2}^l + RT \ln x_{\text{SiO}_2} + RT \ln \gamma_{\text{SiO}_2}) \end{aligned}$$

The calculations can be carried out when the Gibbs free energy of liquid components (Al_2O_3 and SiO_2), composition of the sub-system SiO_2 -mullite (along the mullite liquidus) as well as activity coefficients of both components (at various temperatures) are known.

$\Delta G_{\text{Al}_2\text{O}_3}^l$ and $\Delta G_{\text{SiO}_2}^l$ are calculated by using two models; (6b) – introduced by Berman and Brown [9] and (7b) – offered by Do et al. [10], i.e. models from two sources have been employed, so that a test of their adequateness can be done. In order to preserve consistency, data values (presented in Table I) were applied to particular models as suggested by their authors [9, 10]. Composition at the mullite liquidus curve was obtained from the phase diagram (line 3 in Fig. 1).

As for the activity coefficients, Margules polynomials were taken in the form [9]:

$$\begin{aligned} RT \ln \gamma_{(\text{SiO}_2 \equiv 1)} = & \quad (10) \\ & = x_2^2 \{ [3(B_1 - B_2) + 2B_2] x_1 + B_3(1 - 3x_1)x_2 \} \end{aligned}$$

$$\begin{aligned} RT \ln \gamma_{(\text{Al}_2\text{O}_3 \equiv 2)} = & \\ & = x_1^2 \{ [3(B_3 - B_2)x_2 + 2B_2] x_2 + B_1(1 - 3x_2)x_1 \} \end{aligned}$$

where B -coefficients are given by [9]:

$$\begin{aligned} B_1 = & 63617.160 - T \times 23.740 & (11) \\ B_2 = & 1642663.510 - T \times 763.870 \\ B_3 = & -106635.220 + T \times 28.130 \end{aligned}$$

As a result of the phase equilibrium application, two sets of ΔG_{MULL}^s values were estimated and presented in Table II; first set was obtained by using Berman's model and data while second set appeared when the model and data revised by Do were used.

Table II
Calculated Gibbs Free Energy by Using the Data from Different Sources

No of point	Liquidus temp. (K)	ΔG_1 (J/mol) Data 9	f_1^* (%)	ΔG_2 (J/mol) Data 10	f_2^* (%)	ΔG_3 (J/mol) Data 3
0	298**	-6 509 592	94.3	-6 507 064	94.2	-6 905 802
1	1860	-7 765 584	95.4	-8 098 052	99.5	-8 140 832
2	1953	-7 854 492	95.2	-8 204 419	99.5	-8 247 337
3	1998	-7 884 431	95.0	-8 243 069	99.3	-8 299 788
4	2013	-7 881 554	94.8	-8 243 133	99.1	-8 317 402
5	2025	-7 879 811	94.6	-8 243 757	99.0	-8 331 540
6	2048	-7 887 137	94.4	-8 255 647	98.9	-8 358 751
7	2059	-7 885 851	94.2	-8 256 562	98.6	-8 371 818
8	2079	-7 906 416	94.2	-8 281 149	98.6	-8 395 663
9	2090	-7 916 486	94.1	-8 293 445	98.6	-8 408 825
10	2101	-7 929 362	94.2	-8 308 557	98.6	-8 422 021
11	2115	-7 948 600	94.2	-8 330 654	98.7	-8 438 863
12	2122	-7 957 977	94.2	-8 341 467	98.7	-8 447 306

* Fraction of ΔG_i ($i = 1, 2$), if ΔG_3 (for 3:2 mullite) is taken as 100%

** Referent state (1 bar, 298 K)

Also, equation (8b), applied to Babushkin's data (for 3:2 mullite), gave the last column in Table II, as for an illustration of early investigations on mullite. Comparative presentation of all three sets of calculated ΔG -values can be seen in Fig. 2.

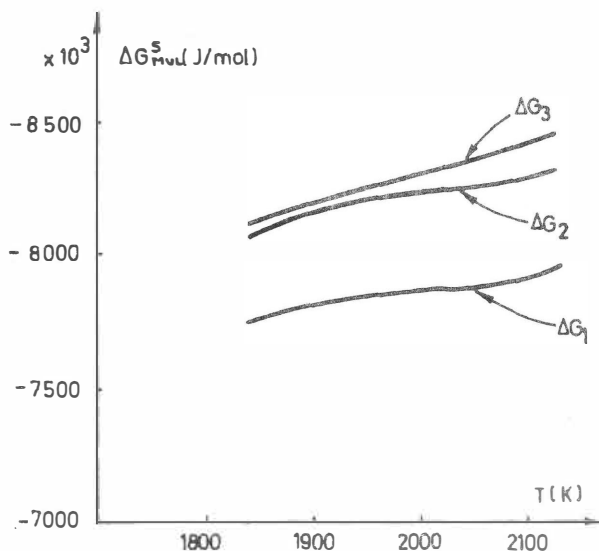


Fig. 2. Gibbs Free Energy of Mullite Calculated by Using Models and Data from Different Sources Legend: ΔG_1 -model and data [9], ΔG_2 -model and data [10], ΔG_3 -model and data [3]

With the ΔG -values, calculated along the liquidus of mullite, the Gibbs free energies at the referent state have been associated. In the case of 2.762:2- mullite, the referent values of both ΔG_1 and ΔG_2 were obtained by linear combining of the constitutional compounds data (presented in Table III). For example:

$$\begin{aligned}
 (\Delta G_1)_{\text{REF}} &= -6\,509\,595 = \\
 &= 2.763(-1\,689\,555) + 2(-921\,522)
 \end{aligned}$$

Referent data for 3:2- mullite were taken from Babushkin [3].

From Table II it is obvious that the calculated ΔG -values of mullite significantly depend on liquid components data. It seems that Berman's data are more correct than those given by Do; therefore ΔG_1 -column will be chosen for a correlating procedure, based on equation (6b) as a mathematical model. The correlating procedure was applied with the aim to determine the value of the last parameter in the heat capacity equation (h), while the values of remaining three parameters (a, c and f) were estimated as the linear combination of adequate parameters of the constitutional compounds (corundum and cristobalite), as presented in the last row in Table IV.

In this way some kind of thermal characterization of mullite was achieved. Its specific heat capacity in terms of temperature was presented in Fig. 3, where the heat capacities of mullite, taken from few sources, were presented as well.

Table III
Referent State Data

Comp.	Ref.	Thermodynamic Data		
		ΔH_{298}° (J/mol)	S_{298}° (J/mol K)	$\Delta G_{298}^{\circ} = \Delta H_{298}^{\circ} - 298S_{298}^{\circ}$
Al ₂ O ₃ ^s	9	-1 674 411	50.82	-1 689 555
SiO ₂ ^s		-908 522	43.625	-921 522
Al ₂ O ₃ ^s	10	-1 675 692	50.82	-1 690 836
SiO ₂ ^s		-905 489	43.625	-918 489
Mull	9	-6 441 767	227.6	-6 509 595
2.762:2	10	-6 439 239	227.6	-6 507 067.5
Mull 3:2	3	-6 829 961	254.5	-6 905 802

Table IV
Heat Capacity Data

Compound	a	c	f	h
Al ₂ O ₃ ^s (corundum)	152.724	-852 486	-522.58	-10 067.9
SiO ₂ ^s (cristobalite)	82.196	-	-	-11 333.6
Mullite (average)*	586.216	-2 354 566	-1 443.37	-50 474.8
Mullite (optimal)**	586.216	-2 354 566	-1 443.37	-36 930.8

* a, c, f and h calculated as linear combinations

** a, c and f as previous; h obtained by the Least square method

Taking all facts (about the referent state of mullite as well as about the heat capacity parameters) into account, following G(T) function can be suggested:

$$\Delta G^T = \quad (12)$$

$$\begin{aligned} &= -6441767 - T 227.6 + 588.216[(T - T_0) - \\ &- T \ln(T/T_0)] - 2354566[1/2T(1/T^2 - 1/T_0^2) - \\ &- (1/T - 1/T_0)] - 1443.7[2(T^{0.5} - T_0^{0.5}) + \\ &+ 2(1/T^{0.5} - 1/T_0^{0.5})] - 36930.8[\ln(T/T_0) + \\ &+ T(1/T - 1/T_0)] \end{aligned}$$

where $T_0 = 298$ (K). When applied to the Gibbs free energy calculation this function gives fairly acceptable values (see column in ΔG_B in Table V), that

can be proved by rather small relative deviations from the ΔG_1 (see column δ_B in Table V).

DISCUSSION OF RESULTS AND CONCLUDING REMARKS

Despite a great number of papers on mullite, there is no general agreement about its formula and consequently about its thermodynamic characteristics. Here, the 2.762:2-mullite was suggested, and its $\Delta G(T)$ -correlation was specified. Mullite formula was proved by Risbud's and Pask's calculation of miscibility gap in the Al₂O₃ - SiO₂- system, at the alumina rich end of the phase diagram [8].

A basis for the correlating procedure is a set of the ΔG_{MULL}^s values, whose preciseness depends markedly

Table V
Relative Deviation of the Gibbs Free Energy Calculated by Berman's Data with
the Correlated Gibbs Free Energy

No of point	Liquidus temp. (K)	ΔG_1 (J/mol) Data 9	ΔG_A (J/mol) $C(T)$ - average	δ_A^* (%)	ΔG_B (J/mol) $C(T)$ - optimal	δ_B^* (%)
1	1860	-7 765 584	-7 644 745	1.556	-7 690 935	0.961
2	1953	-7 854 492	-7 743 193	1.417	-7 792 949	0.784
3	1998	-7 884 431	-7 791 674	1.176	-7 843 166	0.523
4	2013	-7 881 554	-7 807 953	0.934	-7 860 026	0.273
5	2025	-7 879 811	-7 821 020	0.746	-7 873 558	0.079
6	2048	-7 887 137	-7 846 168	0.519	-7 899 599	0.158
7	2059	-7 885 851	-7 858 244	0.350	-7 912 102	0.333
8	2079	-7 906 416	-7 880 280	0.331	-7 918 533	0.361
9	2090	-7 916 486	-7 892 443	0.304	-7 947 508	0.392
10	2101	-7 929 362	-7 904 638	0.312	-7 960 131	0.388
11	2115	-7 948 600	-7 920 201	0.357	-7 976 241	0.348
12	2122	-7 957 977	-7 928 002	0.377	-7 984 315	0.331
				$\bar{\delta}_A^{**} = 0.652$	$\bar{\delta}_B^{**} = 0.389$	

* Relative deviation from ΔG_1

** Mean value of relative deviation (without the greatest and the lowest δ)

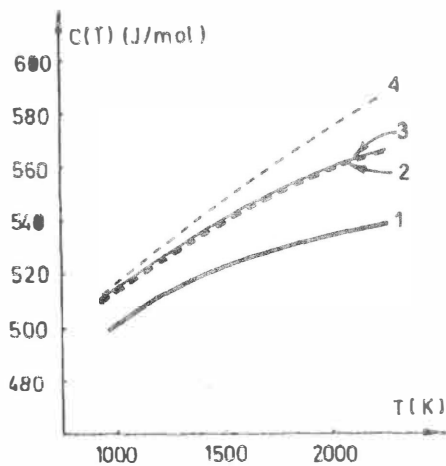


Fig. 3. Heat Capacity of Mullite According to Various Sources Legend: Curve 1 our results for 2.762:2-mullite, Curve 2 ref. [2], Curve 3 results for 3:2-mullite (average), Curve 4 ref. [3]

on the following factors: errors during the measurements, errors in the Gibbs free energy of liquid phase calculation, errors in the prediction of component activities etc. Assuming that the measurement errors were as low as possible, the greatest influence to the final result had the preciseness in the ΔG -liquids cal-

ulation. Therefore, two sources were used and two sets of results (ΔG_1 and ΔG_2 , in Table II) were obtained. They were accomplished by those calculated for the 3:2- mullite (ΔG_3 - values). Graphical presentation of all results can be seen in Fig. 2. The curves, associated with three sets of ΔG - values, represent three different types of function: (6b)–(8b). However, all the functions have $\Delta H_{T_0}^0 - TS^0 + a[(T - T_0) - T \ln T/T_0]$, i.e. the same dominant term (from the point of view of its numerical contribution). As a consequence, all the functions have (almost) the same shapes, but different positions (due to the differences in a - parameter values as well as due to a contribution of remaining terms in equations (6b)–(8b)).

When comparing two sets of values (ΔG_1 and ΔG_2), the advantage was given to the first one. It was found that very small differences between ΔG_2 - values, derived for the 2.762:2- mullite, and those calculated for the 3:2- mullite (ΔG_3 -values) are not acceptable. What's more, comparison among the referent state ΔG - values indicates that the Gibbs free energy of the "light" - mullite should take value of approximately 94% of the value suggested for the "heavy"- mullite. After concluding that the ΔG_1 - values are more likely to be accurate (than the ΔG_2 - values) they were used for a correlating procedure and a $\Delta G(T)$ -function (12) was determined, for the

temperature interval 1860–2122 K as well as the composition range 5–50 mol% Al_2O_3 in the Al_2O_3 – SiO_2 -system. The quality of the correlation was expressed by the relative deviation whose value is fairly small.

As a result of this investigation, the heat capacity equation of mullite was specified, i.e. the parameters (a, c, f and h) for equation (6a) were defined. Specific heats, calculated by applying this equation (curve 1 in Fig. 3), are lower than the values estimated by any other $C(T)$ – function derived for the 3:2 – mullite (curves 2, 3 and 4 in Fig. 3). It is a consequence of lower amount of alumina in a “light” than in a “heavy” molecule. Also, it can be seen that $C(T)$ -values from JANAF tables (curve 2 in Fig. 3) highly agree with the values from equation (8a) whose parameters (a, b and c) are given the average values. But neither of them can be taken as the exact one. The $C(T)$ - relation of mullite, which is suggested for the temperature interval 1860–2122 K, is expressed by equation (6a), with the a, c, f and h-parameters from Table V.

Nomenclature

a		Coefficient of the spec. heat function
b		Coefficient of the spec. heat function
B		Coefficient of the Margules polynomial
c		Coefficient of the spec. heat function
$C(T)$	J/molK	Specific heat
f		Coefficient of the spec. heat function,
		Fraction of the Gibbs free energy
G	J/mol	Gibbs free energy of one mole of a system
ΔG^l	J/mol	Gibbs free energy of liquid
ΔG^s	J/mol	Gibbs free energy of solid
ΔG^T	J/mol	Gibbs free energy at temperature T
h		Coefficient of the spec. heat function
ΔH^0	J/mol	Referent state enthalpy (of forming)
R (= 8.315)	J/molK	Universal gas constant
S^0	J/molK	Referent state entropy
T	K	Temperature
T_0 (= 298)	K	Referent temperature
x		Mole fraction (in the liquid phase)
z		Number of particular oxide in a compound
γ		Activity coefficients
δ		Relative deviation

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Mullit, významná složka nejrůznějších keramických materiálů, byl původně pokládán za tuhý roztok cristobalitu v korundu, s nejpravděpodobnějším složením $2,762\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Toto složení vyhovuje tvaru experimentálně stanovené mezery v rozpustnosti na konci fázového diagramu s vysokým obsahem oxidu hlinitého.

Na tento mullit byla aplikována nezbytná podmínka rovnováhy mezi tuhým fází a taveninou :

$$\Delta G_{\text{MULL}}^s = \quad (1)$$

$$= 2,762(\Delta G_{\text{Al}_2\text{O}_3}^2 + RT \ln x_{\text{Al}_2\text{O}_3} + RT \ln \gamma_{\text{Al}_2\text{O}_3}) +$$

$$+ 2(\Delta G_{\text{SiO}_2}^l + RT \ln x_{\text{SiO}_2} + RT \gamma_{\text{SiO}_2})$$

Členy pravé strany rovnice byly získány takto: a) ΔG kapalin pomocí rovnic ze dvou údajů literatury:

$$\Delta G^T = \Delta H_{T_0}^0 - TS^0 + a[(T - T_0) -$$

$$- T \ln(T/T_0)] + c[1/2T(1/T^2 - 1/T_0^2) -$$

$$- (1/T - 1/T_0)] + f[2(T^{0.5} - T_0^{0.5}) +$$

$$2T(1/T^{0.5} - 1/T_0^{0.5})] +$$

$$h[\ln(T/T_0) + T(1/T - 1/T_0)]$$

$$\Delta G^T = \Delta H_{T_0}^0 - TS^0 + a[(T - T_0) -$$

$$- T \ln(T/T_0)] + b[1/2(T^2 - T_0^2) - (T - T_0)(10^3 + T) +$$

$$+ 10^3 T \ln(T/T_0)] + c[1/3(T^3 - T_0^3) -$$

$$-1/2(T^2 - T_0^2)(2 \times 10^3 + T) + \\ + (T - T_0)(10^6 + 2 \times 10^3 T) - 10^6 T \ln(T/T_0)]$$

b) složení na křivce liquidus fázového diagramu Al_2O_3 - SiO_2 , a c) koeficienty aktivity z Margulových polynomů:

$$RT \ln \gamma_{(\text{SiO}_2 \equiv 1)} = \quad (4) \\ = x_2^2 \{ [3(B_1 - B_2) + 2B_2] x_1 + B_3 (1 - 3x_1) x_2 \}$$

$$RT \ln \gamma_{(\text{Al}_2\text{O}_3 \equiv 2)} = \\ = x_1^2 \{ [3(B_3 - B_2) x_2 + 2B_2] x_2 + B_1 (1 - 3x_2) x_1 \}$$

kde koeficienty B mají následující hodnoty:

$$B_1 = 63617, 160 - T \times 23, 740 \quad (5)$$

$$B_2 = 1642663, 510 - T \times 763, 870$$

$$B_3 = -106635, 220 + T \times 28, 130$$

Tímto způsobem byly získány dvě skupiny hodnot G . Na základě jejich porovnání s hodnotami Gibbsovy energie pro mullit 3:2 byla dána přednost výsledkům, které byly považovány za přesnější. Korelačním postupem pak z nich byla odvozena následující funkce $\Delta G(T)$:

$$\Delta G^T = \quad (6) \\ = -6441767 - T 227, 6 + 588.216[(T - T_0) - \\ - T \ln(T/T_0)] - 2354566[1/2T(1/T^2 - 1/T_0^2) - \\ - (1/T - 1/T_0)] - 1443, 7[2(T^{0.5} - T_0^{0.5}) + \\ + 2(1/T^{0.5} - 1/T_0^{0.5})] - 36930, 8[\ln(T/T_0) + \\ + T(1/T - 1/T_0)]$$

Zároveň byly stejným postupem určeny tepelné vlastnosti mullitu stanovením jeho rovnice měrného tepla.

Protože příslušné experimentální hodnoty použité v těchto výpočtech platí pro teplotní interval 1860–2122 K a koncentrační interval 5–50 mol % Al_2O_3 (ve fázovém digramu Al_2O_3 - SiO_2), korelaci (6) je nutno pokládat za matematický model termodynamického chování mullitu 2,762:2 v daných intervalech.

Obr. 1. Různé křivky liquidus pro mullit dle literatury: křivka 1 [4], křivka 2 [5], křivka [8]

Obr. 2. Gibbsova volná energie mullitu vypočítaná pomocí modelů a hodnot z různých údajů literatury Legenda: ΔG_1 - model a hodnoty dle (9), ΔG_2 - model a hodnoty dle [10], ΔG_3 a hodnoty dle [3]

Obr. 3. Měrné teplo mullitu dle různých údajů literatury Legenda: křivka 1 - naše výsledky pro mullit 2,762:2, křivka 2 - lit. [2], křivka 3 - výsledky pro mullit 3:2 (průměrné hodnoty), křivka 4 - lit. [3]