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Estimation of heat capacities of solid mixed oxides

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Abstract

Some empirical methods for the estimation of standard molar heat capacity (C°_{pm}) of solid mixed oxides are reviewed and the reliability of the obtained data in phase equilibria calculations is examined. Following the comparison of predicted values of C°_{pm}(298.15 K) with more than 300 experimental data the most widely used Neumann–Kopp rule (NKR) is found to be very universal but in some cases the mean deviation of 3.3% is too high, giving rise to a relatively large error in equilibrium calculation results. On the other hand, the method based on binary oxide contributions proposed by Berman and Brown [Contrib. Mineral. Petrol. 89 (1985) 168] for the estimation of temperature dependencies $C^\circ_{pm}(T)$ of silicates and other minerals formed by Al_2O_3, CaO, FeO, Fe_2O_3, K_2O, MgO, Na_2O, SiO_2 and TiO_2 is less general, but more accurate. In comparison with the NKR, the most pronounced drawback of this method is the necessity to know the experimental values of C°_{pm} for a set of mixed oxides, so that the individual contributions of constituent binary oxides can be evaluated.

Keywords: Mixed oxides; Heat capacity; Estimation; Neumann–Kopp rule; Group contribution methods

1. Introduction

The oxide based materials are presently used in a large number of applications. Let us mention only some of the most important ones in the following outline:

- Glasses (system SiO_2–Al_2O_3–B_2O_3–MgO–CaO–PbO–Na_2O–K_2O, special glasses for optical applications, optical fibers).
- Structural ceramics (system SiO_2–Al_2O_3–MgO, zirconia ceramics, sialon).
- Composite materials (oxides are used as a reinforcement in a metallic matrix or, alternatively, as a matrix toughened by non-oxidic fibres).
- Coatings and thin films (protective coatings for gas-turbine parts—system ZrO_2–Y_2O_3–CaO–MgO, dielectric layers in electronics—SiO_2, chemical sensor active layers—ZnO, SnO_2, Fe_2O_3, etc.).
- Materials for magnetic recording (Fe_2O_3, CrO_2, mixed ferrites (Zn,Mn,Cu)Fe_2O_4).
- Structural elements of oxide fuel cells ((La,Ca)-CrO_3, (La,Sr)MnO_3, Y_2O_3–ZrO_2).
- High-temperature superconductors (YBaCuO, BiSrCaCuO, HgBaCaCuO, TlBaCaCuO).

Chemical thermodynamics is frequently used in systematic investigation of processes related with

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material synthesis and processing as the powerful tool to understand the interrelationship between chemical composition, structure and properties. The calculations of thermodynamic equilibria require knowledge of input thermodynamic data for each substance involved, namely the values of enthalpies of formation and entropies at 298.15 K, as well as the coefficients of temperature dependencies of isobaric molar heat capacities. Alternatively, the parameters of temperature dependence of molar Gibbs energy can be directly employed. For a number of solid oxides, such data are tabulated for a wide range of temperatures, see, e.g. [2–9] or available in a form of computer databases. In addition, comprehensive data files for silicates and other oxidic minerals are disposable, e.g. [1,10–16].

The molar heat capacity (C°_{pm}) is one of the fundamental thermodynamic functions of solid substances. Various calorimetric methods being presently applicable from very low temperatures (approx. 10^{-1} K) up to melting points are used for experimental determination of C°_{pm}. The calorimetric measurements have been taken for practically all binary oxides and a considerable number of mixed oxides. The obtained data are available in literature. However, in many cases the experimental data are still missing. Hence, a lot of empirical methods for estimation of C°_{pm} of inorganic compounds have been proposed in order to overcome this lack. These methods are described in some review papers [7,17,18].

The aim of this paper is to summarize the as yet proposed methods for estimation of molar heat capacities of solid mixed oxides,[1] to verify their credibility and to examine the reliability of estimated values in equilibrium calculations in oxide systems. The paper follows the previous study [19] focused to prediction of C°_{pm} for binary oxides.

2. Method description

Let us consider the formation of a ternary oxide $A_{2a}B_{3b}O_x$ from binary oxides A_aO_m and B_bO_n ($x = 2m + 3n$) according to the following equation:

$$2A_aO_m(s) + 3B_bO_n(s) \rightarrow A_{2a}B_{3b}O_x(s) \qquad \text{(R1)}$$

The change of isobaric heat capacity accompanying the reaction, $\Delta C^\circ_{pm}(\text{ox})$, can be expressed as:

$$\Delta C^\circ_{pm}(\text{ox}) = C^\circ_{pm}(A_{2a}B_{3b}O_x) - 2C^\circ_{pm}(A_aO_m) - 3C^\circ_{pm}(B_bO_n) \qquad (1)$$

The values of $\Delta C^\circ_{pm}(\text{ox})$ for more than 300 mixed oxides evaluated from the experimental (calorimetric) data of C°_{pm} using Eq. (1) are plotted in Fig. 1. The dispersion of the obtained values falls roughly in the interval of $\pm 30\ \text{J K}^{-1}\ \text{mol}^{-1}$ and their average is close to zero. All below-mentioned methods can be classified into two essential groups according to whether the condition $\Delta C^\circ_{pm}(\text{ox}) = 0$ is fulfilled or not.

2.1. $\Delta C^\circ_{pm}(ox) = 0$

2.1.1. *Neumann–Kopp rule*

The Neumann–Kopp rule (NKR) represents presumably the simplest approach for estimation of $C^\circ_{pm}(298.15)$ as well as for temperature dependence $C^\circ_{pm}(T)$. Based on this method, the molar heat capacity of a mixed oxide is calculated as a weighted sum of heat capacities of the constituent binary oxides. For example, the heat capacity of the above-mentioned ternary oxide with the stoichiometry $A_{2a}B_{3b}O_x$ reads

$$C^\circ_{pm}(A_{2a}B_{3b}O_x) = 2C^\circ_{pm}(A_aO_m) + 3C^\circ_{pm}(B_bO_n) \qquad (2)$$

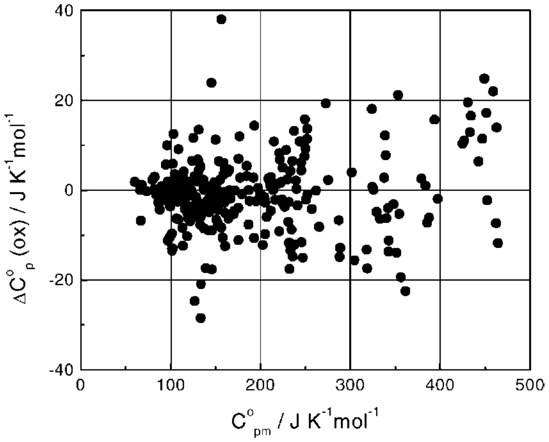

Fig. 1. Heat capacity change, $\Delta C^\circ_{pm}(\text{ox})$, accompanying the formation of mixed oxides from constituent binary oxides at the temperature of 298.15 K.

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[1] The term "mixed oxides" stands here for ternary or higher compounds of oxygen (as an anion O^{2-}) with two or more cations, as well as for compounds consisting of complex anions, which can be considered as salts of oxidic acids (chromates, wolframates) including those cases when the anions form chains, sheets of three-dimensional networks (e.g. silicates).

Such an approximation results in the case of silicates and other natural minerals in the average estimation error of approx. 5% [20]. The main advantage of the NKR lies in the availability of experimental temperature dependencies of $C^\circ_{pm}(T)$ for the respective binary oxides.

As an improvement of basic the NKR let us mention the procedure proposed by Helgeson et al. [20] for the estimation of C°_{pm} of silicates and other oxide minerals. This method is based upon the assumption of zero change of heat capacity in the course of an exchange reaction

$$A_aB_bO_x(s) + C_cO_y(s) = B_bO_z(s) + A_aC_cO_{x+y-z} \tag{R2}$$

between structurally similar substances. The unknown data for a ternary oxide $A_aC_cO_{x+y-z}$ can be thus obtained directly from the data of binary oxides B_bO_z, C_cO_y, and a mixed oxide $A_aB_bO_x$. The accuracy of estimation may be increased to about 2% in this manner. However, the substantial drawback of this method inheres in the dependence, in many cases very important, on the choice of the given exchange reaction (R2).

A method analogous to that of Helgeson has been proposed by Ukleba et al. [21] for the estimation of $C^\circ_{pm}(298.15)$, in which the exchange reaction between two ternary oxides is considered. The mean estimation error for the set of 124 selected ternary oxides amounts to approx. 3%. In case of more possible exchange reactions, averaging of the relevant values is recommended [21].

2.2. $\Delta C^\circ_{pm}(ox) \neq 0$

2.2.1. Contribution methods—atomic and ionic contributions

For the estimation of molar heat capacities of mixed oxides, several contribution methods can be used, which have been reviewed in the previous paper [19] dealing with binary oxides. In cases when the contributions of individual cations (atoms) and the anion O^{2-} (atom O) are considered, the obtained value corresponds to $\Delta C^\circ_{pm}(\mathrm{ox}) = 0$ (for the calculation of $\Delta C^\circ_{pm}(\mathrm{ox})$ according to Eq. (1), the estimated (not experimental) values of C°_{pm} of constituent binary oxides must be used).

Based on the method proposed by Kellogg [22] and later extended by Kubaschewski and Ünal [23], the particular contributions to $C^\circ_{pm}(298.15\ \mathrm{K})$ were evaluated for 25 different complex anions constituted from oxygen and another element (Al, B, Cr, Fe, Ge, Hf, Mo, Nb, Se, Si, Ti, U, V, W, and Zr) [18]. As the complex anion contributions differ from the sum of contributions of respective cations and the anion O^{2-}, the resulting value $\Delta C^\circ_{pm}(\mathrm{ox}) = 0$ in such a case. The evaluated contributions are listed in Tables 1 and 2.

Kubaschewski and Ünal [23] have further proposed the method for estimation of parameters A, B, and C in a simple temperature dependence of $C^\circ_{pm}(T)$ in the form

$$C^\circ_{pm} = A + BT + \frac{C}{T^2} \tag{3}$$

The parameters A and B are estimated using the relations

$$A = \frac{10^{-3}T_m[C^\circ_{pm}(298.15\ \mathrm{K}) + 4.7n] - 1.25n \times 10^5 (T_m)^{-2} - 9.05n}{10^{-3}T_m - 0.298} \tag{4}$$

$$B = \frac{25.6n + 4.2n \times 10^5 (T_m)^{-2} - C^\circ_{pm}(298.15\ \mathrm{K})}{10^{-3}T_m - 0.298} \tag{5}$$

where n is the number of ions (contributions) in the formula unit. The generalized value of the third parameter was set to $C = -4.2n$. The described approach can be employed only for substances whose melting temperature T_m is lower than approx. 2300 K.

The ionic contributions of complex anions consisting of oxygen and other elements (Al, B, Cr, Fe, Ge, Mn, Mo, Nb, Re, Se, Si, Ta, Tc, Ti, U, V, W, and Zr), as well as the contributions of individual cations (in this case differing for unlike valencies) were also evaluated by Kumok [24].

2.2.2. Contribution methods—structural and simple oxides contributions

A number of contribution methods has been developed directly for mixed oxides. The values of $C^\circ_{pm}(298.15\ \mathrm{K})$ or the parameters of $C^\circ_{pm}(T)$ dependence are additively calculated from contributions of constituent oxides or from structural contributions.

Table 1
Cationic contributions to heat capacity at 298.15 K

Cation	Contributions to $C^\circ_{pm}(298)$ (J K^{-1} mol^{-1})		Cation	Contributions to $C^\circ_{pm}(298)$ (J K^{-1} mol^{-1})		Cation	Contributions to $C^\circ_{pm}(298)$ (J K^{-1} mol^{-1})	
	[18,23]	[17,24]		[18,23]	[17,24]		[18,23]	[17,24]
Ag^{2+}	25.73	28.60	Ho^{2+}	23.01	26.10	Se^{6+}	21.34	
Al^{3+}	19.66	17.60	Ho^{3+}	23.01	29.60	Si^{4+}		12.10
As^{3+}	25.10	26.70	In^{+}	24.27	23.70	Sm^{2+}	25.10	35.70
As^{5+}	25.10		In^{2+}	24.27	26.50	Sm^{3+}	25.10	34.40
B^{3+}		6.10	In^{3+}	24.27	25.70	Sn^{2+}	23.43	27.80
Ba^{2+}	26.36	28.40	Ir^{3+}	23.85		Sn^{4+}	23.43	25.80
Be^{2+}	9.62	12.60	Ir^{4+}	23.85		Sr^{2+}	25.52	29.30
Bi^{3+}	26.78	29.00	K^{+}	25.94	28.00	Ta^{3+}	23.01	27.70
Ca^{2+}	24.69	27.30	La^{2+}	25.52	29.50	Ta^{4+}	23.01	
Cd^{2+}	23.01	28.00	La^{3+}	25.52	29.30	Ta^{5+}	23.01	26.30
Ce^{2+}	23.43	27.60	Li^{+}	19.66	20.70	Tb^{2+}		24.30
Ce^{3+}	23.43	31.40	Lu^{3+}		28.70	Tb^{3+}		33.00
Ce^{4+}	23.43	28.20	Mg^{2+}	19.66	22.20	Tc^{4+}		30.50
Co^{2+}	28.03	31.30	Mn^{2+}	23.43	27.90	Th^{2+}	25.52	26.10
Co^{3+}	28.03	12.40	Mn^{3+}	23.43	25.00	Th^{3+}	25.52	29.70
Cr^{2+}	23.01	21.00	Mn^{4+}	23.43	21.20	Th^{4+}	25.52	28.20
Cr^{3+}	23.01	29.10	Mo^{2+}		23.60	Ti^{2+}	21.76	21.30
Cr^{4+}	23.01	21.80	Mo^{4+}		21.40	Ti^{3+}	21.76	23.30
Cr^{6+}	23.01		Na^{+}	25.94	26.80	Ti^{4+}	21.76	25.50
Cs^{+}	26.36	31.10	Nb^{3+}	23.01	23.00	Ti^{5+}	21.76	
Cu^{+}	25.10	25.50	Nb^{4+}	23.01	23.50	Tl^{+}	27.61	30.90
Cu^{2+}	25.10	25.00	Nb^{5+}	23.01	26.70	Tl^{3+}	27.61	
Dy^{2+}		84.00	Nd^{3+}	24.27	28.30	Tm^{3+}		33.30
Dy^{3+}		31.00	Ni^{2+}	27.61	26.70	U^{2+}		30.00
Er^{3+}		29.10	P^{5+}	14.23		U^{3+}	26.78	34.10
Eu^{2+}		29.10	Pb^{2+}	26.78	29.30	U^{4+}	26.78	30.80
Eu^{3+}		33.30	Pb^{4+}	26.78	47.30	U^{5+}	26.78	33.80
Fe^{2+}	25.94	28.70	Pd^{2+}		20.60	U^{6+}	26.78	34.20
Fe^{3+}	25.94	26.20	Pm^{3+}		31.40	V^{2+}	22.18	21.60
Fr^{+}		29.50	Pr^{3+}	24.27	31.50	V^{3+}	22.18	27.10
Ga^{+}	20.92	23.90	Pr^{4+}	24.27		V^{4+}	22.18	26.90
Ga^{2+}	20.92	22.75	Pt^{4+}		24.20	V^{5+}	22.18	
Ga^{3+}	20.92	21.60	Pu^{2+}		40.70	W^{4+}		21.60
Gd^{3+}	23.43	27.80	Pu^{3+}		28.40	Y^{2+}	25.10	22.50
Ge^{2+}	20.08	25.80	Pu^{4+}		35.10	Y^{3+}	25.10	24.00
Ge^{4+}	20.08	23.00	Ra^{2+}		29.60	Yb^{2+}		29.00
Hf^{2+}	25.52		Rb^{+}	26.36	30.80	Yb^{3+}		32.60
Hf^{3+}	25.52		Sb^{3+}	23.85	30.30	Zn^{2+}	21.76	25.50
Hf^{4+}	25.52	20.20	Sc^{3+}		21.20	Zr^{2+}	23.85	24.70
Hg^{+}	25.10	26.30	Se^{4+}	21.34		Zr^{3+}	23.85	25.00
Hg^{2+}	25.10	27.70	Se^{5+}	21.34		Zr^{4+}	23.85	22.90

These methods are confined to a certain family of mixed oxides, though.

Several different methods have been brought in for the estimation of $C^\circ_{pm}(T)$ of silicates and other oxide materials. Robinson and Haas [25] suggested a model based on structural contributions corresponding to individual cations in particular coordination (number of the nearest neighbors O^{2-}). The parameters of the temperature function

$$C^\circ_{pm} = a + bT + \frac{c}{T^2} + fT^2 + \frac{g}{T^{1/2}} \qquad (6)$$

Table 2
Anionic contributions to heat capacity at 298.15 K

Anion	Contributions to $C^\circ_{pm}(298)$ (J K^{-1} mol^{-1})		Anion	Contributions to $C^\circ_{pm}(298)$ (J K^{-1} mol^{-1})	
	[18,23]	[17,24]		[18,23]	[17,24]
$(AlO_2)^-$	49.26	47.40	$(SeO_3)^{2-}$	73.32	72.50
$(AlO_3)^{3-}$	67.73		$(SeO_4)^{2-}$		86.60
$(BO_2)^-$	41.19	40.30	$(SiO_3)^{2-}$	62.93	59.30
$(BO_3)^{3-}$	55.60	52.00	$(SiO_4)^{4-}$	78.34	73.50
$(B_4O_7)^{2-}$	134.26		$(Si_2O_5)^{2-}$	106.79	103.80
$(CrO_2)^-$	62.67	52.40	$(TaO_3)^-$		79.80
$(CrO_3)^{3-}$		84.90	$(TcO_4)^-$		95.30
$(CrO_4)^{2-}$	92.27	86.40	$(TiO_3)^{2-}$	74.45	71.90
$(Cr_2O_7)^{2-}$		166.50	$(TiO_4)^{4-}$	92.52	85.90
$(FeO_2)^-$	63.03	59.70	$(Ti_2O_5)^{2-}$	124.69	120.80
$(GeO_3)^{2-}$	72.08	68.20	$(UO_3)^-$		82.10
$(HfO_3)^{2-}$	78.47		$(UO_4)^{2-}$	107.11	97.90
$(MnO_4)^-$		91.10	$(U_2O_7)^{2-}$		171.40
$(MnO_4)^{2-}$		86.80	$(VO_3)^-$	71.54	70.90
$(MnO_4)^{3-}$		97.50	$(VO_4)^{3-}$	89.20	87.74
$(MoO_4)^{2-}$	92.77	89.80	$(V_2O_7)^{4-}$	163.50	158.90
$(Mo_2O_7)^{2-}$		163.60	$(WO_4)^{2-}$	97.49	89.70
$(NbO_3)^-$	78.00	74.90	$(W_2O_7)^{2-}$		161.30
$(ReO_4)^-$		96.40	$(ZrO_3)^{2-}$	75.06	73.40

Table 3
Contributions of binary oxides to heat capacity at 298.15 K [1]

Oxide	Contributions to $C^\circ_{pm}(298)$ (J K^{-1} mol^{-1})	$C^\circ_{pm}(298)$ (J K^{-1} mol^{-1}) of binary oxide	Difference (%)
Al_2O_3	77.41	79.01	−2.03
CaO	43.18	42.42	1.80
Fe_2O_3	105.17	104.77	0.39
FeO	43.38	48.04	−9.69
K_2O	71.70	84.53	−15.17
MgO	37.31	37.26	0.15
Na_2O	69.18	68.56	0.91
SiO_2	43.95	44.42	−1.05
TiO_2	55.44	55.10	0.61

are calculated additively from such structural contributions. A set of 20 different contributions has been assessed from the available experimental data for 61 minerals. The original experimental values have been reproduced with an accuracy higher than 2%.

For the estimation of the temperature dependence $C^\circ_{pm}(T)$ of minerals formed from binary oxides Al_2O_3, CaO, FeO, Fe_2O_3, K_2O, MgO, Na_2O, SiO_2 and TiO_2 in the form

$$C^\circ_{pm} = k_0 + \frac{k_1}{T^{1/2}} + \frac{k_2}{T^2} + \frac{k_3}{T^3} \qquad (7)$$

Berman and Brown [1] evaluated the contributions of the binary oxides to parameters k_0, k_1, k_2, and k_3. They employed the calorimetric data for 101 minerals for the least square fitting of contributions. The estimation error did not exceed 2% for a large majority of substances even in this case. The calculated values of contributions at 298.15 K for the above-mentioned oxides along with the respective experimental data C°_{pm}(298.15 K) and the relative differences are given in Table 3. These differences are substantial only for FeO and K_2O. Consequently, for the mixed oxides formed by Al_2O_3, CaO, Fe_2O_3, MgO, Na_2O, SiO_2 and TiO_2, the values predicted by the Berman–Brown method will be very close to those ones obtained from the NKR.

Another significant family of mixed oxides is represented by high-temperature superconductors and related phases. The contributions to the estimation of parameters k_0, k_1, and k_2 to the temperature dependence of $C^\circ_{pm}(T)$ according to Eq. (7) have been proposed by Voronin and Uspenskaya [26] for mixed oxides in the system Y–Ba–Cu–O. Analyzing the experimental data for five mixed oxides, they evaluated the contributions for binary oxides Y_2O_3, BaO, CuO, and Cu_2O and predicted the parameters of Eq. (7) for another seven ternary and quaternary oxides.

2.2.3. *Empirical rules in homological series and groups of chemically related substances (oxides)*

Goncharov and Vorobev [27] developed the method for estimation of temperature dependency $C^\circ_{pm}(T)$ for garnets of Fe, Al and Ga with rare earth (RE) elements starting from an assumption of $\Delta C^\circ_{pm}(\mathrm{ox})$ being equal for the same family of substances (e.g. $RE_3Fe_5O_{12}$, $RE_3Al_5O_{12}$, $RE_3Ga_5O_{12}$) irrespective of the particular RE element. Such assumption was found to be well satisfied with the experimental data for ferrogarnets of Y, Sm, Eu, Gd, Tb, and Lu yielding the error did not exceed 2%. Accordingly, the generalized temperature dependence of $\Delta C^\circ_{pm}(\mathrm{ox})$ for $RE_3Al_5O_{12}$ and $RE_3Ga_5O_{12}$ has been obtained from data for $Y_3Al_5O_{12}$ [28] and $Gd_3Ga_5O_{12}$ [29], respectively.

The prediction method of C°_{pm}(298.15 K) using ionic contributions brought in by Aldabergenov et al. [30,31]

was based on the idea that in homologous series like $A_m(B_xO_y)_n$, the molar heat capacity is a linear function of coefficient n specifying the number of complex anions $(B_xO_y)^{z-}$ in the formula unit. Thus for alkaline aluminates, the series

$$AlO_2{}^{-} \xrightarrow{+AlO_2{}^{-}} Al_2O_4{}^{2-} \xrightarrow{+AlO_2{}^{-}} Al_3O_6{}^{3-} \cdots$$

is considered, in which each higher anion differs from the previous one in an increment $(AlO_2)^-$. The higher anion contributions are considered as n-multiples of the primary anion $(AlO_2)^-$, whose value is determined from the available experimental data of $C^\circ_{pm}(298.15\text{ K})$ for $KAlO_2$, $LiAlO_2$ and $NaAlO_2$ as well as from the ionic contributions for the respective cations K^+, Li^+ and Na^+ obtained from their standard molar entropies in an infinitely diluted solution.

3. Comparison of selected methods

In the following part three selected methods, namely the NKR, the Kellogg's method of ionic contributions [22] with ionic contributions taken from Spencer [18] (KK), and the binary oxide contribution method by Berman and Brown [1] (BB) are compared. The values of $C^\circ_{pm}(298.15\text{ K})$ for binary oxides used in the NKR are listed in Table 4. The methods are examined both in terms of their universality, i.e. according to the number of mixed oxides whose

Table 4
Selected values of heat capacity of solid binary oxides at 298.15 K [19]

Oxide	Phase	$C^\circ_{pm}(298)$ (J K^{-1} mol^{-1})	Oxide	Phase	$C^\circ_{pm}(298)$ (J K^{-1} mol^{-1})
Ag_2O	Sol	66.32	MgO	Sol	37.26
Al_2O_3	Sol	79.01	Mn_2O_3	Sol	99.04
B_2O_3	Sol	62.98	MnO	Sol	44.76
BaO	Sol	47.06	MnO_2	Sol	54.42
BeO	Sol-A	24.98	MoO_2	Sol	55.99
Bi_2O_3	Sol-A	112.13	MoO_3	Sol	75.14
CaO	Sol	42.42	Na_2O	Sol-A	68.56
CdO	Sol	44.16	Nb_2O_5	Sol	132.13
Ce_2O_3	Sol	117.05	Nd_2O_3	Sol-A	111.34
CeO_2	Sol	61.53	NiO	Sol-A	44.29
CoO	Sol	55.22	PbO	Red	45.74
Cr_2O_3	Sol	114.26	Pr_2O_3	Sol	116.63
CrO_3	Sol	79.12	Rh_2O_3	Sol	89.12
Cs_2O	Sol	75.90	Sc_2O_3	Sol	93.94
Cu_2O	Sol	62.47	SiO_2	Quartz(L)	44.42
CuO	Sol	42.26	Sm_2O_3	Sol-A	115.82
Dy_2O_3	Sol-A	116.26	SrO	Sol	45.15
Er_2O_3	Sol	108.49	Ta_2O_5	Sol	131.48
Eu_2O_3	Cubic	124.68	TeO_2	Sol	63.88
Fe_2O_3	Sol-A	104.77	TeO_3	Sol	71.47
FeO	Sol	48.04	TiO_2	Rutile	55.10
Ga_2O_3	Sol	93.86	Tl_2O_3	Sol	105.46
Gd_2O_3	Cubic	105.51	Tm_2O_3	Sol-A	116.72
GeO_2	Hexagonal	51.95	UO_2	Sol	63.59
HfO_2	Sol-A	60.26	UO_3	Sol	81.19
HgO	Sol	43.89	V_2O_5	Sol	127.37
Ho_2O_3	Sol	114.96	WO_3	Sol-A	72.80
K_2O	Sol	84.53	Y_2O_3	Sol-A	102.51
La_2O_3	Sol	108.78	Yb_2O_3	Sol-A	115.36
Li_2O	Sol	54.25	ZnO	Sol	41.07
Lu_2O_3	Sol	101.76	ZrO_2	Sol-A	56.21

C°_{pm}(298.15 K) and/or $C^{\circ}_{pm}(T)$ can be obtained, and concerning credibility of the predicted values as well.

3.1. C°_{pm}(298.15 K) experimental data set

The predicted values of C°_{pm}(298.15 K) were compared with available experimental data in order to qualitatively compare the selected estimation methods. 326 mixed oxide phases formed by 71 binary oxides of 57 elements were included into the data set given in Table 5. The values of C°_{pm}(298.15 K) were taken from more than 100 literature sources—data collections, review articles and original papers. The presented data come in all cases either from direct (calorimetric) experiments or from simultaneous processing (optimization) of more experimental data. The accuracy of the calorimetric data depends on the particular method used. The most precise values were obtained by direct measurements of C°_{pm} in adiabatic calorimeters (the determination error does not exceed 0.2–0.5% at an ambient temperature). The experimental error of C°_{pm}(298.15 K) measured in DSC calorimeters (in continuous or stepwise mode) is higher, about 1–2%. Even the higher error (2–3%) must be taken into account in case of heat content measurements, $H_T - H_{\mathrm{Tref}}$, using drop calorimeters. The direct result here is the temperature dependence of the integral function, relative enthalpy, usually measured above 450 °C. The $C^{\circ}_{pm}(T)$ dependence is then obtained by differentiating it with respect to temperature and C°_{pm}(298.15 K) by extrapolation.

In some cases, the available experimental data were not taken into account for assessment of the reliability of the estimation methods. For instance, the values of $C^{\circ}_{pm}(T)$ above 400 K and extrapolated C°_{pm}(298.15 K) reported by Gospodinov et al. for ternary oxides formed by TeO_2 and MnO [32], MgO [33], Al_2O_3, Ga_2O_3, In_2O_3 and Tl_2O_3 [34], or CuO [35] are not treated as much reliable. Indeed, their data of C°_{pm}(298.15 K) for ternary oxides $BaZrO_3$, $CaZrO_3$ and $SrZrO_3$ [36], measured on the same calorimeter and evaluated using the same procedure, are obviously quite different from values reported by other authors [37], and, moreover, some errors have been found in the evaluation of experimental results [38]. Similarly, the data for ternary oxides of Sb_2O_5, BaO, CaO and SrO [39], CoO, NiO and ZnO [40], all reported by Kasenov et al., as well as for quaternary oxides of type $RE_2AE_2Mn_4O_{11}$, (RE: Gd, AE: Ba) [41], (RE: Dy, AE: Sr) [42], (RE: Er, Gd, Ho, La, Lu, Nd, AE: Sr) [43], (RE: La, AE: Ca) [44], and (RE: Er, Gd, Nd, AE: Ca) [45] were not included in the experimental data set. In all latter studies, the conventional calorimeter ICT-400 has been employed for C°_{pm} measurements providing the results with the relatively large error of about 10%. For example, the average value of 181 ± 17 J K^{-1} mol^{-1} resulting from five measurements of $NiSb_2O_6$ is referred in [40], which exceeds severalfold the errors of other data and would therefore, depreciate the comparison of experimental and estimated values.

In addition to complex mixed oxides, the oxides of Me_3O_4 type with a cation of one element in two valence states, $Me^{2+}$and Me^{3+}(Me: Co, Cr, Fe, Mn, Pb), have been also included in the experimental data set. For the sake of completeness, even those mixed oxides are listed in the Table 5, which C°_{pm} cannot be predicted by any of the tested methods.

3.2. Neumann–Kopp rule (NKR)

The NKR is the most universal from all considered methods—within the given experimental data set the total number of 295 values of C°_{pm}(298.15 K) can be estimated using this rule. The NKR cannot be applied only in the following cases:

- The experimental values of C°_{pm}(298.15 K) for binary oxides forming a particular mixed oxide are not available. So far the experimental data for Co_2O_3, CrO_2, MnO_3, Rb_2O, RuO_3 and Tb_2O_3 are missing, and thus only their estimated values are reported in thermodynamic tables. Since the mean prediction error of contribution methods for binary oxides varies by 5% (for C°_{pm}(298.15 K)) [19], the application of the estimated data could significantly decrease the quality of NKR results.
- A given mixed oxide cannot be obtained from a chemical reaction of bare solid binary oxides. Let us mention a quaternary oxide $YBa_2Cu_3O_7$ as the example, which formation can be described as

$$\tfrac{1}{2}Y_2O_3 + 2\,BaO + 3\,CuO + \tfrac{1}{4}O_2 \rightarrow YBa_2Cu_3O_7 \qquad \text{(R3)}$$

Here the gaseous oxygen occurs as one of the starting compounds. The NKR is based on a simple

Table 5

Comparison of experimental and estimated values of heat capacity at 298.15 K of solid mixed oxides

No.	Mixed oxide	Binary oxides combination	Phase	Reference	$C^\circ_{pm}(298)$ ($\mathrm{J\ K^{-1}\ mol^{-1}}$)	$C^\circ_{pm}(298)$(NKR) ($\mathrm{J\ K^{-1}\ mol^{-1}}$)	ΔC°_{pm} (%)	$C^\circ_{pm}(298)$(KK) ($\mathrm{J\ K^{-1}\ mol^{-1}}$)	ΔC°_{pm} (%)	$C^\circ_{pm}(298)$(BB) ($\mathrm{J\ K^{-1}\ mol^{-1}}$)	ΔC°_{pm} (%)
1	Ag_2WO_4	$Ag_2O{\cdot}WO_3$	Sol	[47]	150.36	139.12	−7.48	148.95	−0.94		
2	$Al_{18}B_4O_{33}$	$9Al_2O_3{\cdot}2B_2O_3$	Sol	[6]	823.19	837.05	1.68				
3	Al_2SiO_5	$Al_2O_3{\cdot}SiO_2$	Andalusite	[1]	123.40	123.47	0.06			121.36	−1.65
4	Al_2SiO_5	$Al_2O_3{\cdot}SiO_2$	Kyanite	[1]	122.19	123.47	1.05			121.36	−0.68
5	Al_2SiO_5	$Al_2O_3{\cdot}SiO_2$	Sillimanite	[1]	122.93	123.47	0.44			121.36	−1.28
6	Al_2TiO_5	$Al_2O_3{\cdot}TiO_2$	Sol	[6]	136.40	134.11	−1.68			132.85	−2.60
7	$Al_4B_2O_9$	$2Al_2O_3{\cdot}B_2O_3$	Sol	[6]	222.64	221.00	−0.74				
8	$Al_6Si_2O_{13}$	$3Al_2O_3{\cdot}2SiO_2$	Sol	[1]	325.99	325.87	−0.04			320.13	−1.80
9	$Ba_2Si_3O_8$	$2BaO{\cdot}3SiO_2$	Sol	[8]	224.60	227.38	1.24	222.44	−0.96		
10	Ba_2TiO_4	$2BaO{\cdot}TiO_2$	Sol	[6]	149.15	149.22	0.05	145.24	−2.62		
11	$Ba_3B_2O_6$	$3BaO{\cdot}B_2O_3$	Sol	[48]	215.01	204.16	−5.05	190.28	−11.50		
12	$Ba_3LaNb_3O_{12}$	$(6BaO{\cdot}La_2O_3{\cdot}3Nb_2O_5)/2$	Sol	[49]	387.61	393.77	1.59				
13	$BaAl_2O_4$	$BaO{\cdot}Al_2O_3$	Sol	[6]	113.70	126.07	10.88	112.28	−1.25		
14	$BaAl_2Si_2O_8$	$BaO{\cdot}Al_2O_3{\cdot}2SiO_2$	Sol	[50]	221.71	214.91	−3.07	222.36	0.29		
15	$BaCeO_3$	$BaO{\cdot}CeO_2$	Sol	[51]	111.91	108.59	−2.97				
16	$BaCuO_2$	$BaO{\cdot}CuO$	Sol	[52]	95.00	89.32	−5.98				
17	$BaCuO_{2,09}$		Sol	[53]	96.89						
18	$BaMoO_4$	$BaO{\cdot}MoO_3$	Sol	[54]	122.00	122.20	0.16	119.13	−2.35		
19	$BaSiO_3$	$BaO{\cdot}SiO_2$	Sol	[6]	89.02	91.48	2.77	89.29	0.31		
20	$BaSrFe_4O_8$	$BaO{\cdot}SrO{\cdot}2Fe_2O_3$	Sol	[55]	288.90	301.75	4.45	304.00	5.23		
21	$BaTiO_3$	$BaO{\cdot}TiO_2$	Sol	[6]	102.45	102.16	−0.29	100.81	−1.60		
22	$BaUO_4$	$BaO{\cdot}UO_3$	Sol	[8]	133.50	128.25	−3.93	133.47	−0.02		
23	$BaZrO_3$	$BaO{\cdot}ZrO_2$	Sol	[37]	101.71	103.27	1.53	101.42	−0.29		
24	Be_2SiO_4	$2BeO{\cdot}SiO_2$	Sol	[6]	93.48	94.38	0.96	87.96	−5.90		
25	$Be_3B_2O_6$	$3BeO{\cdot}B_2O_3$	Sol	[6]	138.44	137.92	−0.37	140.06	1.17		
26	$BeAl_2O_4$	$BeO{\cdot}Al_2O_3$	Sol	[6]	104.94	103.99	−0.91	108.14	3.05		
27	$BeAl_6O_{10}$	$BeO{\cdot}3Al_2O_3$	Sol	[6]	261.92	262.01	0.03				
28	$BeWO_4$	$BeO{\cdot}WO_3$	Sol	[8]	96.92	97.78	0.89	107.11	10.52		
29	$Bi_2Ca_2O_5$	$Bi_2O_3{\cdot}2CaO$	Sol	[56]	197.44	196.97	−0.24				
30	Bi_2CaO_4	$Bi_2O_3{\cdot}CaO$	Sol	[56]	151.32	154.55	2.13				
31	Bi_2CuO_4	$Bi_2O_3{\cdot}CuO$	Sol	[57]	151.73	154.39	1.75				
32	$Bi_2Sr_2CuO_6$	$Bi_2O_3{\cdot}2SrO{\cdot}CuO$	Sol	[58]	241.30	244.69	1.40				
33	$Bi_2Sr_2Ca_{1,2}Cu_{1,8}O_{8,5}$		Sol	[59]	346.70						
34	$Bi_2Sr_3Cu_2O_8$	$Bi_2O_3{\cdot}3SrO{\cdot}2CuO$	Sol	[58]	353.28	332.10	−6.00				
35	$Bi_6Ca_4O_{13}$	$3Bi_2O_3{\cdot}4CaO$	Sol	[56]	504.06	506.07	0.40				
36	$Ca_{12}Al_{14}O_{33}$	$12CaO{\cdot}7Al_2O_3$	Sol	[8]	1084.82	1062.11	−2.09			1060.03	−2.29
37	$Ca_2Al_2SiO_7$	$2CaO{\cdot}Al_2O_3{\cdot}SiO_2$	Sol	[1]	205.51	208.27	1.34	210.83	2.59	207.72	1.08

Table 5 (*Continued*)

No.	Mixed oxide	Binary oxides combination	Phase	Reference	$C^\circ_{pm}(298)$ (J K^{-1} mol^{-1})	$C^\circ_{pm}(298)$(NKR) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)	$C^\circ_{pm}(298)$(KK) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)	$C^\circ_{pm}(298)$(BB) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)
38	$Ca_2B_2O_5$	$2CaO{\cdot}B_2O_3$	Sol-A	[6]	147.08	147.82	0.51	146.17	−0.62		
39	$Ca_2Fe_2O_5$	$2CaO{\cdot}Fe_2O_3$	Sol	[1]	192.38	189.61	−1.44			191.53	−0.44
40	$Ca_2MgSi_2O_7$	$2CaO{\cdot}MgO{\cdot}2SiO_2$	Sol	[1]	210.97	210.94	−0.01	210.31	−0.31	211.57	0.28
41	Ca_2SiO_4	$2CaO{\cdot}SiO_2$	Sol-A	[60]	125.76	129.26	2.78	127.72	1.56	130.31	3.62
42	$Ca_3Al_2O_6$	$3CaO{\cdot}Al_2O_3$	Sol	[1]	208.79	206.27	−1.21	209.53	0.35	206.95	−0.88
43	$Ca_3Al_2Si_3O_{12}$	$3CaO{\cdot}Al_2O_3{\cdot}3SiO_2$	Sol	[1]	333.15	339.53	1.92	348.41	4.58	338.80	1.70
44	$Ca_3B_2O_6$	$3CaO{\cdot}B_2O_3$	Sol	[6]	187.86	190.24	1.27	185.27	−1.38		
45	$Ca_3Fe_2Si_3O_{12}$	$3CaO{\cdot}Fe_2O_3{\cdot}3SiO_2$	Sol	[15]	351.38	365.29	3.96	360.97	2.73	366.56	4.32
46	$Ca_3Ga_2Ge_3O_{12}$	$3CaO{\cdot}Ga_2O_3{\cdot}3GeO_2$	Sol	[61]	379.50	376.97	−0.67				
47	$Ca_3MgSi_2O_8$	$3CaO{\cdot}MgO{\cdot}2SiO_2$	Sol	[8]	252.26	253.36	0.44	250.41	−0.73	254.75	0.99
48	$Ca_3Si_2O_7$	$3CaO{\cdot}2SiO_2$	Sol	[60]	211.51	216.10	2.17	215.34	1.81	217.44	2.81
49	Ca_3SiO_5	$3CaO{\cdot}SiO_2$	Sol	[60]	171.61	171.68	0.04			173.49	1.10
50	$Ca_3Ti_2O_7$	$3CaO{\cdot}2TiO_2$	Sol	[6]	239.59	237.46	−0.89	241.04	0.61	240.42	0.35
51	$Ca_4Ti_3O_{10}$	$4CaO{\cdot}3TiO_2$	Sol	[6]	337.77	334.98	−0.83	340.18	0.71	339.04	0.38
52	$CaAl_2O_4$	$CaO{\cdot}Al_2O_3$	Sol	[6]	120.60	121.43	0.69	123.21	2.17	120.59	−0.01
53	$CaAl_2Si_2O_8$	$CaO{\cdot}Al_2O_3{\cdot}2SiO_2$	Sol	[8]	211.31	210.27	−0.49	220.69	4.44	208.49	−1.33
54	$CaAl_2SiO_6$	$CaO{\cdot}Al_2O_3{\cdot}SiO_2$	Sol	[1]	165.82	165.85	0.02			164.54	−0.77
55	$CaAl_4O_7$	$CaO{\cdot}2Al_2O_3$	Sol	[6]	199.57	200.44	0.44			198.00	−0.79
56	CaB_2O_4	$CaO{\cdot}B_2O_3$	Sol	[6]	103.99	105.40	1.36	107.07	2.97		
57	CaB_4O_7	$CaO{\cdot}2B_2O_3$	Sol	[6]	157.85	168.38	6.67	158.95	0.70		
58	$CaCrO_4$	$CaO{\cdot}CrO_3$	Sol	[62]	113.18	121.54	7.39	116.96	3.34		
59	$CaCr_2O_4$	$CaO{\cdot}Cr_2O_3$	Sol-B	[62]	139.31	156.68	12.47	150.03	7.70		
60	$CaFe_2O_4$	$CaO{\cdot}Fe_2O_3$	Sol	[6]	153.65	147.19	−4.20	150.75	−1.89	148.35	−3.45
61	$CaFeSi_2O_6$	$CaO{\cdot}FeO{\cdot}2SiO_2$	Sol	[15]	175.37	179.30	2.24	176.49	0.64	174.46	−0.52
62	$CaHfTi_2O_7$	$CaO{\cdot}HfO_2{\cdot}2TiO_2$	Sol	[63]	206.90	212.88	2.89	217.18	4.97		
63	$CaMgSi_2O_6$	$CaO{\cdot}MgO{\cdot}2SiO_2$	Sol	[1]	166.63	168.52	1.13	170.21	2.15	168.39	1.06
64	$CaMgSiO_4$	$CaO{\cdot}MgO{\cdot}SiO_2$	Sol	[6]	123.22	124.10	0.71	122.69	−0.43	124.44	0.99
65	$CaNb_2O_6$	$CaO{\cdot}Nb_2O_5$	Sol	[6]	177.34	174.55	−1.57	180.69	1.89		
66	$CaSiO_3$	$CaO{\cdot}SiO_2$	Sol-A	[60]	86.42	86.84	0.49	87.62	1.39	87.13	0.83
67	$CaTiO_3$	$CaO{\cdot}TiO_2$	Sol-A	[6]	97.70	97.52	−0.18	99.14	1.48	98.62	0.95
68	$CaTiSiO_5$	$CaO{\cdot}TiO_2{\cdot}SiO_2$	Sol	[1]	139.11	141.94	2.03	140.43	0.95	142.57	2.49
69	$CaUO_4$	$CaO{\cdot}UO_3$	Sol-A	[6]	130.45	123.61	−5.24	131.80	1.04		
70	$CaWO_4$	$CaO{\cdot}WO_3$	Sol	[6]	113.24	115.22	1.75	122.18	7.90		
71	$CaZrO_3$	$CaO{\cdot}ZrO_2$	Sol	[37]	99.91	98.63	−1.28	99.75	−0.16		
72	$CaZrTi_2O_7$	$CaO{\cdot}ZrO_2{\cdot}2TiO_2$	Sol	[64]	211.73	208.83	−1.37	215.51	1.78		
73	$CdTiO_3$	$CdO{\cdot}TiO_2$	Sol-A	[6]	98.50	99.26	0.77	97.46	−1.06		
74	$Ce_2Si_2O_7$	$Ce_2O_3{\cdot}2SiO_2$	Sol-B	[65]	204.41	205.89	0.72	188.13	−7.96		
75	$Ce_2Zr_2O_7$	$Ce_2O_3{\cdot}2ZrO_2$	Sol	[66]	233.74	229.47	−1.83				
76	Co_2SiO_4	$2CoO{\cdot}SiO_2$	Sol	[6]	133.95	154.86	15.61	134.40	0.33		
77	Co_2TiO_4	$2CoO{\cdot}TiO_2$	Sol	[6]	160.49	165.54	3.15	148.58	−7.42		

Table 5 (*Continued*)

No.	Mixed oxide	Binary oxides combination	Phase	Reference	$C^\circ_{pm}(298)$ (J K^{-1} mol^{-1})	$C^\circ_{pm}(298)$(NKR) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)	$C^\circ_{pm}(298)$(KK) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)	$C^\circ_{pm}(298)$(BB) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)
78	Co_3O_4	$CoO{\cdot}Co_2O_3$	Sol	[6]	123.42						
79	$CoFe_2O_4$	$CoO{\cdot}Fe_2O_3$	Sol	[6]	152.58	159.99	4.86	154.09	0.99		
80	$CoTa_2O_6$	$CoO{\cdot}Ta_2O_5$	Sol	[67]	175.59	186.70	6.33				
81	$CoTiO_3$	$CoO{\cdot}TiO_2$	Sol	[6]	107.77	110.32	2.37	102.48	−4.91		
82	$CoWO_4$	$CoO{\cdot}WO_3$	Sol-A	[6]	129.94	128.02	−1.47	125.52	−3.40		
83	Cr_3O_4	$CrO{\cdot}Cr_2O_3$	Sol	[68]	135.64						
84	$CsBO_2$	$(Cs_2O{\cdot}B_2O_3)/2$	Sol	[6]	69.48	69.44	−0.05	67.55	−2.77		
85	$Cs_2Cr_2O_7$	$Cs_2O{\cdot}2CrO_3$	Sol-A	[54]	231.54	234.14	1.12				
86	Cs_2CrO_4	$Cs_2O{\cdot}CrO_3$	Sol-A	[54]	146.06	155.02	6.13	144.99	−0.73		
87	Cs_2MnO_4	$Cs_2O{\cdot}MnO_3$	Sol-A	[69]	149.24						
88	$Cs_2Mo_2O_7$	$Cs_2O{\cdot}2MoO_3$	Sol	[70]	224.14	226.18	0.91				
89	Cs_2MoO_4	$Cs_2O{\cdot}MoO_3$	Sol-A	[6]	148.67	151.04	1.59	145.49	−2.14		
90	Cs_2RuO_4	$Cs_2O{\cdot}RuO_3$	Sol-A	[69]	156.14						
91	$Cs_2Si_2O_5$	$Cs_2O{\cdot}2SiO_2$	Sol	[6]	176.73	164.74	−6.78	159.51	−9.74		
92	$Cs_2Si_4O_9$	$Cs_2O{\cdot}4SiO_2$	Sol	[6]	272.86	253.58	−7.06				
93	Cs_2SiO_3	$Cs_2O{\cdot}SiO_2$	Sol	[6]	122.23	120.32	−1.56	115.65	−5.38		
94	$Cs_2Te_2O_5$	$Cs_2O{\cdot}2TeO_2$	Sol	[54]	193.00	203.66	5.52				
95	$Cs_2Te_4O_{12}$	$Cs_2O{\cdot}TeO_2{\cdot}3TeO_3$	Sol	[54]	343.00	354.19	3.26				
96	$Cs_2Te_4O_9$	$Cs_2O{\cdot}4TeO_2$	Sol	[54]	318.20	331.42	4.16				
97	Cs_2TeO_3	$Cs_2O{\cdot}TeO_2$	Sol	[54]	133.87	139.78	4.42				
98	Cs_2TeO_4	$Cs_2O{\cdot}TeO_3$	Sol	[54]	148.35	147.37	−0.66				
99	$Cs_2U_2O_7$	$Cs_2O{\cdot}2UO_3$	Sol	[54]	231.23	238.28	3.05				
100	$Cs_2U_4O_{12}$	$Cs_2O{\cdot}UO_2{\cdot}3UO_3$	Sol-A	[54]	384.01	383.06	−0.25				
101	Cs_2UO_4	$Cs_2O{\cdot}UO_3$	Sol	[6]	152.75	157.09	2.84	159.83	4.64		
102	Cs_2ZrO_3	$Cs_2O{\cdot}ZrO_2$	Sol	[71]	129.79	132.11	1.79	127.78	−1.55		
103	Cs_3CrO_4	$(3Cs_2O{\cdot}CrO_2{\cdot}CrO_3)/2$	Sol-A	[54]	179.92						
104	$CsAlO_2$	$(Cs_2O{\cdot}Al_2O_3)/2$	Sol	[72]	79.76	77.46	−2.89	75.62	−5.19		
105	$CuFe_2O_4$	$CuO{\cdot}Fe_2O_3$	Sol-A	[6]	148.81	147.03	−1.19	151.16	1.58		
106	$CuFeO_2$	$(Cu_2O{\cdot}Fe_2O_3)/2$	Sol-A	[6]	84.18	85.12	1.12	88.13	4.69		
107	$Dy_3Fe_5O_{12}$	$(3Dy_2O_3{\cdot}5Fe_2O_3)/2$	Sol	[73]	442.72	436.32	−1.45				
108	Dy_3NbO_7	$(3Dy_2O_3{\cdot}Nb_2O_5)/2$	Sol	[74]	251.85	240.46	−4.52				
109	$DyCrO_3$	$(Dy_2O_3{\cdot}Cr_2O_3)/2$	Sol	[75]	102.33	115.26	12.64				
110	$Er_3Fe_5O_{12}$	$(3Er_2O_3{\cdot}5Fe_2O_3)/2$	Sol	[76]	449.52	424.66	−5.53				
111	Er_3NbO_7	$(3Er_2O_3{\cdot}Nb_2O_5)/2$	Sol	[74]	233.02	228.80	−1.81				
112	$ErCrO_3$	$(Er_2O_3{\cdot}Cr_2O_3)/2$	Sol	[75]	101.74	111.38	9.48				
113	$ErMnO_3$	$(Er_2O_3{\cdot}Mn_2O_3)/2$	Sol	[77]	104.81	103.77	−0.99				
114	$Eu_3Fe_5O_{12}$	$(3Eu_2O_3{\cdot}5Fe_2O_3)/2$	Sol	[76]	462.89	448.95	−3.01				
115	Eu_3NbO_7	$(3Eu_2O_3{\cdot}Nb_2O_5)/2$	Sol	[74]	251.01	253.09	0.83				
116	$Fe_2Al_4Si_5O_{18}$	$2FeO{\cdot}2Al_2O_3{\cdot}5SiO_2$	Sol	[15]	464.41	476.20	2.54	491.40	5.81	461.33	−0.66
117	Fe_2SiO_4	$2FeO{\cdot}SiO_2$	Sol	[8]	132.90	140.50	5.72	130.22	−2.02	130.71	−1.65

Table 5 (*Continued*)

No.	Mixed oxide	Binary oxides combination	Phase	Reference	C°_{pm}(298) (J K^{-1} mol^{-1})	C°_{pm}(298)(NKR) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)	C°_{pm}(298)(KK) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)	C°_{pm}(298)(BB) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)
118	Fe_2TiO_4	$2FeO\cdot TiO_2$	Sol	[8]	142.30	151.18	6.24	144.40	1.48	142.20	−0.07
119	Fe_2TiO_5	$Fe_2O_3\cdot TiO_2$	Sol	[1]	163.85	159.87	−2.43			160.61	−1.98
120	$Fe_3Al_2Si_3O_{12}$	$3FeO\cdot Al_2O_3\cdot 3SiO_2$	Sol	[15]	342.74	356.39	3.98	352.16	2.75	339.40	−0.97
121	Fe_3O_4	$FeO\cdot Fe_2O_3$	Sol	[6]	151.78	152.81	0.68	152.00	0.14	148.55	−2.13
122	$FeAl_2O_4$	$FeO\cdot Al_2O_3$	Sol	[15]	131.40	127.05	−3.31	124.46	−5.28	120.79	−8.07
123	$FeCr_2O_4$	$FeO\cdot Cr_2O_3$	Sol	[6]	133.81	162.30	21.29	151.28	13.06		
124	$FeSiO_3$	$FeO\cdot SiO_2$	Sol	[15]	88.12	92.46	4.93	88.87	0.85	87.33	−0.90
125	$FeTa_2O_6$	$FeO\cdot Ta_2O_5$	Sol	[67]	184.87	179.52	−2.89				
126	$FeTiO_3$	$FeO\cdot TiO_2$	Sol	[6]	99.50	103.14	3.66	100.39	0.89	98.82	−0.69
127	$Gd_3Fe_5O_{12}$	$(3Gd_2O_3\cdot 5Fe_2O_3)/2$	Sol	[78]	433.06	420.19	−2.97				
128	$Gd_3Ga_5O_{12}$	$(3Gd_2O_3\cdot 5Ga_2O_3)/2$	Sol	[61]	385.64	392.92	1.89				
129	Gd_3NbO_7	$(3Gd_2O_3\cdot Nb_2O_5)/2$	Sol	[74]	237.49	224.33	−5.54				
130	$GdCrO_3$	$(Gd_2O_3\cdot Cr_2O_3)/2$	Sol	[75]	99.52	109.89	10.42				
131	$Hg_{0,97}Ba_2CuO_{4,05}$		Sol	[79]	189.53						
132	$HgBaO_2$	$HgO\cdot BaO$	Sol	[80]	103.48	90.95	−12.11				
133	$HgCaO_2$	$HgO\cdot CaO$	Sol	[81]	96.31	86.31	−10.38				
134	$HgSrO_2$	$HgO\cdot SrO$	Sol	[80]	89.90	89.04	−0.96				
135	$Ho_3Fe_5O_{12}$	$(3Ho_2O_3\cdot 5Fe_2O_3)/2$	Sol	[82]	451.52	434.37	−3.80				
136	Ho_3NbO_7	$(3Ho_2O_3\cdot Nb_2O_5)/2$	Sol	[74]	252.14	238.51	−5.41				
137	Ho_6WO_{12}	$3Ho_2O_3\cdot WO_3$	Sol	[83]	434.20	417.68	−3.80				
138	$HoCrO_3$	$(Ho_2O_3\cdot Cr_2O_3)/2$	Sol	[75]	101.60	114.61	12.81				
139	$K_2B_4O_7$	$K_2O\cdot 2B_2O_3$	Sol	[6]	170.30	210.49	23.60	186.14	9.30		
140	$K_2B_6O_{10}$	$K_2O\cdot 3B_2O_3$	Sol	[6]	265.34	273.47	3.07				
141	$K_2B_8O_{13}$	$K_2O\cdot 4B_2O_3$	Sol	[6]	319.06	336.45	5.45				
142	K_2CrO_4	$K_2O\cdot CrO_3$	Sol-A	[6]	146.05	163.65	12.05	144.15	−1.30		
143	$K_2Si_2O_5$	$K_2O\cdot 2SiO_2$	Sol-A	[6]	160.95	173.37	7.72	158.67	−1.41	159.60	−0.84
144	$K_2Si_4O_9$	$K_2O\cdot 4SiO_2$	Sol	[84]	247.20	262.21	6.07			247.50	0.12
145	K_2SiO_3	$K_2O\cdot SiO_2$	Sol	[6]	118.70	128.95	8.64	114.81	−3.28	115.65	−2.57
146	$K_2W_2O_7$	$K_2O\cdot 2WO_3$	Sol	[85]	221.00	230.13	4.13				
147	$K_2W_3O_{10}$	$K_2O\cdot 3WO_3$	Sol	[85]	288.10	302.93	5.15				
148	$K_2W_4O_{13}$	$K_2O\cdot 4WO_3$	Sol	[85]	356.40	375.73	5.42				
149	K_2WO_4	$K_2O\cdot WO_3$	Sol-A	[6]	150.81	157.33	4.32	149.37	−0.95		
150	$KAl_3Si_3O_{11}$	$(K_2O\cdot 3Al_2O_3\cdot 6SiO_2)/2$	Sol	[1]	287.37	294.04	2.32	304.53	5.97	283.82	−1.24
151	$KAlSi_2O_6$	$(K_2O\cdot Al_2O_3\cdot 4SiO_2)/2$	Sol	[6]	164.30	170.61	3.84	171.46	4.36	162.46	−1.12
152	$KAlSi_3O_8$	$(K_2O\cdot Al_2O_3\cdot 6SiO_2)/2$	Microcline	[1]	202.84	215.03	6.01	215.32	6.15	206.41	1.76
153	$KAlSi_3O_8$	$(K_2O\cdot Al_2O_3\cdot 6SiO_2)/2$	Sanidine	[1]	205.28	215.03	4.75	215.32	4.89	206.41	0.55
154	$KAlSiO_4$	$(K_2O\cdot Al_2O_3\cdot 2SiO_2)/2$	Sol	[6]	119.90	126.19	5.25	123.94	3.37	118.51	−1.16
155	KBO_2	$(K_2O\cdot B_2O_3)/2$	Sol	[6]	66.96	73.76	10.15	67.13	0.25		
156	$KDyMo_2O_8$	$(K_2O\cdot Dy_2O_3\cdot 4MoO_3)/2$	Sol	[86]	235.90	250.68	6.26				

Table 5 (*Continued*)

No.	Mixed oxide	Binary oxides combination	Phase	Reference	C°_{pm}(298) (J K^{-1} mol^{-1})	C°_{pm}(298)(NKR) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)	C°_{pm}(298)(KK) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)	C°_{pm}(298)(BB) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)
157	$KErMo_2O_8$	$(K_2O\cdot Er_2O_3\cdot 4MoO_3)/2$	Sol	[87]	233.40	246.79	5.74				
158	$KGdMo_2O_8$	$(K_2O\cdot Gd_2O_3\cdot 4MoO_3)/2$	Sol-A	[88]	233.20	245.30	5.19	234.91	0.73		
159	$KHoMo_2O_8$	$(K_2O\cdot Ho_2O_3\cdot 4MoO_3)/2$	Sol	[89]	232.50	250.03	7.54	234.49	0.86		
160	$KLuMo_2O_8$	$(K_2O\cdot Lu_2O_3\cdot 4MoO_3)/2$	Sol	[90]	234.70	243.43	3.72				
161	$KTbMo_2O_8$	$(K_2O\cdot Tb_2O_3\cdot 4MoO_3)/2$	Sol	[91]	236.80						
162	$KYbMo_2O_8$	$(K_2O\cdot Yb_2O_3\cdot 4MoO_3)/2$	Sol	[92]	238.10	250.23	5.09				
163	$KYMo_2O_8$	$(K_2O\cdot Y_2O_3\cdot 4MoO_3)/2$	Sol	[93]	232.10	243.80	5.04	236.58	1.93		
164	La_2CuO_4	$La_2O_3\cdot CuO$	Sol	[94]	151.30	151.04	−0.17				
165	$La_2Mo_3O_{12}$	$La_2O_3\cdot 3MoO_3$	Sol	[6]	329.36	334.20	1.47	329.35	0.00		
166	La_2NiO_4	$La_2O_3\cdot NiO$	Sol	[95]	159.14	153.07	−3.81				
167	$La_2Si_2O_7$	$La_2O_3\cdot 2SiO_2$	Sol-B	[65]	195.18	197.62	1.25	192.31	−1.47		
168	$La_2Zr_2O_7$	$La_2O_3\cdot 2ZrO_2$	Sol	[66]	223.05	221.20	−0.83				
169	La_3NbO_7	$(3La_2O_3\cdot Nb_2O_5)/2$	Sol	[74]	235.68	229.24	−2.74				
170	$LaAlO_3$	$(La_2O_3\cdot Al_2O_3)/2$	Sol	[6]	92.64	93.90	1.36	93.25	0.66		
171	$LaCoO_3$	$(La_2O_3\cdot Co_2O_3)/2$	Sol	[96]	107.51						
172	$LaCrO_3$	$(La_2O_3\cdot Cr_2O_3)/2$	Sol	[75]	111.20	111.52	0.29				
173	$LaFeO_3$	$(La_2O_3\cdot Fe_2O_3)/2$	Sol	[96]	108.65	106.78	−1.72				
174	$LaMnO_3$	$(La_2O_3\cdot Mn_2O_3)/2$	Sol	[97]	102.79	103.91	1.09				
175	$LaMnO_{3,15}$		Sol	[80]	110.10						
176	$Li_2B_4O_7$	$Li_2O\cdot 2B_2O_3$	Sol	[6]	179.32	180.21	0.50	173.58	−3.20		
177	$Li_2B_8O_{13}$	$Li_2O\cdot 4B_2O_3$	Sol	[6]	324.23	306.17	−5.57				
178	$Li_2Si_2O_5$	$Li_2O\cdot 2SiO_2$	Sol-A	[6]	138.77	143.09	3.11	146.11	5.29		
179	Li_2SiO_3	$Li_2O\cdot SiO_2$	Sol	[6]	100.00	98.67	−1.33	102.25	2.25		
180	$Li_2Ti_3O_7$	$Li_2O\cdot 3TiO_2$	Sol	[98]	228.51	219.55	−3.92				
181	Li_2TiO_3	$Li_2O\cdot TiO_2$	Sol-A	[6]	109.68	109.35	−0.30	113.77	3.73		
182	Li_2ZrO_3	$Li_2O\cdot ZrO_2$	Sol	[99]	114.60	110.46	−3.61	114.38	−0.19		
183	Li_4SiO_4	$2Li_2O\cdot SiO_2$	Sol	[100]	155.23	152.92	−1.49	156.98	1.13		
184	$Li_4Ti_5O_{12}$	$2Li_2O\cdot 5TiO_2$	Sol	[98]	361.54	384.00	6.21				
185	Li_8ZrO_6	$4Li_2O\cdot ZrO_2$	Sol	[99]	275.46	273.21	−0.82				
186	$LiAlO_2$	$(Li_2O\cdot Al_2O_3)/2$	Sol	[8]	67.83	66.63	−1.77	68.92	1.61		
187	$LiAlSi_2O_6$	$(Li_2O\cdot Al_2O_3\cdot 4SiO_2)/2$	Sol-A	[6]	158.92	155.47	−2.17	165.18	3.94		
188	$LiAlSiO_4$	$(Li_2O\cdot Al_2O_3\cdot 2SiO_2)/2$	Sol-A	[101]	111.15	111.05	−0.09	117.66	5.86		
189	LiB_3O_5	$(Li_2O\cdot 3B_2O_3)/2$	Sol	[6]	145.52	121.60	−16.44				
190	$LiBO_2$	$(Li_2O\cdot B_2O_3)/2$	Sol	[6]	60.44	58.62	−3.02	60.85	0.68		
191	$LiFeO_2$	$(Li_2O\cdot Fe_2O_3)/2$	Sol	[6]	82.46	79.51	−3.58	82.62	0.19		
192	$Lu_3Fe_5O_{12}$	$(3Lu_2O_3\cdot 5Fe_2O_3)/2$	Sol	[102]	424.90	414.57	−2.43				
193	Lu_3NbO_7	$(3Lu_2O_3\cdot Nb_2O_5)/2$	Sol	[74]	220.14	218.71	−0.65				
194	Lu_6WO_{12}	$3Lu_2O_3\cdot WO_3$	Sol	[83]	393.75	378.08	−3.98				
195	$Mg_2Al_4Si_5O_{18}$	$2MgO\cdot 2Al_2O_3\cdot 5SiO_2$	Sol	[1]	452.38	454.64	0.50	478.84	5.85	449.19	−0.71
196	Mg_2SiO_4	$2MgO\cdot SiO_2$	Sol	[6]	118.43	118.94	0.43	117.66	−0.65	118.57	0.12

Table 5 (*Continued*)

No.	Mixed oxide	Binary oxides combination	Phase	Reference	$C^{\circ}_{pm}(298)$ (J K^{-1} mol^{-1})	$C^{\circ}_{pm}(298)$(NKR) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)	$C^{\circ}_{pm}(298)$(KK) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)	$C^{\circ}_{pm}(298)$(BB) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)
197	Mg_2TiO_4	$2MgO{\cdot}TiO_2$	Sol	[6]	128.17	129.62	1.13	131.84	2.87	130.06	1.48
198	$Mg_3Al_2Si_3O_{12}$	$3MgO{\cdot}Al_2O_3{\cdot}3SiO_2$	Sol	[1]	324.76	324.05	−0.22	333.32	2.64	321.19	−1.10
199	$MgAl_2O_4$	$MgO{\cdot}Al_2O_3$	Sol	[6]	115.96	116.27	0.27	118.18	1.92	114.72	−1.07
200	$MgAl_2SiO_6$	$MgO{\cdot}Al_2O_3{\cdot}SiO_2$	Sol	[15]	160.27	160.69	0.26			158.67	−1.00
201	$MgCr_2O_4$	$MgO{\cdot}Cr_2O_3$	Sol	[6]	126.80	151.52	19.50	145.00	14.36		
202	$MgFe_2O_4$	$MgO{\cdot}Fe_2O_3$	Sol	[1]	142.94	142.03	−0.64	145.72	1.94	142.48	−0.32
203	$MgRh_2O_4$	$MgO{\cdot}Rh_2O_3$	Sol	[103]	129.84	126.38	−2.66				
204	$MgSiO_3$	$MgO{\cdot}SiO_2$	Sol-A	[6]	81.90	81.68	−0.27	82.59	0.84	81.26	−0.78
205	$MgTa_2O_6$	$MgO{\cdot}Ta_2O_5$	Sol	[67]	175.73	168.74	−3.98				
206	$MgTi_2O_5$	$MgO{\cdot}2TiO_2$	Sol	[6]	146.64	147.46	0.56	144.35	−1.56	148.19	1.06
207	$MgTiO_3$	$MgO{\cdot}TiO_2$	Sol	[6]	91.19	92.36	1.28	94.11	3.20	92.75	1.71
208	$MgUO_4$	$MgO{\cdot}UO_3$	Sol	[6]	156.51	118.45	−24.32	126.77	−19.00		
209	MgV_2O_6	$MgO{\cdot}V_2O_5$	Sol	[6]	156.35	164.63	5.30	162.74	4.09		
210	$MgWO_4$	$MgO{\cdot}WO_3$	Sol	[6]	109.89	110.06	0.16	117.15	6.61		
211	$Mn_2Al_4Si_5O_{18}$	$2MnO{\cdot}2Al_2O_3{\cdot}5SiO_2$	Sol	[15]	462.33	469.64	1.58	486.38	5.20		
212	$Mn_2Mo_3O_8$	$2MnO{\cdot}3MoO_2$	Sol	[104]	245.90	257.49	4.71				
213	Mn_2SiO_4	$2MnO{\cdot}SiO_2$	Sol	[6]	129.87	133.94	3.13	125.20	−3.60		
214	Mn_2TiO_4	$2MnO{\cdot}TiO_2$	Sol	[6]	144.60	144.62	0.01	139.38	−3.61		
215	$Mn_3Al_2Si_3O_{12}$	$3MnO{\cdot}Al_2O_3{\cdot}3SiO_2$	Sol	[15]	340.30	346.55	1.84	344.63	1.27		
216	Mn_3O_4	$MnO{\cdot}Mn_2O_3$	Tetra	[6]	140.53	143.80	2.33				
217	$MnMoO_4$	$MnO{\cdot}MoO_3$	Sol	[104]	115.77	119.90	3.57	116.20	0.37		
218	$MnSiO_3$	$MnO{\cdot}SiO_2$	Sol	[6]	86.39	89.18	3.23	86.36	−0.04		
219	$MnTiO_3$	$MnO{\cdot}TiO_2$	Sol	[6]	99.83	99.86	0.03	97.88	−1.95		
220	$MnWO_4$	$MnO{\cdot}WO_3$	Sol	[6]	124.08	117.56	−5.25	120.92	−2.55		
221	$Na_2B_4O_7$	$Na_2O{\cdot}2B_2O_3$	Sol	[6]	186.92	194.52	4.07	186.14	−0.42		
222	NaB_3O_5	$(Na_2O{\cdot}3B_2O_3)/2$	Sol	[6]	121.84	128.75	5.67				
223	$Na_2B_8O_{13}$	$Na_2O{\cdot}4B_2O_3$	Sol	[6]	304.89	320.48	5.11				
224	Na_2CrO_4	$Na_2O{\cdot}CrO_3$	Sol-A	[6]	142.78	147.68	3.43	144.15	0.96		
225	$Na_2Mo_2O_7$	$Na_2O{\cdot}2MoO_3$	Sol	[6]	216.67	218.84	1.00				
226	Na_2MoO_4	$Na_2O{\cdot}MoO_3$	Sol-A	[6]	141.46	143.70	1.58	144.65	2.26		
227	$Na_2Si_2O_5$	$Na_2O{\cdot}2SiO_2$	Sol-A	[6]	156.50	157.40	0.57	158.67	1.39	157.08	0.37
228	Na_2SiO_3	$Na_2O{\cdot}SiO_2$	Sol	[6]	111.81	112.98	1.04	114.81	2.68	113.13	1.18
229	$Na_2Ti_2O_5$	$Na_2O{\cdot}2TiO_2$	Sol	[6]	193.13	178.76	−7.44	176.57	−8.57	180.06	−6.77
230	$Na_2Ti_3O_7$	$Na_2O{\cdot}3TiO_2$	Sol	[1]	249.66	233.86	−6.33			235.50	−5.67
231	$Na_2Ti_6O_{13}$	$Na_2O{\cdot}6TiO_2$	Sol	[105]	397.23	399.16	0.49			401.82	1.16
232	Na_2TiO_3	$Na_2O{\cdot}TiO_2$	Sol-A	[1]	126.77	123.66	−2.45	126.33	−0.35	124.62	−1.70
233	$Na_2U_2O_7$	$Na_2O{\cdot}2UO_3$	Sol-A	[106]	227.26	230.94	1.62				
234	Na_2UO_4	$Na_2O{\cdot}UO_3$	Sol-A	[6]	146.74	149.75	2.05	158.99	8.35		
235	Na_2WO_4	$Na_2O{\cdot}WO_3$	Sol-A	[6]	141.77	141.36	−0.29	149.37	5.36		
236	$Na_2W_2O_7$	$Na_2O{\cdot}2WO_3$	Sol	[107]	214.22	214.16	−0.03				

Table 5 (*Continued*)

No.	Mixed oxide	Binary oxides combination	Phase	Reference	$C^\circ_{pm}(298)$ (J K^{-1} mol^{-1})	$C^\circ_{pm}(298)$(NKR) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)	$C^\circ_{pm}(298)$(KK) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)	$C^\circ_{pm}(298)$(BB) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)
237	$Na_2W_4O_{13}$	$Na_2O{\cdot}4WO_3$	Sol	[107]	354.45	359.76	1.50				
238	Na_2ZrO_3	$Na_2O{\cdot}ZrO_2$	Sol-A	[6]	131.20	124.77	−4.90	126.94	−3.25		
239	Na_4SiO_4	$2Na_2O{\cdot}SiO_2$	Sol	[6]	184.72	181.54	−1.72	182.10	−1.42	182.31	−1.30
240	$NaAlO_2$	$(Na_2O{\cdot}Al_2O_3)/2$	Sol-A	[6]	73.52	73.79	0.36	75.23	2.33	73.30	−0.30
241	$NaAlSi_2O_6$	$(Na_2O{\cdot}Al_2O_3{\cdot}4SiO_2)/2$	Sol	[6]	159.88	162.63	1.72	171.46	7.25	161.20	0.83
242	$NaAlSi_3O_8$	$(Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2)/2$	Sol-A	[6]	204.85	207.05	1.07	215.32	5.11	205.15	0.15
243	$NaAlSiO_4$	$(Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2)/2$	Sol	[8]	115.81	118.21	2.07	123.94	7.02	117.25	1.24
244	$NaBO_2$	$(Na_2O{\cdot}B_2O_3)/2$	Sol	[6]	65.85	65.77	−0.12	67.13	1.94		
245	$NaCrO_2$	$(Na_2O{\cdot}Cr_2O_3)/2$	Sol	[6]	89.41	91.41	2.24	88.61	−0.89		
246	$NaFeSi_2O_6$	$(Na_2O{\cdot}Fe_2O_3{\cdot}4SiO_2)/2$	Sol	[1]	170.17	175.51	3.14	177.74	4.45	175.08	2.89
247	$NaUO_3$	$(Na_2O{\cdot}UO_2{\cdot}UO_3)/2$	Sol	[108]	108.87	106.67	−2.02				
248	Nd_2NiO_4	$Nd_2O_3{\cdot}NiO$	Sol	[109]	160.22	155.63	−2.86				
249	Nd_3NbO_7	$(3Nd_2O_3{\cdot}Nb_2O_5)/2$	Sol	[74]	243.89	233.08	−4.44				
250	$NdAlO_3$	$(Nd_2O_3{\cdot}Al_2O_3)/2$	Sol	[110]	97.05	95.18	−1.93	92.00	−5.20		
251	$NdCrO_3$	$(Nd_2O_3{\cdot}Cr_2O_3)/2$	Sol	[75]	106.48	112.80	5.94				
252	$NdGaO_3$	$(Nd_2O_3{\cdot}Ga_2O_3)/2$	Sol	[111]	105.80	102.60	−3.02				
253	Ni_2SiO_4	$2NiO{\cdot}SiO_2$	Sol	[6]	127.02	133.00	4.71	133.56	5.15		
254	$NiTa_2O_6$	$NiO{\cdot}Ta_2O_5$	Sol	[67]	171.15	175.77	2.70				
255	$NiTiO_3$	$NiO{\cdot}TiO_2$	Sol	[6]	99.25	99.39	0.14	102.06	2.83		
256	Pb_2SiO_4	$2PbO{\cdot}SiO_2$	Sol-A	[6]	136.92	135.90	−0.74	131.90	−3.67		
257	Pb_3O_4	$PbO{\cdot}Pb_2O_3$	Sol	[6]	154.94						
258	Pb_4SiO_6	$4PbO{\cdot}SiO_2$	Sol	[6]	229.73	227.38	−1.02				
259	$PbSiO_3$	$PbO{\cdot}SiO_2$	Sol	[6]	89.13	90.16	1.16	89.71	0.66		
260	$PbTiO_3$	$PbO{\cdot}TiO_2$	Sol-A	[6]	104.40	100.84	−3.41	101.23	−3.04		
261	$PbWO_4$	$PbO{\cdot}WO_3$	Sol	[6]	119.64	118.54	−0.92	124.27	3.87		
262	Pr_2NiO_4	$Pr_2O_3{\cdot}NiO$	Sol	[95]	165.46	160.92	−2.74				
263	Pr_3NbO_7	$(3Pr_2O_3{\cdot}Nb_2O_5)/2$	Sol	[74]	250.21	241.01	−3.68				
264	$PrCrO_3$	$(Pr_2O_3{\cdot}Cr_2O_3)/2$	Sol	[75]	108.92	115.45	6.00				
265	$Rb_2Cr_2O_7$	$Rb_2O{\cdot}2CrO_3$	Sol	[112]	230.17	*236.94*	*2.94*				
266	$Rb_2Mo_2O_7$	$Rb_2O{\cdot}2MoO_3$	Sol	[70]	209.72	*228.98*	*9.18*				
267	$Rb_2Si_2O_5$	$Rb_2O{\cdot}2SiO_2$	Sol	[6]	170.72	*167.54*	*−1.86*	159.51	−6.56		
268	$Rb_2Si_4O_9$	$Rb_2O{\cdot}4SiO_2$	Sol	[6]	270.89	*256.38*	*−5.36*				
269	Rb_2SiO_3	$Rb_2O{\cdot}SiO_2$	Sol	[6]	117.45	*123.12*	*4.83*	115.65	−1.53		
270	$Rb_2U_2O_7$	$Rb_2O{\cdot}2UO_3$	Sol	[72]	258.24	*241.08*	*−6.65*				
271	$RbAlO_2$	$(Rb_2O{\cdot}Al_2O_3)/2$	Sol	[72]	77.31	*78.86*	*1.99*	75.62	−2.19		
272	$RbBO_2$	$(Rb_2O{\cdot}B_2O_3)/2$	Sol	[6]	73.46	*70.84*	*−3.57*	67.55	−8.05		
273	$ScMnO_3$	$(Sc_2O_3{\cdot}Cr_2O_3)/2$	Sol	[113]	102.40	96.49	−5.77				
274	$Sm_3Fe_5O_{12}$	$(3Sm_2O_3{\cdot}5Fe_2O_3)/2$	Sol	[114]	447.10	435.66	−2.56				
275	Sm_3NbO_7	$(3Sm_2O_3{\cdot}Nb_2O_5)/2$	Sol	[74]	240.06	239.80	−0.11				
276	$SmCrO_3$	$(Sm_2O_3{\cdot}Cr_2O_3)/2$	Sol	[75]	101.62	115.04	13.21				

Table 5 (*Continued*)

No.	Mixed oxide	Binary oxides combination	Phase	Reference	$C^\circ_{pm}(298)$ (J K^{-1} mol^{-1})	$C^\circ_{pm}(298)$(NKR) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)	$C^\circ_{pm}(298)$(KK) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)	$C^\circ_{pm}(298)$(BB) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)
277	$SmNiO_3$		Sol	[115]	110.58						
278	Sr_2CuO_3	$2SrO{\cdot}CuO$	Sol	[116]	134.87	132.56	−1.71				
279	Sr_2SiO_4	$2SrO{\cdot}SiO_2$	Sol	[6]	130.80	134.72	3.00	129.38	−1.08		
280	Sr_2TiO_4	$2SrO{\cdot}TiO_2$	Sol	[6]	143.68	145.40	1.19	143.56	−0.09		
281	$Sr_3MgSi_2O_8$	$3SrO{\cdot}MgO{\cdot}2SiO_2$	Sol	[117]	257.35	261.55	1.63	252.90	−1.73		
282	$Sr_3U_{11}O_{33}$	$3SrO{\cdot}3UO_2{\cdot}8UO_3$	Sol	[118]	1064.20	975.74	−8.31				
283	$Sr_3U_2O_9$	$3SrO{\cdot}2UO_3$	Sol	[118]	301.80	297.83	−1.32				
284	$Sr_4Ti_3O_{10}$	$4SrO{\cdot}3TiO_2$	Sol	[6]	341.89	345.90	1.17	343.50	0.47		
285	$Sr_{14}Cu_{24}O_{41}$		Sol	[116]	1730.76						
286	$SrAl_2O_4$	$SrO{\cdot}Al_2O_3$	Sol-A	[6]	119.03	124.16	4.31	124.04	4.21		
287	$SrAl_2Si_2O_8$	$SrO{\cdot}Al_2O_3{\cdot}2SiO_2$	Sol	[50]	221.22	213.00	−3.71	221.52	0.14		
288	$SrCeO_3$	$SrO{\cdot}CeO_2$	Sol	[119]	108.87	106.68	−2.01				
289	$SrCuO_2$	$SrO{\cdot}CuO$	Sol	[116]	86.75	87.41	0.76				
290	$SrMnO_3$	$SrO{\cdot}MnO_2$	Sol	[80]	108.73	99.57	−8.43				
291	$SrMoO_4$	$SrO{\cdot}MoO_3$	Sol	[6]	117.06	120.29	2.76	118.29	1.05		
292	$SrSiO_3$	$SrO{\cdot}SiO_2$	Sol	[120]	89.61	89.57	−0.04	88.45	−1.29		
293	$SrTiO_3$	$SrO{\cdot}TiO_2$	Sol	[6]	99.10	100.25	1.16	99.97	0.87		
294	$SrWO_4$	$SrO{\cdot}WO_3$	Sol	[6]	131.43	117.95	−10.26	123.01	−6.41		
295	$SrZrO_3$	$SrO{\cdot}ZrO_2$	Sol	[37]	103.43	101.36	−2.00	100.58	−2.76		
296	$SrZrSi_2O_7$	$SrO{\cdot}ZrO_2{\cdot}2SiO_2$	Sol	[121]	187.81	190.20	1.27	190.64	1.51		
297	$Tb_3Fe_5O_{12}$	$(3Tb_2O_3{\cdot}5Fe_2O_3)/2$	Sol	[122]	444.40	*425.28*	*−4.30*				
298	Tb_3NbO_7	$(3Tb_2O_3{\cdot}Nb_2O_5)/2$	Sol	[74]	243.48	*229.42*	*−5.78*				
299	$TbFeO_3$	$(Tb_2O_3{\cdot}Fe_2O_3)/2$	Sol	[123]	105.02	*106.84*	*1.73*				
300	$Tl_2Ba_2Ca_2Cu_3O_{10}$	$Tl_2O_3{\cdot}2BaO{\cdot}2CaO{\cdot}3CuO$	Sol	[124]	430.73	411.20	−4.53				
301	$Tl_2Ba_2CaCu_2O_8$	$Tl_2O_3{\cdot}2BaO{\cdot}CaO{\cdot}2CuO$	Sol	[124]	338.70	326.52	−3.60				
302	$Tl_{2,1}Ba_2CaCu_2O_{8,15}$	$1.05\ Tl_2O_3{\cdot}2BaO{\cdot}CaO{\cdot}2CuO$	Sol	[125]	339.56	331.79	−2.29				
303	$Tl_2Ba_2CuO_6$	$Tl_2O_3{\cdot}2BaO{\cdot}CuO$	Sol	[124]	249.37	241.84	−3.02				
304	$Tm_3Fe_5O_{12}$	$(3Tm_2O_3{\cdot}5Fe_2O_3)/2$	Sol	[82]	458.98	437.01	−4.79				
305	Tm_3NbO_7	$(3Tm_2O_3{\cdot}Nb_2O_5)/2$	Sol	[74]	245.52	241.15	−1.78				
306	$TmBa_2Cu_3O_7$		Sol	[126]	288.80						
307	$Y_2Cu_2O_5$	$Y_2O_3{\cdot}2CuO$	Sol	[127]	187.04	187.03	−0.01				
308	$Y_3Al_5O_{12}$	$(3Y_2O_3{\cdot}5Al_2O_3)/2$	Sol	[128]	348.13	351.29	0.91	358.54	2.99		
309	$Y_3Fe_5O_{12}$	$(3Y_2O_3{\cdot}5Fe_2O_3)/2$	Sol	[123]	426.77	415.69	−2.60				
310	Y_3NbO_7	$(3Y_2O_3{\cdot}Nb_2O_5)/2$	Sol	[74]	224.85	219.83	−2.23				
311	Yb_3NbO_7	$(3Yb_2O_3{\cdot}Nb_2O_5)/2$	Sol	[74]	245.21	239.11	−2.49				
312	$YBa_2Cu_3O_{6,7}$		Sol	[129]	285.80						
313	$YBa_2Cu_3O_{6,85}$		Sol	[129]	285.80						

Table 5 (*Continued*)

No.	Mixed oxide	Binary oxides combination	Phase	Reference	$C^\circ_{pm}(298)$ (J K^{-1} mol^{-1})	$C^\circ_{pm}(298)$(NKR) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)	$C^\circ_{pm}(298)$(KK) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)	$C^\circ_{pm}(298)$(BB) (J K^{-1} mol^{-1})	ΔC°_{pm} (%)
314	$YBa_2Cu_3O_{6,9}$		Sol	[130]	282.25						
315	$YBa_2Cu_3O_{6,96}$		Sol	[131]	281.20						
316	$YBa_2Cu_4O_8$		Sol	[130]	320.10						
317	$YbMnO_3$	$(Yb_2O_3 \cdot Mn_2O_3)/2$	Sol	[132]	108.70	107.20	−1.38				
318	$YCrO_3$	$(Y_2O_3 \cdot Cr_2O_3)/2$	Sol	[75]	97.21	108.39	11.50				
319	$YMnO_3$	$(Y_2O3 \cdot Mn_2O_3)/2$	Sol	[132]	98.37	100.78	2.45				
320	Zn_2SiO_4	$2ZnO \cdot SiO_2$	Sol	[6]	121.83	126.56	3.88	121.86	0.02		
321	Zn_2TiO_4	$2ZnO \cdot TiO_2$	Sol	[6]	137.33	137.24	−0.06	136.04	−0.94		
322	$ZnFe_2O_4$	$ZnO \cdot Fe_2O_3$	Sol	[6]	137.33	145.84	6.19	147.82	7.64		
323	$ZnMn_2O_4$	$ZnO \cdot Mn_2O_3$	Sol	[133]	140.30	140.11	−0.14				
324	$ZnWO_4$	$ZnO \cdot WO_3$	Sol	[6]	125.50	113.87	−9.27	119.25	−4.98		
325	$ZrTiO_4$	$ZrO_2 \cdot TiO2$	Sol	[134]	114.03	111.31	−2.39	116.37	2.05		
326	$ZrSiO_4$	$ZrO_2 \cdot SiO_2$	Sol	[6]	98.57	100.63	2.09	102.19	3.67		

assumption that the predominant contribution to C°_{pm} of solids results from the lattice vibrational contribution and does not practically alter during the solid state reaction between the constituent compounds. On the contrary, the translational and, in case of polyatomic molecules, also rotational contributions dominate in gaseous state.

The average error of the estimated values was found 3.3%, whereas for 74 substances (25%) the error did not exceed 1%.

3.3. Kellogg's method

From the ionic contributions proposed by Spencer [18], the values of C°_{pm}(298.15 K) were estimated for 169 mixed oxides with the average error of 3.1%, whereas for 47 substances (28%) the error did not exceed 1%. The accuracy of this method is comparable to that of the NKR—using the same set of substances the average error of the NKR was 3.2% and for 44 compounds did not exceed 1%. As to the universality, the NKR is better than the KK. Indeed, the KK is inapplicable almost for one half of mixed oxides included in the primary set.

3.4. Berman and Brown's method (BB)

Using the BB method the coefficients of $C^\circ_{pm}(T)$ dependence in Eq. (7) were estimated and the values of C°_{pm}(298.15 K) for 68 mixed oxides were evaluated with the average error of 1.5%. For 31 compounds (46%), the error did not exceed 1%. The higher accuracy than for the NKR (average error 2.2% with the same set) is due to smaller universality of the BB method, which is applicable only for the one fifth of substances from the primary set.

4. Influence of C°_{pm} estimation error on the results of equilibrium calculations

Let us consider the formation reaction of the mixed oxide $RE_2Cu_2O_5$ (RE, rare earth element) in order to demonstrate the influence of molar heat capacity error on the results of equilibrium calculations. The reaction from binary oxides is described by the equation

$$2\,CuO(s) + Ln_2O_3(s) \rightarrow Ln_2Cu_2O_5(s) \qquad (R4)$$

As all involved substances are single-species phases, they can all coexist at certain equilibrium temperature, at which $\Delta G^\circ{}_r$ (further denoted ΔG°(ox)) is equal zero. Since in general

$$\Delta G^\circ_r = \Delta H^\circ_r - T\Delta S^\circ_r \qquad (8)$$

this equilibrium temperature is given by the relation

$$T_{eq} = \frac{\Delta H^\circ(ox)}{\Delta S^\circ(ox)} \qquad (9)$$

The standard enthalpy and entropy, ΔH°(ox) and ΔS°(ox), respectively, of reaction (R4) are temperature dependent:

$$\Delta H^\circ(ox) = \Delta H^\circ(ox)(298.15\,K) + \int_{298}^{T} \Delta C^\circ_{pm}(ox)\,dT \qquad (10)$$

$$\Delta S^\circ(ox) = \Delta S^\circ(ox)(298.15\,K) + \int_{298}^{T} \frac{\Delta C^\circ_{pm}(ox)}{T}\,dT \qquad (11)$$

For the numerical calculation, the experimental data for $Yb_2Cu_2O_5$ reported by Jacob et al. [46] will be employed. The standard Gibbs energy of reaction (R4) has been obtained from the EMF measurements with solid electrolyte in the form of the linear temperature dependence

$$\Delta G^\circ(ox) = 9920 - 13.90T(J)$$
$$(T = 970\text{–}1323\,K) \qquad (12)$$

The comparison with Eq. (8) yields for $Yb_2Cu_2O_5$ the values of $\Delta H^\circ(ox) = 9920$ J and $\Delta S^\circ(ox) = 13.9$ J. mol which can be assigned to the mean temperature of 1146.5 K. Under the assumption of both ΔH°(ox) and ΔS°(ox) being independent of temperature, i.e. $\Delta C^\circ_{pm}(ox) = 0$, the equilibrium temperature of $T_{eq} = 714$ K can be calculated from Eq. (9). For more precise calculation, the temperature dependencies of both ΔH°(ox) and ΔS°(ox) (Eqs. (10) and (11), respectively) are to be considered. As the experimental C°_{pm} data for $Yb_2Cu_2O_5$ are not available we have no choice but to use the estimated value. If we use the NKR $C^\circ_{pm}(Yb_2Cu_2O_5)(298.15\,K) = 199.9\,J\,K^{-1}\,mol^{-1}$ with the average estimation error 3.3%. We can expect ΔC°_{pm}(ox) to fall in the interval $\langle -6.6;\ 6.6\rangle$ $J\,K^{-1}\,mol^{-1}$. Then, if ΔC°_{pm}(ox) is temperature independent we obtain $T_{eq} = 750$ K and $T_{eq} = 654$ K for the ultimate values of $\Delta C^{\circ}_{pm}(\mathrm{ox}) = 6.6$ and $-6.6\ \mathrm{J\ K^{-1}\ mol^{-1}}$, respectively.

5. Conclusions

The detailed assessment of three selected empirical methods applicable for prediction of heat capacities of mixed oxides revealed that the NKR can be used for rough estimates of $C^{\circ}_{pm}(298.15\ \mathrm{K})$. This method is highly universal, but in many cases the estimation error can exceed 5% (60 from 278 tested oxides), which is not acceptable in some types of thermodynamic calculations. More accurate values can be obtained using methods based on the individual contributions of binary oxides forming a given mixed oxide. The universality of such an approach is in the first place due to the extent of the evaluated contribution set. For instance, from the file of contributions assessed by Berman and Brown, a number of heat capacities of silicates and other oxide minerals can be predicted. The mean accuracy of such estimates is nearly comparable with experimental errors of DSC or drop calorimetry measurements of heat capacity. Thus a further extension and generalization of this method to other mixed oxide families like high-temperature oxide superconductors and related mixed oxides seem to be very promising. However, the oxygen non-stoichiometry of some phases will have to be taken into account (see Eq. (R3)) by evaluating the oxygen or O^{2-} anion contribution.

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References

[1] R.G. Berman, T.H. Brown, Contrib. Mineral. Petrol. 89 (1985) 168.
[2] O. Kubaschewski, High Temp.—High Press. 4 (1972) 1.
[3] V.P. Glushko, L.V. Gurvich, G.A. Bergman, I.V. Veic, V.A. Medvedev, G.A. Khachkuruzov, V.S. Yungman, Thermodynamic Properties of Individual Substances, Tom I–IV, Nauka, Moskva, 1978–1982 (in Russian).
[4] L.B. Pankratz, Thermodynamic Properties of Elements and Oxides, Bulletin 672, US Bureau of Mines, Washington, 1982.
[5] I.S. Kulikov, Thermodynamics of Oxides, Metallurgiya, Moscow, 1986 (in Russian).
[6] O. Knacke, O. Kubaschewski, K. Hesselmann, Thermochemical Properties of Inorganic Substances, 2nd Edition, Springer, Berlin, 1991.
[7] O. Kubaschewski, C.B. Alcock, P.J. Spencer, Materials Thermochemistry, 6th Edition, Pergamon Press, Oxford, 1993.
[8] I. Barin, Thermochemical Data of Pure Substances, 3rd Edition, Wiley/VCH, Weinheim, 1995.
[9] M.W. Chase, Jr. (Ed.), NIST-JANAF Thermochemical Tables, 4th Edition, J. Phys. Chem. Ref. Data, Monograph No. 9, 1998.
[10] R.G. Berman, J. Petrol. 29 (1988) 445.
[11] T.J.B. Holland, R. Powel, J. Metamorphic Geol. 8 (1990) 89.
[12] S.K. Saxena, N. Chatterjee, Y. Fei, G. Shen, Thermodynamic Data on Oxides and Silicates, Springer, Berlin, 1993.
[13] R.A. Robie, B.S. Hemingway, Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 bar Pressure and at Higher Temperatures, US Government and Printing Office, Washington 1995.
[14] M. Gottschalk, Eur. J. Miner. 9 (1997) 175.
[15] T.J.B. Holland, R. Powell, J. Metamorph. Geol. 16 (1998) 309.
[16] N.D. Chatterjee, R. Kruger, G. Haller, W. Olbricht, Contrib. Mineral. Petrol. 133 (1998) 149.
[17] G.K. Moiseev, J. Šesták, Prog. Cryst. Growth Charact. 30 (1995) 23.
[18] P.J. Spencer, Thermochim. Acta 314 (1998) 1.
[19] J. Leitner, P. Chuchvalec, D. Sedmidubský, Chem. Listy 95 (2001) 2.
[20] H.C. Helgeson, J.M. Delany, H.W. Nesbitt, D.K. Bird, Am. J. Sci. A 278 (1978) 1.
[21] K. Ukleba, G. Gvelesiani, J. Baratashvili, D. Tsagareishvili, J. Omiadze, A. Nadiradze, Bull. Georgian Acad. Sci. 156 (1997) 66.
[22] H.H. Kellogg, in: G.R. Fitterer (Ed.), Applications of Fundamental Thermodynamics to Metallurgical Processes, Gordon and Breach, London, 1967, p. 357.
[23] O. Kubaschewski, H. Ünal, High Temp.—High Press. 9 (1977) 361.
[24] V.N. Kumok, Problem of Correlation Methods for Evaluation of Thermodynamic Characteristics, Direct and Reverse Tasks of Chemical Thermodynamics, Nauka, Novosibirsk, 1987, p. 108 (in Russian).
[25] G.R. Robinson Jr., J.L. Haas Jr., Am. Miner. 68 (1983) 541.
[26] G.F. Voronin, I.A. Uspenskaya, Zh. Fiz. Khim. 71 (1997) 1927.
[27] O.Yu. Goncharov, Yu.P. Vorobev, Zh. Fiz. Khim. 73 (1999) 23.
[28] A.S. Pashinkin, A.S. Malkova, A.A. Ivanov, Neorg. Mater. 31 (1995) 1604.
[29] A.S. Malkova, A.S. Pashinkin, Neorg. Mater. 28 (1993) 240.
[30] M.K. Aldabergenov, G.T. Balakaeva, Zh. Fiz. Khim. 67 (1993) 425.
[31] M.K. Aldabergenov, G.T. Balakaeva, G.T. Kokibasova, Zh. Fiz. Khim. 72 (1998) 808.

[32] G.G. Gospodinov, D.I. Mihov, J. Chem. Thermodyn. 25 (1993) 1249.
[33] G.G. Gospodinov, J. Chem. Thermodyn. 26 (1994) 143.
[34] G.G. Gospodinov, J. Chem. Thermodyn. 26 (1994) 713.
[35] G.G. Gospodinov, J. Chem. Thermodyn. 26 (1994) 1111.
[36] G.G. Gospodinov, V.M. Marchev, Thermochim. Acta 222 (1993) 137.
[37] M.E. Huntelaar, E.H.P. Cordfunke, R.R. van der Laan, Thermochim. Acta 274 (1996) 101.
[38] K. Gavritchev, Thermochim. Acta 343 (2000) 63.
[39] B.K. Kasenov, M.A. Mukhanova, Sh.B. Kasenova, E.S. Mustafin, Zh. Fiz. Khim. 70 (1996) 24.
[40] Sh.B. Kasenova, B.K. Kasenov, E.S. Mustafin, M.K. Aldabergenov, Zh. Fiz. Khim. 71 (1997) 751.
[41] E.S. Mustafin, A.T. Oralova, B.K. Kasenov, Neorg. Mater. 30 (1994) 863.
[42] E.S. Mustafin, A.T. Oralova, B.K. Kasenov, Inorg. Mater. 31 (1995) 914.
[43] A.T. Oralova, B.K. Kasenov, M.M. Mataev, B.Z. Nurgaliev, Zh. Fiz. Khim. 70 (1996) 944.
[44] A.T. Oralova, E.S. Mustafin, B.K. Kasenov, Inorg. Mater. 32 (1996) 111.
[45] A.T. Oralova, B.K. Kasenov, E.S. Mustafin, High Temp. 34 (1996) 645.
[46] K.T. Jacob, T. Mathews, J.P. Hajra, High Temp. Mater. Processes 12 (1993) 251.
[47] P.G. Hall, D.A. Armitage, R.G. Linford, J. Chem. Thermodyn. 17 (1985) 657.
[48] E.H.P. Cordfunke, R.J.M. Konings, R.R. van der Laan, W. Ouweltjes, J. Chem. Thermodyn. 25 (1993) 343.
[49] N.F. Menshenina, A.A. Evdokimov, A.N. Klimenko, Zh. Neorg. Khim. 30 (1985) 568.
[50] I.V. Chernyshova, Yu.V. Semenov, V.M. Agoshov, M. Gambino, P. Gaune, J.P. Bros, Thermochim. Acta 175 (1991) 119.
[51] M.J. Scholten, J. Schoonman, J.C. van Miltenburg, E.H.P. Cordfunke, Thermochim. Acta 268 (1995) 161.
[52] K.S. Gavrichev, V.E. Gorbunov, L.N. Golushina, G.E. Nikiforova, G.A. Totrova, I.S. Shaplygin, Neorg. Mater. 29 (1993) 645.
[53] Yu.F. Minekov, N.I. Matskevich, Yu.G. Stenin, P.P. Samoilov, Thermochim. Acta 278 (1996) 1.
[54] E.H.P. Cordfunke, R.J.M. Konings (Eds.), Thermochemical Data for Reactor Materials and Fission Products, Elsevier, Amsterdam, 1990.
[55] M.E. Huntelaar, E.H.P. Cordfunke, G.D. Elzinga, R.R. van der Laan, J. Chem. Thermodyn. 32 (2000) 671.
[56] P. Abrman, D. Sedmidubský, A. Strejc, P. Voňka, J. Leitner, Thermochim. Acta 381 (2002) 1.
[57] M. Castro, R. Burriel, R. Ibanez, S. Fernando, IEEE Trans. Magn. 30 (1994) 1163.
[58] J. Leitner, D. Sedmidubský, A. Strejc, P. Abrman, B. Doušová, M. Nevřiva, in: B. Taraba (Ed.), Proceedings of the Calorim. Seminar 2000, University Ostrava, Ostrava, 2000, p. 9 (in Czech).
[59] K.S. Gavrichev, V.E. Gorbunov, I.A. Konovalova, V.B. Lazarev, E.A. Tishchenko, I.S. Shaplygin, Izv. Akad. Nauk SSSR, Neorg. Mater. 26 (1990) 1102.
[60] J.R. Taylor, A.T. Dinsdale, CALPHAD 14 (1990) 71.
[61] A.S. Malkova, A.S. Pashinkin, Neorg. Mater. 28 (1993) 240.
[62] M.Y. Lee, C.L. Nassaralla, Thermochim. Acta 371 (2001) 1.
[63] R.L. Putnam, A. Navrotsky, B.F. Woodfield, J.L. Shapiro, R. Stevens, J. Boerio-Goates, Mat. Res. Soc. Symp. Proc. 556 (1999) 11.
[64] B.F. Woodfield, J. Boerio-Goates, J.L. Shapiro, R.L. Putnam, A. Navrotsky, J. Chem. Thermodyn. 31 (1999) 245.
[65] M. Bolech, E.H.P. Cordfunke, A.C.G. van Genderen, R.R. van der Laan, F.J.J.G. Janssen, J.C. van Miltenburg, Thermochim. Acta 284 (1996) 253.
[66] M. Bolech, E.H.P. Cordfunke, A.C.G. van Genderen, R.R. van der Laan, F.J.J.G. Janssen, J.C. van Miltenburg, J. Phys. Chem. Solids 58 (1997) 433.
[67] M.A. White, G. Neshvad, J. Chem. Thermodyn. 23 (1991) 455.
[68] J.R. Taylor, A.T. Dinsdale, Z. Metallkd. 81 (1990) 354.
[69] E.H.P. Cordfunke, R.R. van der Laan, E.F. Westrum Jr., J. Chem. Thermodyn. 24 (1992) 815.
[70] R. Kohli, Thermochim. Acta 237 (1994) 241.
[71] R.P.C. Schram, V.M. Smit-Groen, E.H.P. Cordfunke, J. Chem. Thermodyn. 31 (1999) 43.
[72] R. Kohli, J. Therm. Anal. 49 (1997) 1321.
[73] T.B. Mirianashvili, T.A. Pavleniashvili, V.S. Varazashvili, D.I. Khutsishvili, M.S. Tsarakhov, G.D. Chachanidze, D.Sh. Tsagareishvili, Neorg. Mater. 29 (1993) 876.
[74] A.N. Klimenko, Yu.S. Kozlov, V.S. Sergeev, E.A. Pastukhov, Thermochim. Acta 209 (1992) 331.
[75] H. Satoh, S. Koseki, M. Takagi, W.Y. Chung, N. Kamegashira, J. Alloys Compd. 259 (1997) 176.
[76] V.S. Varazashvili, M.S. Tsarakhov, G.D. Chachanidze, Izv. Akad. Nauk SSSR, Neorg. Mater. 26 (1990) 602.
[77] H. Satoh, T. Shoji, J. Iwasaki, N. Kamegashira, Thermochim. Acta 261 (1995) 47.
[78] V.S. Varazashvili, T.A. Pavleniashvili, M.S. Tsarakhov, D.I. Khutsishvili, Neorg. Mater. 28 (1992) 2029.
[79] V.A. Aleshin, M.V. Gorbacheva, A.F. Maiorova, D.A. Mikhailova, S.N. Mudretsova, Zh. Fiz. Khim. 72 (1998) 421.
[80] D. Sedmidubský, A. Strejc, Unpublished results, 2000.
[81] D. Sedmidubský, J. Leitner, K. Knížek, A. Strejc, M. Veverka, Physica C 329 (2000) 191.
[82] V.S. Varazashvili, T.B. Mirianashvili, M.S. Tsarakhov, D.S. Tsagareishvili, Soobshch. Akad. Nauk Gruz. 142 (1991) 337.
[83] V.P. Marin, A.N. Klimenko, V.A. Levitskii, Yu.V. Menshenin, Yu.Ya. Skolis, Izv. Akad. Nauk SSSR, Neorg. Mater. 20 (1984) 461.
[84] D.W. Fasshauer, B. Wunder, N. Chatterjee, G.W.H. Hohne, Contrib. Mineral. Petrol. 131 (1998) 210.
[85] Q. Chen, S. Liu, P. Zhang, J. Chem. Thermodyn. 31 (1999) 531.
[86] G.I. Frolova, P.V. Klevtsov, I.E. Paukov, Zh. Fiz. Khim. 56 (1982) 710.
[87] G.I. Frolova, S.G. Kozlova, I.E. Paukov, Zh. Fiz. Khim. 55 (1981) 512.
[88] G.I. Frolova, L.P. Kozeeva, I.E. Paukov, Zh. Fiz. Khim. 57 (1983) 2150.

[89] G.A. Berezovskii, L.P. Kozeeva, I.E. Paukov, G.I. Frolova, S.V. Khegai, Zh. Fiz. Khim. 59 (1985) 49.

[90] G.I. Frolova, L.P. Kozeeva, I.E. Paukov, Zh. Fiz. Khim. 54 (1980) 336.

[91] G.A. Berezovskii, L.P. Kozeeva, I.E. Paukov, G.I. Frolova, S.V. Khegai, Zh. Fiz. Khim. 59 (1985) 744.

[92] G.I. Frolova, L.P. Kozeeva, I.E. Paukov, Zh. Fiz. Khim. 58 (1984) 2629.

[93] G.I. Frolova, L.P. Kozeeva, I.E. Paukov, Zh. Fiz. Khim. 57 (1983) 1802.

[94] V.E. Gorbunov, K.S. Gavrichev, G.A. Sharpataya, I.S. Shaplygin, V.L. Zalukaev, Zh. Neorg. Khim. 26 (1981) 547.

[95] M. Castro, R. Burriel, Thermochim. Acta 269/270 (1995) 537.

[96] S. Stølen, F. Grønvold, H. Brinks, T. Atake, H. Mori, J. Chem. Thermodyn. 30 (1998) 365.

[97] H. Satoh, M. Takagi, K. Kinukawa, N. Kamegashira, Thermochim. Acta 299 (1997) 123.

[98] V.I. Kolotyrkin, J.A. Kessler, V.A. Shchelkotunov, I.V. Gordeyev, Yu.G. Metlin, Yu.D. Tretyakov, Thermochim. Acta 43 (1981) 27.

[99] E.H.P. Cordfunke, R.R. van der Laan, G.P. Wyers, J.C. van Miltenburg, J. Chem. Thermodyn. 24 (1992) 1251.

[100] M. Asou, T. Terai, Y. Takahashi, J. Chem. Thermodyn. 24 (1992) 273.

[101] D.W. Fasshauer, N. Chatterjee, L. Cemic, Contrib. Mineral. Petrol. 133 (1998) 186.

[102] T.B. Mirianashvili, V.S. Varazashvili, M.S. Tsarakhov, K.S. Gavrichev, L.M. Golushina, V.E. Gorbunov, D.Sh. Tsagareishvili, Zh. Fiz. Khim. 72 (1998) 16.

[103] J. Nell, H.St.C. O'Neill, Geochim. Cosmochim. Acta 61 (1997) 4159.

[104] V.G. Bessergenev, Yu.A. Kovalenskaya, I.E. Paukov, M.A. Starikov, H. Oppermann, W. Reichelt, J. Chem. Thermodyn. 24 (1992) 85.

[105] M.J. Ferrante, Rep. Invest.—US, Bur. Mines, RI 9018 (1986).

[106] E.H.P. Cordfunke, R.P. Muis, W. Ouweltjes, H.E. Flotow, P.A.G. O'Hare, J. Chem. Thermodyn. 14 (1982) 313.

[107] S. Liu, Q. Chen, P. Zhang, Thermochim. Acta 371 (2001) 7.

[108] W.G. Lyon, D.W. Osborne, H.E. Flotow, H.R. Hoekstra, J. Chem. Thermodyn. 9 (1977) 201.

[109] M. Castro, R. Burriel, Thermochim. Acta 269/270 (1995) 523.

[110] R.R. van der Laan, R.J.M. Konings, A.C.G. van Genderen, J.C. van Miltenburg, Thermochim. Acta 329 (1999) 1.

[111] K.S. Gavrichev, V.E. Gorbunov, L.N. Golushina, G.A. Totrova, E.A. Tishchenko, Yu.G. Nadtochii, Ya.B. Polyarkov, Neorg. Mater. 30 (1994) 1443.

[112] R. Kohli, Thermochim. Acta 237 (1994) 235.

[113] H.W. Xu, J. Iwasaki, T. Shimizu, H. Satoh, N. Kamegashira, J. Alloys Compd. 221 (1995) 274.

[114] T.A. Pavlenishvili, M.S. Tsarakhov, V.S. Varazashvili, D.I. Khutsishvili, G.D. Chachanidze, Izv. Akad. Nauk SSSR, Neorg. Mater. 27 (1991) 99.

[115] J. Peréz, J. Blasco, J. García, M. Castro, J. Stankiewicz, M.C. Sánchez, R.D. Sánchez, J. Magn. Magn. Mater. 196/197 (1999) 541.

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

[117] M.E. Huntelaar, A.S. Booij, E.H.P. Cordfunke, R.R. van der Laan, J. Chem. Thermodyn. 30 (1998) 497.

[118] S. Dash, Z. Singh, R. Prasad, V. Venugopal, J. Nucl. Mater. 279 (2000) 84.

[119] E.H.P. Cordfunke, A.S. Booij, M.E. Huntelaar, J. Chem. Thermodyn. 30 (1998) 437.

[120] M.E. Huntelaar, E.H.P. Cordfunke, E.F. Westrum Jr., J. Phys. Chem. Solids 53 (1992) 801.

[121] M.E. Huntelaar, E.H.P. Cordfunke, J.C. van Miltenburg, Thermochim. Acta 254 (1995) 11.

[122] M.S. Tsarakhov, K.S. Gavrichev, V.S. Varazashvili, V.E. Gorbunov, L.N. Golushina, Zh. Fiz. Khim. 64 (1990) 550.

[123] V.A. Shchelkotunov, V.N. Danilob, L.A. Reznitskii, A.V. Korobeinikova, Izv. Akad. Nauk SSSR, Neorg. Mater. 11 (1975) 1633.

[124] A. Junod, D. Eckert, G. Triscone, V.Y. Lee, J. Muller, Phusica C 159 (1989) 215.

[125] T. Atake, H. Kawaji, M. Itoh, T. Nakamura, Y. Saito, Thermochim. Acta 183 (1991) 143.

[126] T. Atake, H. Kawaji, S. Takanabe, Y. Saito, Thermochim. Acta 139 (1989) 169.

[127] K.S. Gavrichev, V.E. Gorbunov, L.N. Golushina, V.B. Lazarev, G.E. Nikiforova, N.F. Vedernikov, G.A. Totrova, I.S. Shaplygin, Zh. Neorg. Khim. 37 (1992) 1583.

[128] R.J.M. Konings, R.R. van der Laan, A.C.G. van Genderen, J.C. van Miltenburg, Thermochim. Acta 313 (1998) 201.

[129] K.S. Gavrichev, V.E. Gorbunov, I.A. Konovalova, V.B. Lazarev, E.A. Tishchenko, I.S. Shaplygin, Izv. Akad. Nauk SSSR, Neorg. Mater. 24 (1988) 343.

[130] A. Junod, D. Eckert, T. Graf, E. Kaldis, J. Karpinski, S. Rusiecki, D. Sanchez, G. Triscone, J. Muller, Phusica C 168 (1990) 47.

[131] T. Atake, A. Honda, H. Kawaji, Physica C 190 (1991) 70.

[132] H. Satoh, J. Iwasaki, K. Kawase, N. Kamegashira, J. Alloys Compd. 268 (1998) 42.

[133] K. Chhor, J.F. Bocquet, C. Pommier, B. Chardon, J. Chem. Thermodyn. 18 (1986) 89.

[134] B.K. Hom, R. Stevens, B.F. Woodfield, J. Boero-Goates, R.L. Putnam, K.B. Helean, A. Navrotsky, J. Chem. Thermodyn. 33 (2001) 165.