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Some calculation methods as a tool to revise thermodynamic data for the $SrCuO_2$, Sr_2CuO_3, $Sr_{14}Cu_{24}O_{41}$ and $SrCu_2O_2$ double oxides

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Abstract

Various calculation methods were used to review and revise known experimental data of thermochemical properties of the Sr–Cu double oxides in order to estimate the reliable values of ΔH^0_{298}, S^0_{298}, $H^0_{298-}H^0_0$, T and ΔH of phase transformations as well as C_p (T) and C_p at $T > T_{ph.tr}$ for the $SrCuO_2$, Sr_2CuO_3, $SrCu_{24}O_{41}$ and $SrCu_2O_2$ compounds. Calorimetry-based experimental data were treated by the method called "Linear Approximation Rule" which provided satisfactory agreement. For all double oxides the temperature dependences of reduced Gibbs energy were also calculated in the interval for 298–6000 K.

Keywords: Enthalpy; Entropy; Heat capacity; Gibbs energy; Temperature; Thermodynamic calculation; Sr–Cu double oxides

1. Introduction

Thermochemical properties of the double oxides in the SrO–CuO_x system present a definite interest in connection with the synthesis of ceramic superconductors in the SrO–CaO–Bi_2O_3–CuO_x (SCBCO) system. The properties of double oxides in the neighboring SrO–Bi_2O_3 system were present in our previous report [1] and also thoroughly analyzed by Risold et al. [2].

According to Refs. [3–7] the compounds $SrCuO_2$, Sr_2CuO_3, $SrCu_2O_2$ and $Sr_{14}Cu_{24}O_{41}$ can exist in the SrO–CuO_x system at ambient pressure and they usually accompany, as major but unwanted secondary phases, the SCBCO family superconductors. At higher pressures certain non-stoichiometry phases such as $Sr_{n+1}Cu_nO_{1+2n\delta}$ are reported to stabilize [8]. The most common tetragonal $Sr_2CuO_{3+\delta}$ was found to decompose irreversibly to the orthorhombic Sr_2CuO_3 at about 450°C [9]. Phase diagrams were studied by conventional methods of XRD analysis on quenched samples [5,6,10,13] as well as by dynamic thermal analysis technique [11,12,14] showing the peritectic character of melting of $SrCuO_2$, Sr_2CuO_3 and $Sr_{14}Cu_{24}O_{41}$ even at higher oxygen pressures. In general the Sr–Cu–O system was reviewed in [15–18] and the subsystems of Sr–O and Cu–O analysed in detail in [19,20].

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Thermodynamic data of the ternary compounds in question were reported utilizing two sources of experimentation: *Calorimetric* [21–23] and *electrochemical* (EMF) [13,24–26]. They, however, showed certain inconsistency of the reported data respectively obtained. Although the values of formation enthalpies determined by solution calorimetry [22,23] are somehow more negative than the values derived from EMF measurements [13,24–26], they were assumed as being more suitable for our present study and therefore preferred as the basis for further estimations.

In [22] experimental ΔH^0_{298} values were given for both the $SrCuO_2$ and Sr_2CuO_3 compounds as well as for the composition SrO:CuO=3:5 and for the compound $SrCu_{1.667}O_y$ (reduced to one atom of Sr in the molecule). If a similar transformation is made for $Sr_{14}Cu_{24}O_{41}$ one would receive the stoichiometry of $SrCu_{1.714}O_{2.928,}$ i.e. the composition approximately similar to the composition mentioned above [22]. On the other hand, if we assume that this composition consists of a given mixture of Sr_2CuO_3, the associated enthalpy of formation would agree with that determined by EMF measurements. Such thermodynamic behavior seems to be compatible with other data on the Sr–Ca–Cu–O solid solution [21–29] close to ideal enthalpy of mixing for the $(Sr, Ca)_2CuO_3$ solid solution.

The concise study by Risold et al. [21] based on both sorts of calorimetric and EMF measurements reported averaged data, and we used such optimized parameters for comparing our estimations based on preferred calorimetric measurements only.

2. Revision, correction and determination of properties

All double oxides, except $Sr_{14}Cu_{24}O_{41}$, can be presented by following reaction of their formation:

$$x\mathrm{SrO} + y\mathrm{Cu}^{2+}\mathrm{O}(\mathrm{Cu}_2^{+}\mathrm{O}) = \mathrm{Sr}_x\mathrm{Cu}_y^{2+}(\mathrm{Cu}_{2y}^{+})\mathrm{O}_{x+y}. \tag{1}$$

For $Sr_{14}Cu_{24}O_{41}$ the reactions of formation can be presented in two ways:

(A)

$$14\mathrm{SrO} + 24\mathrm{CuO} = \mathrm{Sr}_{14}\mathrm{Cu}_{24}\mathrm{O}_{38} \tag{2}$$

and

$$\mathrm{Sr}_{14}\mathrm{Cu}_{24}\mathrm{O}_{38} + 1.5\mathrm{O}_2 = \mathrm{Sr}_{14}\mathrm{Cu}_{24}\mathrm{O}_{41}; \tag{3}$$

(B)

$$14\mathrm{SrO} + 18\mathrm{CuO} + 3\mathrm{Cu}_2\mathrm{O}_3 = \mathrm{Sr}_{14}\mathrm{Cu}_{24}\mathrm{O}_{41}. \tag{4}$$

Available information about the thermochemical properties of the phase in the $SrO–CuO_x$ system is reviewed in Table 1. The aim of this investigation is the revision of known, as well as the estimation of unknown thermochemical properties for the four above-listed phases existing in the $SrO–CuO_x$ system.

2.1. Standard enthalpy of formation (SEF, ΔH^0_{298})

For such a determination a known dependence is conventionally used in the following form:

$$\Delta H^0_{298}(j) = \sum n_i.\Delta H^0_{298}(i) + \Delta H^0_{298}(\mathrm{ox})_j \tag{5}$$

where n_i is the number of moles at ith simple oxide in the jth complex oxide, $\Delta H^0_{298}(i)$ is the standard enthalpy of ith simple oxide, and $\Delta H^0_{298}(\mathrm{ox})_j$ is the standard enthalpy of formation of the j complex oxide from simple oxides.

The data for SrO, CuO and Cu_2O were taken from Ref. [30], the ΔH^0_{298} Cu_2O_3 value taken from Ref. [31], and the remaining properties of Cu_2O_3 from Ref. [32]. The $\Delta H^0_{298}(\mathrm{ox})_j$ values can be found with the help of different approaches which, for $Sr_{14}Cu_{24}O_{14}$, are described in particular herewith.

2.1.1. Using the data [22] and empirical regularities [33]

Experimental $H^0_{\mathrm{at}}(f)_j$ values (see Table 1) for $SrCuO_2$ and Sr_2CuO_3 are revised and corrected with the use of the Linear Approximation Rule (LAR) developed for relative double inorganic compounds in Ref. [33]. Some additional explanations are worth mentioning: $H^0_{\mathrm{at}}(f)_j$is the standard enthalpy of formation for the jth double oxide from simple oxides presented in kJ (g atom)$^{-1}$, i.e.

$$H^0_{\mathrm{at}}(f)_j = \Delta H^0_{298}(\mathrm{ox})_j/n_j \quad \text{in kJ (g atom)}^{-1}, \tag{6}$$

Table 1
Some known properties of phases in the SrO–CuO$_x$ system

Oxide	ΔH^0_{298} according to [22]			Some properties according to [23] (upper row) and [21] (lower row)			Temperature in K and type of phase transformation	
	ΔH^0_{298} kJ mol^{-1}	ΔH^0_{298} kJ (g atom)$^{-1}$	ΔH^0_{298} (ox) kJ (g atom)$^{-1}$	C_p (298) J K^{-1} mol^{-1}	S^0_{298} J K^{-1} mol^{-1}	$H^0_{298}-H^0_0$ J mol^{-1}	At air atmosphere	At P$_{02}$=10Pa
SrCuO$_2$	−768±2.0	−192.1±0.5	−6.3±0.5	86.752 87.43	96.913 94.32	15765—	1358,IM[b] [5];1350, 1371, 1346, IM [7]	~1080, IM [6]
Sr$_2$CuO$_3$	−1368.3±2.8	−228.05±0.5	−11.8±0.5	134.868 132.5	148.50 150.1	24040—	1498.IM [5];1492, 1513, 1509, IM [7]	~1270, IM [6]
Sr$_3$Cu$_5$O$_y$[a]	−2710.8±4.7[a]	−163,0±0.3[a]	−10±0.3	1730.76	1905.80	302100—	1228,IM [5];1289, IM [6]; 1233, 1224, 1231, IM [7]	—
Sr$_{14}$Cu$_{24}$O$_{41}$	(−12650±22)	(−163.0±0.3)	(−10±0.3)	1691.0	1837.0			
SrCu$_2$O$_2$				108.0	148.0	—	~1513, IM or CM[c] [7]	~1300, IM or CM [7]

[a] In [22] ΔH^0_{298} (Sr$_3$Cu$_5$O$_y$) was determined and these data were used for the calculation. The number of atoms=(ΔH^0_{298} in kJ mol^{-1})/(ΔH^0_{298} in kJ atom^{-1})=−2710.8/−163.0≈16.63; the sum of Sr and Cu atoms is equal to 8, and consequently y=16.63−8=8.63). For such a recalculation related to the composition with 14 atoms of Sr in the molecule we must multiply the initial composition Sr$_3$Cu$_5$O$_{8.63}$ with a value equal 4.6667. As a result we found the composition Sr$_{14}$Cu$_{23.33}$O$_{43.27}$ (the number atoms in the molecule equal to 77.6). For this oxide ΔH^0_{298} in kJ mol^{-1} equal −27.10×4.6667=−12650 or −12650 or −163×77,6≈−12650, and ΔH^0_{298} (ox) in kJ mol^{-1} equal −10×77.6≈−776.

IM[b] and CM[c] means incongruent and congruent melting, respectively.

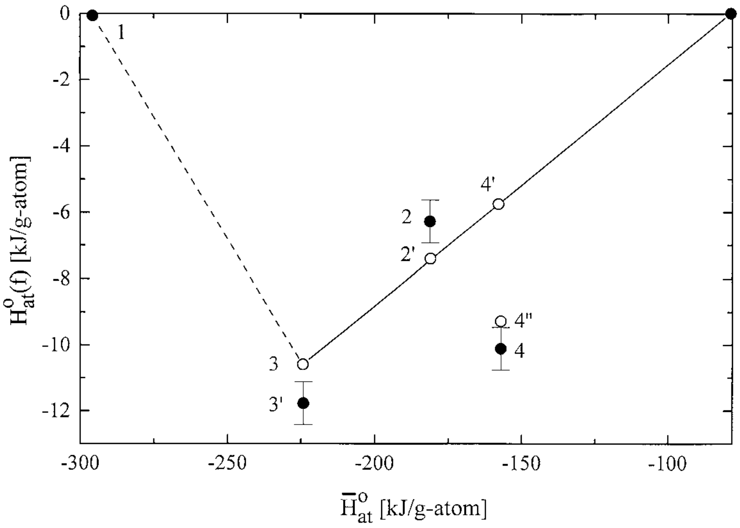

Fig. 1. The application of LAR [33] for the revision and correction of $H^0_{at}(f)_j$ values (in kJ/(g-atom)) [22] for some double oxides in the SrO–CuO$_x$ system:$H^0_{at}(f)$ for: (1) SrO[30], (2) SrCuO$_2$[22], (3) Sr2CuO$_3$ [22], (4) Sr$_{14}$,Cu$_{14}$,O$_{41}$, [22] and (5) CuO [30].Corrected with the use of linear approximation [33] the $H^0_{at}(f)$ for: SrO,2', SrCuO$_2$, 3', Sr$_2$CuO$_3$, 4', Sr$_{14}$Cu$_{24}$O$_{41}$ and 5, CuO; point 4" means the $H^0_{at}(f)$ for Sr$_{14}$Cu$_{24}$O$_{41}$ calculated with the help of Eq. (11).

where n_j is the number of atoms in double oxide molecule.

Values of $H^0_{at}(f)_j = \Delta H_R(j)$, were obtained from Ref. [22]. Then

$$\tilde{H}^0_{at}(f)_j = \Sigma x(i).H^0_{at}(i) \text{ in kJ (g atom)}^{-1}, \qquad (7)$$

where x (i) is the molar fraction of ith simple oxide in the jth double oxide, and H^0_{at} (i) is the standard enthalpy of ith simple oxide conventionally presented in kJ (g atom)$^{-1}$, i.e.

$$H^0_{at}(i) = \Delta H^0_{298}(i)/n_i \qquad (8)$$

where n_i is the number of atoms in a simple oxide molecule. The essence of the LAR is following: The extreme (with minimum $H^0_{at}(f)_j$ value) dependence

$$H^0_{at}(f)_j = f(H^0_{at}(i), \tilde{H}^0_{at}(j), \text{ in kJ (g atom)}^{-1} \qquad (9)$$

for the relative double oxides is described by linear equations (between $H^0_{at}(i)$ and $H^0_{at}(f)j$, min) providing average deviation from reference data less than ±5% [33].

The results of the application of LAR are presented in Fig. 1 (p.p. 2 and 2', p.p. 3 and 3' means data [22] and data after correction for SrCuO$_2$ and for Sr$_2$CuO$_3$ respectively) and also given Table 2, column 4.

According to the LAR, Eq. (9) is given in the from:

$$H^0_{at}(f)j = 5.7213 + 0.072744.\tilde{H}^0_{at}(j) \text{ in kJ (g atom)}^{-1}. \qquad (10)$$

As it is seen from Fig. 1 and Table 2, the $H^0_{at}(f)_j$ values calculated by Eq. (10) agree with the experimental values exhibiting an average difference not more than ±11%.

2.1.2. Using the empirical equation [34] as corrected in the paper [1]

$$\Delta H^0_{298}(ox)_j = (-16.0485 \pm 5.145)m_O(j) \text{ in kJ mol}^{-1}, \qquad (11)$$

where $m_O(j)$ is the number of oxygen atoms in complex oxide molecule.

The results of calculation by Eq. (11) for SrCuO$_2$, Sr$_2$CuO$_3$ and SrCu$_2$O$_2$ are given in Table 2, column 5. It follows that the calculated and experimental data agree with each other satisfactorily.

Table 2

Results of revision and calculation of enthalpy values for complex oxides in the SrO–CuO_2 system investigated by calorimetry [22,46] and averaging calculation methods

Oxide	According to [22] (upper row) and [46] (lower row)		Corrected and calculated ΔH^0_{298}(ox) kJ mol^{-1}		The values taken as reliable	
	ΔH^0_{298} (ox) kJ mol^{-1}	$\Delta H^\circ{}_{298}$ kJ mol^{-1}	According to Eq. (10)	According to Eq. (11)	ΔH^0_{298} (ox) kJ mol^{-1}	ΔH^0_{298} kJ mol^{-1}
$SrCuO_2$	−25.2 −51.4	−768.4±2.0 (−774.5)**	−30.4	−32.1±10.5	−30.4 22.8 [21]	−779.7
Sr_2CuO_3	−70.5 −87.4	−1368.3±2.8 (−1412.1)**	−63.0	−48.1±15.4	−63.0 22.7 [21]	−1403.8
$Sr1_4Cu_{24}O$	−776.0	−12650±22*	−735***a	−658±210.9***b	−735.8 −625.5 [21]	−13010
$SrCu_2O_2$	—	—	—	32.1±10.3	−37.6 −15.5[21]	−792

[*] According to this analysis (see also note to Table 1) the composition of complex oxide in [22] can be presented as $Sr_{14}Cu_{23.33}O_{40.27}$

[**] For ΔH^0_{298} of $SrCuO_2$ and Sr_2CuO_3 in [22] some uncertainty is probable if we take the ΔH^0_{298}(ox) values in kJ/g-atom^{-1} (see Table 1) as reliable, then the ΔH^0_{298}(ox) values in kJ/mol^{-1} would equal (−6.3)×4=−25.2 and (11.8)×6=−70.8 kJ/mol^{-1}, respectively. The ΔH^0_{298} (SrO) and ΔH^0_{298}(CuO) are mutually equal (−592) and (−157.3) kJ/mol^{-1} [30] With the help of Eq. (5) we can find: ΔH^0_{298} ($SrCuO_2$) = (−592) + (157.3) + (−25.2) = −774.5 kJ/mol^{-1} and ΔH^0_{298}(Sr_2CuO_3) =2 (−592)+ (−157.3) + (−70.8) = −1412.1 kJ/mol^{-1}. Therefore we present these data in brackets together with the data published in [22].

[***] The procedures of revision/calculations for this phase are described in detail in the text of article.

2.1.3. Calculation of ΔH^0_{298} values for $Sr_4Cu_{24}O_{41}$

The value of $H^0_{\mathrm{at}}(f)$ ($Sr_{14}Cu_{24}O_{38}$) calculated by Eq. (10) (p4' see Fig. 1.) is then used for the determination of $H^0_{\mathrm{at}}(f)$ of ($Sr_{14}Cu_{24}O_{41}$).

$$H^0_{\mathrm{at}}(f)(\mathrm{Sr_{14}Cu_{24}O_{41}}) = H^0_{at}(f)(\mathrm{Sr_{14}Cu_{24}O_{38}}) + 1.5.\Delta H^0\mathrm{O_2}(i)/\mathrm{n}_i \tag{12}$$

again in kJ (g atom)$^{-1}$, where $\Delta H^0_{O_2}$ is the partial molar enthalpy for joining 1 mole of oxygen and is equal to −184 kJ per 1 mole of O_2 [35], n_i=1.5 is the number of O_2 moles according to reaction (3). The $H^0_{\mathrm{at}}(f)$ value equals 9.31 kJ (g atom)$^{-1}$ and is shown in Fig. 1 (p.4'') to agree with the value taken from [22] (see Table 1). The difference is a mere 5.5%.

The $H^0_{298}(\mathrm{ox})_j$ values determined by the use of Eq. (11) (Table 2) and Eq. (12) satisfactorily correspond with experimental data [22] (Table 2). The use of reaction (4) together with the ΔH^0_{298}(ox) value and Eq. (12) provide

$$\begin{aligned}\Sigma \mathrm{n}_i \Delta H^0_{298}(i) &= 14\Delta H^0_{298}(\mathrm{SrO}) \\ &\quad + 18\Delta H^0_{298}(\mathrm{CuO}) + 3\Delta H^0_{298}(\mathrm{Cu_2O_3}) \\ &= 14(-592) + 18(-157.3) \\ &\quad + 3(-385) - 12214.4\mathrm{kJ}\end{aligned} \tag{13}$$

and is related to the sum of simple oxides, where $\Delta H^0_{298}(Cu_2O_3)$=−355 kJ mol^{-1} [31].

The value of ΔH^0_{298}(ox) was taken to equal −658.0 kJ mol^{-1} regarding Eq. (11). With the use of Eq. (5) the ΔH^0_{298}($Sr\ _{14}Cu\ _{28}O_{41}$) value then equals −12932.4 kJ mol^{-1}. This value shows good agreement with the SEF by Eq. (12) (see Table 2). For $Sr_{14}Cu_{24}O_{41}$ the various methods provide consequently more or less identical ΔH^0_{298} values and the ΔH^0_{298} ($Sr_{14}Cu_{24}O_{41}$) determined by Eq. (12) is taken as most reliable.

Besides reaction (2), the estimation of the remaining thermochemical properties of this phase is made without taking into account any surplus oxygen, i.e. for the composition $Sr_{14}Cu_{24}O_{38}$.

2.2. Standard entropy

Three methods were used:

2.2.1. Additivity method

$$S^0_{298}(j) \approx \Sigma n_i.S^0_{298}(i)\ \mathrm{in\,J\,K\,mol^{-1}}, \tag{14}$$

where n_i is the number of moles and $S^0_{298}(i)$ are the standard entropy of ith simple oxides.

2.2.2. The Gerz method [36]

$$S^0_{298}(j) \approx \mathrm{K_G M}_j / C_{\mathrm{p}(298)^{1/3}}\, x.n_j \ \text{in J K mol}^{-1}, \tag{15}$$

where $\mathrm{K_G}$ is a constant equal to 19.2 according to Ref. [36], M_j is the molecule mass of *j*th oxide, and n_j is the number of atoms in double oxide molecule.

2.2.3. Increments method [37]

$$S^0_{298}(j) \approx \Delta S_{\mathrm{k}}.n_{\mathrm{k}} + \Delta S_{\mathrm{A}}.n_{\mathrm{A}} \ \text{in J K mol}^{-1}, \tag{16}$$

where ΔS_{k} and ΔS_{A} are standard entropies of cation and anion respectively [37]. The values for Sr^{2+}, Cu^{+2}, Cu^{+2} and O^{-2} are taken to equal 43.0, 42.7, 36.5 and 11.7 J K mol^{-1}, respectively; (however for Cu^{+3} the data are unknown); n_{a} and n_{k} are numbers of anions/cations in the compound.

For $\mathrm{SrCuO_2}$ and $\mathrm{Sr_2CuO_3}$ the results of calculations by Eqs. (14)–(16) agree. The mean arithmetic $\bar{S}^0_{298}(j)$, as a reliable value, is presented in Table 3. For the $\mathrm{SrCu_2O_2}$ compound $S^0_{298}(j)$ values calculated by Eq. (15) differ from values calculated by Eqs. (14) and (16) by approximately 15%. The mean arithmetic values obtained by the use of Eqs. (14) and (16) (see Table 3) are therefore taken as reliable data.

2.3. Heat capacity

Temperature dependencies of heat capacities of phases are calculated by two ways: *using the additive method* and *according to the work* [38] (Table 4). The mean arithmetic values of coefficients in the C_{p} (T) equations are taken as reliable.

The heat capacities of double oxides at $T > T$ phase transformation are considered as constant values and calculated by the equation transferred from Ref. [39]:

$$C_{\mathrm{p}}(T > T_{\mathrm{ph.tr.}})_j \approx C_{\mathrm{p}}(T_{\mathrm{ph.tr.}})j + 0.25\Delta S_{\mathrm{ph.tr.}}(j) \ \text{in J (Kmol)}^{-1} \tag{17}$$

2.4. The $H^0_{298} - H^0_0$, T and ΔH data of phase transformation

The enthalpy increments were estimated with the help of Eq. (18)[40]:

$$H^0_{298} - H^0_0 \approx \bar{S}^0_{298}(j).\exp(\bar{S}^0_{298}(j)/17) \ \text{in cal (g atom)}^{-1}, \tag{18}$$

where $\bar{S}^0_{298}(j) = \bar{S}^0_{298}(j)/n_j$ in cal. K^{-1}(g atom)$^{-1}$. The mean arithmetic temperatures $T_{\mathrm{ph.tr}}$. for $\mathrm{SrCuO_2}$ and $\mathrm{Sr_2CuO_3}$ are taken from Refs. [5–7] and are considered as reliable. For $\mathrm{Sr_{14}Cu_{24}O_{41}}$, $T_{\mathrm{ph.tr.}}$=1289 K [6] which is probably an incorrect value, and thus we did not take it into account.

The empirical equation in [41] was used for checking the experimental data, i.e.

$$T_{\mathrm{ph.tr.}}(j) \approx \bar{\mathrm{K}}_t.\Sigma x(i) T_{\mathrm{ph.tr.}}(i), \tag{19}$$

where $\bar{K_t}$ is the empirical correlation coefficient for a group of relative substances and similar types of phase transformations, $x(i)$ and $T_{\mathrm{ph.tr.}}$ (i) are the molar fraction and temperature of melting/decomposition for the *i*th simple oxide, respectively. The $\bar{\mathrm{K}}_{\mathrm{t}}$ values were, respectively, taken equal to 0.79242 (congruent melting – CM), 0.58782 (incongruent melting – IM), and 0.49063 (decomposition in crystalline state – DCS) according to Ref. [1] (Table 5).

Table 3
The standard entropies of complex oxides in the SrO–$\mathrm{CuO_x}$ system

Oxide	S^0_{298} J k^{-1}/mol^{-1} calculated			Mean arithmetic S^0_{298} taken as reliable		S^0_{298} J K^{-1} mol^{-1} according Refs. [23,21]	σ in % between calculated and experimental data
	by Eq. (14)	by Eq. (15)	by Eq. (16)	J K^{-1} atom^{-1}	J K^{-1} mol^{-1}		
$\mathrm{SrCuO_2}$	97.03	100.1	102.9	25.0	100.0	96.9[23]94.3[21]	+3.2
$\mathrm{Sr_2CuO_3}$	151.43	152.73	157.7	25.65	153.9	148.5[23]150.1[21]	+3.6
$\mathrm{Sr_{14}Cu_{24}O_{41}}$	1808.40	1943.5	—	23.75	1876.0	1905.8[23]1837[21]	−1.6
$\mathrm{SrCu_2O_2}$	147.54	(12.46)	151.8	29.90	149.7	−148[21]	—

Table 4
Temperature dependencies of C_p=a+b.10^{-3}. T+c. 10^{5}. T^{-2}+d. 10^{-6}. T^2 J k^{-1} mol^{-1} for complex oxides in the SrO–CuO$_x$ system

Oxide	Calculated with the help of additive method				Calculated with the help of method[38]			Average arithmetic values			
	a	b	c	d	a	b	c	$\bar{a}$	$\bar{b}$	$\bar{c}$	$\bar{d}$
$SrCuO_2$	99.19	13.87	−18.52	—	92.0	12.63	−11.81	95.6	13.25	−15.164	—
Sr_2CuO_3	149.76	20.33	−29.43	—	138.0	18.94	−18.61	143.9	19.64	−24.02	—
$Sr_{14}Cu_{24}O_{41}$	1848.13	311.63	−289.72	—	1817.0	249.46	−245.0	1832.6	280.54	−267.36	—
$SrCu_2O_2$	125.34	−1.15	−21.50	13.05	115.0	15.8	−15.5	120.2	7.32	−18.5	6.52

Table 5
Comparison between experimental [5,7] and calculated phase transformation temperatures for complex oxides in the SrO–CuO$_x$ system

Oxide	$T_{\text{ph.tr}}$ K and type of phase transformation		σ in % between experimental and calculated $T_{\text{ph.tr}}$
	Mean arithmetic values accordingly to [5–7]	Calculated	
$SrCuO_2$	1356, IM^a	1309, IM	+3.4
Sr2CuO$_3$	1503, IM^a	1449, IM	+3.6
$Sr_{14}Cu_{24}O_{41}$	1229, IM	1214, IM	+1.2
$SrCu_2O_2$	1513, IM or CM^{b}1451, IM	1451, IM	+2.2

IM^a and CM^b means incongruent and congruent melting, respectively.

The estimation of $\Delta H_{\text{ph.tr.}}$ values was carried out by a known equation

$$\Delta H_{\text{ph.tr}} = \Delta S_{ph.tr.}.\Delta T_{\text{ph.tr}}, \tag{20}$$

where $\Delta S_{\text{ph.tr}}$ was determined with the use of an empirical dependence

$$\Delta S_{\text{ph.tr}}(j) \approx \Sigma n_j.\Delta S_{\text{ph.tr}}(i). \tag{21}$$

In Eq. (21) n_i is the number of moles of ith simple oxide in complex one, and $\Delta S_{\text{ph.tr}}(i)$ is the entropy change of phase transformation of ith simple oxide.

The values T and $\Delta H_{\text{ph.tr}}$ of simple oxides were taken from Refs. [30,32,42]. For Cu_2O_3, $T_{\text{ph.tr}}$ was taken equal to 1286 K [32], while the $\Delta H_{\text{ph.tr.}}$ value is unknown.

3. Results

The thermochemical properties of four double oxides, proposed as most reliable, are listed in Table 6 and compared with another set of similar data reported by Leitner et al. [45] for practical utilization.

4. Discussion

In our opinion, the reliability the ΔH^0_{298} values for $SrCuO_2$, Sr_2CuO_3 and $Sr_{14}Cu_{24}O_{41}$ given in Table 6 seem to be satisfactory. This reliability assurance, based on the submission of mere calorimetry- based data [22] to the LAR method [33], gives satisfactory agreement between these experimental data and data treated by different calculation ways. It can be assumed as more consistent than data averaging both types of caloric and EMF measurements [21]. The ΔH^0_{298} of $SrCu_2O_2$ was, however, estimated for the first time, and its value can be checked by showing agreement with the estimations provided by Leitner et al. [45].

The experimental $S^0_{298}(j)$, $T_{\text{ph.tr}\cdot}(j)$ and $H^0_{298} - H^{0_j}_0$ values of phases [5–7,23] can also be accounted for as correct because similar data calculated with the help of other methods satisfactorily agree with experimental ones (Table 5 and Table 7). We assume, however, that the phase $SrCu_2O_2$ should melt incongruently (see Table 5).

The comparison of C_p (298)j values with experiments [23] and with the use of equations given in

Table 6
Comparison of two sources of thermochemical properties of complex oxides taken as reliable in the SrO–CuO$_x$ system (upper raw gives our data while lower row shows data proposed by Leitner et al. [45])

Oxide	ΔH^0_{298} k J mol^{-1}	S^0_{298} J K^{-1} mol^{-1}	$H^0_{298} - H^0_0$ kJ mol^{-1}	T K and $\Delta H_{ph.tr.}$ kJ mol^{-1}	Cp=a+b.10^{-3}. T+c.10^{5}.T-2+d.10^{-6}.T2 in J K^{-1}. mol^{-1}				Cp at $T>T_{ph.tr}$. in Jk^{-1} mol^{-1}
					a	b	c	d	
$SrCuO_2$	−779.9	96.9[23]	15765[23]	1356/70.8	96.53	14.054	−12.62	—	125.8
	−770.09	97.2			96.49	12.344	−1.193		
Sr_2CuO_3	−1403.8	148.5[23]	24040[23]	1503/46.8	148.07	20.646	−17.22	—	191.8
	−1388.3	141.9			148.33	17.747	−1.671		
$Sr_{14}Cu_{24}O_{41}$	−13010.0	1905.8	302100[6]	1229/1226.0	1910.64	317.96	−242.9	—	2409.0
	−12531.0	1905.8			1956.62	263.17	−27.056		
$SrCu_2O_2$	−792.6	149.7	21206	1513/103.3	120.2	7.32	−18.5	6.52	162.4
	−777.1	150.6			108.95	30.04	−0.787		

Table 7
Comparison between experimental [23] and calculated values of $H^0_{298} - H^0_0$ and $C^0_p(298)$ for some phases in the SrO–CuO$_x$ system

Oxide	$H^7_{29}0 - H^0_0$ J mol^{-1}		σ %	$C^0_p(297)$ J K^{-1} mol^{-1}		σ %
	According to [23]	Calculated		According to [23]	Calculated with the help of equations from Eq. (4)	
$SrCuO_2$	15765	15196	+3.6	86.75	81.8	+5.7
Sr_2CuO_3	24040	23173	+3.6	134.87	122.7	+9.0
$Sr_{14}Cu_{24}O_{41}$	302100	290173	+3.6	1730.8	1615.1	+6.7

Table 8
The coefficients of temperature dependencies of reduced Gibbs energy (see Eq. (22)) in J K mol^{-1} for some phases in the SrO–CuO$_x$ system

Oxide	Temperature interval K	Coefficients in Eq. (22)[a]				
		φ_1	φ_2	φ_3	φ_4	φ_5
$SrCuO_2$	298–1536	328.21	96.5301	−0.00631	1.78599	70.2701
	1536–6000	375.629	125.8	0	4.54183	0
Sr_{2CuO3}	298–1503	504.789	148.07	−0.00861	2.67801	103.23
	1503–6000	653.056	191.8	0	−4.87592	0
$Sr_{14}Cu_{24}O_{41}$	298–1229	6476.2	1910.64	−0.12145	36.2899	1589.8
	1229–6000	8418.97	2409.0	0	−51.0511	0
$SrCu_2O_2$	298–1513	438.906	120.2	−0.00925	2.12042	36.6
	1513–6000	563.617	162.4	0	−3.53759	0

[a] φ_6 and $\varphi_>$ are equal to zero.

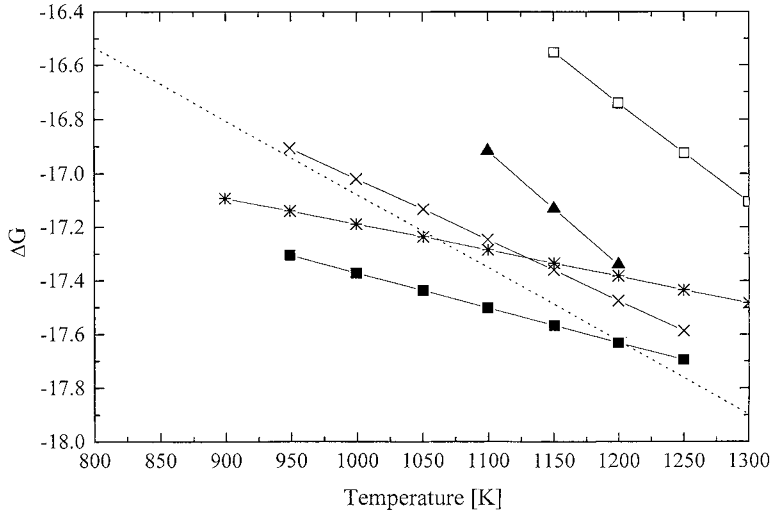

Fig. 2. A graphical representation of Gibbs energy dependence on the temperature using experimental data of Ref. [13] (■, *) and [24] (x) and [25] (□, ▲) for the reaction $SrO+Cu_2O=SrCu_2O_2$ in comparison with our optimized data given in Table 8 (dotted).

Table 4 shows some variations (see Table 7). Taking into account the accuracy of experiments in Ref. [23] we recalculated the $C_p(T)$ dependencies of phases with the use of experimental $C_p\ (298)_j$ data by methods described in refs. [37,43]. The mean arithmetic values taken then as reliable, and the new $C_p\ (T)$ functions, are listed in Table 6. The $C_p\ (298)_j$ values calculated according to these equations agree with experimental data within the limits as low as only 1%.

The data of Ref. [1] and this work show that the methods of SEF for phases containing a surplus oxygen, as well as the use of Eq. (11) can be applied to describing the complex oxides involving SrO, Bi_2O_3 and CuO_x [47].

For application in thermodynamic simulations together with the use of a computer program ASTRA 5 [44] the thermochemical properties of all phases were presented by the temperature dependencies of reduced Gibbs energy in the form of temperature polynomial:

$$\Phi^*(T) = \varphi_1 + \varphi_2 .\ln x + \varphi_3 x^{-2} + \varphi_4 x^{-1} + \varphi_5 x + \varphi_6 x^2 + \varphi_7 x^3, \qquad (22)$$

in $\mathrm{J\,K(mol)^{-1}}$, again where and φ_i are numerical coefficients and $x = T.\ 10^{-4}$ K (see Table 8). For $SrCu_2O_2$ the estimated data are compared with experimental data [13,14,25] in Fig. 2.

5. Conclusion

The known $\Delta H^0_{298}, H^0_{298} - H^0_0, \mathrm{Cp}(298)$ and $T_{\mathrm{ph.tr.}}$ values and the types of phase transformations for $SrCuO_2$, Sr_2CuO_3 and $Sr_{14}Cu_{24}O_{41}$ were reviewed and revised employing various calculation methods. For the above phases, as well as for $SrCu_2O_2$, major thermochemical properties were calculated. In addition to all phases in question the temperature dependencies of reduced Gibbs energy in the interval from 298 to 6000 K were also calculated.

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