

Thermochemical properties of MeCuO_2 and Me_2CuO_3 ($\text{Me}=\text{Ca}, \text{Sr}, \text{Ba}$) mixed oxides

M. Mrovec^a, J. Leitner^{a,*}, M. Nevřiva^b, D. Sedmidubský^b, J. Stejskal^b

^a Department of Solid State Engineering, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic

^b Department of Inorganic Chemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic

Received 13 September 1997; accepted 28 January 1998

Abstract

Optimized experimental data and estimated values are utilized for the assessment of thermochemical functions of alkali-earth cuprates. For the determination of temperature dependences of heat capacities the Neumann–Kopp additive rule was employed. Values of standard enthalpy of formation and molar entropy of Ca_2CuO_3 , SrCuO_2 , Sr_2CuO_3 and BaCuO_2 were optimized from experimental results. For the estimation of enthalpies of formation of CaCuO_2 and Ba_2CuO_3 a linear correlation between enthalpy of formation from oxides and ionic radius of alkali-earth cations was used. Molar entropy of CaCuO_2 and Ba_2CuO_3 was estimated using the modified contribution method. © 1998 Elsevier Science B.V.

Keywords: Enthalpy; Entropy; Heat capacity; Oxides; Superconductors; Thermodynamic properties

1. Introduction

Alkali-earth cuprates (AEC), among others, became a subject of vast experimental and theoretical investigation during the last years on account of the discovery of high-temperature superconductors. Thermochemical properties, i.e. heat capacity, molar entropy and enthalpy of formation, are necessary for the prediction and modeling of the synthesis of these compounds as well as for the determination of the stability of individual phases in the complex oxide systems. Unfortunately, the experimental data on the properties mentioned above are available only for a few substances in the mixed oxide systems, and data for the remaining phase have to be calculated by appropriate correlation or estimation methods.

In this paper, thermodynamic functions for MeCuO_2 and Me_2CuO_3 ($\text{Me}=\text{Ca}, \text{Sr}, \text{Ba}$) binary oxides are assessed. For Ca_2CuO_3 , SrCuO_2 , Sr_2CuO_3 and BaCuO_2 , there is a large number of experimental measurements. The thermodynamic functions of these substances are, thus, mostly optimized from experimental results. Since there is a lack of experimental data for CaCuO_2 and Ba_2CuO_3 phases, other methods have to be used. Several estimation and correlation methods were tested on other complex oxides, and the most reliable ones were chosen to predict the thermochemical functions of CaCuO_2 and Ba_2CuO_3 .

2. Thermochemical properties of basic oxides

For the evaluation of molar entropy and enthalpy of formation for mixed oxides accurate data for simple

*Corresponding author.

oxides are necessary. For CaO and CuO, all thermochemical properties were taken from the JANAF Tables [1]. The value of standard heat of formation of CuO is in good agreement with recently published results [2–5] derived from EMF measurements of Cu₂O/CuO equilibrium. Standard heats of formation of SrO and BaO were also taken from the JANAF Tables [1]. Solution calorimetric measurements, recently performed by Cordfunke et al. [6], confirmed these values. Molar entropies at 298.15 K for SrO and BaO were calculated from low-temperature C_{pm}^0 measurements published by Cordfunke et al. [7]. Temperature dependences of heat capacities for SrO and BaO were derived from data in Ref. [7].

3. Heat capacity

The determination of heat capacity is usually performed in two separate temperature intervals: low-temperature range (from ca. 4 to 300 K) and high-temperature range (>300 K). Above 300 K, the temperature dependence of C_{pm}^0 for solids is customarily expressed by the following equation:

$$C_{\text{pm}}^0(T) = a + bT + c/T^2 \quad (1)$$

The values of C_{pm}^0 were measured by low-temperature calorimetry for four oxides [8–10] (Table 1). Unfortunately, no measurements have been carried out at higher temperatures (above 350 K), and thus temperature dependences of C_{pm}^0 have to be estimated. The most frequent method used for the estimation of $C_{\text{pm}}^0(T)$ of complex solid substances is the Neumann–Kopp rule [11]. This method is based on the assumption

that there is no heat capacity change when a complex substance is formed from its member compounds. An alternative empirical method for the estimation of heat capacities of predominantly ionic binary compounds was proposed by Kubaschewski and Ünal [12]. Heat capacity at 298 K is obtained as a sum of ionic contributions, but for the determination of temperature dependence the melting point is required. Generally, the $C_{\text{pm}}^0(T)$ dependence, as approximated by Kubaschewski, increases more rapidly than that evaluated from the Neumann–Kopp rule. At 1000 K, the difference between them is ca. 6%. The experimental and estimated values of C_{pm}^0 (298 K) are in good agreement except for BaCuO₂. In this case, the experimental value is shifted by 5.7 J K⁻¹ mol⁻¹ to lower values.

Upon optimization of ΔH_{f}^0 (298.15 K) and S_{m}^0 (298.15 K) of Ca₂CuO₃, SrCuO₂, Sr₂CuO₃ and BaCuO₂ (discussed in Sections 4 and 5) temperature dependences by the Neumann–Kopp rule correspond better to experimental results than those calculated using [12]. Therefore, we use the former method for all AEC. For BaCuO₂, the Neumann–Kopp rule was modified by adding a constant increment of 5.7 J K⁻¹ mol⁻¹ to the whole $C_{\text{pm}}^0(T)$ dependence. The coefficients a , b and c for all oxides are listed in Table 2.

4. Standard enthalpy of formation

Standard enthalpies of formation, ΔH_{f}^0 (298.15 K), of the four oxides mentioned above were optimized from experimental data using weighted least square regression analysis. Experimental values of molar

Table 1

Heat capacities of AEC at 298.15 K, EXP, from experimental measurement; NK, estimated by the Neumann–Kopp rule; and KUB, estimated by Kubaschewski and Ünal method

Substance	C_{pm}^0 (EXP)	C_{pm}^0 (NK)	C_{pm}^0 (KUB)
CaCuO ₂	—	84.3	86.4
Ca ₂ CuO ₃	136.1 ^a [8]	134.8 ^a	138.5 ^a
SrCuO ₂	86.8 [9]	87.4	87.2
Sr ₂ CuO ₃	134.7 [9]	132.5	131.1
BaCuO ₂	95.0 [10]	89.3	88.1
Ba ₂ CuO ₃	—	136.4	132.8

^a At $T=350$ K.

Table 2

Heat capacities of AEC

Substance	$C_{\text{pm}}^0(T) = a + bT + cT^{-2}$ [J K ⁻¹ mol ⁻¹]		
	a	$b \times 10^3$	$c \times 10^{-6}$
CaCuO ₂	98.949	11.615	-1.608
Ca ₂ CuO ₃	149.303	15.803	-2.455
SrCuO ₂	98.468	10.457	-1.261
Sr ₂ CuO ₃	148.341	13.487	-1.761
BaCuO ₂	106.841	9.378	-1.300
Ba ₂ CuO ₃	153.687	11.329	-1.839

Table 3

Experimental values of heats of formation of AEC: SC, solution calorimetry (solvent); EMF, electromotive force measurement; and TG, thermogravimetry analysis

Authors and reference	Method	Temperature/ (K)	ΔH_f^0 (kJ mol ⁻¹)	Inaccuracy/ (kJ mol ⁻¹)
<i>Ca₂CuO₃</i>				
Idemoto, 1993 [13]	SC(HClO ₄)	298.15	-1434.0	0.8
Mathews, 1993 [14]	EMF	1110–1260	-1294.4	0.2
Mathews, 1993 [14]	EMF	925–1250	-1310.6	0.3
Suzuki, 1990 [15]	EMF	1000–1220	-1299.9	1.3
<i>SrCuO₂</i>				
Idemoto, 1993 [13]	SC(HClO ₄)	298.15	-771.5	2.0
Alcock, 1990 [16]	EMF	1050–1150	-697.3	0.8
Skolis, 1990 [17]	EMF	1030–1260	-680.4	0.7
Skolis, 1990 [18]	EMF	1060–1250	-679.6	1.7
Jacob, 1990 [19]	EMF	900–1280	-689.0	0.1
Suzuki, 1992 [5]	EMF	923–1223	-686.7	0.9
<i>Sr₂CuO₃</i>				
Idemoto, 1993 [13]	SC(HClO ₄)	298.15	-1410.6	2.8
Alcock, 1990 [16]	EMF	1050–1150	-1243.4	5.7
Skolis, 1990 [17]	EMF	1030–1260	-1242.1	1.1
Jacob, 1992 [19]	EMF	975–1260	-1246.9	0.3
Jacob, 1992 [19]	EMF	900–1280	-1251.1	0.3
Suzuki, 1992 [5]	EMF	923–1223	-1244.2	0.9
<i>BaCuO₂</i>				
Grunin, 1989 [20]	SC(HCl)	298.15	-802.3	2.4
Monaenkova, 1990 [21]	SC(HCl)	298.15	-791.8	3.0
Morss, 1990 [22]	SC(HClO ₄)	298.15	-785.0	10.0
Garzon, 1991 [23]	SC(HClO ₄)	298.15	-804.2	7.9
Idemoto, 1992 [24]	SC(HClO ₄)	298.15	-780.0	4.4
Konkova, 1992 [25]	SC(HCl)	298.15	-772.7	2.1
Zhou, 1992 [26]	SC (2PbO.B ₂ O ₃)	977	-718.0	2.4
Mackevich, 1993 [27]	SC(HCl)	323	-757.0	5.0
Monaenkova, 1994 [28]	SC(HCl)	298.15	-791.9	2.3
Rais, 1995 [29]	SC(HNO ₃)	298.15	-812.0	6.0
Zimmermann, 1995 [30]	SC (2PbO.B ₂ O ₃)	973	-723.1	2.8
Fan, 1989 [31]	EMF	950–1200	-668.2	5.0
Skolis, 1990 [32]	EMF	1101–1182	-656.5	12.6
Voronin, 1990 [33]	EMF	978–1101	-700.0	6.8
Borowiec, 1990 [34]	EMF	1073–1223	-658.6	10.0
Shimpo, 1994 [36]	TG	1100–1173	-606.9	24.0

enthalpies, molar entropies and molar Gibbs energies of the given substance at given temperatures and their inaccuracies were used as input data. These values had to be first recalculated to the desired temperature of 298.15 K by integrating the assumed $C_{pm}^0(T)$ dependence and then averaged, using the inaccuracies as corresponding weights. Input data for Ca₂CuO₃, SrCuO₂, Sr₂CuO₃ and BaCuO₂ are listed in Table 3.

Inaccuracies were estimated from errors of measurements and, in cases where the experimental results were quite inconsistent with other measurements, they were correspondingly higher.

Experimental data for Ca₂CuO₃ and SrCuO₂ are in very good agreement, and optimized values of ΔH_f^0 have low standard deviations. Jacob and Mathews [19] found the data of Alcock and Li [16] on the compound

Table 4

Heats of formation of AEC from simple oxides. Exp. – optimized values from experimental results, ARO – estimated by the Aronson method [37]. TSA, estimated by the Tsagareishvili method [38]; and MRO, estimated by the linear correlation method (this work)

Substance	$\Delta H_{f,ox}^0$ (EXP)/ (kJ mol ⁻¹)	$\Delta H_{f,ox}^0$ (ARO)/ (kJ mol ⁻¹)	$\Delta H_{f,ox}^0$ (TSA)/ (kJ mol ⁻¹)	$\Delta H_{f,ox}^0$ (MRO)/ (kJ mol ⁻¹)
CaCuO ₂	—	-25.3	-58.6	42.9
Ca ₂ CuO ₃	-5.2	-41.2	-87.9	—
SrCuO ₂	-21.6	-16.3	-58.6	—
Sr ₂ CuO ₃	-31.4	-27.9	-87.9	—
BaCuO ₂	-82.5	-9.2	-58.6	—
Ba ₂ CuO ₃	—	-17.2	-87.9	-56.1

Sr₂CuO₃ to be internally inconsistent; therefore, we used a reassessed value, and the experimental error was multiplied by ten. The thermogravimetric measurement on BaCuO₂ reported by Shimpo and Nakamura [36] gives a result that is very far from the rest of experimental values and, thus, the inaccuracy was also higher. Resulting standard enthalpies of formation are listed in Table 4.

For the determination of ΔH_f^0 of CaCuO₂ and Ba₂CuO₃, several estimation and correlation methods were examined. Aronson [37] suggested a method for the estimation of enthalpy of formation for refractory mixed oxides. In this method, a modified Pauling equation

$$\Delta H_f^0 = -96.5n_O(X'_{Me} - 3.50)^2 \quad (2)$$

is applied where n_O is the number of oxygen atoms in the mixed oxide, X'_{Me} the pseudoelectronegativity of the entire metal group, and 3.50 the Pauling electronegativity value of oxygen. X'_{Me} is calculated as the geometric mean from the values of pseudoelectronegativities of individual metal atoms that were determined using Eq. (2) and the known values of ΔH_f^0 of basic oxides. Using this method, enthalpies of formation of all six mixed oxides and, consequently, enthalpies of formation from basic oxides ($\Delta H_{f,ox}^0$) were calculated. All ΔH_f^0 are listed in Table 4.

An empirical method, proposed by Tsagareishvili [38], can be used for the estimation of standard enthalpy of formation of mixed oxides from basic oxides. According to this method $\Delta H_{f,ox}^0 = -29.3n_O$. This method was tested on various systems, including the oxides in the Y–Ba–Cu–O system [39] and good agreement was achieved. Results for AEC are also listed in Table 4.

It follows from a comparison of estimated and experimentally obtained values of $\Delta H_{f,ox}^0$ that the estimation methods mentioned above cannot be successfully applied for AEC. Nevertheless, it was empirically found that there exists a linear dependence of the enthalpy of formation from oxides on ionic radius of alkali-earth cations for titanates, zirconates, hafnates, silicates and molybdates. Fig. 1 shows these dependencies for $\Delta H_{f,ox}^0$ calculated from data of Knacke and Kubaschewski [40] and six-fold coordination ionic radii by Shannon [41]. Supposing the same relationship for 1 : 1 alkali-earth cuprates the value of $\Delta H_{f,ox}^0$ for CaCuO₂ can be estimated from known values for SrCuO₂ and BaCuO₂ using linear extrapolation. The obtained value $\Delta H_{f,ox}^0 = 42.9$ kJ mol⁻¹ indicates that this phase is unstable. This fact can be interpreted in view of the XRD studies [42] that revealed only the existence of nonstoichiometric phase Ca_{1-x}CuO_{2-y}.

For 2 : 1 alkali-earth mixed oxides only a few enthalpies of formation are known. A complete set of data exists only for silicates where the same linear relation was found (Fig. 2). Accordingly, the enthalpy of formation for Ba₂CuO₃ $\Delta H_{f,ox}^0 = -56.1$ kJ mol⁻¹ was estimated from data for Ca₂CuO₃ and Sr₂CuO₃. The values obtained by linear extrapolation method were selected as the most reliable. Enthalpies of formation of all AEC together with enthalpies of formation from oxides are summarized in Table 6.

5. Standard molar entropy

Standard molar entropies of Ca₂CuO₃, SrCuO₂, Sr₂CuO₃ and BaCuO₂ were optimized from experi-

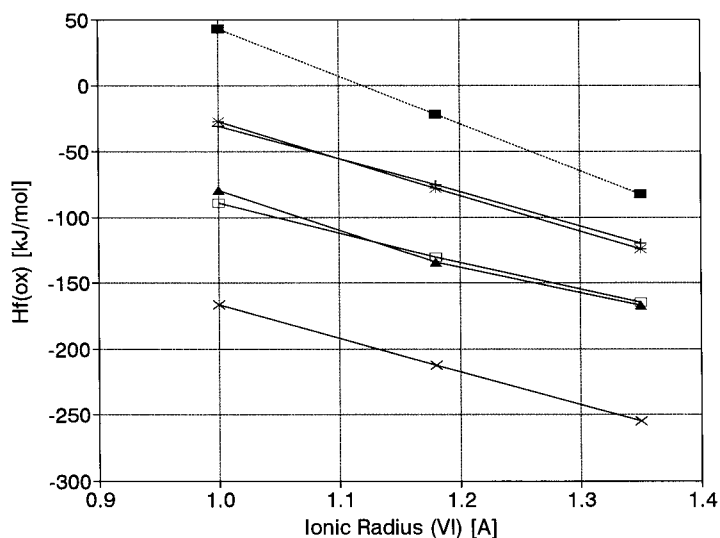


Fig. 1. Dependence of heats of formation from oxides on ionic radii of alkali-earth metals for several 1 : 1 mixed oxides. (■), MeO : CuO; (□), MeO : SiO₂; (Δ), MeO : TiO₂; (+), MeO : ZrO₂; (★), MeO : HfO₂; and (×), MeO : MoO₃.

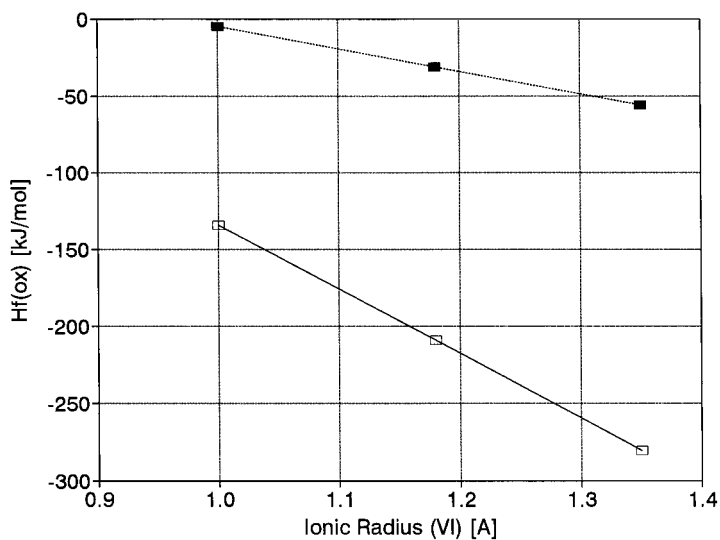


Fig. 2. Dependence of heats of formation from oxides on ionic radii of alkali-earth metals for several 2 : 1 mixed oxides (■), 2MeO : CuO; and (□), 2MeO : SiO₂.

mental data using the method mentioned above for optimization of enthalpies. Input data together with inaccuracies are listed in Table 5. In general, the experimental results show larger scatter than the data for enthalpies of formation, and the resulting deviations for Ca₂CuO₃ and BaCuO₂ reach up to 8%.

Methods proposed for the estimation of standard molar entropy of binary compounds from ionic contributions (for review, see [11,39]) were not proved to be applicable for AEC. In principle, this method yields the molar entropy of formation from oxides ($\Delta S_{f,ox}^0$) equal to zero which does not agree with experimental

Table 5

Experimental values of entropies of AEC. AC, low-temperature adiabatic calorimetry; EMF, electromotive force measurement; and TG, thermogravimetry analysis

Authors and reference	Method	Temperature/ (K)	S_m^0 (J K ⁻¹ mol ⁻¹)	Inaccuracy (J K ⁻¹ mol ⁻¹)
<i>Ca₂CuO₃</i>				
Mathews, 1993 [14]	EMF	1110–1260	331.3	0.7
Mathews, 1993 [14]	EMF	925–1250	317.1	0.7
Suzuki, 1990 [15]	EMF	1000–1220	415.4	1.6
<i>SrCuO₂</i>				
Shaviv, 1990 [9]	AC	298.15	96.9	0.9
Alcock, 1990 [16]	EMF	1050–1150	220.5	1.4
Skolis, 1990 [17]	EMF	1030–1260	230.5	1.4
Skolis, 1990 [18]	EMF	1060–1250	231.2	2.2
Jacob, 1992 [19]	EMF	900–1280	225.5	1.0
Suzuki, 1992 [5]	EMF	923–1223	224.7	1.2
<i>Sr₂CuO₃</i>				
Shaviv, 1990 [9]	AC	298.15	148.5	1.3
Alcock, 1990 [16]	EMF	1050–1150	346.7	1.8
Skolis, 1990 [17]	EMF	1030–1260	346.7	2.1
Jacob, 1992 [19]	EMF	975–1260	345.1	1.5
Jacob, 1992 [19]	EMF	900–1280	340.8	1.5
Suzuki, 1992 [5]	EMF	923–1223	343.6	1.6
<i>BaCuO₂</i>				
Gavrichev, 1993 [10]	AC	298.15	118.3	1.1
Fan, 1989 [31]	EMF	950–1200	234.8	1.5
Skolis, 1990 [32]	EMF	1101–1182	243.7	2.3
Voronin, 1990 [33]	EMF	978–1101	274.0	2.2
Borowiec, 1991 [34]	EMF	1073–1223	257.7	2.2
Azad, 1991 [35]	EMF	736–1102	278.8	2.2
Shimpo 1994 [36]	TG	1100–1173	270.1	2.0

findings. Some other methods were employed based on the assumption that standard molar entropy of mixed oxides can be expressed as a function of a sum of entropies of basic oxides [43]. Although they fit quite well for alkali-earth titanates and zirconates they are not valid in the case of cuprates. In this work, a modified contribution method was used for the determination of unknown values of standard molar entropy of CaCuO₂ and Ba₂CuO₃. According to this method, standard molar entropy of a mixed oxide within a chemically related oxide group is determined as a sum of entropy contributions from constituent basic oxides. The individual entropy contributions are obtained from known experimental values for other mixed oxides. It was confirmed that, in the case of alkali-earth titanates, silicates and aluminates, this

method provides significantly lower deviations (ca. 2%) than simple entropy summing from constituent oxides (deviations from 5 to 18%). Thus, the standard molar entropies of CaCuO₂ and Ba₂CuO₃ were obtained from the following entropy contributions of basic oxides determined before: S(CuO)=44.7, S(CaO)=40.0, and S(BaO)=72.5 J K⁻¹ mol⁻¹. The estimated error was ca. 2%. All standard molar entropies of AEC and molar entropies of formation from oxides are listed in Table 6.

6. Conclusions

In this paper, thermochemical properties of some AEC are presented. In view of the lack of experimental

Table 6
Selected values of heats of formation and entropies of AEC

Substance	ΔH_f^0 (kJ mol ⁻¹)	$\Delta H_{f,ox}^0$ (kJ mol ⁻¹)	S_m^0 (J K ⁻¹ mol ⁻¹)	$\Delta S_{f,ox}^0$ (J K ⁻¹ mol ⁻¹)
CaCuO ₂	-749±7	42.9	84.7±1.7	4.0
Ca ₂ CuO ₃	-1431.1±1.3	-5.2	124.7±9.9	5.9
SrCuO ₂	-769.7±1.6	-21.6	96.6±0.9	0.4
Sr ₂ CuO ₃	-1371.5±3.3	-31.4	148.5±1.0	-1.3
BaCuO ₂	-786.7±7.2	-82.5	117.2±9.6	4.6
Ba ₂ CuO ₃	-1309±13	-56.1	189.7±3.8	7.1

data, several values were estimated and these should be considered as less reliable.

For more accurate data further experimental work is necessary. According to our opinion, these data can be used for successful phase diagram predictions and equilibrium composition calculation. Values recommended in this paper are in quite good agreement with critically assessed data recently published by other authors [30,42,44–48].

Acknowledgements

This work was supported by the Grant Agency of the Czech Republic (Grant No. 104/95/0868) and the Ministry of Education of the Czech Republic (Grant No. VS 96070).

The authors would like to thank Professor J. Šesták for useful discussion on the subject presented.

References

- [1] M.W. Chase Jr., C.A. Davies, J.R. Downey Jr., D.J. Frurip, R.A. McDonald, A.N. Syverud, *J. Phys. Chem. Ref. Data* 14(Suppl.)No. 1 (1985) 1.
- [2] H.S.C. O'Neill, *Amer. Mineralogist* 73 (1988) 470.
- [3] W. Zhang, K. Osamura, *Z. Metallkde.* 81 (1990) 196.
- [4] W. Zhang, K. Osamura, *Metall. Trans. B* 22B (1991) 705.
- [5] R.O. Suzuki, P. Bohac, L.J. Gauckler, *J. Am. Ceram. Soc.* 75 (1992) 2833.
- [6] E.H.P. Cordfunke, R.J.M. Konings, W. Ouweltjes, *J. Chem. Thermodyn.* 22 (1990) 991.
- [7] E.H.P. Cordfunke, R.R. van der Laan, J.C. van Miltenburg, *J. Phys. Chem. Solids* 55 (1994) 77.
- [8] Ch. Krüger, W. Reichelt, A. Almes, U. König, H. Oppermann, H. Scheler, *J. Solid State Chem.* 96 (1992) 67.
- [9] R. Shaviv, E.F. Westrum, T.L. Yang, C.B. Alcock, B. Li, *J. Chem. Thermodyn.* 22 (1990) 1025.
- [10] K.S. Gavrichev, V.E. Gorbunov, L.N. Golushina, G.E. Nikiforova, G.A. Totrova, I.S. Shapligin, *Neorg. Mater.* 29 (1993) 645.
- [11] O. Kubaschewski, C.B. Alcock, P.J. Spencer, *Materials Thermochemistry*, Pergamon Press, Oxford, 1993.
- [12] O. Kubaschewski, H. Ünal, *High Temp.–High Press.* 9 (1977) 361.
- [13] Y. Idemoto, K. Shizuka, Y. Yasuda, K. Fueki, *Physica C* 211 (1993) 36.
- [14] T. Mathews, J.P. Hajra, K.T. Jacob, *Chem. Mater.* 5 (1993) 1669.
- [15] R.O. Suzuki, P. Bohac, L.J. Gauckler, *J. Am. Ceram. Soc.* 77 (1994) 41.
- [16] C.B. Alcock, B. Li, *J. Am. Ceram. Soc.* 73 (1990) 1176.
- [17] Yu. Ya. Skolis, L.A. Khramtsova, *Zh. Fiz. Khim.* 64 (1990) 1681.
- [18] Yu. Ya. Skolis, L.A. Khramtsova, S.V. Kitsenko, M.L. Kovba, I.I. Burchak, *Vestn. Mosk. Universiteta, Ser. Chim.* 31 (1990) 18.
- [19] K.T. Jacob, T. Mathews, *J. Am. Ceram. Soc.* 75 (1992) 3225.
- [20] V.S. Grunin, M.M. Pivovarov, I.B. Patrina, M. Rasumeenko, R.A. Bubnova, M.I. Domnina, M.M. Shults, *Dokl. Akad. Nauk SSSR* 307 (1989) 143.
- [21] A.S. Monaenkova, A.A. Popova, N.V. Zajceva, *Sverkhprodukt: Fiz. Khim. Tekh.* 3 (1990) 955.
- [22] L.R. Morss, S.E. Dorris, T.B. Lindemer, N. Naito, *Eur. J. Solid State Inorg. Chem.* 27 (1990) 327.
- [23] F.H. Garzon, I.D. Raistrick, D.S. Ginley, J.W. Halloran, *J. Mater. Res.* 6 (1991) 885.
- [24] Y. Idemoto, J. Takahashi, K. Fueki, *Physica C* 194 (1992) 117.
- [25] T.S. Konkova, Yu.N. Matyushin, J.H. Greenberg, V.B. Lazarev, I.S. Shapligin, *J. Chem. Thermodyn.* 24 (1992) 225.
- [26] Z. Zhou, A. Navrotsky, *J. Mater. Res.* 7 (1992) 2920.
- [27] N.I. Mackevich, T.L. Popova, V.A. Titov, V.S. Kravchenko, V.P. Shaburova, O.G. Potapova, *Zh. Fiz. Khim.* 67 (1993) 1342.
- [28] A.S. Monaenkova, A.A. Popova, N.V. Zajceva, S.N. Mudrecova, A.F. Majorova, Yu. Ya. Skolis, *Zh. Fiz. Khim.* 68 (1994) 2132.

- [29] A. Rais, M. Ganteaume, M. Desressac, J. Rogez, J.-C. Mathieu, *Ann. Chim. Fr.* 20 (1995) 9.
- [30] E. Zimmermann, K. Hack, A. Mohammad, A. Boudéne, D. Neuschütz, *CALPHAD* 19 (1995) 179.
- [31] Z. Fan, C. Ji, Z. Xi, Z. Guan, *Supercond. Sci. Technol.* 2 (1989) 43.
- [32] Yu. Ya. Skolis, S.F. Pashin, M.L. Kovba, *Sverkhprovodimost: Fiz. Khim. Tekh.* 3 (1990) 2792.
- [33] G.F. Voronin, S.A. Degterov, Yu. Ya. Skolis, *Proc. 3rd German–Soviet Bilateral Seminar on High-Temperature Superconductivity, Karlsruhe, 1990.*
- [34] K. Borowiec, K. Kolbrecka, *J. Alloys Comp.* 176 (1991) 225.
- [35] A.M. Azad, O.M. Sreedharan, K.T. Jacob, *J. Mater. Sci.* 26 (1991) 3374.
- [36] R. Shimpo, Y. Nakamura, *Metall. Mater. Trans. B* 25B (1994) 385.
- [37] S. Aronson, *J. Nuclear Mater.* 107 (1982) 343.
- [38] D.S. Tsagareishvili, G.G. Gvelesiani, I.B. Baratashvili, G.K. Moiseev, N.A. Vatolin, *Zh. Fiz. Khim.* 64 (1990) 2606.
- [39] G.K. Moiseev, J. Šesták, *Prog. Cryst. Growth Charact.* 30 (1995) 23.
- [40] O. Knacke, O. Kubaschewski, K. Hesselmann, *Thermochemical Properties of Inorganic Substances*, Springer-Verlag, Berlin, 1991.
- [41] R.D. Shannon, *Acta Cryst.* A32 (1976) 751.
- [42] D. Risold, B. Hallstedt, L. Gauckler, *J. Am. Ceram. Soc.* 78 (1995) 2655.
- [43] M.M. Lencka, R.E. Riman, *Thermochim. Acta* 256 (1995) 193.
- [44] G. Moiseev, N. Vatolin, J. Šesták, *Thermochim. Acta* 237 (1994) 401.
- [45] G. Moiseev, N. Vatolin, J. Šesták, *Thermochim. Acta* 237 (1994) 409.
- [46] N. Ilynich, S. Zaitzeva, G. Moiseev, J. Šesták, N. Vatolin, *Thermochim. Acta* 266 (1995) 285.
- [47] D. Risold, B. Hallstedt, L. Gauckler, *J. Am. Ceram. Soc.* 78 (1995) 2655.
- [48] D. Risold, B. Hallstedt, L. Gauckler, *J. Am. Ceram. Soc.* 80 (1997) 527.