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Enthalpy of formation of selected mixed oxides in a $CaO–SrO–Bi_2O_3–Nb_2O_5$ system

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ABSTRACT

The heats of drop-solution in $3Na_2O + 4MoO_3$ melt at 973 K and 1073 K for calcium and strontium carbonates, Bi_2O_3, Nb_2O_5 and several stoichiometric mixed oxides in $CaO–Nb_2O_5$, $SrO–Nb_2O_5$ and $Bi_2O_3–Nb_2O_5$ systems were measured using a Setaram Multi HTC-96 calorimeter. The values of enthalpy of formation from constituent binary oxides at 298 K, $\Delta_{ox}H$, were derived for the mixed oxides under investigation: $\Delta_{ox}H(CaNb_2O_6) = -132.0 \pm 23.8$ kJ mol^{-1}, $\Delta_{ox}H(Ca_2Nb_2O_7) = -208.0 \pm 31.9$ kJ mol^{-1}, $\Delta_{ox}H(SrNb_2O_6) = -167.9 \pm 19.1$ kJ mol^{-1}, $\Delta_{ox}H(Sr_2Nb_2O_7) = -289.2 \pm 37.5$ kJ mol^{-1} and $\Delta_{ox}H(BiNbO_4) = -41.9 \pm 11.1$ kJ mol^{-1}. Additionally, the values $\Delta_{ox}H$ for other mixed oxides with different stoichiometries were estimated on the basis of these experimental results.

1. Introduction

Mixed oxides in the system $CaO–SrO–Bi_2O_3–Nb_2O_5(–Ta_2O_5)$ possess many extraordinary electric, magnetic and optical properties for which they are used in fabrication of various electronic components. For example solid solutions $Sr_2(Nb_{1-x}Ta_x)_2O_7$ and $(Sr_{1-y}Ca_y)Bi_2(Nb_{1-x}Ta_x)_2O_9$ are used for ferroelectric memory devices, solid solution $Bi(Nb_{1-x}Ta_x)O_4$ and $CaNb_2O_6$ for microwave dielectric resonators and $Ca_2Nb_2O_7$ as non-linear optical materials and hosts for rare-earth ions in solid-state lasers. To assess the thermodynamic stability and reactivity of these oxides under various conditions during their preparation, processing and operation, a complete set of consistent thermodynamic data, including heat capacity, entropy and enthalpy of formation, is necessary.

Experimental values of enthalpies of formation, $\Delta_f H$, for these mixed oxides are rare. Idemoto et al. [1], using solution calorimetry with $HClO_4$ as a solvent, derived $\Delta_f H(298)$ for a number of mixed oxides in $CaO–Bi_2O_3$ and $SrO–Bi_2O_3$ systems. On the other hand, the Gibbs energies of formation of various mixed oxides from the constituent binary ones, $\Delta_{ox}G$, have been measured by various authors utilizing the EMF method: $CaO–Bi_2O_3$ [2,3], $SrO–Bi_2O_3$ [4], $CaO–Nb_2O_5$ [5–7] and $CaO–Ta_2O_5$ [8,9]. Further, thermodynamic assessments of the $CaO–Bi_2O_3$ [10], $SrO–Bi_2O_3$ [10] and $SrO–Nb_2O_5$ [11] systems have been performed, providing the evaluated Gibbs energies for several relevant mixed oxides from thermodynamic and, in particular, phase equilibrium data.

In a systematic study of the thermochemical properties of complex oxides in the $Bi_2O_3–CaO–SrO–Nb_2O_5–Ta_2O_5$ system, we measured the heat capacities and enthalpy increments of $Bi_2Ca_2O_5$, Bi_2CaO_4, $Bi_6Ca_4O_{13}$, $Bi_{14}Ca_5O_{26}$ [12], $BiNbO_4$, $BiTaO_4$ [13], $BiNb_5O_{14}$ [14], $SrBi_2Nb_2O_9$, $SrBi_2Ta_2O_9$ [15], $SrNb_2O_6$ [16], $Sr_2Nb_2O_7$ [17], $CaNb_2O_6$, $Ca_2Nb_2O_7$ [18], $Sr_2Nb_{10}O_{27}$ and $Sr_5Nb_4O_{15}$ [19]. Furthermore, the values of the molar entropies at 298.15 K were evaluated from low-temperature heat capacity measurements.

In the present contribution, we report the results of calorimetric measurements of the enthalpies of drop-solution, $\Delta_{ds}H$, in a sodium oxide–molybdenum oxide melt for $CaCO_3$, $SrCO_3$, Bi_2O_3, Nb_2O_5 and several stoichiometric mixed oxides in the $CaO–Nb_2O_5$, $SrO–Nb_2O_5$ and $Bi_2O_3–Nb_2O_5$ systems. The values of enthalpy of formation from constituent binary oxides, $\Delta_{ox}H$, were derived for the mixed oxides under investigation. Additionally, the values of $\Delta_{ox}H$ for other mixed oxides with different stoichiometries were estimated on the basis of the experimental results.

2. Experimental

The samples of mixed oxides, namely, $CaNb_2O_6$, $Ca_2Nb_2O_7$, $SrNb_2O_6$, $Sr_2Nb_2O_7$ and $BiNbO_4$, were prepared by conventional solid-state reactions from the high-purity precursors $CaCO_3$ (99.9%, Aldrich), $SrCO_3$ (99.9%, Aldrich), Bi_2O_3 (99.9%, Aldrich) and Nb_2O_5 (99.85%, Alfa Aesar). Carbonates were dried at 180 °C for 10 h just before the next manipulation. Stoichiometric amounts of the precursors were

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Table 1
Conditions of the synthesis of the investigated mixed oxides.

Substance		Calcination		Firing		PDF reference
Stoichiometry	Structure	Temperature (K)	Time (h)	Temperature (K)	Time (h)	
$CaNb_2O_6$	Orthorhombic	1073	48	1223	162	00-039-1392
$Ca_2Nb_2O_7$	Monoclinic	1073	48	1173	142	01-070-2006
$SrNb_2O_6$	Monoclinic	1273	48	1523	120	00-077-2431
$Sr_2Nb_2O_7$	Orthorhombic	1273	48	1673	120	00-052-0321
$BiNbO_4$	Orthorhombic	–	–	1073	80	00-016-0295

ground and calcinated in a platinum crucible in air atmosphere. After regrinding, the mixtures were fired. The experimental conditions of this two-step procedure are summarized in Table 1.

The phase-purity of the samples was assessed by XRD at room temperature. X-ray powder diffraction data were collected at room temperature with an X'Pert PRO (PANalytical, Netherlands) θ–θ powder diffractometer with a parafocusing Bragg–Brentano geometry using CuK_α radiation ($\lambda = 1.5418$ Å, $U = 40$ kV, $I = 30$ mA). The data were scanned over the angular range of 5–60° (2θ) with an increment of 0.02° (2θ) and a counting time of 0.3 s step^{-1}. The data evaluation was performed using the HighScore Plus software package.

The heats of drop-solution were determined using a Multi HTC 96 high-temperature calorimeter (Setaram, France). A sodium oxide–molybdenum oxide melt of the stoichiometry $3Na_2O + 4MoO_3$ was used as the solvent. The ratio of solute/solvent varied from 1/250 up to 1/500. The measurements were performed at temperatures of 973 and 1073 K in argon or air atmosphere. The method consists in alternating dropping of the reference material (small spherules of pure platinum) and of the sample (small pieces of pressed tablets 10–40 mg), being initially held near room temperature (T_0), through a lock into the working cell (a platinum crucible with the solvent) of the preheated calorimeter at temperature T. Two or three samples were examined during one experimental run. The delays between two subsequent drops were 30–60 min. The total heat effect ($\Delta_{ds}H$) includes the heat of solution ($\Delta_{sol}H$), the heat content of the sample ($\Delta_T H$), and, for the carbonates, the heat of decomposition ($\Delta_{decomp}H$) to form solid CaO or SrO and gaseous CO_2. Using appropriate thermochemical cycles, the values of the enthalpy of formation of mixed oxides from the binary oxides and from the elements at 298 K were evaluated. The temperature dependence of the heat capacity of platinum according to the SGTE database [20] was used for the calculation of the sensitivity of the calorimeters.

3. Results and discussion

The XRD analysis revealed that the prepared samples were without any observable diffraction lines from unreacted precursors or other impurities [13,16–18]. The powder diffraction patterns of the samples matched the PDF references, which are given in Table 1. No other chemical or spectral analyses were performed to verify the weighted metallic elements ratio as well as their valence state. However there is a sound reason to believe niobium occurs in Nb^{5+} state in our samples. Atuchin et al. [21], using X-ray photoelectron spectroscopy (XPS), clearly ascertained a pure Nb^{5+} oxidation state in $Sr_2Nb_2O_7$ powder sample prepared by the same procedure as in the present work and Nb^{5+} valence was also confirmed by XPS for other niobates including $Ca_2Nb_2O_7$ [22].

The heats of drop-solution for the calcium and strontium carbonates and for the bismuth and niobium oxides were measured first. These data are necessary for the evaluation of the $\Delta_{ox}H$ values for the mixed oxides, and furthermore, these data could be compared with the literature data [23–26]. For the $AECO_3$ carbonates, the measured heat effect consists of three contributions:

$$\Delta_{ds}H(AECO_3, T) = \Delta_T H(AECO_3, T_0 \rightarrow T) + \Delta_{decomp}H(AECO_3, T) + \Delta_{sol}H(AEO, T) \quad (1)$$

The measurements were performed at 973 K. The values of $\Delta_{ds}H(AECO_3, 973\,K)$ are given in Table 2 along with the values of $\Delta_{ds}H(AEO, 973\,K)$, which were derived based on the following thermochemical cycle ($T_0 \approx 298$ K):

$$AECO_3(s, T_0) \rightarrow AEO(melt, T) + CO_2(g, T); \quad \Delta_{ds}H(AECO_3) \quad (2)$$

$$AECO_3(s, T_0) \rightarrow AEO(s, T_0) + CO_2(g, T_0); \quad \Delta_{decomp}H(AECO_3) \quad (3)$$

$$CO_2(g, T_0) \rightarrow CO_2(g, T); \quad \Delta_T H(CO_2) \quad (4)$$

$$AEO(s, T_0) \rightarrow AEO(melt, T); \quad \Delta_{ds}H(AEO) \quad (5)$$

$$\Delta_{ds}H(AEO) = \Delta_{ds}H(AECO_3) - \Delta_{decomp}H(AECO_3) - \Delta_T H(CO_2) \quad (6)$$

The values $\Delta_{decomp}H(CaCO_3, 298\,K) = 178.8 \pm 1.6\,kJ\,mol^{-1}$, $\Delta_{decomp}H(SrCO_3, 298\,K) = 233.9 \pm 1.8\,kJ\,mol^{-1}$ and $\Delta_T H(CO_2, 298 \rightarrow 973\,K) = 32.0\,kJ\,mol^{-1}$ [23–25,27] were used for the calculations.

Next, the $\Delta_{ds}H$ values of the binary oxides Bi_2O_3 and Nb_2O_5 were measured. Because the dissolution of Nb_2O_5 and of the mixed oxides at 973 K proceeds rather slowly, the higher temperature of 1073 K was used. The measured values of $\Delta_{ds}H$ are also given in Table 2.

It is obvious from the data in Table 2 that the uncertainties of our results are noticeably larger than those of the literature values. The experimental values of $\Delta_{ds}H$ for $SrCO_3$ and $CaCO_3$ are in quite good agreement with the literature data [23–25]. On the other hand, the present and the published [26] values of $\Delta_{ds}H(Nb_2O_5)$ are quite different. It should be noted that a more endothermic value $\Delta_{decomp}H(SrCO_3, 298\,K) = 249.4\,kJ\,mol^{-1}$ is presented in the literature [31], which results in more exothermic value for $\Delta_{ds}H(SrO)$ by $15.5\,kJ\,mol^{-1}$.

$\Delta_{ds}H$ for the mixed oxides was measured at 1073 K. The following thermochemical cycle was used for the calculation of $\Delta_{ox}H$ for

Table 2
Enthalpy of drop-solution in $3Na_2O + 4MoO_3$ melt.

Substance	T (K)	$\Delta_{ds}H$ (kJ mol^{-1})[a]	$\Delta_{ds}H$ (kJ mol^{-1})
$CaCO_3$	973	128.4 ± 10.1 (10)	119.70 ± 1.02[b]
CaO	973	−82.39 ± 10.2[c]	−90.70 ± 1.69[b]
CaO	1073	−77.04 ± 10.2[d]	
$SrCO_3$	973	131.4 ± 9.1 (7)	130.16 ± 1.66[e] 134.48 ± 1.89[f]
SrO	973	−134.47 ± 9.3[c]	−135.82 ± 2.48[e] −131.42 ± 1.89[f]
SrO	1073	−129.25 ± 9.3[g]	
Bi_2O_3	973	26.0 ± 2.9 (12)	
Bi_2O_3	1073	39.6[h]	
Nb_2O_5	1073	141.8 ± 6.0 (11)	91.97 ± 0.78[i]

[a] Data from the present work. The uncertainty is two standard deviations of the mean (95% confidence level), the number in parentheses is the number of experiments performed.

[b] From Ref. [23], $T = 976$ K.

[c] The uncertainty was calculated according to the error propagation law considering the uncertainties of $\Delta_{ds}H$ and $\Delta_{decomp}H$ and neglecting the uncertainty of $\Delta_T H(CO_2)$.

[d] The value $\Delta_T H(CaO, 973 \rightarrow 1073\,K) = 5.35\,kJ\,mol^{-1}$ [28] was used for the calculation.

[e] From Ref. [24], $T = 975$ K.

[f] From Ref. [25], $T = 974$ K.

[g] The value $\Delta_T H(SrO, 973 \rightarrow 1073\,K) = 5.22\,kJ\,mol^{-1}$ [29] was used for the calculation.

[h] The value $\Delta_T H(Bi_2O_3, 973 \rightarrow 1073\,K) = 13.61\,kJ\,mol^{-1}$ [30] was used for the calculation.

[i] From Ref. [26], $T = 973$ K.

calcium and strontium niobates ($T_0 \approx 298$ K):

$$AE_xNb_2O_{5+x}(s, T_0) \rightarrow xAEO(melt, T) + Nb_2O_5(melt, T); \quad \Delta_{ds}H(AE_xNb_2O_{5+x}) \qquad (7)$$

$$AEO(s, T_0) \rightarrow AEO(melt, T); \quad \Delta_{ds}H(AEO) \qquad (8)$$

$$Nb_2O_5(s, T_0) \rightarrow Nb_2O_5(melt, T); \quad \Delta_{ds}H(Nb_2O_5) \qquad (9)$$

$$xAEO(s, T_0) + Nb_2O_5(s, T_0) \rightarrow AE_xNb_2O_{5+x}(s, T_0); \quad \Delta_{ox}H(AE_xNb_2O_{5+x}) \qquad (10)$$

$$\Delta_{ox}H(AE_xNb_2O_{5+x}) = x\Delta_{ds}H(AEO) + \Delta_{ds}H(Nb_2O_5) - \Delta_{ds}H(AE_xNb_2O_{5+x}) \qquad (11)$$

An analogous scheme was applied to calculate $\Delta_{ox}H(BiNbO_4)$. All of the experimental and calculated values are summarized in Table 3. The $\Delta_{ox}H$(298 K) values derived from high-temperature EMN measurements [5–7] for the $CaO–Nb_2O_5$ oxides and the assessed the values from the phase diagram for the $SrO–Nb_2O_5$ oxides [11] are also presented in Table 3. Our values for the calcium niobates are in good agreement with Raghavan's data [6,7], while the data from Dneprova et al. [5] are quite different. Moreover, a relation, $\Delta_{ox}H(CaNb_2O_6) > \Delta_{ox}H(Ca_2Nb_2O_7)$, that holds for the values from the work of Dneprova et al. is rather unexpected. The $\Delta_{ox}H$ values for strontium niobates obtained based on the binary $SrO–Nb_2O_5$ phase diagram evaluation [11] are substantially more exothermic than our calorimetric data. These large differences in the $\Delta_{ox}H$ values are not surprising in view of simultaneous differences in the $\Delta_{ox}S$ values from the assessment [11] and those derived from low temperature dependencies of the molar heat capacity of $SrNb_2O_6$ and $Sr_2Nb_2O_7$ [16,17].

There are other mixed oxides in the $CaO–Nb_2O_5$, $SrO–Nb_2O_5$ and $Bi_2O_3–Nb_2O_5$ systems with stoichiometries of $Ca_3Nb_2O_8$, $Ca_4Nb_2O_9$, $Sr_2Nb_{10}O_{27}$, $Sr_5Nb_4O_{15}$, $Sr_4Nb_2O_9$, $Sr_6Nb_2O_{11}$, $Bi_2Nb_{12}O_{33}$, $BiNb_5O_{14}$, $Bi_8Nb_{18}O_{57}$, and $Bi_5Nb_3O_{15}$ [32] for which $\Delta_{ox}H$ values have not yet been determined. As a rough estimate, the values of $\Delta_{ox}H$ calculated according to an empirical method proposed by the authors [33] can be used. In this case the following relation holds for $\Delta_{ox}H$:

$$\frac{\Delta_{ox}H}{n_{Nb} + n_{Me}} = -2 \cdot 96.5\alpha y x_{Nb} x_{Me}^{\delta} (X_{Nb} - X_{Me})^2 \qquad (12)$$

where X_{Nb} and X_{Me} (Me = Ca, Sr or Bi) are Pauling's electronegativities of the relevant elements, x_{Nb} and x_{Me} are the molar fractions of the oxide-forming elements ($x_{Nb} = n_{Nb}/(n_{Nb} + n_{Me})$, etc.), y is the number of oxygen atoms per one atom of oxide-forming elements

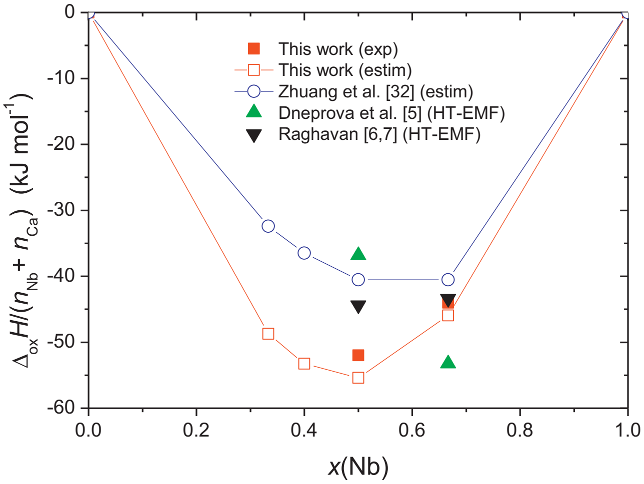

Fig. 1. Values of enthalpy of formation of the mixed oxides from constituent binary oxides in the $CaO–Nb_2O_5$ system (lines serve only as a guide for the eyes).

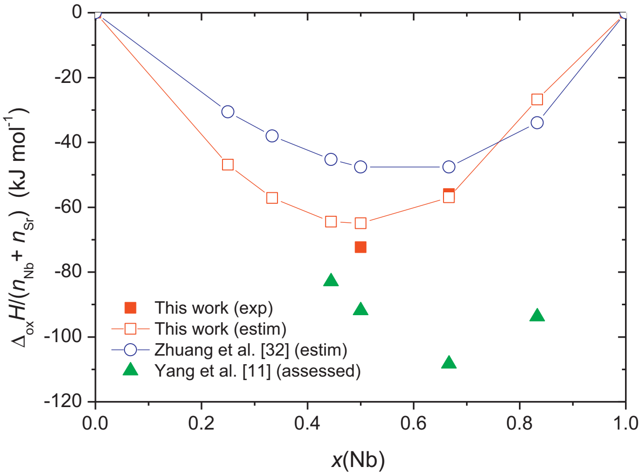

Fig. 2. Values of enthalpy of formation of the mixed oxides from constituent binary oxides in the $SrO–Nb_2O_5$ system (lines serve only as a guide for the eyes).

and α and δ are the model parameters. Using Pauling's electronegativities, $X_{Nb} = 1.60$, $X_{Ca} = 1.00$, $X_{Sr} = 0.95$, and $X_{Bi} = 2.02$, and the calorimetric values of $\Delta_{ox}H$ obtained in this work (see Table 3), the values of $\alpha = 2.576$ and $\delta = 1.50$ were derived from the least-squares fit. The estimated $\Delta_{ox}H$ values are shown in Figs. 1–3. The values of $\Delta_{ox}H$ that were calculated according to an empirical method proposed by Zhuang et al. [34] are displayed for comparison.

Table 3
Enthalpy of drop-solution in $3Na_2O + 4MoO_3$ melt ($\Delta_{ds}H$) and enthalpy of formation from constituent binary oxides ($\Delta_{ox}H$).

Substance	T (K)	$\Delta_{ds}H$ (kJ mol^{-1})[a]	$\Delta_{ox}H$(298 K) (kJ mol^{-1})[b]	$\Delta_{ox}H$(298 K) (kJ mol^{-1})
$CaNb_2O_6$	1073	196.8 ± 20.7 (8)	−132.0 ± 23.8	−159.8 ± 7.5[c] −130.1 ± 1.0[d]
$Ca_2Nb_2O_7$	1073	195.7 ± 27.8 (8)	−208.0 ± 31.9	−147.3 ± 15.1[c] −177.5 ± 1.0[e]
$SrNb_2O_6$	1073	180.50 ± 15.7 (4)	−167.9 ± 19.1	−325.0[f]
$Sr_2Nb_2O_7$	1073	167.54 ± 34.7 (4)	−289.2 ± 37.5	−367.4[f]
$BiNbO_4$	1073	132.61 ± 8.9 (7)	−41.9 ± 11.1	

[a] Data from the present work. The uncertainty is two standard deviations of the mean (95% confidence level), the number in parentheses is the number of experiments performed.

[b] The experimental data from the present work. The uncertainty was calculated according to the error propagation law.

[c] From Ref. [5].

[d] From Ref. [6].

[e] From Ref. [7].

[f] From Ref. [11], the uncertainty is not quoted.

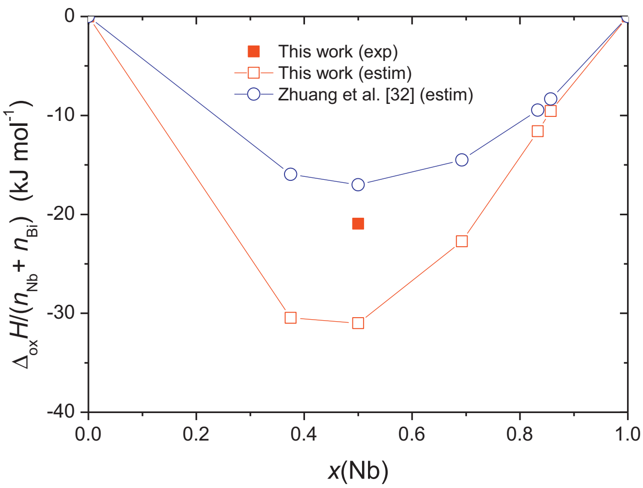

Fig. 3. Values of enthalpy of formation of the mixed oxides from constituent binary oxides in the Bi_2O_3–Nb_2O_5 system (lines serve only as a guide for the eyes).

The obtained data were included in a thermodynamic database FeRAM [35] compatible with the FactSage software [36], which makes it possible to calculate various phase diagrams for the CaO–SrO–Bi_2O_3–Nb_2O_5–Ta_2O_5 system.

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