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Short communication

Thermochemical investigations of bismuth oxide doped by yttrium

N.I. Matskevich[a,*], M.V. Chuprova[a], R. Punn[b], C. Greaves[b]

[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk 630090, Russia*
[b] *School of Chemistry, University of Birmingham, Birmingham B15 2TT, United Kingdom*

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Abstract

The enthalpy of mixing of bismuth oxide and yttrium oxide to form $Bi_{1.5}Y_{0.5}O_3$ has been determined by solution calorimetry by combining the solution enthalpies of Bi_2O_3, Y_2O_3, $Bi_{1.5}Y_{0.5}O_3$ in 2 M HCl at 323.15 K. For the reaction $0.75Bi_2O_3(s) + 0.25Y_2O_3(s) = Bi_{1.5}Y_{0.5}O_3(s)$, $\Delta_{ox}H = -77.1 \pm 2.5$ kJ/mol. $Bi_{1.5}Y_{0.5}O_3$ is stable with respect to decomposition to binary oxides and reaction with CO_2.

Keywords: Bismuth oxide; Yttrium; Enthalpy of mixing; Calorimetry

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1. Introduction

Compounds with the δ-Bi_2O_3 structure stabilized by a variety of elements can exhibit very high oxide ion conductivity and electrocatalytic activity at temperatures below 800 K [1–5]. Moreover, these phases have lower synthesis temperatures than stabilized zirconia phases.

The thermodynamic stabilities of these phases are not well understood so detailed studies of the ternary Bi–RE–O systems are interesting and important to underpin further investigations. The thermodynamics of the Bi–Y–O systems have been little studied. Author of paper [4] devoted to phase equilibria in the system Bi_2O_3–Y_2O_3 reports that the stabilization of the δ-Bi_2O_3 phase with Y_2O_3 is thermodynamically impossible. It is contradicting to results of paper [5] that stabilization of δ-phase at low temperatures is effective. There are no any thermodynamic values for compounds in the Bi–Y–O system both in paper [4] and in investigation [5]. Thermodynamic properties linked to structural characteristics have been used to develop systematic structure–stability relationships in other classes of ternary oxides such as perovskites, spinels, etc.

This initial study focuses on the Bi–Y–O system for obtaining preliminary thermodynamic data on δ-Bi_2O_3 phases, and to understand more completely the stability problems. We have investigated thermochemistry of $Bi_{1.5}Y_{0.5}O_3$, which has the highest oxide ion conductivity in the Bi_2O_3–Y_2O_3 system.

2. Experimental

2.1. Preparation and characterization of samples

$Bi_{1.5}Y_{0.5}O_3$ was synthesised by heating a stoichiometric (Bi_2O_3:Y_2O_3 = 34.95:5.64) and intimate mixture of Bi_2O_3 and Y_2O_3 at 1073 K in air for two periods of 12 h with an intermediate grinding of the sample. The product was shown to be single phase with the δ-Bi_2O_3 structure by X-ray powder diffraction (Siemens D5000, Cu Kα_1, primary beam Ge monochromator, position sensitive detector, transmission geometry). The content of bismuth and yttrium was determined by the spectrophotometry [6]. It was calculated for $Bi_{1.5}Y_{0.5}O_3$: Bi, 77.22; Y, 10.95. Found: Bi, 77.09 ± 0.31; Y, 10.91 ± 0.06. The stoichiometric coefficient of oxygen was determined by iodometric titration with accuracy better than ±0.03 [6]. According to paper [7] all bismuth ions in $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ ($0.10 < x < 0.43$) exist as Bi^{3+}. Our investigation confirms these data [7].

2.2. Investigation method

Solution calorimetry was performed in calorimeter earlier described together with the calorimetric procedure [8]. The calorimeter was calibrated by dissolution of KCl at 298.15 K, and the enthalpy obtained (17.529 ± 0.009 kJ/mol) was in a good

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[*] Corresponding author. Tel.: +7 3833 306449; fax: +7 3833 309489.
E-mail address: nata@che.nsk.su (N.I. Matskevich).

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agreement with literature data (17.524 ± 0.007 kJ/mol) [9]. Two molar of HCl was used to measure solution enthalpies for Bi_2O_3, Y_2O_3, and $Bi_{1.5}Y_{0.5}O_3$ at 323.15 K. A thermochemical cycle was constructed in such a way as to allow comparison of the enthalpies of solution of a mixture of Bi_2O_3 and Y_2O_3 with that corresponding to $Bi_{1.5}Y_{0.5}O_3$. The calorimetric reactions are:

$$0.75Bi_2O_3(s) + \text{solution I} = \text{solution II} \quad 0.75\Delta_{sol}H_1^\circ \tag{1}$$

$$0.25Y_2O_3(s) + \text{solution II} = \text{solution III} \quad 0.25\Delta_{sol}H_2^\circ \tag{2}$$

$$Bi_{1.5}Y_{0.5}O_3(s) + \text{solution I} = \text{solution III} \quad \Delta_{sol}H_3^\circ \tag{3}$$

$$0.75Bi_2O_3(s) + 0.25Y_2O_3(s) = Bi_{1.5}Y_{0.5}O_3(s) \quad \Delta_{ox}H_4^\circ \tag{4}$$

where $\Delta_{ox}H_4^\circ = 0.75\Delta_{sol}H_1^\circ + 0.25\Delta_{sol}H_2^\circ - \Delta_{sol}H_3^\circ$; solution I is 2 M HCl.

3. Results

The measured enthalpies of solution of $Bi_{1.5}Y_{0.5}O_3$, Bi_2O_3 and Y_2O_3 were determined as: −104.4 ± 1.9 ($n = 5$) kJ/mol ($Bi_{1.5}Y_{0.5}O_3$), −114.4 ± 2.1 ($n = 5$) kJ/mol (Bi_2O_3), −382.7 ± 1.8 ($n = 6$) kJ/mol (Y_2O_3). Errors are the 95% confidence interval. Solution enthalpy of Y_2O_3 is in a good agreement with literature data [10].

Combining reactions (1)–(3), we obtain:

$$0.75Bi_2O_3 + 0.25Y_2O_3 = Bi_{1.5}Y_{0.5}O_3 + \Delta_{ox}H^\circ$$

where $\Delta_{ox}H^\circ = 0.75\Delta_{sol}H_1^\circ + 0.25\Delta_{sol}H_2^\circ - \Delta_{sol}H_3^\circ = -77.1 \pm 2.5$ kJ/mol.

The results indicate that $Bi_{1.5}Y_{0.5}O_3$ is stable at room temperature with respect to decomposition to the constituent binary oxides. The negative values of the heat of mixing of oxide solid solutions were observed by us [8] in the system Sm–Ba–Cu–O. Here, situation is the same. It is also necessary to note that the phase $Bi_{1.5}Y_{0.5}O_3$ can be not the most stable one for this stoichiometry at 298 K. According to paper [4] a number of low-temperature stable intermediate phases with variable stoichiometry exist. This is our further work to study stability of $Bi_{1.5}Y_{0.5}O_3$ with respect to decomposition to other Bi–Y–O phases.

Information about phase diagram of Bi_2O_3–Y_2O_3 in the temperature range 873–1423 K is given in Ref. [4] where it is suggested that the cubic structure (δ-Bi_2O_3) is metastable at low temperatures and the thermodynamically stable form is hexagonal. Isomorphous phases were identified in the systems Bi_2O_3–Ln_2O_3 (Ln = La, Pr–Eu) as well as Bi_2O_3–MO (M = Ca, Sr and Ba) [11,12]. There are thermodynamic data only for $BiBaO_3$ [13].

The transition from the hexagonal to the high temperature modification occurs at 993 K. We have no data to check the thermodynamics of this transition in $Bi_{1.5}Y_{0.5}O_3$. As it was discovered for $Bi_{1.75}Tm_{0.25}O_3$ [14], this phase was decomposed at high pressure and a temperature of 1023 K.

We may assume that $Bi_{2-x}Y_xO_3$ solid solution is stable with respect to reaction with oxygen at normal conditions. However, it is useful to consider reaction with CO_2 because many similar complex oxides undergo such reactions. For example, phases such as $SrCeO_3$, $BaCeO_3$, $YBa_2Cu_3O_y$ are thermodynamically unstable with respect to reaction with CO_2 [15–17]

To understand if $Bi_{1.5}Y_{0.5}O_3$ reacts with carbon dioxide, we considered the following reaction:

$$Bi_{1.5}Y_{0.5}O_3 + 3CO_2 = 0.75Bi_2(CO_3)_3 + 0.25Y_2(CO_3)_3 \tag{5}$$

The possibility of interaction was estimated by using formation enthalpies of $Bi_2(CO_3)_3$ (−1692.8 ± 4.2 kJ/mol) and $Y_2(CO_3)_3$ (−3301.6 ± 6.3 kJ/mol), formation enthalpies of Bi_2O_3 (−577.6 ± 4.2 kJ/mol), Y_2O_3 (−1904.8 ± 4.2 kJ/mol), CO_2 (−393.51 ± 0.05 kJ/mol) taken from [18]. The calculated heat of reaction (5) was +72.0 ± 6.0 kJ/mol, which indicates that the compound is stable with respect to interaction with CO_2. This is very unusual and highlights the potential applications of such materials.

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