Note

Formation enthalpy, thermodynamic stability, lattice energy of (Er,Co)-doped Bi$_2$O$_3$

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A R T I C L E   I N F O

A B S T R A C T

Solution calorimetry, using 1 mol dm^{-3} HCl as a solvent, has been used to study for the first time the thermochemistry of Bi$_{2.67}$Er$_{0.33}$CoO$_{5.83}$. For the first time, the standard formation enthalpy of the phase has been determined as following: $\Delta_f H^o$(Bi$_{2.67}$Er$_{0.33}$CoO$_{5.83}$, s, 298.15 K) = −1406.9 ± 8.6 kJ mol^{-1}. The thermodynamic stability at room temperature has been assessed. The results show that investigated phase is thermodynamically stable with respect to decomposition to the constituent binary oxides. It is important to establish thermodynamic stability for solving problem of Bi$_2$O$_3$ stabilization. It is shown that the lattice energies for Bi$_{2.67}$Er$_{0.33}$CoO$_{5.83}$ calculated on the basis of Born-Haber cycle and Kapustinskii rule are in a good agreement. For the first time, we measured the magnetic characteristics of Bi$_{2.67}$Er$_{0.33}$CoO$_{5.83}$ and established that the Bi$_{2.67}$Er$_{0.33}$CoO$_{5.83}$ phase has paramagnetic properties.

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1. Introduction

Compounds on the basis of bismuth oxides are widely used for gas monitoring and combustion control, in metallurgy, petrology, chemical kinetics, in solid state electrolyte fuel cells, etc. [1–10]. The most commonly used electrolyte material is yttria-stabilized zirconia (YSZ) with a high operating temperature near 1300 K which has a low corrosion. However, as was established in a number of papers the conductivity of Bi$_2$O$_3$ can be two orders of magnitude higher than that of yttria-stabilized zirconia at the same temperatures. The delta form of bismuth oxide shows the highest value of the conductivity. The δ-Bi$_2$O$_3$ phase is stable only in the temperature range from 1000 K to its melting temperature of 1100 K. A lot of papers are devoted to stabilization of δ-Bi$_2$O$_3$. However, δ-Bi$_2$O$_3$ can be stabilized by dopants which include iso-valent or aviovalent cations such as rare earth elements, tungsten, molybdenum and others [11–15]. Unfortunately, the conductivity is reduced by substituting dopants. New materials with high conductivity were synthesized by doubly doping Bi$_2$O$_3$ with rhenium and a rare earth cation [1,3,12,16–17]. The phases obtained [1,3,12,16–17] are related to cubic δ-Bi$_2$O$_3$ but have low-temperature oxide ion conductivities that are significantly higher than previously reported for δ-Bi$_2$O$_3$ phases and comparable to those of Bi$_4$V$_{2-x}$M$_x$O$_{11-\delta}$ (M = Cu, Zn, Ni etc.) materials (the BIME-VOX family).

It is known that the delta form of bismuth oxide has a fluorite structure where bismuth has tetrahedral environment. Authors [18] synthesized phase Bi$_3$ReO$_8$. Compound of Bi$_3$ReO$_8$ contains ReO$_4$ tetrahedral in a distorted fluorite structure. This structure is unique, since the rare-earth rhenium oxides Ln$_3$ReO$_8$ contain the Re^{+7} ions in octahedral coordination.

Since rhenium is expensive element we decided to replace rhenium by cobalt. Cobalt also has a tetrahedral oxygen environment in some compounds. We decided to synthesize phase Bi$_3$CoO$_x$ and to add 10% of the rare earth element as in papers [16,17]. It was interesting to understand whether this phase is stable or not at room temperature. It is very important to study stability for practical application.

In the present study we measured the dissolution enthalpy, calculated enthalpy of formation and thermodynamic stability of the Bi$_{2.67}$Er$_{0.33}$CoO$_x$ phase. In addition, we calculated the lattice energy by two ways according to the Kapustinskii rule and compared this value with the lattice enthalpy calculated by the Born-Haber cycle using the experimental data obtained by us. In addition, we measured the magnetic properties of Bi$_{2.67}$Er$_{0.33}$CoO$_x$ in the temperature range of 2–300 K.

In future we plan to investigate thermochemical properties of some other compounds with general formula Bi$_{3-x}$R$_x$CoO$_y$ (R – rare earth elements) and to find correlation "thermodynamic properties – structural characteristics". It is very important to find correlation

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between thermochemical data and structural parameters [19]. It will give possibility to predict the thermodynamic properties of uninvestigated compounds.
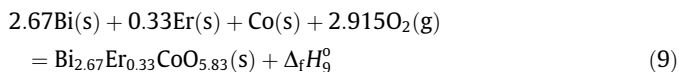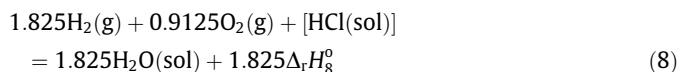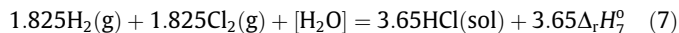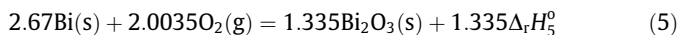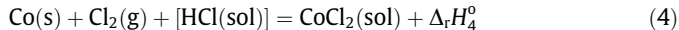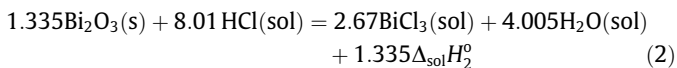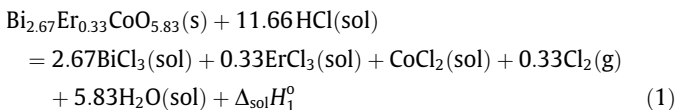
2. Experimental part

2.1. Synthesis of compound

The compound with composition $Bi_{2.67}Er_{0.33}CoO_{5.83}$ was synthesized from bismuth oxide (Bi_2O_3), erbium oxide (Er_2O_3) and cobalt (II, III) oxide (Co_3O_4). Synthesis was performed by solid state reaction. Synthesis was performed according to the following process: $1.335\ Bi_2O_3 + 0.165\ Er_2O_3 + 0.333Co_3O_4 \rightarrow Bi_{2.67}Er_{0.33}CoO_{5.83}$. The following reagents were used for preparation: Bi_2O_3 (>99.99%, Aldrich, ABCR), Co_3O_4 (>99.7%, Alfa Aesar GmbH), Er_2O_3 (>99.9%, Aldrich Chemical Company Inc.). Before synthesis the erbium oxide was treated at 1100 K. The temperature of synthesis was above 973 K. The samples $Bi_{2.67}Er_{0.33}CoO_{5.83}$ were prepared by the following way. Initial reagents were mixed in an agate mortar and ground for about 70 h with 10 intermediate regrounds in a planetary ball mill (FRITSCH pulverisette 5). The rate was varied from 50 up to 180 rpm. Then the mixtures were pressed (pellet Ø 14 mm, press Herzog (5.5 t)), placed in a furnace (Carbolite) and heat treated. The phase purity was analyzed by powder X-ray diffraction (STADI-P, Stoe diffractometer, Germany, Mo radiation). X-ray analysis showed that phases were pure. Phases were indexed in monoclinic structure (P 2/m space group) [20]. Cell parameters for $Bi_{2.67}Er_{0.33}CoO_{5.83}$ are a = 0.564390 nm, b = 0.644945 nm, c = 0.392756 nm, β = 109.3332°. Synchrotron analysis performed in the photon energy range 775–800 eV showed that cobalt has valence 2.7+. All compounds (Bi_2O_3, Co_3O_4, Er_2O_3, $Bi_{2.67}Er_{0.33}$-$CoO_{5.83}$) were analyzed with atomic absorption methods (the standard uncertainty is 0.1–0.5%). The results of chemical analysis showed that the $Bi_{2.67}Er_{0.33}CoO_{5.83}$ compound has mass fraction purity more than 99%. The detailed information about employed compounds are presented in Table 1.

2.2. Thermochemical cycle

A thermochemical cycle was constructed in such a way that investigated compound ($Bi_{2.67}Er_{0.33}CoO_{5.83}$) was dissolved in $1\ mol\,dm^{-3}$ HCl. We also dissolved Bi_2O_3 in $1\ mol\,dm^{-3}$ HCl. The calorimetric reactions are:

$$Bi_{2.67}Er_{0.33}CoO_{5.83}(s) + 11.66\,HCl(sol)$$
$$= 2.67BiCl_3(sol) + 0.33ErCl_3(sol) + CoCl_2(sol) + 0.33Cl_2(g)$$
$$+ 5.83H_2O(sol) + \Delta_{sol}H_1^o \tag{1}$$

$$1.335Bi_2O_3(s) + 8.01\,HCl(sol) = 2.67BiCl_3(sol) + 4.005H_2O(sol)$$
$$+ 1.335\Delta_{sol}H_2^o \tag{2}$$

$$0.33ErCl_3(s) + [HCl(sol)] = 0.33ErCl_3(sol) + 0.33\Delta_{sol}H_3^o \tag{3}$$

$$Co(s) + Cl_2(g) + [HCl(sol)] = CoCl_2(sol) + \Delta_r H_4^o \tag{4}$$

$$2.67Bi(s) + 2.0035O_2(g) = 1.335Bi_2O_3(s) + 1.335\Delta_r H_5^o \tag{5}$$

$$0.33Er(s) + 0.495Cl_2(g) = 0.33ErCl_3(s) + 0.33\,\Delta_r H_6^o \tag{6}$$

$$1.825H_2(g) + 1.825Cl_2(g) + [H_2O] = 3.65HCl(sol) + 3.65\Delta_r H_7^o \tag{7}$$

$$1.825H_2(g) + 0.9125O_2(g) + [HCl(sol)]$$
$$= 1.825H_2O(sol) + 1.825\Delta_r H_8^o \tag{8}$$

$$2.67Bi(s) + 0.33Er(s) + Co(s) + 2.915O_2(g)$$
$$= Bi_{2.67}Er_{0.33}CoO_{5.83}(s) + \Delta_f H_9^o \tag{9}$$

Here: $\Delta_f H_9^o$ – standard formation enthalpy of $Bi_{2.67}Er_{0.33}CoO_{5.83}$;

$$\Delta_f H_9^o = -\Delta_r H_1^o + 1.335\Delta_r H_2^o + 0.33\Delta_r H_3^o + \Delta_r H_4^o + 1.335\Delta_r H_5^o$$
$$+ 0.33\Delta_r H_6^o - 3.65\Delta_r H_7^o + 1.825\Delta_r H_8^o$$

This thermochemical cycle allows us to calculate the standard formation enthalpy for $Bi_{2.67}Er_{0.33}CoO_{5.83}$. In the paper we measured the dissolution enthalpy of $Bi_{2.67}Er_{0.33}CoO_{5.83}$, dissolution enthalpies of bismuth oxide and erbium chloride. The weight of $Bi_{2.67}Er_{0.33}CoO_{5.83}$ was about 50 mg.

Solution calorimetry was performed in calorimeter earlier described together with the calorimetric procedure [21,22]. The calorimeter consists of a Dewar vessel placed in a brass glass. The brass glass was closed with a lid, which is arranged by mixer, thermometer, device for breaking and washing ampoules, and a heater for calibration. The temperature of thermometer was controlled by voltmeter (SOLARTRON 7061), which was connected with computer. Calibration was carried out using the calibration block by supplying a stabilized voltage. Voltage and current were measured in each calorimetric experiment by precision voltmeter SOLARTRON 7061. The calorimeter was calibrated by dissolution of potassium chloride at 298.15 K [21,22]. The enthalpy obtained ($17.529 \pm 0.09\ kJ\,mol^{-1}$) was in a good agreement with literature data ($17.524 \pm 0.007\ kJ\,mol^{-1}$) [23].

2.3. Magnetic measurements

The magnetic properties of the samples were studied using a superconducting quantum interference device (Quantum Design MPMS XL). A SQUID (for superconducting quantum interference device) is a very sensitive magnetometer used to measure extremely subtle magnetic fields, based on superconducting loops containing Josephson junctions. This Quantum Design MPMS XL system is equipped with the optional reciprocating sample and low temperature measurement options allowing a nominal sensitivity of $1 \cdot 10^{-11}\ A\cdot m^2$ and measurements from room temperature to 1.9 K. Standard uncertainty for temperature $u(T) = 0.01$ K; relative standard uncertainty for reverse magnetic susceptibility (χ^{-1}): 0.02.

Table 1
Characterization of chemical samples used in this study.

Chemical Name	Chemical Formula	Source	State	Mass Fraction Purity	Analysis Method
Bismuth oxide	Bi_2O_3	Aldrich, ABCR	solid	>0.9999	Atomic absorption
Cobalt (II,III) oxide	Co_3O_4	Alfa Aesar GmbH	solid	>0.997	Atomic absorption
Erbium oxide	Er_2O_3	Aldrich Chemical Company Inc.	solid	>0.999	Atomic absorption
Bismuth-cobalt oxide doped by erbium	$Bi_{2.67}Er_{0.33}CoO_{5.83}$	synthesis	solid	>0.99	Atomic absorption, Synchrotron analysis
Hydrochloric acid	HCl	Mark "Ultrapure"	solution	>0.999	–

The standard uncertainty of atomic absorption method is 0.1–0.5%.