J. Chem. Thermodynamics 127 (2018) 80–85

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Heat capacity of bismuth-cobalt oxide doped by erbium in the temperature range of 193–547 K

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ARTICLE INFO

Article history:
Received 14 April 2018
Received in revised form 12 July 2018
Accepted 22 July 2018
Available online 23 July 2018

ABSTRACT

For the first time the heat capacities of compound $Bi_{12.5}Er_{1.5}CoO_{22.3}$ have been measured in the temperature range of 193–547 K. Differential scanning calorimetry has been used for measurements. The temperature dependence of heat capacity has been well described by a polynomial $C^{o}_{p,m}$ $(T) = 665.46 + 0.82227\,T - 3.9692{\cdot}10^{-4}\,T^2 - 5.3798{\cdot}10^{6}/T^2$. On the basis of smoothed heat capacities the enthalpy and entropy increments have been calculated (T = 193–547 K).

1. Introduction

As known, increasing requirements for modern devices involve the necessity to search new materials with improved characteristics. In particular, there is a problem to decrease the operating temperatures in devices where high temperatures are used. Mixed oxides are promising materials for using in fuel cells, oxygen ceramic generators, etc. [1–5]. Ones of the promising materials with high ionic conductivity are compounds on the basis of bismuth oxide [6–10]. Fluorite structure of δ-Bi_2O_3 provides exceptionally high oxide ion conductivity. But δ-Bi_2O_3 exists only in very narrow temperature interval from 1000 K up to 1100 K (melting point). For successful application it is necessary to stabilize delta form of bismuth oxide up to room temperature. δ-Bi_2O_3 has cubic structure (Space Group Fm-3m) that is very perspective for application for the following reasons. The ionic conductivity can depend on directions but dependence of conductivity from direction in cubic structure is limited.

A lot of papers are devoted to attempts of stabilization of δ-Bi_2O_3 up to room temperature. [11–15]. Bismuth oxide was substituted by rare–earth oxides, and also tungsten, molybdenum, etc. Prof. C. Greaves substituted bismuth oxide by sulphur and rhenium [16,17] and the following new compounds were synthesized: $Bi_{14}O_{20}(SO_4)$, $Bi_{14}ReO_{24.5}$. But the compounds are not good ionic conductors. Presently the new compounds with general formula $Bi_{12.5}R_{1.5}ReO_{24.5}$ (R – rare-earth elements) were prepared where strategy of "co-doping" (doping by two or more elements) by rhenium and rare-earth elements were used [18–22]. The compounds are related to cubic δ-Bi_2O_3 and have high ionic conductivity which comparable to those of BIMEVOX materials [23]. But rhenium is very expensive element. In addition, perrhenates can easily interact with water vapor. Therefore, we attempted to replace rhenium with cobalt. A new compound with general formula $Bi_{12.5}Er_{1.5}CoO_{22.3}$ was prepared by us. The compound has cubic structure of fluorite (space group Fm3m). It is necessary to perform the detail physical and chemical analysis to understand the perspective of the compound application. In particular, it is very important to know the presence or absence of phase transitions under operating conditions of compound.

In the paper we for the first time measured heat capacities of compound $Bi_{12.5}Er_{1.5}CoO_{22.3}$ in the temperature range of 193–547 K. The differential-scanning calorimetry method was used for investigations. In the future, we plan to measure the heat capacity of $Bi_{12.5}R_{1.5}CoO_{22.3}$ compounds where R is a rare-earth element and find the relationship with structural parameters.

Knowledge of relationships "thermodynamic property-structural property –functional property" is very important to understand the nature of properties change of compounds [24].

2. Experimental part

The $Bi_{12.5}Er_{1.5}CoO_{22.3}$ powder was synthesized via a solid state reaction from bismuth oxide (Bi_2O_3), erbium oxide (Er_2O_3), and Co_3O_4. Before synthesis the erbium oxide was treated at 1100 K up to constant weight to avoid possible vapor of water and carbon dioxide.

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

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https://doi.org/10.1016/j.jct.2018.07.022
0021-9614/

(>99.9%, Aldrich Chemical Company Inc.). The sample $Bi_{12.5}Er_{1.5}CoO_{22.3}$ was prepared by the following way. Initial reagents were mixed in an agate mortar and ground for several hours with intermediate reground in a planetary ball mill (FRITSCH pulverisette 5). The mixture was then pressed, placed in a furnace (Carbolite) and heated. Finally, the precursors were calcined at temperature higher than 973 K.

Powder X-ray diffraction (XRD) patterns were recorded using STADI-P, Stoe diffractometer (Germany, $Cu_{K\alpha}$ radiation). X-ray analysis showed that phase was pure. The phase was identified as cubic structure (Space Group Fm-3m). The structure is delta form of bismuth oxide (δ-Bi_2O_3). Lattice parameters were calculated using program FullProf. Lattice parameters: a = 0.551109 ± 0 .000008 nm, V = 0.167383 nm^3. Here the standard uncertainty is presented. Photoemission spectroscopy which was performed in the photon energy range 775–800 eV showed the $Bi_{12.5}Er_{1.5}CoO_{22.3}$ phase included 35% Co^{2+} и 65% Co^{3+}.

All compounds (Bi_2O_3, Co_3O_4, Er_2O_3, and $Bi_{12.5}Er_{1.5}CoO_{22.3}$) were analyzed with atomic absorption methods (the standard uncertainty is 0.1–1%). The results of chemical analysis showed that the $Bi_{12.5}Er_{1.5}CoO_{22.3}$ compound has mass fraction purity more than 99%. The detailed information about employed compounds are presented in Table 1. The results of the chemical analysis for $Bi_{12.5}Er_{1.5}CoO_{22.3}$ allow us to conclude that the phase has the following composition: $Bi_{12.46\pm0.09}Er_{1.49\pm0.02}CoO_{22.12\pm0.12}$.

Heat capacity was measured by comparison method using DSC 204 F1 Phoenix (firm NETZSCH, Germany) in the temperature range of 193–547 K. Al_2O_3 was used as standard. The sample mass for $Bi_{12.5}Er_{1.5}CoO_{22.3}$ was 39.210 mg (molar mass is 3278.86482 g mol^{-1}). The sample mass for Al_2O_3 was 39.460 mg. Six series were performed for measurements of $Bi_{12.5}Er_{1.5}CoO_{22.3}$ heat capacities. Detailed procedure of DSC measurements was described in papers [25,26].

DSC measurements of sample and standard of Al_2O_3 were perform by heat flow measurement method at a constant heating rate of 6 K min^{-1} in aluminum crucible covered with a lid in 25 mL min^{-1} Ar flow. The baseline signal obtained by heating of two empty crucibles was subtracted from the experimental results of samples. Al_2O_3 was used as standard to calculate heat capacity. Temperature calibration was performed by melting of standard samples (C_6H_{12}, Hg, KNO_3, In, Sn, Bi, Pb, Cd, Zn, CsCl). The detailed information about standard samples is presented in Table 1. The heat capacities for Al_2O_3 were attached with documentation for DSC 204 F1 Phoenix [27] and were in a good agreement with data [28].

3. Results and discussion

The measured heat capacity data for $Bi_{12.5}Er_{1.5}CoO_{22.3}$ in the temperature range of 193–547 K are shown in Fig. 1 and are given

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	$Bi_{12.5}Er_{1.5}CoO_{22.3}$	synthesis	solid	>0.99	Atomic absorption. Synchrotron analysis
Mercury, Lead, Tin, Zinc, Indium, Cadmium, Bismuth, Aluminum oxide, Cesium chloride	Hg, Pb, Sn, Zn, In, Cd, Bi, Al_2O_3, CsCl	Netzsch Group	solid	>0.99999	Netzsch Group analysis [27]
Cyclohexane	C_6H_{12}	Netzsch Group	solid	>0.999	Netzsch Group analysis [27]
Potassium nitrate	KNO_3	Netzsch Group	solid	>0.9999	Netzsch Group analysis [27]

The standard uncertainty of atomic absorption method is 0.1–1%.

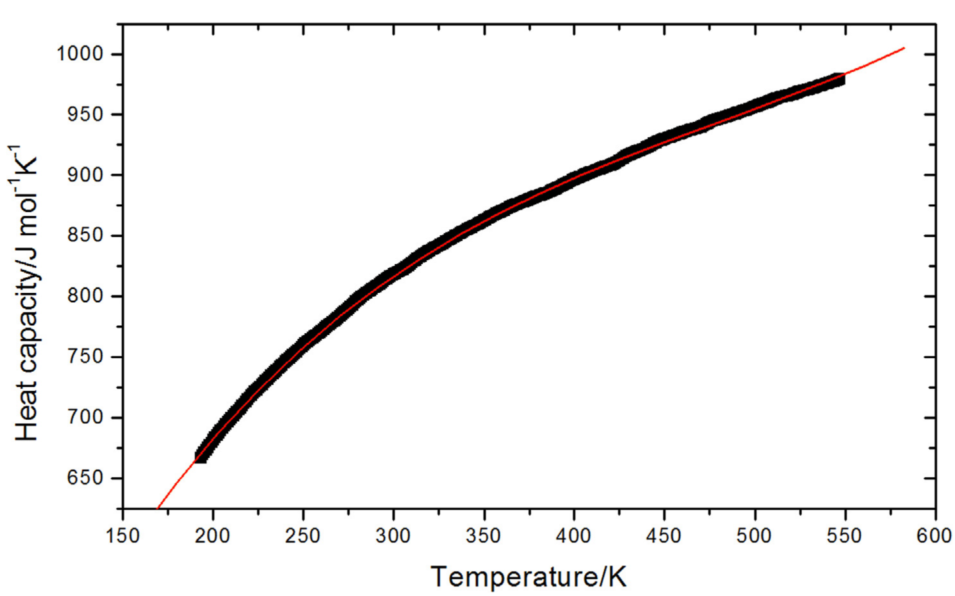

Fig. 1. Heat capacity of $Bi_{12.5}Er_{1.5}CoO_{22.3}$.