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# Thermodynamic functions of bismuth perrhenate doped by neodymium and indium

N.I. Matskevich [a,*], Th. Wolf [b]

[a] Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk 630090, Russia
[b] Karlsruhe Institute of Technology, Institute of Solid State Physics, Karlsruhe D-76344, Germany

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ABSTRACT

For the first time the heat capacities of phase $Bi_{12.5}Nd_{1.4}In_{0.1}ReO_{24.5}$ have been measured in the temperature range of 175–550 K. Differential scanning calorimetry has been used for measurements. The temperature dependence of heat capacity is well described by a polynomial $C^{o}_{p,m}(T) = 542.62 + 1.5107\,T - 1.0402 \cdot 10^{-3}\,T^2 - 2.7875 \cdot 10^{6}/T^2$. On the basis of smoothed heat capacities the enthalpy and entropy increments were calculated ($T$ = 175–550 K).

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## 1. Introduction

At present all over the world the search for promising materials to be used in devices operating at high temperatures, in particular in fuel cells, oxygen ceramic generators etc. is carried out intensively. Mixed oxides on the basis of rare-earth elements are promising materials for these purposes [1–10]. The δ-form of $Bi_2O_3$ possesses one of the highest ionic conductivities, 1 S cm$^{-1}$ at 1023 K, which is 2 orders of magnitude larger than the value of *Y*-stabilized zirconia. The disadvantage of δ-bismuth oxide is its very narrow stability range, only 1000–1100 K.

A lot of scientific papers were devoted to the problem of stabilizing bismuth oxide to room temperature. In first experiments to stabilize δ-$Bi_2O_3$ using rare earth elements a satisfactory solution was not found. Substitution of VI group elements like sulfur, tungsten, and others led to a steep decrease of the ionic conductivity.

About 10 years ago new compounds with the general formula $Bi_{12.5}Ln_{1.5}ReO_{24.5}$ (Ln – lanthanides) were synthesized [11–15]. Measurements of the conductivity showed that the compounds were well-conductive and their conductivity was comparable with bismuth compounds doped by vanadium and copper. Bismuth compounds doped by neodymium and lanthanum possessed the highest conductivity. To learn more about the perspectives of these materials further detailed studies are necessary.

At the same time it was shown in papers [16–18] that adding indium to mixed oxides leads to an increasing stability of the compounds. Therefore we synthesized new compounds with the general formula $Bi_{12.5}Nd_{1.4}In_{0.1}ReO_{24.5}$.

In this paper we present for the first time heat capacities of bismuth perrhenate doped by neodymium and indium ($Bi_{12.4}Nd_{1.4}In_{0.1}ReO_{24.5}$). Heat capacities were measured by differential scanning calorimetry in the temperature range of 175–550 K. In future we plan to measure thermodynamic functions for compounds $Bi_{12.5}(Ln,In)_{1.5}ReO_{24.5}$ with different lanthanides to construct dependence "thermodynamic property-structural property". Knowledge of these relationships is very important to understand the nature of properties change [19].

## 2. Experimental part

We prepared $Bi_{12.5}Nd_{1.4}In_{0.1}ReO_{24.5}$ phase by solid state reaction. The initial reagents for synthesis were: $Bi_2O_3$, $NH_4ReO_4$, $Nd_2O_3$, $In_2O_3$. Detailed information about precursors is presented in Table 1. $Nd_2O_3$ and $In_2O_3$ were treated before synthesis at high temperatures up to constant weight. Starting reagents were mixed in an agate mortar and ground for about several hours with several intermediate reground in a planetary mill. Then the mixture was pressed and heated in air at temperature higher than 900 K. The procedures of reground and heating were repeated until $Bi_{12.5}Nd_{1.4}In_{0.1}ReO_{24.5}$ became a phase pure ceramic.

The phase purity was analyzed with X-ray diffractometer (STADI-P, Stoe diffractometer, Germany, Cu $K_\alpha$ radiation). XRD pattern is presented in Fig. 1. X-ray diffraction indicated that the sample was single phase and that δ-$Bi_2O_3$ structure had been stabilized to room temperature. Using the FullProf program we determined

* Corresponding author.
*E-mail address:* nata.matskevich@yandex.ru (N.I. Matskevich).

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**Table 1**
Purity of initial compounds for synthesis.

| Compounds | Content of compounds (%) and method | Production company |
|---|---|---|
| $Bi_2O_3$ | 99.999%, Spectrophotometric method | ABCR, Karlsruhe |
| $Nd_2O_3$ | 99.9%, Spectrophotometric method | Reacton, Johnson Matthey Company |
| $In_2O_3$ | 99.99%, Spectrophotometric method | Reacton, Johnson Matthey Company |
| $NH_4ReO_4$ | >99%, Fluorescence analysis | Alfa Aesar, Johnson Matthey Company |

the lattice parameters and space group. Space group was Fm-3m (cubic structure). We determined the lattice parameter for $Bi_{12.5}Nd_{1.4}In_{0.1}ReO_{24.5}$ as $a = 0.56116\ (16)$ nm.

Sample $Bi_{12.5}Nd_{1.4}In_{0.1}ReO_{24.5}$ was characterized by chemical analysis as well. For the analysis of Bi, Nd, In a spectrophotometric method was used. The ARL ADVANT'XP sequential X-ray Fluorescence Spectrometer was used to analyze Re content. The oxygen content was determined by reducing melting method. Detailed information is presented in Table 2. According to the results of the analysis, the sample $Bi_{12.5}Nd_{1.4}In_{0.1}ReO_{24.5}$ was found to be single phase with an accuracy of about 0.1%.

Differential scanning calorimetry was used to measure heat capacities of $Bi_{12.5}Nd_{1.4}In_{0.1}ReO_{24.5}$ in the temperature range of 175–550 K. We used calorimeter of Netzsch DSC 204 F1 Phoenix.

DSC measurements of the sample and standard of $Al_2O_3$ were performed by the heat flow measurement method at a constant heating rate of 6 K $min^{-1}$ in an aluminum crucible in an Ar flow of 25 ml $min^{-1}$. The sample mass for $Bi_{12.5}Nd_{1.4}In_{0.1}ReO_{24.5}$ was 24.62 mg (molar mass is 3403.8653 g $mol^{-1}$). The mass of $Al_2O_3$ was 24.78 mg. The baseline signal obtained by heating 2 empty crucibles was subtracted from the experimental results of samples. $Al_2O_3$ was used as standard to calculate heat capacity. Temperature scale graduation was performed by determination of the melting points of standard samples ($C_6H_{12}$, Hg, $KNO_3$, In, Sn, Bi, Pb, Cd, Zn, CsCl).

**Table 2**
Results of chemical analysis of $Bi_{12.5}Nd_{1.4}In_{0.1}ReO_{24.5}$.

| Compounds | Content of elements (experimental data (%)) and methods of analysis | Content of elements (calculated data (%)) | Impurities and method of analysis |
|---|---|---|---|
| $Bi_{12.5}Nd_{1.4}In_{0.1}ReO_{24.5}$ | Bi, 76.68 ± 0.07; Nd, 5.99 ± 0.05; In, 0.31 ± 0.03; Re, 5.49 ± 0.04; O, 11.48 ± 0.05 | Bi, 76.74; Nd, 5.93; In, 0.34; Re, 5.47; O, 11.52 | Ho, Dy, Eu, Yb, La, Tm, Er, Pr, Sm, Ce, Te, Ca, Mg, Mn, Pb, Ag are presented at the level $10^{-3}$–$10^{-4}$ at.% |
| | Bi, Nd, In – spectrophotometric method; Re – X-ray fluorescence analysis; O – reducing melting method | | Mass spectrometry method |

Here the expanded uncertainty with 0.95 level of confidence is provided.

## 3. Results and discussion

We measured 169 experimental points for heat capacities of $Bi_{12.5}Nd_{1.4}In_{0.1}ReO_{24.5}$ in the temperature range of 175–550 K (Table 3). The measurements of heat capacity showed that the curve of the heat capacity is smooth (Fig. 2) in the temperature interval. The relative standard uncertainty for the heat capacities $u_r(C_{p,m}) = 0.015$.

To calculate the smoothed values of heat capacities as well as the increment enthalpy and entropy we approximated our experimental data on the heat capacity by different polynomials.

As it was shown our data can be well described by a polynomial $C^{o}_{p,m}(T) = 542.62 + 1.5107\,T - 1.0402 \cdot 10^{-3}\,T^2 - 2.7875 \cdot 10^{6}/T^2$ (sum of squares of discrepancy is 1094.1). Preliminary the data were approximated by polynomials: (1) $C^{o}_{p,m}(T) = 360.55 + 2.2328\,T - 1.7996 \cdot 10^{-3}\,T^2$ (sum of squares of discrepancy is 1938.7);

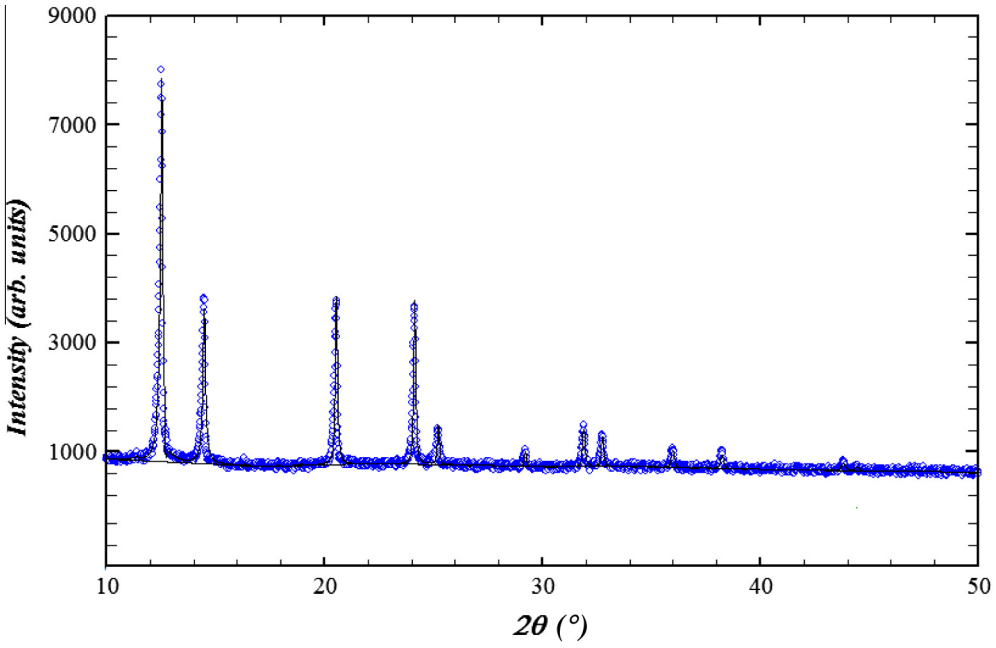


**Fig. 1.** Experimental and calculated patterns for $Bi_{12.5}Nd_{1.4}In_{0.1}ReO_{24.5}$.

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