

New phases $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$: Thermodynamics and influence of dopant size on lattice energy (Ln – lanthanide)

Matskevich, N.i.; Wolf, Th.; Greaves, C.; Adelman, P.; Vyazovkin, I.v.; Matskevich, M.yu.

DOI:

[10.1016/j.jct.2015.07.036](https://doi.org/10.1016/j.jct.2015.07.036)

License:

Creative Commons: Attribution-NonCommercial-NoDerivs (CC BY-NC-ND)

Document Version

Peer reviewed version

Citation for published version (Harvard):

Matskevich, NI, Wolf, T, Greaves, C, Adelman, P, Vyazovkin, IV & Matskevich, MY 2015, 'New phases $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$: Thermodynamics and influence of dopant size on lattice energy (Ln – lanthanide)', *The Journal of Chemical Thermodynamics*, vol. 91, pp. 234-239. <https://doi.org/10.1016/j.jct.2015.07.036>

[Link to publication on Research at Birmingham portal](#)

Publisher Rights Statement:

After an embargo period, this document is subject to the terms of a Creative Commons Non-Commercial No Derivatives license.

Checked October 2015

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Accepted Manuscript

New phases $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$: thermodynamics and influence of dopant size on lattice energy (Ln – lanthanide)

N.I. Matskevich, Th. Wolf, C. Greaves, P. Adelman, I.V. Vyazovkin, M.Yu. Matskevich

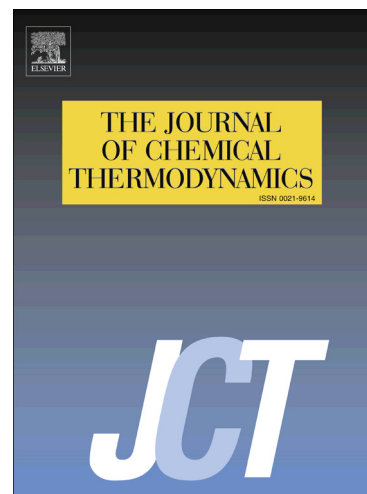
PII: S0021-9614(15)00260-8
DOI: <http://dx.doi.org/10.1016/j.jct.2015.07.036>
Reference: YJCHT 4333

To appear in: *J. Chem. Thermodynamics*

Received Date: 4 February 2015
Revised Date: 24 July 2015
Accepted Date: 25 July 2015

Please cite this article as: N.I. Matskevich, Th. Wolf, C. Greaves, P. Adelman, I.V. Vyazovkin, M.Yu. Matskevich, New phases $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$: thermodynamics and influence of dopant size on lattice energy (Ln – lanthanide), *J. Chem. Thermodynamics* (2015), doi: <http://dx.doi.org/10.1016/j.jct.2015.07.036>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



New phases $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$: thermodynamics and influence of dopant size on lattice energy (Ln – lanthanide)

N.I. Matskevich^{1,2*}, Th. Wolf², C. Greaves³, P. Adelman², I.V. Vyazovkin¹, M.Yu. Matskevich¹

¹Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, 630090, Russia

²Karlsruhe Institute of Technology, Institute of Solid State Physics, Karlsruhe, D-76344, Germany

³Birmingham University, School of Chemistry, Birmingham, B15 2TT, United Kingdom

CORRESPONDING AUTHOR: Phone: +7 913 7489299; Fax: +49 721608 24624; E-mail: nata.matskevich@yandex.ru

Abstract

On the basis of experimental data the lattice energies for the new compounds $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$ have been calculated using a Born-Haber cycle. It has been discovered that there is a linear dependence between lattice energies and inverse radii of lanthanide ions. It has been established that calculated and experimental lattice energies for $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$ are in a good agreement. For the first time the compound $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$ has been synthesized, its lattice parameters have been determined and its thermochemical characteristics have been measured. The determined unit cell parameters of $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$ suggest that the structure is of cubic type, space group $\text{Fm}\bar{3}\text{m}$, $a = 0.55590$ (6) nm.

Key words: Bismuth oxide, Thermodynamic Stability, Size effect of rare-earth radii

Introduction

Compounds on the basis of bismuth oxides possess a wide set of unique properties and they can be quite perspective in various areas [1-19]. So, they can be used as ecological inorganic pigments applied in paints, plastics, ceramics and etc. The majority of inorganic pigments include toxic elements such as Cd, Hg, Sb, Se. Pigments on the basis of bismuth oxides do not contain any toxic elements and therefore seem to be more promising. They provide colors from yellow to orange.

The delta-form of bismuth oxide ($\delta\text{-Bi}_2\text{O}_3$) is a perspective material for applications in electrochemical devices such as high-purity oxygen generators and electrochemical sensors. δ -

Bi_2O_3 shows conductivity two orders of magnitude higher than zirconia-based electrolytes such as yttrium stabilized ZrO_2 (YSZ) at relatively lower temperatures. $\delta\text{-Bi}_2\text{O}_3$ has a cubic fluorite structure. The δ -phase Bi_2O_3 is only stable over a narrow temperature range (1100 - 1200 K), so much work has been carried out to stabilize this phase to room temperature through forming solid solutions with other oxides. $\delta\text{-Bi}_2\text{O}_3$ structure has been stabilized by isovalent or nonisovalent cations.

It was supposed in papers [1, 4, 20] that substituting small amounts of Bi in Bi_2O_3 by tetrahedrally coordinated M(VI) or M(VII) ions could lead to stable superstructures of a cubic fluorite unit cell. This is based on the existence of a stable $\text{Bi}_{12}\text{SiO}_{20}$ compound where SiO_4^{4-} ion has a tetrahedral coordination. There were attempts to stabilize Bi_2O_3 by tetrahedral ions ReO_4^- and SO_4^{2-} [4, 20]. A new bismuth oxide sulfate with the composition $\text{Bi}_{14}\text{O}_{20}(\text{SO}_4)$ has been synthesized by a thermal treatment of an intimate mixture of Bi_2O_3 and $(\text{NH}_4)_2\text{SO}_4$ in the mole ratio 1:0.14 [20]. $\text{Bi}_{14}\text{O}_{20}(\text{SO}_4)$ has a non-cubic fluorite structure with a body-centered tetragonal unit cell ($I4/m$; $a = 0.8664(1)$ nm, $c = 1.7282(2)$ nm). A new phase, $\text{Bi}_{28}\text{Re}_2\text{O}_{49}$, has been synthesized and characterized [4]. It has a tetragonal structure, space group $I4/m$, $a = 0.87216(1)$ nm, $c = 1.74177(2)$ nm. The conductivities of $\text{Bi}_{14}\text{O}_{20}(\text{SO}_4)$ and $\text{Bi}_{28}\text{Re}_2\text{O}_{49}$ were determined in the range of 700-900 K [4, 20]. It has been shown that the observed conductivities are lower than the conductivities of Y-stabilized δ - Bi_2O_3 phase, $(\text{Bi}_{0.75}\text{Y}_{0.25})_2\text{O}_3$ or Bi_3YO_6 .

A new perspective family with the composition of $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Er}, \text{Eu}$) has been prepared [1]. These compounds exhibit exceptionally high oxide ion conductivities at low temperatures. Their conductivities approach that of the best low-temperature conductor, the 2-dimensional BICUVOX ($\text{Bi}_2\text{V}_{0.9}\text{Cu}_{0.1}\text{O}_{5.35}$). The structure of $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$ is similar to $\delta\text{-Bi}_2\text{O}_3$.

As the practical application of ionic conductors has grown, great efforts have been made to gain a unified understanding of their physical and critical properties, their phase equilibria, and their compatibility with other materials and the environment. An important characteristic of materials is their thermodynamic stability. Thermodynamic investigations of bismuth oxide compounds with a general formula of $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Gd}, \text{Dy}, \text{Lu}$) were performed [9, 10, 21]. The thermodynamic stability with respect to binary oxides was studied. Since it is difficult to get experimental data for all lanthanide compounds, it is very important to find a correlation [22] between thermochemical data and structural parameters on the basis of some experimental data, and then to predict the thermodynamic properties for all lanthanides.

The aim of our paper is to determine whether lattice energies for $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Lu}$) depend on $1/r_{\text{Ln}}$ (r_{Ln} – ionic radius of lanthanide) and then to

check this dependence. For checking the dependence the lattice energy of an unknown compound $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$ will be estimated using a constructed dependence. After that a new compound $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$ will be prepared, its lattice parameters and thermodynamic properties will be determined, and experimental values will be compared with the estimated ones. Also, the thermodynamic properties of $\text{Bi}_{14}\text{ReO}_{24.5}$ and reactions with its participation will be studied.

Experimental

In the past a series of new compounds were prepared with the general formula of $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$ for $\text{Ln} = \text{La, Nd, Sm, Gd, Dy, Ho, Lu}$ [9, 10, 17, 21, 23]. The compounds were synthesized by solid state reactions from mixtures of Bi_2O_3 , NH_4ReO_4 , and Ln_2O_3 or Bi_2O_3 , Re_2O_7 , and Ln_2O_3 . The powders were mixed in an agate mill and then pressed in pellets and treated at 1100 K. The analysis of the samples obtained was performed by X-ray fluorescence analysis, chemical analysis, X-ray and neutron diffraction. Thermochemical data were measured by solution calorimetry in a calorimeter with an isothermal jacket.

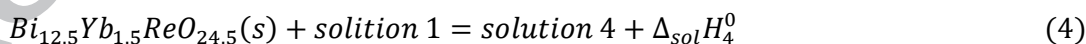
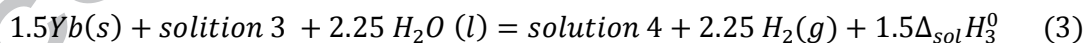
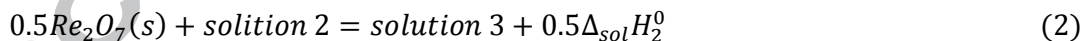
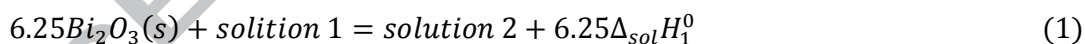
This paper presents a new polycrystalline compound, $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$ prepared by a conventional solid state technique according to the reaction: $6.25\text{Bi}_2\text{O}_3 + \text{NH}_4\text{ReO}_4 + 0.75\text{Yb}_2\text{O}_3 = \text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5} + \text{NH}_3 + 0.5\text{H}_2\text{O}$. Further on the compound $\text{Bi}_{14}\text{ReO}_{24.5}$ was synthesized. The following reagents were used for preparation: Bi_2O_3 (99.999%, ABCR), NH_4ReO_4 (>99%, Alfa Aesar, Johnson Matthey Company), Yb_2O_3 (99.99%, ChemPur). Yb_2O_3 was treated before synthesis at 1073 K up to constant weight. 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 250 rpm. Then the mixtures were pressed (pellet 14 mm, press Herzog (5.5t)), placed in furnace (Carbolite) and reacted in air at 1073 K for 80 h. The reaction completion was monitored by X-ray powder diffraction. Prolonged heating at high temperatures was avoided in order to minimize Bi_2O_3 volatilization. The phase purity was analyzed by powder X-ray diffraction (STADI-P, Stoe diffractometer, Germany, $\text{Cu K}\alpha_1$ radiation). X-ray analysis showed that samples were a single phase.

All compounds were characterized by chemical analysis [9, 13]. Analytical results are presented in Table 1. For the analysis of Bi, Yb a spectrophotometric method (spectrophotometer SF-46) 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. According to results of analysis the investigated compounds ($\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$ and $\text{Bi}_{14}\text{ReO}_{24.5}$) correspond to above-mentioned formulas with accuracy < 1%.

Solution calorimetry method was chosen to investigate thermodynamic properties. The calorimeter construction and the calorimetric procedure were described earlier [24-26]. The calorimeter consists of a Dewar vessel placed in a brass glass. It was closed by a brass lid with a teflon lining. A platinum thermometer, heater, mixer, and a device to break and wash ampules were placed on the brass lid. The thermometer sensitivity was 1×10^{-4} K. The thermometer resistivity was measured by a voltmeter (Solartron 7061). The calorimeter was placed in a thermostat with constant temperature 298.15 K and calibrated by KCl dissolution at 298.15 K. The potassium chloride used in this work was marked as “High purity 16-5”. The certificate included the information: “The sample consists of highly purified potassium chloride, > 99.9%”. The sample was recrystallized two times from distilled water and dried at $T = 773$ K. The mass fraction of potassium was determined by tetraphenylborate method. The method is based on potassium sedimentation by sodium tetraphenylborate with subsequent drying and weighing of obtained potassium tetraphenylborate. Results of analysis are presented in Table 1. The enthalpy obtained (17.529 ± 0.009 kJ mol⁻¹, the molality of the final solution was 0.028 mol kg⁻¹, $T = 298.15$ K) was in a good agreement with literature data (17.524 ± 0.007 kJ mol⁻¹) [27].

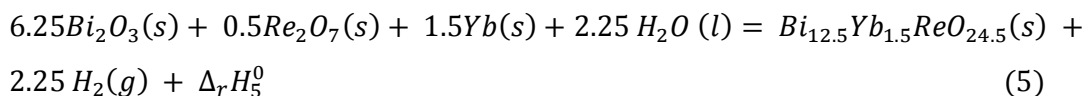
2 mol dm⁻³ HCl was used to measure the solution enthalpies for Bi₂O₃, Re₂O₇, Ln₂O₃ and Bi_{12.5}Yb_{1.5}ReO_{24.5}, Bi₁₄ReO_{24.5} at 298.15 K. Preparation of 2 mol dm⁻³ solution of HCl (mass fraction is 7.06%) was carried out at 298 K using hydrochloric acid marked as “Chemically Pure” which contained 36% of HCl.

A thermochemical cycle was constructed in such a way as to allow comparing the solution enthalpies of Bi₂O₃, Re₂O₇ and Yb mixture with that of corresponding to Bi_{12.5}Yb_{1.5}ReO_{24.5}. Yb was chosen for thermochemical cycles because ytterbium oxide (Yb₂O₃) does not solve in HCl. The calorimetric reactions are:



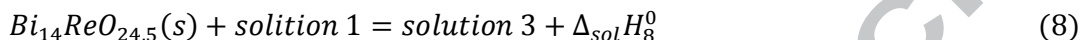
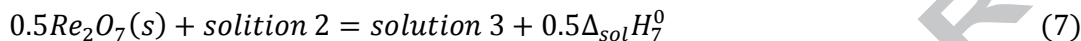
Here, solution 1 is 2 mol dm⁻³ hydrochloric acid.

The measured enthalpies of dissolution (1)–(4) were used to calculate the reaction enthalpy:

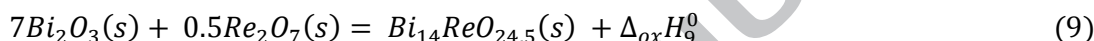


where: $\Delta_r H_5^0$ is the enthalpy of reaction (5).

The thermochemical cycle to determine the formation enthalpy from oxides for $\text{Bi}_{14}\text{ReO}_{24.5}$ is the following:



Dissolution reaction enthalpies (6)-(8) were used to calculate the reaction enthalpy:



$$\text{Here: } \Delta_{\text{ox}} H_9^0 = 7\Delta_{\text{sol}} H_6^0 + 0.5\Delta_{\text{sol}} H_7^0 - \Delta_{\text{sol}} H_8^0$$

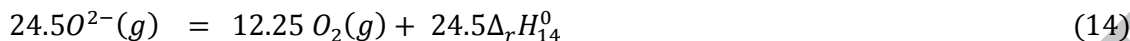
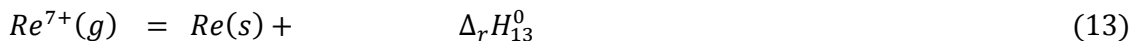
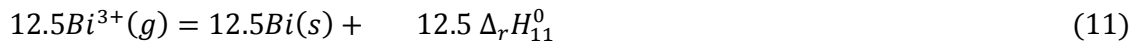
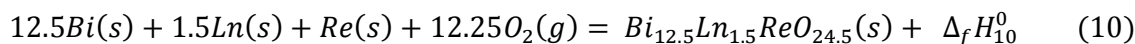
In this work and earlier to optimize calorimetric cycle the following sequence of solution was chosen: 1) Bi_2O_3 ; 2) Re_2O_7 ; 3) rare-earth metal or oxide. We also checked that in our thermochemical cycle within uncertainty the dissolution enthalpies do not depend on change of dissolution sequence.

The weight of samples $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$, $\text{Bi}_{14}\text{ReO}_{24.5}$ involved in calorimetric investigation was about 0.2 g (volume of solvent was 0.25 dm^3). Experimental temperature was $T = 298.15 \pm 0.01\text{ K}$, pressure was $100 \pm 0.15\text{ kPa}$.

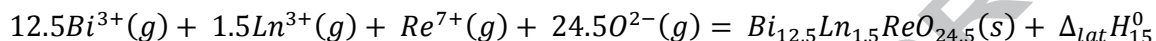
Results and discussion

The compounds prepared earlier [9, 10, 17, 21, 23] had the general formula $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$ ($\text{Ln} = \text{La, Nd, Sm, Gd, Dy, Ho, Lu}$). Lanthanides radii are taken from Shannon [28] and the lattice parameters obtained by us are presented in Table 2.

As there is no data on the lattice energy for $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$ in literature, the lattice energy for $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$ ($\text{Ln} = \text{La, Nd, Sm, Gd, Dy, Ho, Lu}$) was calculated using the experimental data [9, 10, 17, 21, 23] on standard formation enthalpies. Born-Haber cycle was used for the calculation. The calculation schema is presented below.



On the basis of reactions (10)-(14) the lattice energies can be calculated as follows:



$$\text{where: } \Delta_{lat} H_{15}^0 = \Delta_f H_{10}^0 + 12.5 \Delta_r H_{11}^0 + 1.5 \Delta_r H_{12}^0 + \Delta_r H_{13}^0 + 24.5\Delta_r H_{14}^0$$

The values used to calculate the lattice energies were taken from our earlier papers [9, 10, 17, 21, 23] and reference book [27]. They are presented in Table 3, 4. The calculated values of the lattice energy are presented in Table 5.

To construct the dependence of lattice energies on structural parameters Kapustinskii formula was used which connects lattice energies with structural parameters suggesting that there is ionic binding.

$$U = 256.1 \frac{E_n W_k W_a}{r_a + r_k}$$

Here: U - a lattice energy, E_n - a number of structural units, W_k - a cation valence, W_a - an anion valence, r_a - a cation radius, r_k - an anion radius.

After some mathematic transformations Kapustinskii formula can be written for compounds $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$ as follows:

$$U = A + \frac{B}{r_{Ln}}$$

where: A, B - constant values for series of $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$ compounds and r_{Ln} - a lanthanide radius.

A linear dependence between the lattice energy and the inverse value of the lanthanide radius is expected from this equation. Based on the data calculated the dependence U versus $1/r_{Ln}$ was constructed (see Fig. 1). One can see that there is practically a linear dependence of

lattice energies on $1/r_{Ln}$ for the series of $Bi_{12.5}Ln_{1.5}ReO_{24.5}$ compounds. Using this dependence the lattice energy of $Bi_{12.5}Yb_{1.5}ReO_{24.5}$ was calculated for which no thermochemical data are available. We obtained a lattice energy $-125020 \text{ kJ mol}^{-1}$. To check the reliability of our estimation we prepared and characterized samples of $Bi_{12.5}Yb_{1.5}ReO_{24.5}$ and $Bi_{14}ReO_{24.5}$. The results are given below.

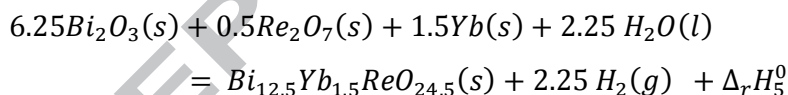
X-ray diffraction data were used to calculate the lattice parameters of a new compound $Bi_{12.5}Yb_{1.5}ReO_{24.5}$. The observed X-ray pattern of $Bi_{12.5}Yb_{1.5}ReO_{24.5}$ at room temperature is presented in Figure 2. This phase crystallizes in a cubic structure (space group Fm-3m) with a lattice parameter: $a = 0.55590(6) \text{ nm}$. The detailed information is presented in Table 6. $Bi_{14}ReO_{24.5}$ was found to crystallize in a tetragonal structure, space group I 4/m with parameters $a = 0.87124(10) \text{ nm}$, $c = 1.7400(3) \text{ nm}$. The X-ray pattern for $Bi_{14}ReO_{24.5}$ is presented in Figure 3. $Bi_{12.5}Yb_{1.5}ReO_{24.5}$ lattice parameters are not available in literature, $Bi_{14}ReO_{24.5}$ lattice parameters are in good agreement with reference [4].

$Bi_{12.5}Yb_{1.5}ReO_{24.5}$, $Bi_{14}ReO_{24.5}$ and Yb solution enthalpies were measured in 2 mol dm^{-3} HCl. The following values were obtained: $\Delta_{sol}H_3^0(Yb) = -681.5 \pm 3.6 \text{ kJ mol}^{-1}$, $\Delta_{sol}H_4^0(Bi_{12.5}Yb_{1.5}ReO_{24.5}) = -861.7 \pm 4.2 \text{ kJ mol}^{-1}$, $\Delta_{sol}H_8^0(Bi_{14}ReO_{24.5}) = -613.5 \pm 4.5 \text{ kJ mol}^{-1}$.

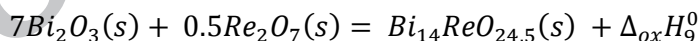
The error was calculated for 95% confidence interval using the standard procedure of processing experimental data.

Bi_2O_3 , Re_2O_7 solution enthalpies which were necessary to calculate $Bi_{12.5}Yb_{1.5}ReO_{24.5}$ and $Bi_{14}ReO_{24.5}$ formation enthalpies were taken from our earlier papers [9].

So, the following values were obtained:

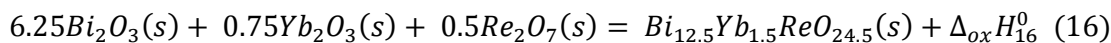


$$\Delta_r H_5^0 = -889.1 \pm 6.7 \text{ kJ mol}^{-1}$$



$$\Delta_{ox}H_9^0 = -200.9 \pm 5.4 \text{ kJ mol}^{-1}$$

Then, using H_2O and Yb_2O_3 standard formation enthalpies [26] the reaction enthalpy was calculated:



$$\Delta_{ox}H_{16}^0 = -171.3 \pm 7.0 \text{ kJ mol}^{-1}$$

To calculate the standard formation enthalpies of $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$ and $\text{Bi}_{14}\text{ReO}_{24.5}$ the standard formation enthalpies of Bi_2O_3 , Re_2O_7 , and Yb_2O_3 were taken from a reference book [27]. The formation enthalpies obtained are:

$$\Delta_f H^0(\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}, s, 298.15 \text{ K}) = -5779.6 \pm 7.0 \text{ kJ mol}^{-1},$$

$$\Delta_f H^0(\text{Bi}_{14}\text{ReO}_{24.5}, s, 298.15 \text{ K}) = -4881.5 \pm 5.4 \text{ kJ mol}^{-1}.$$

Using the experimental value of the standard formation enthalpy of $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$ the lattice energy was calculated with Born-Haber cycle. This value is:

$$U_{ex}(\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}, 298.15 \text{ K}) = -125063 \text{ kJ mol}^{-1}.$$

Comparing the experimentally obtained value of $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$ lattice energy and the value estimated according to U versus $1/r_{Ln}$ in Fig. 1 the following is revealed:

$$\text{Experimental value: } U_{exp}(\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}, 298.15 \text{ K}) = -125063 \text{ kJ mol}^{-1}.$$

$$\text{Estimated value: } U_{cal}(\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}, 298.15 \text{ K}) = -125020 \text{ kJ mol}^{-1}.$$

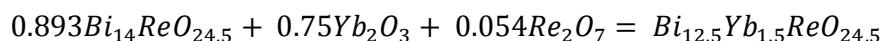
As it is possible to see, experimental value of lattice energy (U_{exp}) is in a good agreement with value calculated according to the U versus $1/r_{Ln}$ dependence (U_{cal}).

Next, the problem of phase thermodynamic stabilities, namely, that of $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$, $\text{Bi}_{14}\text{ReO}_{24.5}$ will be considered. One can see that the formation enthalpies of $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$ and $\text{Bi}_{14}\text{ReO}_{24.5}$ both are negative. To see whether a phase is stable or not one has to know its Gibbs free energy: $\Delta G = \Delta H - T\Delta S$. As there are no entropy data of $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$, $\text{Bi}_{14}\text{ReO}_{24.5}$ available in literature we used estimated values of entropies. It has been shown that it is possible to estimate the entropy of mixed oxides with good accuracy as a sum of entropies of binary oxides [29]. With this approximation the Gibbs free energies for reaction (9) and (16) could be obtained as:

$$\Delta_{ox} G_9^0 = -200.9 \pm 5.4 \text{ kJ mol}^{-1}$$

$$\Delta_{ox} G_{16}^0 = -171.3 \pm 7.0 \text{ kJ mol}^{-1}$$

Again, Gibbs free energies are negative. Therefore, the compounds under consideration are thermodynamically stable with respect to the decomposition to binary oxides. After that $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$ thermodynamic stability will be examined with respect to its decomposition to $\text{Bi}_{14}\text{ReO}_{24.5}$. The following reaction can be written:



The Gibbs free energy was calculated as:

$$\Delta_r G^0 = +8.2 \pm 6.2 \text{ kJ mol}^{-1}$$

This value is positive, which signifies that $Bi_{12.5}Yb_{1.5}ReO_{24.5}$ is thermodynamically unstable with respect to decomposition into mixtures including $Bi_{14}ReO_{24.5}$, Yb_2O_3 , and Re_2O_7 at room temperature. However, it is formed at the temperature range of 1000-1100 K, that is at existence temperatures of δ - Bi_2O_3 . In order that reaction

$Bi_{12.5}Yb_{1.5}ReO_{24.5} = 0.893Bi_{14}ReO_{24.5} + 0.75Yb_2O_3 + 0.054Re_2O_7$ proceeds at room temperatures the long time will be required. Authors checked that at least within 6 months after synthesis compound $Bi_{12.5}Yb_{1.5}ReO_{24.5}$ remains at room temperature in the same form as after synthesis, namely cubic form $Bi_{12.5}Yb_{1.5}ReO_{24.5}$.

Conclusions

Based on experimental data the dependence of the lattice energy versus $1/r_{Ln}$ for a series of $Bi_{12.5}Ln_{1.5}ReO_{24.5}$ compounds has been constructed. Born-Haber cycle has been used to calculate the lattice energy. Experimental value of lattice energy for $Bi_{12.5}Yb_{1.5}ReO_{24.5}$ is in a good agreement with value calculated according to the U versus $1/r_{Ln}$ dependence. The compound $Bi_{12.5}Yb_{1.5}ReO_{24.5}$ has been prepared for the first time. We have synthesized $Bi_{14}ReO_{24.5}$ phase as well. $Bi_{14}ReO_{24.5}$ and $Bi_{12.5}Yb_{1.5}ReO_{24.5}$ standard formation enthalpies have been measured. The phases have been shown to be thermodynamically stable with respect to the decomposition into binary oxides. Yet, $Bi_{12.5}Yb_{1.5}ReO_{24.5}$ is thermodynamically unstable as to the decomposition into a mixture including $Bi_{14}ReO_{24.5}$ at room temperature.

Acknowledges

This work was supported by Karlsruhe Institute of Technology, RFBR (Project 13-08-00169) and Program of Fundamental Investigation of Siberian Branch of the Russian Academy of Science.

References

1. R. Punn, A.M. Feteira, D.C. Sinclair, C. Greaves, *J. Amer. Chem. Soc.* 128 (2006) 15386-15387.
2. I. Diop, N. David, J.M. Fiorani, R. Podor, M. Vilasi, *J. Chem. Thermodynamics* 41 (2009) 420-432.
3. M. Aspiala, D. Sukhomlinov, P. Taskinen, *J. Chem. Thermodynamics* 75 (2014) 8-12.
4. T.E. Crumpton, J.F.W. Mosselmans, Greaves C. *J. Mater. Chem.* 15 (2005) 164-167.
5. T. Atake, *J. Chem. Thermodynamics* 41 (2009) 1-10.
6. S.J. Skinner, J.A. Kilner, *Materials Today* 6 (2003) 30-37.
7. R. Ganesan, T. Gnanasekaran, R.S. Srinivasa, *J. Chem. Thermodynamics* 35 (2003) 1703-1716.
8. S. Phapale, D. Das, R. Mishra, *J. Chem. Thermodynamics* 63 (2013) 74-77.
9. A.N. Bryzgalova, N.I. Matskevich, C. Greaves, C.H. Hervoches, *Thermochim. Acta* 513 (2011) 124-127.
10. N.I. Matskevich, Th. Wolf, C. Greaves, A.N. Bryzgalova, *J. Alloys Comp.* 582 (2014) 253-256.
11. A. Zahariev, N. Kaloyanov, V. Parvanova, C. Girginov, *Thermochim. Acta* 594 (2014) 11-15.
12. E.E. McCabe, I.P. Jones, D. Zhang, N.C. Hyatt, C. Greaves, *J. Mater. Chem.* 17 (2007) 1193-1200.
13. N.I. Matskevich, A.N. Bryzgalova, Th. Wolf, P. Adelman, D. Ernst, T.I. Chupakhina, *J. Chem. Thermodynamics* 53 (2012) 23-26.
14. R. Ganesan, T. Gnanasekaran, R.S. Srinivasa, *J. Chem. Thermodynamics* 38 (2006) 739-747.
15. A. Zahariev, N. Kaloyanov, C. Girginov, V. Parvanova, *Thermochim. Acta* 528 (2012) 85-89.
16. M. Drache, P. Roussel, J.P. Wignacourt, *Chem. Rev.* 107 (2007) 80-96.
17. N.I. Matskevich, Th. Wolf, P. Adelman, A.N. Bryzgalova, *J. Alloys Comp.* 604 (2014) 325-326.
18. C. Vernochet, R.N. Vannier, M. Huvé, C. Pirovano, G. Nowogrocki, G. Mairesse, G. Van Tendeloo, *J. Mater. Chem.* 10 (2000) 2811-2817.
19. A. Zahariev, V. Parvanova, N. Kaloyanov, *Thermochim. Acta* 502 (2010) 90-93.
20. M. G. Francesconi, A. L. Kirbyshire, C. Greaves, O. Richard, G. Van Tendeloo, *Chem. Mater.* 10 (1998) 626-632.

21. N.I. Matskevich, A.N. Bryzgalova, Th. Wolf, P. Adelman, D. Ernst, T.I. Chupakhina, J. Chem. Thermodynamics 53 (2012) 23–26.
22. L.M. Sprunger, J. Gibbs, A. Proctor, W.E. Acree, Jr., M.H. Abraham, Y. Meng, C. Yao, J.L. Anderson, Ind. Eng. Chem. Res. 48 (2009) 4145-4154.
23. N.I. Matskevich, Th. Wolf, J. Alloys Comp. 538 (2012) 45–47.
24. N.I. Matskevich, Th. Wolf, J. Chem. Thermodynamics 42 (2010) 225-228.
25. N.I. Matskevich, Th. Wolf, Thermochim. Acta 467 (2007) 113-116.
26. N.I. Matskevich, Th. Wolf, Yu.I. Pochivalov, Inorg. Chem. 47 (2008) 2581-2584.
27. V.P. Glushko, Termicheskie Konstanty Veshchestv (Thermal Constants of Substances). VINITI: Moscow. 1965-1982, issued 1-10.
28. R. D. Shannon, Acta Cryst. A32 (1976) 751-761.
29. Yu.F. Minenkov, N.I. Matskevich, Yu.G. Stenin, P.P. Samoilov, Thermochim. Acta 278 (1996) 1-8.

ACCEPTED MANUSCRIPT

Table 1. Results of chemical analysis of $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$, $\text{Bi}_{14}\text{ReO}_{24.5}$ and potassium chloride

Compounds	Experimental data (%)	Calculated data (%)	Method of analysis
KCl	K, 52.42 ± 0.02	K, 52.44	Weight method with sodium tetraphenylborate
$\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$	Bi, 75.66 ± 0.07 ; Yb, 7.58 ± 0.05 ; Re, 5.42 ± 0.05 ; O, 11.31 ± 0.04	Bi, 75.72; Yb, 7.52; Re, 5.40; O, 11.36	Bi, Yb – spectrophotometric method; Re - X-ray Fluorescence analysis; O – reducing melting method
$\text{Bi}_{14}\text{ReO}_{24.5}$	Bi, 83.42 ± 0.08 ; Re, 5.36 ± 0.05 ; O, 11.15 ± 0.05	Bi, 83.50 ; Re, 5.31; O, 11.19	Bi – spectrophotometric method; Re - X-ray Fluorescence analysis; O – reducing melting method

ACCEPTED MANUSCRIPT

Table 2. Lattice parameters and ion radii of $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$

Compounds	Ion radii of lanthanides/nm	Lattice parameters/nm
$\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}$	0.1032	0.56456 (3)
$\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}$	0.0983	0.56184 (4)
$\text{Bi}_{12.5}\text{Sm}_{1.5}\text{ReO}_{24.5}$	0.0958	0.55958 (1)
$\text{Bi}_{12.5}\text{Gd}_{1.5}\text{ReO}_{24.5}$	0.0938	0.55818 (1)
$\text{Bi}_{12.5}\text{Dy}_{1.5}\text{ReO}_{24.5}$	0.0912	0.55677 (1)
$\text{Bi}_{12.5}\text{Ho}_{1.5}\text{ReO}_{24.5}$	0.0901	0.55723(2)
$\text{Bi}_{12.5}\text{Lu}_{1.5}\text{ReO}_{24.5}$	0.0861	0.55689(5)

ACCEPTED MANUSCRIPT

Table 3. Standard formation enthalpies for $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$

Compounds	$\Delta_f H^0$ (298.15 K)/ kJ mol^{-1}
$\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}$	-5659.7 ± 8.8
$\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}$	-5702.6 ± 9.0
$\text{Bi}_{12.5}\text{Sm}_{1.5}\text{ReO}_{24.5}$	-5760.1 ± 8.2
$\text{Bi}_{12.5}\text{Gd}_{1.5}\text{ReO}_{24.5}$	-5760.3 ± 8.5
$\text{Bi}_{12.5}\text{Dy}_{1.5}\text{ReO}_{24.5}$	-5788.0 ± 8.6
$\text{Bi}_{12.5}\text{Ho}_{1.5}\text{ReO}_{24.5}$	-5815.0 ± 9.1
$\text{Bi}_{12.5}\text{Lu}_{1.5}\text{ReO}_{24.5}$	-5819.4 ± 8.3

ACCEPTED MANUSCRIPT

Table 4. Ion formation energies ($A_{(s)} = A^{n+}(g)$)

Ions	$\Delta E / \text{kJ mol}^{-1}$
Bi ³⁺	4994
Re ⁷⁺	28088
La ³⁺	3885
Nd ³⁺	4028
Sm ³⁺	4088
Gd ³⁺	4153
Dy ³⁺	4189
Ho ³⁺	4224
Lu ³⁺	4334

ACCEPTED MANUSCRIPT

Table 5. Lattice energies for $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$

Compounds	$U/\text{kJ mol}^{-1}$
$\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}$	-124189
$\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}$	-124446
$\text{Bi}_{12.5}\text{Sm}_{1.5}\text{ReO}_{24.5}$	-124579
$\text{Bi}_{12.5}\text{Gd}_{1.5}\text{ReO}_{24.5}$	-124693
$\text{Bi}_{12.5}\text{Dy}_{1.5}\text{ReO}_{24.5}$	-124773
$\text{Bi}_{12.5}\text{Ho}_{1.5}\text{ReO}_{24.5}$	-124853
$\text{Bi}_{12.5}\text{Lu}_{1.5}\text{ReO}_{24.5}$	-125023

ACCEPTED MANUSCRIPT

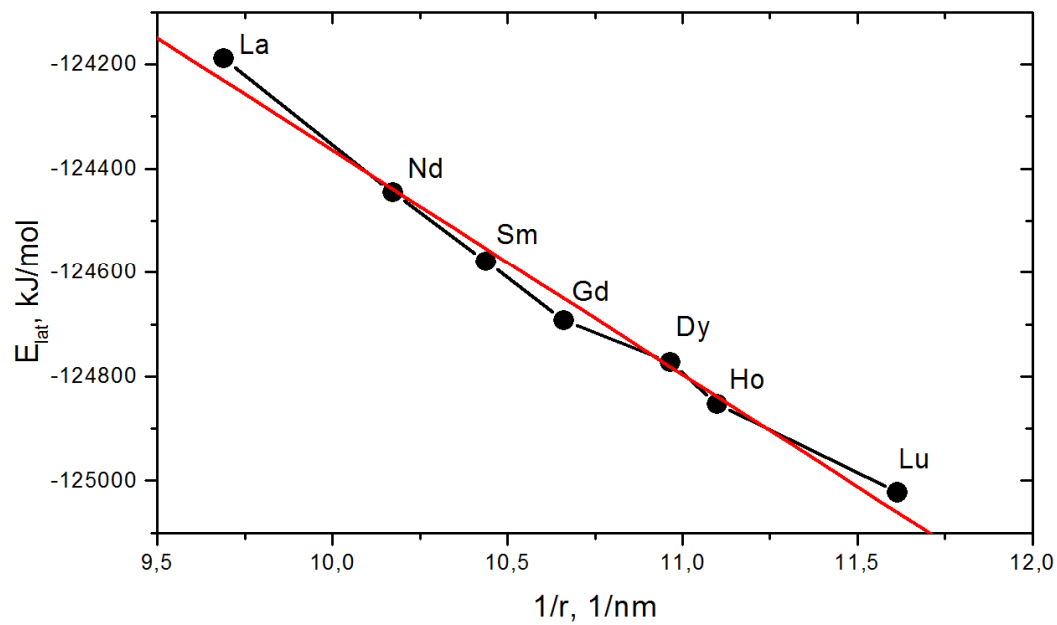


Figure 1. Dependence of lattice energies for $\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$ compounds as the function of $1/r$ (r – an ion radius of lanthanide)

ACCEPTED

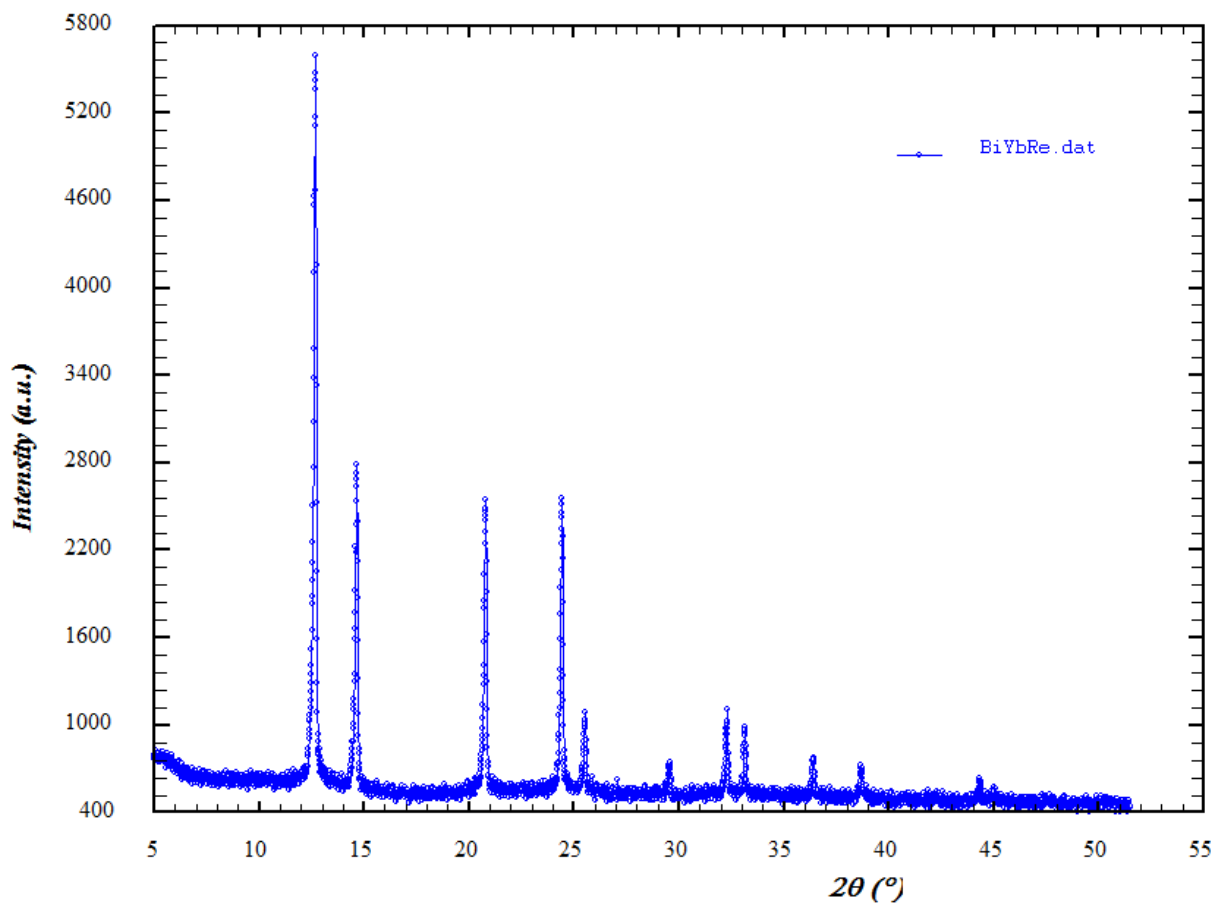


Figure 2. X-ray diffraction pattern of $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$

ACCEPTED

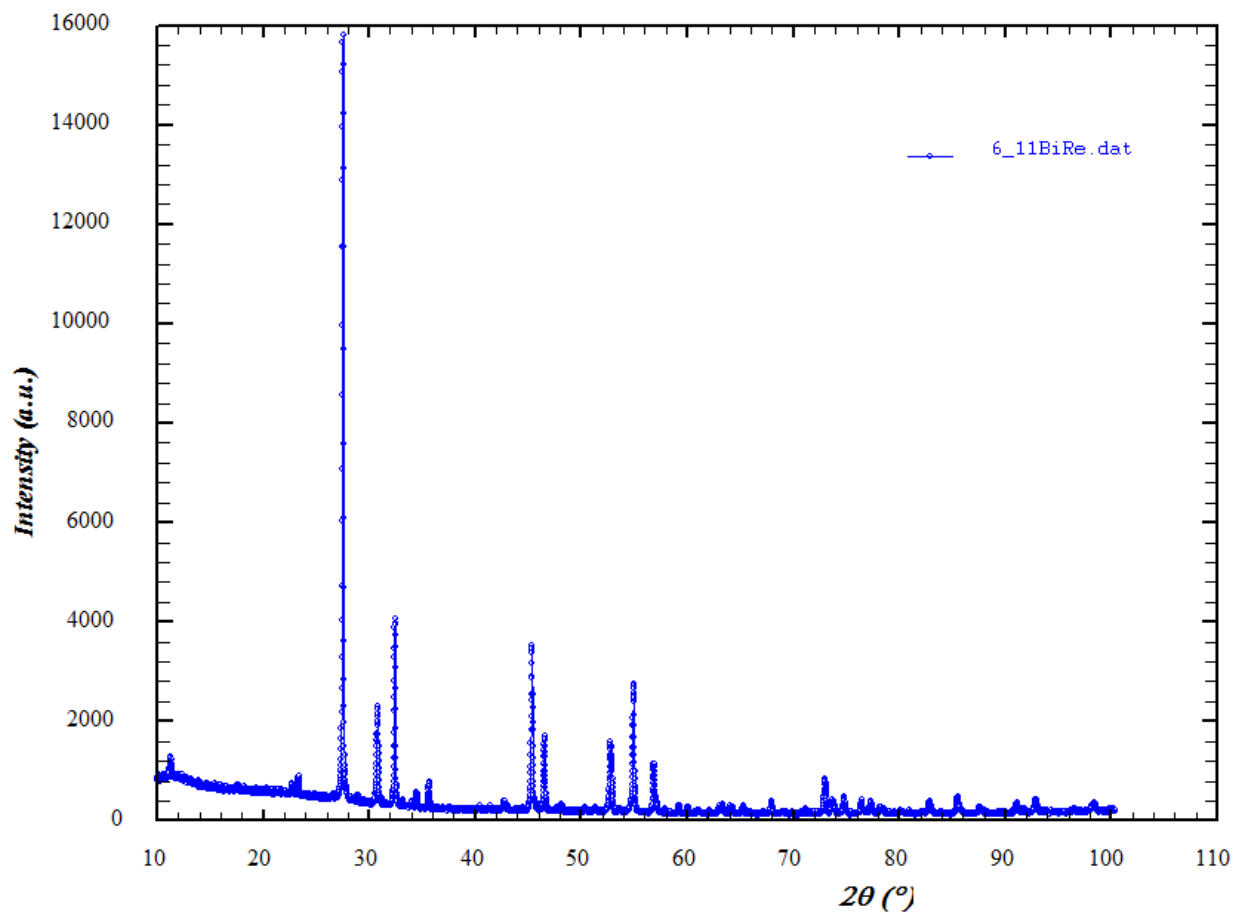


Figure 3. X-ray diffraction pattern of $\text{Bi}_{14}\text{ReO}_{24.5}$

ACCEPTED

Table 6. Power X-ray diffraction data for $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$

N	2Th [obs]	H	K	L	2Th[calc]	obs-calc	Int.	d[obs]	d[calc]
1	12.684	1	1	1	12.688	-0.0045	100.0	3.2106	3.2095
2	14.661	2	0	0	14.661	0.0003	49.6	2.7795	2.7795
3	20.794	2	2	0	20.791	0.0027	45.5	1.9652	1.9654
4	24.433	3	1	1	24.431	0.0017	45.3	1.6760	1.6761
5	25.540	2	2	2	25.535	0.0041	18.7	1.6045	1.6048
6	29.574	4	0	0	29.569	0.0049	13.2	1.3895	1.3898
7	32.293	3	3	1	32.292	0.0011	18.4	1.2753	1.2753
8	33.149	4	2	0	33.155	-0.0052	17.1	1.2432	1.2430
9	36.420	4	2	2	36.425	-0.0051	13.7	1.1349	1.1347
10	38.714	5	1	1	38.719	-0.0052	12.8	1.0700	1.0698
11	44.350	5	3	1	44.349	0.0010	11.4	0.9396	0.9397
12	45.016	6	0	0	45.012	0.0039	9.9	0.9264	0.9265

We synthesized new compound $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$.

We measured formation enthalpies of $\text{Bi}_{12.5}\text{Yb}_{1.5}\text{ReO}_{24.5}$ and $\text{Bi}_{14}\text{ReO}_{24.5}$.

$\text{Bi}_{12.5}\text{Ln}_{1.5}\text{ReO}_{24.5}$ lattice energies dependence on rare-earth reverse radii was done.

ACCEPTED MANUSCRIPT