



## Formation enthalpies and thermodynamics of some reactions of the $\text{Bi}_{12.5}\text{R}_{1.5}\text{ReO}_{24.5}$ ( $\text{R} = \text{Y}, \text{Nd}, \text{La}$ ) compounds

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### ABSTRACT

Solution calorimetry, using 2.0 M HCl ( $T=298.15\text{ K}$ ) as a solvent, is used to study the thermochemistry of  $\text{Bi}_{12.5}\text{R}_{1.5}\text{ReO}_{24.5}$  ( $\text{R}=\text{Nd}, \text{La}, \text{Y}$ ). For the first time, the standard formation enthalpies of these phases have been determined as follows:  $\Delta_f H^\circ$  ( $\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}, \text{s}, 298.15\text{ K}$ ) =  $-5659.7 \pm 8.8\text{ kJ/mol}$ ;  $\Delta_f H^\circ$  ( $\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}, \text{s}, 298.15\text{ K}$ ) =  $-5702.6 \pm 9.0\text{ kJ/mol}$ ;  $\Delta_f H^\circ$  ( $\text{Bi}_{12.5}\text{Y}_{1.5}\text{ReO}_{24.5}, \text{s}, 298.15\text{ K}$ ) =  $-5727.6 \pm 8.8\text{ kJ/mol}$ . The thermodynamic stability at room temperature has been assessed. The results show that investigated phases are thermodynamically stable with respect to binary oxides and stable with respect to interaction with  $\text{H}_2\text{O}$  at ambient temperatures.  $\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}$  and  $\text{Bi}_{12.5}\text{Y}_{1.5}\text{ReO}_{24.5}$  are thermodynamically stable but  $\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}$  is thermodynamically unstable with respect to interaction with  $\text{CO}_2$ .

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### 1. Introduction

The high oxide ion conductivities of mixed oxides of bismuth and rare-earth element's oxides resulted in significant interest as materials for use as electrolytes for solid oxide fuel cells (SOFCs), ceramic oxygen generators, etc. [1–7]. In particular, they have high ionic conductivity and electrocatalytic activity in the temperature range of 600–800 K. Substituted bismuth vanadium oxides (BIMEVOX materials) show even higher conductivities, but have the disadvantage of low mechanical strength. Unfortunately, bismuth-containing oxides are susceptible to reduction at the anode of SOFCs, which seriously limits their applicability for this application. Nevertheless, it is still important to seek materials, which exhibit the following characteristics at relatively low temperatures: (1) ionic conductivity similar to that of BIMEVOX; (2) isotropic structure; (3) low thermal expansion coefficient. The new compounds of general formula  $\text{Bi}_{12.5}\text{R}_{1.5}\text{ReO}_{24.5}$  ( $\text{R} = \text{rare-earth elements}$ ) were discovered in papers [1,2]. Their conductivity in the temperature range of 600–800 K is practically the same as seen in BIMEVOX materials, but they are isotropic [1].

Previously the structure and conductivity of some of these Re-containing compounds were investigated [1]. However, further information is needed for practical application of these phases. In particular, one of the important aspects of practical application is thermodynamic stability.

The aim of this paper is to measure thermodynamic characteristics of the  $\text{Bi}_{12.5}\text{R}_{1.5}\text{ReO}_{24.5}$  ( $\text{R} = \text{Y}, \text{La}, \text{Nd}$ ) phases and to study their thermodynamic stability.

The thermodynamic stability of compounds  $\text{Bi}_{12.5}\text{R}_{1.5}\text{ReO}_{24.5}$  ( $\text{R} = \text{Y}, \text{La}, \text{Nd}$ ) was investigated using calorimetric methods to explore stability with respect to: (1) the decomposition to binary oxides; (2) reaction with the external reagents  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . These values are useful for assessing the potential of such materials. Another interesting feature is the possible correlation between thermodynamic stability and ionic conductivity. There are no thermodynamic data for these compounds in literature.

### 2. Experimental

#### 2.1. Sample preparation and characterization

Reagents  $\text{Bi}_2\text{O}_3$  (99.99% Alfa),  $\text{Nd}_2\text{O}_3$  (99.99%, Purathem, STREM Chemicals, New Buryport, USA),  $\text{La}_2\text{O}_3$  (99.99% Alfa),  $\text{Y}_2\text{O}_3$  (99.99% Alfa),  $\text{NH}_4\text{ReO}_4$  (99.99% Alfa) were used for synthesis of oxide compounds in the  $\text{Bi}_2\text{O}_3\text{--R}_2\text{O}_3\text{--Re}_2\text{O}_7$  system and for the calorimetric experiments.

Compounds have been synthesized by conventional solid state methods using reactions between stoichiometric mixtures of bismuth oxide ( $\text{Bi}_2\text{O}_3$ ), rare-earth oxides ( $\text{Nd}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ) and ammonium perchlenate ( $\text{NH}_4\text{ReO}_4$ ), to give a ratio of bismuth to rare-earth metal and to rhenium of 12.5:1.5:1. The reactants were carefully weighed and mixed in a planetary mill, pressed and heated in air at 1073 K for 36 h. The samples were characterized using powder diffraction (collected at Studsvik, Sweden; 10 K; wavelength

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**Table 1**  
Thermochemical data on dissolution enthalpies and formation enthalpies of binary oxides.

Phases	Bi <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	La <sub>2</sub> O <sub>3</sub>	Nd <sub>2</sub> O <sub>3</sub>	Re <sub>2</sub> O <sub>7</sub>	Ref.
$\Delta_{\text{sol}}H^\circ$ (kJ/mol) <sup>a</sup>	-114.4 ± 1.1	-382.7 ± 1.8	-474.4 ± 2.2	-434.7 ± 2.0	-27.2 ± 0.1	This work
$\Delta_fH^\circ$ (kJ/mol)	-578.0 ± 0.2	-1905.0 ± 0.3	-1794.2 ± 0.2	-1808.3 ± 0.3	-1271.9 ± 8.4	[12]

<sup>a</sup> All experimental values were calculated as the average value from six parallel experiments. The errors were calculated for 95% confidence interval using standard procedure of treatment of experimental results [14].

1.4703 Å) and X-ray diffraction using power X-diffraction (STADI-P, Stoe diffractometer, Germany; CuK<sub>α1</sub> radiation). The patterns agree well with the patterns known from the literature [1]. The materials were found to be single. Structural analysis confirms that Bi<sub>12.5</sub>R<sub>1.5</sub>ReO<sub>24.5</sub> was single. The Bi<sub>12.5</sub>R<sub>1.5</sub>ReO<sub>24.5</sub> has space group Fm3m [1].

All compounds were also characterized by chemical analysis. For the analysis of Bi, Nd, La, Y a spectrophotometric method (spectrophotometer SF-46) was used. The content of impurities was determined by spectral methods (mass-spectrometer “Element”, Finnigan Mat, Germany) [8]. The analyses indicated that impurities of Ho, Dy, Eu, Yb, La, Tm, Er, Pr, Sm, Ce, Te, Ca, Mg, Mn, Pb, Ag metals were present at the level 10<sup>-3</sup>–10<sup>-4</sup> at. %. The oxygen contents were determined by iodometric titration using 0.01 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O according to the method described in paper [9]. According to the results of the analyses the involved compounds were found to be single with an accuracy of about 1%.

### 3. Experimental technique

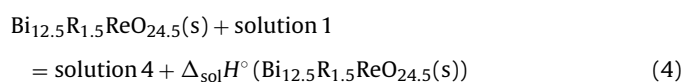
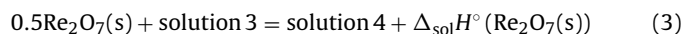
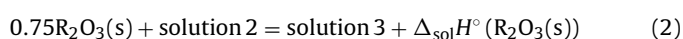
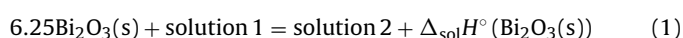
To determine the thermodynamic characteristics of compounds, the solution calorimetric experiments were carried out using a calorimeter with an isothermal shield. The calorimeter was fully automated, with the enthalpies of solution being calculated by computer. The calorimeter consists of a Dewar vessel with a brass cover and volume of 200 cm<sup>3</sup>. The platinum resistance thermometer, calibration heater, cooler, mixer, and device to break the ampoules were mounted on the lid closing the Dewar vessel. The construction of the solution calorimeter and the experimental procedure are described elsewhere [10–11]. The calorimetric vessel was maintained at  $T=298.15$  K with temperature drift less than 0.0003 K for 10 h. Dissolution of potassium chloride in water was performed to calibrate the calorimeter. The dissolution heat of KCl obtained was 17.41 ± 0.08 kJ/mol (the molality of the final solution was 0.028 mol/kg,  $T=298.15$  K). The literature data are: 17.42 ± 0.02 kJ/mol [12], 17.47 ± 0.07 kJ/mol [13].

The experiments were performed at 298.15 K. The amount of Bi<sub>12.5</sub>R<sub>1.5</sub>ReO<sub>24.5</sub> was about 0.2 g.

All compounds were stored in a dry box to prevent interaction with moisture or CO<sub>2</sub>.

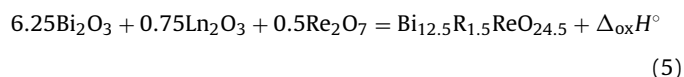
### 4. Thermochemical cycles

The thermochemical cycle for determination of formation enthalpies of Bi<sub>12.5</sub>R<sub>1.5</sub>ReO<sub>24.5</sub> (R=Nd, La, Y) was constructed in such a way that bismuth oxide and phases of Bi<sub>12.5</sub>R<sub>1.5</sub>ReO<sub>24.5</sub> were dissolved in 2 M HCl. The rare-earth oxide was dissolved in solution 2 (2 M HCl with dissolved Bi<sub>2</sub>O<sub>3</sub>) and rhenium oxide was dissolved in solution 3 (2 M HCl with dissolved Bi<sub>2</sub>O<sub>3</sub> and rare-earth oxide). Then the enthalpy of dissolution of mixture Bi<sub>2</sub>O<sub>3</sub>, R<sub>2</sub>O<sub>3</sub>, Re<sub>2</sub>O<sub>7</sub> was compared with the solution enthalpy of Bi<sub>12.5</sub>R<sub>1.5</sub>ReO<sub>24.5</sub>. The reactions showing the principal scheme from which the formation enthalpies from binary oxides are calculated are presented below:



Here, solution 1 is 2 M hydrochloric acid.

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

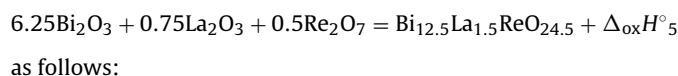


where  $\Delta_{\text{ox}}H^\circ$  is the formation enthalpy of Bi<sub>12.5</sub>R<sub>1.5</sub>ReO<sub>24.5</sub> from binary oxides.

### 5. Results and discussion

To determine the formation enthalpy of Bi<sub>12.5</sub>La<sub>1.5</sub>ReO<sub>24.5</sub> we measure the solution enthalpies of bismuth oxide, lanthanum oxide, rhenium oxide and solution enthalpy of Bi<sub>12.5</sub>La<sub>1.5</sub>ReO<sub>24.5</sub>. The dissolution enthalpies for binary oxides are presented in Table 1 together with data on enthalpies of formation, which were taken from [12]. It is necessary to mention that after our work [10] we measured the dissolution enthalpy of Bi<sub>2</sub>O<sub>3</sub> again to decrease error but used value of the Y<sub>2</sub>O<sub>3</sub> dissolution enthalpy taken from our paper [10]. The solution enthalpy of investigated compound is  $\Delta_{\text{sol}}H^\circ(\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}(\text{s})) = -1019.0 \pm 2.9$  kJ/mol. All experimental values were calculated as the average value from six parallel experiments. The errors were calculated for 95% confidence interval using standard procedure of treatment of experimental results [14].

The measured enthalpies of dissolution were used for calculating the enthalpy of Bi<sub>12.5</sub>La<sub>1.5</sub>ReO<sub>24.5</sub> from binary oxides:



$$\Delta_{\text{ox}}H^\circ_5 = 6.25\Delta_{\text{sol}}H^\circ_1 + 0.75\Delta_{\text{sol}}H^\circ_2 + 0.5\Delta_{\text{sol}}H^\circ_3 - \Delta_{\text{sol}}H^\circ_4$$

Then, we calculated the standard formation enthalpy according to formula:

$$\begin{aligned} \Delta_fH^\circ(\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}) \\ = \Delta_{\text{ox}}H^\circ_5 + 6.25\Delta_fH^\circ(\text{Bi}_2\text{O}_3) + 0.75\Delta_fH^\circ(\text{La}_2\text{O}_3) \\ + 0.5\Delta_fH^\circ(\text{Re}_2\text{O}_7) \end{aligned}$$

In this way, we obtained the values for formation from binary oxides and standard formation enthalpy of Bi<sub>12.5</sub>La<sub>1.5</sub>ReO<sub>24.5</sub> as following:

$$\Delta_{\text{ox}}H^\circ = -65.6 \pm 7.6 \text{ kJ/mol—the formation enthalpy from binary oxides;}$$

$$\Delta_fH^\circ = -5659.7 \pm 8.8 \text{ kJ/mol—the standard formation enthalpy.}$$

Thermochemical data for compound Bi<sub>12.5</sub>Nd<sub>1.5</sub>ReO<sub>24.5</sub> were obtained in similar fashion. The solution enthalpy was measured to be:  $\Delta_{\text{sol}}H^\circ = -956.7 \pm 3.6$  kJ/mol (calculated as average

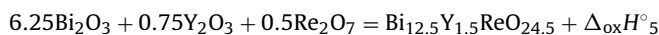
from six parallel experiments). Using the same scheme as for  $\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}$  based on solution enthalpies of  $\text{Bi}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Re}_2\text{O}_7$ ,  $\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}$  we calculated the formation enthalpy from binary oxides:  $\Delta_{\text{ox}}H^\circ = -97.9 \pm 7.9 \text{ kJ/mol}$  – enthalpy of formation of  $\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}$  from binary oxides. The solution enthalpies, necessary for the calculation, are presented in Table 1.

Using equation:

$$\Delta_f H^\circ = \Delta_{\text{ox}} H^\circ + 6.25 \Delta_f H^\circ(\text{Bi}_2\text{O}_3) + 0.75 \Delta_f H^\circ(\text{Nd}_2\text{O}_3) + 0.5 \Delta_f H^\circ(\text{Re}_2\text{O}_7)$$

the calculation of standard formation enthalpy was possible:  $\Delta_f H^\circ = -5702.6 \pm 9.0 \text{ kJ/mol}$  – standard formation enthalpy of  $\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}$ .

The solution enthalpy obtained for  $\text{Bi}_{12.5}\text{Y}_{1.5}\text{ReO}_{24.5}$  was  $-965.21 \pm 2.9 \text{ kJ/mol}$  and the enthalpy from oxides was calculated using formula:



Here:  $\Delta_{\text{ox}} H^\circ_5 = 6.25 \Delta_{\text{sol}} H^\circ_1 + 0.75 \Delta_{\text{sol}} H^\circ_2 + 0.5 \Delta_{\text{sol}} H^\circ_3 - \Delta_{\text{sol}} H^\circ_4$ .

Again, the standard formation enthalpy was estimated using the formula:

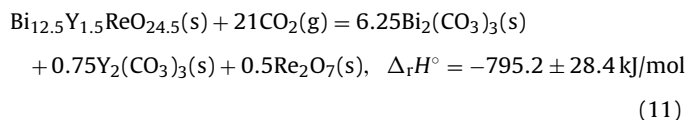
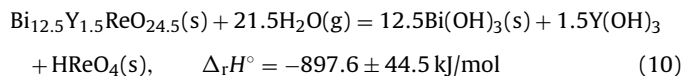
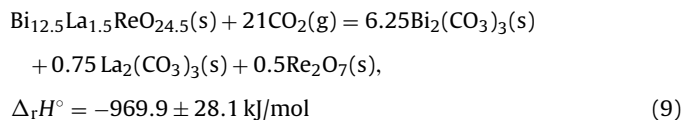
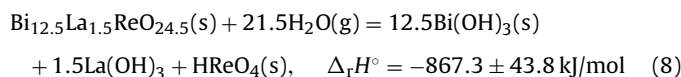
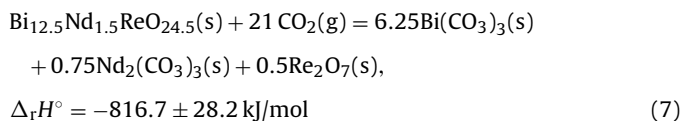
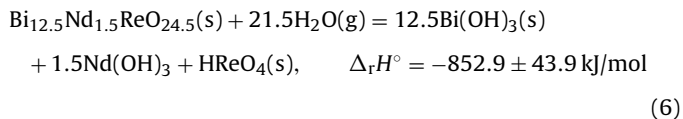
$$\Delta_f H^\circ(\text{Bi}_{12.5}\text{Y}_{1.5}\text{ReO}_{24.5}) = \Delta_{\text{ox}} H^\circ_5 + 6.25 \Delta_f H^\circ(\text{Bi}_2\text{O}_3) + 0.75 \Delta_f H^\circ(\text{Y}_2\text{O}_3) + 0.5 \Delta_f H^\circ(\text{Re}_2\text{O}_7)$$

In this way, the formation enthalpy of  $\text{Bi}_{12.5}\text{Y}_{1.5}\text{ReO}_{24.5}$  from binary oxides was determined as  $\Delta_{\text{ox}} H^\circ = -50.4 \pm 7.6 \text{ kJ/mol}$ , and the standard formation enthalpy was  $\Delta_f H^\circ = -5727.6 \pm 8.8 \text{ kJ/mol}$ .

The results indicate that  $\text{Bi}_{12.5}\text{R}_{1.5}\text{ReO}_{24.5}$  (R = La, Nd, Y) is stable at room temperature with respect to decomposition to the constituent binary oxides. To understand whether the  $\text{Bi}_{12.5}\text{R}_{1.5}\text{ReO}_{24.5}$  phases decompose to the  $6.25\text{Bi}_2\text{O}_3 + 0.75\text{R}_2\text{O}_3 + 0.5\text{Re}_2\text{O}_7$  mixture it is necessary to know the Gibbs energy. There are no entropies for the  $\text{Bi}_{12.5}\text{R}_{1.5}\text{ReO}_{24.5}$  (R = La, Nd, Y) compounds. As known the entropy of complex oxide is close to entropy of sum of binary oxide mixture [15–17]. So, the entropy of mixture  $6.25\text{Bi}_2\text{O}_3 + 0.75\text{R}_2\text{O}_3 + 0.5\text{Re}_2\text{O}_7$  is close to  $\text{Bi}_{12.5}\text{R}_{1.5}\text{ReO}_{24.5}$  and the Gibbs energy of reaction (5) is practically the same as the formation of enthalpy of this reaction. On the basis of this value, it is concluded that the  $\text{Bi}_{12.5}\text{R}_{1.5}\text{ReO}_{24.5}$  phase is thermodynamically stable with respect to decomposition according to reaction (5) at room temperature.

The other interesting aspect is to consider reactions of  $\text{Bi}_{12.5}\text{R}_{1.5}\text{ReO}_{24.5}$  with  $\text{CO}_2$  and water vapour because many similar compounds [10,11] are thermodynamically unstable with respect to reactions with  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

To understand if  $\text{Bi}_{12.5}\text{R}_{1.5}\text{ReO}_{24.5}$  reacts with carbon dioxide, we considered and calculated the formation enthalpies of following reactions:



The formation enthalpies of above reactions were calculated by using formation enthalpies of  $\text{Bi}_2(\text{CO}_3)_3$ ,  $\text{Nd}_2(\text{CO}_3)_3$ ,  $\text{La}_2(\text{CO}_3)_3$ ,  $\text{Y}_2(\text{CO}_3)_3$ ,  $\text{Bi}(\text{OH})_3$ ,  $\text{Y}(\text{OH})_3$ ,  $\text{Nd}(\text{OH})_3$ ,  $\text{La}(\text{OH})_3$ ,  $\text{HReO}_4$ ,  $\text{Re}_2\text{O}_7$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  taken from paper [12]. The calculated values of above reactions are negative.

It is necessary to note that the direction of any chemical transformation is determined by sign of the Gibbs energy  $\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$ . Below we will calculate the Gibbs energies for reactions (6)–(11). The values of the entropies of  $\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}$ ,  $\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}$ ,  $\text{Bi}_{12.5}\text{Y}_{1.5}\text{ReO}_{24.5}$  were estimated using entropies of  $\text{Bi}_2\text{O}_3$ ,  $\text{Re}_2\text{O}_7$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  taken from Ref. [12]. The Gibbs energies for processes (6)–(11) were calculated as:

$$\begin{aligned} \Delta_r G^\circ (298.15 \text{ K}) &= +77.0 \pm 43.9 \text{ kJ/mol} \text{ [for reaction (6)]} \\ \Delta_r G^\circ (298.15 \text{ K}) &= +4.0 \pm 28.2 \text{ kJ/mol} \text{ [for reaction (7)]} \\ \Delta_r G^\circ (298.15 \text{ K}) &= +61.3 \pm 43.8 \text{ kJ/mol} \text{ [for reaction (8)]} \\ \Delta_r G^\circ (298.15 \text{ K}) &= -151.2 \pm 28.1 \text{ kJ/mol} \text{ [for reaction (9)]} \\ \Delta_r G^\circ (298.15 \text{ K}) &= +30.3 \pm 44.5 \text{ kJ/mol} \text{ [for reaction (10)]} \\ \Delta_r G^\circ (298.15 \text{ K}) &= +28.4 \pm 28.4 \text{ kJ/mol} \text{ [for reaction (11)]} \end{aligned}$$

As it is possible to see, all compounds do not react with  $\text{H}_2\text{O}$  (g), i.e., they are stable with respect to interaction  $\text{H}_2\text{O}$  (g). As to reactions with  $\text{CO}_2$ , two compounds ( $\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}$ ,  $\text{Bi}_{12.5}\text{Y}_{1.5}\text{ReO}_{24.5}$ ) do not react with  $\text{CO}_2$ , but  $\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}$  reacts with  $\text{CO}_2$ . The fact that the  $\text{Bi}_{12.5}\text{R}_{1.5}\text{ReO}_{24.5}$  compounds do not react with  $\text{H}_2\text{O}$  (g) is unusual and these compounds are perspective for application. It is better to apply the  $\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}$ ,  $\text{Bi}_{12.5}\text{Y}_{1.5}\text{ReO}_{24.5}$  phases because they also do not react with  $\text{CO}_2$ .

As a conclusion, it was established that all the compounds are thermodynamically stable with respect to the decomposition to binary oxides. It is also interesting to study the thermodynamic stability of the  $\text{Bi}_{12.5}\text{R}_{1.5}\text{ReO}_{24.5}$  compounds with respect to mixtures including other stable ternary oxides in subsystems  $\text{Bi}_2\text{O}_3\text{–R}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3\text{–Re}_2\text{O}_7$ ,  $\text{R}_2\text{O}_3\text{–Re}_2\text{O}_7$  but there are no thermodynamic data available now on these phases.

The  $\text{Bi}_{12.5}\text{R}_{1.5}\text{ReO}_{24.5}$  phases do not react with  $\text{H}_2\text{O}$  (g),  $\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}$ ,  $\text{Bi}_{12.5}\text{Y}_{1.5}\text{ReO}_{24.5}$  do not react with  $\text{CO}_2$ , whereas  $\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}$  reacts with  $\text{CO}_2$ . The thermodynamic stability seems to increase from  $\text{Bi}_{12.5}\text{Y}_{1.5}\text{ReO}_{24.5}$  to  $\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}$  to  $\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}$ . There seems no obvious correlation between stability and the ionic conductivity (see, in detail, paper [1]). The values of ionic conductivity are:  $\text{Bi}_{12.5}\text{Y}_{1.5}\text{ReO}_{24.5}$   $1.95 \times 10^{-5} \text{ S cm}^{-1}$  at 600 K,  $\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}$   $1.10 \times 10^{-3} \text{ S cm}^{-1}$  at 600 K,  $\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}$   $2.04 \times 10^{-4} \text{ S cm}^{-1}$  at 600 K.

## 6. Conclusions

1. The enthalpies of solution of  $\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}$ ,  $\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}$ ,  $\text{Bi}_{12.5}\text{Y}_{1.5}\text{ReO}_{24.5}$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Re}_2\text{O}_7$  were measured using 2 M HCl at 298.15 K.
2. Using measured solution enthalpies of  $\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}$ ,  $\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}$ ,  $\text{Bi}_{12.5}\text{Y}_{1.5}\text{ReO}_{24.5}$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Re}_2\text{O}_7$  and literature data on standard enthalpies of  $\text{Bi}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Re}_2\text{O}_7$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$  the standard formation enthalpies of  $\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}$ ,  $\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}$ ,  $\text{Bi}_{12.5}\text{Y}_{1.5}\text{ReO}_{24.5}$  and formation enthalpies from binary oxides were calculated for the first time. It was discovered that the thermodynamic stability is increased with increasing number of rare-earth elements from  $\text{Bi}_{12.5}\text{Y}_{1.5}\text{ReO}_{24.5}$  to  $\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}$  to  $\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}$ . It was established that above compounds do not react with  $\text{H}_2\text{O}$  (g).  $\text{Bi}_{12.5}\text{Nd}_{1.5}\text{ReO}_{24.5}$  and  $\text{Bi}_{12.5}\text{Y}_{1.5}\text{ReO}_{24.5}$  do not react with  $\text{CO}_2$ , but  $\text{Bi}_{12.5}\text{La}_{1.5}\text{ReO}_{24.5}$  reacts with  $\text{CO}_2$ .

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