Heat capacity of bismuth cobalt oxides doped by neodymium and holmium in the temperature range of 319-1000 K

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Abstract. The heat capacity of bismuth cobalt oxides doped by neodymium and holmium was measured for the first time by differential scanning calorimetry in the temperature range of 319-1000 K.

1. Introduction

Compounds, based on bismuth oxide are promising materials for ecological pure technologies, new energy, oxygen ceramic generators, etc. [1-5]. One of the promising areas for the application of bismuth-based mixed oxides is premised on the high ionic conductivity of the delta form of bismuth oxide. The delta form of bismuth oxide has a cubic structure (space group Fm-3m) and is one of the most promising solid-state ionic conductors. The problem is that the delta form of bismuth oxide is stable only in the narrow temperature range from 1000 to 1100 K. To expand the stability range, the delta form of bismuth oxide is doped by elements of III, VI, VII groups, in particular, rare earth elements. Progress in the development of ecological pure technologies requires creating new materials with improved characteristics.

In our research, the bismuth cobalt oxides doped by neodymium and holmium of general formula Bi$_{12.5}$R$_{1.5}$CoO$_{22.3}$ (R = Nd, Ho) were obtained for the first time, and their thermodynamic studies were performed.

2. Experimental

Bismuth cobalt compounds with the composition of Bi$_{12.5}$Nd$_{1.5}$CoO$_{22.3}$, Bi$_{12.5}$Ho$_{1.5}$CoO$_{22.3}$ were synthesized by solid-state reaction at temperatures above 1000 K. For the synthesis of compounds, the following precursors were used: Bi$_2$O$_3$ (99.999%, NIIC SB RAS), Co$_3$O$_4$, Nd$_2$O$_3$, and Ho$_2$O$_3$ (> 99.9%, Novosibirsk Rare Metals Plant). Before the synthesis, oxides of rare earth elements (Nd$_2$O$_3$, Ho$_2$O$_3$) were calcined up to constant weight at a temperature of 900 K to remove traces of water and carbon dioxide. Further, the precursors (Bi$_2$O$_3$, Nd$_2$O$_3$, Ho$_2$O$_3$, Co$_3$O$_4$) were weighed in stoichiometric quantity, mixed in corundum glass, and milled in Fritsch Pulverisette 6 planetary mill for more than 30 h with several intermediate grinding. Next, the mixture was pressed into pallets, placed in SNOL 4/1300 furnace, and heated for more than 50 h.

The characterization of samples was carried out by X-ray, fluorescence, mass spectrometric, and chemical analyzes.
X-ray powder diffraction was performed using Shimadzu XRD-7000 diffractometer, Cu-Kα radiation. Impurities were determined by mass spectrometry.

Differential scanning calorimetry was used to measure the heat capacity of Bi\(_{12.5}\)Nd\(_{1.5}\)CoO\(_{22.3}\), Bi\(_{12.5}\)Ho\(_{1.5}\)CoO\(_{22.3}\) samples in the temperature range of 319-1000 K. DSC 404 F1 calorimeter (NETZSCH company) was used for measurements. The operation principle and measurement procedure were described in detail in papers [6-7].

### 3. Results and discussion

X-ray analysis showed that obtained phases Bi\(_{12.5}\)R\(_{1.5}\)CoO\(_{22.3}\) (R = Nd, Ho) were individual and did not contain any impurity phases. The phases were identified as cubic, fluorite structure, space group \(Fm-3m\). The phase structure was the structure of the delta form of bismuth oxide (\(\delta\)-Bi\(_2\)O\(_3\)). A typical diffraction pattern of Bi\(_{12.5}\)R\(_{1.5}\)CoO\(_{22.3}\) (R = Nd, Ho) compounds is presented in figure 1. The lattice parameter for Bi\(_{12.5}\)Ho\(_{1.5}\)CoO\(_{22.3}\) was \(a = 0.55218\) nm.

![X-ray diffraction pattern for Bi\(_{12.5}\)R\(_{1.5}\)CoO\(_{22.3}\) (R = Nd, Ho).](image)

**Figure 1.** Typical X-ray diffraction pattern for Bi\(_{12.5}\)R\(_{1.5}\)CoO\(_{22.3}\) (R = Nd, Ho).

Photoemission spectroscopy, which was performed in energy range of 775-800 eV, showed that phases Bi\(_{12.5}\)Nd\(_{1.5}\)CoO\(_{22.3}\), Bi\(_{12.5}\)Ho\(_{1.5}\)CoO\(_{22.3}\) contain 35% Co\(^{2+}\) and 65% Co\(^{3+}\).

The results of chemical analysis showed that compounds of Bi\(_{12.5}\)Nd\(_{1.5}\)CoO\(_{22.3}\), and Bi\(_{12.5}\)Ho\(_{1.5}\)CoO\(_{22.3}\) have purity of more than 99%.

The samples 5 mm in diameter and 1.5 mm thick were cut from synthesized tablets of Bi\(_{12.5}\)Nd\(_{1.5}\)CoO\(_{22.3}\) and Bi\(_{12.5}\)Ho\(_{1.5}\)CoO\(_{22.3}\) compounds to determine the heat capacity. Such samples were tightly inserted into the measurement crucible, which provided good contact with it.
The mass of samples was weighed on AND GH-252 electronic balance with an error of no more than 0.3 mg and equaled to 117.45 mg and 117.20 mg for Bi$_{12.5}$Nd$_{1.5}$CoO$_{22.3}$ and Bi$_{12.5}$Ho$_{1.5}$CoO$_{22.3}$, respectively. Before each thermal cycle, the working volume of the calorimeter was evacuated up to a vacuum of 1 Pa and flushed several times with argon, whose purity was 99.992 vol.%. Sapphire weighing 85.28 mg was used as a calibration sample. The measurements were carried out using platinum crucibles with corundum inserts and platinum caps at a heating rate of 6 K/min in a flowing argon atmosphere (20 ml/min).

The heat capacity of Bi$_{12.5}$Nd$_{1.5}$CoO$_{22.3}$ and Bi$_{12.5}$Ho$_{1.5}$CoO$_{22.3}$ was measured in the temperature range of 319-1000 K. Three thermal cycles were performed for each sample. The data on the heat capacity of samples in the first thermal cycle differed from data on the heat capacity of samples in the second and third thermal cycles. This was due to the release of stresses, existing in samples, and the removal of absorbed substances.

The heat capacity data, obtained for both samples in second and third thermal cycles were reproduced within measurement error up to ~ 800 K for Bi$_{12.5}$Nd$_{1.5}$CoO$_{22.3}$ and in the entire investigated temperature range for Bi$_{12.5}$Ho$_{1.5}$CoO$_{22.3}$. Both samples manifested anomalies associated with phase transitions.

The heat capacity of Bi$_{12.5}$Ho$_{1.5}$CoO$_{22.3}$ sample in the entire investigated temperature range is shown in figure 2.

![Figure 2. Heat capacity of Bi$_{12.5}$Ho$_{1.5}$CoO$_{22.3}$.](image)

The heat capacity of Bi$_{12.5}$Nd$_{1.5}$CoO$_{22.3}$ sample had complex behavior. The results of the third heating of the heat capacity for Bi$_{12.5}$Nd$_{1.5}$CoO$_{22.3}$ sample in the temperature range of 920-1000 K are shown in figure 3.
Figure 3. Heat capacity of Bi$_{12.5}$Nd$_{1.5}$CoO$_{22.3}$.

The temperature of maximum phase transition according to results of third heating for Bi$_{12.5}$Nd$_{1.5}$CoO$_{22.3}$ was 981 K, and for Bi$_{12.5}$Ho$_{1.5}$CoO$_{22.3}$ was 875 K.

As is seen, the phase transition temperature was decreased from bismuth cobaltate, doped by neodymium, to bismuth cobaltate, doped by holmium. It was correlated with decreasing radii of rare earth elements from Nd to Ho ($r_{\text{Nd}} = 0.0983$ nm, $r_{\text{Ho}} = 0.0901$ nm).

Earlier, using reaction calorimetry, we measured standard formation enthalpies of Bi$_{12.5}$Nd$_{1.5}$CoO$_{22.3}$ and Bi$_{12.5}$Ho$_{1.5}$CoO$_{22.3}$. The calorimeter and measurement procedure were described in the paper [8]. The thermochemical cycle to determine standard formation enthalpies for Bi$_{12.5}$Nd$_{1.5}$CoO$_{22.3}$, Bi$_{12.5}$Ho$_{1.5}$CoO$_{22.3}$ was similar to the thermochemical cycle for determining the standard formation enthalpy of Bi$_{12.5}$Er$_{1.5}$CoO$_{22.3}$, which was presented in paper [9]. Using Born-Haber cycle, based on measured standard formation enthalpies for compounds of Bi$_{12.5}$Nd$_{1.5}$CoO$_{22.3}$ and Bi$_{12.5}$Ho$_{1.5}$CoO$_{22.3}$, the lattice enthalpies for above mentioned compounds were calculated as following values: $\Delta_{\text{lat}}H$(Bi$_{12.5}$Nd$_{1.5}$CoO$_{22.3}$, 298.15 K) $= -98630$ kJ mol$^{-1}$; $\Delta_{\text{lat}}H$(Bi$_{12.5}$Ho$_{1.5}$CoO$_{22.3}$, 298.15 K) $= -99080$ kJ mol$^{-1}$. As is seen, decreasing in temperature of phase transition from Bi$_{12.5}$Nd$_{1.5}$CoO$_{22.3}$ up to Bi$_{12.5}$Ho$_{1.5}$CoO$_{22.3}$ correlated with increasing in lattice enthalpy, namely, when the lattice was becoming to be more stable, the phase transition temperature was decreasing.

4. Conclusion

For the first time, the compounds of Bi$_{12.5}$Nd$_{1.5}$CoO$_{22.3}$ and Bi$_{12.5}$Ho$_{1.5}$CoO$_{22.3}$ were synthesized by solid-state reaction. The compounds had cubic structure, space group $Fm-3m$. The heat capacity of Bi$_{12.5}$Nd$_{1.5}$CoO$_{22.3}$ and Bi$_{12.5}$Ho$_{1.5}$CoO$_{22.3}$ compounds was measured by differential scanning calorimetry in the temperature range of 319–1000 K. It was found that both compounds had phase transitions. The phase transition temperature decreased from Bi$_{12.5}$Nd$_{1.5}$CoO$_{22.3}$ up to Bi$_{12.5}$Ho$_{1.5}$CoO$_{22.3}$. This correlated with decreasing radius of rare earth elements from neodymium to holmium and also with increasing in lattice enthalpy from Bi$_{12.5}$Nd$_{1.5}$CoO$_{22.3}$ up to Bi$_{12.5}$Ho$_{1.5}$CoO$_{22.3}$.
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References
[1] Punn R, Feteira A M, Sinclair D C and Greaves C 2006 J. Am. Chem. Soc. 128 15386
[2] Dziegielewska A, Malys M, Wrobel W, Hull S, Yue Y, Krok F and Abrahams I 2021 Solid State Ionics 360 115543
[3] Mitrofanova A V, Fortalnova E A, Safronenko M G, Politova E D, Mosunov A V and Verskovskii N U 2020 Russ. J. Inorg. Chem. 65 1654
[4] Parwin S and Parui J 2021 J. Chem. Thermodyn. 156 106347
[5] Bryzgalova A N, Matskevich N I, Greaves C and Hervoches C H 2011 Thermochim. Acta 513 124
[6] Matskevich N I, Wolf T, Le Tacon M, Adelman P, Stankus S V, Samoshkin D A and Tkachev E N 2017 J. Therm. Anal. Calorim. 130 1125
[7] Matskevich N I, Wolf T, Pischur D and Kozlova S G 2016 J. Therm. Anal. Calorim. 124 1745
[8] Matskevich N I, Kuznetsov F, Feil D and Range K J 1998 Thermochim. Acta 319 1
[9] Matskevich N I, Kellerman D G, Gelfond N V, Zaitsev V P and Martynetz V G 2020 Russ. J. Inorg. Chem. 65 720