

УДК 536.63

High-Temperature Heat Capacity of Bismuth Oxide and Bismuth-Zinc Double Oxide with the Sillenite Structure

Liliy A. Irtyugo, Nataliy V. Belousova,
Viktor M. Denisov*, Liubov T. Denisova,
Sergei D. Kirik and Liubov G. Chumilina
*Siberian Federal University
79 Svobodny, Krasnoyarsk, 660041 Russia ¹*

Received 05.06.2012, received in revised form 12.06.2012, accepted 19.06.2012

Experimental data on the heat capacity of bismuth oxide and bismuth-zinc double oxide with the sillenite structure (446-939 K) were presented.

Keywords: bismuth oxide, bismuth-zinc double oxide, heat capacity.

Introduction

Bismuth oxide and Bi₂O₃-based compounds are of practical importance in view of their valuable properties and for a long time attract considerable attention of scientists [1 – 4]. At the same time, there are certain problems relating to the obtaining materials. It is attributed to the fact that many Bi₂O₃-based oxide compounds can be in metastable state [4 – 6]. Phase equilibria in such systems can be improved with the use of thermodynamic modeling. To do this would require data on the thermodynamic properties of original oxides as well as complex oxide compounds over a wide temperature interval. Although Bi₂O₃-based compounds are used extensively, their properties call for additional investigations. In the first place, this is true for pure Bi₂O₃. It forms α , β , γ and δ polymorphous modifications in different temperature ranges [7].

By now there are data on the heat capacity of Bi₂O₃. The values of C_p for this oxide at 298-800 K are given in [8] by Eq. (1), J/(mole·K):

$$C_p = a + bT - cT^{-2}, \quad (1)$$

where $a = 103,60$; $b = 33,50 \cdot 10^{-3}$; $c = 0$. From this equation it follows that C_p is a linear function of the temperature.

* Corresponding author E-mail address: antluba@mail.ru

¹ © Siberian Federal University. All rights reserved

V.E. Gorbunov et al [9] have studied the heat capacity of Bi_2O_3 at 11-50 K with the use of an adiabatic microcalorimeter. Based on these results and the data of other researchers, they obtained smoothed values of the thermodynamic functions of Bi_2O_3 to $T = 298,15$ K: $C_{p298,15} = 113,4$ J/(mole·K); $H_{298,15}^\circ - H_0^\circ = 21530$ J/mole; $S_{298,15}^\circ - S_0^\circ = 150,0$ J/(mole·K). It should be noted that the close values of $C_{p298,15} = 113,804 \pm 1,255$ J/(mole·K) and $S_{298,15}^\circ - S_0^\circ = 151,460 \pm 4,184$ J/(mole·K) were presented in [10]. At the same time, different value of the enthalpy was given in [10]: $H_{298,15}^\circ - H_0^\circ = 13054,08 \pm 209,2$ J/mole. The cause of such difference in the magnitude of the enthalpy is only stated by the authors of [9].

To obtain consistent results on the thermodynamic properties of Bi_2O_3 , O. V. Kuznetsova et al [11] used data on the low-temperature heat capacity (11 – 300 K) [7, 9, 10, 12] and high-temperature ones (400 – 800 K) [13] which were processed by the Reshetnikov's function [14].

We found no information on direct calorimetric measurements of C_p in the range of temperatures from 400 to 1003 K (to the $\alpha \rightarrow \delta$ phase transition temperature (1003 K [4])).

The thermodynamic properties of $\text{Bi}_2\text{O}_3 - \text{ZnO}$ system were investigated by S. Serena et al [15], but the aim of that work was the thermodynamic analysis of the $\text{Bi}_2\text{O}_3 - \text{ZnO}$ phase diagram in the field of Bi_2O_3 .

The purpose of the present work is to measure the heat capacity of Bi_2O_3 at 403 – 960 K and $\text{Bi}_{12}(\text{Bi}_{0,67}\text{Zn}_{0,33})\text{O}_{19,33}$ at 446 – 939 K.

Experimental procedure

$\text{Bi}_{12}(\text{Bi}_{0,67}\text{Zn}_{0,33})\text{O}_{19,33}$ ceramics was obtained by the solid-phase sintering with matching optimal regime. The total time of the synthesis at 1008 K was 45 hours. 9 intermediate grindings were performed, accompanied by the pressing. X-ray diffraction (XRD) data were collected on a PANalytical X'Pert Pro powder diffractometer ($\text{CuK}\alpha_{1,2}$ radiation). The record was carried out with the use of a high-speed PIXcel detector and a graphite monochromator in an angle range of $5 - 80^\circ 2\theta$ with the pitch angle of $0,026^\circ$. The identification was performed by PDF-ICDD [Powder diffraction file sets 1-58. JCPDS-ICDD, Pennsylvania 19073-3273 USA]. The lattice parameters were refined by the profile-fitting method (Le Beil method): $a = 10,2030(1)$ Å, $V = 1062,14$ Å³, space group I23. These data are in agreement with those obtained previously [4]. Fig 1 shows a XRD pattern of $\text{Bi}_{12}[\text{Bi}_{0,67}\text{Zn}_{0,33}]\text{O}_{19,33}$ sample.

The heat capacity (C_p) measurements were carried out in platinum crucibles by the differential scanning calorimetry with a STA 449 C Jupiter device (NETZSCH). The experimental procedure was similar to described one [16, 17].

Results and discussion

The C_p temperature dependence of bismuth oxide is presented in Fig. 2. It can be seen that, in the temperature range under investigation, the values of C_p increase regularly and the dependence $C_p = f(T)$ does not exhibit any extrema. Near 1000 K the magnitudes of C_p rise sharply and a jump of C_p is observed at the $\alpha \rightarrow \delta$ phase transition temperature (not shown in Fig. 2). The smoothed values of $C_p = f(T)$ can be described by Eq. 2, J/(mole·K):

$$C_p = 113,79 + 24,46 \cdot 10^{-3} T. \quad (2)$$

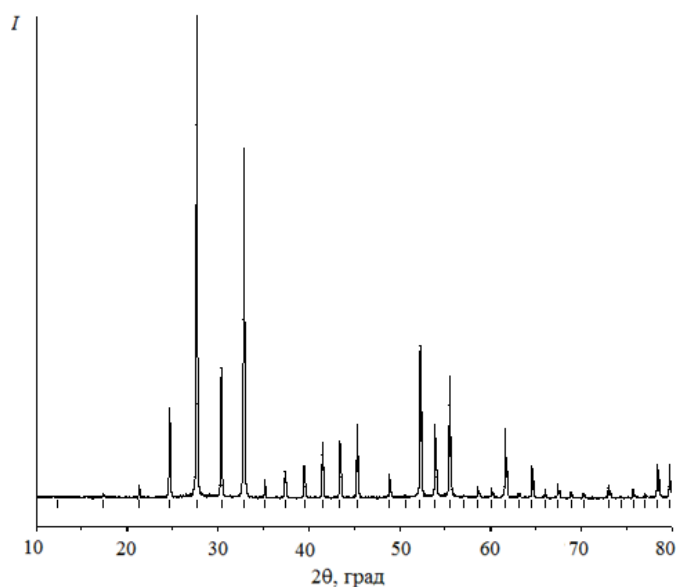


Fig. 1. XRD pattern of $\text{Bi}_{12}[\text{Bi}_{0.67}\text{Zn}_{0.33}]\text{O}_{19.33}$ sample

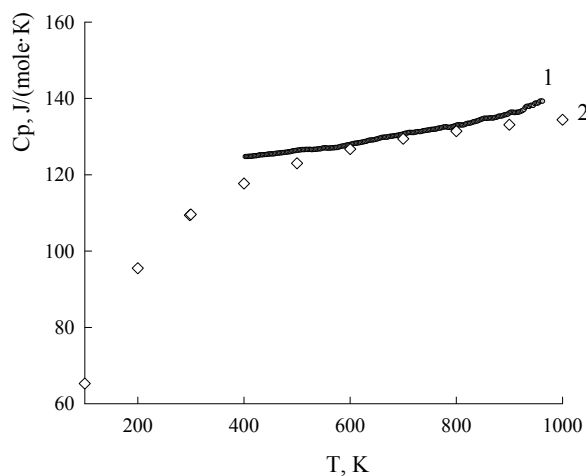


Fig. 2. Influence of the temperature on the heat capacity of Bi_2O_3 . 1 – our data, 2 – [11]

The comparison of this expression and Eq. 1 shows that they differ slightly. It is not inconceivable that this fact is accounted for the different temperature interval: 298-800 K (Eq. 1) and 403 – 960 K (Eq. 2). At the same time our experimental values of C_p agree satisfactory with those calculated in [11] (Fig. 2).

Data on the heat capacity of $\text{Bi}_{12}(\text{Bi}_{0.67}\text{Zn}_{0.33})\text{O}_{19.33}$ is presented in Fig. 3. The values of C_p are seen to increase almost linearly with increased temperature. The obtained temperature dependence of C_p takes the form, $\text{J}/(\text{mole}\cdot\text{K})$:

$$C_p = 726,54 + 155,78 \cdot 10^{-3} T. \quad (3)$$

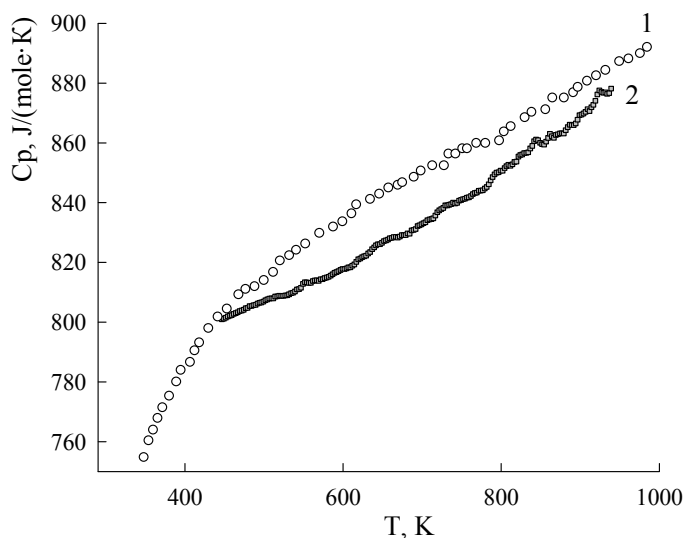


Fig. 3. The temperature dependence of the $\text{Bi}_{12}[\text{Bi}_{0.67}\text{Zn}_{0.33}]\text{O}_{19.33}$ heat capacity. 1 – [18], 2 – our data

A comparison of our data with the results obtained in [18] demonstrates (Fig. 3) that they are reasonably close but our values are slightly below.

According to the equilibrium diagram, $\text{Bi}_{12}(\text{Bi}_{0.67}\text{Zn}_{0.33})\text{O}_{19.33}$ compound melts incongruently [15, 19] (data of [19] are shown in Fig. 4). Because of this, G.S. Suleimenova and V.M. Skorikov obtained single crystals of this compound from Bi_2O_3 -based solution-melt [18]. As noted in the process, the crystals can contain impurities of a metastable phase (δ^* -phase of Bi_2O_3) as a result of some excess of Bi_2O_3 in the initial mix stipulated by the techniques of the crystal growing from the solution-melt and by the melt superheating. This is likely to be responsible for the difference between our data and the values presented in [18] (Fig. 3).

Discussing $\text{Bi}_{12}\text{M}_x\text{O}_{20\pm\delta}$ crystals having a sillenite structure the authors of [18] supposed that a lattice contribution in the heat capacity of $\text{Bi}_{12}\text{GeO}_{20}$ and $\text{Bi}_{12}\text{SiO}_{20}$ is less than in the case of other crystals and the values of the heat capacity is above for crystals with lattice distortions. By [4, 20], the sillenite structural type has approximately 60 individual phases, the generalized formula of which can be presented as $\text{Bi}_{12}\text{M}_x\text{O}_{20\pm\delta}$ (M are elements of the II-VIII groups of Mendeleev's periodic table). These compounds crystallize in the cubic system (space group I23, SG № 197). $\text{Bi}_{12}\text{GeO}_{20}$ has an “ideal” lattice but the rest of the crystals contain structural defects. The greatest disorder was noticed for the lattice of compounds with M^{3+} and M^{2+} cations, in which 1/2 or 2/3 of the regular $[\text{MO}_4]$ -tetrahedra are substituted by the umbrella-type $[\text{BiO}_3\text{E}]$ groups with the simultaneous formation of oxygen vacancies and the occurrence of $[\text{BiO}_4\text{E}]$ polyhedra [20].

It may be suggested that the aforesaid conditions a specific character of the heat capacity of sillenites including $\text{Bi}_{12}(\text{Bi}_{0.67}\text{Zn}_{0.33})\text{O}_{19.33}$.

Conclusion

Data on the high-temperature heat capacity of Bi_2O_3 (403 – 960 K) and $\text{Bi}_{12}(\text{Bi}_{0.67}\text{Zn}_{0.33})\text{O}_{19.33}$ (446 – 939 K) were refined and extended.

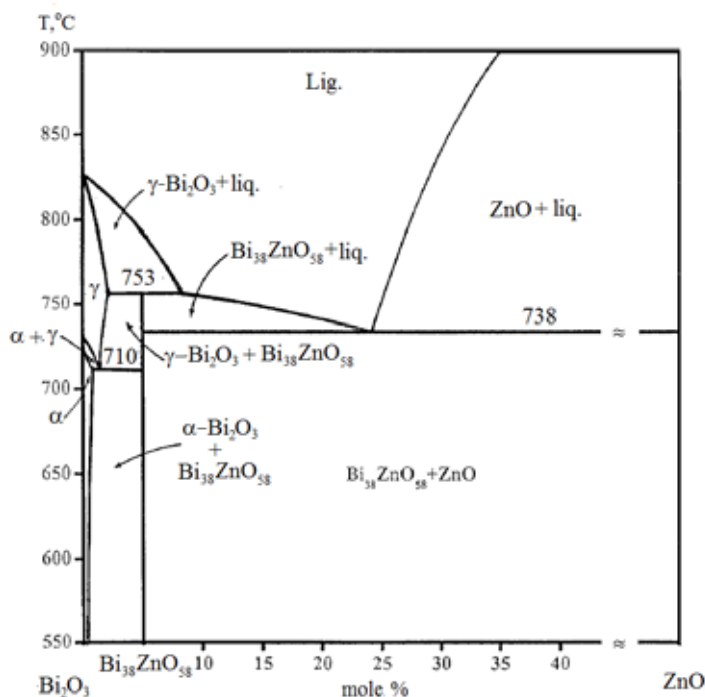


Fig. 4. The phase diagram of Bi₂O₃ – ZnO system

References

1. Moiseev G.K., Vatolin N.A., Belousova N.V. Modeling of the synthesis of bismuth oxides // Russ. J. Phys. Chem. 2000. V. 74. № 9. P. 1415-1423.
2. Denisov V. M., Belousova N. V., Moiseev G. K., Bakhvalov S. G., Istomin S. A., E. A. Pastukhov, *Bismuth-Containing Materials: Structure and Physicochemical Properties* / Yekaterinburg: Ural Branch of the Russian Academy of Sciences, 2000, 526 p. [in Russian].
3. Yukhin Yu. M. and Mikhailov Yu. I., *Chemistry of Bismuth-Containing Compounds and Materials* / Novosibirsk: Siberian Branch of the Russian Academy of Sciences, 2001, 360 p. [in Russian].
4. Kargin Yu. F., Burkov V. I., Mar'in A. A., and Egorysheva A. V. Crystals Bi₁₂M_xO_{20±δ} with the Sillenite Structure: Synthesis, Structure, and Properties / Moscow: MFTI, 2004. 316 p. [in Russian].
5. Zhereb V.P. *Metastable Equilibria Bismuth-Containing Oxide Systems* Moscow: MAKSPress, 2003, 162 p. [in Russian].
6. Zhereb V.P., Skorikov V.M. Metastable states in bismuth-containing oxide systems // Inorganic Materials. 2003. V. 39. Suppl. 2. P. S121-S145.
7. Harwig N.A., Gerards A.G. The polymorphism of bismuth sesquioxide // Thermochim. Acta. 1979. V. 28. № 1. P. 121-131.
8. *The Oxide Handbook* / Ed. by G. V. Samsonov. Moscow: Metallurgiya, 1978. 472 p.; Springer, Berlin, 1982).
9. Gorbunov V.E., Gavrichev K.S., Sarakhov V.A., Lazarev V.B. Thermodynamic functions of Bi₂O₃ in the temperature range 11-298 K // Russ. J. Inorg. Chem. 1981. V. 26. № 2. P. 297.

10. *Thermal constants of substances*. Issues 1-10 / Ed. by V.P. Glushko. Moscow: VINITI, 1965-1981.
11. Kuznetsova O. V., Semenikhin V. I., Rudnyi E. B., Sidorov L. N. Determination of the Enthalpy of Formation of BiO^\cdot and BiO_2^\cdot by the Method of Ion-Molecule Equilibria // *Zh. Fiz. Khim.* 1992. V. 66. № 12. P. 3160-3165 [in Russian].
12. Levin E.M., Roth R.S. Polymorphism of bismuth sesquioxide. I. Pure Bi_2O_3 // *J. Res. Nat. Bur. Stand.* 1964. V. 68A. № 2. P. 189-195.
13. Barin I., Knake O. Thermochemical properties of inorganic substances. Heidelberg; N.Y.: Springer Verlag. 1973.
14. Reshetnikov M.A. Equation for corundum heat capacity from 0 to 2000° // *Zh. Neorg. Chim.* 1969. V. 11. № 7. P. 1489-1496 [in Russian].
15. Serena S., De La Rubia M.A., Caballero A.C. et al. Thermodynamic study of the rich- Bi_2O_3 region of the Bi_2O_3 -ZnO system // *Bol. Soc. Esp. Ceram.* 2006. V. 45. № 3. P. 150-153.
16. Denisov, V.M., Irtyugo, L.A., and Denisova, L.T., High-Temperature Heat Capacity of Oxides in the GeO_2 -PbO System // *Phys. Solid State*. 2011. V. 53. № 4. P. 689-693.
17. Denisova L.T., Irtyugo L.A., Denisov V.M., Biront V.S. Heat capacity, thermal conductivity and thermal extension of $\text{Bi}_{12}\text{SiO}_{20}$ single crystals // *J. Sib. Fed. Univ. Eng. & Technologies*. 2010. V. 3. № 2. P. 214-219 [in Russian].
18. Suleimenova G.S., Skorikov V.M. Thermochemical study of gamma bismuth oxide based single crystals // *Thermochim. Acta*. 1992. V. 196. P. 203-211.
19. Guha J.P., Kulnej S., Suvorov D. Phase equilibrium relations in the binary system Bi_2O_3 -ZnO // *J. Mater. Sci.* 2004. V. 39. P. 911-918.
20. Avdeev G., Milenov T., Egorysheva A., Petrov K., Skorikov V., Titorenkova R., Rafailov P. Crystal structure of $\text{Bi}_{36}\text{MgP}_2\text{O}_{60-\delta}$ // *Russ. J. Inorg. Chem.* 2011. V. 56. № 6. P. 913-918.

Высокотемпературная теплоемкость оксида висмута и висмут цинкового оксида со структурой силленита

**Л.А. Иртюго, Н.В. Белоусова, В.М. Денисов,
Л.Т. Денисова, С.Д. Кирик, Л.Г. Чумилина**
*Сибирский федеральный университет
Россия 660041, Красноярск, пр. Свободный, 79*

Получены экспериментальные данные теплоемкости для оксида висмута и висмут цинкового оксида со структурой силленита (446-939 K).

Ключевые слова: оксид висмута, висмут цинкового оксида, теплоемкость.
