

THE FORMATION AND STABILITY OF A BODY-CENTERED-CUBIC γ -Bi₂O₃ SOLID SOLUTION IN THE Bi₂O₃-ZnO SYSTEM**Špela Kunej, Jyoti P. Guha, and Danilo Suvorov***Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia**Received 22-12-2003***Abstract**

Minor additions of ZnO to Bi₂O₃ result in the transformation of the face-centered-cubic crystal structure of the high-temperature polymorph of Bi₂O₃ to a body-centered-cubic solid solution (γ -Bi₂O₃). In the binary system Bi₂O₃-ZnO, the b.c.c.-solid solution exists in the Bi₂O₃-rich part of this system and extends to a composition of 1.5 mol% ZnO. Beyond the solid-solubility limit, the solid solution coexists with a binary compound Bi₃₈ZnO₅₈. On cooling below 700 °C, the γ -Bi₂O₃ solid solution transforms to the low-temperature monoclinic polymorph α -Bi₂O₃ and Bi₃₈ZnO₅₈.

Key words: γ -Bi₂O₃, solid solution, Bi₂O₃-ZnO system

Introduction

Bismuth oxide, Bi₂O₃ is known to occur in several polymorphic forms with different crystal structures. The room-temperature polymorph, commonly known as α -Bi₂O₃, has a monoclinic structure that transforms into a high-temperature polymorph with a face-centered-cubic structure, referred to as δ -Bi₂O₃. The stability of these polymorphic forms of Bi₂O₃ is known to depend on various conditions such as temperature, thermal treatment and chemical doping, etc.^{1,2} Thus, minor doping of Bi₂O₃ with various oxides results in the formation of a body-centered-cubic solid solution (b.c.c), referred to as γ -Bi₂O₃. The b.c.c. phase of Bi₂O₃ has the space group *I*23 and $a_0 \approx 10 \text{ \AA}$, and is known to possess a sillenite-type crystal structure.^{2,3} For pure Bi₂O₃ this sillenite crystal structure is metastable, but under controlled cooling the crystal structure can be stabilized with minor additions of several cations, such as Si⁴⁺, Ge⁴⁺, Ti⁴⁺, etc.^{3,4,5} In general, compounds with a sillenite structure are represented by the stoichiometric composition Bi₁₂MO₂₀, where M is a cation of the additive oxide or a combination of oxide cations.^{2,6} However, in a recent publication by Valant and Suvorov,⁷ the sillenite composition has been corrected to Bi₁₂(Bi_{4/5-nx}Mⁿ⁺_{5x})O_{19.2+nx}. The sillenite phases display a variety of physical properties, and can, as result, be used in a variety of

electro-optic, acoustic and piezotechnics applications.^{8,9,10} Recently, sillenites have been used as dielectric materials in microwave-electronic technology.¹³ The major advantage of these materials compared to other microwave dielectric materials is their low sintering temperature (≤ 850 °C), which allows the application of these materials in low-temperature cofired ceramic (LTCC) technology. The low sintering temperature also means that silver, with a melting point of 960 °C, can be used as an electrode material for these dielectrics. One of the problems accompanying the firing of LTCCs is the formation of several unwanted phases during sintering.¹⁴ In microwave applications of LTCC in the form of tapes, it is necessary to minimize the number of phases in order to simplify the system. When co-firing an LTCC module that is composed of more than one type of ceramic layer, all the different layers must be compatible in terms of properties such as sintering parameters, thermal expansion coefficients and a chemical compatibility between all the ceramic materials in the system, as well as between all the materials present in the LTCC and the electrode. Thus, a basic understanding of the compatibility relations between the various phases that form during firing is essential.

Previous studies of the Bi_2O_3 -ZnO system have reported somewhat contradictory results regarding the formation and stability of the binary compounds that occur in this system. The Bi_2O_3 -ZnO phase diagram reported by Levin and Roth¹⁵ shows a binary compound with a chemical composition close to $6\text{Bi}_2\text{O}_3:\text{ZnO}$. This compound, which has a body-centered-cubic structure, was found to melt congruently at approximately 800 °C. Furthermore, this phase diagram shows the presence of a eutectic between Bi_2O_3 and the $6\text{Bi}_2\text{O}_3:\text{ZnO}$ compound at a composition close to 8 mol% ZnO, with a melting point of 750 °C. Safronov et al.¹⁶ reported a phase diagram of the system Bi_2O_3 -ZnO in which a binary compound with the chemical composition $\text{Bi}_{48}\text{ZnO}_{73}$ ($24\text{Bi}_2\text{O}_3:\text{ZnO}$) was shown to occur. In contrast to the study reported by Levin and Roth,¹⁵ this compound was found to melt incongruently at 750 °C. In the Safronov phase diagram a binary eutectic between $\text{Bi}_{48}\text{ZnO}_{73}$ and ZnO was shown to occur at a composition close to 14 mol% ZnO with a melting point of 740 °C. However, no solid solution was shown to exist at the Bi_2O_3 -end of the Bi_2O_3 -ZnO system. Bruton et al.¹⁷ prepared single crystals from the Bi_2O_3 -ZnO system using the top-seed solution technique and reported the existence of a compound with the chemical composition $\text{Bi}_{16}\text{ZnO}_{25}$ ($8\text{Bi}_2\text{O}_3:\text{ZnO}$). The

compound was found to melt congruently at 760 °C and form two eutectics: one at a composition close to 9 mol% and the other at 12 mol% ZnO, with melting points of 745 °C and 740 °C, respectively. However, Wang and Morris¹⁸, who have investigated several compositions in this system, observed the formation of a compound with a Bi₂O₃/ZnO molar ratio of 20:1. Subsequent crystal-structure studies reported by several workers^{4,6,19} have shown the existence of a binary compound in the system Bi₂O₃-ZnO with the chemical formula Bi₃₈ZnO₅₈ (19Bi₂O₃:1ZnO). In contrast to the previously reported Bi₂O₃-ZnO phase diagrams, we have observed the formation of a body-centered-cubic solid solution in the Bi₂O₃-rich area of this system. The results reported in this study primarily deal with the nature and formation of this solid solution and its compatibility with the binary compounds that occur in this system.

Experimental

The samples were prepared using the solid-state reaction technique and high-purity (>99.99%) powders of Bi₂O₃ and ZnO. Before weighing, the powders were dried at 400 °C for several hours to remove any moisture present in the materials. Several specimens with the general composition (1-x)Bi₂O₃:xZnO, where x = 0–0.1, were prepared from the Bi₂O₃ and ZnO powders. The powders were weighed with an accuracy of ±0.0002, mixed in an agate mortar with acetone, and then pressed into pellets. The pellets were placed in an Al₂O₃ crucible over an Au-foil and calcinated at 700–730 °C for 4–5 hours with intermediate cooling, crushing, mixing and pressing to achieve homogeneity. Some of the calcinated specimens were heat-treated at 700–780 °C. The phases present in the calcinated and heat-treated specimens were determined by X-ray powder diffraction (XRD) (ENDEAVOR D4, Bruker axs) using CuK α radiation at a scanning rate of 0.02°/2s and 2 θ = 10–70°. The microstructures and individual phases of the heat-treated specimens were examined using scanning electron microscopy (SEM) (Jeol JXA840A, Japan) combined with energy-dispersive spectroscopy (EDS) (Tracor Northern, Model NORAN Series II, USA). Prior to the microstructure examination, the specimens were first ground, then polished with 1 μ m diamond paste, and finally etched in a HNO₃-HF-water solution.

Results and discussion

The Bi_2O_3 -ZnO binary phase diagram proposed by Safronov et al.¹⁶ (Figure 1) shows a compositional area located between Bi_2O_3 and $\text{Bi}_{48}\text{ZnO}_{73}$ below 740 °C, in which the low-temperature monoclinic α - Bi_2O_3 coexists with $\text{Bi}_{48}\text{ZnO}_{73}$. However, no solid solution is shown in the Bi_2O_3 -rich area of this phase diagram.

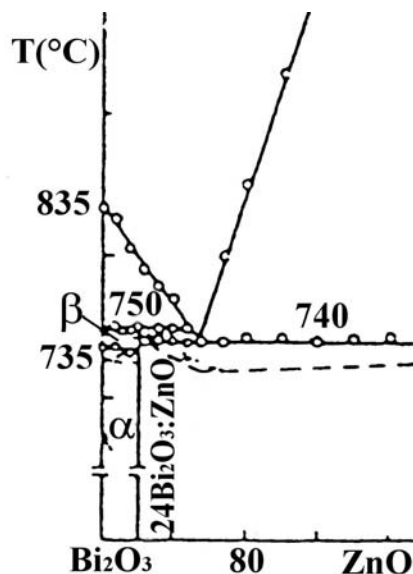


Figure 1. Equilibrium phase diagram of the Bi_2O_3 -ZnO system (Safronov et al.¹⁶).

In our study, an effort was made to stabilize the high-temperature f.c.c.-based crystal structure of the δ - Bi_2O_3 polymorph with minor additions of ZnO. The XRD results indicated that a small amount ZnO enters into the f.c.c. δ - Bi_2O_3 lattice to form a solid solution with a b.c.c.-based, γ - Bi_2O_3 crystal structure. The XRD patterns of several samples containing various proportions of Bi_2O_3 and ZnO that were heat-treated at 700–750 °C are shown in Figure 2. The solid-solubility limit of ZnO in Bi_2O_3 , as evident from the XRD and SEM analyses of several compositions, extends to a composition of 1.5 mol% ZnO.

An SEM micrograph of a sample containing 1.5 mol% ZnO, which was fired at 750 °C and quenched to room temperature, is shown in Figure 3. The microstructure shows a near-single-phase γ - Bi_2O_3 solid solution with a small amount of $\text{Bi}_{38}\text{ZnO}_{58}$ at the grain boundaries.

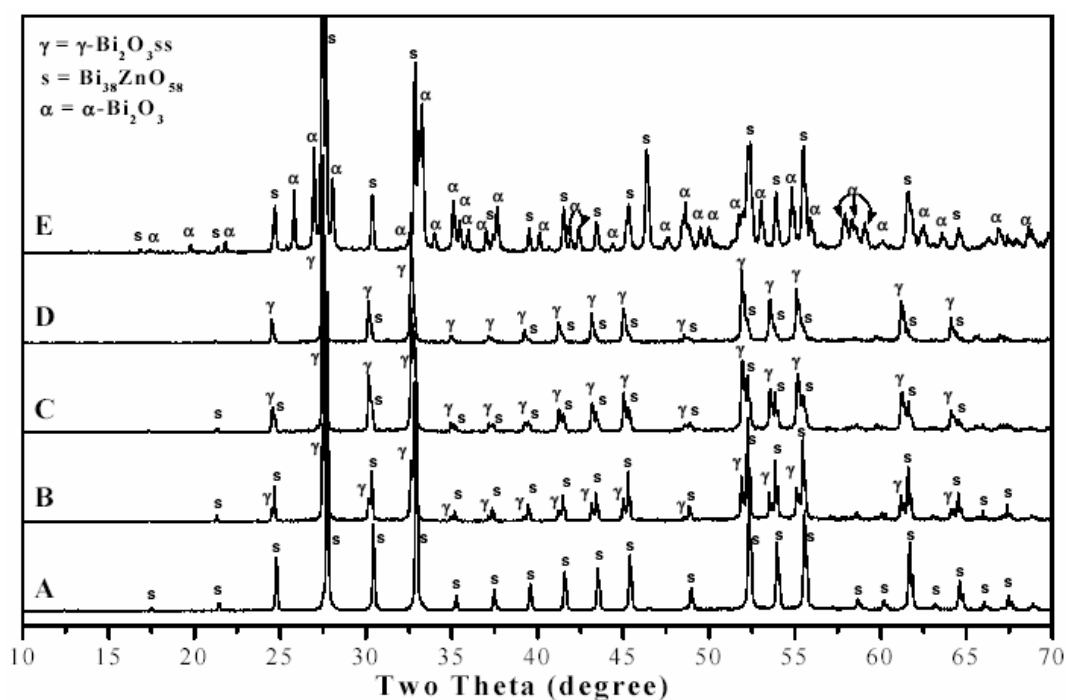


Figure 2. XRD patterns of a series of binary compositions containing: **A)** compound $\text{Bi}_{38}\text{ZnO}_{58}$, **B)** 3.5 mol% ZnO, **C)** 2 mol% ZnO; heat-treated at 740 °C and quenched to room temperature, and **D)** 1.5 mol% ZnO; heat-treated at 750 °C and quenched to room temperature, **E)** 2 mol% ZnO; heat-treated at 740 °C and slowly cooled ($\gamma = \gamma\text{-Bi}_2\text{O}_3,ss$; $s = \text{Bi}_{38}\text{ZnO}_{58}$; $\alpha = \alpha\text{-Bi}_2\text{O}_3$).

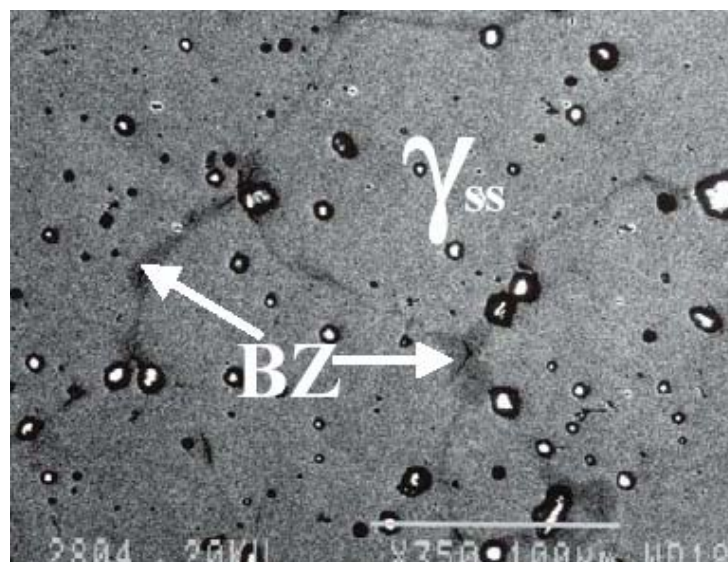


Figure 3. SEM backscattered micrograph of a sample with 1.5 mol% ZnO, heat-treated at 750 °C and quenched to room temperature ($\gamma_{ss} = \gamma\text{-Bi}_2\text{O}_3,ss$ and $BZ = \text{Bi}_{38}\text{ZnO}_{58}$).

It is evident from these XRD patterns (Figures 2a-d) that the b.c.c-based $\gamma\text{-Bi}_2\text{O}_3$ solid solution has a similar crystal structure to that of the compound $\text{Bi}_{38}\text{ZnO}_{58}$. As a

result, it is difficult to distinguish the solid solution from the compound by an XRD analysis of the heat-treated samples. However, the microstructure examination of several samples clearly shows the existence of two different phases. An SEM micrograph of a sample containing 2 mol% of ZnO that was fired at 740 °C and quenched to room temperature is shown in Figure 4. The microstructure shows two phases: i.e., the γ -Bi₂O₃ solid solution and Bi₃₈ZnO₅₈.

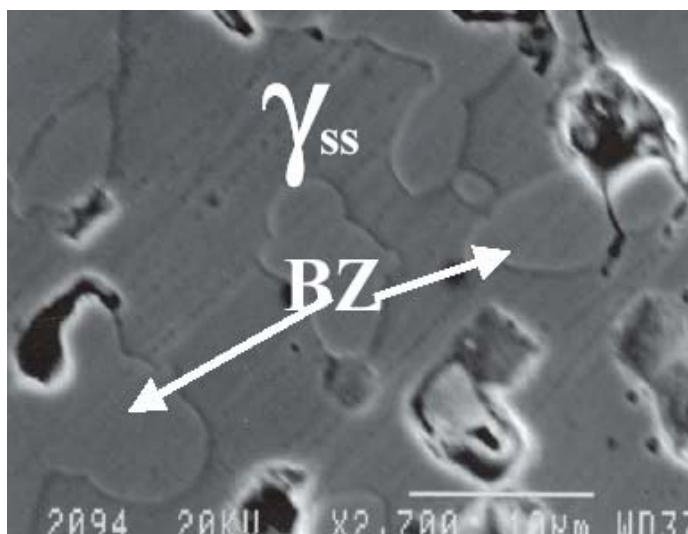


Figure 4. SEM micrograph of a sample with 2 mol% ZnO, heat-treated at 740 °C and quenched to room temperature (γ_{ss} = γ -Bi₂O_{3,ss} and **BZ** = Bi₃₈ZnO₅₈).

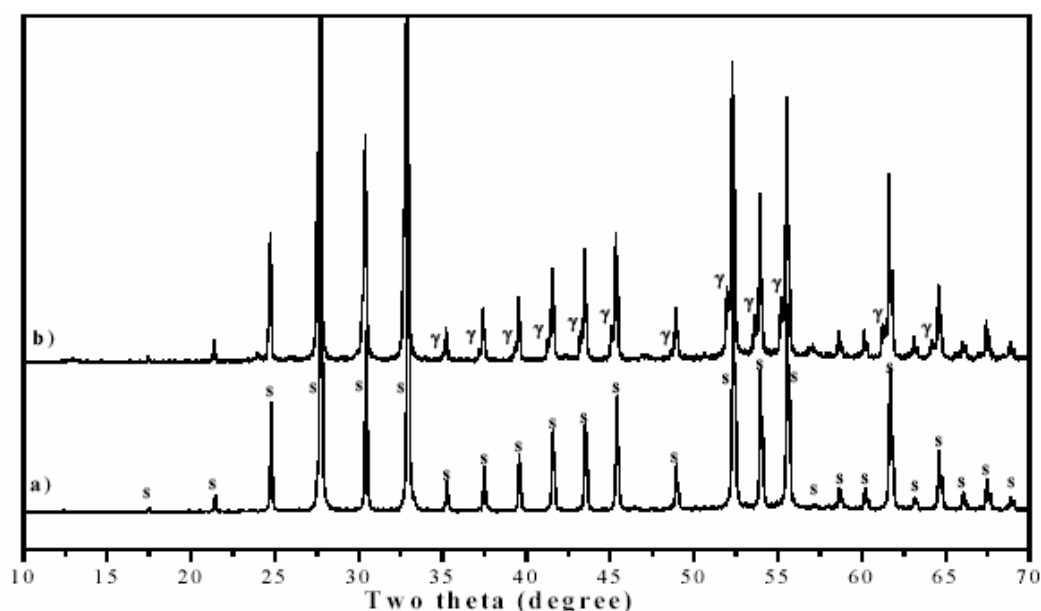


Figure 5. XRD patterns of Bi₃₈ZnO₅₈ at temperature a) 740 °C and b) 755 °C (γ = γ -Bi₂O_{3,ss} and s = Bi₃₈ZnO₅₈).

The XRD patterns of $\text{Bi}_{38}\text{ZnO}_{58}$, which was obtained after firing at 740–755 °C, are shown in Figure 5. It was found from these XRD patterns that the $\text{Bi}_{38}\text{ZnO}_{58}$ compound melts incongruently at 755 °C to form the $\gamma\text{-Bi}_2\text{O}_3$ solid solution and a liquid. This result supports the earlier literature data.^{5,16}

The XRD patterns of several samples indicated that the $\gamma\text{-Bi}_2\text{O}_3$ solid solution is not stable when cooled to room temperature. Thus, the samples that were fired at 750 °C and then slowly cooled to room temperature revealed the presence of $\alpha\text{-Bi}_2\text{O}_3$ and $\text{Bi}_{38}\text{ZnO}_{58}$. The XRD pattern of a sample containing 2 mol% ZnO is shown in Figure 2e. The evidence obtained in our study indicated that on cooling to room temperature the b.c.c.-based $\gamma\text{-Bi}_2\text{O}_3$ transforms to the low-temperature monoclinic $\alpha\text{-Bi}_2\text{O}_3$ and $\text{Bi}_{38}\text{ZnO}_{58}$. The various results obtained in our study seem to differ significantly from those proposed by Safronov et al.¹⁶ for the $\text{Bi}_2\text{O}_3\text{-ZnO}$ binary phase diagram (Figure 1). First, the formation of the $\gamma\text{-Bi}_2\text{O}_3$ solid solution at the Bi_2O_3 -end is not shown in the phase diagram. Second, a two-phase-field area between the $\gamma\text{-Bi}_2\text{O}_3$ solid solution and the $\text{Bi}_{38}\text{ZnO}_{58}$ compound occurs in this system. Unlike the previously reported melting of this compound,^{15,17} $\text{Bi}_{38}\text{ZnO}_{58}$ melts incongruently at 755 °C. Thus, it is apparent from the various results obtained in this study that a revision of the $\text{Bi}_2\text{O}_3\text{-ZnO}$ phase diagram must be undertaken to take into account these new findings.

Conclusions

Minor additions of ZnO to the f.c.c Bi_2O_3 ($\delta\text{-Bi}_2\text{O}_3$) result in the formation of a b.c.c.-based solid solution ($\gamma\text{-Bi}_2\text{O}_3$) at the Bi_2O_3 -rich end of the $\text{Bi}_2\text{O}_3\text{-ZnO}$ system. The solid solubility is limited to the composition 1.5 mol% ZnO. The $\text{Bi}_{38}\text{ZnO}_{58}$ compound melts incongruently at 755 °C to form the $\gamma\text{-Bi}_2\text{O}_3$ solid solution and a liquid. The $\gamma\text{-Bi}_2\text{O}_3$ solid solution is stable at high temperatures, and on cooling to room temperature it transforms to the low-temperature monoclinic $\alpha\text{-Bi}_2\text{O}_3$ and $\text{Bi}_{38}\text{ZnO}_{58}$.

References

1. E. M. Levin, R. S. Roth, *J. Res. Natl. Bur. Stand.* 68A (2), **1964**, 189–195.
2. E. M. Levin, R. S. Roth, *J. Res. Natl. Bur. Stand.* 68A (2), **1964**, 197–206.
3. N. M. Sammes, G. A. Tompsett, H. Näfe, F. Aldinger, *J. Europ. Ceram. Soc.* **1999**, 19, 1801–1826.
4. D. C. Craig, N. C. Stephenson, *J. Solid State Chem.* **1974**, 15, 1–8.
5. S. Chehab, P. Conflant, M. Drache, J. C. Boivin, G. McDonald, *Mat. Res. Bull.* **2003**, 38, 865–874.
6. T. M. Bruton, J. C. Brice, O. F. Hill, P. A. C. Whiffin, *J. Crystal Growth* **1974**, 23, 21–24.

7. M. Valant, D. Suvorov, *Chem. Mater.* **2002**, *14*, 3471–3476.
8. V. Tassev, G. Diankov, M. Gospodinov, *Mat. Res. Bull.* **1995**, *30*, 1263–1267.
9. V. Tassev, G. Diankov, M. Gospodinov, *Optical Mat.* **1996**, *6*, 347–351.
10. J. Žmija, M. T. Borowiec, A. Majchrowski, H. Szymczak, T. Zayarnyuk, *Crys. Engin.* **2002**, *5*, 273–282.
11. R. Metz, H. Delalu, J. R. Vignalou, N. Achard, M. Elkhatib, *Mat. Chem. Phys.* **2000**, *63*, 157–162.
12. C.-H. Lu, N. Chyi, H.-W. Wong, W.-J. Hwang, *Mat. Chem. Phys.* **2000**, *62*, 164–168.
13. M. Valant, D. Suvorov, *J. Am. Ceram. Soc.* **2001**, *84*, 2900–904.
14. M. Valant, D. Suvorov, *Mat. Chem. Phys.* **2003**, *79*, 104–110.
15. E. M. Levin, R. S. Roth, *J. Res. Natl. Bur. Stand.* *68A* (2), **1964**, 199.
16. G. M. Safronov, V. B. Batog, T. V. Stepanyuk, P. M. Fedorov, *Russ. J. Inorg. Chem.* **1971**, *16*, 460–461.
17. T. M. Bruton, O. F. Hill, P. A. C. Whiffin, J. C. Brice, *J. Crys. Growth* **1976**, *32*, 27–28.
18. J. Wong, W. G. Morris, *Am. Ceram. Soc. Bull.* **1974**, *53*, 816–820.
19. S. F. Radaev, L. A. Muradyan, V. I. Simonov, *Acta Crystallogr. SecB: Structural Science*, **1991**, *47*, 1–6.

Povzetek

Dodatek ZnO k visoko temperaturni modifikaciji Bi_2O_3 , ki ima ploskovno centrirano celico, omogoča nastanek $\gamma\text{-Bi}_2\text{O}_3$ trdne raztopine s telesno centrirano celico. Ugotovili smo, da trdna raztopna $\gamma\text{-Bi}_2\text{O}_3$ obstaja do sestave 1.5 mol% ZnO v binarnem sistemu $\text{Bi}_2\text{O}_3\text{-ZnO}$. Pri presegu maksimalne trdne topnosti pa trdna raztopina soobstaja z binarno spojino $\text{Bi}_{38}\text{ZnO}_{58}$. Pri ohlajanju $\gamma\text{-Bi}_2\text{O}_3$ trdne raztopine, nastopi pri temperaturi pod 700 °C transformacija, pri kateri iz trdne raztopine nastaneta nizko temperaturna modifikacija Bi_2O_3 z monoklinsko celico in spojina $\text{Bi}_{38}\text{ZnO}_{58}$.