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Phase equilibrium relations in the binary system Bi_2O_3-ZnO

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Phase equilibria in the binary system Bi_2O_3-ZnO were studied by quenching technique. Heat-treated compositions were subjected to X-ray diffraction for phase identification, and differential thermal analysis, optical and scanning electron microscopy were used to determine the solid-liquid equilibria occurring in this system. The data thus obtained revealed that incorporation of a small amount of ZnO to the high-temperature face-centered cubic lattice of Bi_2O_3 leads to the formation of a body-centered cubic solid solution (γ-Bi_2O_3), which extends up to a composition of 2.2 mol% ZnO at a temperature near 750°C. On cooling, the γ-Bi_2O_3 solid solution undergoes a eutectoid transformation at a temperature of 710°C to yield the low-temperature monoclinic polymorph of Bi_2O_3 (α-Bi_2O_3) and $Bi_{38}ZnO_{58}$. The eutectoid occurs at a composition of 1.8 mol% ZnO. The compound $Bi_{38}ZnO_{58}$ has a crystal structure analogous to the body-centered cubic γ-Bi_2O_3 solid solution and melts incongruently at a temperature near 753 ± 2°C to yield γ-Bi_2O_3 and liquid. A binary eutectic occurs between $Bi_{38}ZnO_{58}$ and ZnO at a composition near 25 ± 1.0 mol% ZnO with a melting temperature of 738 ± 2°C. Based on the data obtained in this study, a revised phase diagram of the binary system Bi_2O_3-ZnO is proposed.
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1. Introduction

Compositions based on ZnO with minor additions of Bi_2O_3 have been, for many years, known to exhibit non-linear current voltage characteristics and are extensively used commercial as varistor materials [1–4]. In general, development of the characteristic properties of Bi_2O_3-doped ZnO varistors are attributed to several reaction products that form during processing, which remain mostly in the grain boundaries of the sintered materials. Additionally, a liquid phase is formed in the grain boundaries of the materials during processing, the presence of which in the ceramics results in an enhancement of the densification process leading to a significant microstructural change with a corresponding change in the varistor properties. Thus, a knowledge of the reaction chemistry and an understanding of the phase equilibria involved in the Bi_2O_3-ZnO system are considered to be very important for the development of the characteristic microstructures that control the final properties of the varistors.

Another area that has become technologically important in recent years is the development of glass-free low-temperature co-fired ceramics, commonly referred to as LTCC, which are mostly used for high-performance dielectric applications [5–7]. The main advantage of the Bi_2O_3-based LTCC over several known commercial products lies in their ability to render these materials into high-density products by processing at a comparatively low temperature, especially, below 1000°C. As a result, highly conductive silver and/or copper metals having low-melting temperatures can be effectively used as internal electrodes for designing and fabrication of various electronic devices.

Among the many Bi_2O_3-based compositions reported so far, those based on the compounds occurring in the ternary system Bi_2O_3-ZnO-Nb_2O_5 have received considerable attention during the last several years and become the subject of numerous investigations [8–11]. In general, these compounds, which possess an oxygen-deficient pyrochlore structure, exhibit moderately high dielectric constant (k), low dielectric losses (high Q-values) and near zero temperature coefficient of permittivity. Furthermore, with minor substitutions of several cations in the A- and B-sites of the pyrochore lattice, a wide variety of solid solutions exhibiting improved dielectric properties have been obtained [12, 13]. However, these solid solutions undergo a significant microstructural change during sintering with a corresponding change in the dielectric properties of the materials. Until now, only limited information is available on the nature of the phase assemblages that form during processing of these materials. Thus, it is apparent that certain knowledge of the phase equilibria involved in the Bi_2O_3-based systems is desirable to obtain materials with improved dielectric properties. The study reported herein, which forms a part of an investigation on phase equilibria involved in the ternary system Bi_2O_3-ZnO-Nb_2O_5, primarily deals with the binary system Bi_2O_3-ZnO.

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Earlier reported studies [14–16] on the nature and stability of a compound that occur in the Bi_2O_3-ZnO system have indicated somewhat conflicting results. For instance, Levin and Roth [14] have reported a partial phase diagram of the system Bi_2O_3-ZnO showing the existence of a body-centered cubic (b.c.c.) phase with a chemical composition $Bi_{12}ZnO_{19}$ ($6Bi_2O_3{\cdot}ZnO$). In this study, it has been shown that this b.c.c-based cubic phase melts congruently at a temperature near 750°C and forms a binary eutectic with ZnO in the system Bi_2O_3-ZnO. However, based on the data obtained by heating curves and X-ray powder diffraction of several compositions containing variable proportions of Bi_2O_3 and ZnO, Safronov *et al.* [15] have proposed a phase diagram of the system Bi_2O_3-ZnO showing the occurrence of a b.c.c-based compound with a chemical composition $Bi_{48}ZnO_{73}$ ($24Bi_2O_3$:ZnO). The compound $Bi_{48}ZnO_{73}$ melts incongruently at 750°C and forms a eutectic with ZnO at a composition near 14 mol% ZnO. Bruton *et al.* [16] and Bruton [17] have grown single crystals of a compound from melt and reported the formation of a b.c.c-based phase in this system having a composition of $Bi_{16}ZnO_{25}$ ($8Bi_2O_3$:ZnO). On the other hand, Wang and Morris [18] have carried out X-ray diffraction analysis of a number of sintered compositions in this system and confirmed the existence of a b.c.c-based compound with a composition $Bi_{48}ZnO_{73}$. Furthermore, these workers have observed that upon slow cooling and quenching to room temperature, almost all heat-treated specimens transformed into two distinctly different phases identified as α-Bi_2O_3 (the low-temperature polymorph of Bi_2O_3) and ZnO. Notwithstanding of the data reported in the aforementioned studies, Craig *et al.* [19] and Radaev *et al.* [20], who have performed crystal structure studies on this body-centered cubic phase in the system Bi_2O_3-ZnO, assigned a chemical composition $Bi_{38}ZnO_{58}$ ($19Bi_2O_3$:ZnO) to this compound. The X-ray powder diffraction pattern of this compound has also been reported in the JCPDS File for inorganic minerals and compounds [21, 22].

In the present investigation, a series of binary compositions containing variable proportions of Bi_2O_3 and ZnO were heat-treated at temperatures between 650 and 950°C and then cooled and/or quenched to room temperature in air. The specimens were analyzed by X-ray powder diffraction, thermal analysis, optical and scanning electron microscopy and the data thus obtained were used to construct a revised Bi_2O_3-ZnO phase diagram.

2. Experimental

The starting materials used in this study were Bi_2O_3 (99.975%) and ZnO (99.99%) obtained from Alfa Aesar, Karlsruhe, Germany in the form of fine powders. The as-received powders were dried at 500°C and then used for the preparation of a series of binary mixtures containing variable proportions of Bi_2O_3 and ZnO. The weighed mixtures were pressed into pellets and then placed on sacrificial discs made from the same compositions inside alumina crucibles having tightly-fitted lids. Preliminary heat-treatment of several compositions indicated that a liquid phase, identified as a eutectic with a melting temperature near 740°C, was formed which led to the segregation of a Bi_2O_3-rich liquid from the specimens. To avoid this problem, all compositions were heat-treated at 730°C for 15 h at 5 h intervals with intermittent cooling, crushing, mixing and pressing to promote homogeneity and to attain equilibrium. At the end of the heat-treatment process, the specimens were quenched to room temperature in air and the phases present were analyzed by X-ray powder diffraction (XRD) (model D-5000, Siemens Corporation, Germany). The diffraction patterns were obtained with Ni-filtered Cu K_α radiation at a scanning rate of 0.02° 2θ/min at diffraction angles (2θ) ranging from 10 to 70°.

For melting experiments, small portions of the equilibrated specimens were placed in alumina crucibles and then slowly inserted into the hot-zone of a tube furnace that has been previously heated to a predetermined temperature. The specimens were progressively heated to temperatures ranging from 750 to 950°C until complete melting was accomplished. The specimens were held at the melting temperatures for periods ranging from 15 min to 1 h, depending on the Bi_2O_3 content of the mixtures, and then cooled and/or quenched to room temperature in air. During melting, it was observed that the specimens, especially, those with a high ZnO content reacted with the alumina crucible at temperatures above 950°C. Thus, the melting experiments were restricted to a maximum temperature of 950°C. No appreciable weight-loss was observed when the specimens were melted up to this temperature.

Microstructures of both the heat-treated and melted specimens were examined by optical and scanning electron microscopy to determine the eutectic and the peritectic compositions as well as to delineate the various phase-field areas that occur in this system. For this purpose, polished and etched specimens were examined under reflected-light using an optical microscope (BX50F, Olimpus Optical Co., Japan). Selected compositions were analyzed by a scanning electron microscope (SEM) (Model 480, JEOL, Japan) equipped with an energy dispersive X-ray analyzer (EDX) (Tracor Northern, Wisconsin, USA). Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) (STA-409, Netzsch Thermal Analyzer, Selb, Germany) were performed on equilibrated specimens to determine the melting points of the eutectic and peritectic compositions and also to ascertain the solidus and the liquidus temperatures of various compositions that occur in this system. The DTA/TGA runs were carried out at a heating rate of 10°C/min. up to a maximum temperature of 950°C. For specimens with a high Bi_2O_3 content (>95 mol%), the DTA/TGA runs were restricted to a temperature below the melting point of Bi_2O_3 (825°C). The apparatus was periodically checked with the melting points of Au (1063°C) and GeO_2 (1115°C).

3. Results and discussion

3.1. Solid solubility in the Bi_2O_3-rich region of the system Bi_2O_3-ZnO

XRD patterns of a series of binary mixtures containing variable proportions of Bi_2O_3 and ZnO, which were

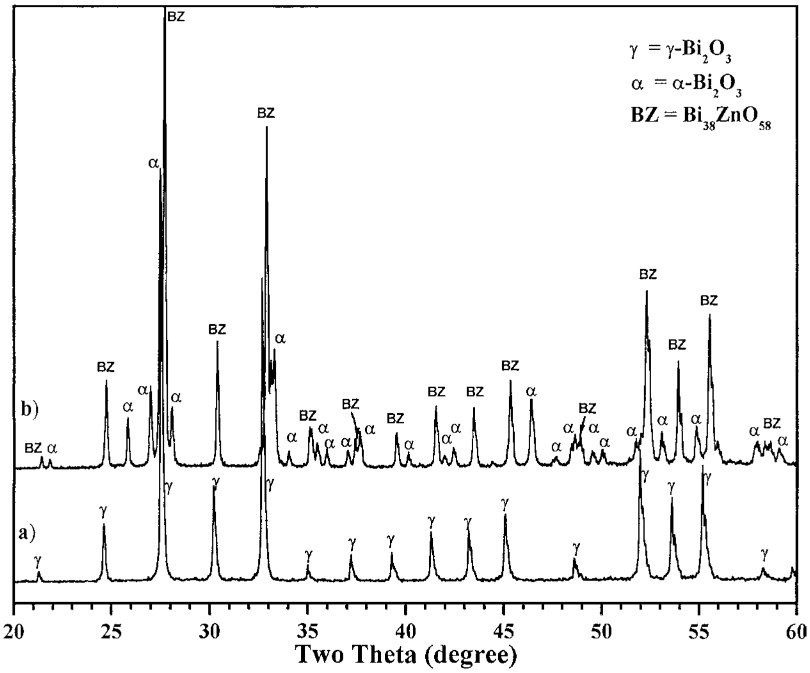

Figure 1 X-ray diffraction patterns of a composition containing 2 mol% ZnO: (a) heat-treated at 730°C for 15 h and quenched in air and (b) slowly cooled to room temperature after heat-treating at 730°C.

heat-treated at subsolidus temperatures (<738°C) and quenched to room temperature in air, indicated that a small amount of ZnO enters into the face-centered cubic (f.c.c.) lattice of the high-temperature polymorph of Bi_2O_3 (δ-Bi_2O_3) to yield a body-centered cubic (b.c.c.) solid solution, hereafter, referred to as γ-Bi_2O_3 solid solution. The extent of the solid solution was difficult to determine accurately by XRD analysis because of the narrow compositional range within which the solid solution occurs in this system. Nevertheless, SEM/EDX analyses of the heat-treated specimens containing small amounts of ZnO, ranging from 0.5 to 5 mol% ZnO, indicated that the solid solubility region extends up to a composition of 2.2 mol% ZnO. The XRD pattern of a composition containing 2 mol% ZnO, which was heat-treated at 730°C and quenched to room temperature, is shown in Fig. 1a. The XRD pattern of this specimen revealed a single-phase material consisting of b.c.c-based γ-Bi_2O_3 solid solution. When heat-treated at 730°C and then slowly cooled to room temperature (at a rate of approximately 10°C/min.), this composition was found to transform into two distinctly separate phases. From the XRD pattern as shown in Fig. 1b, these phases were identified as the low-temperature monoclinic polymorph of Bi_2O_3(α-Bi_2O_3) and $Bi_{38}ZnO_{58}$.

Microstructural examination of several compositions, which were heat-treated at temperatures between 650 and 770°C and then slowly cooled to room temperature, revealed that the γ-Bi_2O_3 solid solution undergoes a eutectoid transformation at a temperature near 700°C according to the following reaction:

$$\gamma\text{-Bi}_2\text{O}_3 \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha\text{-Bi}_2\text{O}_3 + \text{Bi}_{38}\text{ZnO}_{58}$$

A SEM micrograph of a composition containing 2 mol% ZnO, which was heat-treated at 770°C and quenched to room temperature, is shown in Fig. 2. The microstructure shows a single-phase material consisting of large and elongated grains of γ-Bi_2O_3 solid solution that seems to have developed in presence of a liquid phase. By contrast, the microstructure of the slowly cooled specimen of the same composition, as shown in Fig. 3, reveals that upon cooling through the eutectoid temperature, the single-phase γ-Bi_2O_3 solid solution has transformed into several regions or colonies composed of alternate lamellae of α-Bi_2O_3 and $Bi_{38}ZnO_{58}$. The lamellae seem to have formed initially at the grain boundaries and then advanced into the adjoining matrix by simultaneous growth of these two phases. Evidence obtained by both XRD and SEM of several compositions, which were first heat-treated at 730°C for a prolonged period (to yield γ-Bi_2O_3 solid solution) and then slowly cooled to room temperature, indicated that the eutectoid composition is located at a composition of 1.8 mol% ZnO and undergoes a transformation at a temperature near 710°C to yield α-Bi_2O_3 and $Bi_{38}ZnO_{58}$.

3.2. The phase equilibrium diagram of the binary system Bi_2O_3-ZnO

The phase diagram of the binary system Bi_2O_3-ZnO as established in the present study is shown in Fig. 4. In contrast to the earlier reported study [15], the phase diagram, as proposed herein, is characterized by the presence of three invariant points, namely, a eutectoid at a composition of 1.8 mol% ZnO with a transformation temperature of 710°C, a peritectic at a composition near 9.0 ± 1.0 mol% ZnO with a melting temperature of 753 ± 2°C, and a eutectic between $Bi_{38}ZnO_{58}$ and ZnO at a composition near 25 ± 1.0 mol% ZnO with a melting temperature of 738 ± 2°C.

The XRD patterns of a series of binary compositions containing variable proportions of Bi_2O_3 and ZnO,

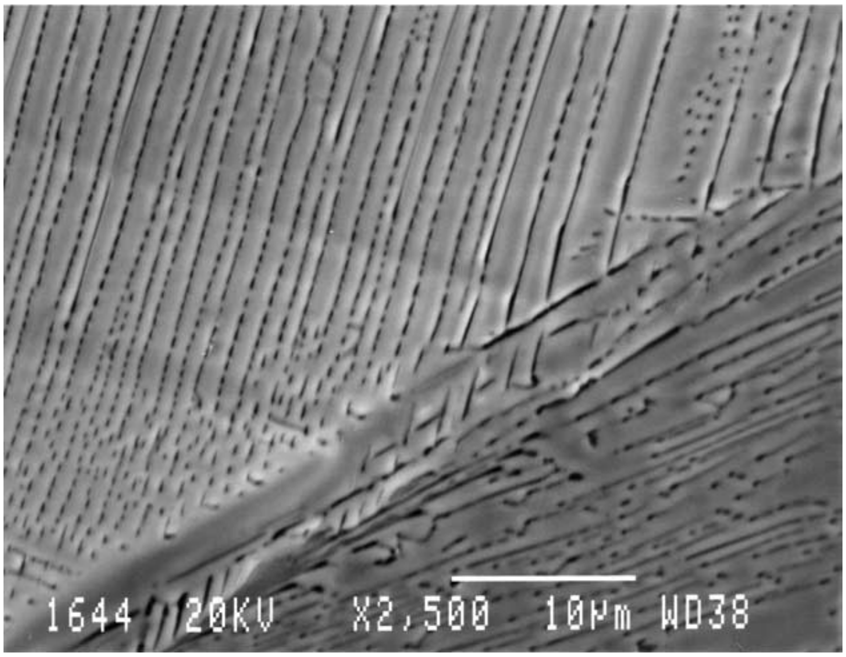

Figure 2 Scanning electron micrograph of a composition containing 2 mol% ZnO, heat-treated at 730°C for 15 h and then at 775°C for 1 h followed by quenching in air to room temperature.

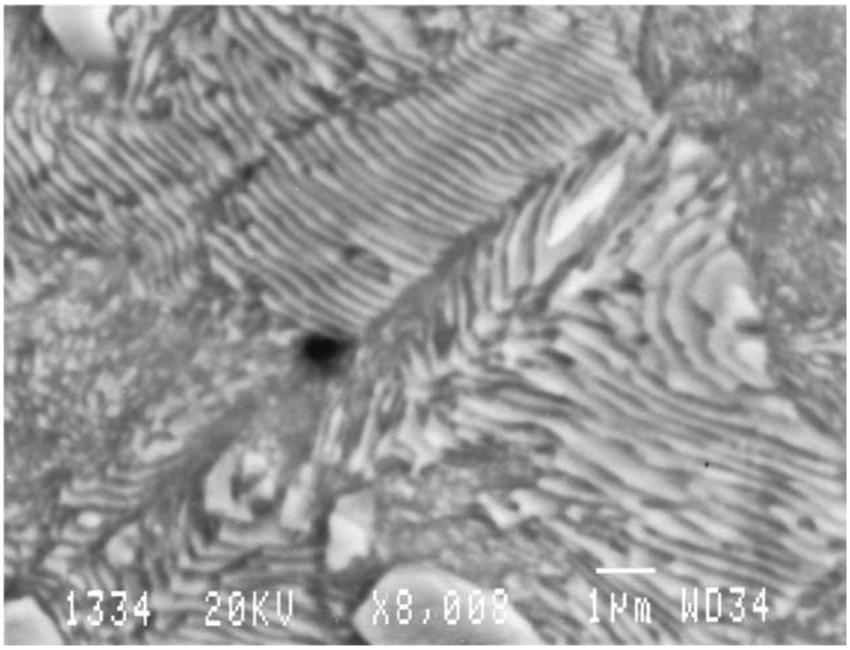

Figure 3 Scanning electron micrograph of a composition containing 2 mol% ZnO, heat-treated at 730°C for 15 h followed by cooling to room temperature at a rate of 10°C.

which were equilibrated at 730°C and then quenched to room temperature, are shown in Fig. 5. The XRD pattern of a composition containing 2 mol% ZnO corresponds to a single-phase b.c.c-based γ-Bi_2O_3 solid solution (Fig. 5a). As mentioned earlier, at a temperature near 750°C, the γ-Bi_2O_3 solid solution extends up to 2.2 mol% ZnO. Beyond this solid solubility region, two distinctly different phases with identical crystal structures consisting of γ-Bi_2O_3 solid solution and $Bi_{38}ZnO_{58}$ were identified. The crystal structure of $Bi_{38}ZnO_{58}$ is analogous to that of the b.c.c-based γ-Bi_2O_3 solid solution and these two phases were distinguished from one another by a slight shift of the d-spacings in the XRD patterns (Fig. 5b). The compound $Bi_{38}ZnO_{58}$ occurs as a single-phase material with a Bi_2O_3:ZnO ratio of 19:1 (Fig. 5c), which agrees with the earlier reported studies [19, 20]. XRD and DTA results revealed that $Bi_{38}ZnO_{58}$ melts incongruently at 753°C to yield γ-Bi_2O_3 solid solution and liquid according to the reaction:

$$Bi_{38}ZnO_{58} \underset{\text{cooling} <753^\circ\text{C}}{\overset{\text{heating} >753^\circ\text{C}}{\rightleftharpoons}} \gamma\text{-}Bi_2O_{3_{\text{s.s.}}} + \text{liquid}$$

This is consistent with the data as shown in the previously published phase diagram [15]. Compositions with a higher ZnO content to that of the compound $Bi_{38}ZnO_{58}$ (5 mol% ZnO) were found to occur within

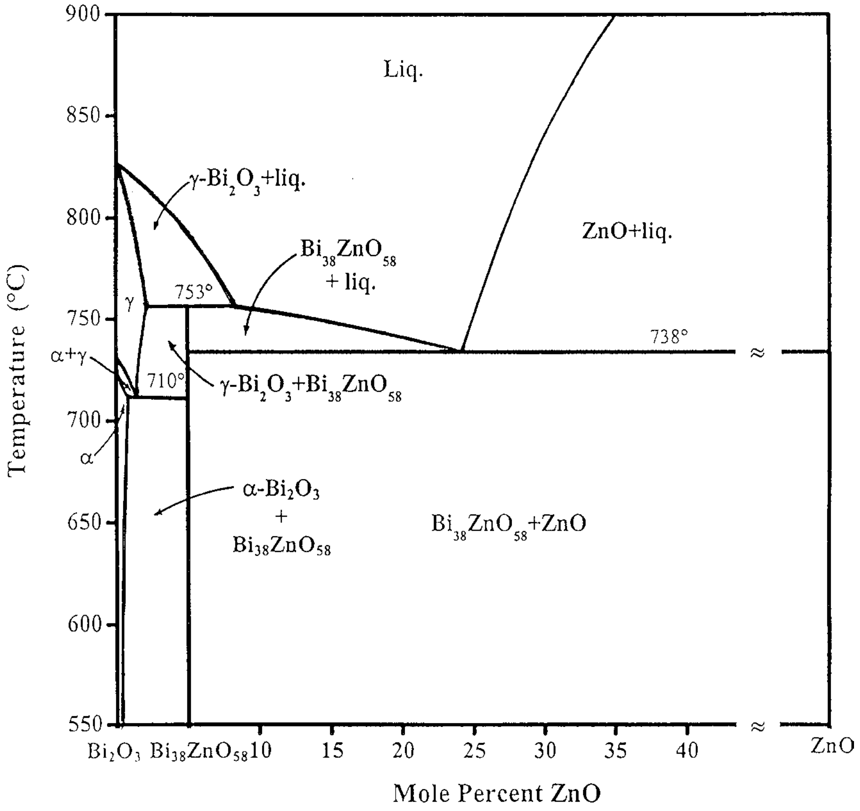

Figure 4 The phase diagram of the binary system Bi_2O_3-ZnO (α = low-temperature monoclinic Bi_2O_3, γ = body-centered-cubic solid solution, liq = liquid).

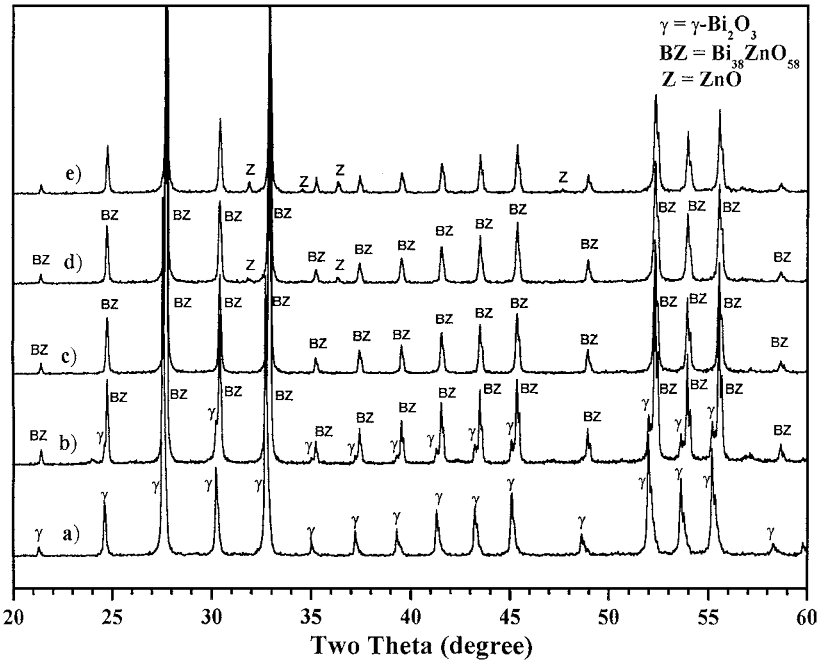

Figure 5 X-ray diffraction patterns of Bi_2O_3 containing variable proportions of ZnO, specimens heat-treated at 730°C for 15 h followed by quenching in air to room temperature.

a two-phase field region in which $Bi_{38}ZnO_{58}$ and ZnO coexist with one another (Fig. 5d and e).

The incongruent melting behavior of the compound $Bi_{38}ZnO_{58}$ was confirmed by the microstructural characteristics of a partially melted specimen representing the compound and is shown in Fig. 6. As can be seen from this microstructure, the γ-Bi_2O_3 solid solution, which formed by incongruent melting of $Bi_{38}ZnO_{58}$, has crystallized on the periphery of the $Bi_{38}ZnO_{58}$ grains on cooling below the peritectic temperature (753°C). With increasing additions of ZnO to $Bi_{38}ZnO_{58}$, the melting temperature was progressively lowered from the peritectic temperature at 753°C and a composition 9.0 mol% ZnO to the melting point of the eutectic at 738°C and a composition 25 mol% ZnO. As is apparent from the phase diagram (Fig. 4), the liquidus

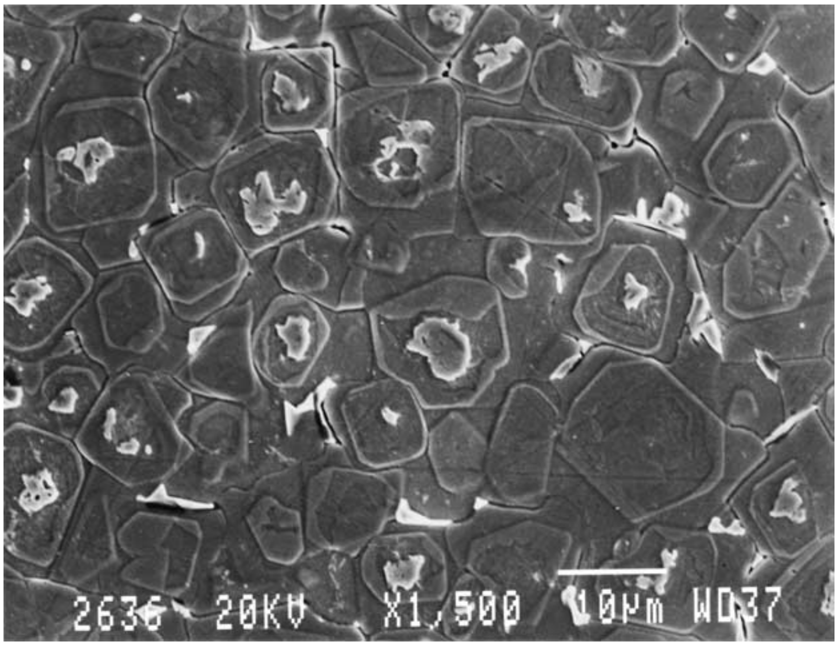

Figure 6 Scanning electron micrograph of a composition representing the compound $Bi_{38}ZnO_{58}$, specimen partially melted at 760°C and then slowly cooled to room temperature.

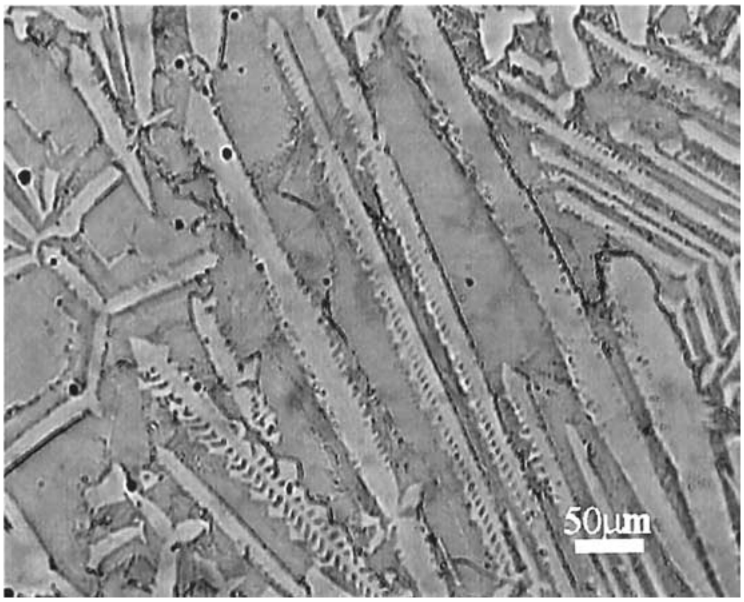

Figure 7 An optical micrograph of a composition containing 15 mol% ZnO, specimen melted at 750°C and cooled to room temperature.

at the $Bi_{38}ZnO_{58}$-rich side of the eutectic composition is nearly flat. The compositions located in this area, especially those lying in the vicinity of the eutectic, were found to melt completely at temperatures above 750°C. By contrast, the liquidus on the ZnO-rich side of the eutectic composition is very steep and as a result, the compositions located in the primary phase-field area of ZnO required significantly higher temperatures to accomplish complete melting.

The microstructures of several compositions, which were examined by an optical microscope for locating the eutectic composition, as well as, for the delineation of various phase-field areas occurring in this system, are elucidated by the following micrographs. The microstructure of a composition containing 15 mol% ZnO, which was melted at 750°C and then cooled to a temperature below the solidus, is shown in Fig. 7. The microstructure shows the presence of numerous dendrites of $Bi_{38}ZnO_{58}$ coexisting with the eutectic liquid. This is typical of the microstructures in which the primary phase, on cooling from a temperature above the liquidus, almost always appeared in the form of dendrites. It is worthy of mention at this point that for the microstructure development of various melted compositions, especially, those located in the vicinity of the eutectic, the cooling rate used for quenching the specimens was found to be much too fast to accomplish complete crystallization of the equilibrium phases. In most cases, a small amount of liquid, on cooling, remained intact in the specimens in the form of glass. The resulting microstructures were found to be far from being effective for the determination of the eutectic

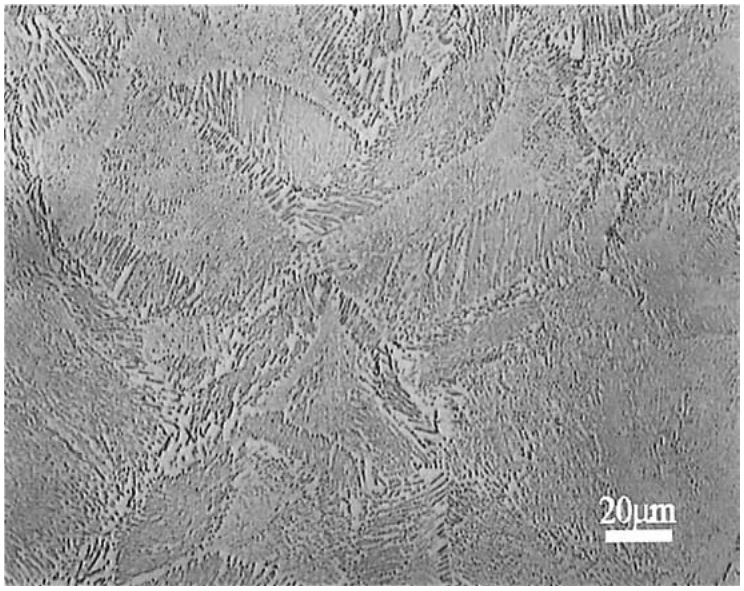

Figure 8 An optical micrograph of a composition containing 25 mol% ZnO, specimen melted at 750°C and cooled to room temperature.

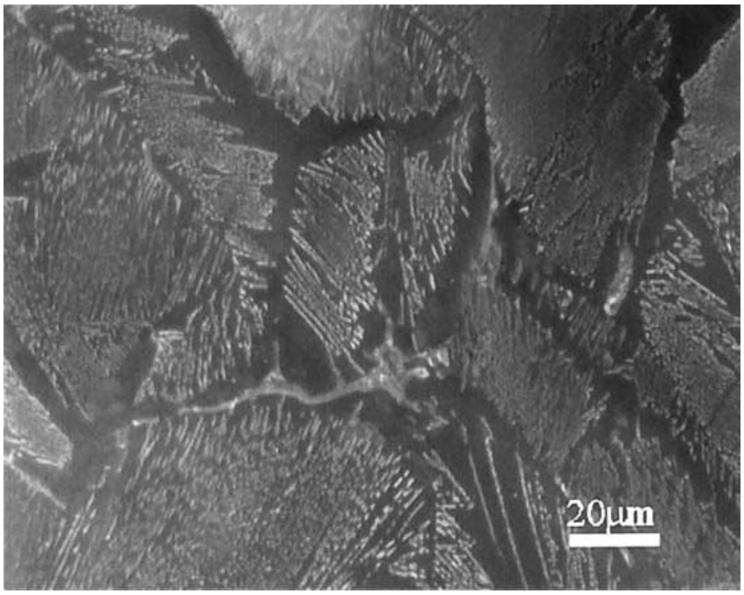

Figure 9 An optical micrograph of a composition containing 30 mol% ZnO, specimen melted at 860°C and cooled to room temperature.

composition as well as for the delineation of the various phase boundaries that occur in this system. Thus, it was found necessary to employ a slower rate of cooling (at a rate of approximately 20°C/min.) to allow sufficient time for completion of the crystallization process.

The microstructure of the eutectic, which was obtained by melting a composition containing 25 mol% ZnO at 750°C followed by cooling to room temperature, is shown in Fig. 8. As visible in this micrograph, the morphology is typical of a eutectic and consists of alternate layers of $Bi_{38}ZnO_{58}$ and ZnO that formed during cooling by crystallizing from the melt. Specimens with ZnO content higher than that of the eutectic composition revealed a two-phase microstructure. A micrograph of a composition containing 30 mol% ZnO, which was melted at 860°C and cooled below the solidus temperature (738°C) is shown in Fig. 9. The microstructure shows the presence of ZnO appearing mostly in the form of grey dendrites coexisting with the eutectic liquid. The solid solubility of Bi_2O_3 in ZnO, as explored earlier in several studies [23, 24], has been found to be negligible (<0.02 mol% ZnO). In the present study, the absence of any detectable shift of the characteristic d-lines in the XRD patterns of several Bi_2O_3-doped ZnO specimens has confirmed the earlier findings.

4. Conclusions

In the binary system Bi_2O_3-ZnO, incorporation of a small amount of ZnO into the high-temperature face-centered-cubic lattice of Bi_2O_3 (δ-Bi_2O_3) gives rise to the formation of a body-centered-cubic solid solution (γ-Bi_2O_3). The maximum solid solubility of ZnO in Bi_2O_3 occurs at a temperature near 750°C and is limited to a composition of 2.2% ZnO. On cooling, the γ-Bi_2O_3 solid solution undergoes a eutectoid transformation at a temperature near 710°C to yield the low-temperature monoclinic polymorph of Bi_2O_3 (α-Bi_2O_3) and $Bi_{38}ZnO_{58}$. The eutectoid occurs in the Bi_2O_3-rich region of the Bi_2O_3-ZnO system at a composition near 1.8 mol% ZnO. The compound $Bi_{38}ZnO_{58}$ has a crystal structure analogous to that of the b.c.c-based γ-Bi_2O_3 solid solution and melts incongruently at 753 ± 2°C to yield γ-Bi_2O_3 and liquid. A binary eutectic between $Bi_{38}ZnO_{58}$ and ZnO occurs at a composition of 25 ± 1.0 mol% ZnO with a melting temperature of 738 ± 2°C.

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