

Thermodynamic study of the rich-Bi₂O₃ region of the Bi₂O₃-ZnO system

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Precise knowledge of the Bi₂O₃-ZnO system is fundamental to control the functional microstructure of ZnO-based varistors. Also the potential applications of materials based on ZnO and Bi₂O₃ as dielectric materials in the high frequency range have renewed the interest in this binary system.

The aim of the present work is to carry out a thermodynamic analysis of the Bi₂O₃-ZnO phase diagram, taking into account the existing experimental information. Thermodynamic calculation has been performed according CALPHAD methodology (CALculation of PHase Diagrams), using the software Thermo-Calc.

Keywords: Thermodynamic modelling, Phase diagram, Bi₂O₃-ZnO, varistor

“Estudio termodinámico de la región rica en Bi₂O₃ del sistema Bi₂O₃-ZnO.”

El conocimiento preciso del sistema Bi₂O₃-ZnO es una herramienta básica para conseguir el control de la microestructura de los varistores basados en ZnO. Recientemente otros materiales basados en óxidos de cinc y bismuto han mostrado un gran potencial para su uso en aplicaciones como dieléctricos a frecuencias altas, renovando el interés por dicho sistema binario.

El objetivo del presente trabajo es realizar una evaluación termodinámica del diagrama de fases consistente para el sistema Bi₂O₃-ZnO teniendo en cuenta la información experimental existente del mismo. La evaluación termodinámica del sistema se ha llevado a cabo mediante la metodología CALPHAD (CALculation of PHase Diagrams), empleando el software Thermo-Calc.

Palabras clave: Cálculo Termodinámico, Diagrama de Fases, Bi₂O₃-ZnO, varistores.

1. INTRODUCTION

Due to its highly non-linear behaviour in the intensity-voltage response, the principal application of ZnO-Bi₂O₃ based materials is the fabrication of varistors (variable resistor or Voltage Dependent Resistor) (1). Precise knowledge of the Bi₂O₃-ZnO phase diagram is fundamental to understand the sintering behaviour of these materials and control their microstructure, responsible of the varistor behaviour. However, despite of its technological importance, there are nowadays some controversial features of the system. In this sense, the possible presence of Bi₂O₃ methastables polymorphs and the stoichiometry of the intermediate compounds of Bi₂O₃ and ZnO, cause the rich-Bi₂O₃ region of the system to be on discussion in our days.

The aim of this paper is to achieve a thermodynamic calculation of the Bi₂O₃-ZnO system by means of CALPHAD methodology (2), using the software Thermo-Calc (3). This method implies a critical review of the experimental information of the system and a description of the Gibbs free energy functions (G) of all the phases according to the proper thermodynamic models. Thermodynamic assessment of some Bi₂O₃ containing systems (Bi-O-X (X= Ca, Sr)) (4,5) have been recently reported. The CALPHAD methodology offers realistic estimation of ternary or higher order phase diagram by extrapolation from their binary subsystems (6). In this sense, it is important to establish consistent thermodynamic description of Bi-O-X systems to obtain reliable approach to

high order systems, necessary to discuss the behaviour of real materials (5).

2. EXPERIMENTAL

2. Review of experimental data.

Bi₂O₃ present four polymorphic (8,9) forms at normal pressure, which are known as the α -, β -, γ -, and δ -forms. All polymorphic modifications have been structurally characterized and their powder diffraction patterns discussed (8,9,10). At atmospheric pressure, the monoclinic α -Bi₂O₃ is stable up to 729°C, above this temperature transforms to the cubic δ -Bi₂O₃ that is stable up to the melting point of 824°C. Two methaestable phases, tetragonal β -Bi₂O₃ and cubic γ -Bi₂O₃ may appear during cooling at 650° and 639°C respectively.

ZnO presents only a hexagonal wurzite-tipe crystalline structure up to its fusion at 1977°C.

First works on the Bi₂O₃-ZnO system point out to the existence of an intermediate compound with sillenite structure, however its concrete stoichiometry has been recently discussed. Most accepted stoichiometry was the 24Bi₂O₃:ZnO (11,12). Afterwards, Graig and Stephenson (13) observed the formation of a compound with sillenite structure, having a Bi₂O₃:ZnO ratio close to 19:1. This result was confirmed by

Radaev et al (14) who refined the crystalline structure of the Bi₁₂[Bi_{0.67}Zn_{0.33}]O_{19.33} compound with a Bi₂O₃:ZnO ratio very close to 19:1. On the other hand, the maximum content of Zn in the sillenite structure, estimated by Valant et al (15) was the corresponding to the structural formula Bi₁₂(Bi_{2/33}+M_{1/3+2})O_{19.33}. These results were in line with provided by Chehab et al (16) showing the stoichiometry 19Bi₂O₃:ZnO for the intermediate compound in the Bi₂O₃-ZnO system.

The first phase equilibrium diagram for Bi₂O₃-rich region of the system Bi₂O₃-ZnO proposed by Levin and Roth in 1967 (17) suggested the existence of a narrow solid solution region about 13 mol% ZnO that melts congruently, and a eutectic point at 8 mol% ZnO and ~750°C. Bruton et al (18) studied the Bi₂O₃-rich region of the system Bi₂O₃-ZnO and proposed a liquidus boundaries basically agree with that proposed by Levin and Roth (17) except for the different compositions assigned to the intermediate compound.

The Bi₂O₃-ZnO phase diagram was investigated over the entire composition range by Safronov et al (11). The proposed diagram drastically differs of the previously published. This work established the existence of a single incongruently melting intermediate compound 24Bi₂O₃:ZnO and the existence of a eutectic point at ~86 mol% Bi₂O₃ and 740°C.

The ZnO-rich region of the system has been studied too. In this sense, the presence of a solid solutions of Bi₂O₃ in ZnO was observed in various indirect studies based on the sintering behaviour of ZnO-rich specimens (19,20). The maximum solubility of Bi₂O₃ in ZnO between 740° up to 1100°C established by Hwang in 1994 (12) is ~0.25 mol% of Bi₂O₃.

In a recent work, J. P. Guha et al (21) suggest important modifications to the rich-Bi₂O₃ region of the system. Their data reveal that incorporation of a small amount of ZnO to the high-temperature δ-Bi₂O₃ polymorph, leads to the formation of a γ-Bi₂O₃ solid solution, with a crystal structure analogous to the 19Bi₂O₃:ZnO compound. The eutectic point suggested by these authors was located in 25 mol% ZnO at a temperature of 738°C.

Recently de la Rubia et al (22,23) observed the presence of the 19Bi₂O₃:ZnO compound as stable phase in the rich-Bi₂O₃ region of the system. According with their results, the eutectic point of the system should be located at higher fraction of ZnO than the proposed by Safronov et al (11), close to the suggested by Guha et al (21). Also the peritectic point of decomposition of 19Bi₂O₃:ZnO should be located at higher contents of ZnO than the proposed by Guha et al (21). On the other hand, no evidences of the presence of γ-Bi₂O₃ as a stable phase was found by these authors, contrasting with the reported by Guha et al (21).

3. THERMODYNAMIC MODELS

The liquid phase has been described by the two-sublattice model for ionic liquids (24,25). According this model, cations and anions are assumed to mix freely in their respective sublattice. The liquid can then be represented by the formula (Bi³⁺,Zn²⁺)_p(O²⁻)_q, where p and q vary with composition to maintain electroneutrality. Hypothetical vacancies with an induced charge are introduced in the second sublattice to make the model continuous to the metal liquid. In this case, p and q are given by

$$p=2 ; q=3y_{Bi^{3+}}+2y_{Zn^{2+}} \quad [1]$$

where y_s is the site fraction, i. e. the fraction of the species s in a particular sublattice.

The molar Gibbs free energy of the liquid is

$$G_m^{Liq} = y_{Bi^{3+}} y_{O^{2-}}^0 G_{Bi^{3+};O^{2-}}^{Liq} + y_{Zn^{2+}} y_{O^{2-}}^0 G_{Zn^{2+};O^{2-}}^{Liq} + pRT(y_{Bi^{3+}} \ln y_{Bi^{3+}} + y_{Zn^{2+}} \ln y_{Zn^{2+}}) + E G_m^{Liq} \quad [2]$$

where the excess Gibbs free energy, is given by Ec. 3

$$E G_m^{Liq} = y_{Bi^{3+}} y_{Zn^{2+}} L_{Bi^{3+},Zn^{2+};O^{2-}}^{Liq} \quad [3]$$

A comma is used the separate species on the same sublattice, and a colon is used to separate species on different sublattices. The term $L_{Bi^{3+},Zn^{2+};O^{2-}}^{Liq}$ represents the interaction

between Bi₂O₃ and ZnO, and a regular interaction parameter has been optimized in this work, as A_{Bi₂O₃+ZnO} · T.

Most authors point out that α-Bi₂O₃ and δ-Bi₂O₃ are the stable forms, so these have been the only polymorph of bismuth oxide considered in this work. The phases α-Bi₂O₃ and δ-Bi₂O₃ have been described as pure phases and their G have been taken from SSUB database (Thermo-Calc P) (26).

Some works referred in the bibliographic review show the presence of little contents of Bi₂O₃ in the ZnO lattice however, the experimental data are very scarce to tackle the calculation of G for this solid solution. On the other hand, all the results reveals that the solid solution of Bi₂O₃ in the ZnO is very low (<0.25 mol% Bi₂O₃) (12), so that the ZnO has been considered as a pure phase and its G has been taken from SSUB database (Thermo-Calc P) (26).

According the most recent works (14-16,21-23), 19Bi₂O₃:ZnO has been considered as stable phase in the present assessment. The phase Bi₃₈ZnO₅₈ has been described as a stoichiometric compound, with Gibbs free energy given relative to α-Bi₂O₃ and ZnO.

$$G^{Bi_{38}ZnO_{58}} = 19 G_{Bi_2O_3}^{\alpha} + 0 G_{ZnO}^{ZnO} + A_{Bi_{38}ZnO_{58}} + B_{Bi_{38}ZnO_{58}} \cdot T \quad [4]$$

where A and B are the parameters to be optimized.

4. RESULTS AND DISCUSSION

The optimization of the described parameters, as well as all calculations, has been performed using the PARROT module in the Thermo-Calc data-bank system (3). Table I shows the thermodynamic parameters optimized in the present work. The low number of parameters used to reproduce the experimental data put in evidence that the used models accurately describe the real behavior of the system.

The resulting phase diagram calculated for the Bi₂O₃-ZnO system is shown in the Figure 1 and 2, and the calculated invariant points are the collected in Table II.

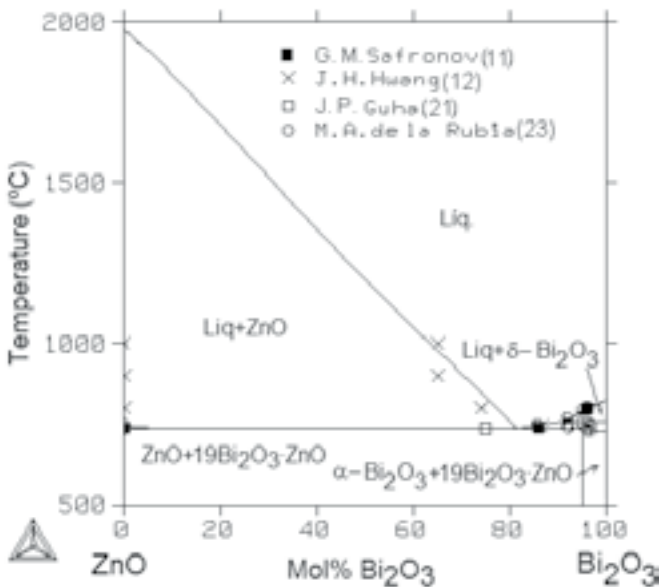
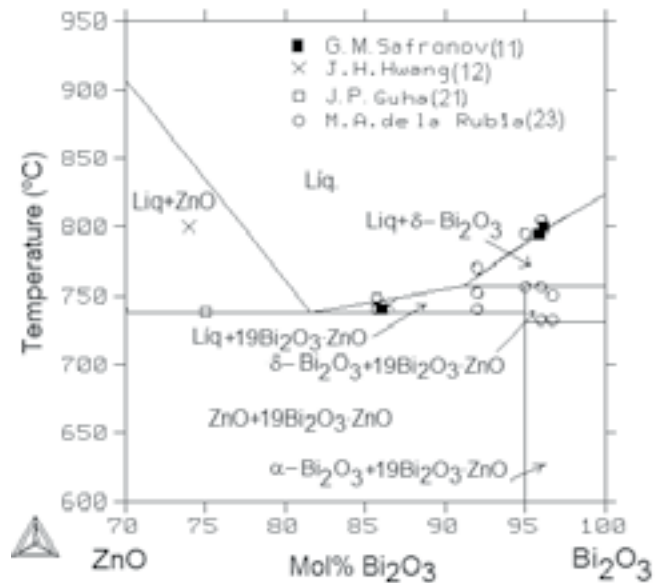
Figure 1 shows the whole Bi₂O₃-ZnO system whit the different compatibility fields of the stable phases in the system; liquid, α-Bi₂O₃, δ-Bi₂O₃, ZnO and 19Bi₂O₃:ZnO. The system present the invariant point presented in Table II. Calculated phase diagram is in good agreement with the scarce experimental information of the Liquid+ZnO coexistence field.

TABLE I. THERMODYNAMIC PARAMETERS FOR THE Bi_2O_3 -ZnO SYSTEM OPTIMIZED IN THE PRESENT WORK. ALL PARAMETERS ARE GIVEN IN SI UNITS (J, MOL, K; $R=8.31451$ J/(MOL·K)⁻¹).

Phase	Parameter
Liquid $(\text{Bi}^{3+}, \text{Zn}^{2+})_p(\text{O}^{2-})_q$ $p=2; q=3y_{\text{Bi}^{3+}}+2y_{\text{Zn}^{2+}}$	$L_{\text{Bi}^{3+}, \text{Zn}^{2+}, \text{O}^{2-}}^{\text{Liq}} = A_{\text{liq}} + B_{\text{liq}} \cdot T$ $A_{\text{Liq}} = -4793.61; B_{\text{Liq}} = 0$
$19\text{Bi}_2\text{O}_3 \cdot \text{ZnO}$	$G^{\text{Bi}_{38}\text{ZnO}_{58}} = 19^0 G^{\alpha\text{-Bi}_2\text{O}_3} + 0 G^{\text{ZnO}} + A_{\text{Bi}_{38}\text{ZnO}_{58}} + B_{\text{Bi}_{38}\text{ZnO}_{58}} \cdot T$ $A_{\text{Bi}_{38}\text{ZnO}_{58}} = -2520.54; B_{\text{Bi}_{38}\text{ZnO}_{58}} = 0$

TABLE II. INVARIANT POINTS CALCULATED IN THE Bi_2O_3 -ZnO SYSTEM.

Invariant Point	T. (°C)	Phase	% mol Bi_2O_3
Eutectic: $\text{Liq.} \rightarrow \text{ZnO} + 19\text{Bi}_2\text{O}_3 \cdot \text{ZnO}$	737	Liq.	81.58
		ZnO	0
		$19\text{Bi}_2\text{O}_3 \cdot \text{ZnO}$	95.00
Peritectic: $19\text{Bi}_2\text{O}_3 \cdot \text{ZnO} \rightarrow \text{Liq.} + \delta\text{-Bi}_2\text{O}_3$	756	$19\text{Bi}_2\text{O}_3 \cdot \text{ZnO}$	95.00
		Liq.	91.15
		$\delta\text{-Bi}_2\text{O}_3$	100

Fig. 1- Calculated phase equilibrium diagram for the Bi_2O_3 -ZnO system. Symbols represent the limits of the stability field proposed by various authorsFig. 2- Bi_2O_3 -rich region of the calculated phase equilibrium diagram for the Bi_2O_3 -ZnO system. Symbols represent the limits of the stability field proposed by various authors.

The invariant eutectic point calculated is located between those suggested by Guha et al (21), Safronov et al (11) and Hwang et al (12). Also the temperature of the eutectic point is accordance with the suggested by the different authors.

In the rich- Bi_2O_3 region of the system, Figure 2, the liquidus line fits with the data reported by Safronov et al (11) and de la Rubia et al (22,23) at higher temperatures. In this region, the incongruent fusion of the $19\text{Bi}_2\text{O}_3 \cdot \text{ZnO}$ compound can be observed. The location of this peritectic

point is indicated in the Table II. There is no data on the composition of the composition of the peritectic liquid, so that, the thermodynamic assessment of the system offer a friable estimation of this point. The location of the peritectic liquid in the system is in good agreement with the extension of the compatibility field proposed by de la Rubia et al (22,23) in this range of compositions.

5. CONCLUSIONS

A thermodynamic assessment for the Bi₂O₃-ZnO system has been performed. An optimal set of thermodynamic functions for the binary system have been obtained from the selected phase diagram and thermodynamic data by using the CALPHAD technique. The comparison shows that the experimental information is reasonably well accounted for by the present description of the system and support the consistence of the phase diagram proposed for the system

The thermodynamic study support the existence in the system of the 19Bi₂O₃·ZnO compound and the presence of δ-Bi₂O₃ as a stable phase in the rich-Bi₂O₃ region of the system.

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