

Equilibrium phases in the Bi_2O_3 -rich region of the ZnO – Bi_2O_3 system

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Abstract

Varistors manufacturing is one of the most important applications of ceramic materials based in ZnO – Bi_2O_3 system. This system ZnO – Bi_2O_3 is especially relevant for both the formation of the microstructure that originates the varistor behavior and the sintering behavior. However, despite of its technological relevance, many aspect related to these materials remain unclear. Phase equilibrium diagram, specially the Bi_2O_3 -rich region of the ZnO – Bi_2O_3 , is still controversial. The $24\text{Bi}_2\text{O}_3\cdot\text{ZnO}$ phase with sillenite structure is reported to be at equilibrium, however recent works point to the existence of $19\text{Bi}_2\text{O}_3\cdot\text{ZnO}$ as the equilibrium phase. In this work, a set of samples have been studied in order to elucidate this point. Equilibrium phases and thermal behaviour of the samples have been analysed by XRD, SEM and DTA. Presented results show that the stoichiometry at equilibrium is $19\text{Bi}_2\text{O}_3\cdot\text{ZnO}$ which is agreement with the recent published results.

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1. Introduction

Ceramic materials based in Bi_2O_3 doped ZnO have their main application as varistors due to their highly non-linear current–voltage response. Recently, materials containing ZnO and Bi_2O_3 have attracted interest because of their possible application as microwave dielectrics. Compounds like $\text{Bi}_{12}(\text{Bi}_{0.67}\text{Zn}_{0.33})\text{O}_{19.33}$ with sillenite structure and others in the ZnO – Bi_2O_3 – Nb_2O_5 system with pyrochlore structure show interesting properties. However, in order to tailor the material processing and properties, a basic understanding is still lacking. Despite of the importance of the ZnO – Bi_2O_3 system, its phase equilibrium diagram and the possible existence of metastable phases in the Bi_2O_3 -rich region is still under discussion. In early works,^{1–5} a body centered cubic phase with sillenite structure was proposed to be at equilibrium; however there was a lack of agreement on the exact composition. Hwang and Mason reported $24\text{Bi}_2\text{O}_3\cdot\text{ZnO}$ as the composition of the phase at equilibrium, in agreement with previous results.⁶

On the other hand, Valant et al.⁷ have proposed recently that the maximum Zn content within the sillenite structure

is not higher than the expected according to the structural formula $\text{Bi}_{12}(\text{Bi}_{2/3}^{3+}\text{M}_{1/3}^{2+})\text{O}_{19.33}$. This result is in agreement with those obtained by Chehab et al.,⁸ showing that the stoichiometry of the compound is $\text{Bi}_{38}\text{ZnO}_{58}$. In a recent paper, Guha et al.⁹ propose a phase equilibrium diagram with $\text{Bi}_{38}\text{ZnO}_{58}$ as the phase at equilibrium.

In the present paper, a set of samples have been analysed in order to establish the actual phases at equilibrium.

2. Experimental

Five different compositions were prepared with the following $\text{Bi}_2\text{O}_3/\text{ZnO}$ ratios (in mol%): composition 1 (96.7/3.3), composition 2 (96/4) with $24\text{Bi}_2\text{O}_3\cdot\text{ZnO}$ stoichiometry, composition 3 (95/5) with $19\text{Bi}_2\text{O}_3\cdot\text{ZnO}$ stoichiometry, composition 4 (88.75/11.25), and composition 5 (85.714/14.286) which corresponds to the eutectic composition. High purity raw materials (99.99%) were used: ZnO commercial powder (Sigma–Aldrich) with an average particle size of $1\ \mu\text{m}$ and hexagonal wurtzite-type structure, and commercial Bi_2O_3 powder (Sigma–Aldrich) with an average size of $15\ \mu\text{m}$ and characterized by XRD as monoclinic α - Bi_2O_3 . Compositions were attrition milled in attrition during four hours in ethanol and dried at $60\ ^\circ\text{C}$. Pellets

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(8 mm diameter and 2 mm thick) were uniaxially pressed at 3000 kg/cm².

Thermal treatments were carried out in a small chamber furnace previously calibrated with an external thermocouple placed beside the furnace own thermocouple, yielding a temperature gradient of $\pm 2^\circ\text{C}$. For compositions 1 and 4, thermal treatments were carried out up to 745 °C/72 h followed by quenching in air. Compositions 2 and 3 were heated up to 720 °C/72 h and air quenched. Finally composition 5 was heated to 745 °C/30 min, slowly cooled (24 h) to 735 °C and then quenched in air. The sintered samples were then grounded and re-heated applying again their respective thermal treatments. The phases present were identified by XRD and SEM. Thermal evolution of the samples was studied by DTA.

3. Results and discussion

Fig. 1 shows the phase diagram of the Bi₂O₃ rich region of the ZnO–Bi₂O₃ binary system reported by Guha et al.⁹ Experimental points described in the present paper are marked in the Figure. Composition 1 lies in the γ -Bi₂O₃–Bi₃₈ZnO₅₈ field according to Guha et al. However, XRD (Fig. 2) shows the presence of Bi₃₈ZnO₅₈ (JCPDS 42-0183) and α -Bi₂O₃ (JCPDS 71-0465). DTA curve for this composition (Fig. 3) shows three endothermic peaks. The first peak at 730 °C seems to indicate the α -Bi₂O₃ to δ -Bi₂O₃ transformation, clearly observed in the DTA curve of pure Bi₂O₃. The kinetic of δ to α transformation during cooling is fast enough to avoid the high temperature phase quenching, therefore XRD measurements detect the low temperature phase. The second

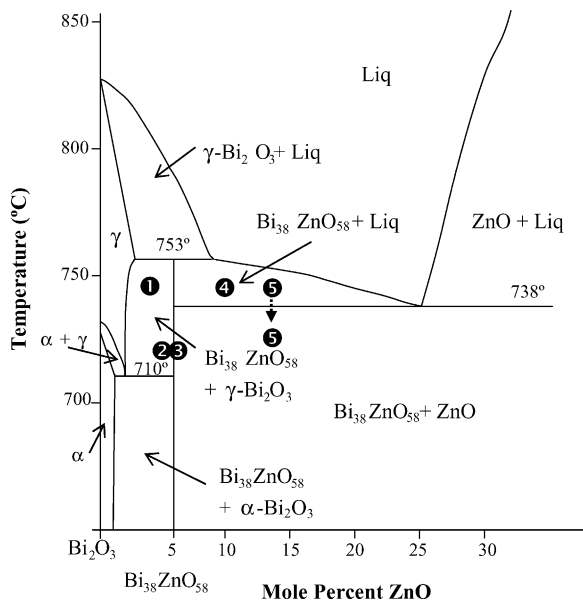


Fig. 1. Proposed Bi₂O₃-rich region of the binary phase diagram ZnO–Bi₂O₃ reported by Guha et al.⁹ Numbers in the black circles represent the prepared compositions.

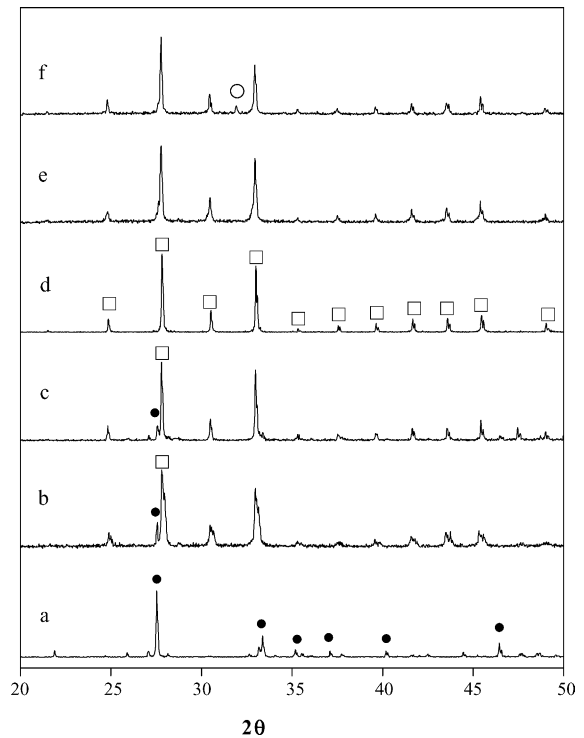


Fig. 2. XRD of (a) pure Bi₂O₃, (b) composition 1, (c) 24Bi₂O₃·ZnO, (d) 19Bi₂O₃·ZnO, (e) composition 4 and (f) composition 5 α -Bi₂O₃ (●), ZnO (○) and 19Bi₂O₃·ZnO (□).

DTA peak observed at 750 °C corresponds to the incongruent melting of the Bi₃₈ZnO₅₈ phase and the third one indicates the temperature of the liquidus line. Composition 2 according to Safronov et al.² is expected to be a single 24Bi₂O₃·ZnO phase. However, the sample behaves in the same way that

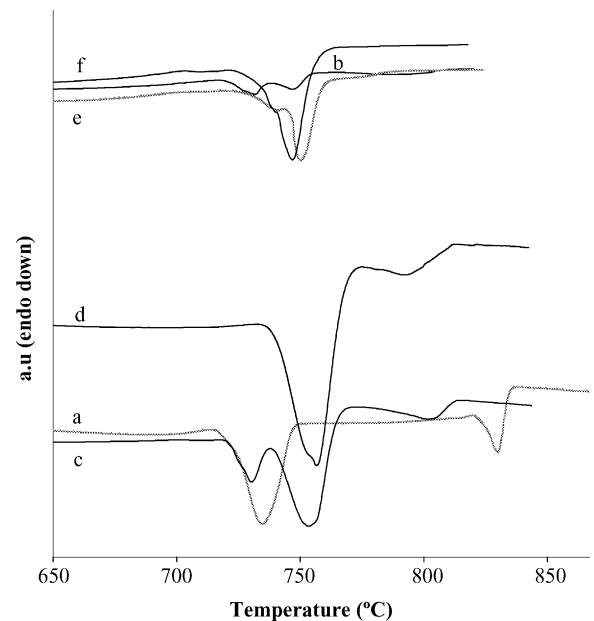


Fig. 3. DTA (a) pure Bi₂O₃, (b) composition 1, (c) 24Bi₂O₃·ZnO, (d) 19Bi₂O₃·ZnO, (e) composition 4 and (f) composition 5.

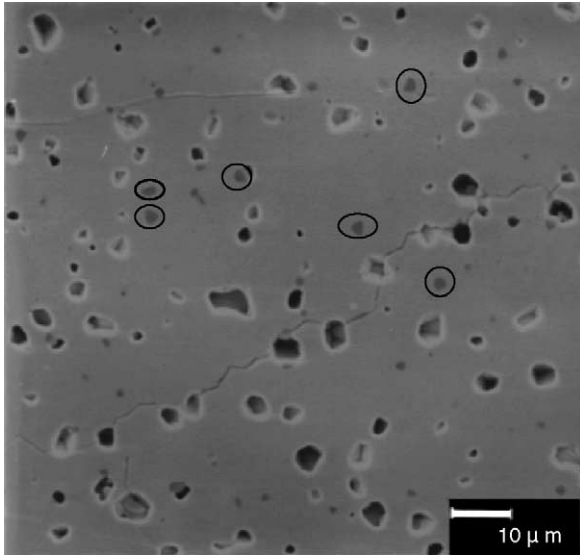


Fig. 4. SEM micrograph for composition 4. ZnO phase is marked with black circles.

composition 1, differences in XRD are only quantitative, related to the amount of the phases observed (see Fig. 2). Composition 3 corresponds to the $\text{Bi}_{38}\text{ZnO}_{58}$ stoichiometry and DRX scan only shows this phase. DTA curve shows two endothermic peaks as expected. According to the results obtained up to this point, it is evidenced that $\text{Bi}_{38}\text{ZnO}_{58}$ is the actual phase at equilibrium. However, no evidence has been found on the existence of $\gamma\text{-Bi}_2\text{O}_3$ as an equilibrium phase. Composition 4 lies in the $\text{Bi}_{38}\text{ZnO}_{58}$ + liquid field. DTA curve shows three endothermic peaks: the first at 740°C corresponds to the eutectic melting, the second one at 750°C reflects the incongruent melting of $\text{Bi}_{38}\text{ZnO}_{58}$ and the third one at 770°C indicates the liquidus temperature. XRD scan of this sample shows only the presence of $\text{Bi}_{38}\text{ZnO}_{58}$ however, ZnO is evidenced in SEM micrographs (Fig. 4). ZnO is not detected by XRD because of its low concentration and low

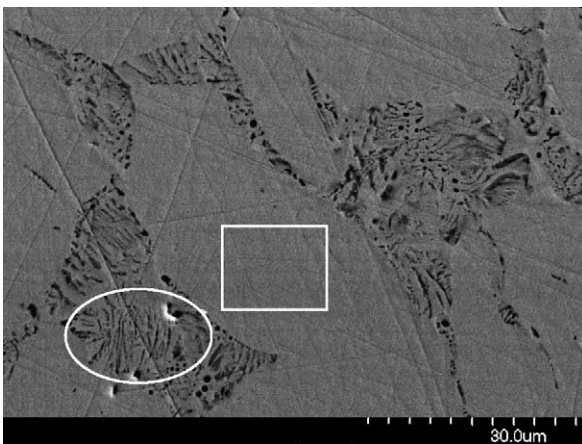


Fig. 5. SEM micrograph of composition 5 showing $19\text{Bi}_2\text{O}_3\cdot\text{ZnO}$ phase (white square) and eutectic crystallization (white circle).

X-ray scattering factor. According to this results the peritectic point seems to occur at a higher ZnO concentration than reported by Guha et al.⁹ Composition 5, that is eutectic composition according to Safronov et al.² shows two overlapped endothermic peaks: the first at 740°C corresponds to the eutectic melting and the second one at 750°C to the liquidus line. This indicates that the composition 5 is not the eutectic one. SEM micrograph of the sample (Fig. 5) show the eutectic crystallization together with large grains of $\text{Bi}_{38}\text{ZnO}_{58}$. This morphology also indicates that is not the eutectic composition as proposed by Safronov and is in agreement with Guha et al.⁹

4. Conclusions

The presence of $\text{Bi}_{38}\text{ZnO}_{58}$ as the phase at the equilibrium and the compositional shift of the eutectic point to higher ZnO concentration have been observed. These results are in agreement with the modifications proposed by Guha et al. On the other hand no evidence has been found of the existence of $\gamma\text{-Bi}_2\text{O}_3$ as an equilibrium phase. Peritectic point occurs for a higher ZnO concentration than that proposed by Guha et al.

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