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Influence of chemical composition on sintering of bismuth–titanium-doped zinc oxide

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Liquid-phase sintering (LPS) of ceramics issued from powders of bismuth–titanium-doped zinc oxide, made of spherical grains constituted of small crystallites, were studied by dilatometry. A correlation can be established between the shape of the shrinkage curves and the microstructure of the ceramics. During sintering the spherical grains are destroyed as soon as the liquid phase appears and the rearrangement proceeds directly between crystallites. Systematic studies were carried out on bismuth–titanium-doped ZnO. For small Bi contents, the beginning of a solid-phase sintering process occurs. For 1 at% Bi in the binary system Bi-doped ZnO, rapid shrinkage leads to a well-densified ceramic with a grain size of 70 μm on average. The influence of the amount of titanium in y% Ti–1% Bi-doped ZnO is discussed. Whatever the amount of Ti, LPS is observed. The shrinkage curves depend greatly on the amount of Ti: only a Ti content of $y = 0.6$% leads to an increase in grain size (100 μm on average).

1. Introduction

Zinc oxide ceramics with a small amount of other metal oxides such as Bi_2O_3, Co_3O_4 or Mn_2O_3 exhibit non-linear current voltage characteristics [1]. They are widely used for electronic devices. The microstructure developed during sintering has an important effect on the electrical properties. The solid-phase sintering process of pure zinc oxide has been studied in detail by many workers [2–8]. However, the sintering of Bi_2O_3-doped zinc oxide ceramics occurs in the presence of a liquid phase at low temperature. Only a few studies have been carried out on this process.

The mechanism of liquid-phase sintering (LPS) of metals and oxides has been studied by many authors [9–14]. The main feature is the solution of a solid in the liquid phase, followed by its precipitation. Thus good wetting and an appreciable solubility of the solid in the liquid phase are required [9]. The sintering process involves several steps: (i) rearrangement of the particles as soon as the liquid phase occurs; (ii) shape accommodation of the grains; and (iii) microstructural evolution.

The kinetics of shrinkage during these steps are quite different: rearrangement is very fast, as indicated by dilatometry measurements. "Primary" and "secondary" rearrangements have been distinguished depending on whether the liquid fills pores between aggregates, or boundaries between crystallites inside the aggregates themselves [11]. Solid skeletons necessarily take part in the LPS process, but do not always lead to densification ceasing [11]. Rearrangement can continue, if the solid phase dissolves into the liquid phase [10]. When a small fraction of the volume is liquid, this liquid will tend to migrate towards the more densely packed regions, leading to the best densification in these parts and leaving large pores in the deserted parts [12]. These pores can vanish in the latest stages of sintering if liquid redistribution allows them to be filled [12]. The elimination of large pores is made easier by a great grain growth which decreases the coordination of pores, thus facilitating their filling [13, 14].

Nevertheless, the sintering mechanism of ZnO in the presence of a liquid phase (such as Bi_2O_3) is not yet clear. Stanisic *et al.* [15] have shown that, for small amounts of Bi_2O_3 in the $ZnO–Bi_2O_3$ system, a solid solution is formed. For a Bi_2O_3 content of 5 mol %, a compound $6Bi_2O_3–ZnO$ is formed in addition to the diffusion of bismuth into the ZnO lattice. However, Kim *et al.* [16] ruled out the possibility of solid-solution formation. They proposed that, when the additive content is small (< 0.1 mol %), the majority of Bi segregates at the surface ZnO grains. Wong [17], Asokan *et al.* [18] and Kim *et al.* [16] have shown that a Bi_2O_3-rich liquid phase enhances grain growth of ZnO during sintering. Recently, Senda and Bradt [19] have determined the kinetics of grain growth, and concluded that the grain-growth process is controlled by phase-boundary reaction of ZnO with the Bi_2O_3-rich liquid, rather than by diffusion of ZnO into the liquid phase during heat treatment.

From studies on complex systems where several metal oxides are added to ZnO, Sung *et al.* [20] have inferred that a small addition of TiO_2 also improves the grain size. For their part, Trontelj *et al.*, after having detected a $Bi_4Ti_3O_{12}$ phase in ceramics obtained from the $ZnO–Bi_2O_3–Co_3O_4–Mn_2O_3–TiO_2$ system [21] have investigated the chemical reactions and new phases which occur during sintering in the $ZnO–Bi_4Ti_3O_{12}$ system [22].

Thus although many studies have been devoted to the $ZnO-Bi_2O_3$ binary system, the $ZnO-Bi_2O_3-TiO_2$ system has not been explored. In this paper, an attempt is made to study the influence of the chemical composition on sintering, densification and grain size of bismuth–titanium-doped ZnO, using dilatometry and scanning electron microscopy.

2. Experimental procedure

2.1. Green ceramics

Powders of doped zinc oxide, prepared by coprecipitation, are made of spherical grains with diameters between 1 and 10 μm. Each sphere consists of a multitude of small crystallites with a size of 50–100 nm (Fig. 1). In the following, the amounts of dope are given as atomic percentage of the total amount of metal atoms. In any case the expected composition of the powder has been confirmed by plasma emission spectroscopy.

The oxide powders were mixed with an organic binder and pressed into disc form (diameter 6 mm, 5 mm thick) by applying a uniaxial pressure of 350 MPa. On average the density of the green ceramic is about 55% of the theoretical density.

2.2. Physical measurements

The thermal treatments and the concomitant measurements of shrinkage were performed in air atmosphere using a NETZSCH 402E electronic dilatometer. The thermal cycle was as follows: heating at a rate of 7 °C min^{-1} up to 250 °C, held for 2 h to burn off the binder, then heating up to the final sintering temperature of 1250 °C, held for 6 h and finally cooling at a rate of 5 °C min^{-1}. The heating was relatively fast to avoid bismuth oxide evaporation. In the dilatometer, the sample was separated from both support and alumina driving rod by thin platinum leaves to avoid diffusion between sample and gauge. The pressure exerted by the driving rod on to the sample was 18 kPa. An air flow of 0.1 l min^{-1} was blown through the furnace to remove vapour of bismuth oxide.

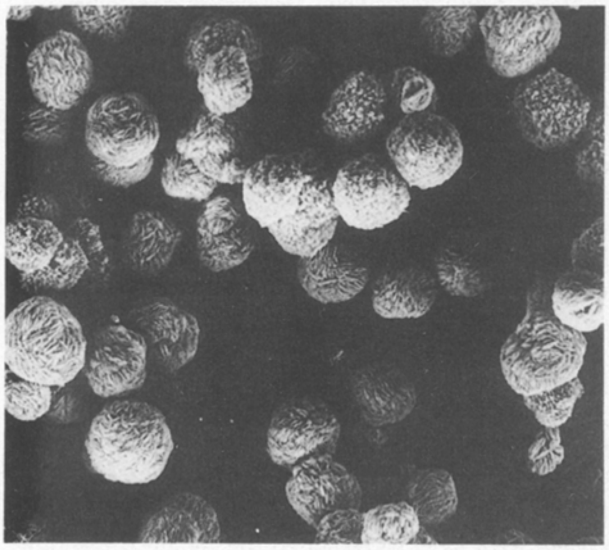

Figure 1 SEM of powder 1 at% Bi-doped ZnO. Magnification × 2000.

2.3. Microstructural examination

The sintering pellets (90–95% of theoretical density) were polished and mild-etched with 1 N chloridric acid for 5 s for delineating the grain boundaries. The surface structure was examined by scanning electron microscopy (SEM).

Grain size, D, was analysed using the linear intercept method: 200 intercept lengths were measured and the average grain size $\bar{D}$ was obtained as described by Mendelson [23]: $\bar{D} = 1.56\,\bar{L}$, where $\bar{L}$ is an average grain boundary intercept length of a series of random lines on the micrograph.

3. Results and discussion

3.1. Sintering of undoped ZnO

Undoped Zn oxide ceramic presents a shrinkage (Fig. 2a) which begins a little before 700 °C and becomes important and linear from 780–920 °C, and then slows down to the sintering temperature of 1250 °C. The derived curve shows a phenomenon spread over a temperature range of 300 °C. The microstructure (Fig. 3a) reveals mainly polygon-shaped grains, of average size 12 μm. The pores are situated at the grain boundaries, and most of the time at triple boundaries. Grain boundaries are flat and often 120° apart from each other. All these features show that the ceramic is quite close to stability. Therefore extending the sintering time would not lead to grains of a greater size. The conditions of solid-phase sintering of undoped zinc oxide can lead to superficial diffusion [3], evaporation, condensation [7, 8] and volume diffusion [2], which depend on firing conditions when powders are prepared by coprecipitation [6]. The systematic study of solid-state sintering conditions of ZnO has not been undertaken here. The results above are only given for the sake of comparison with bismuth or titanium-doped ZnO ceramics.

3.2. Sintering of bismuth-doped ZnO

The shrinkage curves of all Bi-doped samples (Fig. 2b–f) are very different from those of an undoped sample (Fig. 2a). In fact, the rapid shrinkage stage is indicated on the derived curve by a sharp peak occurring at a temperature depending on the amount of Bi. This stage is unquestionably that of rearrangement, characterized by rapid kinetics which occur as soon as the liquid phase appears [9].

All Bi-doped ceramics (from 0.2%) present grains with average sizes larger than those of undoped ceramics obtained by the solid-phase sintering process: 12 μm with undoped ZnO, 31 μm with 0.2% Bi, and 56 μm with 0.5% Bi. So it is obvious that, even with a small quantity of Bi, the LPS process is predominant.

3.2.1. Dilatometry

For samples of the same composition and the same green density, the reproductibility of shrinkage curves

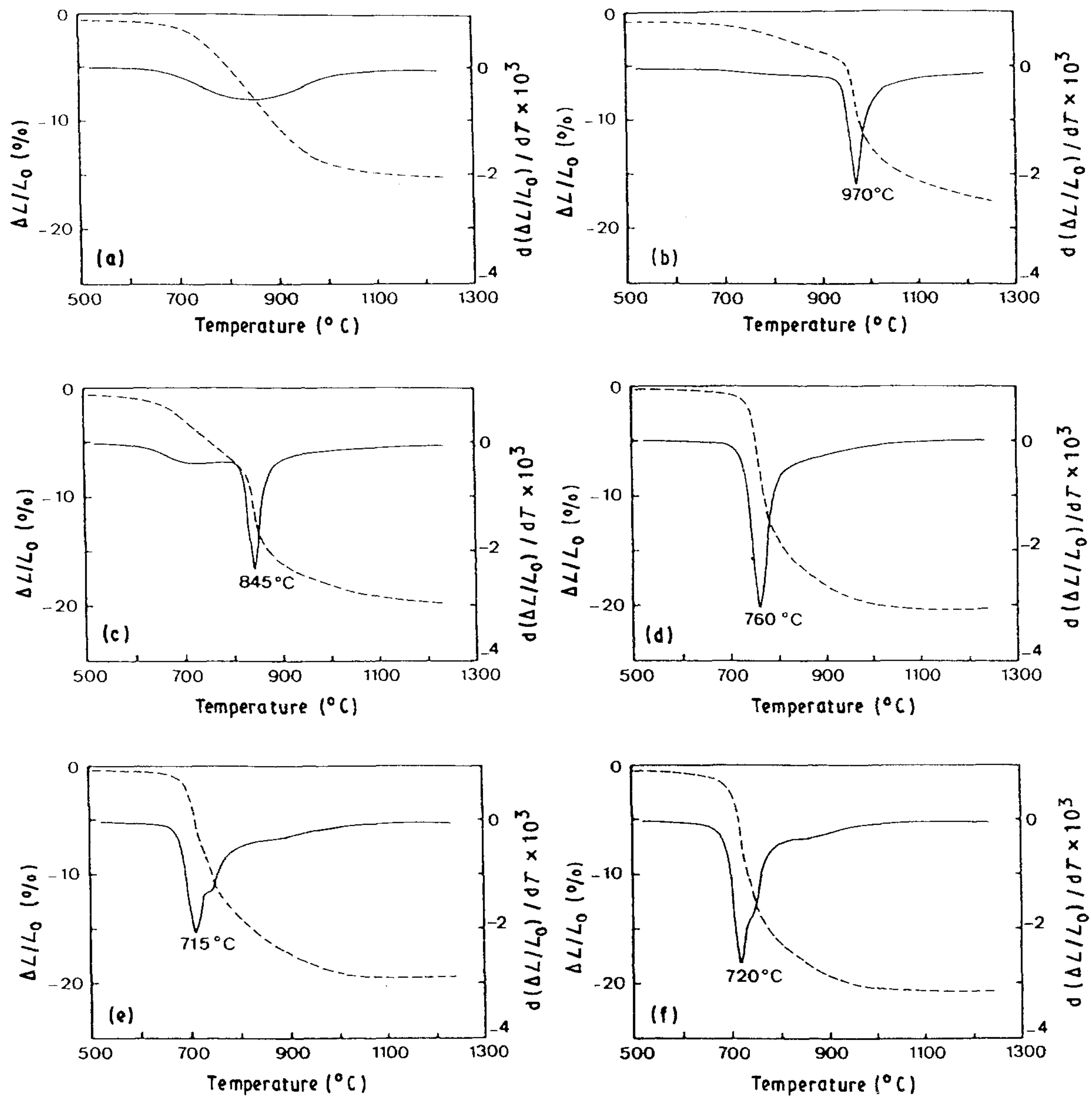

Figure 2 Dimension changes $\Delta L/L_0$ (dotted line) and its derived curves $d(\Delta L/L_0)/dT$ (solid line) as a function of temperature during sintering of samples of (a) pure ZnO, and bismuth-doped ZnO: (b) 0.2; (c) 0.5; (d) 1.0; (e) 2.0; (f) 3.0% Bi.

was checked. It was observed that variations of 10% in green density have a repercussion on the relative magnitude of the shrinkage, but do not shift the peaks of the derived curve (i.e. the observed temperature of the events). In the same way, the differences in magnitude of shrinkage displayed by the curves in Fig. 1a–f, for example, are ascribed to green density differences as the powder morphology depends on the chemical composition.

To discuss the dilatometry measurements with assurance, the stress of 18 kPa applied by the collector on the sample must be taken into account. For each sample, the axial-to-radial shrinkage ratio has been estimated by measuring the sample sizes before and after sintering. This ratio is roughly 1.15, and does not depend on the composition of the sample. Load dilatometry experiments carried out on the MgO–Bi_2O_3 system have shown that 27.5 or 55.0 kPa stresses have no influence on the grain size of the obtained ceramics [24]. Thus the stress applied by the collector amplifies the axial shrinkage, but this effect is not correlated to the composition parameter, the influence of which is the question of this study.

3.2.1.1. Small Bi contents (0.2 and 0.5 at %). With 0.2 and 0.5% Bi (Fig. 2b and c), two successive and very different shrinkages can be noticed: (i) a slow and limited phenomenon, nearly linear as a function of temperature; and (ii) a rapid phenomenon characteristic of the rearrangement when the liquid phase appears. The first phenomenon leads to a shrinkage very similar to that previously observed for the undoped zinc oxide. The linear part especially is very clear on a temperature range of 130 °C for 0.5% Bi. We therefore believe that a solid-phase sintering process occurs at this stage. Taking into account the rather low temperature and the still not very densified state, as well as the small size of crystallites, superficial diffusion plays an essential part, which is why the shrinkage remains very limited [25].

The second stage, a rearrangement phenomenon,

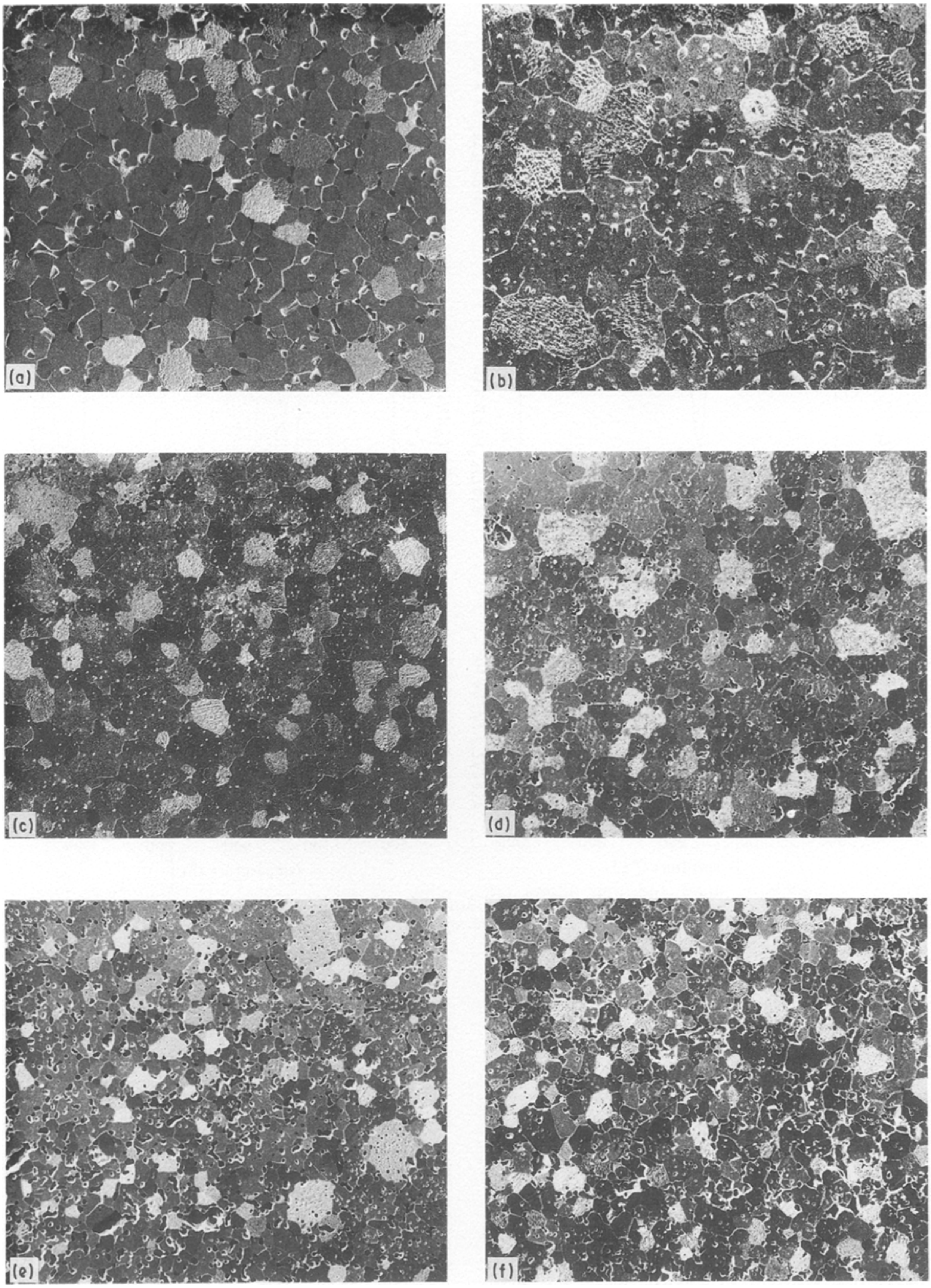

Figure 3 SEMs of polished and etched samples of (a) pure ZnO, and bismuth-doped ZnO: (b) 0.2; (c) 0.5; (d) 1; (e) 2; and (f) 3 at % Bi. (a, b) × 300; (c–f) × 100.

starts at 950 °C for 0.2% Bi (Fig. 3b) and at 825 °C for 0.5% Bi (Fig. 3c), while eutectic melting can occur as low as 750 °C [26]. A dilatometry study carried out on ceramics made from mixtures of oxides shows a delayed densification for 0.2% or less Bi [16]. That delay was assigned to Bi segregation at the surface of particles and at grain boundaries. Other works concerning the grain growth of ceramics made in the same way have led the author to propose the existence of a solid solution for small Bi content [15]. Notice that, with small Bi contents, the solid-phase diffusion is slowed down without being stopped on the one hand, and on the other, the occurrence of the liquid phase is delayed. The formation of a solid solution limited to the surface of crystallites, not easy to show, would explain both. An important Bi segregation at grain boundaries at these temperatures (700 to 900 °C) would behave like a diffusion barrier, and would not allow us to explain the sudden appearance of liquid phase around 950 °C for a 0.2% Bi content.

3.2.1.2. 1 at % Bi. For 1 at % Bi (Figs 2d and 4), liquid phase appears at around 740 °C, at about the eutectic melting temperature [26]. The rearrangement is done very rapidly, without any shrinkage discontinuity. Previous works on liquid-phase sintering of alumina powder with spherical grains showed that, depending on sintering agent, the rearrangement is either done between spheres and then between crystallites, or directly between crystallites [10]. In the first case, a shrinkage discontinuity appears, making obvious the two stage rearrangement far less rapidly than in the second case. Therefore, in our case, the rearrangement proceeds directly between crystallites, the spherical grains being destroyed as soon as a melted phase occurs; this is easily explained by the homogeneous Bi distribution in the initial powder.

3.2.1.3. Large Bi contents (2 and 3 at %). Above 1% Bi, the liquid phase appears as soon as 700 °C (Fig. 2e and f; Fig. 4), a lower temperature than expected from the ZnO–Bi_2O_3 partial-phase diagram [26, 27]. The derived dilatometry curve shows a shoulder at about 740 °C which may originate from the occurrence of an extra quantity of liquid phase, which increases the volumetric fraction of liquid and thus allows the rearrangement to speed up.

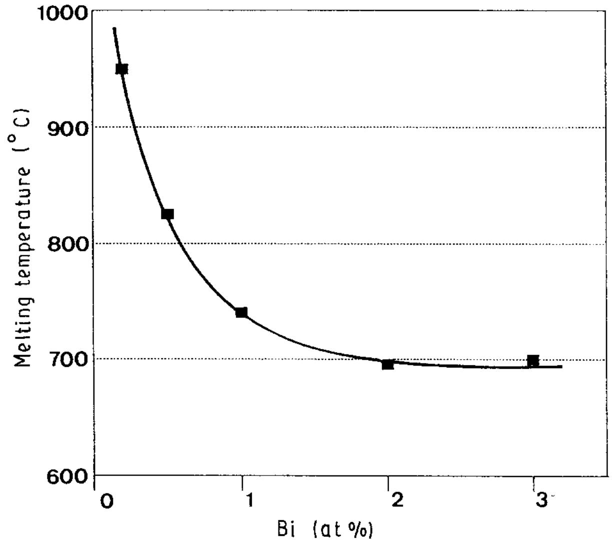

Figure 4 Temperature of occurrence of a liquid phase (about 20 °C under peak temperature of derived curve of dimension change) as a function of at % Bi during sintering of bismuth-doped ZnO.

So it is not impossible that, in addition to the eutectic melting at 750 °C, another melting of the same kind occurs at about 700 °C.

3.2.2. Microstructure

As already shown by several authors [16, 17] the ceramics which display the largest grains are obtained with 1% Bi (Figs 3d and 5). The distribution of the relative densities is very similar to that of the average grain size (Fig. 6) with a maximum of 93.4% for 1% Bi.

The microstructure examination (Fig. 3b–e) shows irregularly shaped grains, mainly for 1% Bi. Porosity is at the same time on grain boundaries (doubles or triples) and within the grains themselves. Samples with a large Bi content (2–3%) display an important intergrain porosity, obviously showing a bad sintering.

For small Bi contents (0.2 and 0.5%), the solid-phase presintering leads to the constitution of a solid

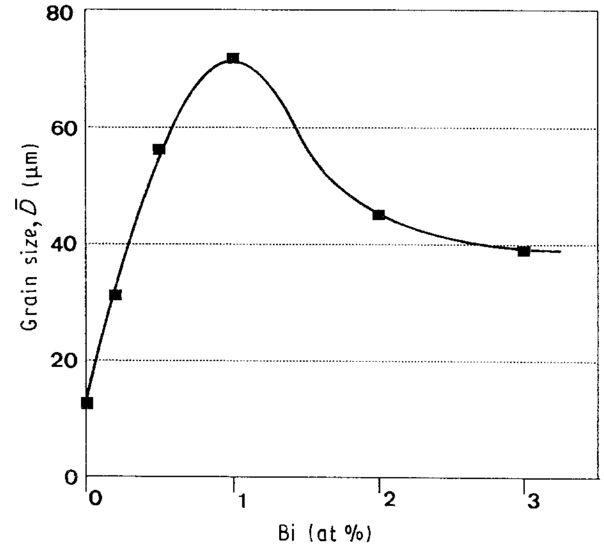

Figure 5 Average grain size $\bar{D}$ of samples of pure ZnO and bismuth-doped ZnO as a function of at % Bi.

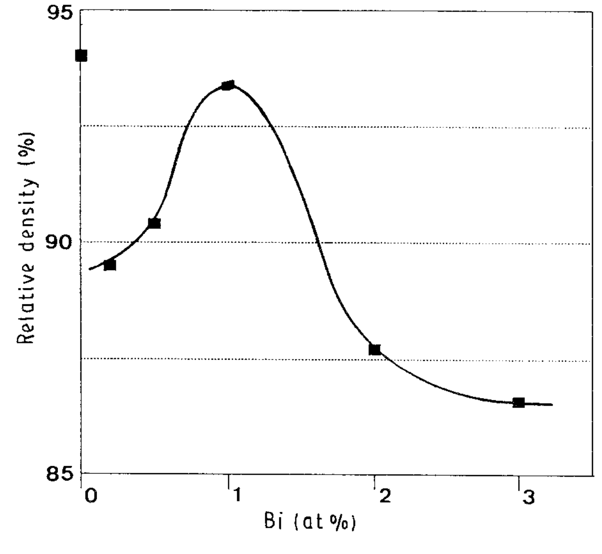

Figure 6 Relative density of samples of pure ZnO and Bi-doped ZnO as a function of at % Bi.

skeleton formed by small particles. Because of the presence of this skeleton, and also because of the small liquid volumic fraction probably being insufficient to wet all the boundaries immediately, the rearrangement is carried out more slowly which hampers both densification and grain growth. Moreover, this small quantity of liquid leaves the less densely packed region [12–14], thus increasing the porosity of these regions and leading to a lower overall density.

It has already been observed that increasing Bi content leads to more porous ceramics, presenting smaller grains [16, 17, 19] particularly for heat treatment at about 1200 °C [18]. This increase in porosity was assigned to the evaporation of Bi_2O_3 [18], as already pointed out by mass-loss studies [17]. This important porosity at grain boundaries decreases the mobility of boundaries and consequently the grain-growth speed [19]. It was also proposed that increasing the Bi content increases the probability of skeleton formation by the constitution of boundaries low in energy and unwettable, by the melted phase [16]. Such skeleton formation is probably due to brownian movement between particles, amplified by the increase of the melt volume, and thus would be limited to the very beginning of sintering, when the size of crystallite does not exceed 1 μm [11]. It might also be a consequence of the density difference between the solid phase and the melt rich in bismuth [11], which would lead to a skeleton in the upper part of the sample, partly deserted by the denser liquid.

In all these cases, a slower shrinkage will be observed during the final part of densification, as grain growth and shape accommodation play an important part in the final stage of the shrinkage [16]. That is what we observe in effect for 2 and 3% Bi content, between 750 and 1000 °C (Fig. 2e and f).

It is thus not surprising to note that a Bi content of 1%, which gives at the same time higher density and larger grain size, corresponds with the quicker shrinkage (Fig. 2d) leading without discontinuity to a maximum densification at about 1100 °C. This Bi content seems to be the best compromise to obtain grains of large size, irrespective of the powder used in ceramic making.

Thus to study the influence of titanium content in the ternary system bismuth–titanium-doped ZnO, the 1% bismuth content has been retained.

3.3. ZnO doped with 1% Bi and y% Ti (y = 0.4, 0.6, 0.8, 1.0)

Bi–Ti-doped ZnO samples lead, like 1% Bi-doped ceramic, to shrinkage curves presenting the phenomenon of rapid rearrangement, indicated on the derived curve by a sharp peak (Fig. 7a–d). In addition, the microstructure (Fig. 8a–d) shows large grains, always much larger than those obtained for undoped zinc oxide. These features once again indicate the LPS process.

3.3.1. Dilatometry

For 0.4 and 0.6% Ti, dilatometric curves as well as derived curves (Fig. 6a and b) had the same shape as

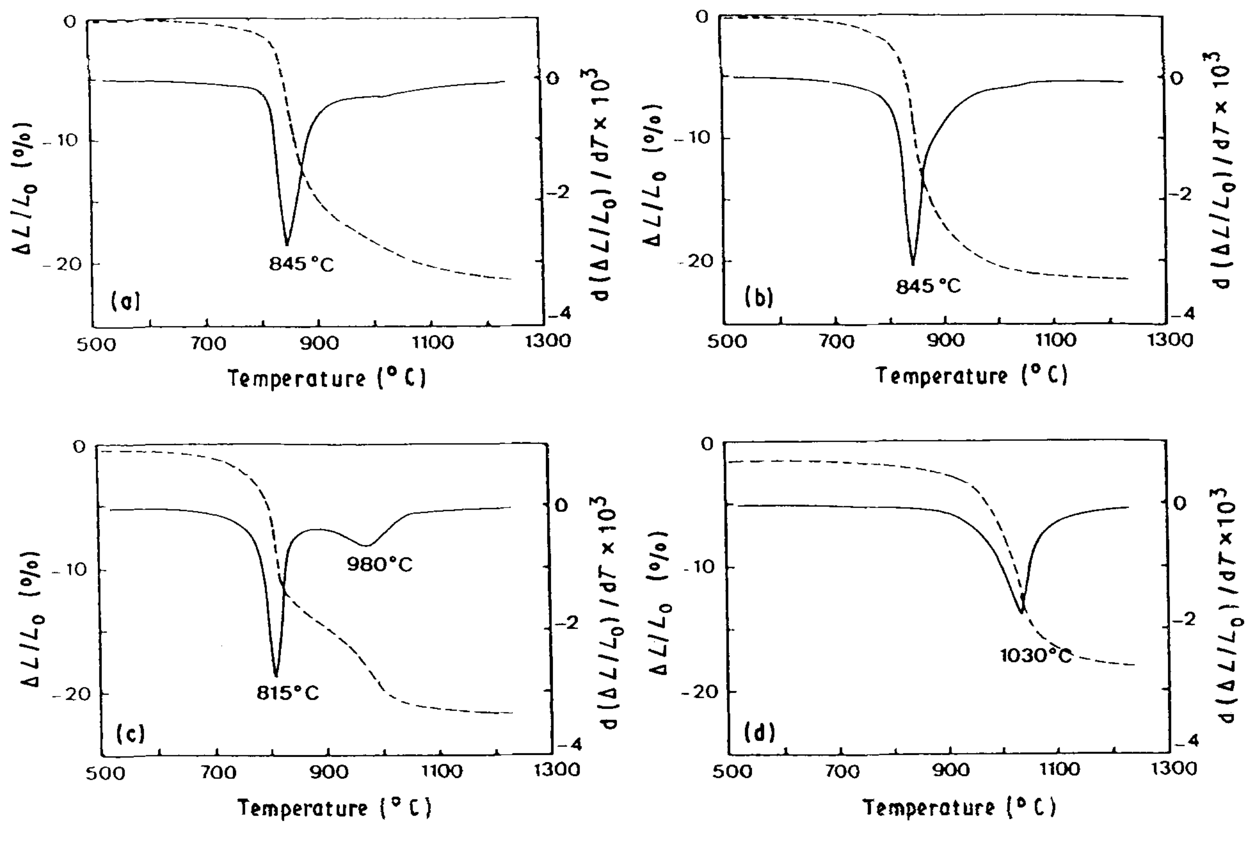

Figure 7 Dimension changes $\Delta L/L_0$ (dotted line) and its derived curves $d(\Delta L/L_0)/dT$ (solid line) as a function of temperature during sintering of samples of Bi–Ti-doped ZnO. Bi: 1 %; Ti: (a) 0.4; (b) 0.6; (c) 0.8; (d) 1.0 %.

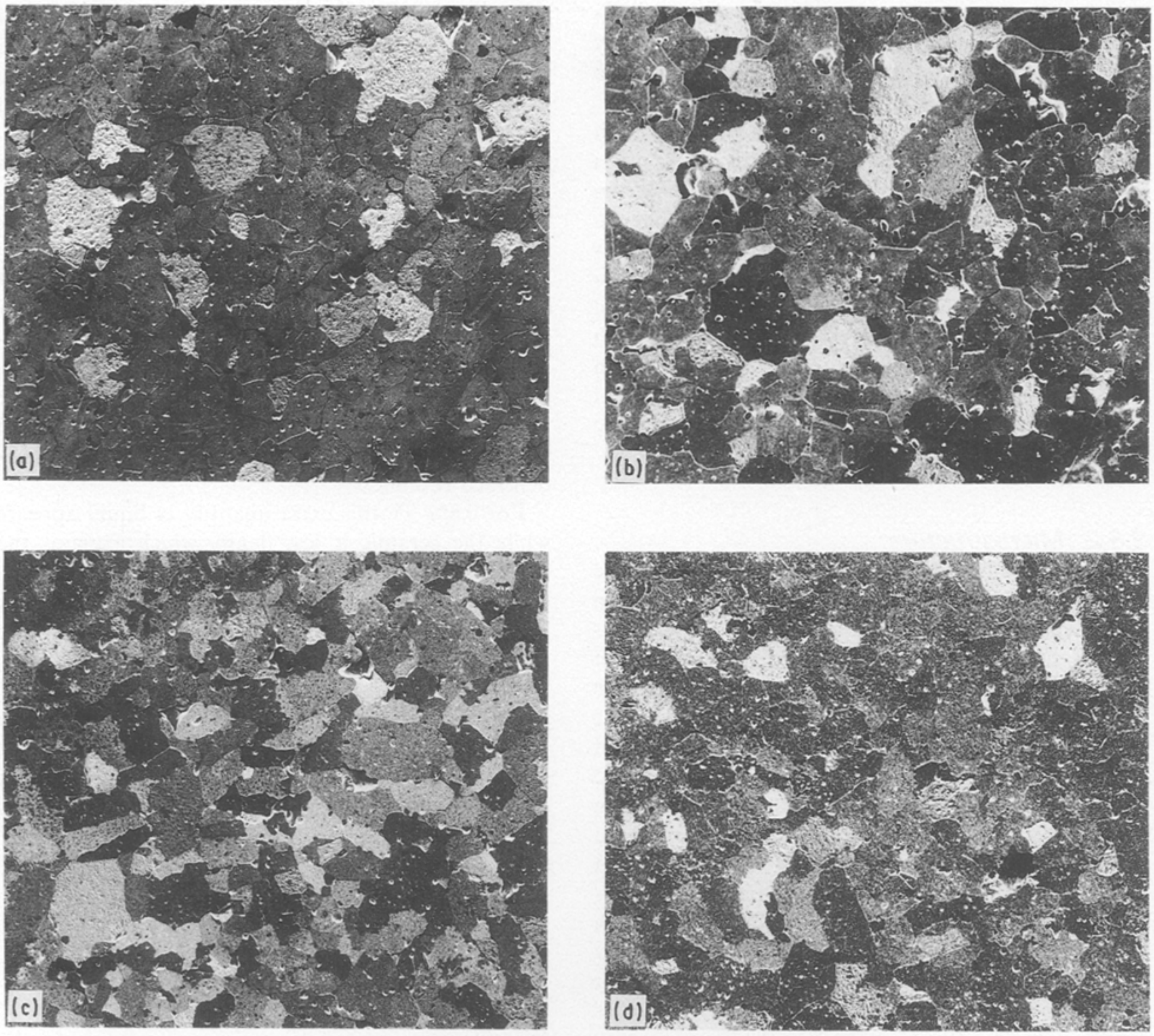

Figure 8 SEMs of polished and etched samples of 1% Bi–Ti-doped ZnO (a) 0.4; (b) 0.6; (c) 0.8; (d) 1 at % Ti. × 100.

that observed before adding Ti to the 1% Bi binary, but shifted towards the high temperatures as the liquid phase appeared only around 825 °C instead of 740 °C. So melting occurs at the same temperature as for the binary system 0.5% Bi. It can be through this mechanism a part of the bismuth has formed: not easily melting mixed oxides with titanium, such as, for example $Bi_4Ti_3O_{12}$ noted by several authors [22, 28], as reducing the amount of Bi available to form the easily melting phase at about 800 °C. The rearrangement then proceeds with a liquid volumic fraction similar to that of the 0.5% Bi binary system.

The 0.8% Ti ternary system presents a more complex shrinkage curve (Fig. 7c) to which we shall return later.

For 1% Ti, the dilatometric curve (Fig. 7d) has the usual shape with a single peak derived curve, but strongly shifted towards high temperatures. Some authors have shown the formulation of $Bi_4Ti_3O_{12}$ in such systems [28] and its decomposition around 1040 °C according to the reaction

$$Bi_4Ti_3O_{12} + 6ZnO \Rightarrow 2Bi_2O_3 + 3Zn_2TiO_4 \quad (1)$$

resulting in a spinel phase and a Bi_2O_3-rich melt.

It can be assumed that for 1% Ti, all the Bi is combined with Ti in the form of $Bi_4Ti_3O_{12}$ to around 950 °C. From this temperature, the reaction would occur with slow kinetics, releasing enough melt for the rearrangement to proceed. Furthermore it can be noted that the peak on the derived curve is asymmetrical (Fig. 7d): the first part of the rearrangement is slower than usual as it is controlled by the kinetics of the reaction which governs the occurrence of the liquid phase. According to the stoichiometry of $Bi_4Ti_3O_{12}$, the titanium does not seem to lie as a whole in this mixed oxide, as it is only for 1% Ti that the lack of Bi-rich fusible phase can be seen before 950 °C. So the existence of TiO_2 in this system cannot be ruled out.

Let us now return to the shrinkage curve obtained for 0.8% Ti (Fig. 7c). The derived curve presents two peaks: shrinkage begins as usual a little before 800 °C; around 820 °C, it suddenly slows down and keeps a steady slow speed over a temperature range of 100 °C; and over 940 °C, shrinkage speeds up clearly until 980 °C. For this composition, there is enough Bi left not mixed with Ti for the liquid phase to appear as early as 800 °C. Yet the liquid-phase amount seems to be not enough to lead to densification as fast as for 0.6% Ti. As a matter of fact, the liquid has probably migrated to the more densely packed regions, to the prejudice of the others [12–14].

The rearrangement phenomenon in the zones first deserted by the liquid phase and the filling of big pores by liquid phase are effective only after 950 °C, when reaction 1 releases an extra quantity of liquid. In addition, for all these ternary compositions, and particularly with 1% Bi and 1% Ti, no important shrinkage phenomenon is noticed before the rapid step of rearrangement. Contrary to what has been seen with 0.2 and 0.5% Bi, there is no important diffusion in solid phase before the liquid phase appears. Real diffusion barriers are thus formed at the surface of the crystallites when Bi and Ti coexist in a sample.

3.3.2. Microstructure

0.6% is the only content leading to a microstructure with really larger grains (average size 103 μm) than in the absence of titanium (Figs 8a–d and 9). The evolution of densities in terms of Ti percentage is not significant: they are around 91%, a little below those obtained without Ti (93.4% for the 1% Bi binary). The microstructure of ceramics made of zinc oxide doped with several oxides, among which are Bi_2O_3 and TiO_2, has already been studied [20–22]. It has been particularly pointed out that grain growth is enhanced for 0.5 and 1% TiO_2, whereas higher contents are not as favourable because of the precipitation of phases containing TiO_2 which interfere with grain growth [21]. Adding TiO_2 to these systems favours grain anisotropy at the same time as grain growth [20]. For these systems it has been proposed that TiO_2 dissolves rapidly in melted Bi_2O_3, increasing the liquid reactivity towards the ZnO matrix, and thus speeds up the grain growth [21].

We have noticed that in our systems, prepared by coprecipitation with no other doping elements than Bi and Ti, a significant increase in the average size of grains is obtained only for 0.6% Ti, while a content of 1% is prejudicial (Fig. 9). These results, as well as dilatometric curves (Fig. 7a–d) *vide supra* lead us to propose the same hypotheses to explain the evolution of microstructures in the Ti–Bi-doped systems.

As in the case of binary systems, the largest grain size is obtained for the composition corresponding to the fastest shrinkage (Fig. 7b). For this composition, a two-step process of densification can be proposed: (i) at 820 °C a liquid phase is formed with the Bi, not combined to Ti, in sufficient amount to allow a complete rearrangement which leads to an important densification at 950 °C; (ii) above 950 °C an extra quantity of liquid phase is produced gradually by reaction 1 allowing the growth mechanisms to be completed under the favourable conditions of an already well-densified ceramic.

For 0.8% Ti, this extra quantity of liquid appears while the ceramic is less dense, which explains the moderate enhancement of growth (Fig. 8c). For 1% Ti, rearrangement is not really advanced until 1100 °C: growth phenomena are considerably delayed and the average grain size obtained after a complete cycle is thus smaller than for other compositions (Fig. 9).

It is useful to check whether a 0.6% Ti ternary, with 1.5% instead of 1% Bi, would not lead to larger grains. The shrinkage is rapid (Fig. 10a) very like that obtained with 1% Bi and 0.6% Ti although shifted

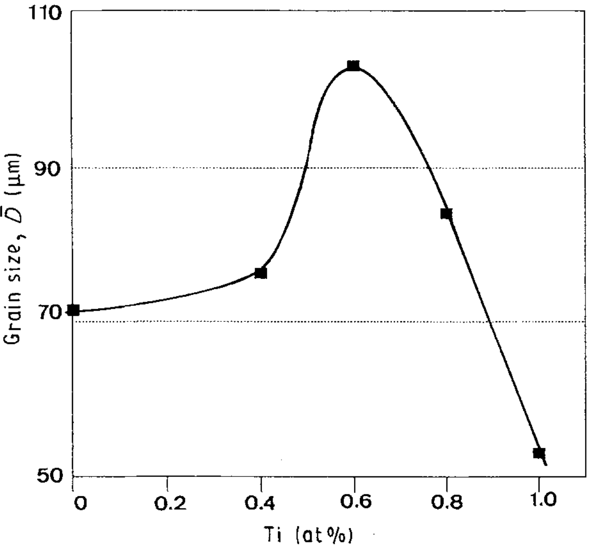

Figure 9 Average grain size $\bar{D}$ of samples of 1% Bi–Ti-doped ZnO as a function of at % Ti.

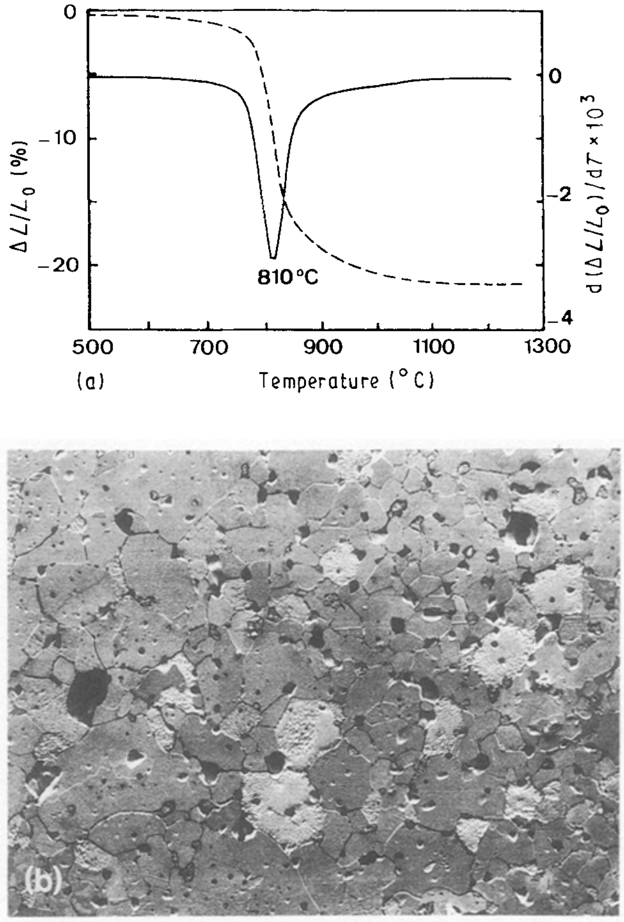

Figure 10 Sample of 1.5% Bi–0.6% Ti-doped ZnO. (a) Dimension change $\Delta L/L_0$ (dotted line) and its derived curve $d(\Delta L/L_0)/dT$ (solid line) as a function of temperature during sintering. (b) SEM of polished and etched sample. × 100.

40 °C towards a lower temperature. However the microstructure (Fig. 10b) reveals an average grain size of 54.5 μm, much under that obtained for 1% Bi–0.6% Ti compositions (103 μm). We believe that rearrangement begins at a lower temperature because the quantity of Bi not mixed with Ti is more important. We have noticed during the study of binaries that the temperature at which liquid phase appears decreases when the Bi content increases. Up to 950 °C, rearrangement proceeds very quickly; above this temperature, reaction 1 releases too great a quantity of liquid, giving rise to the difficulties already mentioned for the 2 and 3% Bi binary systems. It is therefore crucial to keep the Bi content around 1%, so that grain growth proceeds under good conditions above 1000 °C.

4. Conclusions

The liquid-phase sintering of zinc oxide powders doped with bismuth and titanium, whose few microns spherical grains consist of 50–100 nm crystallites, was systematically investigated. During sintering, rearrangement proceeds directly between crystallites, spherical grains being destroyed as soon as a liquid phase appears. The sintering behaviour of Bi-doped ZnO depends on the amount of Bi. A Bi content of 1.0 at % leads to the largest grains (70 μm on average) in a well densified ceramic; such samples are characterized by rapid shrinkage. For small Bi contents (0.2 and 0.5 at%), the LPS is preceded by the beginning of a solid phase-sintering process, and the liquid phase appears at higher temperature, during the melting of a solid solution located on the surface of the crystallites. For 2 and 3% Bi, the densification is insufficient because of bismuth evaporation and/or because of the more marked tendency to skeleton formation.

Whatever the amount of titanium in the y % Ti–1% Bi-doped ZnO, a LPS process is observed. According to the titanium content, all or a part of the bismuth is combined with titanium as $Bi_4Ti_3O_{12}$ up to 950 °C, which has an influence on the sintering behaviour. In the y% Ti–1% Bi-doped ZnO system, only the Ti content $y = 0.6\%$ leads to an increase in grain size (100 μm on average). The quantity of uncombined Bi then allows an important densification under 950 °C. Above this temperature $Bi_4Ti_3O_{12}$ decomposes and gradually releases an extra quantity of liquid, thus improving the conditions of grain growth.

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