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Combustion process in the synthesis of $ZnO–Bi_2O_3$

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Abstract

Combustion synthesis of homogeneous $ZnO–Bi_2O_3$ powder mixtures has been investigated, with emphasis on the reaction mechanism. The reaction uses salts containing the zinc and bismuth ion (oxidizer) and a fuel. The self-sustaining reaction leads to high temperatures that promote oxide formation and crystallization in a short period of time. The resulting $ZnO–Bi_2O_3$ powders show characteristics that favor applications in the field of electronic ceramics, such as varistors. Such characteristics, namely particle morphology and crystallinity degree, were accessed by X-ray diffraction and scanning electron microscopy, showing that combustion synthesis is a promising alternative method to produce adequate powders for the manufacture of varistors. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

1. Introduction

ZnO ceramics sintered in the presence of a small amount of Bi_2O_3 and other metal oxides exhibit nonlinear current-voltage characteristics [1,2] that have wide applications as electronic materials for circuit protectors to guard against voltage transients and power overloads. Some researchers [3,4] report that a Bi_2O_3-rich liquid phase enhances densification and increases the final grain size of $ZnO–Bi_2O_3$ ceramics. They also suggest that the grain growth process in $ZnO–Bi_2O_3$ ceramics is controlled by the phase boundary reaction of the ZnO with the Bi_2O_3-rich liquid rather than by diffusion of ZnO within the liquid phase during firing. The presence of other additive oxides, such as Sb_2O_3, MnO CoO Cr_2O_3, improves the nonlinear ohmic coefficient. As a result of the interest shown in ZnO varistors, several studies have been made in order to observe the influence of additives on the microstructure and properties, as well as other techniques to produce these varistors [1–6]. This paper presents a new method for preparing $ZnO–Bi_2O_3$ ceramics through the process of synthesis by combustion reaction, which is an alternative powder producing method whose advantage is its simplicity when compared to other methods, such as: combustion hydrolysis of metal–organic, sol–gel, coprecipitation and other sophisticated and costly processes.

The combustion technique employed in the area of propellants and explosives involves a mixture of reagents that transformed to the oxide easily (such as nitrates) and a fuel [such as $CO(NH_2)_2$] that act as a reagent reducer. The method is actually self-sustainable after the reaction has initiated and, owing to the exothermic characteristic of the reaction, high temperatures guarantee the crystallization and formation of oxides in a short period of time. This normally prevents the agglomeration of particles being formed [7] instantaneously.

This method also offers the advantage of high chemical homogeneity since the initial reagents are mixed in the form of an aqueous solution and, as a result, favor the production of phases or multicomponent ceramics [7].

Using the oxidizer relation of $(O)/\text{fuel}(F)=1$, the energy released is at its maximum and an explosion reaction occurs, which is sustainable and self-propagating, transforming the initial mixture (salts containing the desired metallic ions) into ceramic oxides (powders).

Some authors have employed this combustion technique, using urea as a fuel, to produce submicron powders such as mullite [8], zircon [9], calcium aluminate [10] and some oxide materials [9]. Conversely, other authors have used the combustion technique with other types of fuel such as carbohydrazide [11] and tetraformol triazine [7].

The combustion reaction process is promising for the production of powders for varistor applications compared to the conventional oxide mixtures and the sophisticated techniques that so often make production on an industrial scale impractical due to the high costs involved. Moreover, because the method of combustion reaction quickly converts a liquid solution into a solid,

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Table 1
Characteristics of the ZnO and ZnO–Bi_2O_3 powders synthesized by combustion reaction

	Properties						
			Lattice parameters		Particle size (μm)		
Powders	Surface area (m^2/g)	D_{BET} (μm)	$a=b$	c	< 90	50	< 10
ZnO	2.753	0.389	3.252 ± 0	3.278 ± 0.0062	10.2	4.3	1.0
ZB	2.295	0.467	5.207 ± 0	5.197 ± 0.113	10.2	4.3	1.0

segregation of ions can be avoided, resulting in improved chemical homogeneity.

The fuel used in this study was urea and a mixture of zinc nitrate and bismuth nitrate as oxidizer reagents. X-ray diffraction, electronic microscopy scanning, transmission electron microscopy, particle size distribution and BET specific surface area evaluated the characteristics of the powders resulting from this process.

2. Materials and methods

The combustion reaction synthesis technique involved a mixture of zinc nitrate and bismuth nitrate (reagents, which oxidize easily,) and a fuel that acts as reagent reducer.

The materials used were zinc nitrate $Zn(NO_3)_2{\cdot}6H_2O$ (99.5 mol%–Carlo Erba), $Bi(NO_3)_3$ $5H_2O$ (0.5 mol%) and urea (NH_2CONH_2) (synth.), reagent grades.

The proportions of the initial mixture were calculated according to the valences of the reacting elements in order to supply the relation [oxidizer (O)/fuel(F)] = 1, based on the pre-established stoichiometric ratio of the metallic ions to form the desired phase.

The mixture, placed in a vitreous silica basin, was homogenized and then heated on a hot plate up to ~300°C. Initially, the solution underwent melting and dehydration, followed by decay and accompanied by the release of large amounts of gases. When the mixture had taken on a more viscous appearance it was placed in a furnace, where it rapidly generated a small explosion, producing a dry oxide. The high temperatures that were reached allowed for very fast crystallization and formation of a zinc oxide and ZnO–Bi_2O_3 (ZB) powder.

The powders resulting from the combustion reactions were then ground in a mortar, sieved (≠200), and subjected to characterization by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Particle size distribution was determined with a Micromeritics - Sedigraph 5100 apparatus and the BET specific surface area was determined using a Quantachrome Quantasorb apparatus.

3. Results

By means of a combustion reaction between zinc nitrate and bismuth nitrate (reagents which transformed to the oxides easily) and urea acting as reagent reducer, it was possible to obtain fine crystalline powders that maintain the stoichiometric composition. Because the reactants were dissolved in an aqueous solution directly in a vitreous basin, the possibility of contamination was minimized.

The results below will be compared with the ZnO powders previously obtained through the same

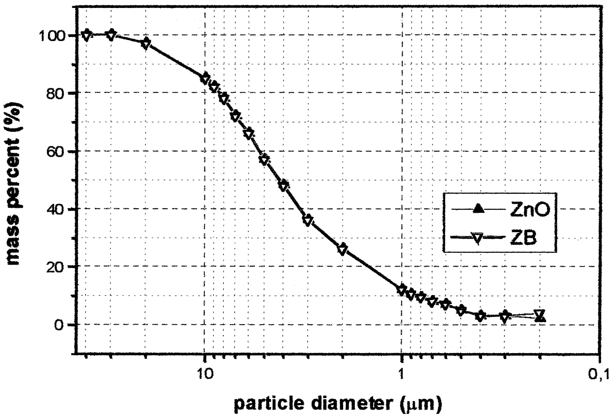


Fig. 1. Particle distribution of ZnO and ZB powders obtained through synthesis by combustion reaction.

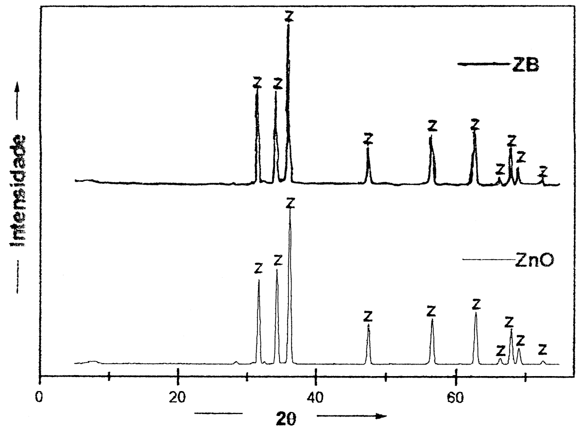


Fig. 2. X-ray diffraction patterns of ZnO and ZB powders obtained through synthesis by combustion reaction.

technique, which is discussed in detail in the literature [12].

Table 1 presents the surface area and particle size of ZnO and ZnO–Bi_2O_3 (ZB) systems calculated by BET. The particle diameter increases when the Bi_2O_3 is present. These results agree with the results reported by Wong and Asokan [3,4].

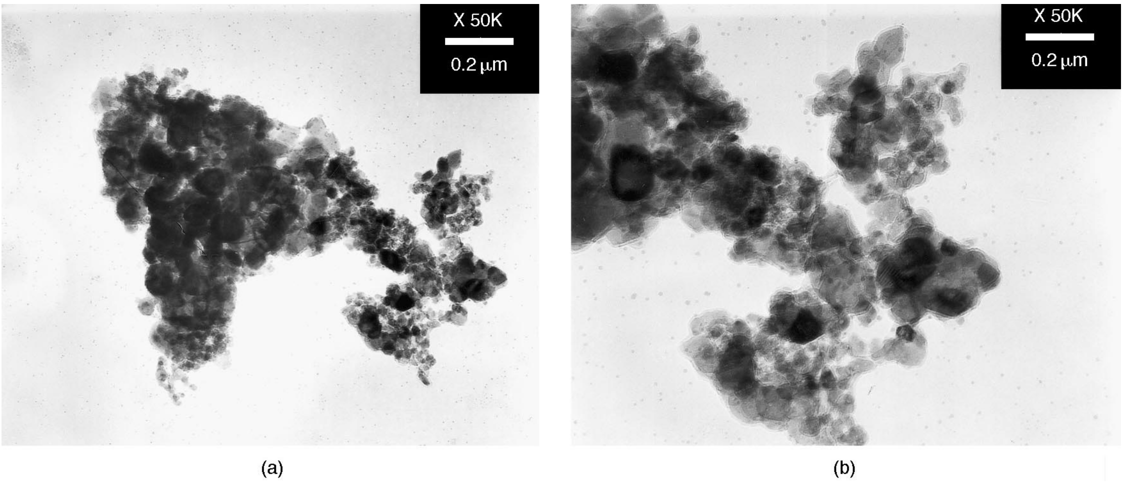
Fig. 1 shows the particle distribution of the ZnO powders produced by combustion reaction, with and without Bi_2O_3. The results agree with those obtained by the BET technique and appear to be correlated to the aggregated aspects of the as-prepared powders.

Fig. 2 compares the X-ray diffraction patterns of the ZnO powders produced by combustion reaction, with and without Bi_2O_3.

The Bi_2O_3 was not detected, probably because of the small amount used in the mixture. However, from the ZnO–Bi_2O_3 binary diagram [11] and under the conditions used [0.5 mol% Bi_2O_3 and the high temperatures reached during the reaction ($>700°C$)], it is possible to predict the formation of γ-Bi_2O_3 which crystallizes in a cubic structure.

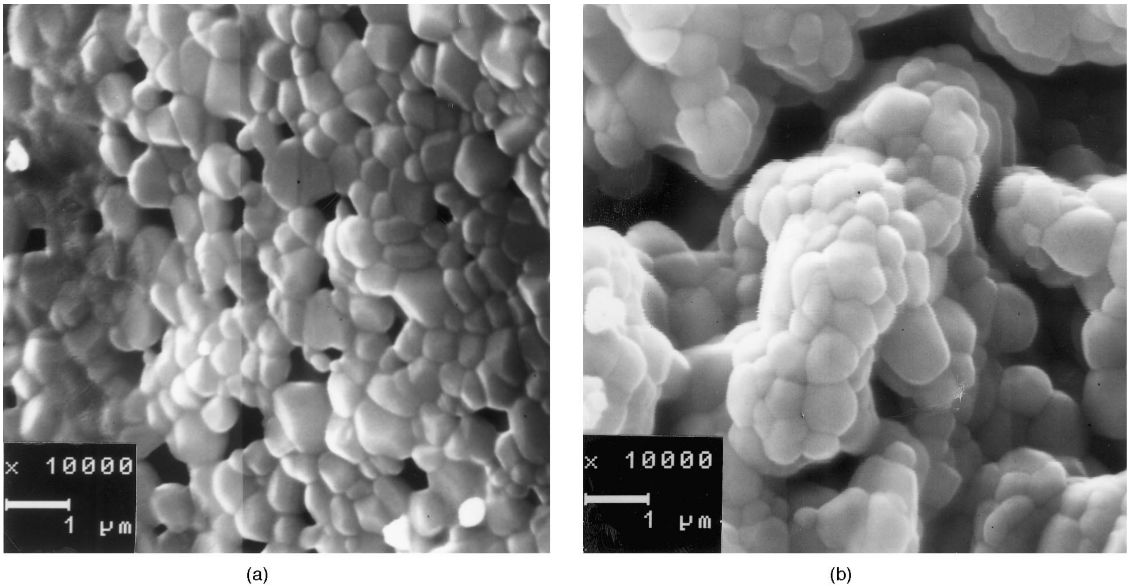
The lattice parameters (Table 1) agree with the literature results [13] that suggest, in the case of γ-Bi_2O_3, that all the a values were greater than that of the Joint Committee on Powder Diffraction Standards (JCPDS) (3.249) and, on the other hand, that all the *c* values were smaller than that of JCPDS (5.206).

The morphological appearance of the ZnO and ZB powders obtained by combustion reaction can be observed in Figs. 3 and 4.



(a) (b)

Fig. 3. Transmission electron micrographs showing typical morphology of (a) individual as-prepared ZnO and (b) ZB crystallites produced by combustion reaction.



(a) (b)

Fig. 4. Scanning electron micrographs showing typical morphology of (a) as-prepared ZnO and (b) ZB powders produced by combustion reaction.

Fig. 3a and b shows typical morphologies of individual ZnO and ZB crystallites (<400 nm), and confirm that the average particle size increases when the Bi_2O_3 is present (Fig. 4b), although both systems become somewhat aggregated.

The scanning electron micrographs (Fig. 4) shows that sintering of particles was initiated and resulted in small aggregates. The high temperature reached during the reaction can explain this result. When the Bi_2O_3 is present, the initial sintering process is favored because the high temperature reached allows the Bi_2O_3 to melt (melting point 750°C). The liquid phase formation leads to particle aggregation since it favors the possibility of diffusion through particle contact.

4. Conclusions

The combustion reaction can be used to prepare ZnO and ZnO–Bi_2O_3 powders in an aqueous solution of zinc and bismuth nitrates in single step reaction.

The combustion reaction has been shown to be a simple, inexpensive and efficient technique for the stoichiometric and high purity grained ZnO and ZnO–Bi_2O_3 powders.

The foam-like structures of as-prepared powders can be easily dispersed and subsequently used.

The results extend the use of the combustion reaction method for preparation of varistor compositions by the introduction of the desired ions into the precursor solution.

Acknowledgements

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