TEM Characterization of ZnO - Bi_2O_3 - Sb_2O_3 – CoO Ceramics Obtained by Combustion Process

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Abstract

Combustion synthesis of homogeneous ZnO. Bi_2O_3. Sb_2O_3. CoO powders from stoichiometric mixtures of the relevant water – soluble metal nitrates, as cation precursors, and urea as fuel, was investigated. Which is an alternative powder producing method whose advantage is its simplicity (one - step reaction), pureness, reactivity and high chemical homogeneity when compared to other methods. The resulting ZnO. Bi_2O_3. Sb_2O_3. CoO sample characterized by TEM, SEM showed that the sintering of the particle was initiated resulting and small micro aggregates (5μm). The self- sustaining reaction leads to high temperatures that promote formation of oxide powders showing characteristics in the electronic ceramic field, such as ceramic varistors.

Key words: Combustion reaction, powder, ZnO, varistors

Introduction

Very fine crystalline multicomponent oxide ceramic powders are often difficult to produce by other synthesis routes. Several conventional synthesis techniques are available, including solid state synthesis, co-precipitation, freeze-drying, and spray drying. Each method has its own characteristic degree of purity, compositional homogeneity, powder morphology and degree of agglomeration. The process of combustion synthesis [1-12] is also an important powder preparation process, by which several hundred compounds can be prepared. The process of combustion reaction uses nitrates as oxidizers and urea as fuel, which allow for the use of **lower** firing temperatures and reduce the time required to obtain the product. Thus, the main purpose of this type of combustion reaction is the continuous formation of well-crystallized single-phase fine powders through the chemical energy released during combustion. In this study, we propose to investigate the morphology of the ZnO- Bi_2O_3-Sb_2O_3-CoO powders obtained by combustion reaction [1, 13] using a mixed solution of metal nitrates and urea to obtain fine uniform powders, as well as the microstructural and electrical characteristics after sintering pellets at 1050°C/1,5 hours.

Materials and Methods

The combustion synthesis of this study involved mixing $Zn(NO_3)_2.6H_2O$ (98 mol %) with $Bi(NO_3)_3$ $5H_2O$ (0,5 mol %), $Co(NO_3)_2.6H_2O$ (0,5 mol %), Sb_2O_3 (mol %)(ZBSC) (reagents used as cation precursors) and $CO(NH_2)_2$, a fuel that acts as a reducing reagent. This mixture, placed in a vitreous silica basin, was homogenized and then heated on a hot plate to ~300°C. Upon taking on a more viscous appearance, the mixture was placed in a box furnace preheated to 700°C in which ignition took place, producing a dry fragile foam. This foam was then lightly ground in the silica basin with a porcelain pestle and the powder sieved through a # 200 mesh and characterized by scanning electron microscopy (SEM) (MODEL Carl Zeiss DSM 940 A), and transmission electric microscopy (TEM) (LaB_6 field emission HITACHI S-4100). After the powder was

characterized, it was pressed uniaxially into pellets of approximately 0,1 cm thickness and 1,2 cm diameter at 130 MPa and subsequently sintered at 1050°C / 1,5 hours. Following sinterization, the samples were analyzed by SEM and X-ray energy dispersion spectroscopy (EDS). Current-tension measurements were taken using High voltage measure unit (KEITHLEY Model 248).

Results and Discussion

Figure 1 presents the morphological appearance of the ZnO-Bi_2O_3-Sb_2O_3-CoO powder obtained by the combustion reaction method, showing the typical

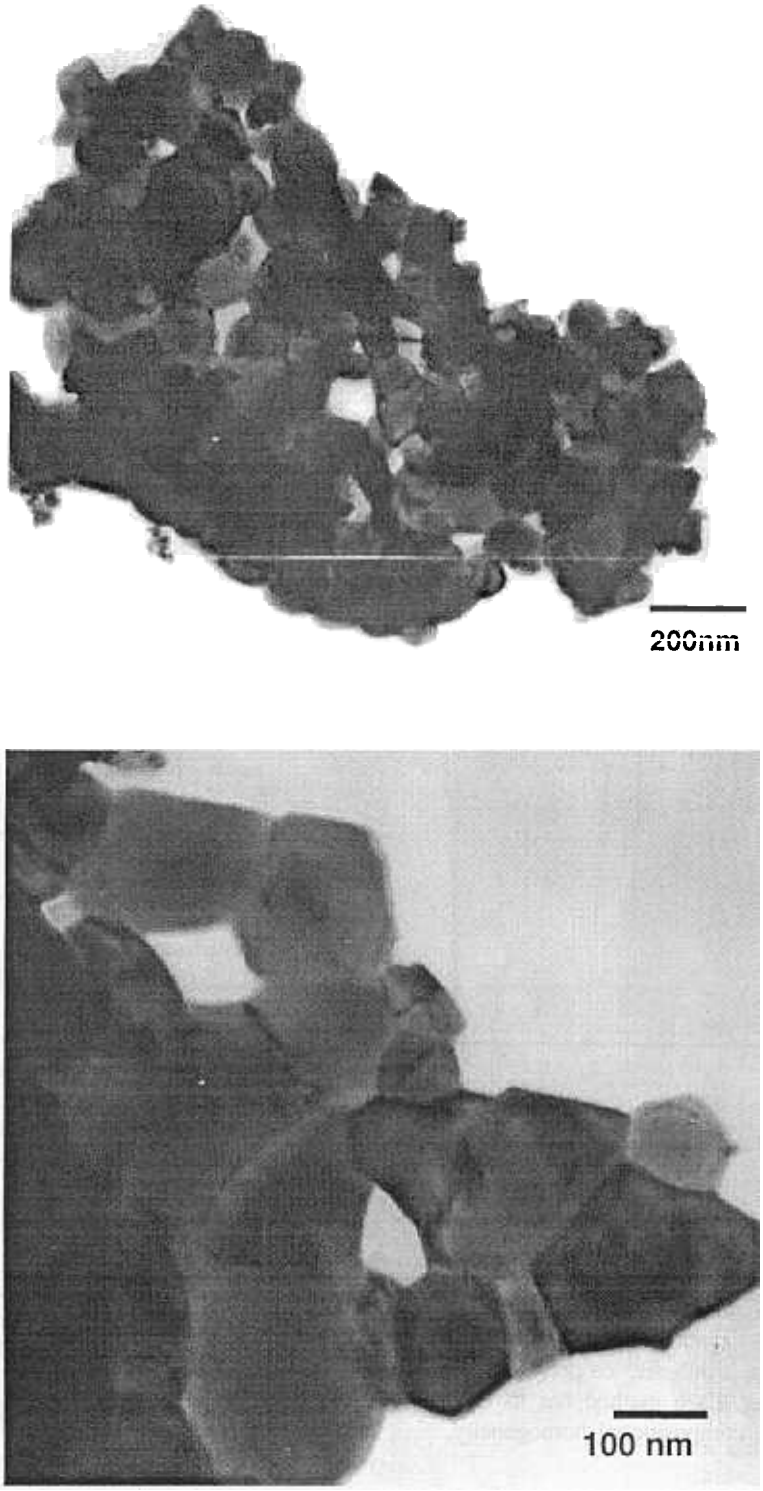

Figure 1. TEM - Transmission electron microscopy of ZBSC powders produced by combustion reaction

morphology of individual crystallites (<122 nm). The micrographs of Figures 1 and 2 indicate that particle sintering began and that it resulted in small micro-aggregates. Figure 2 also shows the agglomeration of these micro-aggregates, with small particles acting as anchors between two others, thereby favoring mass transport through the boundary (necking). Some darker areas may characterize regions of higher electric absorption resulting from the presence of very fine particles, which favor intense disordered mass transport. Table I presents some of the characteristics of the stoichiometric powders obtained after combustion synthesis, which make up the ZBSC system. As can be seen from this table, the ZBSC powder consists of small

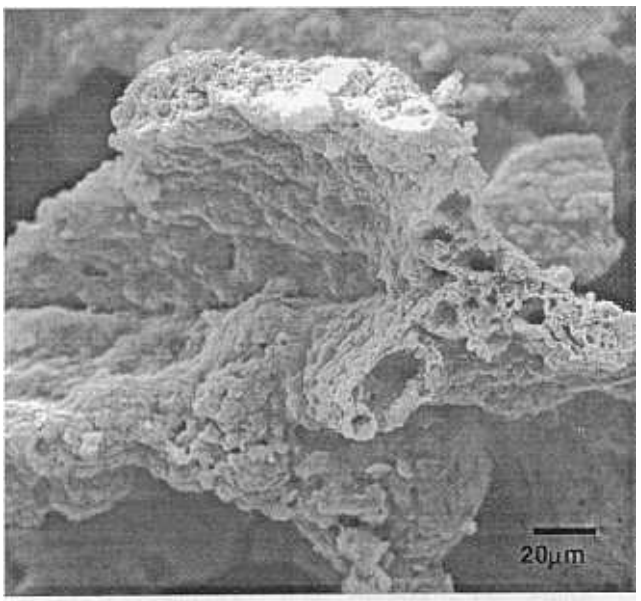

Figure 2. SEM - Scanning electron micrographs showing typical morphology of ZBSC powders produced by combustion reaction.

sized particles. The particle sizes revealed in these micrographs coincide with the particle sizes of the powders calculated by BET and TEM and observed through scanning electronic microscopy (SEM). Figure 3 presents the microstructure of the ZBSC sample after sinterization at 1050°C/1.5h, showing the spinel phase ($3Zn_7Sb_2O_{12}$) between the ZnO grains distributed homogeneously throughout the microstructure. These results were confirmed by EDS, which revealed the presence of Bi and Sb segregated in specific regions, indicating the preferential formation of the spinel ($3Zn_7Sb_2O_{12}$) and pyrochlore ($2Zn_2Bi_3O_{14}$) phases along the ZnO grain contours. The Co shows a dispersed pattern in the matrix (ZnO), indicating the formation of a solid solution with ZnO or intermediate phases. Figure 4 and Table II show the current density curve as a function of the electric field.

Table I. Characteristics of stoichiometric powder

Properties	
Surface area (m^2/g)	8,76
D_{BET} (nm)	122
D_{TEM} (nm)	165

Based on the linear regression of this curve on a logarithmic scale, the value of the coefficient of nonlinearity (α) was determined at approximately 6. This α value is low because other additives, such as MnO_2 and Cr_2O_3, are required to obtain better electrical properties.

Conclusions

The combustion reaction can be used to successfully produce ZnO – Bi_2O_3 – Sb_2O_3 - CoO varistors, since it has proven to be a simple, inexpensive and efficient technique to produce stoichiometric and high purity grained ZnO varistors.

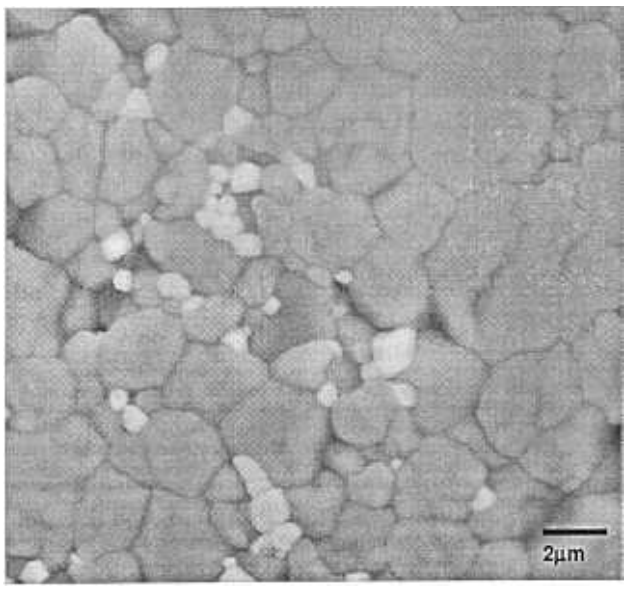

Figure 3. SEM – Microstructure of the ZBSC system samples sintered at 1050°C for 1.5 h, polished with alumina and subjected to thermal attack.

Table II. Characteristics of ZBSC varistor

Properties	
Apparent density (g/cm^2)	5,16 ± 0,15
Relative density (%)	92,09 ± 0,75
Grain size (µm)	2,1
Non linear coefficient (α)	6,31 ± 0,48
Breakdown electric field (E_r)	

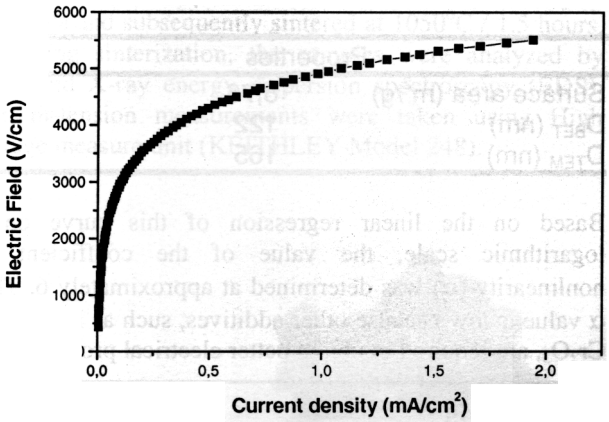

Figure 4. Electric field as a function of the current density of the ZBSC system samples obtained from combustion reaction sintered at 1050°C.

Acknowledgments

The authors gratefully acknowledgment the Department of Ceramics and Glass Engineering at the University of Aveiro, who hosted part of this work, and the financial support of FAPES—State of São Paulo Research Support Foundation, Brazil, and FCT—Foundation for Science and Technology, Portugal.

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