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Parallel Development of Microstructure and Electrical Properties in Doped-Zinc Oxide

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Abstract

Zinc oxide (ZnO) is semiconductor ceramics having highly non-ohmic current-voltage characteristics which originate at the grain boundaries and the electrical properties are closely correlated with the particle size and morphology of ZnO grains. Hence, in this research the parallel evolution of the electrical properties with microstructure changes was investigated. Polycrystalline ZnO doped with bismuth oxide (Bi₂O₃) and cobalt oxide (CoO) was synthesized by using the high energy ball milling (HEBM) technique for 12 hours and sintered from 500 to 1300 °C with 100 °C increments. ZnO nanopowder with average particle size of 10.08 nm was successfully proved by Transmission Electron Microscopy (TEM). Decreasing in particle size would lead to improved grain growth control and homogeneity for better electrical characteristics. The HEBM technique produced good electrical properties due to the proper microstructure formed at low-sintering temperature and improved grain boundary characteristics.

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Introduction

Ceramic materials based on zinc oxide (ZnO) with minor additions of other oxides such as bismuth oxide (Bi₂O₃), antimony oxide (Sb₂O₃), cobalt oxide (CoO), manganese oxide (MnO) and chromium oxide (Cr₂O₃) exhibit highly nonlinear current-voltage (I-V) characteristic and, therefore are widely used as varistors devices to protect electronic equipment against overvoltage. In the normal case, varistors are subjected to a voltage below their characteristic breakdown and pass only a leakage current. When the overvoltage exceeds the breakdown voltage, the varistor becomes highly conducting and draws current through it, usually to ground. When the voltage returns to normal, the varistor returns to its highly resistive state [1]. ZnO is a typical material controlled by grain boundaries and it is expected that the properties of the samples will be modified because of many defects at grain boundaries especially for nanostructured materials due to large grain boundary volumes. The high performance of doped-ZnO samples can be improved by reducing the grain size, which allows the increased grain boundary per unit volume and improves the breakdown voltage. Other important factors to achieve high performance of doped-ZnO samples are to have the dopants distribution homogeneously throughout the grain boundary [2, 3] and to start with fine powders such as nanopowders as the starting materials so that fine grains and homogeneous dopants distribution are retained even after sintering. High energy ball milling (HEBM) is one of the simple, effective and cost intensive techniques used to synthesize ZnO nanopowder. Ever since nanotechnology has become popular, there have been many techniques developed to make nanocrystalline ZnO powders, which include sol-gel [4] coprecipitation [5], intensive mechanical milling [6,7], microemulsion [8], metallorganic method [9], solution coating [10,11] and combustion synthesis [12,13]. Microstructurally, the doped-ZnO samples consist of highly conductive n-type ZnO grains surrounded by electrically insulating grain boundary

regions. This property is attributed to the interface layer which is chemically related to the bismuth-rich phase and has been found to be essential for forming non-ohmic behavior. The properties of the doped-ZnO samples are similar to a pair of back-to-back avalanche diode [14]. In the ZnO grains, there is an abundance of mobile electrons where the electrons tend to diffuse away to reach the interface layers and be trapped by the trapping states, leaving behind a positive fixed charge of ionized donors in the neighborhood of the interface layers. Consequently, a depletion region is formed on both sides of the grain boundary and thus there are a series of double Schottky barrier diodes in the doped-ZnO samples [15]. Therefore, the nature of the interface layer is of considerable interest, the knowledge of which plays an important role in understanding the highly non-ohmic property of the doped-ZnO samples.

Research on nonlinear coefficient, α of doped-ZnO samples is well known and accepted. However a systematic study on microstructure-property relationship in cobalt doped-ZnO from low sintering temperature (nanometer size regime) to high sintering temperature (micrometer size regime) has not been done before. Hence, in this paper, we report the results of an attempt to experimentally track and explain the relationship between electrical properties and microstructure as they evolved in parallel from low sintering temperature to high sintering temperature.

Experimental

Materials & Methods

Samples of the doped-ZnO samples with the composition of ZnO-Bi₂O₃-CoO were prepared by high energy ball milling (HEBM) technique. The high purity powders of ZnO, Bi₂O₃ and CoO were weighed in stoichiometric ratio and milled for 12 hours. Then the milled powder was granulated by monodisperse granulation technique where in this technique the milled powder

were mixed with polyvinyl alcohol (PVA) until it was fully wet and dried under fluorescent lamp. After drying, the powder was ground and sieve through a 150 nm sieve. The resulting powder was then pressed into disc-shapes samples by uniaxial pressing and sintered at 500, 600, 700, 800, 900, 1000, 1100, 1200 and 1300 °C. The densities of the samples after sintering measured using the Archimedes method and the particles sizes of the milled powder were obtained by transmission electron microscope (TEM). The crystalline phase of the samples was analyzed by using X-ray diffraction (XRD) characterization. The microstructure of the samples after sintering was observed by field scanning electron microscope (FESEM) and the average grain size was measured by the intercept method from the cross-sectional surface of the FESEM images of ZnO grains. Electrical measurements were performed to obtain their (I-V) characteristic using an electrometer (Keithley 6517). For the electrical measurement, both surfaces of the disc-shaped samples were polished to give a final thickness of 0.7 mm and sandwiched between two cooper electrodes and the currents measured relative to the applied voltage. Electrical contacts were applied to both surfaces using conducting silver paint. The coefficient of nonlinearity (α) was defined as follows:

$$\alpha = \frac{\log I_2 - \log I_1}{\log V_2 - \log V_1} \quad (1)$$

where V_1 and V_2 are the voltages at the currents I_1 (1.0 mA) and I_2 (10 mA), respectively.

Results and Discussion

Structure and Microstructure

The XRD patterns of the doped-ZnO samples are shown in Figure 1. The XRD pattern reveals the presence of primary phase ZnO and secondary phases of $\text{Bi}_{12}\text{ZnO}_{20}$. The peaks are (100), (002), (111), (102) and (110) shown in the patterns can be identified as the hexagonal wurtzite structure of ZnO ceramic. From the XRD spectra it was shown that as the sintering temperature increased the diffraction peaks became sharper and stronger, indicating the crystallinity improvement of the samples. Additional peak of $\text{Bi}_{12}\text{ZnO}_{20}$ was found for all sintered samples and the existence of $\text{Bi}_{12}\text{ZnO}_{20}$ phase induced the nonlinear-characteristics in ZnO samples, thus contributing to Bi_2O_3 -rich liquid phase along the grain boundaries.

The average particle size of the milled ZnO powder was found to be 10 nm as shown in Figure 2 and the TEM result proved that the nanoparticles powder was successfully obtained from HEBM technique. From Figure 3, as expected the density of the samples increased as the sintering temperatures increased due to the larger grain size and diminished pores. The elemental distribution was verified by EDAX analysis from Figure 4 and from the observation it clearly shows the presence of Zn, Bi, O and Co element for sample sintered from 500 until 1100 °C. Meanwhile, the sample sintered at 1200 and 1300 °C, only showed Zn, O and Co elements as detected by EDAX due to the diminishing Bi-rich phase when the sintering temperature increased. The higher percentage of Bi element has been observed at the 1100 °C sintering temperature and the existence of thin bismuth oxide layer at the grain boundaries was necessary to form a potential barrier for improving the electrical properties of doped-ZnO samples. Due to the similar ionic radius of Co^{2+} (0.58) with Zn^{2+} (0.60) ions, the Co ions can easily be substituted into Zn sub lattice and can be observed in all spectrums in Figure 4.

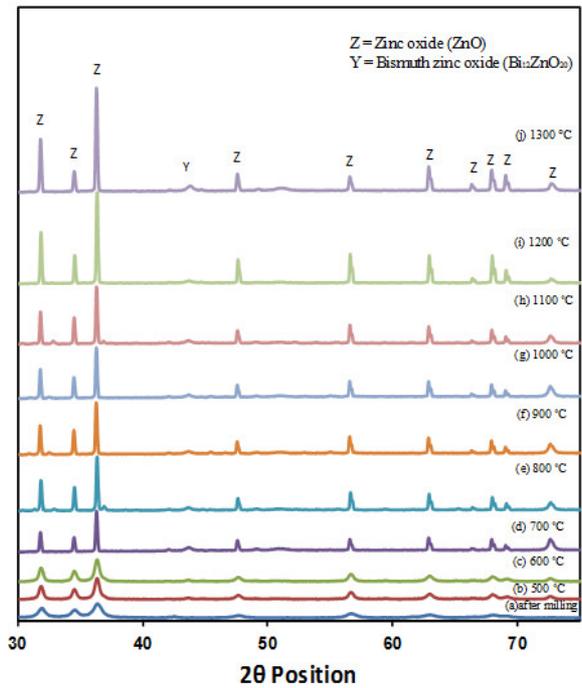


Figure 1: X-ray diffraction (XRD) patterns of ZnO-Bi₂O₃-CoO samples

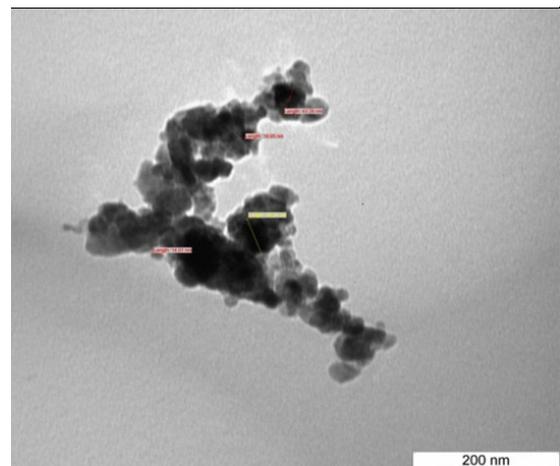


Figure 2: Transmission electron microscope (TEM) micrograph of ZnO-Bi₂O₃-CoO powder milled for 12 hours

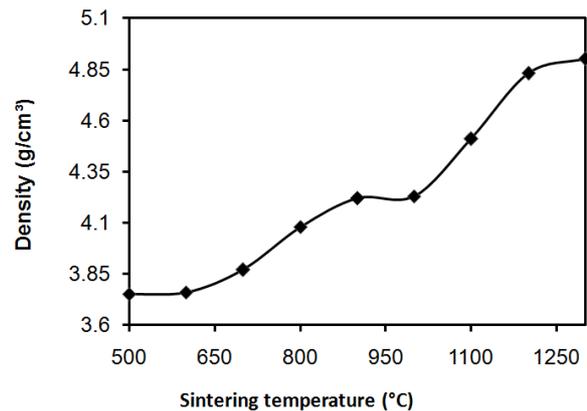


Figure 3: Density for ZnO-Bi₂O₃-CoO disc

Figure 5 shows FESEM micrographs and distribution of grain size of the ceramic samples at different sintering temperatures. It was found that the microstructure for all samples consists of two kinds of grains which are big grains as primary phases and small

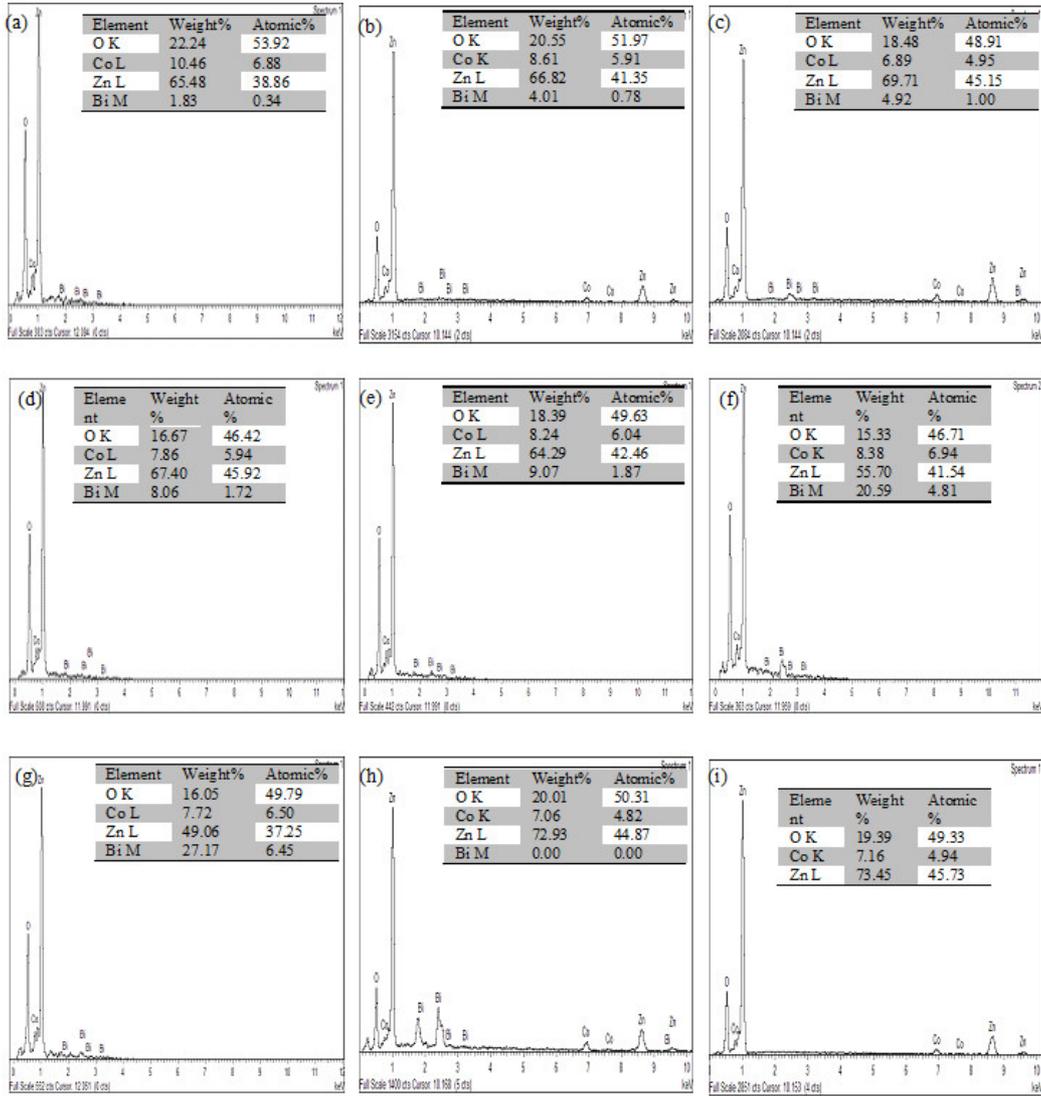


Figure 4: EDAX measurement for ZnO-Bi₂O₃-CoO samples sintered at (a) 500, (b) 600, (c) 700, (d) 800, (e) 900, (f) 1000, (g) 1100, (h) 1200 and (i) 1300 °C

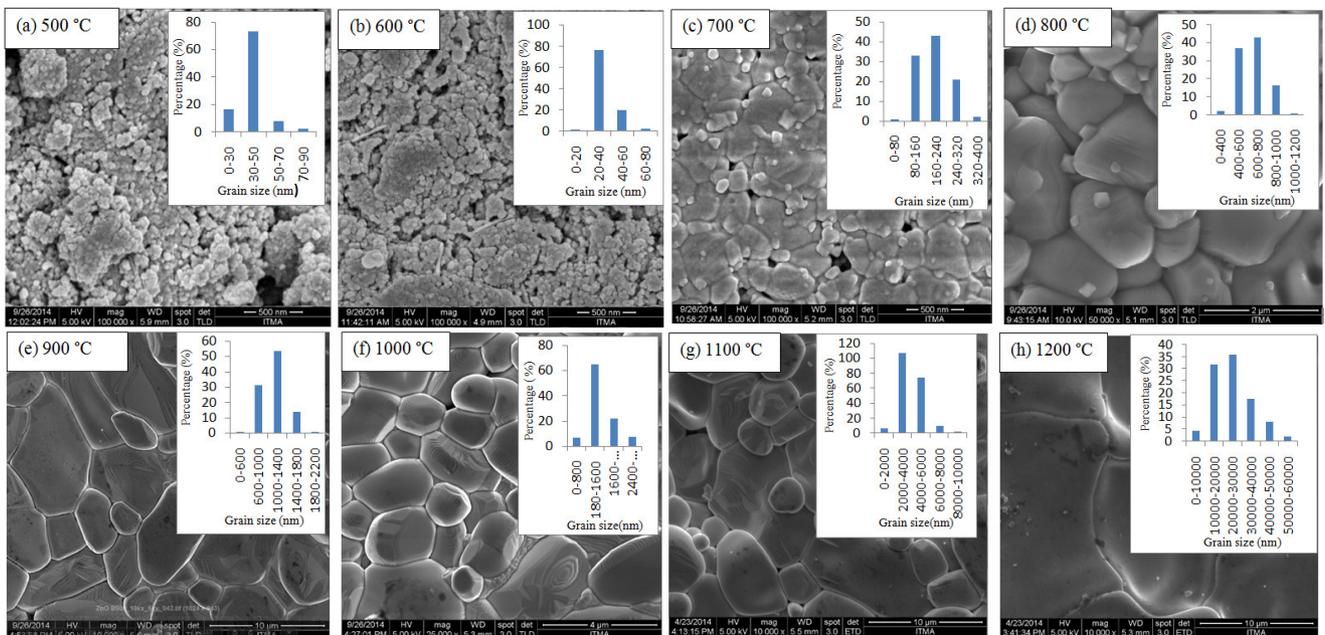


Figure 5: FESEM images of ZnO-Bi₂O₃-CoO samples sintered...

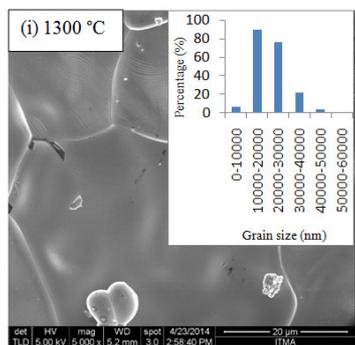


Figure 5: FESEM images of ZnO-Bi₂O₃-CoO samples sintered at (a) 500, (b) 600, (c) 700, (d) 800, (e) 900, (f) 1000, (g) 1100, (h) 1200 and (i) 1300 °C

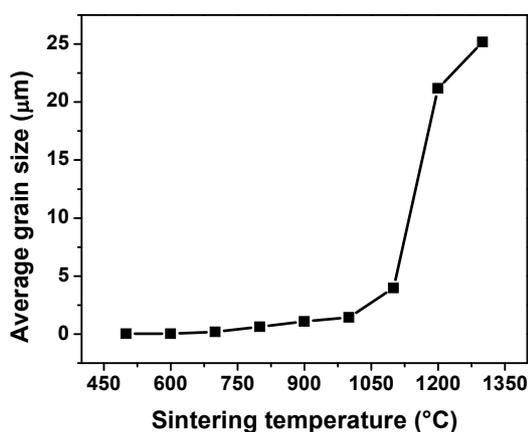


Figure 6: Variation in average grain size of ZnO-Bi₂O₃-CoO with different sintering temperatures

intergranular grains as secondary phases. When the sintering temperature increased, the average grain size gradually increased, indicating that the microstructure became more compact with less grain boundaries and reduced discontinuity between the grains. The average grain size ranges from 0.04 to 25.17 µm with the increased of sintering temperature, as observed from Figure 6. It was observed that the grain growth has a linear relationship with sintering temperatures. A high sintering temperature is known to provide a larger driving force for internal atomic diffusion responsible for grain growth and pore elimination. The presence of the second phase increases the diffusion distance between ZnO grains. Bi₂O₃ also helps in densification and for wetting of ZnO grains [16] because addition of Bi₂O₃ will form liquid phase during sintering and hence encourages ZnO grains to grow. Table 1 shows that the nanograin can only be observed at 500 °C and as the sintering temperature increases, the average grain size abruptly increased. This kind of rapid grain growth resulted from capillary driving forces at high temperatures [16] and the grain boundaries of nanograin ZnO can drastically change the physical properties.

Nonlinear current-voltage (I-V) Characteristics

One of the most important parameters in the doped-ZnO samples is the nonlinear coefficient, α , which characterizes the native properties of the samples itself. The doped-ZnO properties are characterized by non-ohmicity in the I-V characteristics [17]. The degree of nonlinearity is determined by the flatness of breakdown/threshold field. The flatter the I-V curves in this region, the better the nonlinear properties [18]. The variation of α as a function of grain size is exhibited in Figure 7. Thus, this nonlinear plot can clearly and strikingly indicate the three groups: the first group was at grain size ranges from 0.04 to 0.43 µm (500

– 700 °C) showed slightly increase value of α ranges from 1.40 to 2.06, meanwhile, the second group was at grain size ranges from 0.64 until 3.98 µm (800–1100 °C) showed abrupt increase value of α ranges from 2.20 to 8 and the third group was at grain size ranges from 21.18 and 25.17 µm (1200 and 1300 °C) showed decrement value of α from 3.53 to 3.26.

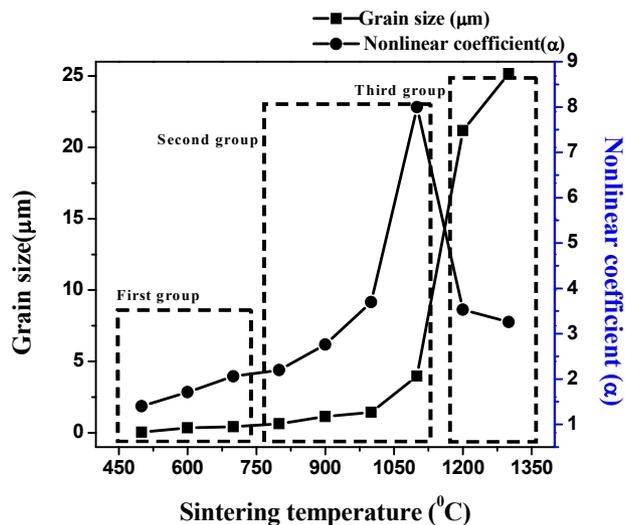


Figure 7: Nonlinear coefficient (α) characteristics of ZnO-Bi₂O₃-CoO sintered samples for different average grain size

It was observed that α value in Table 1 initially increases and then decreases with increasing grain size. The increment of α value with the sintering temperature was due to the increase of grain size and amount of Bi-rich phase.

Table 1: List of the nonlinear coefficient (α) values for ZnO-Bi₂O₃-CoO samples and sintered at different sintering temperatures

Group	Sintering temperature (°C)	Grain size (µm)	Nonlinear coefficient (α)
First group	500	0.04	1.40
	600	0.35	1.71
	700	0.43	2.06
Second group	800	0.64	2.20
	900	1.13	2.76
	1000	1.44	3.70
Third group	1100	3.98	8.00
	1200	21.18	3.53
	1300	25.17	3.26

Hence, the existence of the Bi-rich phase causes a resistance path where it caused difficulty for the current to flow in the samples and lead to a higher value of α . Meanwhile, the decrease of α with increasing grain size at higher sintering temperature (21.18 and 25.17 µm) was attributed to the decrease in the number of grain boundaries caused by the increase in the ZnO grain size and furthermore reduced the Bi-rich phase segregated at the grain. Reducing the amount of secondary phase existed around the grain boundary affecting the electron movement, hence cause the deterioration of electrical properties of the sample. The variations in nonlinear property with grain size are closely related to the Schottky barrier height according to the variation of the electronic states at the grain boundary. The grain boundary material is assumed to consist of the same semiconducting material but contains defects and dopants. Electrons which come from the grain are trapped by the defects and dopants at the grain boundary. The

sintering temperature changes the density of the interface states with the transport of the defect ions toward the grain boundary [19]. It is also known that transition the metal oxide such as Co and Mn generally improve the coefficient of nonlinearity at lower current density region because of increase in barrier height by trapping of electrons. Similar ionic radius of Co and Zn lead to complete substitution of Co in the Zn lattice [20]. The presence of Co^{2+} ions found in the grain, neglecting the existence of pores and other vacancies. Furthermore, Co dopant increases the defect concentration, lead to high resistance and caused uneasy for the current to flow in the samples, hence, lead to a change in α value.

Conclusions

ZnO-Bi₂O₃-CoO was successfully prepared using a high energy ball milling (HEBM). The XRD patterns reveal wurtzite structure for all sintered samples. The microstructure of doped-ZnO samples consist of conducting grains of various size surrounded by thin insulating layers of Bi-rich phase which is plays the dominant role in α value. Interestingly, three different groups of α values were clearly distinguishable, which is an evident of the microstructural factor associated with certain grain-sizes ranges that supporting the evolution trends in our study. It has been observed that increase in α value correspond to an increase in the grain size. However, a sudden drop was observed in α value after sintering above 1100 °C, which suggests the existence of larger grain size and diminishing of Bi₂O₃ phase in the grain boundaries at higher sintering temperature.

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