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Microstructural and electrical properties of multicomponent varistor ceramics with PbO–ZnO–B_2O_3 glass addition

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Abstract Zinc oxide based ceramics are widely used materials in varistors because of their excellent nonlinearity. Traditionally these ceramics are sintered at high temperatures (about 1,100–1,300°C). In this work a novel zinc oxide-based material with a low sintering temperature (900–1,000°C) was investigated. This material can be used in varistors consisting of several ceramic layers with embedded silver/palladium thick-film electrodes. This paper explains the research procedure employed with this novel varistor material, including the effect of sintering aid addition on the final electrical properties and fired microstructure. The electrical properties achieved are compared to the values measured from the original zinc oxide composition without sintering aid addition. Especially the I–V characteristics, nonlinearity coefficient α, breakdown voltage V_{bk} and leakage current density J_L are investigated. The sintering properties are also reported. It was found that by adding 10 wt.% of glass and using a 900 °C sintering temperature, the material had good varistor characteristics, as V_{bk}=378 V/mm, α=33 and J_L=15 μA/cm^2. The investigated varistor material can be applied to protect electrical circuits against surges.

Keywords Varistor · ZnO · LTCC

1 Introduction

Modern electronics require miniature, highly integrated, inexpensive, and low power consumption devices. Multilayer ceramic chip varistors used as low-voltage surge protection devices in surface mounted hybrid integrated circuit technology, are one important step in fulfilling this requirement [1].

Semiconductive zinc oxide is one of the most important varistor materials. The mixtures used in practice commonly contain more than 90% of ZnO as the main component with several metal oxides used as minor dopants [2–5]. The main purpose of these dopants is to enhance the electrical nonlinearity and/or stability against degradation. A number of dopants are, however, added to affect grain growth, which is important because both the switch voltage and the energy-handling capability in both high- and low-voltage varistors increase with the number of grains (per unit area) between the electrodes. Additionally, dopants affect the dewetting characteristics of the liquid phase and the electronic defect states that control overall varistor characteristics [3]. These compositions, fabricated using conventional ceramic processing methods to form bulk varistors are commonly sintered at about 1,100–1,300°C [6].

Multilayer-chip varistors are formed by an alternate configuration of electrode layers and ceramic inner layers stacked together into a monolithic block [7]. The compositions commonly used, ZnO with a lead zinc borosilicate glass system, also require high sintering temperatures

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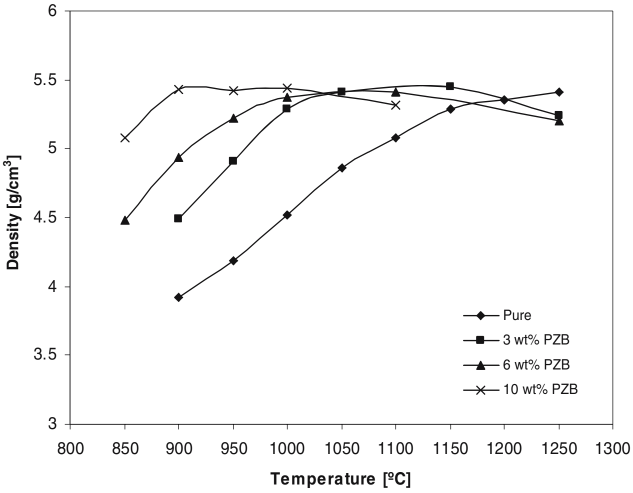

Fig. 1 Density as a function of the sintering temperature for different compositions

(1,100–1,250°C) [1, 8, 9]. Thus, these materials permit neither embedded high conductive, inexpensive silver or silver/palladium electrodes nor wider integration into Low Temperature Co-fired Ceramic (LTCC) modules.

Little has been reported about varistor compositions that fulfill the requirements of LTCC technology, and although compositions sinterable below 900°C have been prepared, special manufacturing processes, like a polymerized complex method are required, increasing the final price of the devices [10–12].

The main target of this work is to develop the commonly used ZnO-based varistor composition in such a way that it can be sintered at 900–950°C without special powder or heat treatment processes. An effective additive enabling this is introduced, and the sintering behaviour, microstructural and electrical properties of the material are presented. The electrical properties achieved are compared to the values measured from a traditional bulk ceramic varistor without sintering aid addition.

2 Experimental procedure

Basic varistor powder with the nominal composition 95.8 mol% ZnO+1.0 mol% Bi_2O_3, 1.0 mol% Sb_2O_3, 0.5 mol% Co_3O_4, 0.4 mol% Cr_2O_3, 0.5 mol% MnO and 0.8 mol% NiO was prepared by the classical ceramic procedure. Reagent grade oxides were mixed in proper ratios and homogenized in distilled water by ball-milling. After drying the powder was pressed into discs and calcined at 1250°C for one hour followed by further ball-milling and screening through a 200 μm mesh sieve.

In order to lower the sintering temperature, several low melting point glasses (<950°C) were investigated. One of these compositions was found to be very effective sintering aid for the basic varistor powder while maintaining its electrical properties within very useful level. This glass, consisted of 20 mol% ZnO, 40 mol% PbO and 40 mol% B_2O_3 (labelled PZB), is typically used for radiation shielding and glass solder for sealing [13, 14]. The glass was prepared by weighing the starting materials (Johnson Matthey Gmbh, Germany) and mixing them in distilled water for one hour in a ball-mill jar with agate balls. The slurry was dried and the powder was pressed into pellets. After melting in a platinum crucible at temperature of 950°C for 30 minutes, the material was quenched in distilled water. The glass was then wet-ground in the ball-mill for 4 hours, dried and screened through a 200 μm mesh sieve.

Samples with 0, 3, 6 and 10 wt.% of glass were prepared by mixing appropriate amounts of glass and ceramic powder by ball-milling together with PVA as a binder and PEG as a plasticizer and distilled water. To ensure uniform distribution of the sintering aid, 24 h ball-milling time was used. This action also decreased the particle size of the mixtures, when compared to pure varistor material.

The particle size and distribution of the varistor powder and the glass powder were measured with a Beckman Coulter LS 230 Particle Size Analyzer. In order to investigate the properties of the obtained mixtures, green powders were pressed into pellets by using uniaxial press at 80 MPa. Pellets were sintered with heating rate of 2°C/min and holding time of 2 h at peak temperature.

Density of the sintered pellets was estimated from their dimensions and weights. The microstructures of the fired ceramics were studied with a scanning electron microscope equipped with a energy dispersive spectrometer, SEM/EDS (Jeol JEM-6400, Tokyo, Japan). Both polished and thermally etched samples were prepared for SEM. The average ZnO grain size for each fired sample was determined using 400–800 measurements of grain size per sample. The surface of each grain was measured and its size was calculated as a diameter for circular geometry. An X-ray diffractometer was used to identify the crystalline phases (Siemens D5000, Karlsruhe, Germany). Disc-like samples were prepared for electrical measurements. The size of the samples was about 9 mm in diameter and 1 mm in thickness. Thick-film silver electrodes were printed on both faces of the samples with DuPont 6160 paste.

The voltage-current (V–I) properties of the samples were characterized using a Stanford Research Systems PS310 high voltage power supply as a voltage source and an Agilent 34401A multimeter as a current meter. The voltage level was incremented by one volt and after that the current was measured. After each measurement step the voltage source's output was switched off for two seconds to prevent heating of the sample. The electrical field (E) was calculated from the voltage level and the thickness of the sample, and the current density (J) was measured from the current level and the area of the sample. The nonlinear coefficient (α) was estimated from current densities varying from 0.5 to 5 mA/cm^2. The breakdown voltage (V_{bk}) was measured at a current density of 0.5 mA/cm^2 and the leakage current (J_L) was measured at 0.8 $\mathrm{V_{bk}}$. The capacitances of the samples were measured using a Hewlett-Packard 4285A precision LCR meter. The stimulus signal was 1 V_{p-p} and the frequency was 100 kHz. Relative real permittivity (ε) was calculated from the measured capacitances values (Cp) and the dimensions of the samples.

3 Results

3.1 Materials characterization

After 24 h ball-milling, the particle size of the mixtures (D_{50} values) varied from 4.8 to 6.2 μm, depending on the amount of additive. The fired densities of the samples with 3, 6 and 10 wt.% of glass are presented in Fig. 1. The composition without any glass addition (referred later as pure varistor material), sintered at 1,250°C, has a density value of 5.4 g/cm^3. According to the reference [13], the density of PZB glass is also 5.4 g/cm^3.

The microstructures of the polished samples (Fig. 2) show that the white area surrounding the main phase increased when the amount of glass addition increased. According to the SEM-EDS analysis (Fig. 2b–d), the white areas consisted mainly of zinc, bismuth and lead oxides, the dark grey areas corresponded mainly to zinc oxide and the light grey areas showed an excess amount of antimony and minor dopants compared to the other phases. Although the lightest element of the PZB glass, boron, could not be detected with EDS, the white area was the only one showing trace of glass added since only this contained Pb. The microstructure investigation of samples sintered at different temperatures (900, 950 and 1,000°C) showed that a higher sintering temperature led to growth in average ZnO grain size being 2.5, 3.0 and 3.1 μm, respectively, for fired samples containing 10 wt.% glass addition.

Crystalline phases according to the XRD measurements were ZnO and $Zn_7Sb_2O_{12}$. The results were similar for all the samples, regardless of the amount of added glass or even the sintering temperature. Due to the lack of peaks indicating a crystalline Pb or B -containing phase, it can be assumed that the glass phase has remained amorphous.

3.2 Electrical properties

The electrical properties of the samples were characterized by their electrical field-current density properties (E–J) and relative permittivity (ε). Figure 3 shows the E–J characteristics of the samples with 3, 6 and 10 wt.% addition of glass sintered at 900, 950 and 1,000°C. In these figures, the E–J plot for the pure varistor composition without glass addition

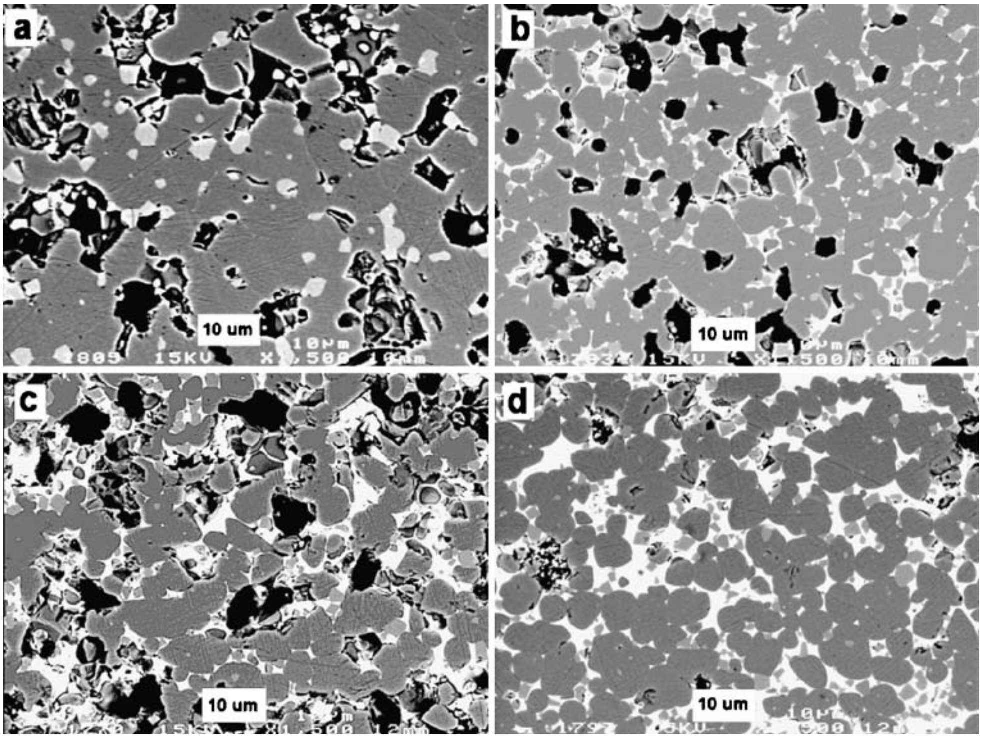

Fig. 2 Microstructures of varistor ceramics with various amounts of glass: **a** 0 wt.% **b** 3 wt.% **c** 6 wt.% and **d** 10 wt.%. The sintering temperature was 1,250°C for the sample (**a**) and 950°C for the samples (**b**)–(**d**)

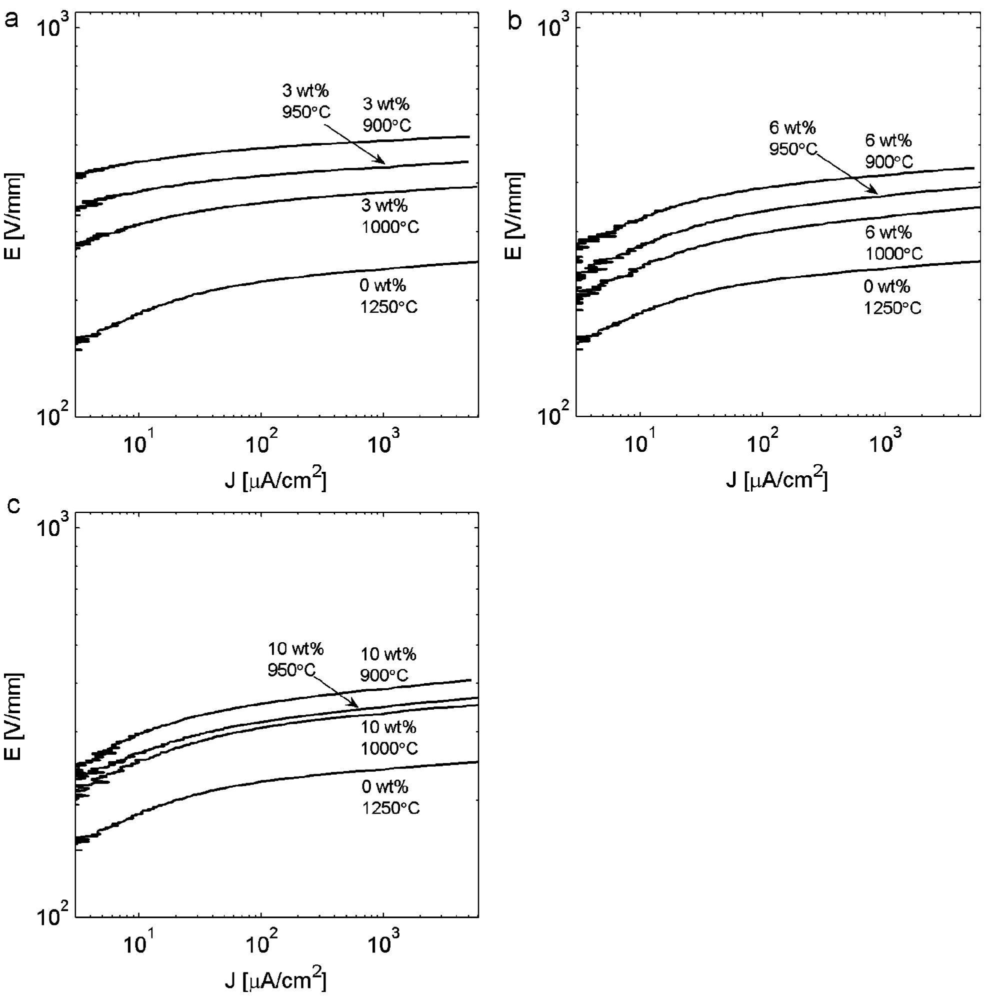

Fig. 3 E–J characteristics of varistor material with **a** 3 wt.%, **b** 6 wt.% and **c** 10 wt.% of glass additive sintered at different temperatures

is also shown. The varistor parameters were calculated from the E–J characteristics and are shown in Fig. 4 and summarized in Table 1.

The nonlinear coefficient (α) of the varistor material without a glass additive was ~40. Figure 4a shows the α values as a function of the sintering temperature with different glass addition levels. The samples with 3 wt.% of glass had better α values when compared to the pure material sample. The samples with 6 and 10 wt.% of glass had lower nonlinear coefficients compared to ones with 3 wt.% glass addition, but were still close to the value of the pure varistor material sample. When 6 and 10 wt.% glass additions were used, the nonlinear coefficients were rather insensitive to sintering temperature.

The leakage current (J_L) of pure varistor material was about 14 μA/cm^2. When 3 wt.% of glass was added (Fig. 4c), J_L decreased to the values of 3–8 μA/cm^2. By adding 6 or 10 wt.% of glass the J_L returned, however, to the same level as with the pure varistor material samples. In general, the leakage current is related to nonlinear coefficients in such a way that the bigger the α value, the smaller the J_L value.

The breakdown voltage (V_{bk}) of a pure varistor sample was ~250 V/mm and the next lowest ones, ~320 V/mm, were obtained with the samples containing 6 and 10 wt.% glass addition sintered at 1,000°C. Figure 4b shows that samples with 3 wt.% glass had the largest V_{bk} (510 V/mm, sintered at 900°C) and it also decreased a lot as a function of sintering temperature (370 V/mm sintered at 1,000°C). The smallest variation in V_{bk} was achieved when 10 wt.% of glass was added, showing almost the same kind of stability as measured for its nonlinear coefficient value. However, the observed decrease of the V_{bk} as a function of sintering temperature (Table 1) can not be explained by density.

Figure 4d shows that the relative permittivity (ε) measured at 100 kHz generally increases as a function of the sintering temperature. The relative permittivity of the samples containing 3 and 6 wt.% glass was more sensitive to the sintering temperature compared to the 10 wt.% samples. However, the relative permittivity of the pure varistor sample was clearly higher (~800) than the maximum relative permittivity measured for doped samples (~560).

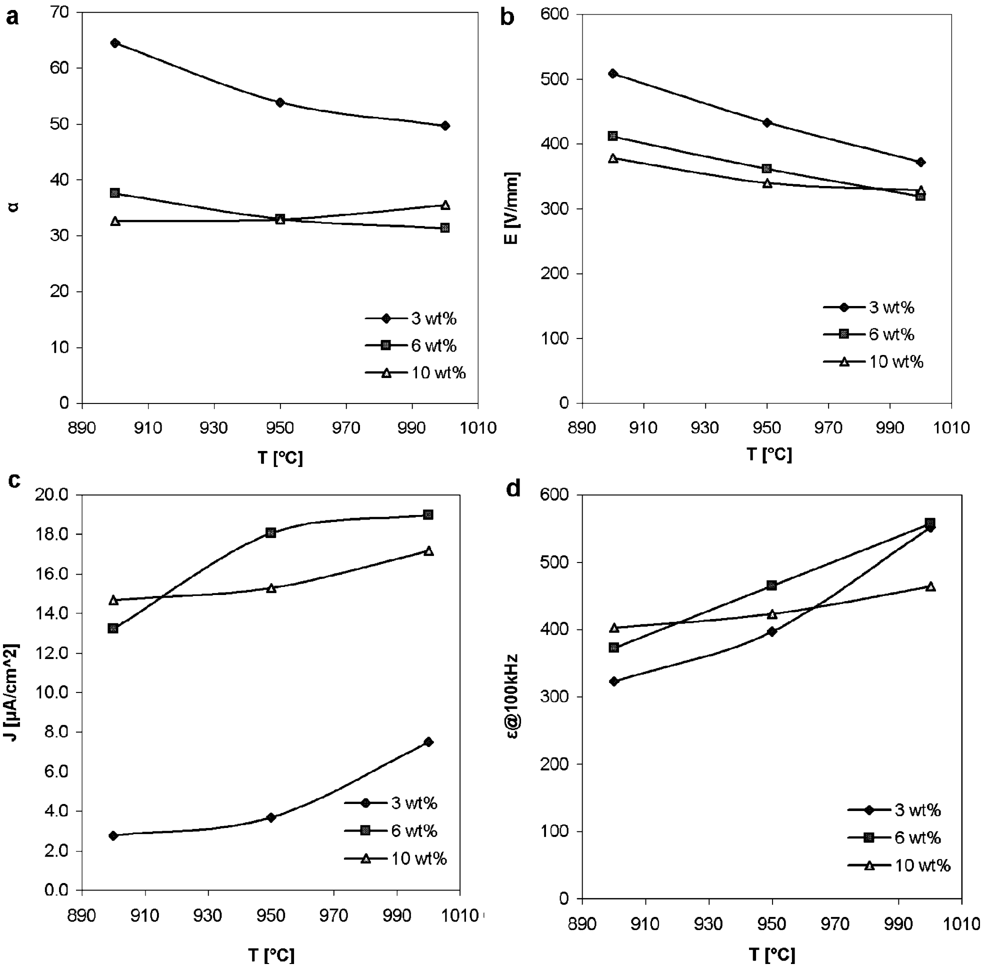

Fig. 4 **a** Nonlinear coefficients, **b** breakdown voltage, **c** leakage current density and **d** relative permittivity (100 kHz) as a function of sintering temperature for different samples

4 Discussion

The results show that doping the ZnO -based varistor material with the PZB glass effectively decreased the sintering temperature. The samples with 3 and 6 wt.% glass addition had density values of 4.5 and 4.9 g/cm^3, respectively, when sintered at 900°C. However, increasing the amount of the PZB glass to 10 wt.% showed density of ~5.4 g/cm^3, which is close to the value measured for the pure varistor material sintered at 1,250°C. For comparison, the density of the pure varistor sample sintered at 900°C was 3.9 g/cm^3.

Taking the values of the pure varistor samples as a starting point, the PZB glass addition clearly decreases its relative permittivity and raises the breakdown voltage, but the nonlinear constant and the leakage current stay at the same level. Previously, it has not been possible to make functional varistor using this kind of ZnO varistor materials sintered at low temperature (900°C). Much research has been done with ZnO–V$_2$O$_5$ ceramics, but the reported

Table 1 Parameters of ZnO-based varistor materials.

wt.%	T [°C]	ρ [g/cm^3]	α	V_{bk} [V/mm]	J_L [µA/cm^2]	ε@100 kHz
0	1,250	5.4	40	236	13.9	803
3	900	4.5	64	508	2.8	323
3	950	4.9	54	433	3.7	397
3	1,000	5.3	50	372	7.5	552
6	900	4.9	38	411	13.2	373
6	950	5.2	33	362	18.1	465
6	1,000	5.4	31	319	19.0	557
10	900	5.4	33	378	14.7	403
10	950	5.4	33	340	15.3	423
10	1,000	5.4	36	328	17.2	464

nonlinear coefficients have been lower than with ZnO–Bi_2O_3 ceramics [15–19]. Functional varistor compositions sinterable at 900°C using the polymerized complex methods have also been researched. They show, however, very high V_{bk} partly caused by the small grains, as also mentioned by the authors [10–12].

The variation in densities and breakdown voltages is the largest with samples containing 3 wt.% glass and the smallest in samples with the 10 wt.% content, as shown in Figs. 1 and 4b. In general lower sintering temperatures produced lower densities and the corresponding V_{bk} values were higher. However, the densities of the samples with 10 wt.% glass addition remained the same where as V_{bk} decreased when the sintering temperature increased (Fig. 4b).

It is well known fact that V_{bk} value is effected by the grain size of the varistor material [6]. On the other hand according to the SEM images, the sintering temperature increased the ZnO grain size. In the case of the samples containing 10 wt.% PZB glass the average ZnO grain size sintered at 900, 950 and 1,000°C were 2.5, 3.0 and 3.1 μm, respectively. Increased grain size decreases the number of grain boundaries between the electrodes. V_{bk} across a varistor depends on the amount of grain boundaries between the electrodes, as follows:

$$V_{bk} = \frac{V_{gb}D}{d} = V_{gb}n \tag{1}$$

V_{gb} is the grain barrier voltage, D is the distance between the electrodes, d is the average grain size and n is the amount of grain boundaries. [6, 20] Using the average ZnO grain size values and the V_{bk} values from the Table 1 of the 10 wt.% samples sintered at different temperature, the V_{gb} value was in the range of 1.01–1.10 V. For common ZnO base varistor materials sintered at high temperatures, the V_{gb} value is about 3 V [6]. As a conclusion, the average ZnO grain size explains mainly the variation of the V_{bk} as a function of sintering temperature.

In the case of the samples sintered in 950°C the calculated V_{gb} for 3, 6 and 10 wt.% glass addition were 1.62, 1.51 and 1.08 V, respectively. The decrease of the V_{gb} can be explained by the conductive properties of glass additive [21]. This PZB phase is surrounding the ZnO grains shown by the SEM image in Fig. 2.

When comparing the relative permittivity (ε) in Fig. 4d to the densities in Table 1, it can also be seen that permittivity depends on density, but also on the amount of glass additive and the sintering temperature. This can be seen clearly in the case of the 10 wt.% glass addition samples, which the relative permittivity remain lower than the value of the pure varistor sample although their densities were the same.

Previously produced compositions with a low sintering temperature have achieved high α values along with high V_{bk} values. [10–12, 15]. However, the low-temperature sintered composition here researched with 10 wt.% of glass PZB showed V_{bk} value low enough for low voltage applications [6].

The next step is to integrate this material into LTCC modules in the tape form or in the form of thick-film paste.

5 Conclusions

The microstructural and electrical properties of ZnO-based varistor ceramics were investigated with various PZB glass contents and with various sintering temperatures. The amount of PZB glass added effected strongly on the sintering temperature of varistor ceramics.

The advantage of the additive is that the sintering temperature could be decreased from 1,250°C to around 900°C, thus allowing the use of this material in the LTCC process. The varistor ceramics which contained 10 wt.% of the PZB glass and which were sintered at 900°C had good varistor characteristics with the breakdown voltage of 378 V/mm, the nonlinear exponent of 33 and the leakage current of 15 μA/cm^2.

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