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Effect of Firing on Some Physical Properties of Ti_2O_3 Doped ZnO

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Abstract: The present study deals with the physical properties of Ti_2O_3 doped ZnO in the range of 1–4 wt % TiO_2, which fired at temperatures range of 1000°C-1300°C for different soaking times. Densification of the suggested mixes is deduced from the physical properties in terms of firing shrinkage, bulk density, water absorption and apparent porosity. A decrease in absorption and consequently in porosity was recorded with rise in maturing temperature and increase in time of soaking. The results of firing shrinkage and bulk density showed an increase with rise in temperature and soaking time. A decrease in water absorption and apparent porosity were recorded with rise in maturing temperature and increase in time of soaking. Also densification decreased with increasing TiO_2 doping.

Key words: ZnO powder · Aqueous precipitation · Varistor · Electric properties · Homogeneity

INTRODUCTION

ZnO is known to be a metal excess n-type semiconductor while pure ZnO is an insulating semiconductor. Single crystal ZnO is always observed to exhibit metal excess or oxygen deficiency which is reflected as zinc interstitial or oxygen vacancies. The conductivity arises on heat treatment when sintering is achieved. This conductivity is derived from holes donor levels in the ZnO associated with oxygen vacancies when sintered at 1200°C [1]. ZnO varistors are ceramic semiconductor devices with highly non-linear voltage-current (V-I) characteristics. The voltage-current characteristics of ZnO varistors are expressed approximately as follows.

$$I = (V/C)^{\alpha}$$

Where V is the voltage across the sample, I is the current flowing through the sample, C is the constant and α is the nonlinearity parameter.

The V-I characteristics are measured with a cover tracer (Tektronix type 576.577). The nonlinearity parameter (α) is calculated from the following equation.

$$\alpha = [\log I_2 - \log I_1]/[\log V_2 - \log V_1]$$

Where V_1 and V_2 are the voltages at currents of I_1 and I_2 respectively [2]. Typical values for the exponent o f non linearity α, defined by $I \propto V^{\alpha}$, lie in the region $2 \leq \alpha \leq 6$, which is similar to the nonlinearity exhibited by Cerva and Russwurm [3]. A series of multi component ZnO based ceramic varistors with properties greatly superior to those attained on the binary systems have been developed by Matsuoka *et al.* [4, 5]. Fabrication of ZnO varistors follows standard ceramic techniques. The components are mixed, for example by milling in a ball mill and spray drying afterwards. The mixed powder is dried and pressed to the desired shape. The resulting pellets are sintered at high temperature, typically 1000-1400°C. The effects of dopants are classified into three categories: forming basic microstructure [5, 7] of sintered body; as Bi_2O_3 and BaO, improving non-ohmic properties; CoO and MnO and improve reliability; NiO and glass frit [2, 8, 9]. Additives are usually added to improve the electric properties of varistors; increase the non linearity behavior or to improve the breakdown voltage of ZnO. Thus they may form a conducting layer surrounding the ZnO-grains that are responsible for the electric properties played by the ceramic body.

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Early work on ZnO-based varistors was largely limited to binary systems comprised of ZnO and few mol % of second insulating oxide component. Valeyev *et al.* [10] investigated quite extensively the fabrication of varistors in the ZnO-SiO_2, ZnO-SnO_2 and ZnO-SiO_2-glass systems. Their work is demonstrated in a number of publications on the production of metal oxide varistors using mixtures of ZnO-Bi_2O_3 [11], ZnO-Al_2O_3 [12] and ZnO-TiO_2 [13, 14].

Nahm and Kim [15] investigated in quaternary system ZnO-Pr_6O_{11}-CoO-Dy_2O_3, the varistors with Pr_6O_{11}/CoO=0.5/1.0 exhibited much higher non-linear properties than any other Pr_6O_{11}/CoO mole ratio. In particular, the varistor sintered at 1350°C exhibited the highest non-linearity, in which the nonlinear exponent is 37.76 and the leakage current is 5.36 μA, whereas the varistors having high density and poor non-linearity exhibited a high stability for DC accelerated aging stress. Asokan [16] studied the effect of the calcinations temperature on compositions subjected to different grinding time, the average particle size recorded range between 7 and 1 μm for 5 and 20 hours, respectively. The distribution of dopants was also considerably affected. Thus, uniform distribution of Bi_2O_3 took place at the intergranular region leading to good non-linear characteristics. But, the distribution of other additives such as Sb_2O_3, CoO, Cr_2O_3 and NiO was not affected significantly by the variation of particle size. ZnO grains are controlled by the second phase forming and sintering temperature although liquid phase sintered ZnO has a propensity for coarsening. Yoshitugu *et al.* [17] reported that the wurtzite structure was found to exist in ultrafine ZnO particles less than 50 nm in size. This fact indicates that ZnO particles have the wurtzite structure from the early stages of growth. The particles tend to grow along the C-axis with increasing size. Sossina *et al.* [18] confirmed that the uniform size distribution and uniform coating of this powder with appropriate dopants allowed fabrication of varistor with improved properties over those fabricated from conventionally ball-milled and calcined powders. The improved properties were a high coefficient of non- linearity (~44) in the non–ohmic region, a sharp change in electrical behavior from ohmic to non-ohmic and a high resistivity (5×10^{12} Ω.cm) at low voltage. Karakas and Lee [19] reported that sintering to high density occurs after short times (30 min.) at low temperatures (1150°C) producing a fine grained (<3 μm) varistor.

Hongyu *et al.* [20] reported that with increasing Er_2O_3 content, the ZnO grain size decreases due to the Er-rich phases inhibiting grain growth; and non-linear coefficient (α) decreases because of the decrease of barrier height (ψ_B), the breakdown voltage (E_B) and density increase, whereas leakage current (I_L) decreases with increasing Er_2O_3 content. The barrier height (ψ_B), donor concentration (Nd), density of interface states (N_S) decrease and barrier width (w) increases with increasing Er_2O_3 content due to acceptor effect of Er_2O_3 in varistor ceramics.

MATERIALS AND METHODS

Reagent grade raw materials were used in compositions suggested, thus ZnO and Ti_2O_3 chemical grade oxides were used. Four mixes were suggested to study the effect of titanium oxide alone in a binary system ZnO plus Ti_2O_3 and is given in Table 1.

The prepared ZnO was wet ground in a ball for a period of 3 hours to pass 200 mesh sieves is shown in Figure 1. The slurry was dried overnight and used to fulfill the above mentioned mixes. The mixes were weighted in suggested proportions, wet milled to ensure thorough mixing of the different compositions then dried at 110°C. Two discs were used, the first one has 1.2 cm diameter and 0.2 cm thickness and the second disc has 5 cm diameter and 0.2 cm thickness. These two discs were processed by a semi–dry press method under 70 kN. Small specimens were subjected to thermal treatment to select the proper maturing temperature for each mix. Three discs were always fired in muffle kiln with a rate of heating of 5°C/min in the temperature range between 1000 to1300°C and for 1 to3 hours. The sinterability of the different samples was determined in terms of physical properties.

The grain size distribution of ZnO is determined by sedimentation method. The optimum firing temperature for each mix was deduced from the determination of the following parameters; firing shrinkage, apparent porosity, bulk density and water absorption. The method given is according to the ASTM standard (C71, 72, 73) [21]. The dried specimens were exceedingly friable i.e it was difficult to locate a mark on them as the specifications demand. Therefore, the diameter of specimens was measured from more than one side (at least 2-3 measurements) for three representative specimens, the average of each disc was represented by (L_0). Specimens were measured in the some way after firing at the respective temperature interval or soaking period.

Table 1: The mixes chosen for the study

Mix/Oxides	T_0	T_1	T_2	T_3	T_4
ZnO (wt %)	100	99	98	97	96
Ti_2O_3 (wt %)	-	1	2	3	4

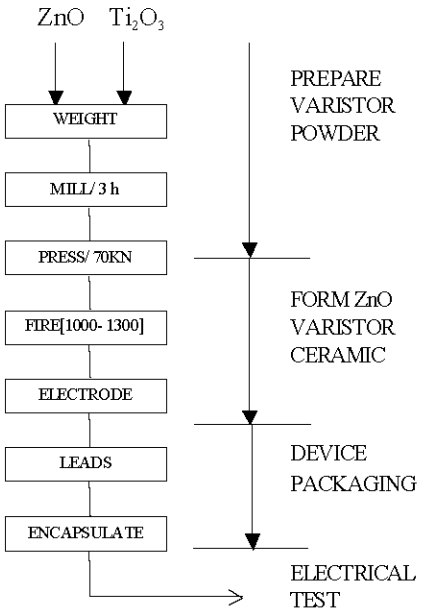

Fig. 1: Simplified flow diagram for the fabrication of ZnO varistors

The average values were designated (L). Linear firing shrinkage was determined from the following relation.

$$S = \frac{Lo - L}{Lo} \text{x} 100$$

Three disc specimens from each mixture fired at different temperature intervals or soaking period in the rang mentioned, were immersed in hot water, left to boil for 2 hours and then allowed to cool over night. Specimens were weighed, soaked with water (M) and then suspended in water (S). All specimens were dried in an electric oven overnight at 110°C and then weighed again (D) as dry weight. Bulk density, percent of water absorption and percent of apparent porosity were calculated from the following relations.

$$\text{Bulk density} = \frac{D}{M - S} \text{g/cm}^3$$

$$\text{Water Absorption} = \frac{M - D}{D} \text{x } 100$$

$$\text{Apparent Porosity} = \frac{M - D}{M - S} \text{x } 100$$

According to these calculations and the data obtained, the respective maturing temperature and soaking time of each mix were selected. Specimens fired at the selected maturing temperature for each mix were ground in an agate motter to pass through a 350 mesh sieve. Powders were dried at 110°C. Clean and dry pyknometers were weighed (P). A known weight (S) from each mix was placed in pyknometer, partially filled with previously filtered kerosene and them agitated in an ultrasonic bath for 20 minutes to expell any entrapped air, followed by evacuation a vacuum desicator to a pressure less than 25 mm Hg overnight. The pyknometers were completed with kerosene up to volume and weighed (M). Volume of the pyknometer were calculated from their weights when empty and then filled with kerosene alone (O). The density of kerosene was determined with respect to distilled water and was found to be equal to 0.79 g/cm^3. Specific gravity was calculated from the following formula

$$\text{Specific gravity} = \frac{S \times 0.79}{(O - P) - M - (P - S)}$$

$$\text{True porosity} = \frac{1 - \textit{Bulk density}}{\textit{Specific gravity}} \text{x} 100$$

Percentage closed pores = True porosity – Apparent porosity

$$\text{Relative density} = \frac{\text{Bulk density}}{\text{Specific gravity}}$$

The starting materials namely ZnO and Ti_2O_3 were examined by XRD, using Philips apparatus type 170, a copper target (λ =1.54 Å) and Ni-filter in Metallurgy Research Center, Egypt. A continuous plot of intensity for 2Θ values 4 to 66 was made at a scanning speed of 1°/minute, with a paper speed of 10 mm/min. Electric properties in terms of V-I characteristics were measured. The V-I measurements were carried out on specimens at the selected temperature for each mix using d.c. power supply in a current range up to 100 mA. To avoid heating of the sample at high current ranges, the current was allowed to flow for only the short time necessary for taking the reading in pulses. Disc specimens with the following dimensions; diameter 1.5-3 cm and thickness about 0.2-0.4 cm were fired at the selected temperature for each mix and the required time interval. Silver paint (Gunison) was applied to cover both surface were painted central circle (Figure 2) or the samples were placed between parallel conducting plates from gold. The connection of varistor sample in electric circuit is shown in Figure 3.

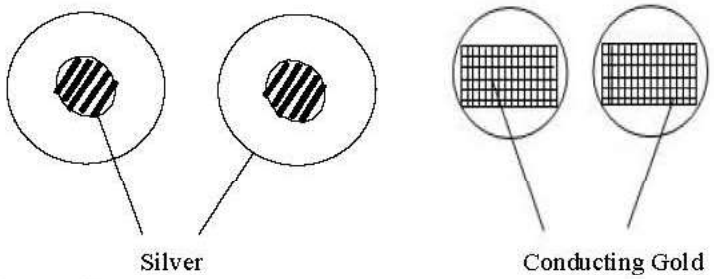

Fig. 2: Sliver paint on the sample

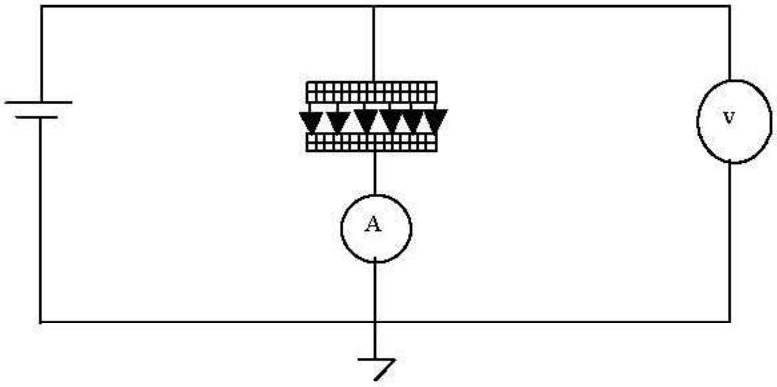

Fig. 3: The position of varistor sample in electric circuit

RESULTS AND DISCUSSION

The size of ZnO grains governs their application, low voltage varistors are characterized by large grains [22] of about 50µm, while high voltage on the other hand, requires a small grain size as possible of about 5–15 µm. The results of grain size distribution of starting ZnO indicates that material have a more or less uniform grain size, about 90 % was less than 2 µm, as shown in Table 2.

Sinterability of the suggested mixes is deduced from the results of physical properties in terms of water absorption, apparent porosity, bulk density and firing shrinkage as presented in Tables 3-6 and Figures 4-7. The results of firing shrinkage and bulk density showed an increase with rise in temperature and in time of soaking. Maximum values were attained in mixes fired at 1300°C for 3 hours. The mixes showed an increase in firing shrinkage with increase in Ti_2O_3 added, a maximum of 14 % was displayed in mix containing 4 wt % Ti_2O_3 (T_4). A maximum density of 5.55 g/cm was achieved by mix T_2. Firing the mixes more than 1300°C for 3 hours caused the start of deformation of different mixes. Therefore, it recommended to increase the soaking time more than 3 hours as the increase in bulk density displayed there after did not show remarkable change with soaking time.

Table 2: Grain size distribution of ZnO

Mµ	8-63	2-8	< 1-2
Weight (%)	9.04	0.025	90.7

Table 3: Firing shrinkage percent of different mixes

Mix	T_0	T_1	T_2	T_3	T_4
1000°C/1h	1.6	4.8	0.8	0.8	0.8
1100°C/1h	7.2	7.2	6.4	7.2	6.4
1200°C/1h	10.4	8.6	9.6	9.6	10.4
1300°C/1h	13.6	11.2	11.2	12.8	13.6
1000°C/2h	4.8	5.6	2.4	4.0	3.2
1100°C/2h	8.8	7.2	7.2	8.0	7.2
1200°C/2h	11.2	10.4	9.6	10.4	11.2
1300°C/2h	14.4	14.4	13.6	14.4	14.4
1000°C/3h	6.4	6.4	4.8	5.6	5.6
1100°C/3h	10.4	8.0	8.0	9.6	8.8
1200°C/3h	12.8	10.4	10.4	11.2	12.8
1300°C/3h	12.9	11.2	11.3	12.4	14.0

Table 4: Water absorption percent of different mixes

Mix	T_0	T_1	T_2	T_3	T_4
1000°C/1h	4.4469	5.9730	5.7008	6.2581	6.87190
1100°C/1h	2.9016	4.3831	4.0564	5.2915	4.41530
1200°C/1h	1.8451	3.0298	3.3631	3.9771	2.41090
1300°C/1h	0.2130	1.8656	2.1871	2.5660	0.08438
1000°C/2h	3.9027	5.0438	4.7638	6.1470	6.23080
1100°C/2h	2.8900	4.2898	3.9831	5.2856	3.97500
1200°C/2h	1.2254	2.9309	2.9725	3.7021	2.14210
1300°C/2h	0.0000	1.3588	1.7367	1.6097	0.81960
1000°C/3h	3.4052	4.4378	4.1157	5.6655	5.03980
1100°C/3h	1.9690	3.5587	3.5613	4.0925	2.74360
1200°C/3h	0.6949	2.2925	2.6914	3.2920	1.28440
1300°C/3h	0.4241	2.0080	2.4621	1.9867	1.00420

Table 5: Apparent porosity of different mixes

Mix	T_0	T_1	T2	T_3	T_4
1000°C/1h	16.0577	24.9281	23.5545	25.7456	28.6099
1100°C/1h	8.7710	18.4916	17.4296	22.0441	18.8244
1200°C/1h	4.5913	12.5128	14.9729	17.3922	11.9785
1300°C/1h	1.0220	9.5762	10.0838	12.1046	4.1230
1000°C/2h	14.0639	21.4165	20.4713	25.1379	25.7281
1100°C/2h	7.9220	18.1885	17.7855	21.9913	17.7872
1200°C/2h	3.1142	11.9892	13.4077	16.2747	10.1521
1300°C/2h	0.0000	5.9629	8.1311	7.5923	4.0165
1000°C/3h	12.7414	18.2827	17.1186	23.5248	21.2484
1100°C/3h	5.0110	12.5890	15.4793	17.5435	12.5272
1200°C/3h	1.4219	10.7991	12.2636	15.3385	6.1768
1300°C/3h	1.2466	11.2247	13.7138	11.0063	5.5532

Table 6: Bulk density of different mixes at different temperatures (1000-1300)°C/1 h

Temp\Mix	T_0	T_1	T_2	T_3	T_4
10000C	5.55	5.48	5.44	5.36	5.32
11000C	5.58	5.52	5.45	5.44	5.43
12000C	5.59	5.53	5.48	5.47	5.46
13000C	5.61	5.57	5.55	5.53	5.48

Results of water absorption and apparent porosity are shown in Figures 4-7 respectively. A decrease in water absorption and consequently in porosity was recorded with rise in maturing temperature. Minimum water absorption was displayed in specimens fired at 1300°C for 3 hours.

The content of pores both closed and open governs the degree of densification reached at maturity. Minimum apparent porosity does not mean maximum densification. Also the content of closed pores affect to a greater extent the sinterability of the body produced. Usually a percent not exceeding 83 % was displayed by different mixes as shown in Table 7. Standard mix (T_0) without additions shows max densification. Lenel [23] and German [24] studied sintering of ZnO grain in the system ZnO-Bi_2O_3 and reported that better densification was achieved in the presence of liquid phase. According to the binary system ZnO-Bi_2O_3, a eutectic reaction occurs at 740°C, resulting in the presence of ZnO-$4Bi_2O_3$ and ZnO which is of low density. Nahm *et al.* [25] studied

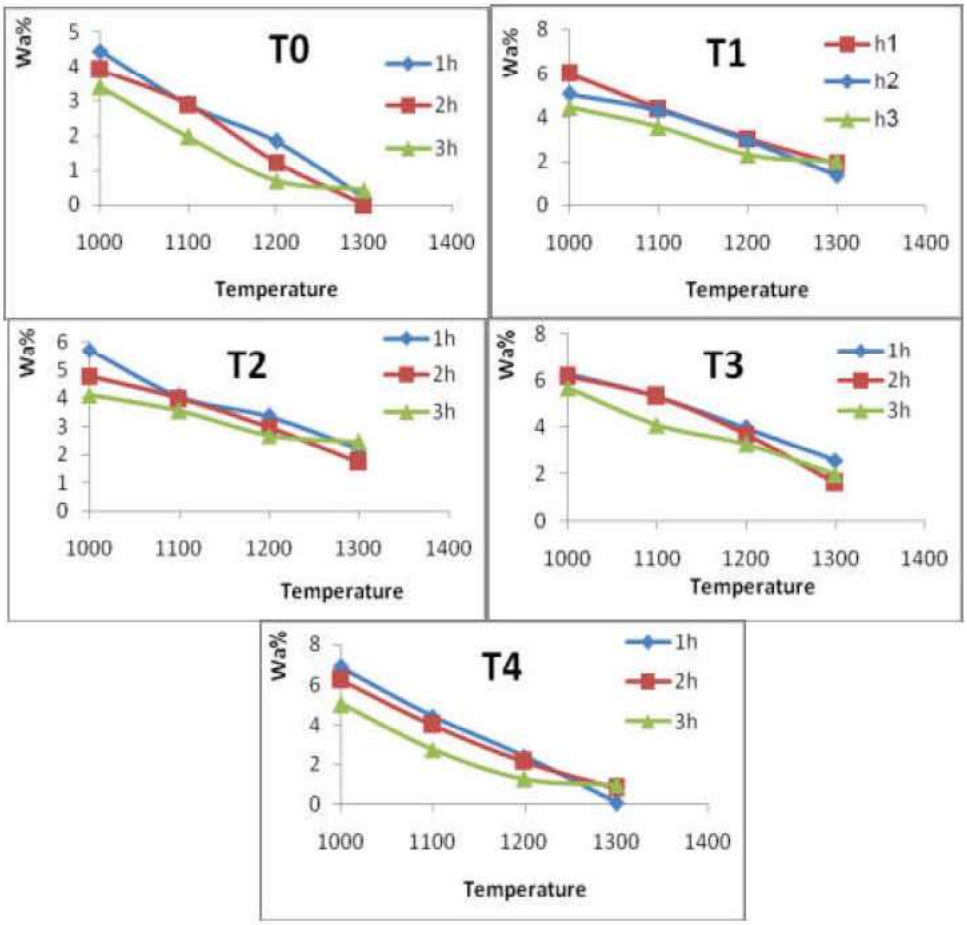

Fig. 4: Water absorption of different mixes

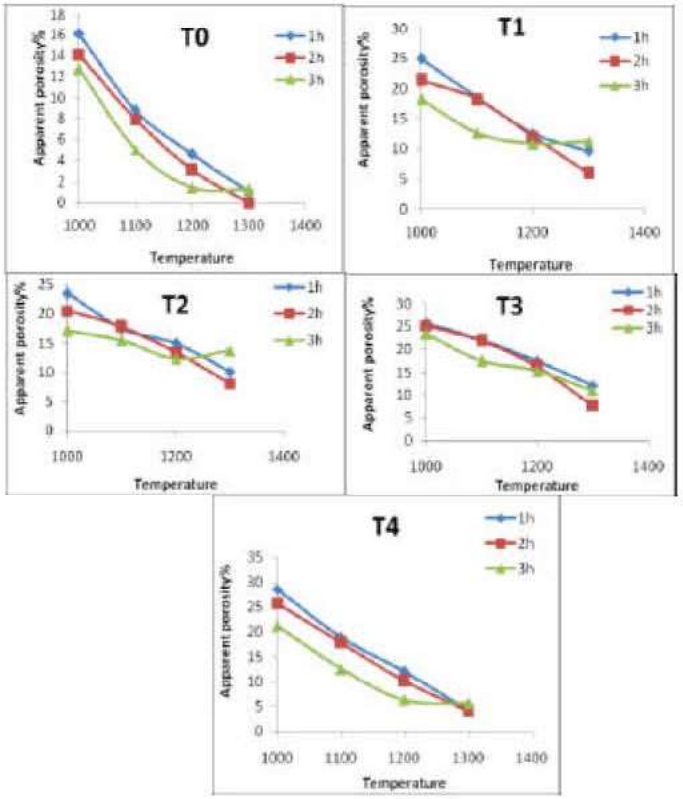

Fig. 5: Apparent porosity of different mixes

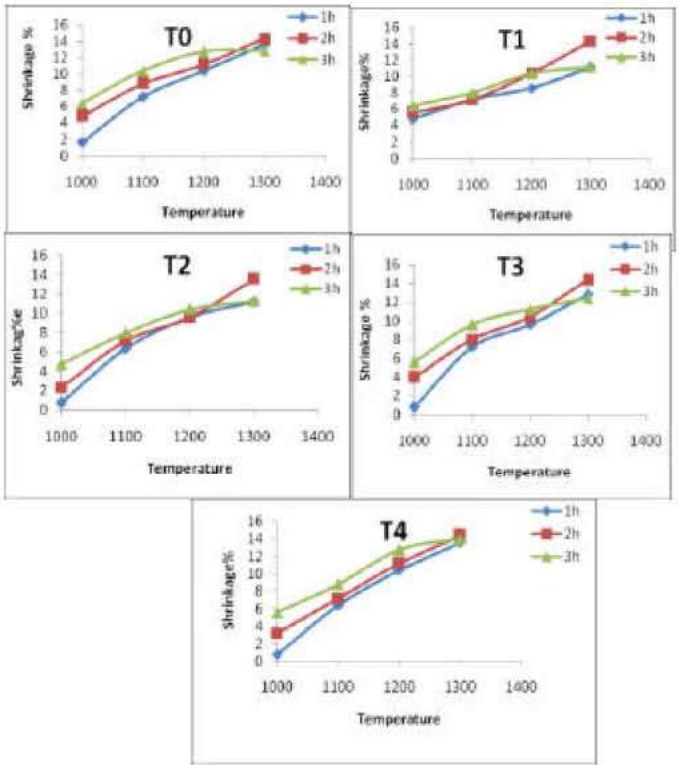

Fig. 6: Firing shrinkage of different mixes

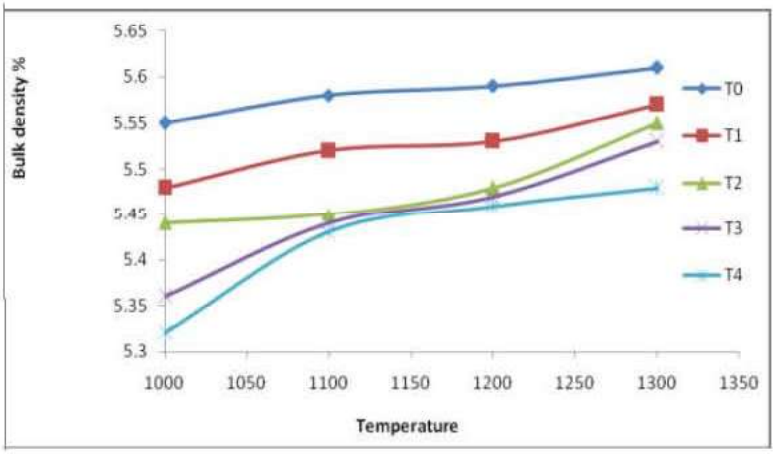

Fig. 7: Bulk density of different mixes at different temperatures (1000-1300)°C/1 h

Table 7: Degree of densification of different mixes at different temperatures

	1000°C			1100°C			1200°C			1300°C		
Mix	1 h	2 h	3 h	1 h	2 h	3 h	1 h	2 h	3 h	1 h	2 h	3 h
T0	80.8	80.79	63.79	86.68	86.74	88.63	88.53	90.62	93.61	96.54	97.25	96.54
T1	73.3	73.27	74.93	76.05	76.10	76.66	77.71	78.86	80.53	80.75	81.61	80.76
T2	75.4	75.65	75.73	75.75	76.18	76.56	78.56	78.6	80.07	81.88	81.91	81.94
T3	73.4	73.53	73.71	73.95	75.81	76.10	77.15	77.98	82.71	83.73	83.73	83.74
T4	69.1	69.27	70.73	71.52	76.60	77.90	79.51	80.68	81.97	81.97	82.01	82.11

(Degree of densification = Bulk density/specific gravity)

that the microstructure, non-linear properties and dielectric characteristics of the varistors, which are composed of $ZnO–Pr_6O_{11}–CoO–Cr_2O_3–Dy_2O_3$ based ceramics were investigated at various CoO contents.

The increase of CoO content improved the densification of ceramics as increasing density in the range of 5.25–5.55 g/cm^3. The CoO served as a prompter of grain growth as increasing average grain size from 9.9 to 27.2 μm. The increase of sintering temperature led to more densified ceramics, whereas, it decreased the non-linear properties and varistor voltage. The highest non-linearity was obtained from the varistors sintered at 1230°C, with 77.9 in nonlinear exponent and 0.4 μA in leakage current. The varistors sintered at 1260°C exhibited the highest stability, with % $\Delta V1$ mA of +1.9 %, % $\Delta\alpha$ of ?10.6 % and % ΔI_L of +20 %. As a result, the non-linear properties and stability of ZnO– Pr_6O_{11}-based varistors can be said to be affected by the sintering temperature. Karakas and Lee [19] reported that sintering to high density occurs after short times (30 min.) at low temperatures (1150°C) producing a fine grained (<3 μm) varistor.

From the above mentioned results, it is evident that better densification and less water absorption are achieved in all mixes fired at 1300°C for 3 hours. Therefore, this temperature was selected as proper maturing temperature for all mixes, above 1300°C, all mixes were totally deformed. Addition of Ti_2O_3 to ZnO leads to better densification. i.e Ti_2O_3 improved densification by minimizing the percent of closed pores as shown in Table 7. From XRD of mix T3 sintered at 1200°C/1h, ZnO was the main phase and only very small quantities of secondary phases were detected, these secondary phases were found to be zinc titanates (Zn_2TiO_4) as shown in Figure 8.

The V-I characteristics were measured at voltage between 0-5 kV and current between 0-10 mA. The relation between I and V for the different mixes are present in Figure 9. It is evident, that mixes show clearly non-linear behaviour. Asokan *et al.* [16, 27] studied the binary systems between ZnO and other oxides like Nb_2O_3, Bi_2O_3, MnO_2, Sb_2O_3 and Cr_2O_3 and found that Nb_2O_3 shows the non-linear behavior of ZnO when added up to 0.2 wt. α was around 7, further addition negatively affected it.

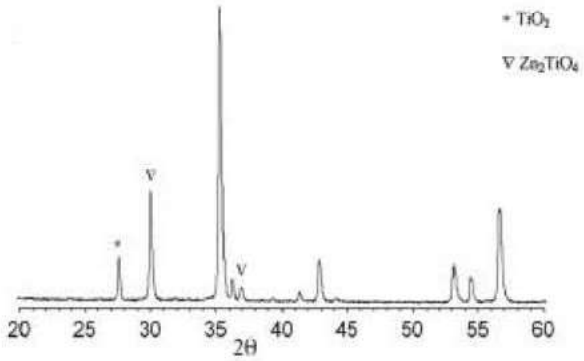

Fig. 8: XRD of Mix T_3 which containing 3 wt % Ti_2O_3

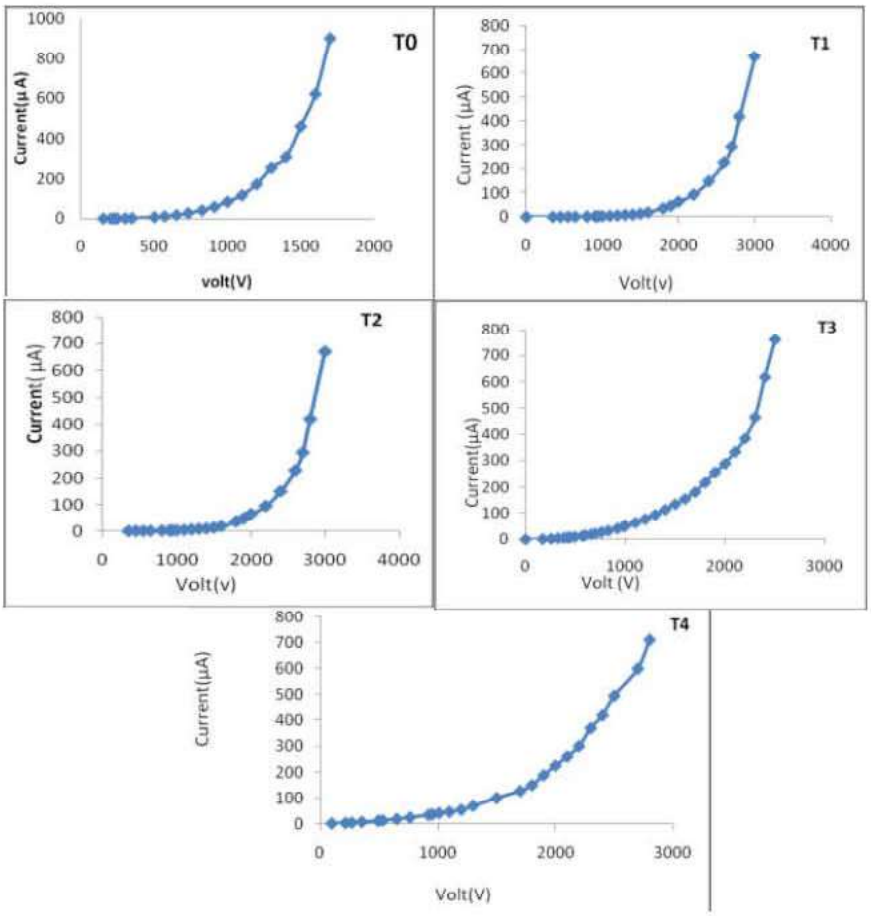

Fig. 9: I-V characteristics of different mixes sintered at 1200°C/2 h.

Also α increases with temperature up to 1100°C, then decreases again. Non linearity coefficient was greatly improved by the addition of a mix of Bi_2O_3, Sb_2O_3, MnO_2, NiO and Al_2O_3. It reaches about 40, although any of the above oxides did not show non linearity in binary system with ZnO. This was not observed in the present study. The calculated non linearity coefficient in the ZnO along the range of potential applied showed high values indicating the relation is non ohmic and is shown in Figure 9. i.e addition of Ti_2O_3 improved the non linearity coefficient.

According to Morris [27], the non linear volt–ampere characteristics of the ceramic are intimately connected with the conduction mechanism in the inter granular

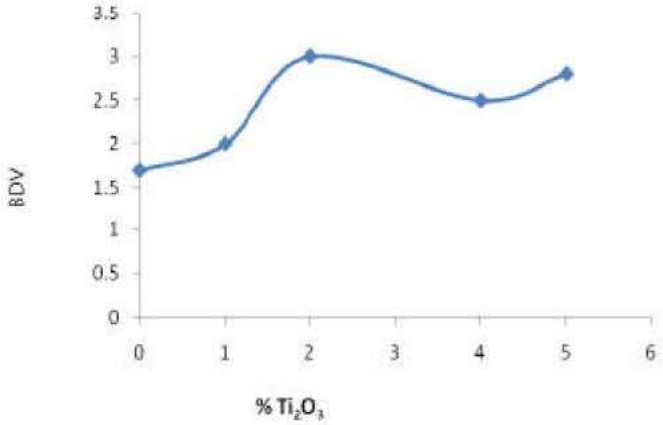

Fig. 10: The effect of wt % Ti_2O_3 on break down voltage of different mixes sintered at 1200°C/2 h.

Table 8: Break down voltage of different mixes

Ti_2O_3	0	1	2	3	4
BDV [Kv]	1.7	2	3	2.5	2.8

phase which is in case of ZnO-Bi2O3 is a conduction of electron hopping an tunneling in thin layer of amorphous Bi2O3–ZnO. The effect of % Ti2O3 on break down voltage is present in Table 8 and Figure 10.

CONCLUSIONS

Homogeneous low voltage ZnO varistor powder prepared by chemical processing and single step has been successfully fabricated. The physical properties of Ti_2O_3 doped ZnO in the range of 1–4 wt % TiO_2, was studied. The result showed that, a decrease in absorption and consequently in porosity was recorded with rise in maturing temperature and increase in time of soaking. The results of firing shrinkage and bulk density showed an increase with rise in temperature and soaking time. A decrease in water absorption and apparent porosity were recorded with rise in maturing temperature and increase in time of soaking. Also densification decreased with increasing TiO_2 doping.

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