The Microstructure and Electrical Behavior of TiO$_2$ Varistors Processed by Magnetized Water

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Abstract. A comparative study of the microstructures of two kinds of TiO$_2$ based varistor materials processed from the slurry using magnetized water and regular deionized water is conducted. The additives in the form of oxides of Nb, Ce, Ca, and Si were used in the recipe. The electrical behavior reveals that the water magnetized at 0.2 T yielded lower varistor voltage while the water magnetized at 0.3 T yielded higher varistor voltage compared to the regular deionized water. A second phase comprising of Ce, Si, and Ti was found in each of these samples. The distribution of second phase was found strongly dependent on the type of water used. Thus, the magnetized water shows influence on the TiO$_2$ varistor microstructures. It apprehended that the application of magnetized water in the general arena of advanced electronic ceramics may bring novel experimental results as demonstrated in the present work.

Introduction

Varistors are devices that exhibit nonlinear electrical behavior. The current-voltage (I-V) characteristics can be expressed by [1]

$$I = KV^{\alpha}, \tag{1}$$

where α is the nonlinear coefficient. As of today's technology the most common and best performing varistors are made from zinc oxide (ZnO) based polycrystalline ceramics. It is widely used in various situations to protect electrical or electronic systems against transient over-voltage. The ZnO varistor is one of the electronic ceramic materials whose properties are controlled and dictated by the grain boundary phenomena. However, it is generally accepted that the breakdown voltage of single grain boundary in ZnO ceramics is finite and

may be assumed to be near a constant in the vicinity of 3 V [2]. The total breakdown voltage along the single thread direction of the current flow is the product of breakdown voltage of each grain boundary and the number of grain boundaries. Thus, it is rather restricted for ZnO varistors to be used in low-voltage systems.

In a recent work [3] the relationship between the breakdown electric field and the thickness of various ZnO varistors is reported. As a part of the continued effort the nonlinear properties of the TiO$_2$ based varistor materials have been studied to understand the behavior of the low voltage varistors. A number of low voltage varistor materials are reported in the literature [4, 5] such as based on TiO$_2$, SrTiO$_3$, etc. These materials exhibit larger terminal dielectric constant value as well as lower varistor voltage than the ZnO varistor materials. Thus, these are attracting a great deal of attention for obtaining better performing characteristics involving noise absorption and multifunction properties. Yan and Rhodes [4] reported that (Nb, Ba)-added TiO$_2$

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ceramics have useful varistor properties with α of about 3 to 4. Yang and Wu [6, 7] conducted extensive work on (Nb, Ba, Bi)-added TiO_2 ceramics. It is revealed that Ba dominates the varistor action in the material system. Pennewiss and Hoffman [8] studied the effect of oxidizing condition on the electrical properties of Al-doped TiO_2. The voltage-dependent resistivity was attributed to the surface oxidation layer rather than the grain boundary effect which is quite similar to the $SrTiO_3$ varistor materials [5].

In this paper microstructures and electrical response of the TiO_2 varistor materials prepared by using magnetized water is addressed. Two types of magnetized water as well as ordinary deionized water are used in the preparation of TiO_2 ceramics. In the history of advanced *electronic ceramics* (electroceramics) processing the use of deionized water is the usual tradition. Thus, it is anticipated that the introduction of magnetized water instead of deionized water in the ceramic slurry processing may lead to novel devices as it is already reported in the literature that the magnetized water has a significant effect in agriculture and relevant industrial issues including daily life consumption [9, 10].

Experimental

Traditional ceramic processing technique was employed in preparing the TiO_2 varistor materials. Three types of water were used in the processing of the slurry using these conditions: (1) regular deionized water yielding varistor samples denoted as #0 and also designated as the reference varistor samples, (2) deionized water treated with a magnetic field of 0.2 T yielding varistor samples denoted as #1, and (3) deionized water treated with a magnetic field of 0.3 T yielding varistor samples denoted as #2. Deionized water passed through the magnetizers at these magnetic fields resulted in #1 and #2 magnetized water, respectively, used in preparing the slurry upon collecting them in various vessels. The raw chemicals used in making TiO_2 based varistors in this study were the reagent grade TiO_2, Nb_2O_5, SiO_2, CeO_2, and $CaCO_3$. The TiO_2 used in this study was the anatase powder. The compositions were designed in mole in the ratio of TiO_2:Nb:Ce:(Ca + Si) = 100:0.2:0.5:0.5. The internal ratio of Ca to Si was 1:1. The water was added at a ratio of 80 weight% of the solid materials. The powders were mixed via conventional wet ball-milling for 5 h in a polyethylene bottle

wherein ZrO_2 balls were used as the milling media. The ball-milled slurry contained PVA (polyvinyl alcohol) as a binder. The slurry was then dried using an oven at 105°C to obtain the granulated powders. These powders were pressed into disks of 12 mm in diameter and 1.2 mm in thickness. These samples were sintered at a temperature of 1350°C for 4 h (soak-time or hold-time), and then cooled inside the furnace with power shut-off condition. Each of these samples was polished and then electroded using Ag paste on the opposite parallel faces. This Ag paste was dried at 550°C for 20 minutes in an oven.

The varistor voltage $V_{1\,mA}$ and $V_{10\,mA}$ were measured by using JN2711 meter, a set up arrangement used in China. The nonlinear coefficient α was calculated using [1]:

$$\alpha = \frac{\log(I_2/I_1)}{\log(V_2/V_1)} = [\log(V_{10\,mA}/V_{1\,mA})]^{-1}, \quad (2)$$

where the current 1 mA ($=I_1$) corresponds to the voltage $V_{1\,mA}$ ($= V_1$) and the current 10 mA ($=I_2$) corresponds to the voltage $V_{10\,mA}$ ($=V_2$). In general, the nonlinear coefficient and varistor voltage $V_{1\,mA/cm^2}$ corresponding to the current density 1 mA/cm^2 are the two most important electrical parameters for any varistor material [11]. In this study, the dimension and electrode area of the samples were maintained the same. Thus, varistor voltages corresponding to 1 mA and 10 mA are consistent in discussing the electrical behavior of the device. The low voltage TiO_2 varistors reported earlier [8] are identical to the varistors achieved in this work although these varistors comprised of small amount of additives. It is apprehended that the role of the finite existence of the second phase in the SrO-TiO_2 system [12] is still not certain in controlling the nonlinear coefficient as well as the functional behavior when exposed in the application field.

The capacitance C and the dielectric loss tangent (tan δ) were measured using an LCR meter (2693D: made in China) at a fixed measurement frequency of 1 kHz. This measurement frequency is selected arbitrarily. The microstructures were evaluated using SEM (XL–30 FEG Technology). Since most of the grains exhibited non-spherical shape the distance in the horizontal direction was defined as the *horizontal distance* while the distance in the vertical direction was defined as the *vertical distance*. For every sample studied both horizontal and vertical distances were measured and the average value is called the grain size of this specific

grain. The average grain size represents the *average grain size* of more than 150 grains and described recently [3]. The powder X-ray diffraction (XRD–Rigaku D/max III B) pattern of the phases as well as the energy dispersive spectroscopy (EDAX–XL– 30 FEG technology) was carried out to analyze the grains and the dried granules of various slurries.

Results and Discussion

The reference TiO_2 varistor samples were prepared using the regular deionized water. These samples were used in comparing the varistor samples made by using the magnetized water. The slurry prepared with the magnetized water is easy to deal and handle in terms of reduced flocculation, reduced non-Newtonian colloidal fluidity via improved dispersion, and reduced surface sticking behavior of the solid particles when compared to the slurry preparation utilizing regular deionized water. The granular behavior of the dried slurry possesses higher flow rate and uniform granular size. Thus the density distribution, uniformity, and consistency of the sintered samples were favorable over the samples processed by using the regular de-ionized water. The apparent distinction among the granules and then the microstructures of the sintered bodies were attributed to the magnetized water as such features were not observed for the regular deionized water processed samples.

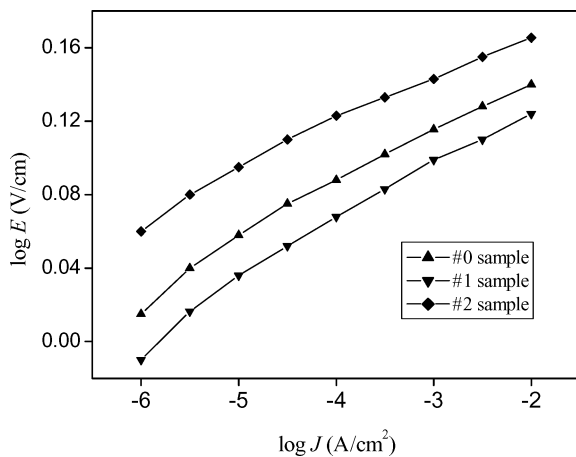The current-voltage (I-V) behavior of the varistor samples are depicted in Fig. 1. It is evident that the

Table 1. The influence of magnetized water on the measured electrical parameters of the TiO_2 varistors.

Sample	$V_{1\ mA}$ (V)	$V_{10\ mA}$ (V)	α	C(nF)	$\tan\delta$
#0 water	14.30	25.25	4.02	36.52	0.25
#1 water	9.79	17.38	4.01	56.19	0.27
#2 water	26.95	45.17	4.45	28.57	0.22

voltage gradient is enhanced for the samples as the high magnetized water is used for making the slurry. The nonlinear coefficient α is in the vicinity of 4 and, thus, similar to the SiC varistors [13]. However, such a response is expected to improve with the introduction of further cations and internal adjustment of the overall additives to TiO_2.

The electrical performance parameters are listed on Table 1. These parameters are $V_{1\ mA}$, $V_{10\ mA}$, nonlinear coefficient α, capacitance C (at 1 kHz) and dielectric loss tangent ($\tan\delta$ at 1 kHz). The values for each of these parameters represent average of at least 10 samples. Three typical I-V curves of the TiO_2 samples, prepared by using of the above three types of water, are shown in Figure 1. Furthermore, in order to investigate the consistency within various samples, the error bars of $V_{1\ mA}$ and V_{10mA} have been introduced in Fig. 2.

It is observed from Table 1 and Fig. 1 that #1 samples lead to lower varistor voltage and higher capacitance with respect to the reference #0 samples. Likewise the #2 samples yielded higher varistor voltage and lower capacitance when compared to the #0 samples. Nevertheless, the nonlinear coefficient and
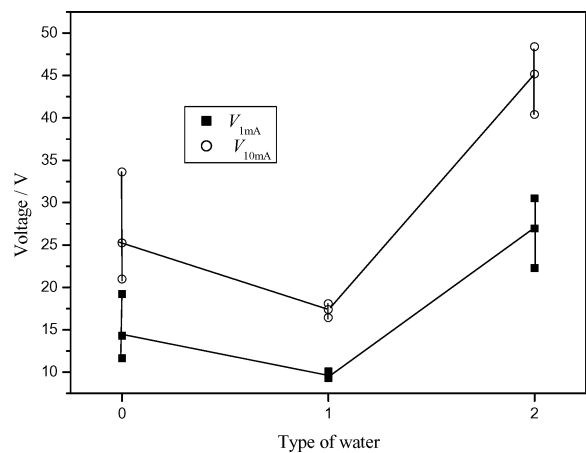

Fig. 1. The current (I-V) characteristics of various TiO_2 varistor samples.

Fig. 2. The relation between varistor voltage and different types of water used in making these varistors.

tanδ may be considered as identical for each of these samples.

Combining Table 1 with the results contained in Fig. 2 suggests that the lower magnetic field treated (0.2 *T*) water can facilitate improved consistency via narrow dispersion of the measured electrical parameter for the samples. However, higher magnetic field of 0.3 *T* exhibits slight variation in the same parameter. Since the samples were prepared in the same way except for using the type of water, the consistencies among the samples shown in Fig. 2 is mainly attributed to the type of the obtained slurry property. Thus, it is suggested that the electrical properties of the varistor samples can be perturbed via water treated at various magnetic fields. Reiterating the same statement it may be asserted that the varistor behavior may be improved per desired characteristics based on not only the cation additives but in conjunction with the adjustment of the type of the magnetized water.

In order to investigate the role of the magnetized water on the microstructure of the TiO$_2$ varistor materials, examination with scanning electron microscopy was carried out for the microstructures and they are displayed in Fig. 3. Figure 3(a) shows the microstructure of the sample prepared by ordinary deionized water. Fig. 3(b) and 3(c) show the microstructure of the samples prepared by #1 and #2 magnetized water, respectively. Since the sintering temperature of each of these three types of samples is the same, it is observed that using magnetized water in preparing ceramic slurry yielded large grain size. The samples prepared by using ordinary deionized water showed an average grain size of about 4.2 μm and the grain surface is covered by a random second phase making an obstacle for direct and successive TiO$_2$ grain to TiO$_2$ grain contact. As #1 magnetized water is used in the sample shown in Fig. 3(b), the average grain size of samples measured as about 5.5 μm and the second phase is located around the grains in a nearly uniform manner. There are a few voids observed despite having compact-like grains and their uniform distribution.

Large grain size in Fig. 3(b) accounts for a low varistor voltage and large capacitance of the samples. This is quite reasonable as the grain boundary junctions are fewer causing low varistor voltage, and the net depletion layer width across the grain boundaries is also small attributing to the large terminal capacitance. Of course the assumption on the capacitance is primarily based on the geometric contributions. Figure 3(b) and (c) exhibited identical type of microstructures except
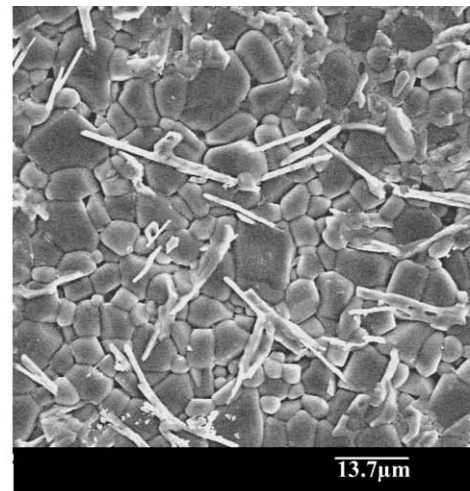
(a)
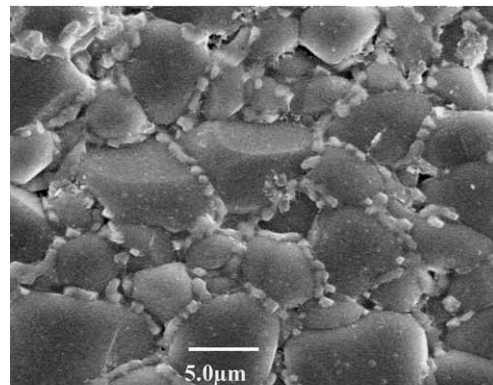
(b)
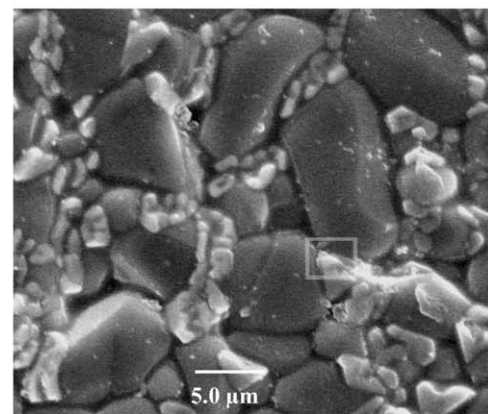
(c)

Fig. 3. SEM micrographies of three varistor samples prepared by using (a) deionized Water, (b) 0.2 T magnetized water, and (c) 0.3 T magnetized water.

for the average size distribution. The average grain size obtained in Fig. 3(c) is about 6.4 μm. A few irregular grain dimensions are evident in Fig. 3(c), which are often surrounded by the second phase in addition to the presence of some smaller grains. Such distribution of the grains may have led to higher varistor voltage and lower capacitance of the samples. Invariably this is attributed to the thickness of the insulating second phase as well as to the individual resistivity of the second phase apart from the number of the grain boundaries contained within the same geometry of the samples. Thus, the role of the second phase becomes predominant in the measurement of the electrical response. This is an ongoing investigation.

To examine the physical property of the second phase, the structural investigation is carried out using the powder XRD technique via JCPDS files. The patterns of the *three* types of the samples are identical confirming the presence of similar phases in each of the microstructures with the exception of the grain size and/or grain boundaries. Thus, one XRD pattern is provided in Fig. 4. It is clear that the basic XRD pattern possesses the *rutile* phase with major intensity peaks corresponding to 2θ at 27.45°, 36.08°, 41.22°, 54.32°, etc. However, there are two additional peaks appeared in the spectrum with $2\theta = 29.44°$ and 30.64°. The intensity corresponding to $2\theta = 29.44°$ is 10% while the intensity corresponding to $2\theta = 30.64°$ is 11%. These two peaks represent the second phase and consequently marked with "S" in the spectrum as recently also reported in the literature [14]. The anatase phase is transformed to the rutile phase as the varistor samples
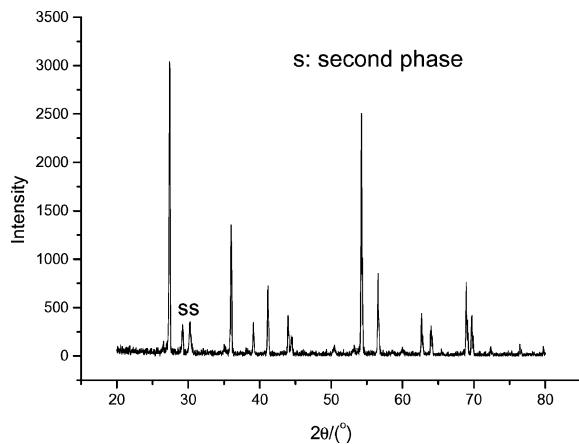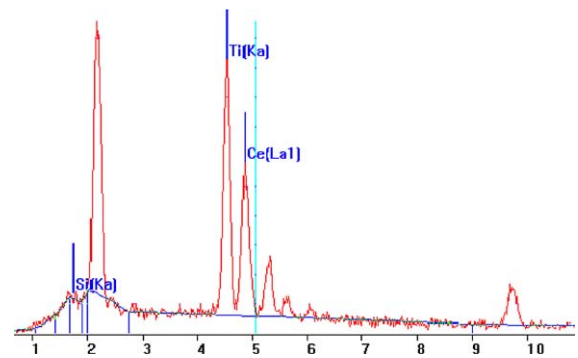

Fig. 5. EDAX results on the second phase in the TiO_2 varistor materials.

were sintered at 1350°C. Similar phase transformation has been reported earlier for the anatase-based sensor materials [15].

The energy dispersive spectroscopy (EDAX) was conducted to obtain the composition of the second phase. The results are shown in Fig. 5. It is understood that the second phase is primarily composed of Ce, Si, and Ti. It was suggested that the second phase located on the surface of TiO_2 grain [16] is electrically insulating. Based on the above experimental results, it is revealed that the magnetized water can influence electrical parameters and thereby affecting electrical properties via the microstructures of the TiO_2 varistor materials. The water treated at a magnetic field of 0.2 T can facilitate nearly homogeneous grain distribution and achieving lower varistor voltage while the water treated at 0.3 T leads to the asymmetrical type grain microstructures and elevating the varistor voltage.

In order to explain the foregoing situation, it is proposed in the literature that the gas-liquid interface is perturbed by the action of the applied magnetic field [17]. Since carbon dioxide has high density among the gases; it is then approximated to be close to the gas/liquid interface. When treated in magnetic field, carbon dioxide hydrolyzes in water and yields carbonic acid which subsequently dissociates into bicarbonate and hydrogen ion. This process can be described by the following equations:

$$CO_2 + H_2O \Leftrightarrow H_2CO_3, \qquad (3)$$

$$H_2CO_3 \Leftrightarrow H^+ + (HCO_3)^-. \qquad (4)$$
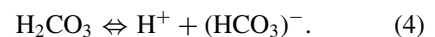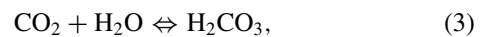
Again it is revealed that most oxide surfaces are hydrated. For an oxide of a metal M, there will be MOH

Fig. 4. Powder XRD pattern of the TiO_2 varistor material showing the second phase.

groups on the surfaces. In this study, the additives are submitted to form the slurry in the form of oxides. Thus, possible hydrated ions in the slurry may be formed during the dispersion process of the slurry. When the deionized water is treated in the magnetic field, there will be H^+ ions produced according to Eq. (4). In such a suspension adsorption of H^+ ions is preferential in the surface of various hydrated ions and a positively charged surface is consequently obtained.

It is quite legitimate to conceptualize electrical double layers for the particles in the slurry. According to the DLVO (after Derjaguin, Landau, Verwey and Overbeek) theory [18], two forces will act on the particles in a suspension. These are attractive van der Waals force and repulsive electrical force. As the distance between the successive two particles decrease, the overlap layers causes the potential to increase thereby leading to a repulsive force. The repulsive force is fairly weak when the particle surface is neutral. If the double layer repulsion force is less than the van der Waals attraction force, the slurry attains an unstable situation. Thus unstable situation can result in time dependent variation in the zeta potential measurement. However, if magnetized water is used in the slurry a greater repulsive electrical force is expected among various oxide particles due to the charging effect of the particle surfaces. In this case, stable and uniform slurry can be achieved.

Now probing to the magnetized water it may be reasonable to note that higher magnetic field may lead to more H^+ ions according to Eqs. (3) and (4). However, it can also lead to oscillatory (time dependent) changes of the interparticle forces of various cationic (metal) oxides after magnetic treatment [19], which can well explain the variation in the results obtained for the $0.2\ T$ and $0.3\ T$ treated magnetic water. This implies that when $0.3\ T$ water is used it is more than likely that there may be oscillatory changes in the interparticle forces, which in turn lead to the granules that are causing the microstructures responsible for the higher varistor voltage.

Although the magnetized water in the slurry is affecting the measured electrical parameters of the TiO_2 based varistor materials, it is still not very transparent about the total role of the magnetized water at this stage. However, it is presumed that the grain-to-grain interfaces are altered via the surface states and thereby affecting potential barriers across the grain boundaries. Continued study is expected to reveal surface-interface properties of the grains via traps or defect states. It is expected that the application of magnetized water

in the field of advanced ceramics may allow preparing some novel electronic materials as well as producing useful resulting products. The *zeta potential* of the Newtonian-like (of course non-Newtonian) colloidal slurry requires revisiting for the total comprehension of the processing as well as the total electrical behavior of the device. Consequently, it is of great significance to explore the role of magnetized water in further details besides determining the optimum electrical response via steady performance characteristics for potential applications.

Conclusions

The magnetized water in conjunction with the organic dispersant and binder in the processing of the TiO_2 varistor materials reveals microstructural differences for various magnitudes of the magnetized water. Thus, electrical responses are affected. The $0.2\ T$ magnetized water yielded lower varistor voltage via less variation in the microstructural features while $0.3\ T$ magnetized water yielded higher varistor voltage and a variation in the grain size distribution. The TiO_2 grains obtained in the microstructures are *rutile* for every sample investigated. Therefore, there is no influence on achieving the rutile grains other than the type of the distribution in conjunction with the defect states at the grain surfaces and/or the grain boundary interfaces. The second phase composed of Ce, Si and Ti is observed and presumed to play identical role in the electrical behavior of the device. The $0.2\ T$ magnetized water can facilitate a uniform distribution of the second phase around the TiO_2 grains. The role of the magnetized water was conceptualized via the perturbation of the gas-liquid interface which is likely to change the inter-particle forces with time of the metal oxide particles. The magnetized water causes charged surfaces, presumably positive at this time, for the particles and achieve uniformly dispersed slurry. Henceforth, the electrical performance parameters of the TiO_2 based varistor materials may be controlled via desired microstructures.

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