The effect of magnetized water on TiO$_2$ based varistors

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Abstract

The effect of magnetized water on TiO$_2$ based varistors was investigated. The results of the electrical behavior reveal that the water magnetized at 0.2 T yielded lower varistor voltage and the water magnetized at 0.3 T yielded higher varistor voltage compared to non-magnetized deionized water. The XRD and EDAX results show that the main polycrystalline phase is rutile TiO$_2$ surrounded by the second phase composed of Ce, Si, and Ti. The SEM micrographs suggest more preferable microstructure may be obtained by using the 0.2 T magnetized water. The role of the magnetized water was examined by the perturbation of the gas-to-liquid interface that changes inter-particle forces, and consequently leads to higher electrostatic stabilization of the slurries.
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1. Introduction

It is reported in the literature[1,2] that the magnetized water may enhance the growth rate of plants and animals, accelerate the healing of the fractured and broken bones including the soft tissues, inhibit the scaling of metallic surfaces, and improve the compressive strength of the cement. Thus, use of the magnetized water in agriculture, in industry, and in relevant daily life is more than likely to be extended with growing demand. From another standpoint water is necessary in the conventional and advanced ceramic processing technology. The state-of-the-art ceramic powders are prepared from the water based slurry apart from the multi-directional processing methods that are employed to obtain various novel electroceramic systems. In general, deionized water is used in the ceramic processing technology. Based on the available information in the published literature, till to date, very little effort has been put on the application of the magnetized water in the processing of the ceramic systems.

The effect of slurry preparation on the ceramic microstructure and obtaining desired functional behavior have drawn extensive technological attention in the recent years.[3,4] It is already proven that the stabilization of the slurry is of great significance on the physical properties of the ceramic granules. Thus, the ceramic granules may influence the microstructural features resulting from the sintering and relevant heat treatment steps, and thereby the electrical response of the ceramic body. The role of the magnetized water in achieving stable and uniform slurry is a necessary objective for understanding and controlled usage. To achieve such slurry a bidirectional stabilization effort may be directed. These stabilization processes include electrostatic stabilization and polymeric stabilization.[5] Usually the investigators employ various organic polymers such as organic dispersants or binders to achieve polymeric stabilization of the slurry. Thus, associated free flowing properties of the slurry are achieved via the reduction of the non-Newtonian colloidal behavior. However, only rare effort has been directed toward making an evolution of the water despite being the most common vehicle of the ceramic processing.

In this paper, efforts were concentrated to investigate the role of the magnetized water in the ceramic processing.

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The preparation of the TiO_2 based varistor was chosen as a sample study. This is because such varistors are known as low voltage varistors[6] whose applications are extensive. Also electrical and microstructural characterization processes are identical to those employed for the ZnO based varistors.[7] Thus, the preliminary relations of the processing–microstructure–property are evaluated for potentially novel applications of such a varistor material.

2. Experimental

Traditional ceramic processing technique was employed in preparing the TiO_2 varistors using various types of water in the processing of the slurry. Three types of water were used in the processing of the slurry using these cationic ratios. These are: (1) ordinary or regular deionized water (varistor samples made of this water is denoted as #0 or designated as the reference varistor samples), (2) deionized water treated with a magnetic field of 0.2 *T* (varistor samples made of this water is denoted as #1), and (3) deionized water treated with a magnetic field of 0.3 *T* (varistor samples made of this water denoted as #2). Deionized water passed through the magnetizers under different applied magnetic fields such as 0.2 *T* and 0.3 *T* resulted in #1 and #2 magnetized water, respectively. In order to achieve magnetized water, a 30 cm long pipe-like glass tubing (outer diameter 7 cm and inner diameter 5 cm) was used in applying various magnetic fields while flowing deionized water. The flow rate was kept the same value of 100 ml/min at each applied magnetic field around the tubing. Then the magnetized water was collected in the glass vessel and retained for about 0.5 h in air for making slurry. Each magnetized water sample was tested for pH and found to be 6.5 for each sample which was the same as before magnetization. Each magnetized water sample was chemically evaluated and also found identical for each sample. Thus, no observable difference was noticed for any of the magnetized water used in preparing the slurry. There was no evidence that the glass vessel having collected water contributed as a source of contamination that modified the physical properties of the magnetized water. The chemistry of the magnetized water, thus far, is not a subject of suspicion for possible contamination and thereby altered the flocculation behavior of the slurry. A detailed study of the behavior of the magnetized water is a subject of the future publication.

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 the ratio of TiO_2:Nb:Ce:(Ca + Si) = 100:0.2:0.5:0.5 (in mol). The internal ratio of Ca to Si was 1:1. The water

was added at a ratio of 80 wt.% 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 min in an oven.

The varistor voltage $V_{1\ mA}$ and $V_{10\ mA}$ were measured by using JN2711 meter. The nonlinear coefficient α was calculated using:[8]

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

where 1 mA ($= I_1$) corresponds to $V_{1\ mA}$ ($= V_1$) and 10 mA ($= I_2$) corresponds to $V_{10\ mA}$ ($= V_2$). In general, the nonlinear coefficient and varistor voltage V_{1mA/cm^2} corresponding to the current density 1 mA/cm^2 are the two most important electrical parameters for any varistor material.[9] In this work, the dimension and electrode area of the samples were maintained the same. Thus, varistor voltages corresponding to 1 mA and 10 mA are used in discussing the electrical behavior. The low voltage TiO_2 varistors reported earlier[6] 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[10] is still not certain to control the nonlinear coefficient as well as the functional behavior when exposed in the application field.

The capacitance C and the dielectric loss tangent (tanδ) were measured using an LCR meter (2693D) at a fixed measurement frequency of 1 kHz. This measurement frequency is selected arbitrarily. The microstructures were evaluated using SEM (XL-30 FEG Technology). 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.

3. 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 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 deionized 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 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.[11] 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 (tanδ 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 Fig. 1. Furthurmore, in order to investigate the
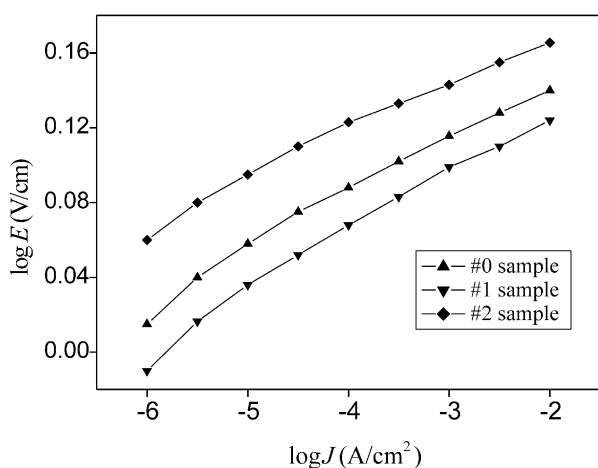
consistency within various samples, the error bars of $V_{1\ mA}$ and $V_{10\ mA}$ have been introduced in Fig. 2.

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 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 parameter within 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. Fig. 3(a) shows the microstructure of the sample prepared by ordinary deionized water. Fig. 3(b) and (c) show the microstructure of the samples prepared by #1 and #2 magnetized water, respectively. A complete view of various samples was carried out. Since the sintering temperature of each of these three types of samples is the same, it is reasonable to propose that using magnetized water in preparing ceramic slurry

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

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

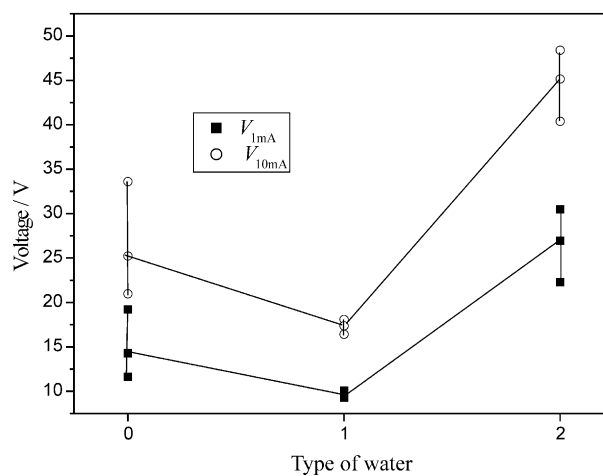| Sample	$V_{1\ mA}$ (V)	$V_{10\ mA}$ (V)	α	C(nF)	tanδ
#0 water	14.30	25.25	4.02	36.52	0.25
#1 water	9.79	17.38	4.01	56.19	0.27
#2 water	26.95	45.17	4.45	28.57	0.22

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

provide large grain size. To achieve the average grain size, minimum 150 grains were measured for each sample. 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. Thus, a more preferable microstructure is obtained by using #1 magnetized water.

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. Fig. 3(b) and (c) exhibited identical type of microstructures except 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 behavior. Overall, this is a subject of further investigatgion.

To examine the physical property of the second phase, the structural investigation is carried out using the powder XRD technique. The patterns of the *three* types of the samples are identical confirming the presence of similar phases in each of the microstructures. 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
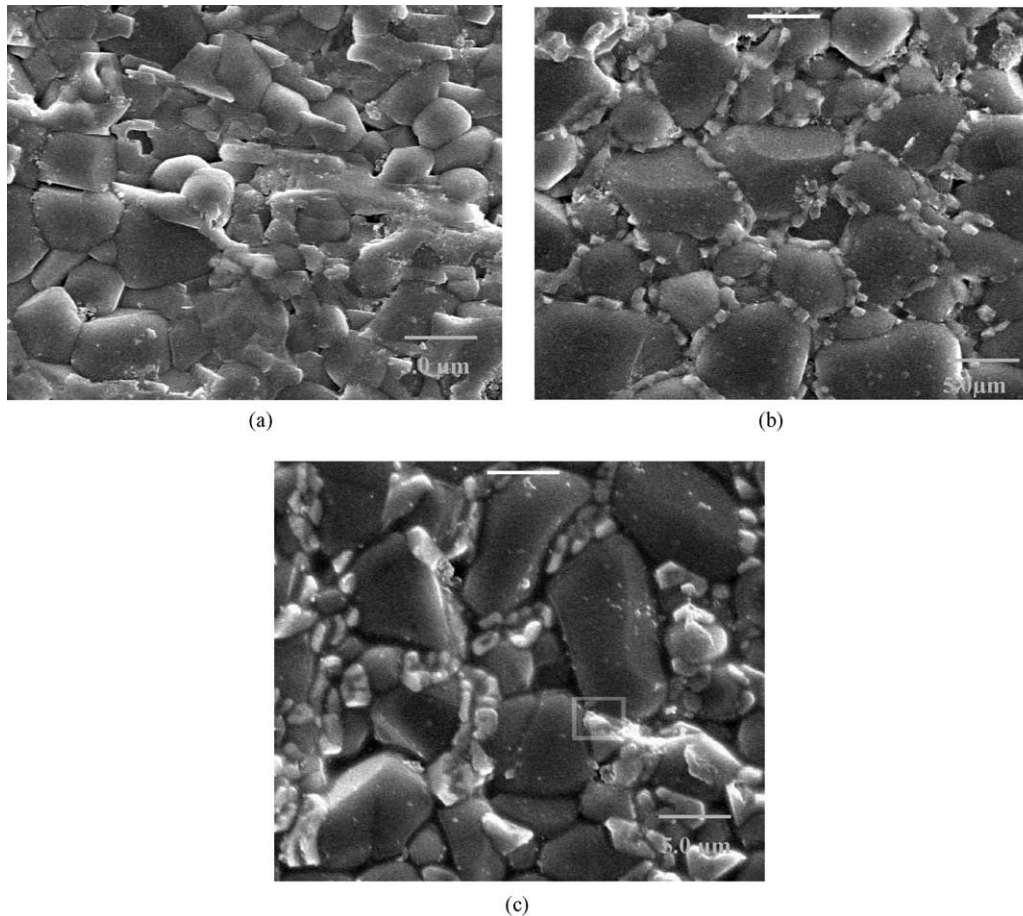

(a)

(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.

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. The anatase phase is transformed to the rutile phase as the varistor samples were sintered at 1350 °C. Such phase transformation takes place around 946 °C.[12,13]

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 in the intergranular regions between the successive TiO_2 grains[14] 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.
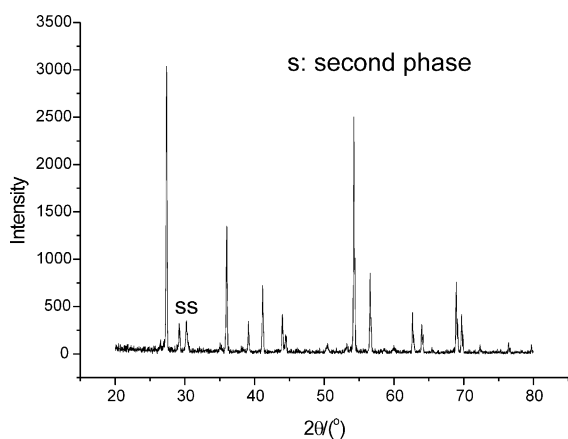

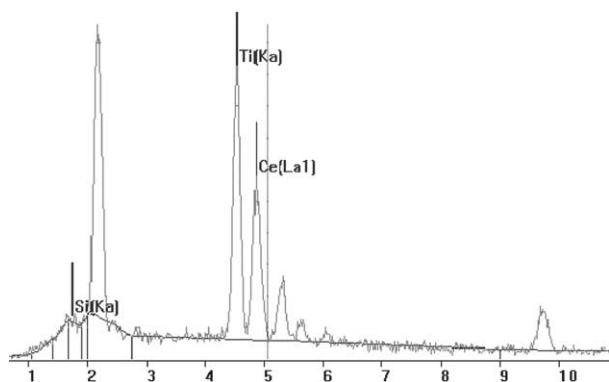Fig. 4. Powder XRD pattern of the TiO_2 varistor material showing the second phase.

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

Since three types of samples were prepared using the same recipe and following the processing route, it is suggested that the resulting electrical properties can only be affected by the nature of the slurries obtained. The physical properties of the slurry can be influenced by several factors. These factors[3] include interparticle forces, zeta-potential (surface charging effect), deflocculating behavior, surface sticking behavior, particulate volume fraction, particle size, particle size distribution, mixed but distinctive phase(s), pH, etc. In this work, slurries had the same particulate volume fraction and mixed phases. Thus, two possible hypotheses may be considered for the slurry behavior. The first is that magnetized water lead to unmasking the surface charging effect thereby affecting zeta potential and the dispersion process. Thus, the influence of the distribution of the particle size on the slurry is reduced via reduced surface charging effect. The surface surging effect causes the zeta potential resulting from the dangling bonds of the particles. The second is that the magnetized water is conducive to the alteration of the potentially existing interparticle forces. Either of these hypotheses them can result in changing the physical properties of the slurry.

To investigate the role of the magnetized water on the particle size in the slurry, the analysis of the granules was carried out. Two compositions were used for this purpose. One composition is the same as noted in the experimental section. The other composition is designed using the internal ratio for TiO_2:Nb:Bi:Ba = 100:0.2:0.5:0.5 (in mol). For the two compositions only two types of water (#0 and #1) were used. These slurries are designated as A and B respectively. The granule analysis of two slurries for each recipe comprising of a total of four slurries is shown in Table 2. The comparison chart depicts the granule concentration corresponding to 16, 50, and 84%, and specific surface. A finite difference in the results is evident when the deionized water and the magnetized water are used for both the compositions. However, the assessment is based on the single-handed (one person's judgment using the same instrument) identical method of measurements. Based on this fact, it is clear that the magnetized water show little influence on the particle size distribution (granule effect) of the TiO_2 based slurry. Therefore, the effect of the magnetized water is attributed to the change or alteration in the interparticle force within the slurry.

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.[15] 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:

Table 2
The granule analysis of the powders prepared from the slurries obtained using various types of water

Items	A		B	
	#0 water	#1 water	#0 water	#1 water
Granularity (μm)				
16%	1.21	1.24	1.08	1.11
50%	1.77	1.74	1.68	1.65
84%	2.33	2.58	2.22	2.18
Specific surface $(m^2\,g^{-1})$	0.92	0.86	1.04	0.98

$$CO_2 + H_2O \Longleftrightarrow H_2CO_3, \tag{2}$$

$$H_2CO_3 \Longleftrightarrow H^+ + (HCO_3)^-. \tag{3}$$
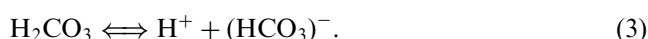
Again it is revealed that most oxide surfaces are hydrated. For an oxide of a metal M, there will be MOH groups on the surfaces.[5] In this study, the additives are submitted to form the slurry in the form of oxides. Thus, possible hydrated ions in the slurry may be formed during the dispersion process of the slurry. When the deionized water is treated in the magnetic field, there will be H^+ ions produced according to Eq. (3). 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. The above process is illustrated in Fig. 6.

It is quite legitimate to conceptualize electrical double layers for the particles in the slurry.[3] According to the DLVO (after Derjaguin, Landau, Verwey and Overbeek) theory,[5] 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
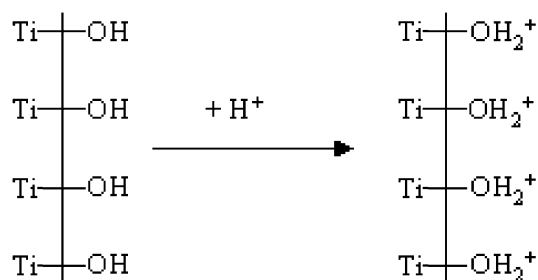

Fig. 6. Illustration of the surface charges produced by the adsorption of the H^+ ions.

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. (2) and (3). However, it can also lead to oscillatory (time dependent) changes of the interparticle forces of various cationic (metal) oxides after magnetic treatment,[16] 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. Such an oscillatory change is demonstrated in Fig. 2. Since water is known as a strong polarized molecule, thus, in general, water exists in the form of large clusters. It is already shown that under proper magnetized field the large clusters of water disintegrates into small clusters[16] that lead to better distribution of solid particles in ceramic slurry and, thus, a good consistency of results at 0.2 *T* can be achieved as shown in Fig. 2. The results of 0.3 *T* in Fig. 2 shows a poor consistency compared with the results of 0.2 *T*.

It is anticipated that a change in the inter-particle force may have an impact on the particle size distribution via preventing agglomeration. According to the results shown in Table 2, it is reasonable to propose that the change in water clusters play a significant role on the observed results. Thus, variation in the electrical results as well as in the microstructural features are feasible despite identical particle size distribution for each type of slurry prepared at various applied magnetic fields.

It is beyond doubt that hydrogen and hydroxide ions are potentially determining ions for the metal oxides. If the particle surfaces in the slurry can be adjusted by the appropriate processing parameters, an electrostatic stabilization can be achieved. This stabilized situation causes the magnetized water to reach at equilibrium of the surface charging effect of the particles in the slurry. However, in practice, investigators are exposed to the polymeric stabilization. Various organic polymers such as organic dispersants and binders are used in the slurries to achieve polymeric stabilization. Till to date seldom research was carried out to study the achievement of the electrostatic stabilization beside some basic variations such as the adjustment of the pH values of slurries. This is achieved by adjusting the solid to liquid ratio or vice versa. Often the organic materials are adjusted in such a way so that the dispersion attains

stability via time invariant zeta potential value. 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. Furthermore, the underlying mechanism of magnetized water still remains unclear as how an applied magnetized field influences the equilibrium between CO_2 and bicarbonate ions. At this stage only a hypothesis structured but needs additional studies to confirm the exact role of the magnetized water on the preparation of the slurry. It is expected that the application of the magnetized water in the technology of electronic ceramics may bring out some novel experimental results based on the results of the present work. Consequently, it is of great significance to explore the role of magnetized water in further details.

4. Conclusions

The magnetized water in the processing of the TiO_2 varistor materials reveals some interesting phenomena. Nevertheless, a few observations can be outlined from the results obtained in this study. The 0.2 T magnetized water yielded lower varistor voltage via desired microstructural features while 0.3 T magnetized water yielded higher varistor voltage and a variation in the grain size distribution. These observations are provided when compared with the regular deionized water. The TiO_2 grains obtained in the microstructures are *rutile* for every sample investigated. Therefore, there is no influence on achieving the rutile grains. The second phase composed of Ce, Si and Ti is found in both cases. 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 examined by the concept portrayed in the perturbation of the gas–liquid interface which changes the interparticle forces with time of the metal oxide particles. The magnetized water causes positively charged surfaces for the particles and achieve uniformly dispersed slurry. Thus, the electrical parameters of the TiO_2 based varistor materials may be improved via desired microstructures.

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