Dielectric properties and microstructure of BaTiO$_3$-SiO$_2$ nanocomposites using vacuum treated barium titanate nanoparticles

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Abstract

Effect of vacuum treatment on the microstructure and dielectric properties of BaTiO$_3$(BT)-SiO$_2$ nanocomposites is systematically studied using BT nanoparticles with a process of vacuum treatment, and coated with a SiO$_2$ layer by a wet chemical process. It is found that the vacuum treatment induced not only the oxygen vacancies but also permanent changes in the crystal structure of nanocomposites. Comparing with the nanocomposites sintered from untreated BT nanoparticles, the nanocomposites sintered from vacuum treated BT exhibit a significantly higher dielectric constant, a lower loss and, therefore, a higher energy storage density. It is believed that the electric dipoles formed by the treatment caused defects are responsible for the high dielectric performance observed. The dipoles also result in a pinching effect in the polarization - electric field hysteresis loop. For the composites with 20.0 wt% SiO$_2$, the composites sintered from BT treated at 950 °C exhibit a dielectric constant that is more than 6 times of that of the composites sintered from untreated BT and this high dielectric constant is almost independent of the temperature over a temperature range from −50 to 140 °C.

1. Introduction

In electronic circuits, devices, and systems, dielectric materials are necessary for three primary functions: insulation, capacitor, and energy storage [1–3]. For these applications, dielectrics with a high electrical breakdown field ($E_b$) and a large dielectric constant ($\varepsilon_r$) are critical. In general, the polar inorganic materials, especially ferroelectric ceramics/crystals, exhibit a larger $\varepsilon_r$ (up to $10^3$) with a lower $E_b$ ($\sim 10^6$ MV m$^{-1}$) [4–6], while polymers (such as polypropylene) and non-polar inorganic materials (such as silica) exhibit a higher $E_b$ ($10^2 \sim 10^5$ MV m$^{-1}$) with a small $\varepsilon_r$ (~$10^0$) [5, 7, 8]. Therefore, it is interesting to study dielectric composites by combining the properties of these two types of dielectrics to develop dielectrics with a relatively high $\varepsilon_r$ and $E_b$ [3]. It should be mentioned that the temperature dependence of dielectric properties is also very critical for many applications, in which the temperature can change over a wide range, such as the electronics used in space exploration [9]. The polar materials usually exhibit a strong temperature dependence of dielectric properties [10], while polymers and non-polar materials exhibit a weak temperature dependence of dielectric properties [8]. Regarding the study of dielectric composites, plenty of efforts were given to the development of polymer-based composites, in which the polymers with a high $E_b$ are used as matrices [5]. In this field, the composites using different matrices with enhanced dielectric properties have been reported [5, 11–13]. However, it is well known that the polymer-based composites have a very limited working temperature range [9]. For the purposes of improving dielectric stability in a wider temperature range, the dielectric composites using glasses as the matrix are highly desirable [14, 15].
For the development of glass-based composites, the lead-free ferroelectrics with a high $\varepsilon_r$, such as BaTiO$_3$ (BT), were intensively studied as fillers $[1, 5]$. In the research of composites using BT as fillers, different glassy materials have been used as the matrix, such as SiO$_2$ $[16]$, Al$_2$O$_3$ $[17]$, B$_2$O$_3$ $[18]$, and the mixture of multiple metal oxides $[14, 15, 19, 20]$. Actually, both SiO$_2$ and Al$_2$O$_3$ have been widely used as the sintering agents in the fabrication of BT ceramic capacitors. In this case, the amount of SiO$_2$ used is usually about 1.0 wt%, while Al$_2$O$_3$ is about 2.5 wt% $[21]$. The sintering agent is used to achieve a dense morphology in the BT ceramic. Therefore, the usage of a small amount of these additives results in the ceramics exhibit a high dielectric constant with a slightly improved $E_b$ $[21, 22]$. For these materials, the containing of ferroelectric phase results in the strong temperature dependence of dielectric properties since the BT has the phase transitions at about 0 °C and 120 °C, respectively $[1, 21]$. To further increase the $E_b$ of ferroelectric BT, the glass compounds with a higher content (up to 65 wt%) $[23]$ was added during the sintering process to form composites, in which the raw material is either the glass-coated BT particles $[24]$ or the mixture of BT and glass particles $[22, 25]$. For some of the BT-glass composites, the reaction between BT and glass might result in the formation of new phases. For example, the formation of both Ba$_2$TiSi$_2$O$_8$ and BaTiSiO$_5$ phases has been found in the BT-SiO$_2$ composite system $[25, 26]$. In this case, although the $E_b$ of the ceramic-glass composite was increased as the SiO$_2$ content increases, the $\varepsilon_r$ was significantly reduced $[19, 25, 26]$. To further improve the $\varepsilon_r$ of a BT-glass composite such as BT-SiO$_2$, the utilization of vacancies in BT are potential $[27, 28]$. The electric/dielectric properties of BT may be effectively modified by changing the concentration of vacancies $[29]$. By the pretreatment under vacuum or different gas atmospheres with suitable temperatures, the conductivity ($\sigma$) of BaTiO$_3$ may vary within a large range between $10^{-7}$ and $10^{-10}$ Ω·cm, which can be used for obtaining the dielectric constant improvement of ceramics $[30, 31]$. Actually, BT with oxygen vacancies has already been used in the development of polymer-based 0–3 composites. It has been reported that for the polyester-styrene reactive resin filled with BT nanoparticles, the $\varepsilon_r$ was increased to more than twice by using BT particles treated in vacuum at 1000 °C $[32, 33]$. Therefore, it is interesting to determine the effects of vacancies on the dielectric properties of BT-glass composites.

In this work, BT-SiO$_2$ nanocomposites are sintered in air at 1230 °C from BT nanoparticles in 200 nm. Prior to the sintering process, the BT nanoparticles were pretreated in vacuum at different temperatures: 850 °C, 900 °C, 950 °C, and 1000 °C, respectively, to induce the oxygen vacancies. The pretreated BT nanoparticles were then, coated with a layer of SiO$_2$ using a wet chemical process. It is found that the composites sintered from both pretreated and untreated BT nanoparticles exhibit a low dielectric loss, but the composites sintered from the pretreated BT nanoparticles exhibit a significantly higher dielectric constant than the nanocomposites sintered from the untreated BT.

### 2. Experiments

#### 2.1. Vacuum treatment of BaTiO$_3$ nanoparticles

BT nanoparticles with 99% purity and an average particle size of 200 nm were purchased from US Research Nanomaterials and used as received. For the study on the influence of vacuum treatment, the nanoparticles were pretreated under vacuum (below $5 \times 10^{-3}$ Torr) at different temperatures: 850 °C, 900 °C, 950 °C, and 1000 °C, respectively, for 4 h. Here, the BT nanoparticles were labeled as BT(V850), BT(V900), BT(V950), and BT(V1000) based on the temperature of vacuum treatment, while the untreated BT was labeled as BT(V0). The treatments under low oxygen pressure lead to the formation of vacancies in varying degrees $[26]$. After pretreatment, the vacancies introduced nanoparticles were used as the raw materials for the preparation of BT-SiO$_2$ nanocomposites.

#### 2.2. Creation of BT-SiO$_2$ core–shell structures

In the preparation of glass–ceramic composites, the pretreated BT nanoparticles were utilized as the ceramic core. SiO$_2$ shell was obtained by the chemical reaction between tetraethylorthosilicate (TEOS) and H$_2$O in suspension environment according to stöber process $[34]$. In the experiments, the content of SiO$_2$ was controlled based on the mass. Following constant of SiO$_2$ was designed and prepared: 2.5, 5.0, 10.0, 15.0, 20.0 wt%. Prior to coating SiO$_2$, the surface of the BT nanoparticles was activated by placing the nanoparticles in the mixture of ethanol and acetic acid and sonicated at 40 °C for 30 min. Then, TEOS was added to the suspension and the 28–30 wt% ammonia-water solution from VWR International was slowly added during the stirring and wait for 30 min to complete the chemical reaction. The obtained mixture was washed with ethanol and deionized water at room temperature and, then, heated to 80 °C for 3 h and then to 120 °C for 12 h to evaporate all the solvent. The final products were SiO$_2$ coated BT nanoparticles.
2.3. Preparation of BT-SiO$_2$ nanocomposites

First of all, the green body in a diameter of 10 mm and a thickness of 1 mm were prepared by pressing the nanoparticles (i.e. without or with different SiO$_2$ coating) at 20 MPa using a 5 wt% PVA-water solution as the binder. The green bodies were, then, sintered in air in a 46 100 Barnstead Thermolyne furnace to fabricate the BT-SiO$_2$ ceramic-glass nanocomposite disks. In the sintering process, the green bodies were put into an alumina crucible. The furnace was firstly heated up to 600 °C with a heating rate of 2 °C min$^{-1}$ and, then, kept at 600 °C for 1 h to remove PVA. The furnace was further heated to 1230 °C from 600 °C with a heating rate of 2 °C min$^{-1}$ and the nanocomposites were sintered at 1230 °C for 5 h. Finally, the furnace was cooled down with a cooling rate of 2 °C min$^{-1}$ to 700 °C and, then, followed by a natural cooling to room temperature. The prepared ceramics and composites were labeled as BT(Vy)$_x$SiO$_2$, where x is the content of SiO$_2$ in weight percentage and y = 0 means untreated.

3. Characterization and measurement

The coating layer of SiO$_2$ on BT nanoparticles was examined using Hitachi H-7650 TEM (Transmission Electron Microscope); the morphology and uniformity of composites were examined using JEOL JSM 7000F FE-SEM (Scanning Electron Microscopy); the crystalline of the ceramic-glass composites were examined by Bruker D8 Discovery XRD (x-ray diffraction). For the characterization of dielectric properties, the samples were polished to reduce the thickness (0.2 ~ 0.3 mm) and obtain smooth surfaces. The gold electrodes in a diameter of 3.0 mm were sputtered on both sides of the films to make a parallel plate capacitor. An Agilent 4294A impedance analyzer was used to characterize and record the dielectric spectrum in a frequency range from 100 Hz to 1 MHz by using the Cp-D function and calculation form the parallel plate capacitance. A Precision-LC100 Ferroelectric Testers with a High Voltage Supplier/Amplifier was used to determine the $E_d$ and P-E loop of composite samples.

4. Results and discussion

The effect of coating by the process as introduced above was firstly examined by the TEM. The picture of BT nanoparticle coated with 10.0 wt% SiO$_2$ was shown in figure 1(a), in which the continuous and uniform coating of SiO$_2$ thin layer was obtained. It is observed that the uniform SiO$_2$ shells were formed on the surface of BT nanoparticles, and therefore the thickness of the SiO$_2$ coating layer can be controlled by the amount of TEOS. From TEM, the thickness of SiO$_2$ coating layer was determined to be 3.0, 5.8, 12.8, 21.9, and 32.2 nm for the BT nanoparticles. The thickness of SiO$_2$ coating layer is close to the estimated results calculated by the density of SiO$_2$ (2.2 g cm$^{-3}$) and BT (6.0 g cm$^{-3}$). The morphology and microstructure of the nanocomposites are shown in figures 1(b)–(d), where the SEM images of the cross-sections of the BT(V950) ceramics and both BT(V950)-2.5SiO$_2$ and BT(V950)-15SiO$_2$ ceramic-glass are presented as some examples. It was indicated the coating of SiO$_2$ has a strong influence on the interaction between the components. For the BT ceramics without SiO$_2$, the grains with clear contours had a non-spherical phase reflecting the growth of the grains during the sintering. For the ceramic-glass nanocomposites, the contours of grains are not clearly defined and the samples have a dense microstructure structure than the BT ceramics. This may indicate the formation of glass phase between the grains. That is, the ceramic-glass composites were formed and the growth of BT grains was suppressed due to the SiO$_2$ additive.

The influence of the vacuum treatment on the crystalline structure of the BT nanoparticles was evaluated using XRD results as shown in figure 2(a), where the XRD patterns of BT nanoparticles with different treatment temperatures are presented. For the untreated nanoparticles, a single peak of (101)/(110) was observed, which indicated that the nanoparticles are in cubic phase. For the standard tetragonal phase of BT, the intensity of the (112) peak is less than half of that of (211) phase and the intensity of the (002) peak is less than that of (200) peak. Therefore, the observed (112)/(211) and (002)/(200) peaks being asymmetrical indicates that the nanoparticles should be at its tetragonal phase. For the BT(V850), BT(V900), and BT(V950) nanoparticles, the similar XRD patterns are observed as shown in figures 2(a1)–(a3). That is, the peak of the (101)/(001) is symmetric and the peaks of the (002)/(200) and (112)/(211) are asymmetrical. However, as the temperature of treatment increases, all these peaks shift to higher angles. For the BT(V1000), both of (112)/(211) and (002)/(200) peaks are splitted into two; the intensity of (211) and (200) peak is higher than that of (112) and (002) peak, respectively, as shown in figures 2(a2)–(a3), which is consistent with the standard XRD results of tetragonal BT. All these indicate that the BT nanoparticles at room temperature are at its tetragonal phase. To analyze the crystalline structure, it was assumed that the crystalline structure of all the BT nanoparticles was pure tetragonal phase so that the lattice constants, a and c, and the volume of the lattice unit, a$^2$c, were obtained as shown in figure 2(b), where the ratio of c/a is also presented. From the results, one can conclude that the c/a ratio of the
Figure 1. (a) TEM image of BT nanoparticle coated with 10.0 wt% of SiO$_2$; SEM images of: (b) cross section of BT(V950) ceramics; (c) BT(V950)-2.5SiO$_2$, and (d) BT(V950)-15SiO$_2$.

Figure 2. (a) XRD patterns of BT nanoparticles treated at different temperatures in vacuum; (b) lattice constants (a and c) and c/a ratio of BT nanoparticles treated at different temperatures; (c) lattice constants and c/a ratio of BT-2.5SiO$_2$ sintered from the BT nanoparticles treated at different temperatures.
tetragonal phase increases and the volume of lattice unit decreases, with increasing treatment temperature. For the BT(V1000) nanoparticles, the ratio of $c/a$ is about 1.009, which is close to the ratio of $c/a$ (∼1.01) for the bulk BT [35]. However, the intensity of (101) peak is higher than that of (110) peak as shown in figure 2(a1), which is against to the standard XRD results of the bulk tetragonal BT. This may indicate that besides the oxygen vacancies some other changes in BT nanoparticles were also induced by the vacuum pretreatment. It was reported that if the oxygen vacancy concentration was high, the intrinsic disorders including both Schottky and Frenkel defects would be induced in the BT [36, 37]. Regular BT has an ABO$_3$ structure, in which the barium and titanate ions take the A site and B site, respectively, of the lattice. Thus, the intrinsic disorders mean that the barium and titanate ions can take the locations other than A and B site of the lattice, respectively. For example, barium ions can take the B site and the interstitial site. Therefore, the treatment-induced intrinsic disorders would result in a different distribution of the elements/atoms/ions so that the XRD patterns were changed.

The XRD patterns of the BT(V0) ceramics and BT(V0)-xSiO$_2$ ceramic-glass composites are shown figure 3(a), where the standard peak position and intensity of BaTi$_5$Si$_3$O$_{15}$ and Ba$_2$Ti$_3$Si$_2$O$_{10}$ compounds from PDF are marked at the bottom of each figure, while the standard peaks of tetragonal BT at room temperature from the PDF are marked with dotted lines and its index. To show the details of the peaks associated with tetragonal BT, three figures, (a1)–(a3), are presented at the right of figure 3(a). Clearly, besides the peaks associated with tetragonal BT, new XRD peaks are observed. The intensity of these new peaks increases, while the intensity of the peaks associated with BT decreases, with increasing SiO$_2$ content. This is consistent with other reports [16]. The XRD results of the BT-2.5SiO$_2$ nanocomposites sintered from both untreated and pretreated BT nanoparticles are shown in figure 3(b). Clearly, the BT in these composites is at its tetragonal phase. For the tetragonal phase of BT in these composites, the lattice constants of the crystalline structure were determined from the XRD data shown in figure 3(b). The results are shown in figure (c). Comparing with the BT nanoparticles, the crystalline structure of BT in the BT-2.5SiO$_2$ nanocomposites have a smaller lattice constant and lattice unit.

Figure 3. XRD patterns of nanocomposites sintered from BT(V0)-xSiO$_2$ (a), BT-2.5SiO$_2$ (b); BT-20SiO$_2$ (c).
Therefore, the XRD results shown in figure 3(b), one can also find that besides the peaks associated with the tetragonal phase of BT some new peaks, especially the one at 29.0°, can be seen, but the intensity of the new peaks is small. For the BT-20SiO2 composites, the intensity of these new peaks is much stronger, while the peaks associated with the tetragonal BT can be seen but their intensity is much weak, as shown in figure 3(c). Interestingly, it is found that the intensity of peaks associated with the tetragonal BT is also dependent on the temperature used to treated BT nanoparticles. That is, the higher is the treatment temperature, the weaker is the intensity of the peaks associated with tetragonal BT in the nanocomposites. For example, the intensity of the peaks associated with tetragonal BT obtained in the nanocomposites sintered from BT(V0) and BT(V850) is much stronger than that in the nanocomposites sintered from BT(V900), BT(V950) and BT(V1000). Regarding the peaks associated with the new compound(s), one can find from figure 3(c) that the intensity of these peaks obtained from the nanocomposites sintered from BT(V1000) and BT(V950) is clearly the strongest and second strongest, respectively, among all the composites. Therefore, one can conclude that the higher is the temperature used to treat the BT nanoparticles, the less amount of BT is left in the nanocomposites from the reaction between the BT and SiO2.

Regarding the new compounds formed in the BT-SiO2 composites, there are many possibilities. Based on the BT-SiO2 phase diagram [38], following compounds can be formed: BaTiSi3O9, Ba2TiSi2O7, and BaTiSi2O8. Additionally, the Ba2TiSi2O8 has been reported in the BT-SiO2 system [16] and BaO, BT, and SiO2 system [19]. From the PDF database, the XRD peaks of two compounds (BaTiSi3O9 and Ba2TiSi2O7) were found and marked in figure 3. One can find that the peaks associated with these two compounds are very close. However, Ba2TiSi2O8 has a unique and week peak, (220) at 29.6° that is at the right side of the strongest peak, (211) at 29.0°. Therefore, the XRD results shown in figure 3(c) indicate that Ba2TiSi2O8 was formed in the nanocomposites. Based on the chemical formula, it is expected that 20.5 wt% SiO2 in the BT-SiO2 system would consume all barium atoms in the system if the reaction is completed. Considering the fact that about 1.0 wt% SiO2 should be used as the sintering agent in BT ceramics [21], the BT-20SiO2 composites would consume about 93 wt% barium in the system if the reaction is completed. In this case, one would also expect the formation of TiO2 since the chemical reaction formula is: 2BaTiO3 + 2SiO2 = Ba2TiSi2O8 + TiO2. However, no peak associated with TiO2 was found from XRD results. In other words, the new compounds formed during sintering may be more than one (Ba2TiSi2O8). For example, the Schottky and Frenkel defects and oxygen vacancies in the BT nanoparticles would provide new locations available for the silicon atoms to fill in the crystal. That is, the silicon can take the A site, B site and interstitial sites.

To determine the influence of the treatment on the properties of BT-SiO2 ceramic-glass, the dielectric constant and loss at 1 kHz for all the nanocomposites at room temperature are presented in figure 4. First of all, for the nanocomposites sintered from BT nanoparticles with the same condition of treatment, the dielectric constant of the composites decreases with increasing SiO2 content. This is the same as others reported for BT-SiO2 system sintered using untreated BT [16]. Secondly, for the nanocomposites with the same SiO2 content, the nanocomposites sintered from the pretreated BT nanoparticles, especially the BT(V950)-xSiO2, exhibit a significantly higher dielectric constant than the nanocomposites sintered from untreated BT nanoparticles. For example, BT(V0)-20SiO2 at room temperature exhibits a dielectric constant of 20 at 1 kHz, that is the same as reported by others [16], while the BT(V950)-20SiO2 exhibits a dielectric constant of about 123 at 1 kHz. That is, by using BT nanoparticles treated at 950 °C, the dielectric constant is enhanced about 6 times. Similarly, the BT(V950)-15SiO2 exhibit a dielectric constant that is more than 8 times higher than the dielectric constant.

Figure 4. (a) dielectric constant and (b) dielectric loss at 1 kHz of the nanocomposites at room temperature versus the temperature used to treat the BT nanoparticles.
obtained in the BT(V0)-15SiO2. In addition, all the composites at room temperature exhibit a low loss. One can find that the BT(V950)-xSiO2 exhibits a lower dielectric less than BT(V0)-SiO2. A higher dielectric constant with a lower dielectric loss makes the nanocomposites sintered from the BT(V950) nanoparticles the best candidate for the development of the high-performance dielectric materials.

It was well known that the dielectric constant (~3.9) of SiO2 is much smaller than that (~10^3) of BT [1, 7]. In addition, as discussed above about the XRD results, there were reactions between the SiO2 and BT during sintering process, which resulted in the formation of new compound in the composites. Therefore, the experimental results that the dielectric constant decreases with increasing SiO2 indicate that the dielectric constant of the new compound should be smaller than that of BT. That is why the BT(V0)-20SiO2 composites exhibit a dielectric constant of only 20. From the XRD results discussed above, it is known that the BT(V950)-20SiO2 had less BT left from the reactions between the BT and SiO2 than BT(V0)-20SiO2. Therefore, one would expect that the BT(V950)-20SiO2 exhibited a lower dielectric constant than the BT(V0)-20SiO2. Similarly, the BT(V950)-15SiO2 composites would exhibit a lower dielectric constant that the BT(V0)-15SiO2.

However, these are against the experimental results shown in figure 4(a). That is, there are some significant differences between the BT(V0)-xSiO2 and the nanocomposites sintered from the pretreated BT nanoparticles, which should originate from the structural differences between the treated and untreated BT nanoparticles.

As discussed above, the dielectric properties of the BT-SiO2 nanocomposites are strongly dependent on both the SiO2 content and the treatment of BT nanoparticles used. For the BT ceramics (i.e. x = 0) sintered from BT nanoparticle treated at different temperatures, it is found that the dielectric constant does not change much with the treatment, but the dielectric loss increases significantly with the treatment temperature. For example, for the materials at room temperature, the loss at 1 kHz obtained in the BT(V0) ceramics is less than 2%, but it obtained in BT(V850), BT(V900), BT(V950) and BT(V1000) ceramics was experimentally determined to be 13%, 16%, 22% and 26%, respectively. This confirmed the oxygen vacancies and some other crystal defects were induced in the BT nanoparticles by the vacuum treatment. Furthermore, the results in figure 4 indicate that these defects induced by the vacuum treatment cannot even be completely recovered by the sintering. Considering the fact that the sintering temperature was higher than the temperature used to treat the BT in vacuum, it could be conclude that permanent changes in the BT were induced during treatment. It is also found that the higher was the temperature used to pretreat the BT nanoparticles, the higher was the dielectric loss obtained in the BT ceramics sintered from the treated nanoparticles. In other words, the higher was the temperature used to pretreat the BT nanoparticles, the more was the permanent changes induced by the vacuum treatment. The permanent changes in the BT nanoparticles can be the results of the intrinsic disorders induced by the high-concentration oxygen vacancies.

The dielectric response of the nanocomposites under strong electric field was characterized using the P-E hysteresis loops. The P-E loops of all the nanocomposites measured at an electric field lower than the E_b are shown in figure 5, where only the nanocomposites sintered from pretreated nanoparticles are included. For the nanocomposites sintered from the BT nanoparticles with the same treatment condition, the saturated polarization P_s (the maximum polarization measured at the highest electric field used) decreases with increasing SiO2 content, which is the same as reported in untreated BT-SiO2 by others [16]. It should be mentioned that a pinching effect is observed on the P-E loop, especially in the BT-5SiO2 composites as shown in figure 5(e). It was believed that the pinching effect observed in these ceramics was due to the dopants. That is, when an electric field was applied, the point defects in BT kept the original symmetry during the domain-switching process, which led to the pinching effect in the P-E loop [39-41]. For the BT-SiO2 nanocomposites sintered from the vacuum treated BT nanoparticles, both donor and acceptor dopants exist as discussed above. Therefore, the pinching effect observed in the P-E loop of the nanocomposites reported here supports the discussion above about the defects in the nanocomposites. From the data shown in figures 5(a)–(d), it is also found that except BT-20SiO2, all other composites, especially BT-10SiO2 composites, exhibit a lossy loop. Recall that these composites exhibit a low dielectric loss as shown in figure 4(b), there are two possibilities for the lossy loop observed in the nanocomposites: (1) the electric conductivity at high field is high, (2) the orientation response of the defect-associated dipoles at high field has a longer response time.

For all the BT-20SiO2 nanocomposites, an almost linear P-E loop is observed, which is consistent with the XRD results that in the BT-20SiO2 nanocomposites almost all BT is reacted with SiO2. Therefore, the P-E obtained in BT-20SiO2 should reflect the response of the new compounds under the high field. To further study it, the P-E loop of all the BT-20SiO2 nanocomposites is replotted in figure 5(f). One can find that the nanocomposites sintered from the pretreated BT nanoparticles exhibit a higher P_s than that from the untreated BT nanoparticles. The highest P_s is obtained in the BT(V950)-20SiO2, which is consistent with the dielectric constant shown in figure 4(a). However, the results obtained in BT(V950)-20SiO2 exhibit a clear loop. This indicates that the BT(V950)-20SiO2 have a higher loss than others, which is different with the dielectric loss shown in figure 4(b). This again indicates the response of the defect-associated dipoles. In a short summary, both the dielectric behavior (i.e. dielectric constant and loss) of the composites at weak electric field and the P-E loop
of the composites under high field indicate that the response of the defect-related dipoles is an important part of the experimental results, which is consistent with the conclusion made from the structure analysis: (1) the vacuum treatment induces some permanent change including intrinsic defects; and (2) the reaction between SiO$_2$ and BT with the permanent defects results in the formation of electrical dipoles between the acceptor and donor dopants. Regarding the $E_b$ observed in the nanocomposites sintered from the pretreated BT nanoparticles, it was found that the $E_b$ increased with increasing SiO$_2$ content. These results are close to what was reported by others for the composites using untreated BT.[26] Interestingly, it was experimentally found that the nanocomposites sintered from the pretreated BT nanoparticles exhibited a higher $E_b$ (about 5 MV m$^{-1}$ higher) than the nanocomposites sintered from BT(V0).

From the P-E loops of all nanocomposites, the $P_s$ and $P_r$ (the polarization at zero field) and $U_{charge}$ (the charging energy density) are summarized in figure 6. From the data, it can be found that for the nanocomposites with the same SiO$_2$ content, the composites sintered from pretreated BT nanoparticles, especially BT(V950) nanoparticles, exhibit a higher $P_s$ and a higher $P_r$-$P_s$ than the composites sintered from BT(V0). Clearly, for the nanocomposites with the same SiO$_2$ content, the nanocomposites sintered from BT(V950) nanoparticles exhibit the highest energy density. As discussed previously, the reaction between the SiO$_2$ and BT was influenced by the oxygen vacancies and intrinsic disorders existed in BT nanoparticles during sintering, and the silicon ions may
take A sites, B sites and interstitial sites due to the existence of the vacancies and disorders. When these occurred, a barium ion located at a B site and interstitial site can be treated as the donor and acceptor dopants, respectively; a titanate or silicon ion at an A site and interstitial site can be treated as the acceptor dopants. These acceptor and donor dopants can form electric dipoles. The defect-related dipoles should have a large dipole moment since the distance between the defects is long and the charge carried by each defect is larger $(2e \text{ to } 4e)$. The external electric field will have an orientation effect on these dipoles, which is a typical dielectric relaxation response. This relaxation response should be the reason behind the high polarization obtained in the nanocomposites sintered from the vacuum treated BT nanoparticles. On the other side, it was reported that the defects with a high concentration may block the dipoles to decrease the polarization $[{39}]$. Therefore, the suitable concentration of defect will lead to the maximal increase of polarization. In this work, the critical temperature associate with the suitable concentration was experimentally determined to be $950 \degree C$.

The temperature dependence of the dielectric constant and loss of the nanocomposites with different SiO$_2$ contents are shown in figure 7. For all the nanocomposites as presented, a clear frequency dispersion is observed that the dielectric constant decreases with increasing frequency. This is a typical result of the dielectric relaxation. Based on above discussion, the frequency dispersion observed here is the direct result of the defect-associated dipoles. Additionally, it is found that the dielectric constant increases with increasing temperature. However, for the nanocomposites with high SiO$_2$ content, the change in the dielectric constant with the temperature is pretty small. For example, the change in the dielectric constant of BT(V950)-20SiO$_2$ over the entire temperature range studied here (−50 $\degree$C to 140 $\degree$C) is less than 9%. The data shown in figure 7 also indicate that the nanocomposites exhibit a low loss over the entire temperature range (−50 $\degree$C to 140 $\degree$C). For example, the loss of the BT(V950)-20SiO$_2$ over the entire temperature range is less than 2%. An almost temperature independent and high dielectric constant with a low dielectric loss makes the BT(V950)-20SiO$_2$ is a strong candidate for dielectric applications.

5. Conclusions

In this work, the BT-SiO$_2$ ceramic-glass nanocomposites using 200 nm BT nanoparticles that were pretreated in vacuum are studied. It is concluded that vacancies and other permanent changes were induced in the BT crystals by the treatment. It is indicated that the condition of vacuum treatment is important for the formation of new
phase during the sintering process. The higher is the treatment temperature, the less is the BT left from the reaction between the BT and SiO$_2$. Regarding the dielectric properties, it is found that the nanocomposites sintered from pretreated BT nanoparticles, especially BT(V950) nanoparticles, exhibit a significantly higher dielectric constant, a higher $E_b$ and a lower loss than the nanocomposites sintered from untreated BT nanoparticles. It is believed that the permanent changes induced by the vacuum treatment act as dopants, and the electric dipoles formed by the defects increases the dielectric constant of nanocomposites. These dipoles also result in the pinching effect in the P-E loop of the nanocomposites. It is found that the composites sintered from the vacuum treated nanoparticles, especially BT(V950)-$20$SiO$_2$, exhibit a higher $P_s$, a higher $P_s-P_r$, and, therefore a higher energy storage density. The nanocomposites sintered from the vacuum treated nanoparticles with a high SiO$_2$ content, especially BT(V950)-20SiO$_2$, exhibit a high dielectric constant and a low loss over the entire temperature range studied here (−50 to 140 °C). More interestingly, the dielectric constant of BT(V950)-20SiO$_2$ exhibits a very weak temperature dependence.

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