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ORIGINAL PAPER

Investigating the dielectric properties of barium titanate nanocomposites using transmission electron microscopy image processing

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Abstract

Barium titanate (BTO) is a ferroelectric perovskite material used in energy storage applications because of its high dielectric constant. A previous study showed that the dielectric constant for BTO nanoparticles drastically increases to over 15,000 at a particle size of 70 nm. This result is highly contested, but its implications to energy storage motivated our investigation into the dielectric constants of BTO nanoparticles that are incorporated into a polymer matrix. We developed a novel method of using image processing techniques on transmission electron microscope images of BTO-polymer nanocomposites. Data on the positions, shapes, sizes, and orientations of BTO nanoparticles were used to build more realistic computational models that simulate the dielectric behavior of the nanocomposites. Here, we investigate the relationship between regions of enhanced electric field and the composite dielectric constant.

Introduction

Novel energy storage technologies aim to solve problems including the intermittent nature of some renewable energy sources, fast response demands of the electric grid, and electric vehicle charging. The advancement of electrostatic capacitors, which store energy in the form of an electric field, could help overcome such challenges. Since the discovery of the high dielectric constant of barium titanate (BTO), ceramics have been widely used as a dielectric material for capacitors [1–3]. Displacement of the titanium atom in BTO unit cells, visualized in Fig. S1, causes spontaneous polarization and ferroelectricity, which are the characteristics that are responsible for the high dielectric constant of BTO [4].

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In 2003, Wada et al. reported that BTO nanoparticle size greatly affects dielectric constant [5]. Specifically, powders with diameters > 300 nm were found to have a dielectric constant of 4000, whereas the dielectric constant surpassed 15,000 for a diameter of 70 nm [5]. These results indicate BTO may revolutionize energy storage, but are highly contested. Several other studies report BTO dielectric constants peaking at ~ 5000–6000 for particles with a 1000 nm diameter, then decreasing significantly with decreasing particle size [1, 6, 7]. Disagreement between studies into the effect of BTO particle size on dielectric constant motivates further research.

In 2018, Kaufman et al. investigated the dielectric constants of BTO nanoparticles using finite element analysis (FEA) [2]. All particles were assumed to be spherical and agglomerates were modeled as simple cubic arrangements of particles with zero separation between particles. Composites were built by embedding agglomerates in a polymer matrix, then adding randomly distributed particles around the cubic arrangements [2, 8]. This approach was used to study various degrees of agglomeration in a controlled context to quantify effects of agglomeration on dielectric constant. Despite generating new knowledge, especially regarding enhanced field regions, the FEM developed by Kaufman et al. assumed cubic arrays of particles rather than real particle arrangements within the composite [2].

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Here, we present a more realistic model of BTO nanocomposites by introducing ellipsoid particles of sizes, shapes, rotations, and arrangements directly obtained from transmission electron microscopy (TEM) images of fabricated nanocomposites. As depicted in Fig. 1, the Python programming language was used to extract particle information from TEM images and directly inform model geometry. COMSOL Multiphysics was used to build three-layer nanocomposites and calculate dielectric constants. Finally, the model was used to visualize how energy is stored within the composite. Regions of enhanced electric field (REEF), resembling those reported by Kaufman et al., were also observed.

Materials and methods

Sample preparation and transmission electron microscopy

200 nm BTO particles were incorporated into epoxy composites of 20% volume loading (vol%) as described in Section S3. The composite was cut along the edge around the copper plating on the surface and embedded in epoxy resin and then microtomed as described in Section S4. Finally, the slices were removed from water and mounted on a copper TEM grid using an inoculating loop. The resulting grid was imaged on a JEOL JEM 1200EX at different magnifications to achieve optimal resolution.

Python image processing pipeline

An image processing pipeline was created using Python's OpenCV computer vision library. Pre-processing and transformation steps detailed in Section S5.3 enable extraction of particle information. The pipeline centers around a watershed segmentation algorithm to obtain particle boundaries, as shown in Fig. S3 [9, 10].

Once particle contours are obtained, the longest and perpendicular short chord lengths are computed and particle rotations in the *X*–*Y* plane are calculated. Since TEM images are two-dimensional, the third dimension is extrapolated. If both calculated radii are smaller than the actual radius of the imaged nanoparticles, or expected radius, the third radius is set as the expected radius. If any calculated radius is longer than the expected radius, the third radius is set as the average of the two calculated radii. Three TEM images are combined to form a layered model in which particles within a TEM image form a single layer of the composite, as shown in Fig. 1. The *z*-positions are randomized within layers.

Data are saved as a text file containing particle positions, radii, and rotations. Composite information including total particle numbers, BTO volume fraction, and electrode separation is also appended. Software was developed as described in Section S5.5 and the code repository for our project can be found in Section S1.

Fig. 1 Combining 3 TEM images of fabricated BTO nanocomposites embedded in an epoxy matrix into a three-layer COMSOL Mutliphysics model. Scale bar represents 200 nm

COMSOL multiphysics model

COMSOL Multiphysics was used to model the nanocomposite from data obtained through the image processing pipeline. The model consists of a rectangular prism with copper electrodes on the top and bottom faces. Between these plates, ellipsoids representing BTO nanoparticles were suspended in a polymer matrix.

Data output by the Python pipeline was imported to COMSOL using MATLAB LiveLink. Once geometries were loaded, the matrix was set to epoxy. After meshing the model, an electrostatics study was run and surface integration across the copper plates was evaluated to calculate composite dielectric constant.

Electric field visualizations

Electric field visualizations were used to characterize particle interactions. The composite dielectric constant is calculated using internal energy and relates to electric field as shown in (1). Isosurface plots were generated by obtaining the magnitude of electric field from COMSOL's calculated values for electric potential. These visualizations provided insight on the locations of enhanced field regions.

The energy stored within any given region of the composite is

$$U = \iiint \frac{1}{2}\varepsilon\varepsilon_0 E^2 \, \mathrm{d}x\mathrm{d}y\mathrm{d}z, \tag{1}$$

where ε_0 is the vacuum permittivity, E the electric field magnitude, and ε the dielectric constant of the material at the point of integration.

Results

In producing a computational model of BTO nanocomposites in COMSOL, it is crucial to model REEF occurring between particles and between particles and electrodes. Equation (1) shows that the energy stored within any given region of the composite is proportional to the square of the electric field magnitude E. Therefore, increases in E are expected to significantly impact U and the composite dielectric constant ε_c (see Section S6).

Kaufman et al. observed E increasing when REEF were created by reducing distance between particles to the order of 1 nm in the applied field's direction. [2]. Kaufman et al. argued that the local electric field's magnitude can be increased by increasing agglomeration and decreasing distance between particles. The work done by Kaufman et al. modeled agglomerates as tightly packed spherical particles, but our model represents agglomeration using relative particle positions and rotations extracted from TEM images.

Quantifying the effects of REEF between particles involved exploring the relationship between layer spacing and ε_c. Figure 2a shows the relationship between the composite dielectric constant and distances between particles in the z-direction for a three-layered model derived from TEM images and a cubic array model, both at 20 vol%. Model creation and the method of moving particles closer together is described in Section S7. Figure 2a shows that decreasing particle-particle distance in the direction of the electric field from 10 nm to 1×10^{-13} nm causes ε_c to increase in both the three-layer and cubic array models. The increase in dielectric constant reaches a plateau when the negative log of distance between particles is equal to 3, or 1×10^{-3} nm.

Fig. 2 Composite dielectric constant versus particle-particle distance (**a**) and particle-electrode distance (**b**) for two different models. For the TEM-obtained three-layer model, the x-values are upper bounds for the distances rather than exact values. Error bars are standard deviations

Fig. 3 Isosurfaces showing regions of high energy density within a TEM-obtained three-layer model. Only one energy density threshold value is shown in each plot and that value is constant along all the colored surfaces in that plot. As the energy density threshold increases, there are fewer regions with such high internal energy per unit volume. These regions are usually between particles and between particles and electrodes

In the cubic array, particles are positioned directly above and below each other, increasing particle-particle electrostatic interactions between layers and thus ε_c.

Particle-electrode distances were decreased to further investigate the effects of REEF. Decreasing z-direction particle-electrode distance to less than 10 nm was found to increase ε_c. The three-layer model was used to generate Fig. 2a with a z-direction particle-particle distance of 1×10^{-13} nm as a starting point. Next, the electrodes were incrementally pushed closer. Figure 2b compares this data with that obtained when the same procedure was used on the cubic array model in Fig. 2a with z-distances between particles set to 0 nm. Figure 2b shows decreasing particle-electrode distance in the direction of the electric field that causes ε_c to increase in the three-layer and cubic array models. There's a stronger correlation in the latter, likely from the larger number of REEF for particles equidistant from the electrodes. In the three-layer model, the effective spacing to capture interactions was found to be 0.0001 nm. Decreasing particle-electrode distance further does not significantly impact ε_c (notice the plateau in Fig. 2b).

Given the importance of REEF on ε_c, locations of these regions and the magnitude of internal energy stored were investigated using isosurface plots of internal energy per unit volume. These plots allow visualization of regions of the composite that meet a specific energy density threshold. Figure 3 shows the plots generated for a 13 vol% model of 200 nm BTO in epoxy at various energy density thresholds. Notably, the composite has regions with an energy density as high as 200,000 Jm^{-3}. These regions of high energy density are mostly found between particles and the electrodes, but also exist where two particles are extremely close in the z-axis or are oriented toward one another. At lower energy densities such as 10,000 Jm^{-3}, the volume of the composite meeting the threshold is far larger and comprised mainly of regions between close-packed particles, z-axis extremities of particles, and regions between particles and electrodes. REEF from particle-electrode proximity comprise less volume, but contain far higher energy densities.

REEF from relative particle orientation alongside particle-particle and particle-electrode separation are critical in constructing a model wherein effects of BTO nanoparticles on dielectric constant are captured. Effects of electrode positioning are presented in Section S8. While the model is still in development (see Section S9), use of ellipsoidal particles with parameters sourced from TEM images captures the importance of REEF and the effects of non-spherical BTO particle agglomeration on composite dielectric constant.

Conclusion

The ability to model composites using TEM images has great promise in analyzing nanocomposites. The novel Python image processing pipeline enables the reconstruction of nanocomposites with geometric parameters of cross-section lengths, rotations, and relative particle placements sourced from experimental data. This pipeline may also be applied to analyze images from different applications containing agglomerated ellipsoids. Furthermore, the method of determining effective spacing between layers of particles as well as between the particles and the electrodes enables the modeling of REEF in three dimensions. This allows for in-depth physics-based analysis to be conducted on how the geometry of nanoparticles within a composite impacts dielectric constant. Computational modeling of nanocomposites using FEM presents great promise in developing new energy storage technologies and extracting the dielectric constant of discrete nanoparticles. The model's tunability to various TEM images lends itself to an understanding of the impact of the geometry of experimentally fabricated composites on energy storage capacity. Future work will focus on comparing composite dielectric constants from generated models to experimental data to understand what electromagnetic factors contribute to these values.

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Data availability The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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Supplementary Materials for

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S1 GitHub Repository

https://github.com/akshaytrikha/BTO-TEM-Processing

S2 BTO Unit Cell

Fig. S1 At room temperature, the BTO unit cell has a tetragonal crystal structure. The slight vertical offset of the titanium atom (0.02 Å) gives rise to a spontaneous polarization and ferroelectricity in the material, which are responsible for its dielectric properties

S3 Sample Fabrication

The fabrication of BTO epoxy nanocomposites was carried out in three stages: a ball milling stage, a mixing stage and casting and curing stage. In the first stage, 19 g of agglomerated BTO nanoparticles were dispersed in ethanol and

tert-Butylphosphonic Acid (surfactant). The mixture was ball milled with 95 g of zirconia grinding balls for 8 hours at 150 rpm. Next, the dispersed BTO nanoparticles and ethanol were filtered through a mesh filter into a planetary mixing container (PMC), adding ethanol as needed. Epoxy was added to the PMC to obtain a 20 vol% mixture which was then mixed in a planetary mixer for 180 seconds. A fritted glass disk nucleator was added to the PMC to create sites for ethanol to evaporate without bursting. In nucleator-aided evaporation ethanol bubbles were generated in close proximity to the nucleator, implying quicker boiling. The ethanol was evaporated in a vacuum oven at a pressure of 1693.19 Pa at 75°C for 2 hours. Next, an appropriate amount of hardener was added to the PMC and the resulting mixture was mixed in a planetary mixer for 180 seconds. In preparation for curing, the mixture was moved to a new PMC with silicone base. The contents were mixed in a planetary mixer until the mixture laid flat on the bottom of the container. The mixture was cured in the oven at 50°C. The density of the prepared nanocomposites was obtained analytically from their measured mass and volume. Next, both sides of the nanocomposites were sputtered with a 100 nm thick layer of gold. These gold layers functioned as electrodes, allowing for the measurement of the capacitance of the nanocomposites, which enabled the composite dielectric constant to be determined. The sputtered nanocomposites were then ready to be imaged.

S4 Sample Preparation

The size of the cut varied, but was small enough to fit the mold with some space on all sides. Next, the composite was embedded in EpoThin™ 2 epoxy resin in a trapezoidal silicone mold of dimensions 15mm x 6mm x 3mm. This was cured at room temperature for 24 hours, then shaved down into a smaller trapezoid using a polytetrafluoroethylene coated razor blade. The resulting cross-section at the top measured about 1 mm x 1 mm. Once the BTO composite was smooth and exposed at the cross-section, a Leica EM UC7 Ultramicrotome was used to section the sample. Rough cuts were made with a glass blade. When the sample smoothed out enough to have a slightly reflective surface, a DiATOME Ultra 45° diamond blade was used to slice the composite. The boat on the knife was filled with water to allow the slices to pull away from the knife's edge. The slices were approximately 60-70nm thick, allowing optimal TEM imaging. If samples were cut too thick, the beam did not penetrate the epoxy. In contrast, if samples were cut too thin, the beam ripped the epoxy. A continuous interference color and thickness scale for thin sections was used as a general guide to asses thickness.

S5 Python Image Processing Pipeline Visuals

S5.1 Pre-processing Steps

Before analyzing an image for its particles, a series of pre-processing steps were performed to reduce the dimensionality of the data and create necessary intermediate images. An input color image was first converted to grayscale using the

OpenCV library's `cvtColor()` function, such that each RGB pixel mapped to a single channel pixel ranging from 0 to 255 using the following formula:

$$\text{Pixel} = 0.299\text{R} + 0.587\text{G} + 0.114\text{B}$$

as specified in the OpenCV documentation.

The input TEM images are potentially noisy in the sense that the microscope picks up random, undesirable, fluctuations in brightness or color. In order to get rid of these unwanted pixels and smoothen out potentially sharp edges in the image, we apply a Gaussian blur transformation using the OpenCV library's `gaussianBlur()` function. This convolves the image with a predefined matrix resulting in a blurring transformation.

A binary threshold is then applied such that any pixel value higher than the threshold is set to 1, and any less than or equal to the threshold is set to 0. The threshold value itself was determined by the user.

The distance transform, depicted in Figure S2 (a), is generated by mapping the distance between a light pixel, of value 1, and its closest background pixel, of value 0, to a pixel brightness value. Brighter pixels mean that a pixel is further away from its boundaries, while duller pixels are interpreted as closer to a boundary. The distance transformed image is particularly useful because it allows us to visually inspect the centers of particles that the pipeline is finding. Another useful piece of information that we can see from the distance transformed image is if there are pixels bridging two bright centers of particles then we know those particles to be touching in the TEM image.

(a) **(b)** **(c)** **(d)**

Fig. S2 (a) Distance transform (b) Sure foreground (c) Sure Background (d) Unknown region, difference between sure foreground and background

S5.2 Obtaining Watershed Markers

Watershed markers, shown in Figure S3 (a) are required for the watershed segmentation algorithm. Approximate particle centers, which serve as the watershed markers, were extracted using a very high threshold value of the distance transform. The sure foreground, or sure particle area, in Figure S2 (b) was extracted by using a moderately high threshold value of the distance transform. The sure background, in Figure S2 (c) or sure epoxy matrix area, is extracted by eroding the particles to remove noise and then morphologically dilating particles. The unknown region, depicted in Figure S2 (d) will be determined to be either part of a particle or background through running the watershed algorithm. Finally, once approximate particle centers, or watershed markers, are obtained, the watershed algorithm is used to determine particle contours.

(a) **(b)**

Fig. S3 (a) Markers signifying where to start the watershed algorithm for each particle. (b) Result of performing watershed segmentation

S5.3 Watershed Segmentation

Much like a geological watershed, the watershed segmentation algorithm divides regions based on catchment basins. It imagines the centers of particles at a topographically higher elevation than their potential contours. Then, starting from particle centers, the algorithm tries to find the closest local minima of pixels. Basins where watersheds from two particles intersect are labelled as boundary regions representing particle contours.

S5.4 Breaking Up Agglomerates

Separating agglomerated particles in the TEM images was addressed by using the expected radius of the particles in each TEM image. Two different methods have been developed for breaking up agglomerated particles. The first method of breaking agglomerates into individual particles is incrementally increasing the threshold until the largest ellipse formed using the long and short chord lengths has an area less than four times the expected area. This method was effective for 200 nm particles. However, it was unsuccessful at breaking up 500 nm particles because there were not discernible edges of particles within agglomerates. Therefore, another method of placing particles was developed in which the agglomerate was replaced with evenly spaced spheres positioned within the contour of the agglomerate with the radius set to be that of the expected particle radius.

S5.5 Software Development

A machine learning based approach was not possible because of the small amount of data, which was due to the difficult nature of producing TEM images. Using a Jupyter notebook during development allowed for easily accessible visual feedback of each transformation step. The composite was visualized using the `plot_wireframe()` function in the Matplotlib Python library as seen in Figure

Fig. S4 Wireframe visualization of the composite

S4. Once the functionality was working as intended, the Numba just-in-time compiler library was used to translate computationally heavy functions directly into machine code and decrease runtime by approximately 25 times. A faster pipeline helped accelerate the development of newer features as well as the generation of data to input into the COMSOL model.

S6 Relationship Between Electric Field, Internal Energy and Composite Dielectric Constant

The energy stored within any given region of the composite is given by

$$U = \iiint \frac{1}{2}\varepsilon\varepsilon_0 E^2 \; dxdydz, \tag{2}$$

where ε_0 is the vacuum permittivity, E is the electric field magnitude and ε is the dielectric constant of the material at the point of integration. The composite dielectric constant ε_c can be calculated from the composite internal energy U as follows

$$\varepsilon_c = \frac{2Ud}{\varepsilon_o V^2 A}, \tag{3}$$

where d is the distance between the capacitor plates, A is the plate area and V is the voltage across the plates. Equation (2) defines the internal energy U to be quadratically dependent on the electric field magnitude E. By (3) the composite dielectric constant ε_c is proportional to U. Therefore, an increase in the electric field magnitude E can cause a significant increase in the dielectric constant ε_c. Hence, it is important to understand the development of regions of enhanced electric field (REEF) so that they can be accurately modeled.

S7 Measuring Particle-Particle Interactions

For the three layer model, particles were added to a single layer until a 20 vol% loading was obtained. This was repeated three times, with the middle layer rotated

by 180 degrees around the axis perpendicular to the layer's plane and intersecting its center point. The cubic array consisted of four layers, each containing 16 spherical particles arranged in a 4x4 matrix with distances between particles in the x- and y-directions set to zero.

For the three-layer model, particles were pushed together by pushing particles in the top and middle layers down onto the particles in the layer below them until the distance between particles was the desired distance. Therefore, the particles in the bottom layer were all centered in the same plane and the bottom of the composite was relatively flat, but the top of the composite was very uneven. For the cubic array, particles were pushed together by pushing all of the layers closer to the center of the composite by the same amount.

S8 Changing Electrode Positions

To investigate the impact of relative particle position in the direction of the applied electric field on the presence of REEF, isosurface plots were generated for two different models where the position of the electrodes were swapped from the xy-plane to the xz- and yz-planes (the XY, XZ and YZ positions) as seen in Figures S5 and S6. Each model consisted of three different layers obtained from three different TEM images. Each layer is named a, b and e, so the name bae indicates the order of the layers, where b is the bottom layer, a is the middle layer, and e is the top layer. Model bea differs from model bae in that the position of two of the layers has been switched. Now, layer e is in the middle and layer a is on top. The model is also different from model bae in that the z-positions of particles are not the same as they were as they are randomly assigned within a layer each time the order of the layers is changed.

Changing the position of the electrodes was found to have a non-negligible impact on the total energy stored within the composite volume. The total energy stored, here referred to as composite internal energy, was calculated in COMSOL by volume integration as described in Equation (2). Each time the electrodes were moved into a new position, the voltage between the plates was adjusted to maintain the background electric field constant. More specifically, since the model composites were cuboids, the distance between the electrodes changed depending on their position. Consider the electric field E defined as

$$E = \frac{V}{d}, \tag{4}$$

where V and d are the voltage across and distance between the capacitor plates, respectively. From (4) we learn that electric field and plate distance are inversely proportional. The model with the electrodes in the XY position was arbitrarily chosen to be the standard. By (4) this model had a background electric field of 9.5×10^6 Vm^{-1}. Therefore, when the electrodes were moved into the positions XZ and YZ, the voltage was adjusted so that the resulting electric field for these models would be unchanged at 9.5×10^6 Vm^{-1}. Because of the constant electric field, the BTO nanoparticles were assumed to polarize to the same extent in all three models regardless of the electrode position, allowing for valid composite internal energy caparisons.

Changing the position of the electrodes not only affected the composite internal energy but also the isosurfaces. These show that with the electrodes parallel to the xy-plane (XY position) the particle-electrode REEF were maximized for the three arrangements (Figures S5 and S6). For the $20,000$ Jm^{-1} internal energy threshold, up to 15 particle-electrode isosurfaces can be counted in the bae model when the electrodes are in the XY position. This large number of particle-electrode REEF are thought to be responsible for the notably larger value for composite internal energy when the electrodes are in the XY position. When the electrodes are in the XZ and YZ positions, the isosurfaces show almost no particle-electrode interactions. This lack most likely accounts for the lower composite internal energy for these two models.

Finally, the increased number of particle-electrode interactions for the XY position can be rationalized by the fact that in this arrangement, the electrodes are parallel to the nanoparticle layers in the model. Furthermore, isosurfaces for the XY position model arguably also show more pronounced particle-particle REEF. However, this is not as evident as with the particle-electrode REEF.

Fig. S5 Model bae. Isosurfaces showing regions of high energy density within a the TEM-obtained three layer model. Only one energy density value is shown in each plot and that value is constant along all the colored surfaces in that plot. For the same model, varying the electrodes' position leads to different isosurfaces and different composite internal energies. The composite internal energy is highest when the electrodes are in the xy-position and REEF are maximized, especially between particles and electrodes

Fig. S6 Model bea. Isosurfaces showing regions of high energy density within a the TEM-obtained three layer model. Only one energy density value is shown in each plot and that value is constant along all the colored surfaces in that plot. For the same model, varying the electrodes' position leads to different isosurfaces and different composite internal energies. The composite internal energy is highest when the electrodes are in the xy-position and REEF are maximized, especially between particles and electrodes

S9 Volume Loading

The main challenge in reconstructing 3D models from TEM data arises in accurately recreating models of composites with equivalent volume loading to their experimentally fabricated counterparts. The biggest issue when trying to maintain experimental volume loading while extracting particles from TEM images is that by centering particles in a plane, particles that are between layers and their accompanying volume are lost. Another thing that impacts volume loading is the loss of some particles and the loss of volume for some particles. While the novel python image processing pipeline is able to extract particle size, position, and rotation data, in selecting an appropriate threshold to do so, some pixel data is lost. This results in a COMSOL model with a lower volume fraction than the experimentally fabricated nanocomposites from which the TEM images are derived. The underestimation of volume fraction in the model is a hurdle to overcome in using COMSOL modelling to extract the particle dielectric constant of BTO.