SIZE EFFECT OF SUBMICRON BARIUM TITANATE PARTICLES ON THEIR DIELECTRIC PROPERTIES

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The dielectric properties of a heterogeneous system consisting of submicron barium titanate particles of different sizes and oleic acid were studied. On the basis of these results the dielectric permittivity and electrical conductivity of the particles for each size were determined. The dielectric permittivity of 100 nm size particles has the lowest value, which is explained by the absence of ferroelectricity at these sizes. Particles with a size of 200 nm, on the other hand, have an explicitly high value of dielectric permittivity, indicating their monodomain structure. The electrical conductivity of barium titanate particles increases with their size. Qualitative explanations of the obtained results are given.

Keywords: ferroelectrics, barium titanate, dielectric permittivity, dielectric relaxation, conductivity.
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INTRODUCTION

Barium titanate ($BaTiO_3$) is a ferroelectric material from perovskite family with very high spontaneous polarization (26 μC/cm^2 at room temperature) and is widely used as elements in various electronic devices: memory elements, nonlinear capacitors and supercapacitors, infrared sensors, actuators, ultrasonic generator, voltage sensor, positive temperature coefficient thermistors, laser frequency doubler etc. [1-4]. Amorphous barium titanate thin film improves the light trapping in solar cells [5]. The constructive combination of the features of submicron barium titanate particles and nanoparticles and other functional materials can lead to qualitatively new effects, which makes it possible to expand their applications [6,7]. Particularly, barium titanate based polymer composites and $BaTiO_3$ particles are used in charge and energy storage devices, multilayer ceramic capacitors etc. [8-10]. In the last two decades a large number of papers on liquid crystalline colloids with barium titanate particles have appeared [11-12]. The researchers hope that in the future, $BaTiO_3$ particles can be used in liquid crystal displays, because the addition of these particles to liquid crystals in small amounts drastically improves some of the characteristics of electro-optical effects in the liquid crystal, such as driving voltage, response time etc. [13-15]. In some cases, the addition of particles into the liquid crystal has led to qualitatively new effects, e.g., a memory electromechanical effect was observed in the isotropic phase of liquid crysral [16]. To optimize the charac-teristics of barium titanate based composites and colloid systems, it is necessary to clarify how the properties of submicron $BaTiO_3$ particles are changed in comparison with a bulk sample of a $BaTiO_3$ crystal. In this work, the dielectric properties of monodisperse $BaTiO_3$ particles with a size of 100, 200, 300, 400 and 500 nm has been investigated.

EXPERIMENT

$BaTiO_3$ particles were purchased from company US Nano. Scanning electron micrograph of these particles in JOEL JSM-767F shows the sufficiently monodispersity of powders (Fig. 1a). To prevent strong aggregation of polarized $BaTiO_3$ particles, the surfaces of these particles must be coated with suitable surfactant. For this purpose, the stabilizer oleic acid was added to the barium titanate powder in a weight amount of 16% (volume fraction 57%).

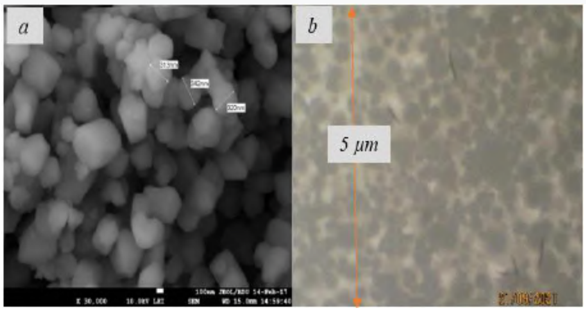

Fig. 1. a) SEM photography of 300 nm sized barium titanate powder; b) micrograph of 300 nm sized barium titanate – oleic acid mixture in optic microscope equipped with high resolution camera.

Dielectric measurements of obtained slurry type mixture were carried out in a special cell consisting of two parallel plane glass substrates, the inner surfaces of which are covered with a transparent ITO electrode. The sample thickness is fixed with a special 30μm Teflon spacer. An example of micrograph of the thin layer of 300nm particles $BaTiO_3$-oleic acid taken with optic microscope Carl Zeiss equipped with 14MP camera is shown in fig.1b. The capacitance-frequency of the cell was measured using IET 1920 RLC-meter in the frequency range from 20Hz to 1MHz. The amplitude of the test signal was 1V.

RESULTS AND DISCUSSION

Figures 2,3 and 4 show frequency dependences of the real and imaginary parts of the dielectric permittivity, as well as conductivity of mixtures of olive acid and BT particles with different sizes, espectively.

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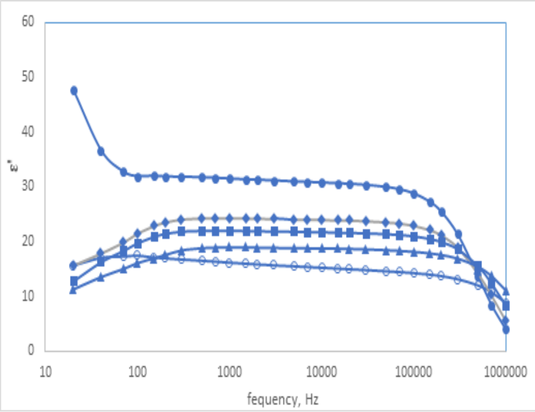

Fig. 2. The frequency dependence of real part of barium titanate – oleic acid mixture: empty circles–100nm $BaTiO_3$; filled circles–200nm $BaTiO_3$; triangles–300nm $BaTiO_3$; squares– 400nm $BaTiO_3$; rhombs–100nm $BaTiO_3$.

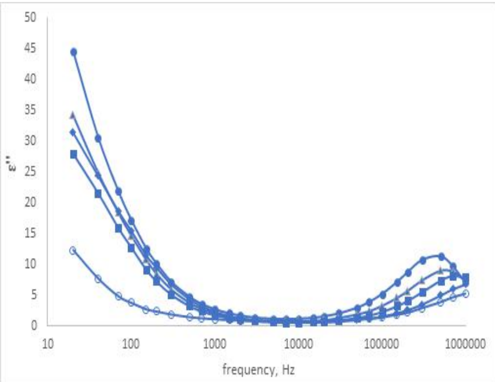

Fig. 3. The frequency dependence of imaginary part of barium titanate–oleic acid mixture: empty circles–100nm $BaTiO_3$; filled circles–200nm $BaTiO_3$; triangles–300nm $BaTiO_3$; squares–400nm $BaTiO_3$; rhombs–100n m $BaTiO_3$.

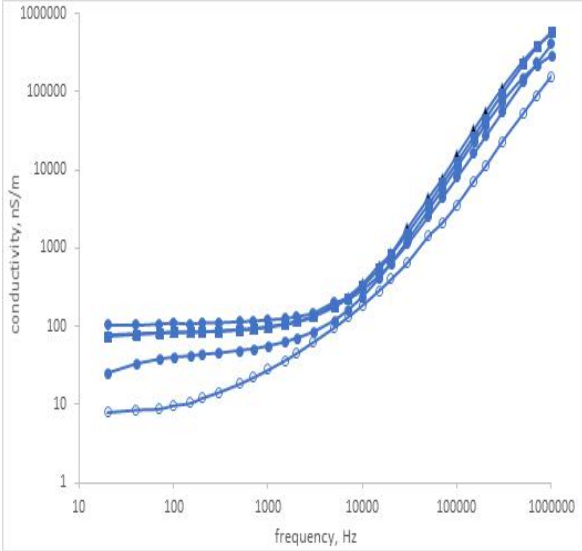

Fig. 4. The frequency dependence of electric conductivity of barium titanate–oleic acid mixture: empty circles–100nm $BaTiO_3$; filled circles–200nm $BaTiO_3$; triangles–300nm $BaTiO_3$; squares–400nm $BaTiO_3$; rhombs–100nm $BaTiO_3$.

The second and third rows of the table present the values of dielectric constant and electric conductivity of mixtures at 2kHz, for each barium titanate particles size.

For mixtures, corresponding to barium titanata particle size of 200nm, 400nm and 400nm a dispersion of dielectric permittivity is observed at frequencies less than 1MHz (instrument upper frequency limit). The fourth row of Table 1. shows the frequencies corresponding to the dielectric absorption maximum.

Table 1.

Presents some important data extracted from these dependencies.

Size of particle	100 nm	200 nm	300 nm	400 nm	500 nm
Dielectric permittivity at 2 kHz	15.9	31.3	24.3	22.1	19.2
Electric conductivity at 2 kHz, nS/m	45,3	70,9	113,3	116.1	133.8
Relaxation frequency, kHz	-	700	650	750	-
Dielectric permittivity of particles	24.3	228.2	97.2	69.7	43.6

Using the formula for effective dielectric permittivity of two-component heterogeneous systems [17]:

$$\sqrt[3]{\varepsilon_{eff}} = f\sqrt[3]{\varepsilon_m} + (1-f)\sqrt[3]{\varepsilon_p} \qquad (1)$$

We can calculate the dielectric permittivity of $BaTiO_3$ particles with different sizes, which are shown in the third row of Table 1.

Analysis of the data in the table allows us to establish:

1) the dielectric permittivity of barium titanate particles is greatest at 200nm, and gradually decreases with increasing particle size;
2) the dielectric permittivity dispersion is observed for particles of 200nm, 300nm, and 400nm; and for particles of 100nm and 500nm the dispersion is most likely outside the measurement range of the instrument (1MHz).
3) the electrical conductivity of the mixture increases with the size of the BT particles.

The decrease in the size of BT particles is reflected in their structure, hence in many physical properties, including dielectric properties [18]. According to US Nano Database, BT particles with a size of 100nm have cubic symmetry, so they lack the ferroelectric property and for them the dielectric permittivity has a small value.

According to modern concepts, ferroelectric BT particles are characterized by the core-shell structure [19, 20]. The non-ferroelectric shell with a thickness of about 10nm has a cubic structure. The ferroelectric core has a tetragonal structure. In most cases, the core is in a polydomain state: it consists of several domains on the order of 100nm, separated by thin walls. Such sizes of BT particles are possible when the core consists of a single domain. This case was first discovered in Wada's work at the size of BT particles of 140nm and the colloid with such particles was called superparaelectric by analogy with superparamagnetics. For some mixtures there is a dispersion of dielectric permittivity in the limit of RLC-metra measurement. The fourth line of Table 1 shows the frequencies corresponding to the dielectric absorption maximum.

The dielectric dispersion of oleic acid is not observed between 20Hz and 1MHz (Figure 5). This means that in mixtures with VT particle sizes of 200, 300 and 400nm the dielectric dispersion is related to these particles. The reason for this, in our opinion, is the following. The oscillation of the lattice atoms with respect to each other in an alternating sinusoidal field is hampered by permanent (permanent) surface charges due to the presence of spontaneous polarization.

The electrical conductivity of the mixtures is at least an order of magnitude greater than that of pure oleic acid (3.3nS·m). This can be explained on the basis of two assumptions:

1) $BaTiO_3$ particles play a dominant role in the electrical conductivity of the mixture;

2) there is a percolation relationship between these particles. The increase in the electrical conductivity of mixtures with an increase in the size of BT particles is associated with a change in the band gap width [18].

CONCLUSIONS

The structure and physical properties of submicron particles of $BaTiO_3$ differ from its bulk samples because of the increased role of the surface. This is clearly reflected in the values of dielectric permittivity and electrical conductivity. Ferroelectricity is not observed in particles with a size of 100nm. Relatively large particles retain the ferroelectric property and have a polydomain structure. 200nm sized particles have a monodomain structure. Consequently, $BaTiO_3$ particles at these sizes have the highest dielectric permittivity. The smaller the size of the BT particle, the smaller its electrical conductivity. This is explained by the increase in the band gap width. The observed dielectric dispersion of about 700kHz for particles with a size of 200-400nm, most likely, is associated with the influence of surface charges arising from the presence of spontaneous polarization.

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