Synthesis and Study The Dielectric Properties of La-Doped And Undoped Barium Titanate Nanopowders

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ABSTRACT

Lanthanum doped $Ba_{1-x}La_xTiO_3$ (BLT) with (x = 0.005, 0.015, 0.02, 0.025) and undoped Barium titanate $BaTiO_3$ (BT) nanopowders were synthesized at Room temperature via a semi-oxalate method with adjusting a pH of the solution around (5.5).Crystallization processes and Particles size of prepared powders were studied, measured and calculated by using X-ray diffraction. XRD analysis and Scanning Electron Microscopy SEM techniques, and the particles size were found to be about 65 nm. The dielectric properties (real ϵ' and imaginary ϵ'' part of dielectric constant) of polymer/BT, polymer/BLT nanocomposites, and UPE (unsaturated polyester resin) samples were studied at different frequencies in the range of (20kHz-5MHz) using LCR meter, while theoretical dielectric constant of the prepared samples were calculated by using Bruggeman rule of mixture. The results of dielectric measurements found that the real dielectric constant and tangent loss of the nanocomposites samples decreases with increasing Lanthanum content.

Keywords: Barium titanate, $BaTiO_3$, Piezoelectric, (Ba-La) TiO_3, and Nanopowders.

تحضير ودراسة خصائص العازل للمساحيق النانوية للباريوم تيتانيت المطعم وغير المطعم باللنثانيوم

الخلاصة

تم تحضير المساحيق النانوية لتيتانيت الباريوم المطعمة بايونات اللنثانيوم (BLT) $Ba_{1-x}La_xTiO_3$ بالنسب (x = 0.005, 0.015, 0.02, 0.025) والغير مطعمة $BaTiO_3$ (BT) بالتقنية الشبيهة بطريقة الاوكزالات (semi-oxalate) عند درجه حرارة الغرفة مع ضبط الأس الهيدروجيني (pH) للمحلول عند حدود القيمة (5.5). تمت دراسة عمليات التبلور وحجم الدقائق للمساحيق المحضرة باستخدام تقنيات تحليل حيود الاشعة السينية (XRD) والمجهر الالكتروني الماسح (SEM) , ووجد ان حجم الدقائق المحضرة قد بلغ حوالي (65 nm) .وكما تمت دراسة

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خواص العازل (بجزئيه الحقيقي 'ϵ والخيالي"ϵ لثابت العزل المركب) للمتراكبات (بوليمر/ تيتانيت الباريوم),
BT(بوليمر/ تيتانيت الباريوم اللنثانيوم BLT) و بوليمر راتنج البولي استر الغير مشبع (UPE) كدالة للتردد في
المدى (20 kHz - 5 MHz) باستخدام منظومة LCR meter ,كما تم حساب ثابت العزل النظري للنماذج
المحضرة باستخدام قانون بروكمان للمخاليط . ومن نتائج قياسات ثابت العزل للمتراكبات وجدت بأنها تتناقص مع
زيادة نسب التطعيم باللنثانيوم.
الكلمات المفتاحية: تيتانيت الباريوم, $BaTiO_3$, الاجهادية الكهربائية , $(BaLa)TiO_3$, والدقائق النانوية.

INTRODUCTION

In 1945, barium titanate ($BaTiO_3$), the first ceramic material in which ferroelectric behavior was reported [1]. With its much simpler structure (perovskite), better ferroelectric properties, chemical and mechanical stability, barium titanate (BT) became one of the most extensively studied ferroelectric materials [2]. $BaTiO_3$ is used for practical applications due to. their ferroelectric, piezoelectric, and thermoelectric properties [3-5], $BaTiO_3$ is mainly used for capacitors such as multilayer ceramic capacitors (MLCCs) and integral capacitors in printed circuit boards (PCB),[6]. $BaTiO_3$ is also a semiconducting and a nonlinear optical materials when doped with other elements, and therefore can be used for resistors with positive temperature coefficient of resistivity (PTCR) [7], temperature–humidity-gas sensors [8] as well as electro-optic devices [9]. Among these applications, performance and characteristics are strongly dependent on the size, shape, composition, morphology, and impurities of the $BaTiO_3$ nanoparticles.

The solid-state method is widely used for the production of cheap bulk titanates. However, growing demands for high-pure, homogeneous and nano-sized titanate move the research investigations toward wet chemical methods and synthesis of nano-sized titanate powders [10-12]. Lanthanum as a donor dopant commonly substitutes Ba in the lattice of barium titanate. Since La^{3+} has a different valence than Ba^{2+} this change produces a charge imbalance and induces n-type semiconductivity. Therefore, charge compensation requires the production of electrons, electron holes or titanium (V_{Ti}) and oxygen (V_O) vacancies in the material, causing modification of electrical properties [13].

In the present work La-doped barium titanate (BLT) and undoped $BaTiO_3$ (BT) nanopowders with different concentration of lanthanum were synthesized at room temperature using a semi-oxalate method. The structural characteristics were studied using XRD and SEM. The real (ε') and imaginary (ε'') parts of dielectric constant were investigated in the frequency ranges of 20 kHz to 5.0 MHz at room temperature.

Dielectric Characteristics

Dielectric constant has a real part; a real dielectric constant (ε'), is a measure of the capacity and polarization, and imaginary part; is a measure of the energy loss when there is an application of a.c. (absorption of energy by the dielectric molecules from the applied field) called an imaginary dielectric constant (ε''),[14].

The tangent of loss angle ($\tan\delta$) is a measurement of dielectric ability, at lower value of ($\tan\delta$), dielectric ability of material increase. Dielectric parameters (ε', ε'', $\tan\delta$) are affected by many factors, the most important are a temperature and field frequency, as well as influenced by the properties of material, density, porosity, impurities in addition to mineral composition of the dielectric material. Real Dielectric Constant ε', Imaginary

Dielectric Constant ϵ'' and Loss tangent $\tan\delta$ were measured as a function of frequencies in the range (50 Hz to 5 MHz) at room temperature by using LCR - meter device (type: Agilent 4294A Precision Impedance Analyzer, 40 Hz to 110 MHz). Bruggeman rule of mixture model were used to calculate the dielectric constant for all composite specimens [15-16].

Materials and Methods
Raw materials
The following high purity raw materials were used to prepare BT and BLT:
Titanium dioxide TiO_2 (99.8 % ,Riedelde haen, Germany), Barium nitrate Ba $(NO_3)_2$ (99 %, Fluka, Switzerland), Lanthanum nitrate La $(NO_3)_3$.$6H_2O$ (99 % , BDH, England), Oxalic acid $(COOH)_2$.$2H_2O$ (99.% , B.D.H Laboratory, England), Ammonia solution NH_3 (25%, India) and Unsaturated Polyester resin (UPE, Intermediate Petrochemicals Industries IPI). Barium titanate ($BaTiO_3$) and Barium Lanthanum titanate ($Ba_{1-x}La_xTiO_3$) were prepared via a semi-oxalate method and can be described as follows:

Preparation of Barium Titanate
An aqueous solution of 0.12 molar $Ba(NO_3)_2$ was prepared using de-ionized water. Required amount (Ba /Ti = 1:1) of TiO_2 powder was added to Ba $(NO_3)_2$ solution with constant stirring (magnetic stirrer).The suspension was ultrasonicated for 20 minutes to break TiO_2 agglomerates. Oxalic acid (0.4 molar solutions) was added drop wise into the mixture under vigorous stirring. The pH of the resultant mixture was adjusted to (pH=5.5) by adding ammonia solution. The resulting precipitates (white powder) were then washed repeatedly using deionized water, followed by drying at 80 ^oC for 12 hours in an oven. The powders (purified products) were calcined in air at temperatures 920^oC for 3 hours in an electric furnace (Carbolite, England).

Preparation of Lanthanum Doped $BaTiO_3$
Barium Lanthanum titanate was Prepared by adding the Lanthanum nitrate (La $(NO_3)_3$.$6H_2O$) to Barium nitrate (Ba $(NO_3)_2$) to prepare the formula Ba_{1-x} La_xTiO_3 (where , x = 0.005, 0.015, 0.02 and 0.025).The same procedure mentioned above steps were repeated (for preparation $Ba_{1-x}La_xTiO_3$).

Preparation of Composite Specimens
Disc specimens of (UPE), (UPE/BT) and (UPE/BLT) Composites with a diameter 15 mm and thickness 1–2.5 mm, were prepared using vigorous stirring and ultrasonic mixing device (for 30 minutes) to make homogeneous distribution of the powders in the UPE and inhibit particle agglomerations, then samples placed in a drying oven for 12 hours at a temperature 60°C. Finally, polishing operation was performed for specimens' surfaces.
Dielectric properties were measured (Dielectric constants; Real dielectric constant ϵ', Imaginary dielectric constant ϵ'' and Loss tangent $\tan\delta$), for all specimens (UPE, UPE /BT and UPE /BLT) at room temperature. The symbol representations for each composite sample are listed in the Table (1).

Table (1): Symbol representation for synthesized composite samples

Composite samples	La-doped value (x)	Symbols
100% UPE	Pure UPE	UPE
5% ($BaTiO_3$) +95% (UPE)	0	BT/UPE
5%($Ba_{1-x}La_xTiO_3$)+95% (UPE)	x	BLT/UPE
5%($Ba_{1-x}La_xTiO_3$)+95% (UPE)	0.005	BLT1/UPE
5%($Ba_{1-x}La_xTiO_3$)+95 (UPE)	0.015	BLT2/UPE
5%($Ba_{1-x}La_xTiO_3$)+95% (UPE)	0.020	BLT3/UPE
5%($Ba_{1-x}La_xTiO_3$)+95% (UPE)	0.025	BLT4/UPE

Results and Discussion
Structural Characteristics

The $BaTiO_3$ and $Ba_{1-x}La_xTiO_3$ powders were prepared by semi-oxalate route. The synthesized powders were characterized by X-ray diffraction. XRD pattern were obtained using Cu Kα radiation and the figure (1) shows the XRD pattern of the La-doped and undoped BaTiO3 range from 20-60o in 2θ scale. According to JCPDS no.05-0626, all the peaks in the patterns are matching and no evidence of the precursor phases $BaCO_3$, TiO_2. No intermediate phases were detected by XRD and all the matched hkl values are indexed in the figure (1).
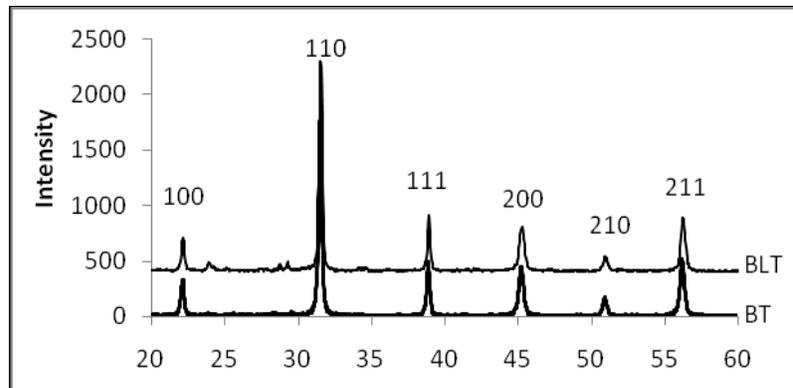

Figure.(1): The XRD patterns for BT and $Ba_{1-x}La_xTiO_3$ nanopowders were prepared at pH = 5.5 and calcined at 920 °C.

Only the (002) peak of the cubic phase, lying between two tetragonal phases, may overlap due to broadening of the peaks. In the present case, the splitting of cubic (200) into tetragonal (200) and (002) reflections cannot be clearly observed. Accordingly, the synthesized $BaTiO_3$ phases indicate a cubic structure. XRD patterns show that the peak shifts toward right indication a decrease in lattice parameter due to the smaller Lanthanum (1.06 A[0]) ionic radius than that of Barium (1.34 A[0]).Crystallite size of the BT

were calculated using Scherrer equation for the peaks (110) listed in the figure (1) and found to be in the range of 65-80 nm.
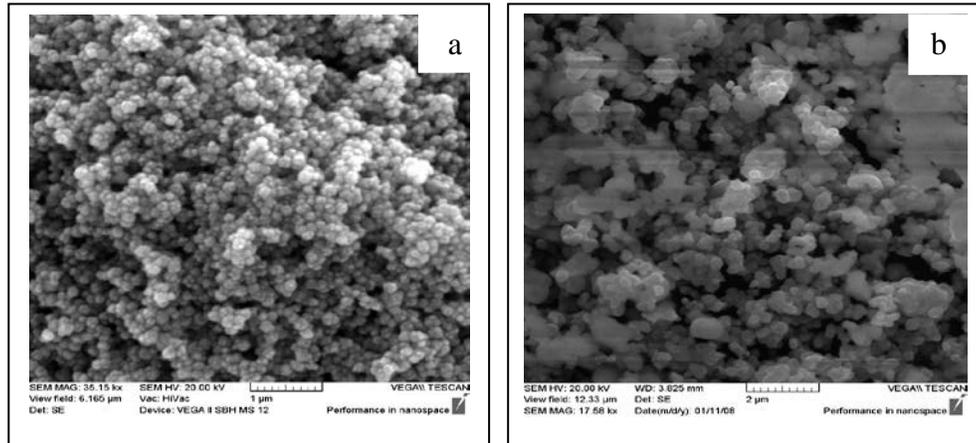

Figure. (2): (a) SEM images for BaTiO$_3$ (BT) nanopowders, (b) SEM images for Ba$_{0.975}$La$_{0.025}$TiO$_3$ (BL$_{0.025}$T) nanopowders

As can be seen in figures (2-a) for BaTiO$_3$ (BT) powder at high magnification the scans conclusively showed that the samples were cubic BaTiO$_3$, which forms sphere-like particles. The particle found through SEM is around 50-80 nm which is in good agreement with the particle size found from the XRD using the Scherer's formula. Average particle size measurements were obtained in the range of 65-80 nm from the x-ray data using Scherer's formula. Figure (2-b) shows SEM images for Ba$_{0.975}$La$_{0.025}$TiO$_3$ (BL$_{0.025}$T) nanopowders prepared from oxalate precursors. The crystallite size in both composition phases is around 50-80 nm, this size is consistent with cubic symmetry; and the result agreement with XRD analysis for BLT.

Dielectric constant

The dielectric constant and loss tangent of the BT/UPE or BLT/UPE composites showed lower values because the polarity of the hydroxyl groups on BT or BLT were suppressed physically by the UPE molecules, i.e., interface polarization between the UPE and BT or BLT were repressed by the UPE molecules encapsulated on the BT or BLT, and forming the semi-interpenetrating polymer network. Therefore, polymer encapsulation of BT or BLT plays an important role in controlling the dielectric constants of the composites.

The real dielectric constant of pure UPE samples will marginally decrease with increasing the frequency due to reduction in the polarizations caused by dipolar groups. Similarly, the real dielectric constant in BT/UPE and BLT/UPE composite samples also reduces with increasing frequency.

Figure (3) showed that the real dielectric constant of BT/UPE composite value is high at low frequencies, but decrease rapidly with increase frequency and becomes not depend clearly on the frequency, especially at high frequencies, because at low frequencies

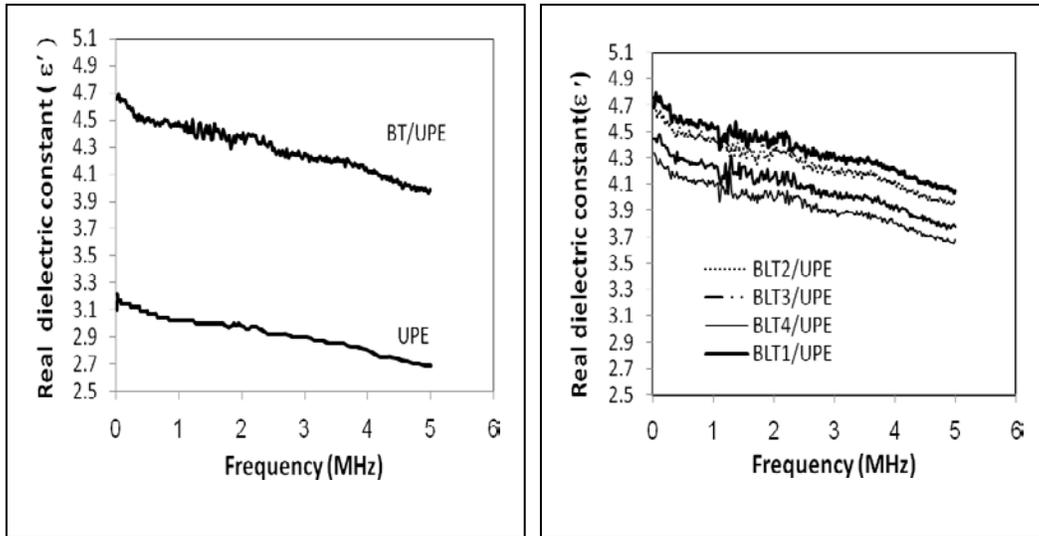dielectric dipoles possess enough time to guide itself entirely parallel to the applied electric field.

Figure. (3): Variation of real dielectric constant value vs. frequency for UPE and BT/UPE composite samples.

At high frequencies, electric field is reflected very fast periodically, making difficult for dipole alignment with the electric field. Dielectric constant of nanocomposites is decrease with increasing Lanthanum ratio in BLT. The doping by La^{3+} brings more electrons into the system, increases dielectric constant up to a critical doping level and the material converts from insulator to n-type semiconductor and back to insulator.

Nano-filler (BT and BLT) is a reinforced in UPE, the variations of dielectric constant at low filler concentration will be determined by orientation polarization effects (where dipoles tend to orient themselves to an applied electric field).

The nanocomposite effective permittivity will be governed by the occurrence of two processes – minimum effect of nano-filler permittivity and strong polymer nanoparticles interactions, as well as Cubic $BaTiO_3$ has paraelectric properties which show no displacement of ions, and hence, results in low dielectric permittivity.

This is probably the reasons why the lowest effective permittivity in both BT and BLT filled UPE nanocomposites are observed. Figure (4) shows the experimental real dielectric constant and theoretical real dielectric constant from rule of Mixture by the Bruggeman model.
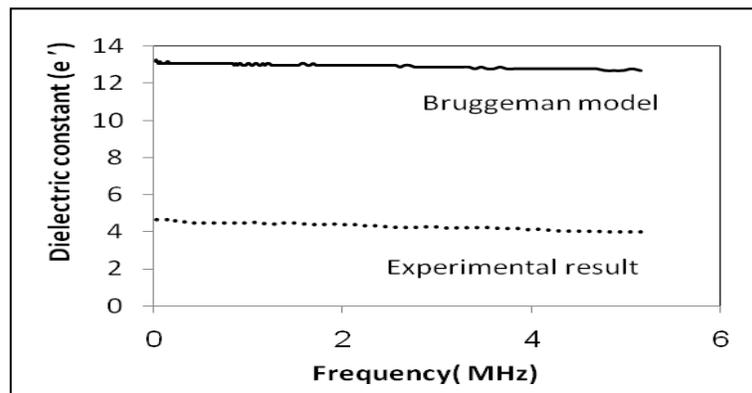
**Figure. (4): The experimental dielectric constant and theoretical dielectric constant
from rule of mixture by the Bruggeman model vs. frequency.**

Imaginary Dielectric constant

Space charge effect on dielectric loss value (ε'' and $\tan\delta$) as a result of (interfacial polarizability) that appears when the heterogeneity of the composite sample or due their isolated   phases   formed   inside   the   material   or the result of impurity atoms that appears impedance barriers effect on movement of free charges in the material. Thus the charges accumulate at this barriers, lead to appearance opposite charges on the edge of the barriers. These charges were separated inside the material, leading to appearance the dipoles in the material and polarize these dipoles when exposed to the external electric field.

The frequency increase at this region causes an increase in the dielectric loss until it reaches the limit in which the dielectric loss at maximum value, so-called (Resonance Absorption), where dipole absorbs maximum of energy of the applied field, any increase in frequency more than limit value, dielectric loss begins decreases. It has been found that this region of the absorption appear in materials that contain more than phase predominantly.
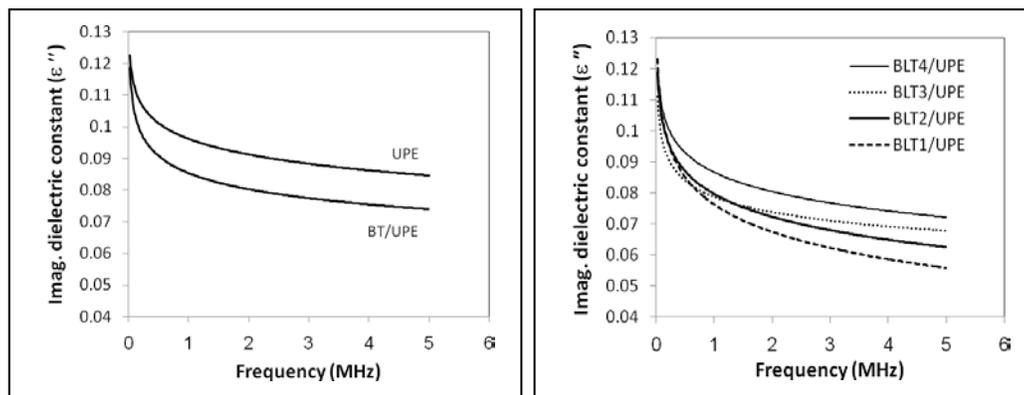

**Figure. (5) Variation of imaginary dielectric constant value vs. frequency for
UPE and BT /UPE nanocomposite samples.**

Figure (5) represents change in imaginary dielectric constant with frequency for UPE and BT/UPE nanocomposites, which shows decreases the imaginary dielectric constant with increasing frequency due to the dipoles absorption of the electric field energy at low frequencies (high loss) so as to overcome the impedance viscous area that surrounds the dipole during the rotation, frequency increase reduces imaginary dielectric constant value.

Also this figure shows increase in the imaginary dielectric constant values with increasing (x) values due to the presence of Lanthanum in the BT system, therefore the material (BT) changes from insulator to n-type semiconductor.

Tangent loss (tan δ)

For any electrical insulation system, a low tan (δ) value is always desired in the dielectric material whereas the desired dielectric constant of the material must be high depending on application.

In pure UPE or their composites (BT/UPE) and (BLT/UPE); loss tangent is a function of the electrical conductivity (which depends on the charge carrier mobility) and the applied excitation frequency. At lower frequency ranges, the incorporation of fillers does not introduce too much variation in the tan (δ) values with respect to the unfilled UPE value, clearly shows the dielectric loss value is decreased when nanofiller is added, as it appears in figure (6).
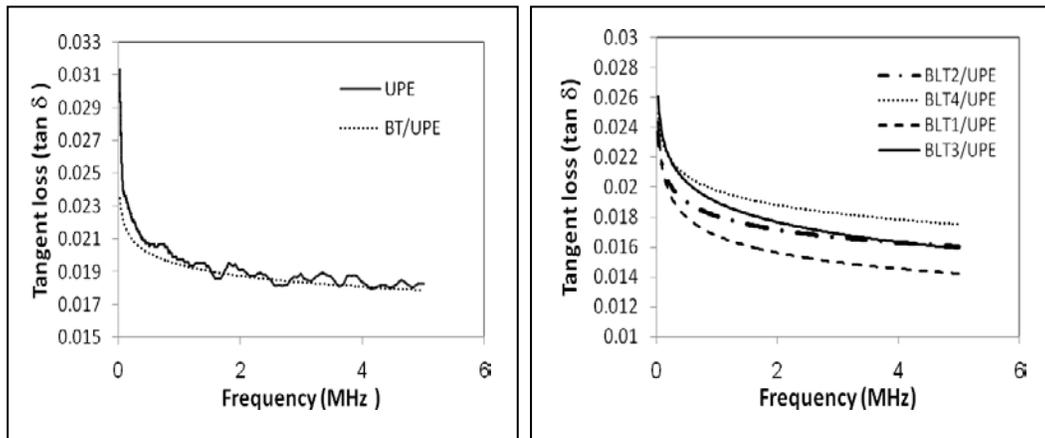

Figuire. (6) Variation of tangent of loss angle value vs. field frequency for UPE (100%) and BT (5%) with UPE(95%).

It can be seen from figure (6) that in both BT(5%) and $BL_XT(5\%)$ filled UPE(95%) nanocomposites, there is a marginal (but continuous) decrease in tan(δ) values with increasing frequency. As the frequency increases, the (tan δ) values in filled UPE are observed to reduce in comparison with the unfilled UPE (100%). Figure (6) clearly shows how the dielectric loss value increase when (x) value for (BL_XT) increase (x = 0.005, 0.015, 0.02, 0.025) because BT dielectric material changes from insulator to n-type semiconductor.

Conclusions

The main conclusions of this work can be summarized as follows:

1-   Single phase, stoichiometric $BaTiO_3$ and $Ba_{1-x}La_xTiO_3$ nanopowders were prepared by semi-oxalate route followed by heat treatment at 920°C for 3 h in air.

2-   Particle size of BT and BLT powders were found to be about 50-80 nm in both XRD and SEM techniques

3-   With increasing the amount of La^{3+} in the BLT/UPE nanoparticles composite compared to the undoped one, Real dielectric constant(ϵ') values decrease with increasing La^{+3} doping, while the tangent loss (tan δ) and Imaginary dielectric constant(ϵ'') values increase with increasing La doping .

4-   The doping of La^{3+} on $BaTiO_3$ decreases the dielectric constant and the material changes from insulator to n-type semiconductor.

5-   Polymer nanocomposites could be advantageous over traditionally filled polymers in dielectric properties from the stand point of dielectrics insulation. This feature will technologically result in compact design of electrical equipments with high reliability and thereby in significant cost reduction for system integration and maintenance.

6-   In order to obtain excellent but low cost polymer nanocomposites, existing material processing technologies should be more advanced so as to match dielectrics and electrical insulation.

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