



The Room-Temperature Sodium-Free Organosol Precipitation of Barium Titanate Nanocrystals

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ABSTRACT

The purpose of this research was to produce high-purity monodisperse barium titanate nanocrystals (BTO-NCs). To this end, a modified and very high-yield organosol precipitation method was developed. The novelty of this method was its purely organic approach, which stopped the application of inorganic bases such as caustic soda (NaOH) and avoided the risk of the presence of undesirable ions in the synthesized dielectric material. Results showed that an absolutely-organic base, such as the methylamine aqueous solution could ensure the basic condition required for high-yield organosol precipitation. X-ray diffraction, scanning electron microscopy, dynamic light scattering, and high-resolution transmission electron microscopy analyses were utilized to ensure the formation of monodisperse NCs. It was also found that monodisperse precursor crystals of about 3 nm have been achieved. Using oleic acid as the capping agent allowed generating uniformly small size and excellent dispersibility of the precipitate in the nonpolar solvents. Thus, the synthesized NCs could be easily redispersed in different nonpolar solvents to produce various suspensions of nm-size BTO-NCs without adding any surfactant. The obtained transparent suspensions, which include well-dispersed nm-size crystals, are promising for many applications in nanotechnology such as advanced electro-optic devices.

1. INTRODUCTION

Nanostructured ferroelectric materials such as ferroelectric nanoparticles (NPs), nanodots, and nanocrystals (NCs) have attracted broad interest due to a wide range of applications in different miniaturized nanodevices. Ferroelectric nanoparticles and nanodots are widely used in advanced dielectric and piezoelectric polymer matrix nanocomposites [1]. Ferroelectric nanodots are promising nanostructures for the next generation of high-density flash memories [2]. Moreover, ferroelectric NCs are fascinating objects from the fundamental physics point of view since the reduction of the structural dimensions emerges new phenomena and properties dramatically different from those of bulk ferroelectrics [3]. It is believed that the

length scales in ferroelectrics can, in essence, decrease to several nanometers [3]. Therefore, researchers are greatly interested in producing monodisperse near-ferroelectric NCs of below 10nm -or even below 5nm-, size.

Barium titanate (BTO) is a very basic dielectric and ferroelectric material for electronic applications, which is the first ceramic material with ferroelectric behavior [4] and often discussed in the textbooks as a sample ferroelectric perovskite material. This material is ideal for explaining "Ferroelectricity," from the crystal structure perspective, in the materials with spontaneous charge displacement [5]. Furthermore, BTO has been the first material, which was artificially developed as a piezoceramic and fabricated at large scale to generate and detect acoustic and ultrasonic signals [6].

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Moreover, it has played a major role in demonstrating that ferroelectric ceramics get a piezoelectric response through the poling process [5]. Nowadays, BTO has many commercial applications in ceramic multi-layer capacitors, chemical sensors, nonvolatile memories [7], pyroelectric detectors, infrared imaging systems, nonlinear optics, electrooptic modulators, optical memories, and microelectromechanical devices [8].

Organometallic methods, such as the organosol precipitation, are well-known synthesis methods for producing different nanomaterials. These methods provide an ideal environment to control the growth of the NCs because nucleation and growth of the NCs are two separate stages in these methods [9]. Moreover, the organosol precipitation approach can exhibit various advantages including high yield, low process temperature, short reaction time, as well as low cost of the reagents [10].

The organosol precipitation of BTO-NCs has been reported by others [7]. High-yield organosol precipitation methods require highly-basic environments. Generally, there is no organic base with base dissociation constant (K_b) parameter comparable to the well-known inorganic bases such as caustic soda (NaOH). Therefore, many of the previous researchers have applied NaOH for the hydrolysis and precipitation reactions to raise the pH value above 13 to effectively precipitate BTO crystals [7, 11, 12]. Hence, sodium (Na^+) ions are conventionally a common impurity in organosol BTO precipitation while the risk of the presence of undesirable Na^+ ions in the dielectric materials is well-known [13, 14]. It has been reported that the presence of mobile Na^+ ions in dielectric materials results in severe consequences such as undesirable dielectric breakdown.

The novelty of the current research is that an absolutely organic base has successfully been used in the organosol precipitation method for complete hydrolysis and precipitation reactions. For this purpose, a pure organic base, methylamine, is utilized. Synthesis of high-purity monodisperse nanocrystals is a crucial requirement to fabricate reliable nanoelectronic devices. Therefore, the present study is a breakthrough to synthesize high-purity monodisperse BTO-NCs for nanoelectronic applications.

2. EXPERIMENTAL PROCEDURES

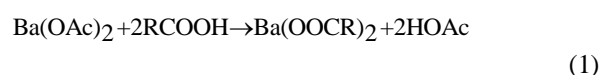
2.1. Materials and methods

The precursor materials for BTO-NCs include barium acetate, $Ba(CH_3COO)_2$, 99%, and titanium isopropoxide, $Ti(OCH(CH_3)_2)_4$, 97%, as the barium and titanium precursors, respectively. A methylamine solution, CH_3NH_2 , 40wt% in water, was used as the

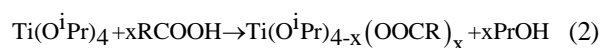
organic base. The mentioned chemicals were purchased from Sigma-Aldrich, Steinheim, Germany. Furthermore, oleic acid, $[(CH_2)_7CH]CH(CH_2)_2COOH$, 65% AppliChem, and toluene, C_7H_8 , 99.5% Fisher Chemicals, were used. Some previous researchers have used other barium precursors such as barium hydroxide. The use of barium acetate is reported useful to decrease the possible formation of barium carbonate because barium acetate displays lower sensitivity to CO_2 [11].

2.2. Synthesis procedure

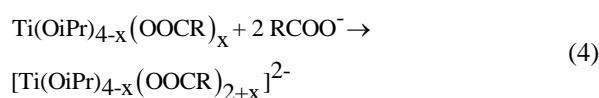
Typically, barium acetate was added to 40ml oleic acid to synthesize 2.33g, 10mmol, of BTO nanopowder, 2.58g, 10mmol, which was mixed magnetically under a dry nitrogen flow. Then, the prepared barium acetate/oleic acid mixture was gradually heated up to $450^\circ C$ above the boiling temperature of oleic acid to ensure complete decomposition of the acetate and reaction of barium with oleic acid (1)[7]:



Where RCOOH denotes oleic acid. Thus, a bright-orange transparent solution of barium oleate was formed, which was cooled down to room temperature. In a separate flask, 3.05mL, 10mmol, titanium isopropoxide was dissolved in toluene, 40 mL, and stirred magnetically under nitrogen flow to ensure that a homogenous solution has been formed. The prepared titanium isopropoxide/toluene solution was added to the Ba-oleate solution and mixed magnetically for two hours for complete reaction and obtaining a homogenous BTO precursor solution (2).

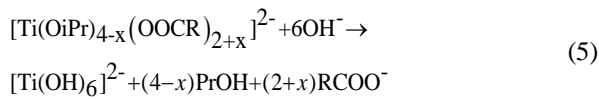


Where, "RCOO" and "Ac" represent the entire oleate and acetate ligands, respectively. Since $RCOO^-$ is a nucleophilic molecule, it can be absorbed by Ti^{4+} cations, which may result in ionic dissociation of Ba-oleate into the oleate and Ba^{2+} ions. Therefore, oleate may remove two electrons from barium (3) after adding the titanium precursor solution and nucleophilically attack Ti^{4+} ions (4). Since the coordination number in the Ti-O bond is 6, a maximum number of two agents can attack each Ti^{4+} cation (4)[7].



2.3. Precipitation in water phase

An appropriate amount of the methylamine 40wt% aqueous solution was added to the oleate precursor solution, which raises its pH value up to about 13. In such a strongly basic condition, fast hydrolysis of the chemically-modified titanium precursor occurred (5). Since Ba^{2+} ions are available, a yellow-colored precipitate of BTO-NCs can be formed through the reaction of these ions with titanium hydroxide in a water phase in the final suspension (6). The final suspension was centrifuged to rapidly separate the precipitated BTO-NCs from this phase. After centrifuging, the prepared BTO-NCs were dried in a vacuum evaporator at room temperature.



2.4. Avoiding BaCO_3 Formation and Effective BaCO_3 Removal

Washing and neutralizing the precipitate is necessary due to the highly basic and organic nature of the current organosol approach. Moreover, BaCO_3 (BCO) may form on the surface of BTO [15]. The formed BCO layer may work as a passivation layer on the surface of the synthesized NCs in aqueous media, but the formation of BCO impurities on the surface of the BTO-NCs will dramatically affect their dielectric properties [16]. Therefore, a washing step was employed to neutralize the precipitated NCs and remove their BCO content while care was also taken to minimize BCO formation during the synthesis - nucleation and precipitation of the NCs - as follows:

Depending on the pH, BCO is partially soluble in water, which releases Ba^{2+} cations into the water. Ba^{2+} ions can be specifically adsorbed on the surface of BTO-NCs, changing their electrochemical properties [12]. Therefore, all the reactions were carried out under N_2 purge to avoid BCO formation to block CO_2 adsorption. Thus, the methylamine solution was reacted with the oleate precursor solution under N_2 to minimize BCO formation and ensure precipitation of BTO-NCs. The solubility of the BCO composition increases at $\text{pH} \geq 6$. Below that pH region, carbonic acid (H_2CO_3) begins to dissociate into the CO_2 gas. Therefore, acid washing within this pH range will increase the risk of deficient Ba stoichiometry on the surface of BTO-NCs. This significant change of the solubility of BCO can lead to an undesirable composition because it results in large changes in the Ba content. Thus, a concentrated acetic acid solution was selected for washing the

precipitated BTO powder. Acetic acid may react with the remaining methylamine to produce acetyl amide and water (Figure 1), which decreases pH in the synthesized nanopowder. Therefore, the pH of the powder suspension can be decreased below 2. The solution was stirred magnetically for effective BCO removal. The pH of the final powder was neutralized by adding an appropriate amount of an ammonia solution in ethanol after washing. Thus, the washed BTO-NCs can be easily separated from the neutralized solution by centrifuging. Both Acetyl amide and aminoacetate are slightly soluble in both water and ethanol. Therefore, the byproducts of the washing stage can be easily removed after neutralizing the solution. The complete reaction of acetic acid with methylamine is:

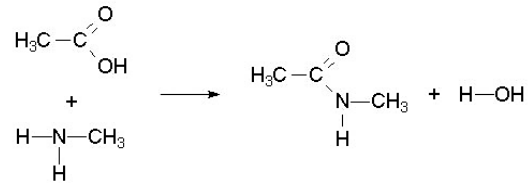


Figure 1. Schematic reaction of acetic acid with methylamine

2.5. Characterization

The size of the synthesized NCs was measured by dynamic light scattering (DLS) using a NanoFlex system, ParticleMetrix. An environmental scanning electron microscope (ESEM) Quanta 400 FEG, FEI system was utilized to examine the size and morphology of the precipitated NCs (the aggregates). The composition and the crystalline structure of the grown NCs were determined by a Vertex 70 model, Siemens Bruker D5000 X-ray diffraction (XRD) system. The size and morphology of the redispersed NCs were investigated by high-resolution transmission electron microscopy (HR-TEM) on a JEOL 2200FS field emission HR-TEM system.

3. RESULTS AND DISCUSSION

3.1. Hydrolysis-Assisted Precipitation

The completed hydrolysis reaction will result in complete aggregation and precipitation of the BTO-NCs in a water phase (Figure 2). After this stage, the precipitated BTO-NCs were centrifuged out of the water phase and subsequently dried. Then, they were characterized through both DLS and ESEM.

3.1.1. DLS Measurement of the Precipitated BTO-NCs

The hydrolysis reaction may result in fast precipitation of the BTO-NCs in a highly basic phase due to the formation of large aggregates (Figure 2). The DLS

measurement of the precipitated BTO-NCs confirms this hypothesis (Figure 2).

Figure 2 illustrates the effect of the hydrolysis reaction on the DLS measurement of the prepared BTO-NCs. The DLS sample in this figure was directly sampled from the water phase containing BTO-NCs (Figure 2) without size selection.

Figure 2 displays a very broad size distribution including both nm- and μ m-size objects, which indicates aggregation of the NCs. Hence, many NCs have been aggregated into microparticles during the hydrolysis stage due to the high pH of the water phase.

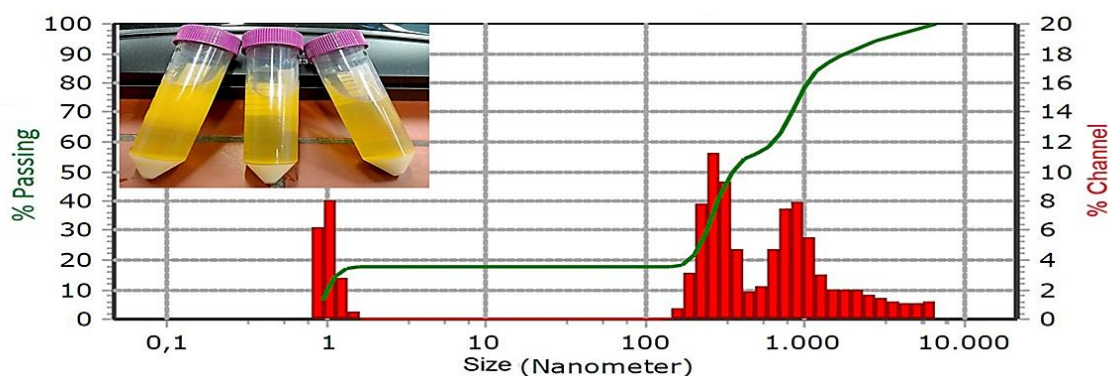


Figure 2. [The arrowed graphs] the DLS measurement of the precipitated BTO-NCs and [Inset] the BTO-NCs precipitated from a water phase

3.1.2. Studying the Precipitated BTO-NCs by SEM

SEM investigations were performed to determine the size and morphology of the precipitated NCs. Figure 3 reveals the SEM image of the precipitated BTO-NCs. These crystals have been hydrolyzed by the methylamine solution at room temperature. It is observed that the powder sample in Figure 3 consists of some aggregates of different sizes. Therefore, both DLS and SEM investigations confirm that the utilized organic base, i.e., the methylamine solution, has effectively hydrolyzed the BTO-NCs.

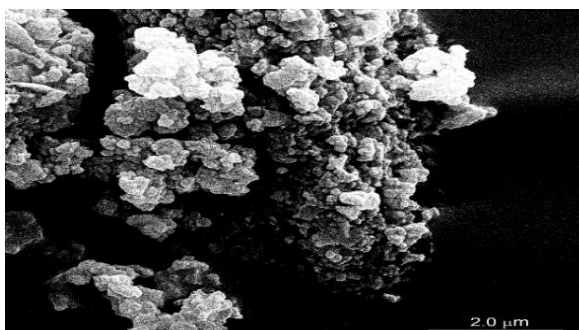


Figure 3. The SEM micrograph of the precipitated NCs

3.2. Redispersing the NCs

The precipitated BTO-NCs could be well redispersed in various nonpolar solvents such as toluene,

chlorobenzene, chloromethane, dichloromethane, hexane, toluene, etc. after drying. Thus, the transparent dispersions of the NCs could be prepared, which were characterized through DLS and HR-TEM methods as follows:

3.2.1. DLS Measurements

The precipitated BTO-NCs could be redispersed in organic nonpolar solvents such as toluene, tetrahydrofuran, chlorobenzene, n-octane, etc. without using any surfactant after drying.

Figure 4 displays the size distribution of the synthesized NCs, which is measured by DLS after NCs are redispersed in toluene. A total amount of 1mg of the precipitated dry BTO nanopowder was mixed with the solvent, toluene, 1mL to prepare DLS sample. The powder was subsequently dispersed in the solvent using an ultrasonic probe.

DLS measurements in Figure 4 confirm fabrication of monodisperse nm-scale objects. Some hundred nm objects are observed in Figure 4, which show the possible formation of solid agglomerates upon hydrolysis stage. Such large aggregates are not destroyed by the ultrasonic vibration because of the powerful bonding of the agglomerated nanoparticles, which indicates that solid agglomerates have been formed due to the strong hydrolysis reaction.

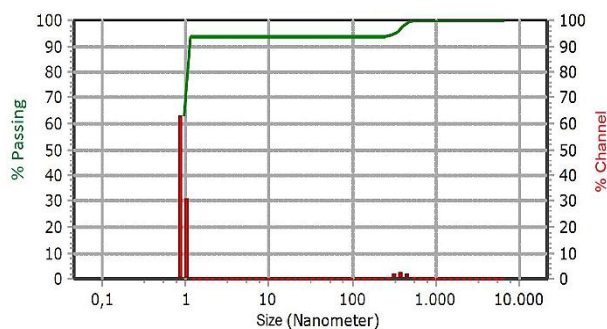


Figure 4. DLS measurement of the precipitated BTO-NCs, which are redispersed in toluene

3.2.2. HR-TEM Investigations

Figure 5 (a) and (b) shows the high-resolution TEM (HR-TEM) image of the precipitated BTO-NCs after redispersing. The BTO-NCs in this figure have been prepared at room temperature for 24h at pH=13 by adding the appropriate amount of the methylamine solution. Then, they were washed in a concentrated acetic acid solution and subsequently neutralized. They were dried in vacuum at room temperature for 12h after separating the washed NCs in a centrifuge system. The HR-TEM samples were directly prepared from the precipitated dry BTO nanopowder without any size selection. The dried BTO-NCs were redispersed in toluene using an ultrasonic probe for HR-TEM sample preparation. Then, one drop was coated on an HR-TEM grid. Many BTO-NCs show low TEM contrast with the amorphous carbon-coated grid due to the small (nm) size of the grown crystals and the capping layer. Some of the NCs are arrowed in both Figure 5 (a) and (b) and Figure 6 using horizontal white arrows.

The inset figures in Figure 5 (a) and (b) can illustrate the periodic structure of the synthesized NCs. The rather low contrast in the bright-field HR-TEM image in these figures is due to the presence of the surfactant layer around the crystal surface. The surfactant layer is arrowed in Figure 6 using one vertical white arrow. Since the redispersed NCs are prepared through modification of BTO precursors with oleic acid, the grown BTO-NCs are capped by a capping oleate layer. Thus, a continuous oleate layer is observed in this figure, which perturbs the TEM contrast of the grown NCs. Thus, the HR-TEM images somehow confirm the obtained DLS data (Figure 4), which indicates that nm-size monodisperse nanocrystals have been formed.

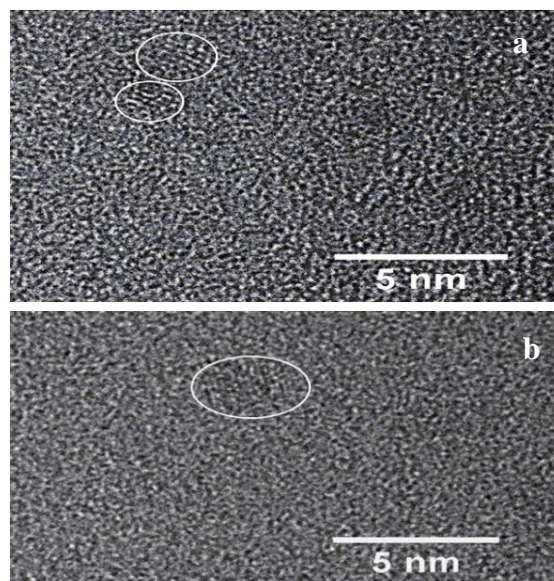


Figure 5. (a) and (b) HR-TEM images of the redispersed NCs, which are prepared at room temperature

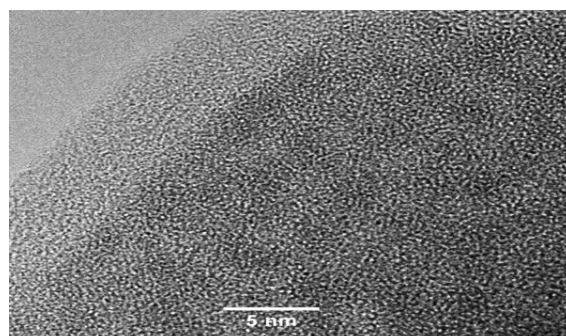


Figure 6. Perturbed TEM contrast of the grown NCs (the horizontal arrows) by the surfactant, the oleate layer (the vertical arrow)

3.3. XRD

The XRD technique was used to examine the composition and crystalline structure of the precipitated nanopowders to confirm the formation of BTO-NCs and the complete removal of BCO (Figure 7). Figure 7(a) shows the XRD pattern of the precipitated nanopowder, which is dried in vacuum at 40°C. An intensive background has hindered the XRD reflections due to both BTO and BCO as well as the organic capping layer and small size of the NCs (Figure 7(a)). Therefore, it is hard to conclude whether BTO and or BCO have formed.

It is necessary to perform heat treatment at elevated temperatures to enlarge the grown nanocrystals for successful phase detection by XRD.

Figure 7 (b) shows the XRD pattern of the precipitated nanopowder in Figure 7(a), which is heat-treated in vacuum at 100°C. The formation of the BCO and BTO crystals is identified in this figure according to the JCPDS Cards No 01-085-0720 and 01-080-0825, for BCO and BTO, respectively.

Figure 7 (c) shows the XRD pattern of the heat-treated nanopowder, which is heat-treated in vacuum at 100°C after washing in concentrated acetic acid. Most of the diffraction peaks have been removed due to a BCO phase. Thus, BCO removal through washing has successfully been monitored by XRD (Figure 7(b) and (c)). Furthermore, few diffraction peaks have been removed due to barium titanate, which may indicate the formation of an amorphous phase upon acid washing. A longtime acid washing of BTO powder or increasing the number of washing with acetic acid will remove BCO. However, it is preferred to minimize the washing cycles to avoid the pH effects on washing a BTO powder because crystalline BTO is not stable in the acidic pH values and can be dissolved to be an amorphous phase [17].

Many previous researchers consider a similar presumption that only an inorganic base such as NaOH is so strong to assure the basic environment required for complete precipitation of BTO nanomaterials [12,18].

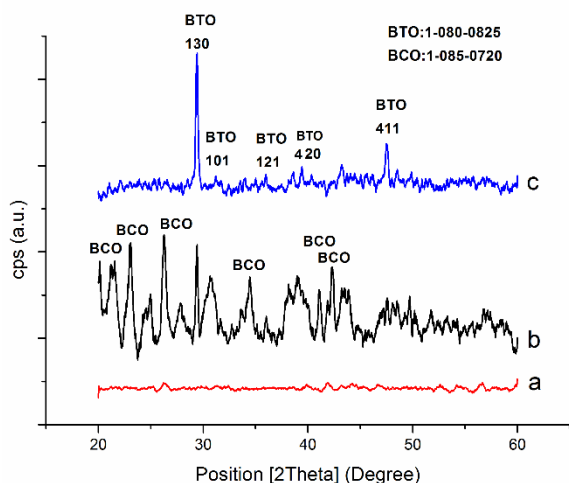


Figure 7. The XRD patterns of the precipitated nanopowder after heat treatment at (a) 40°C and (b) 100°C. (c) The XRD pattern of the nanopowder in Figure (b) after washing in concentrated acetic acid

The use of NaOH will increase the risk of the presence of undesirable Na^+ ions in the precipitated ferroelectric material. The hazards of the presence of undesirable metal ions such as Na^+ ions in the ferroelectric materials are well-known [14,19]. Therefore, the

complete removal of metal ions through the application of successive washing steps is needed to reduce the concentration of the introduced ions. These extra procedures will dramatically reduce not only the production rate, but also the processing efficiency. Moreover, they may result in noncrystalline BTO particles.

It has been shown in this study that an organic base, such as the methylamine solution, can effectively hydrolyze and precipitate BTO-NCs. In this approach, undesirable Na^+ ions are not included in the synthesized ferroelectric material. Furthermore, all the synthesis procedure has been performed in an N_2 environment to minimize BCO formation and the formed BCO is entirely removed by acid washing. Thus, the precipitation of BTO-NCs can be ensured.

The synthesized NCs can be easily dispersed in different nonpolar solvents without adding any surfactant. Therefore, the procedure proposed in the present research can produce the suspensions of nm BTO-NCs in different nonpolar solvents such as chlorobenzene or toluene. It is observed in

Figure 4 and Figure 5 that such suspensions include dispersed nanocrystals of a few-nm size. Also, those figures show that the precipitate includes a uniform and narrow distribution of NC size.

It is notable that the chemistry of a material has a major contribution to its synthesis in a wet synthesis method. The surface chemistry of BTO-NCs highly depends on the pH of the solution [9]. An amorphous Ti-rich surface layer may form within $\text{pH} = 7-8$ and BCO may form on the surface within $\text{pH} = 9-12$ [17]. Thus, the pH of the precursor solution was increased immediately not slowly up to $\text{pH} \sim 13$ to achieve crystalline BTO nanomaterials and avoid BCO formation.

4. CONCLUSION

The results of the research indicated that an organic base can be successfully used for the organosol precipitation of monodisperse barium titanate precursor nanocrystals. A methylamine aqueous solution was successfully utilized for this purpose, which could raise the pH of the oleate precursor solution to about 13 and fix it at $\text{pH} \geq 12$. Therefore, the methylamine aqueous solution could provide a suitable water phase required for the hydrolysis reactions and the precipitation of the precursor BTO-NCs. The hydrolysis reaction resulted in fast aggregation and precipitation of the BTO-NCs in the water phase. DLS studies showed that a very broad size distribution including both nm- and μm -size objects was achieved inside the water phase, which

indicates the aggregation of the NCs in the provided highly basic environment, i.e., the water phase. Thus, many NCs were precipitated during the hydrolysis stage. The methylamine solution was reacted with the oleate precursor solution under N₂ to minimize BCO formation and ensure precipitation of BTO-NCs. A suspension with uniform and narrow distribution of NC size was achieved after redispersing the precipitate in a nonpolar solvent as confirmed by DLS. Detailed HR-TEM studies confirmed that nm-size and monodisperse nanocrystals have been formed. The suggested method offers a low-cost route to synthesize various perovskite nanocrystals.

6. REFERENCES

- Varghese, J., Whatmore, R.W., Holmes, J.D., "Ferroelectric nanoparticles, wires and tubes: synthesis, characterisation and applications", *Journal of Materials Chemistry C*, Vol. 1, (2013), 2618-2638.
- Fu, H., Bellaiche, L., "Ferroelectricity in barium titanate quantum dots and wires", *Physical review letters*, Vol. 91, (2003), 257601.
- Ahn, C. H., Rabe, K. M., Triscone, J.-M., "Ferroelectricity at the nanoscale local polarization in oxide thin films and heterostructures", *Science*, Vol. 303, No. 5657, (2004), 488-491.
- Vijatović, M.M., Bobić, J.D., Stojanović, B.D., "History and challenges of barium titanate: Part I", *Science of Sintering*, Vol. 40, (2008), 155-165.
- Moulson, A.J., Herbert, J.M., "Barium Titanate—The Prototype Ferroelectric Ceramic, in: Electroceramics: materials, properties, applications", John Wiley & Sons, (2003), pp. 71-82.
- Moulson, A.J., Herbert, J.M., "Important Commercial Piezoceramics, in: Electroceramics: materials, properties, applications", John Wiley & Sons, (2003), pp. 362-381.
- Gao, Y., Shvartsman, V.V., Elsukova, A., Lupascu, D.C., "Low-temperature synthesis of crystalline BaTiO₃ nanoparticles by one-step organosol-precipitation", *Journal of Materials Chemistry*, Vol. 22, (2012), 17573-17583.
- Zhou, Z., Bowland, C.C., Patterson, B.A., Malakooti, M.H., Sodano, H.A., "Conformal BaTiO₃ films with high piezoelectric coupling through an optimized hydrothermal synthesis", *ACS applied materials & interfaces*, Vol. 8, (2016), 21446-21453.
- Jiang, B., Iocozzia, J., Zhao, L., Zhang, H., Harn, Y.W., Chen, Y., Lin, Z., "Barium titanate at the nanoscale: controlled synthesis and dielectric and ferroelectric properties", *Chemical Society Reviews*, Vol. 48, (2019), 1194-1228.
- Kolen'ko, Y.V., Kovnir, K.A., Neira, I.S., Taniguchi, T., Ishigaki, T., Watanabe, T., Sakamoto, N., Yoshimura, M., "A novel, controlled, and high-yield solvothermal drying route to nanosized barium titanate powders", *The Journal of Physical Chemistry C*, Vol. 111, (2007), 7306-7318.
- Gao, Y., "Synthesis of Core-Shell Structured Nanocomposite Materials", in: Institute for Material Science, Faculty of Engineering, University of Duisburg-Essen, Essen, Germany, (2015).
- Du, H., Wohlrab, S., Weiß, M., Kaskel, S., "Preparation of BaTiO₃ nanocrystals using a two-phase solvothermal method", *Journal of Materials Chemistry*, Vol. 17, (2007), 4605-4610.
- Chou, N., Eldridge, J., "Effects of material and processing parameters on the dielectric strength of thermally grown SiO₂ films", *Journal of the Electrochemical Society*, Vol. 117, (1970), 1287-1293.
- DiStefano, T., "Dielectric breakdown induced by sodium in MOS structures", *Journal of Applied Physics*, Vol. 44, (1973), 527-528.
- López, M.D.C.B., Fourlaris, G., Rand, B., Riley, F.L., "Characterization of barium titanate powders: barium carbonate identification", *Journal of the American Ceramic Society*, Vol. 82, (1999), 1777-1786.
- Lee, S., Paik, U., Hackley, V.A., Jung, Y.G., Yoon, K.J., "Microstructure and permittivity of sintered BaTiO₃: influence of particle surface chemistry in an aqueous medium", *Materials Research Bulletin*, Vol. 39, (2004), 93-102.
- Adair, J.H., Crampo, J., Mandanas, M.M., Suvaci, E., "The role of material chemistry in processing BaTiO₃ in aqueous suspensions", *Journal of the American Ceramic Society*, Vol. 89, (2006), 1853-1860.
- Park, K.I., Lee, M., Liu, Y., Moon, S., Hwang, G.T., Zhu, G., Kim, J.E., Kim, S.O., Kim, D.K., Wang, Z.L., Lee, K.J., "Flexible nanocomposite generator made of BaTiO₃ nanoparticles and graphitic carbons", *Advanced Materials*, Vol. 24, (2012), 2999-3004.
- Osburn, C.M., Raider, S.I., "The effect of mobile sodium ions on field enhancement dielectric breakdown in SiO₂ films on silicon", *Journal of the Electrochemical Society*, Vol. 120, (1973), 1369-1376.