Soft Combustion Technique: Solution Combustion Synthesis and Low-Temperature Combustion Synthesis; to Prepare $Bi_4Ti_3O_{12}$ Powders and Bulk Ceramics

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Abstract:

$Bi_4Ti_3O_{12}$ (BTO) powders were synthesized using soft combustion techniques, specifically known as Solution Combustion Synthesis (SCS) and Low-temperature Combustion Synthesis (LCS). XRD results showed that the single phase BTO was obtained following calcinations at 800^oC for the sample prepared using SCS; compared to after combustion, for the sample prepared using LCS. The TG/DTA showed a combustion temperature of around 252 - 280^oC, which became stable with a single phase BTO at 500^oC and above. Sintering was carried out at $1,100^oC$ for 3 h, to determine the microstructures, grain orientation, relative density, dielectric, and ferroelectric properties, of the bulk ceramics. It was found that the bulk ceramics prepared using SCS exhibited elongated-like grains, strong (117)-preferred grain orientation, a relative density of 93.3%, ε_r = 320 - 360, tan δ = 0.03 - 0.1, P_r = 6.8 $\mu C/cm^2$, and E_c = 20 kV/cm. Meanwhile, the bulk ceramics prepared using LCS showed plate-like grains, strong c-preferred grain orientation, a relative density of 83%, ε_r = 143 - 195, tan δ = 0.01 - 0.38, P_r = 5.9 $\mu C/cm^2$, and E_c = 30 kV/cm.
Keywords: $Bi_4Ti_3O_{12}$; combustion synthesis; grain orientation; dielectric; ferroelectric

1. Introduction

Recently, ferroelectric materials have been intensively studied as candidates for use in a wide range of new multifunctional applications in piezoelectrics, transducers, and memory devices [1-2]. Bismuth Layer-Structured Ferroelectrics (BLSFs), including $SrBi_2Ta_2O_9$ and $Bi_4Ti_3O_{12}$, consist of a layer structure of $(Bi_2O_2)^{2+}$ and a pseudo-perovskite along the *c*-axis; which is different from a simple perovskite structure. $Bi_4Ti_3O_{12}$ (or BTO) is a BLSFs and is known to have a high Curie temperature (675^oC), a large remanent polarization (P_r = 5 – 6.5 $\mu C/cm^2$), a low coercive field (E_c = ~50 kV/cm), and a low processing temperature (750 – 800^oC); giving this material a high potential in real applications [3-5]. Furthermore, BTO is very familiar as a lead-free ceramic material. For the above reason, BTO was investigated by several other researchers.

BTO is usually prepared using a conventional solid state reaction at a calcinations temperature above 1000^oC. However, this route has several disadvantages, such as inhomogeneity, non-uniformity of grain morphology, high impurity content, a lack of reproducibility, and a necessity for repeated grinding [6]. Moreover, the densification at a

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high sintering temperature is not suitable for ferroelectric applications, because the loss of bismuth ions at high temperature results in the formation of secondary phases [7]. In order to reduce the sintering temperature, a number of wet-chemical methods, including sol-gel synthesis, co-precipitation synthesis, hydrothermal routes, and soft combustion techniques, have been used to synthesize BTO [3, 7-8]. Among these techniques, soft combustion has been chosen and employed in this study, due to its simple and rapid preparation process. In combustion synthesis, the thermal energy required for the reaction to occur is provided by the reaction itself, instead of the external source. Various fuels have been used in combustion synthesis, including citric acid, glycine, urea, and polysaccharide [9-10]. Additionally, other additives have also been used to support the reaction completely, such as ammonia solution [11]. In some cases, the external source e.g. calcinations, is necessary to form the bismuth-layered phase [12]. Hence, an attempt has been made to investigate the soft combustion technique in different approaches on the phase formation, grain morphology, dielectric, and ferroelectric properties, of the BTO material. These approaches are known as Solution Combustion Synthesis (SCS) and Low-temperature Combustion Synthesis (LCS).
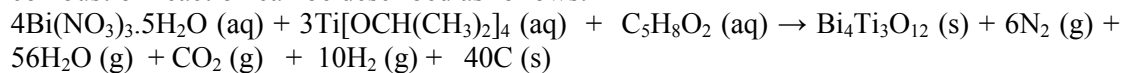
2. Experimental procedure
2.1 Materials used

The starting materials consist of bismuth nitrate pentahydrate, $Bi(NO_3)_3.5H_2O$ (Sigma-Aldrich, 98%), titanium(IV)isopropoxide $Ti[OCH(CH_3)_2]_4$ (Aldrich Chemistry, 97%), 2-Methaoxyethanol (2-ME) $C_3H_8O_2$ (Sigma Aldrich), acetylacetone $C_5H_8O_2$ (Merck), NH_4OH 29% solution, citric acid monohydrate $C_6H_8O_7$ (Sigma Aldrich), and distilled water.

2.2 BTO powder preparation via SCS

$Bi(NO_3)_3.5H_2O$ was dissolved in 2-methaoxyethanol and stirred for 30 minutes in a water bath at 40C. Separately, titanium(IV)isopropoxide was dissolved in a solvent containing 2-ME and acetylacetone and stirred for 30 minutes at 25C. Then, the prepared Ti solution was slowly added into the prepared Bi solution using a dropping funnel, to obtain a precursor solution. The obtained solution was then stirred for another 2 hours at 40C. Then, the temperature was increased to 80C for an evaporation process. A sticky gel was formed, followed by a soft combustion process that formed foam (exothermic chemical reaction that resulted in the production of a flame). This foam was then crushed using a mortar to obtain a fine powder. The powder was then calcined at different temperatures i.e., 600, 650, 700, 750, and 800C for 3 hours, with a heating rate of $5Cmin^{-1}$ and a cooling rate of $5Cmin^{-1}$. The combustion reaction can be described as follows:
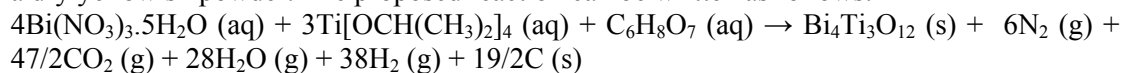
$$4Bi(NO_3)_3.5H_2O \text{ (aq)} + 3Ti[OCH(CH_3)_2]_4 \text{ (aq)} + C_5H_8O_2 \text{ (aq)} \rightarrow Bi_4Ti_3O_{12} \text{ (s)} + 6N_2 \text{ (g)} + 56H_2O \text{ (g)} + CO_2 \text{ (g)} + 10H_2 \text{ (g)} + 40C \text{ (s)}$$

Where, (aq), (g) and (s) refer to liquid, gas, and solid state, respectively.

2.3 BTO powder preparation via LCS

$Bi (NO_3)_3.5H_2O$ was dissolved in distilled water and stirred for 2 hours to obtain a good solubility. The temperature of the water bath was controlled at 40C. A selected fuel agent of citric acid monohydrate was dissolved in distilled water and stirred at 25C. Separately, titanium (IV) isopropoxide was dissolved in 2-ME and stirred for 30 minutes at 25C. After that, the prepared Ti solution was slowly added into the prepared Bi solution containing citric aqueous using a dropping funnel, to form a precursor solution. NH_4OH (29% solution) was

added to enhance fuel reaction for combustion process to occur. The pH of the solution was increased to 7. Then, the precursor was constantly stirred at 60C for 24 hours, to obtain a homogeneous solution. Then, the temperature was raised to 80C for a drying process, prior to the combustion process. The combustion reaction lasted for less than 5 minutes and produced a dry yellowish powder. The proposed reaction can be written as follows:

$4Bi(NO_3)_3.5H_2O$ (aq) + $3Ti[OCH(CH_3)_2]_4$ (aq) + $C_6H_8O_7$ (aq) → $Bi_4Ti_3O_{12}$ (s) + $6N_2$ (g) + $47/2CO_2$ (g) + $28H_2O$ (g) + $38H_2$ (g) + $19/2C$ (s)

Where, (aq), (g) and (s) refer to liquid, gas, and solid state, respectively.

2.4 Bulk ceramic preparation for SCS and LCS

The prepared powders were crushed to break the agglomeration and pressed at a pressure of 100 MPa into pellets, 13 mm in diameter. The sintering process was carried out at 1100 ^oC for 3 hours at a heating rate of 5 ^oC min^{-1} and a cooling rate of 5 ^oC min^{-1}.

2.5 Characterization

Phase identification and structural parameters were investigated using X-ray diffraction, XRD with Cu-Kα radiation (Bruker D8 Advanced). Thermal decomposition temperature of the as-dried powder was investigated using Thermogravimetric-Differential Thermal Analysis (TG-DTA) (Setaram). The grain morphology and microstructure of the bulk samples were observed using Field Emission Scanning Electron Microscopy (FESEM) (Zeiss Supra 55VP PGT/HKL). A Raman spectrometer (Horiba Jobin-Yvon HR800UV) was used to investigate the vibrational modes in the BTO system. The relative density of the bulk samples was measured using the Archimedes method. To investigate the electrical properties, the bulk ceramics were coated with silver conductive paint for an ohmic contact. The dielectric and ferroelectric properties were measured using an impedance analyzer and a Sawyer-Tower circuit, respectively.

3. Results and discussion
3.1 Phase formation and thermal analysis

The as-combusted powders, prepared using different combustion techniques, were initially analyzed using X-ray diffraction (XRD). The standard XRD data for the perovskite BTO in the ICDD PDF (73-2181) was used as a reference pattern. The result is presented in Fig. 1. As shown in Fig. 1(a), the intermediate phases, such as $Bi_{7.7}Ti_{0.3}O_{12.16}$ and $Bi_2Ti_2O_7$, were formed in certain 2θ angle, as marked in the XRD pattern. This analysis implies that the as-combusted powder prepared using SCS, is composed from the mixed perovskite phase. Additionally, the presence of an unwanted phase is associated to the incomplete combustion reaction from the SCS technique. In another technique, the single phase BTO was successfully formed in the powder prepared using LCS, as indicated in the XRD pattern in Fig. 1(b). Further analysis shows that all diffraction peaks were indexed as the orthorhombic structure, with the lattice constants: a: 5.420 Å, b: 5.447 Å, c: 32.775 Å. This result agrees well with the standard data value a: 5.410 Å, b: 5.448 Å, 32.8400 Å. In addition, the crystallite size of the powder was about 25 nm. This basis suggests that the combustion technique plays an important role on the single phase formation. In this work, the perovskite BTO was successfully produced in a single-step synthesis using the LCS technique. However, a similar result was not observed in the as-combusted powder that was prepared using SCS. It is therefore believed that calcinations are necessarily used on that particular powder. To that,

calcinations were studied at different temperatures, in order to eliminate the unwanted phases. The results are shown in Fig. 2.
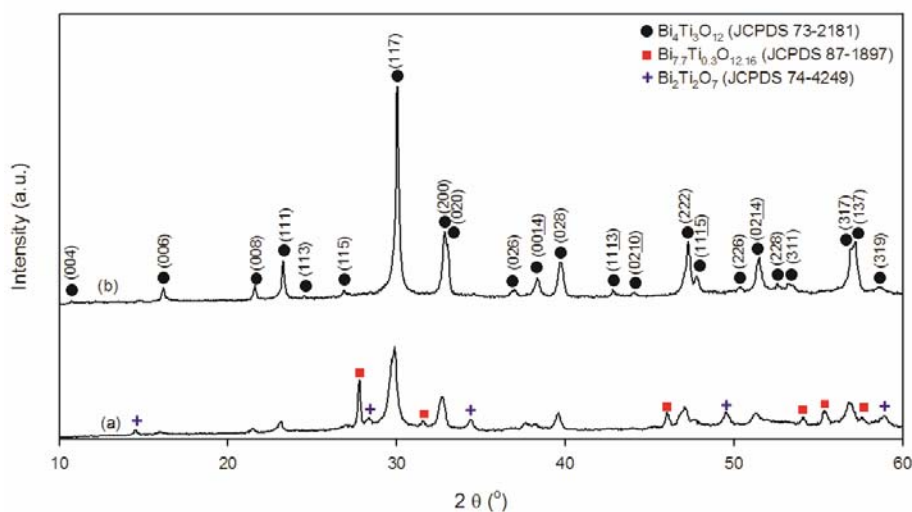

Fig. 1. XRD patterns of the as-combusted powders: (a) SCS and (b) LCS.

Based on calcinations studies, the intermediate phases were gradually eliminated with an increase in calcinations temperature. As can be seen in Fig. 2, the intermediate phases completely disappeared at 750 and 800°C. The result implies that calcinations are essential, in the SCS technique, to form the single phase compound. In addition, the increase in calcinations temperature also implies the improvement of crystallinity. This can be explained by the width of the diffraction lines, which decreased, whilst the intensity increased. The lattice constant, for the powder calcined at 800°C, was determined to be a: 5.4124 Å, b: 5.4429 Å, c: 32.846 Å and the crystallite size was calculated to be 56.7 nm.
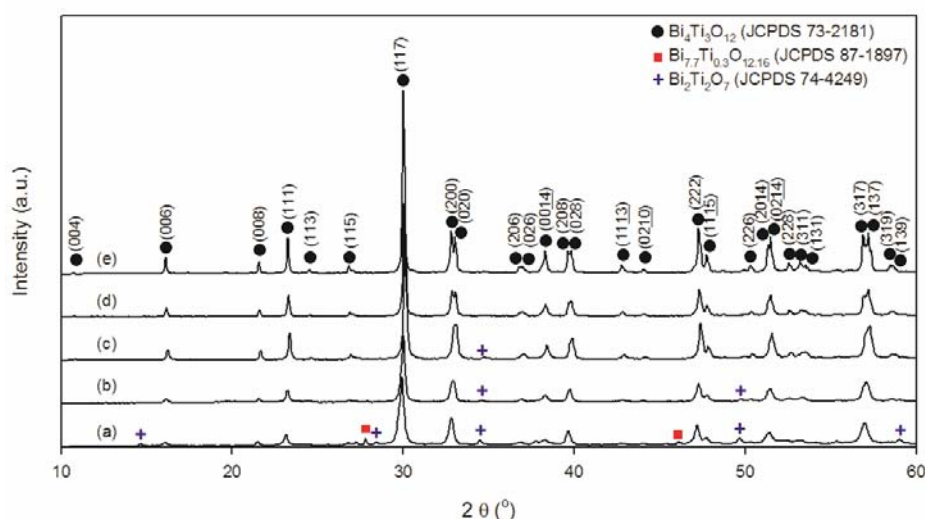

Fig. 2. XRD patterns of the calcined powders at different temperatures: (a) 600°C, (b) 650°C, (c) 700°C, (d) 750°C, and (e) 800°C for 3 hours.

According to both findings, it is necessary to investigate the LCS technique further, because this technique was not engaged with calcinations, in producing the single phase compound. With that, another set of experiments was carried out without NH₄OH addition

into the precursor solution. In order to determine the phase presence, the prepared powder was then analyzed using XRD. It was found that the XRD pattern did not show any diffraction peaks (this result is not shown here). This implies that the amorphous phase is present from the as-combusted powder, when the precursor solution was not added with NH_4OH. This result also suggests that NH_4OH addition is believed to enhance the combustion rate to support the formation of a single phase BTO. Such formation is believed to occur at a very low temperature during the combustion reaction. In order to determine the formation temperature, the as-dried powder (before combustion) was analyzed for its thermal properties. The characteristics of the TG-DTA results are shown in Fig. 3.
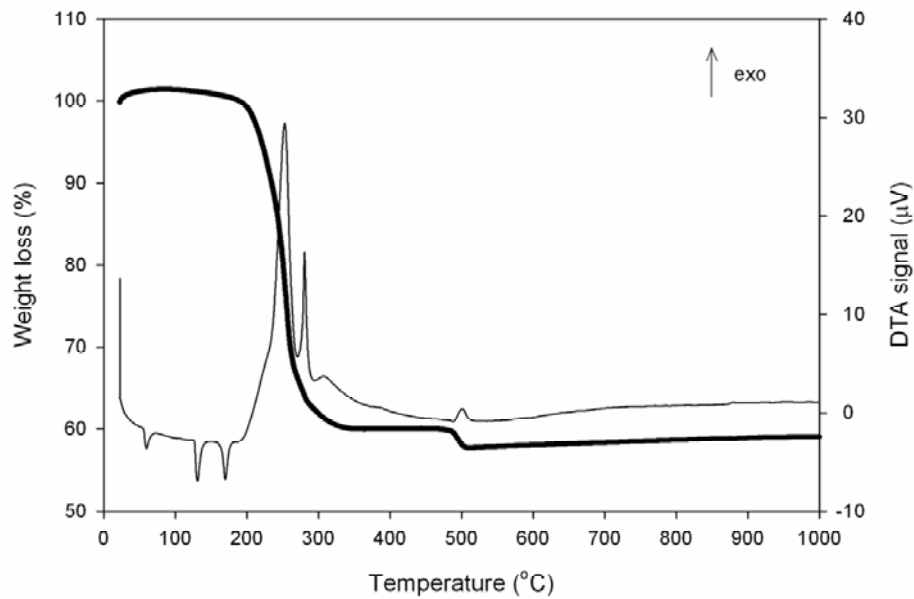

Fig. 3. TG-DTA graphs of the as-dried powder prepared using LCS.

There are three remarkable endothermic peaks and another four noticeable exothermic peaks shown in the DTA graph. The endothermic peaks, corresponding to the adsorption of residual water and remaining solvents, were characterized at 60, 130, and 170°C. The exothermic peaks, corresponding to the combustion of organic species of precursors, were found at 252, 280, and 307°C. This was supported by a major weight loss (of about 40.1%) from 190 to 350°C on the TG curve. Another small exothermic peak (at around 500°C) was attributed to the crystallization of BTO with a minor weight loss. With a further increase in temperature, up to 1,000^{o}C, the DTA curve was free from any peaks and the TG curve was nearly flat. This trend correlates well with the phase detected, based on the XRD analysis, whereby the reaction was stable with the single phase BTO at 500°C and above. As shown in the DTA curve, the area under the exothermic peaks gives the amount of heat produced in the combustion reaction. With that, the large area under the exothermic peaks might be equivalent to the major weight loss on the TG curve. Therefore, the amount of heat produced represents the combustion temperature, approximately in the range of 252 - 280°C.

Fig. 4 shows the XRD patterns of bulk ceramics sintered at 1100°C for 3 hours. Both ceramics were obtained from the calcined powder prepared using SCS and the as-combusted powder prepared using LCS. The XRD patterns show the single phase BTO at this temperature. No peaks from any other phases were observed in the XRD pattern, thus confirming the purity of the ceramics. Nevertheless, there are several peaks that could not be observed in the bulk ceramic prepared using SCS (see Fig. 4(a)), such as (00$\underline{10}$) and (00$\underline{12}$). This result implies that the *c*-axis orientation is not completely formed by SCS. Furthermore,

the peak intensity for (117)-axis is relatively high in the XRD pattern. For comparison, the tremendous increase in peak intensity for (0014)-axis is clearly shown from the bulk ceramics prepared using LCS (see Fig. 4(b)). This result may suggest that the *c*-axis orientation is completely formed by LCS. Thus, it also indicates that the difference in combustion approaches may result in a different preferred grain orientation for highly anisotropic BTO material.
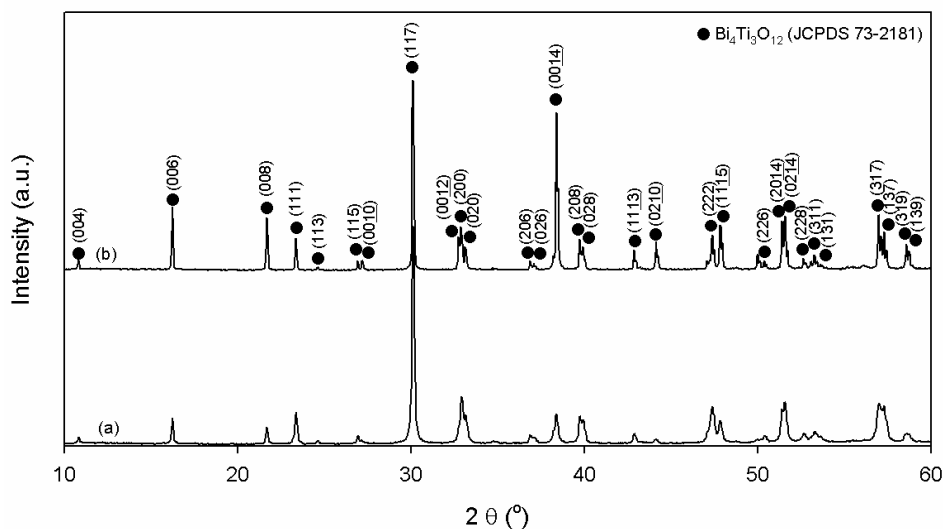

Fig. 4. XRD patterns of the bulk ceramics sintered at $1100^{o}C$ for 3 hours: (a) SCS and (b) LCS.

3.2 Raman analysis

Raman spectroscopy is very useful tool to investigate the structural changes observed in the formation of BTO from the combustion technique. As is known, the increase in Raman peaks implies strong interactions between the ions, which mainly arise from the stretching and bending of the shorter TiO_6 within the anionic groups [13]. In the BTO structure, the TiO_6 octahedron plays an important role in the lattice vibration spectra. Fig. 5 shows the room temperature Raman spectra of powders for different combustion techniques. The spectrum of the powder prepared using SCS, exhibits intense modes at about 268, 539, and 850 cm^{-1}, together with some weak features. By comparison, with the assignment of bulk BTO, the Raman modes at about 229, 268, 328, 539, 566, and 850 cm^{-1} are attributed to the internal vibrational modes of the TiO_6 octahedron. The appearance of vibrational modes of the TiO_6 octahedron indicates that the layered perovskite structure has well formed in such a powder. As shown in Fig. 5, the Raman modes at about 229, 328, 566, and 614 cm^{-1}, disappear in the spectra BTO powder, prepared using LCS. In addition, the intensities of several higher frequency modes, e.g., at 262, 538, and 845 cm^{-1}, appeared both wide and weak. The disappearance of some modes and the decrease of intensities, indicate that the line shape of the Raman modes is strongly dependent on grain size. The morphology of grain size is explained in Section 3.3. Besides that, the increase in intensity with line width decrease reveals the improvement in the crystallinity. In comparison to this study, the BTO powder prepared using SCS showed better crystallinity than the BTO powder prepared using LCS. This result is in agreement with the XRD analysis.
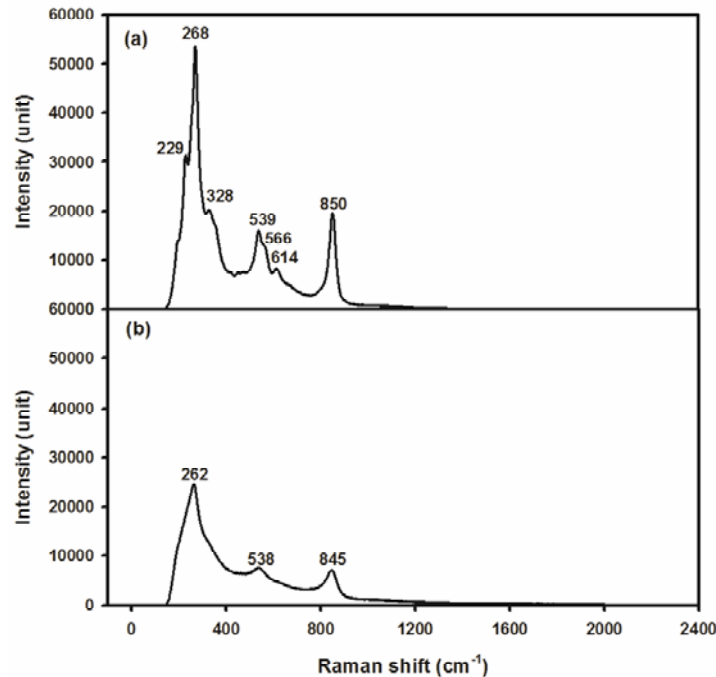
Fig. 5. Room temperature Raman spectra of BTO powders for different combustion techniques: (a) SCS and (b) LCS.

3.3 Microstructure analysis

To gain an insight into the formation of BTO prepared using different techniques in combustion approaches, BTO was monitored by taking FESEM images. Fig. 6 shows the grain morphologies of the powders and the bulk ceramics. As shown in Fig. 6(a), the calcined powder was formed as plate-like grains with an average thickness of 0.31 μm and a length of 2.1 μm. However, the as-combusted powder was formed as a porous structure, as shown in Fig. 6(b). A porous structure is a typical formation for any combustion ceramic material. The formation of such a structure, with different sizes, was mainly attributed to gas release from organic compounds, due to their decomposition during the combustion reaction. Nevertheless, the as-combusted powder consists of small grains approximately 0.1–0.2 μm, with a good homogeneity, as shown by inset Fig. 6(b). The increase in sintering temperature, of 1100°C for 3 hours, is necessary for densification. Fig. 6(c) and 6(d) show the microstructures of the bulk ceramics sintered at 1100°C for 3 hours. It was found that different microstructures are clearly observed after sintering, for both combustion approaches. In Fig. 6(c), the microstructure of the bulk ceramic prepared using SCS, shows a random arrangement of elongated-like grains, several of which are highly elongated. In contrast, the microstructure of the bulk ceramic prepared using LCS (see Fig. 6(d)), shows a random arrangement of plate-like grains. These results are in line to the grain orientation in the XRD pattern, where the elongated-like grain is characterized by the (117)-axis and the plate-like grain is characterized by the *c*-axis.

It is commonly observed that densification during sintering is hindered by the simultaneous growth of randomly aligned, highly elongated grains; particularly when significant elongated grain growth occurs during the earlier stages of sintering. High final densities are difficult to achieve, because matter transport into the interstices between highly elongated grains is normally difficult through solid state diffusion [14]. In the present study,

microstructural observations of bulk ceramics to relative densities are 93.3% and 83%, for the prepared ceramics by SCS and LCS, respectively. The increase in relative density, of 90% and above, indicates that the highly elongated grains start to develop, after significant densification has been achieved. Thus, the effect of the elongated grains is hindered, and densification in the present system is therefore limited. Nevertheless, the decrease in relative density, of the ceramic prepared by LCS, is mainly caused by the porous structure of the as-combusted powder. It is known that this porosity is caused by the out gassing of the absorbed gases and voids, which exist in the compacted sample. This explains the decrease in its relative density.
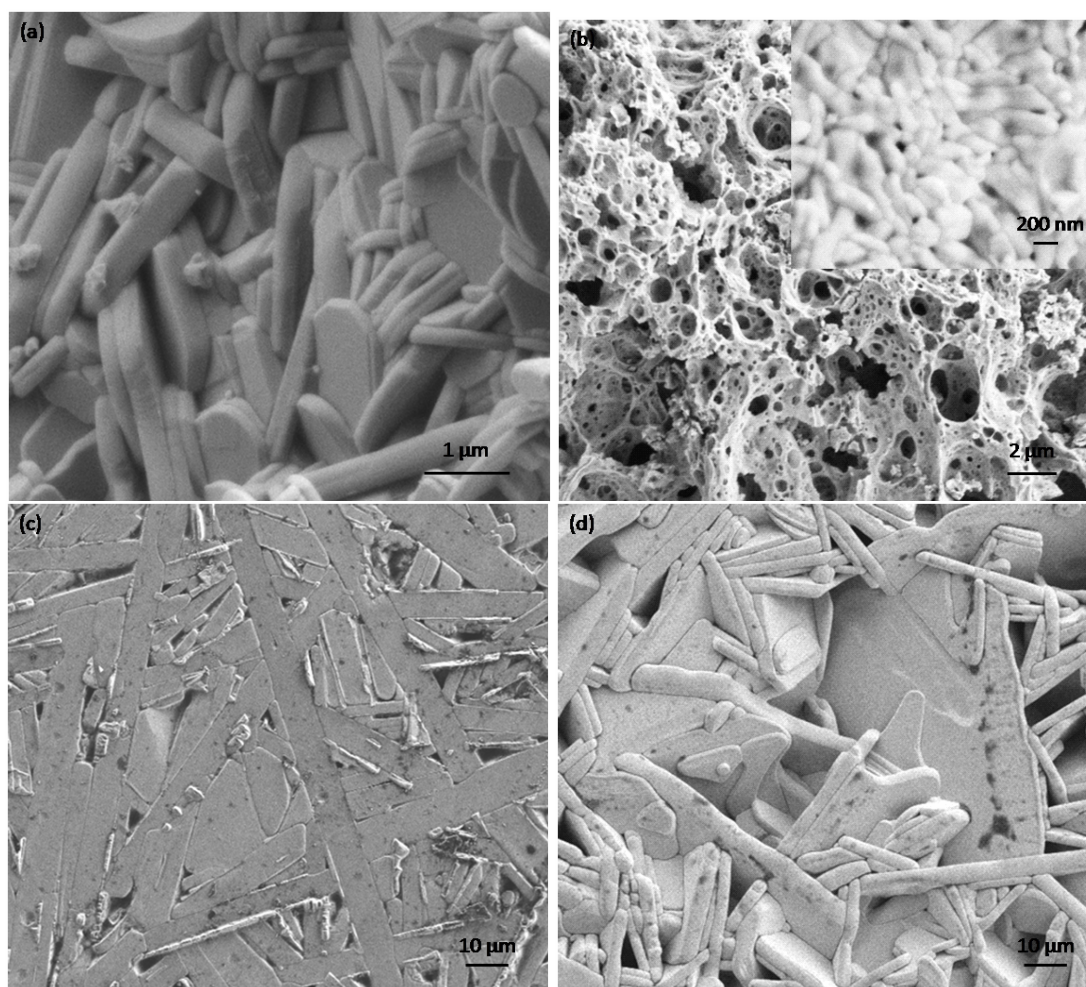

Fig. 6. FESEM images of BTO powder and bulk ceramics: (a) calcined at 800°C for 3 hours, (b) as-combusted for several minutes, and (c) and (d) sintered at 1100°C for 3 hours.

3.4 Dielectric properties

The dielectric properties of the bulk ceramics were studied. Fig. 7 shows the variation of relative permittivity, ε_r and loss tangent, tan δ measured at room temperature, as a function of frequency in the range 1 MHz to 1000 MHz. The dependence of relative permittivity and loss tangent on the combustion technique is clearly shown in Fig. 7. In Fig. 7(a), the bulk ceramic prepared using SCS shows a higher relative permittivity, compared to that of the bulk ceramic prepared using LCS. In Fig. 7(b), the loss tangent of the bulk ceramic prepared using

SCS is given with a lower value, compared to the value given by LCS. These results seem to be caused by differences in bulk ceramic properties. As is known, the increase in relative permittivity is associated with the increase in grain size, and the decrease in the amount of grain boundaries. In particular, the bulk ceramic prepared using SCS has a larger grain size than that of the bulk ceramic prepared using LCS. Therefore, an increase in relative permittivity is expected to occur. The increase in loss tangent is caused by these defects. Compared to that of the bulk ceramic prepared by SCS, the loss tangent of the bulk ceramic prepared using LCS is relatively high when increasing the frequency. Thus, the increase in loss tangent can be explained by the increase of defects, such as high porosity (or low relative density).
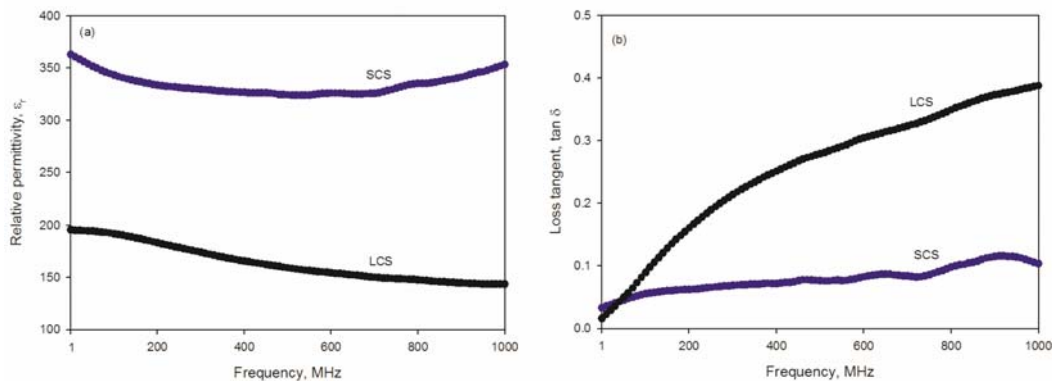

Fig. 7. (a) Frequency dependence of (a) relative permittivity, ε_r and (b) loss tangent, tan δ for the bulk ceramics prepared through different combustion techniques.

3.5 Ferroelectric properties

Fig. 8 shows the hysteresis loops of the bulk ceramics, measured at room temperature, with applied voltages of 5 kV. Well-saturated hysteresis loops were observed for both bulk ceramics.
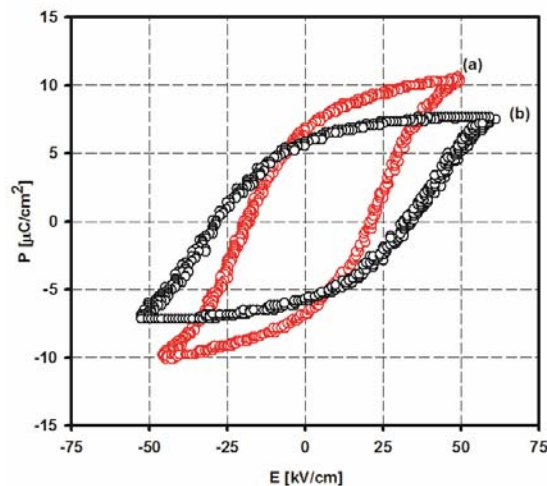

Fig. 8. Hysteresis loops of the bulk ceramics prepared using: (a) SCS and (b) LCS.

The remanent polarization P_r, for the bulk ceramics prepared using both SCS and LCS was 6.8 and 5.9 $\mu C/cm^2$, respectively; whereas the coercive field E_c, was 20 and 30 kV/cm,

respectively. Based on earlier findings, the increase in remanent polarization is contributed to by the increase in the grain size of the bulk ceramics with a strong (117)-preferred grain orientation. In addition, the increase in relative density is crucial, in giving a high remanent polarization. On that basis, the expected result of a low coercive field was also obtained.

3.6 Conclusion

In this work, the BTO powders and the ceramics were successfully prepared using Solution Combustion Synthesis (SCS) and Low-temperature Combustion Synthesis (LCS). Based on all of the findings, the difference in combustion techniques showed a great influence on the single phase formation, structural parameters and crystallite size, grain morphologies and microstructures, preferred grain orientation, relative density, relative permittivity, loss tangent, remanent polarization, and coercive field. In addition, both techniques can be used as an alternative route to prepare BTO bulk ceramics, with better dielectric and ferroelectric properties.

Acknowledgment

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Садржај: *Прах Bi₄Ti₃O₁₂ (ВТО) синтетисан је методом лаганог сагоревања, познатијом као Синтеза Раствора Сагоревањем (СРС) и Ниско-температурска*

Синтеза Сагоревањем (HCC). Рендгено-структурна анализа је показала да је чиста фаза BTO добијена након калцинације на 800 ^{o}C за узорак припремљен методом CPC; у односу на узорак припремљен методом HCC, након сагоревања. Крива TG/DTA показује температуру сагоревања у интервалу 252 – 280 ^{o}C, и постаје стабилна са појавом BTO фазе на 500 ^{o}C и температурама изнад. Синтеровање је вршено на 1100 ^{o}C 3 h, одређивана је микроструктура, оријентација зрна, релативна густина, диелектрична и фероелектрична својства. Утврђено је да керамика припремљена CPC методом има издужена зрна, јаку (117)-оријентацију зрна, релативну густину 93.3 %, ε_r = 320 - 360, tan δ = 0.03 - 0.1, P_r = 6.8 µC/cm^2, и E_c = 20 kV/cm. Даље, керамика припремљена HCC методом има округласта зрна, јаку c-преференцијалну оријентацију зрна, релативну густину од 83 %, ε_r = 143 - 195, tan δ = 0.01 - 0.38, P_r = 5.9 µC/cm^2, и E_c = 30 kV/cm.

Кључне речи*: $Bi_4Ti_3O_{12}$; синтеза сагоревањем; оријентација зрна; диелектрици; фероелектрици.*