Enhanced dielectric properties of Nanocrystalline
Ba\(_{(1-x)}\)Sr\(_x\)TiO\(_3\) (x=0 and 0.3) ceramics

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Abstract. In this paper, we report the enhancement of the dielectric constant of barium titanate (BTO) through partial substitution of strontium to barium and crystallite size reduction through a high power ultrasonic treatment. The sample under investigation is Ba\(_{1-x}\)Sr\(_x\)TiO\(_3\) or BST with x = 0 and 0.3 compositions prepared through mechanical alloying of SrCO\(_3\), BaCO\(_3\) and TiO\(_2\) precursors as the feedstock. All mechanically alloyed samples were crystalline powders with a single phase as confirmed by an x-ray diffractometer (XRD). The mechanically alloyed materials were consisted of multi-crystallite particles as confirmed both by XRD data analysis and particle size evaluation. Subject to an additional ultrasonic treatment, the multi-crystallite particles were fragmented toward mono-crystallite particles with the mean crystallite size about 52 nm after 12 hours irradiation. Even a smaller mean crystallite size (18 nm) with a narrower crystallites distribution then that of BTO was obtained in Ba\(_{1-x}\)Sr\(_x\)TiO\(_3\) with x = 0.3. Such a narrow crystallite size distribution with a small mean crystallite size has superior dielectric constant over those of BTO and doped BTO with a large mean crystallite size. The highest dielectric constant of 3000 was obtained at a frequency of 273 Hz in doped BTO after 12 hours ultrasonic irradiation. The value is 12 times higher than those of BTO and doped BTO with a large crystallite size.

1. Introduction

Barium titanate is a ferroelectric material, which widely used in many applications [1]. For the last few years, research on ferroelectric material have been developing rapidly due to the exponential increase of ferroelectric based materials that required by electronic products producer which should always be able to provide new innovations through improvement in material performances [2]. The characteristics and performance of BTO are influenced by its crystal and materials structure. When refer to previous reports [3,4], it is well known that BTO and Sr substituted BTO or BST possesses a perovskite structure with two different crystal structures, tetragonal and cubic respectively. The BST of both structures could produce unique electrical properties. It was reported that the BST with dopant substituted x≤0. 3 possessed ferroelectric properties with tetragonal crystal structure, while the BST with x≥0. 3 possessed para electric with a cubic crystal structure [4]. Structural modification of BTO like in BST could changes the intrinsic properties of BTO that possesses a better respond to the influence of external field like the changes of electric field, temperature, pressure and electromagnetic wave. Further improvement in properties could be obtained through refining the crystallite size toward nanostructure. There is a large surface to volume ratio in a nanocrystalline system, which expected to
provide the enhancement in properties. Hence, BST based devices should be able to meet the current need of various electronic components with a better performance.

Various synthesis methods to prepare the BST based material have been introduced [5-9]. A few to mention here: sol gel, wet chemical, sonogel, citrate precursor, mechanical alloying and mechanochemical methods. However, among the all mentioned methods, the mechanical alloying has been the one of the most common and the most used because of the following reasons: it is a simple processing method, economically reliable, environmentally friendly and adaptable for a large production capacity [10,11]. The synthesis of strontium titanate based material generated through mechanical alloyed generally have micrometer particle size [12], thus a further treatment in material with nanostructure is required. In spite of various preparation techniques to produce nanometer scale material is available, in the current study, we have selected a mechanical alloying method to prepare the BST crystalline powders coupled with high power ultrasonic irradiation treatment in order to obtain nanoscale powders. It was demonstrated in our previous works [13,14] that crystalline powders with nanometres scale have successfully synthesized through a successive treatment ultrasonically to the mechanically alloyed powders [15,16]. The aim of this study is to increase the dielectric constant of barium titanate (BTO) through partial substitution of Sr\(^{2+}\) ion to Ba\(^{2+}\) during synthesis of the Ba\(_{1-x}\)Sr\(_x\)TiO\(_3\) (BST) by mechanical alloying method coupled with a high frequency of ultrasonic irradiation treatment for further reduction their crystallite sizes.

2. Methodology/experimental

The Ba\(_{1-x}\)Sr\(_x\)TiO\(_3\) with \(x = 0\) and 0.3 were prepared through stoichiometry mixing of the standard research grade BaCO\(_3\), SrCO\(_3\) and TiO\(_2\) precursors of Sigma Aldrich with at least 99% purity level. All precursors were wet-ball milled using alcohol as dispersed media in a planetary ball mill apparatus for 60 hours at a 160 RPM speed. The ratio of ball mill:precursors was 10:1. The mechanical milling process to the precursors has produced heavily deformed powder materials. A 2 wt.% of Poly Vinyl Acetate (PVAc) diluted in a demineralized water were then added to the powder materials for wetting all the particles and let the paste in an oven for drying. The dried particles are poured into a cylindrical die and 10 tons of compacting were employed to make the green compact samples with 25 mm in diameter and 3 mm thickness. The green compact samples were sintered at a temperature of 1200°C for 4 hours. The characterization of polycrystalline samples was performed by X-Ray Diffractometer (XRD) PANalytical Empyrean and analyzed using a High Score Plus (HSP) software. The sintered BST pellet was then hand grounded and re-milled in a ball mill apparatus for 20 hours. The crystalline milled powders were dispersed in aquadest medium, an addition of 0.1% non-ionic surfactant. Ultrasonically irradiated treatments in Qsonica sonicator Q700, operated at 20 kHz with a transducer of 60 \(\mu\)m amplitude for 3, 6, 9 and 12 hours. Particle size characterization of powders was performed by means of particle size analyzers (PSA). The distribution of crystallite size in ultrasonically irradiated powders was calculated from refined XRD employing Whole Powder Pattern Modeling (WPPM) method [17,18].

3. Results and discussion

The diffraction pattern of a polycrystalline sample of \(x = 0\) and 0.3 compositions in the 2 theta range of 20-90° was previously reported along with phase analysis from the pattern [1]. It was shown that for \(x = 0\), the calculated lattice constants of tetragonal structure a and c is respectively 3.99603 Å and 4.02638 Å. While for \(x = 0.3\), the crystal structure changes to cubic with the lattice constants of a and c is 3.97334 Å. Obviously, the lattice changes are due to the presence of a partial Sr\(^{2+}\) ion substitution for Ba\(^{2+}\) in BST in which the ionic radius of Sr\(^{2+}\) is smaller than that of Ba\(^{2+}\) [19].

Figure 1 shows the crystallite size distribution of doped and un-doped BTO, along with their respective cumulative curves. The curve indicates that doped sample (\(x = 0.3\)) has crystallite sizes <140 nm, which were smaller than that of un-doped (\(x = 0\)) sample (<350 nm). Apparently, inhomogeneity of crystallite size in the two samples is the same which indicated by nearly an equal breadth of their
crystallite size distribution. However, the mean crystallite size of the two samples for doped and undoped sample is 19 nm and 52 nm which showing a significant difference.

Figure 1. The crystallite size distribution and cumulative curve of mechanically milled crystalline Ba_{1-x}Sr_xTiO_3 powders.

The crystalite size distribution of particles undergone ultrasonic irradiation at a various irradiation time is compared in figure 2. It shows no significant change in their mean crystallite size, which is in the range 52-64 nm. All treated powders showed almost similar crystallite size distribution.

Figure 2. Crystallite distribution and cumulative curves for un-doped BTO.

Figure 3. Particle size distribution of ultrasonically irradiated powders for un-doped BTO.

In contrary to the crystallites, the ultrasonic treated particles undergone progressive reduction in particle size as the irradiation time was extended from 0 to 12 hours. It is demonstrated in figure 3, the mean particle size of 353 nm in untreated powders was significantly reduced to 52 nm after 12 hours irradiation time. Reduction in particle sizes of mechanically powders was also shown in our previous report [20].

A similar data analysis for doped BTO is shown in figure 4. Trend of crystallite size reduction in doped BTO apparently similar to that of un-doped BTO. Before ultrasonic treatment, the particles have a mean crystallite size 38 nm. After 12 hours irradiation time, the mean crystallite size of
ultrasonic treated particles reduced to 19 nm. It is clear that the treatment has brought devastating effect to the crystallites which fragmented the crystals to the smaller size. Hence, severe effects must also be experienced by the ultrasonically irradiated particles. It is shown in figure 5 which compares plots of the particle size distribution of doped-BTO before and after ultrasonic irradiation.

Prior to the irradiation, the particles are in the range size 100-650 nm. The particle sizes distribution is then gradually changed to the distributions with a much narrower particle size variation after ultrasonic treatment. Plots of particle sizes as shown in figure 5 indicated that the mean size of ultrasonic treated particles is progressively reduced. The longer irradiation time is applied, the smaller the mean size of particles. After the doped-BTO particles experienced ultrasonic treatment for 12 hours, the ultra-fine particles with the mean size of 35 nm was obtained. Plots in figure 5 assures that the increase of ultrasonic irradiation time is not only changing the particle size become smaller but also shows the narrower particle size distribution, which means that the particle size become uniform. It is again showing that the mechanical alloying method coupled with a high power ultrasonic destruction succeeded to produce doped BTO with nanometer scale in crystallite and particle sizes.

Figure 4 is the dielectric constant of the sample made of 12 hours ultrasonically treated particles (BS3T U12) compared with those of ultrasonic treated free (BS3T) and doped free (BTO) samples. The two last samples have an almost similar value of dielectric constant at least in the frequency range 273-1194 Hz. At frequencies lower than 273 Hz, an increase in the dielectric constant of the two samples is observed. At a frequency 203 Hz, the dielectric constant of BS3T sample is more than double of BTO. It was reported that strontium substituted BTO or Ba$_{1-x}$Sr$_x$TiO$_3$ at x=0.3 led to a crystal structure change from tetragonal to cubic, marked with the maximum value of dielectric constant in the whole composition. However, larger values of dielectric constant were obtained from a BS3T U12 sample when compared with the former two in the whole frequency range. At a frequency 203 Hz, the dielectric constant value is 3250 which more than six times larger than that of BTO and about 2.6 times larger than that of BS3T. Hence, the crystal structure and fine crystallite size of BS3T U12 are responsible for the increase in dielectric constant.

In the previous report [21], it was shown that the dielectric constant of the BST (x=0.03) with no additional treatment ultrasonically about 18.55 at a frequency 1 kHz. In another report, the dielectric constant of Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ was 3,870 at a frequency 10 Hz [22]. The improvement of dielectric constant was shown due to the mean crystallite size of material in a nanometer scale that facilitates the grain exchange interaction of electric dipole moments on the surface. The fraction of interacting area will increase the decrease in crystallite size [23].
Materials with fine crystallites size discourage the formation of multi-domain. Single domain grains are formed instead; this resulted in the increase in the dielectric constant of material [24]. The fine crystals with homogeneous single domain microstructure enables the stable and uniform ferroelectric \( \text{BaTiO}_3 \). External strain in grains has also shown a great influenced on the domain structure and nanoparticles is an additional parameter which could influence the domain energy [4].

Figure 7 shows electrical conductivity in the BTO-BS3T-BS3T U12 increased 2.5x10\(^{-8}\); 4.6x10\(^{-8}\); 6.9x10\(^{-8}\) S/cm respectively (f=889 Hz). The AC conductivity increases with increase in the frequency, which may be due to the strong hopping mechanism of ions [25].

4. Conclusion
A single phase of \( \text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3 \) at x=0; 0.3 has successfully synthesized through mechanical alloying method coupled with an additional treatment ultrasonically. The treatment has proven effective to produce monocrystallite particles. Irradiation time to obtain such particles is 12 hrs which led to mono crystallite particles with the mean crystallite size 19 nm in the BS3T-U12 sample. The latter sample has an improved dielectric constant in the whole frequency range 203-1194 Hz over BTO and BS3T samples. A slight distorted cubic structure coupled with a fine mean crystallite size responsible for the improvement. The reduction in particle sizes also increased the electrical conductivity from 2.5x10\(^{-8}\) S/cm (BTO) to 6.9x10\(^{-8}\) S/cm (BS3T U12) at a 889 Hz frequency.

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6. References

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