Multistep sintering: its role on density, phase homogeneity, microstructure and electrical properties of (1-x-y)BaTiO3-xPbZrO3-yNaVO3 System

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Abstract. Barium Titanate synthesized by the oxalate coprecipitation method was doped by other perovskite-based material PbZrO3 and NaVO3 to obtain a system of (1-x-y)BaTiO3-xPbZrO3-yNaVO3 with x = 0.15 and y = 0.025. TGA characterization shows an important weight loss that starts at 400°C and finished at 650°C. XRD analysis of calcined powder at 650°C shows that the samples mostly consist of single-phase BaTiO3 perovskite. Sintering process was carried out in two ways; first, a single step sintering up to 1250°C for 2 hours shows increasing secondary phases, until the BaTiO3 phase becomes the minority. Secondly, multistep sintering starting at 1050°C, holding for 2 hours, down to room temperature, and then repeated with similar processes for 1150°C and 1250°C. Characterizations including XRD, SEM for microstructure, and permittivity analysis of the sample after this thermal treatment shows that the majority phase is BaTiO3 with minor secondary BaVO2.9 phase and its electrical properties are enhanced.

1. Introduction
Ferroelectric materials are one group of materials that are being studied in the development of electronics, as it can be used as sensors and capacitors. Barium Titanate (BaTiO3) is one of those ferroelectric materials, with a perovskite structure. Ferroelectric materials are still being researched to the present day and applied in several industrial and commercial applications [1]. Among the ferroelectric materials, the perovskites (ABO3), including BaTiO3 and PbTiO3, are the most important and widely studied [1, 2]. BaTiO3 (BT) is one of the most widely used ferroelectric ceramic due to its excellent dielectric, ferroelectric and piezoelectric properties [3, 4]. Its transforms from initially ferroelectric to paraelectric occurs around 120 °C (Curie temperature, Tc), above which is cubic symmetry, below the curie temperature, the structure is slightly distorted, taking a tetragonal symmetry [5].

Another perovskite material that has also been widely studied is PbZrO3 (PZ), with its high dielectric permittivity [6], and its various potential applications, amongst other as energy storage [7] and digital displacement transducer [8]. The Curie temperature in pure PbZrO3 is 230°C. Below this temperature, the crystal is in an antiferroelectric state, with the structure changing to an orthorhombic one. However, at or near the Curie temperature, the antiferroelectric phase assumes a tetragonal structure [9]. NaVO3 (NV) is another of the perovskite-based material with a melting point that is relatively low, around 630°C [10], so it can be used to help lower the temperature of calcination/sintering.
Methods of sintering for ceramics are an interesting subject to study because sintering is an important part of ceramic fabrication/processing as it affects the microstructure and density of ceramics [11]. Sintering of any material can also cause several categories of reactions, such as dissociation of compounds, sublimation, evaporation/condensation, and formation of new phases [12]. Multistep sintering can help achieve a fully dense and fine-grained microstructured ceramics [13], and in some cases help achieve the desired crystal phase [14]. In this research, BaTiO$_3$ will be doped with PbZrO$_3$ and NaVO$_3$ to obtain a system of (1-x-y)BaTiO$_3$-xPbZrO$_3$-yNaVO$_3$ with x = 0.15 and y = 0.025. The effect of sintering methods and temperatures on density, phase homogeneity, microstructure, and electrical properties of the materials will be studied.

2. Methods
Precursor BaTiO$_3$ was synthesized using the oxalate coprecipitation method [15], with BaCl$_2$, 2H$_2$O, TiCl$_4$, and C$_2$H$_2$O$_4$·2H$_2$O as raw materials. Precursor PbZrO$_3$ was synthesized using a sol-gel auto combustion method [16] with Pb(NO$_3$)$_2$, ZrCl$_4$, C$_6$H$_8$O$_7$, NH$_4$OH and HNO$_3$ as starting materials, and precursor NaVO$_3$ was synthesized using a conventional solid-state method using Na$_2$CO$_3$ and V$_2$O$_5$ as starting materials. All the precursors are mixed using attritor then calcined to match the stoichiometric calculation to obtain a system of (1-x-y)BaTiO$_3$-xPbZrO$_3$-yNaVO$_3$ with x = 0.15 and y = 0.025. TGA/DTA analysis was done to determine the best calcination temperature for the materials. After calcination, the materials are pressed at 40 MPa to obtain a cylindrical pellet and sintered.

The sintering process was done using two methods: single-step and multistep. For the single-step method, the sintering is done by heating the sample to 1250°C using a 3°C/min increment, holding the temperature for 2 hours, and then down to room temperature at the rate of 3°C/min (Figure 1 a). Meanwhile, the multistep sintering is done in a similar manner starting with heating the sample up to 1050°C, holding for 2 hours, down to room temperature, and then repeated for temperatures of 1150°C and 1250°C (Figure 1 b). XRD analysis was done to determine the crystal phase(s) of the materials. The microstructures of the materials are examined with a Scanning Electron Microscope. The electrical properties of the samples are characterized using Impedance Analyzer Solartron SI 1260.

3. Results and Discussions
TGA characterization of the sample after the mixing of precursors is shown in figure 2. After initial mass loss due to water evaporation from 100°C to ~150°C, it shows a mass loss of about 17% starting at ~160°C until ~400°C. This mass loss can be associated with the breaking-off of oxalate bonding from BaTiO$_3$ precursor and the subsequent release of CO$_2$ gas [15]. From ~400°C to ~600°C there is a mass loss for about 7% which can be caused by decarbonization and release of CO$_2$ gas [15]. The mass losses continue from ~650°C to 900°C which indicates the possible formation of unwanted phase(s). The XRD characterization of the sample calcined at 650°C (figure 3) shows that the sample is almost single phased,
with a relatively small amount of $\text{Ba}_2\text{TiO}_4/\text{Ba}_2\text{Ti}_5\text{O}_{12}$ phases, such as those reported in [17, 18]. Meanwhile, for the calcination at 900°C, the peaks of secondary $\text{Ba}_2\text{TiO}_4$ and $\text{Ba}_2\text{Ti}_5\text{O}_{12}$ phases are relatively higher and therefore the molar percentages of the secondary phases are also higher. The excess of barium and oxygen can generally contribute to the formation of $\text{Ba}_2\text{TiO}_4$ phase [19], as is the thermal treatment time of the sample [17]. Because of these results, it is determined that the optimal temperature for the calcination of the sample is at 650°C.

**Figure 2.** TGA characterization of the sample from room temperature to 900°C.

**Figure 3.** XRD spectra of the sample calcined at 650°C and 900°C ($\bigtriangledown = \text{Ba}_2\text{TiO}_4$, $\ast = \text{Ba}_2\text{Ti}_5\text{O}_{12}$).

**Figure 4.** XRD spectra of samples sintered with single-step sintering method at temperatures 1150°C, 1200°C, and 1250°C labeled as ss1150, ss1200 and ss1250 respectively, and also with multistep sintering at temperature of 1250°C labeled as ms1250 ($\text{BT} = \text{BaTiO}_3$, $\text{BV1} = \text{Ba}_3\text{V}_2\text{O}_8$, $\text{BV2} = \text{BaVO}_{2.9}$ and $\text{PZT} = \text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$).

After calcination, the sample is sintered with single-step sintering method at 1150°C, 1200°C, and 1250°C, and also with multistep sintering method up to 1250°C. From figure 4, it can be seen that the peaks of secondary phases in the samples, which are identified to be $\text{Ba}_3\text{V}_2\text{O}_8$ and $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$, is rising in intensity as the temperature of the single-step sintering rises. At the temperature of 1150°C and 1200°C, the $\text{BaTiO}_3$ phase is still a majority and its peaks have the highest intensity. However, at sintering temperature of 1250°C the peaks $\text{BaTiO}_3$ becomes relatively lower than the peaks of $\text{Ba}_3\text{V}_2\text{O}_8$ and $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ phases. For multistep sintering up to 1250°C, the peaks of $\text{BaTiO}_3$ are the highest, with a minor phase of $\text{BaVO}_{2.9}$ and it differs from the single-step sintering method, where at the temperature of 1250°C the $\text{BaTiO}_3$ phase is a minority. For a single-step sample at around $2\theta = 37^\circ$, there is a peak from an unknown phase. The $\text{Ba}_3\text{V}_2\text{O}_8$ phase also has a peak around that 20, but according to the COD database of the $\text{Ba}_3\text{V}_2\text{O}_8$ phase, the intensity of that peak is very low relative to the intensity of the peak observed.
Table 1. Lattice parameters of BaTiO$_3$ phase in each sample derived from Rietveld refinement of XRD spectra.

| Sample               | Lattice parameters (Å) | Unit cell size (Å$^3$) |
|----------------------|------------------------|------------------------|
|                      | a          | B              | C          |                      |
| Multistep 1250°C     | 4.0251     | 4.0251         | 4.0379     | 65.4197              |
| Single-step 1250°C   | 4.0416     | 4.0416         | 4.0197     | 65.6599              |
| Single-step 1200°C   | 4.0214     | 4.0214         | 4.0440     | 65.3982              |
| Single-step 1150°C   | 4.0164     | 4.0164         | 4.0413     | 65.1921              |

It can be seen from Table 1 that lattice parameters and unit cell size of the BaTiO$_3$ phase, which is the main phase in this system of material, is changing with the change of sintering treatment. The crystal unit sizes of the single-step samples are increasing with increasing sintering temperature. This result is consistent with the XRD spectra (figure 4), where the position of the highest peak from BaTiO$_3$ phase at around $2\theta = 32^\circ$ is slightly shifted to the left for single-step sintering samples. The lattice parameters a and b are also increasing with respect to sintering temperature for single-step sintering samples. However, the lattice parameter c for a single-step sintering sample at a temperature of 1250°C shows an anomaly where it is lower than a, making the c/a value lower than 1. This deformation of the tetragonal structure can possibly be attributed to the existence of a relatively large amount of other phases.

Table 2. The density of the samples with different sintering treatments.

| Sintering treatment | Density (g/cc) |
|---------------------|----------------|
| Single-step 1150°C  | 2.3369         |
| Single-step 1200°C  | 3.2372         |
| Single-step 1250°C  | 5.3939         |
| Multistep 1250°C    | 4.8116         |

Figure 5. SEM images of the sample sintered with a single-step method at 1250°C, for SE at 10k (a), and BSE at 10k magnification (b).

Figure 6. SEM images of the sample sintered with a multistep method up to 1250°C, for SE at 10k (a), and BSE at 10k magnification (b).
Table 2 shows the density of samples with different sintering treatment. It can be seen that for single-step sintering at temperatures of 1150°C and 1200°C, the densities of the samples are relatively still very low. Hence, the temperature used for multistep sintering was chosen to be at 1250°C. The density of the sample sintered with a multistep method up to 1250°C is relatively lower than the sample sintered with a single-step method at the same temperature. This result agrees with the SEM images of the single-step and multistep sample in figure 5 (a) and figure 6 (a) where it can be seen that the single-step sample has relatively fewer pores than the multistep sample. However, the single-step sample is shown to have more abnormal (exaggerated) grain growth than the multistep sample. The microstructure of the multistep sintering sample consists mostly of submicronic grains, where the grain size is around 0.5 µm as seen in figure 6 (a). The BSE SEM images for both samples, shown in figure 5 (b) and figure 6 (b), do not show any visible contrast which indicates that there are no different heavy atoms/ions in the grains.

![Figure 7. Relative permittivity versus temperature of single-step and multistep sintering samples at the frequency of 1 kHz.](image)

![Figure 8. Relative permittivity real ($\varepsilon'$) and imaginary ($\varepsilon''$) versus frequency of single-step sintering (a) and multistep sintering (b) samples at room temperature.](image)
The change in relative permittivity to temperatures for both single-step and multistep sintering samples is shown in figure 7. The relative permittivity of the multistep sintering sample is higher than the single-step sample from room temperature to about 280°C, and the difference is relatively high and noticeable from room temperature to about 100°C, which is the operating temperature range for electronic materials. The single-step sample shows a peak of relative permittivity at 170°C, while there is no peak observed for the multistep sample. This indicates that the phases in the single-step sample go through a Curie (ferroelectric) transition (from tetragonal to cubic symmetry) at that temperature, while for the multistep sample the BaTiO$_3$ phase does not go through that transition. The shift in Curie point in the single-step sample from 120°C (for BaTiO$_3$) to 170°C can be attributed to the existence of a relatively high amount of PZT phase, which has Curie point higher than 200°C [9]. Meanwhile, the lack of Curie point in the multistep sample indicates that the BaTiO$_3$ phase in this sample is already in a cubic structure at room temperature or the tetragonality is very low, that is, the symmetry is pseudocubic. This can also be seen from table 1 where the c/a value for the BaTiO$_3$ phase of the multistep sample is relatively low.

Figure 8 shows the frequency versus real relative permittivity ($\varepsilon'$) and imaginary relative permittivity ($\varepsilon''$) of the single-step and multistep sample at room temperature. The dipolar and space charge polarization of each sample is quite visible. It can be seen that the relative permittivity of the multistep sample is higher at the frequency range of 1 Hz to 1 MHz. For the multistep sintering sample (figure 8 b), Debye relaxations related to both space charge and dipolar polarization are visible at frequencies around 1 mHz and 1 MHz respectively. Meanwhile, for the single-step sample (figure 8 a), only Debye relaxation related to space charge polarization is visible at a frequency around 1 Hz. Figure 9 shows the frequency dependence of the real part of impedance ($Z'$) and the imaginary part of impedance ($Z''$) for both single-step and multistep samples. It can be seen that for the single-step sample, the $Z'$ value initially decreases up to about 1 kHz and then remains at almost a constant value with the rise in frequency. Meanwhile, the value of $Z''$ increased initially and attains a peak at around 100 Hz and then decreases with frequency to around 100 kHz, then remains at almost a constant value with the rise of frequency. This independence of $Z'$ and $Z''$ to frequency at high frequencies may be due to the release of space charge polarization [20, 21]. For the multistep sample, the $Z'$ and $Z''$ value shows a similar curve, where the values are decreasing initially and then shows independence to the frequency at around 10 Hz for $Z'$ and around 100 Hz for $Z''$. From this characteristic, it can be inferred that the release of space charge polarization in the multistep sample happens in lower frequency than those in the single-step sample.

![Figure 9](image_url)

**Figure 9.** Impedance real ($Z'$) and impedance imaginary ($Z''$) versus frequency of a single step (a) and multistep (b) samples at room temperature.
Figure 10 shows the change in dielectric loss ($\tan \delta$), quality factor $Q$ and $Qxf$ of the samples. It can be seen that the dielectric loss of both samples are decreasing originally, but the dielectric loss for the single-step sample is much higher. This relatively high difference in dielectric loss at a low frequency can be associated with high impurities and/or microstructural defects (exaggerated grain growth) which existed in the single-step sample [22, 23]. The space charge (interfacial) polarization is associated with the dielectric loss at this low frequency [23]. At higher frequency around 100 kHz, the dielectric loss of the multistep sample began to increase again and become slightly higher than the single-step sample, which might be associated to the dipolar polarization. For the quality factor $Q$ (figure 10 b), which is the reciprocal of $\tan \delta$, it can be seen that both samples have similar curve, where the $Q$ value increases, reach a maximum, and then decreases. It can be noted that the value of quality factor $Q$ is higher for the multistep sample from about 1 Hz to around 50 kHz. The $Qxf$ graph (figure 10 c) also shows similar curve, except that the value of $Qxf$ is not shown to be decreasing.

4. Conclusions
Multistep and single-step sintering of a (1-x-y)BaTiO$_3$-xPbZrO$_3$-yNaVO$_3$ system of material results in different properties for each method of sintering. The XRD characterization of the multistep sintering sample at 1250°C shows that the BaTiO$_3$ phase is a majority, with minor secondary BaVO$_2$ phase. Meanwhile, for the single-step sintering of the sample at 1250°C, the BaTiO$_3$ phase is a minority, with other phases Ba$_3$V$_2$O$_8$ and PbZr$_{0.52}$Ti$_{0.48}$O$_3$ being the majorities. A highly dense sample can be achieved with sintering at 1250°C. The density of the multistep sintering sample at 1250°C is relatively lower than the density of a single-step sintering sample at the same temperature. This is substantiated by the SEM images of the samples where it was shown that the multistep sample has more pores than the single-step sample. However, the single-step sample has more exaggerated grain growth.

The relative permittivity of the multistep sample at 1 kHz is relatively higher than the single-step sample from room temperature to about 280°C. The difference in relative permittivity between the two samples is relatively high and noticeable from room temperature to 100°C, which is the temperature range of most electronic devices. The relative permittivity of the multistep sample at room temperature is also higher than the single-step sample from ~1 Hz to ~1 MHz. The dielectric loss of the single-step sample is higher than the multistep sample at low frequency, possibly due to high impurities or microstructural defects which existed in the single-step sample. Meanwhile, the quality factor $Q$ and $Qxf$ for multistep sample is higher at frequency range from ~1 Hz to ~50 kHz. Thus it can be said, generally, that the electrical (dielectric) properties of multistep sample is better than the single-step sample.

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