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To cite this article: Phan Gia Le, Thuy Linh Pham, Dang Thanh Nguyen, Jong-Sook Lee, John G. Fisher, Hwang-Pill Kim & Wook Jo (2021) Solid state crystal growth of single crystals of 0.75(Na$_{1/2}$Bi$_{1/2}$)TiO$_3$-0.25SrTiO$_3$ and their characteristic electrical properties, Journal of Asian Ceramic Societies, 9:1, 63-74, DOI: 10.1080/21870764.2020.1847426

To link to this article: https://doi.org/10.1080/21870764.2020.1847426

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Published online: 18 Nov 2020.

Article views: 538

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Solid state crystal growth of single crystals of $0.75(Na_{1/2}Bi_{1/2})TiO_3$-$0.25SrTiO_3$ and their characteristic electrical properties

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ABSTRACT

Ceramics of composition $0.75(Na_{1/2}Bi_{1/2})TiO_3$-$0.25SrTiO_3$ (NBT-25ST) show a giant electric field-induced strain, making them attractive for actuator applications. Single crystals generally have improved piezoelectric properties over their ceramic counterparts, but the electrical properties of NBT-25ST single crystals have not yet been studied. In this work, NBT-25ST single crystals are grown by the solid state crystal growth technique and their electrical properties measured for the first time. The single crystals show relaxor ferroelectric behavior typical of an NBT-type material. The ferroelectric and inverse piezoelectric properties depend strongly on crystallographic orientation, with superior properties in the (001) orientation. The inverse piezoelectric properties of the (001)-oriented NBT-25ST single crystal are superior to those of an NBT-25ST ceramic ($S_{\text{max}}/E_{\text{max}} = 1042$ pm/V vs. 739 pm/V).

1. Introduction

Piezoelectric materials have been applied in many areas such as electric fuel injection, autofocus mechanisms, inkjet printers, optical lenses and mirrors [1,2]. A piezoelectric material can be designed based on physical dimensions, displacement (stroke), blocking force, maximum strain, temperature range, frequency range and voltage range [3–5]. Piezoelectric materials must operate in many different environments and are affected by many factors such as temperature, frequency, pressure and humidity [3–5]. At the present time, the global market for piezoelectric materials is dominated by Lead Zirconate Titanate (PZT), which has excellent piezoelectric properties such as $S_{\text{max}}/E_{\text{max}} \approx 700$ pm/V, $e_{33}/\varepsilon_0 = 2300$, $T_c = 250\, ^{\circ}\text{C}$ [2,6–8]. However, the high concentration of lead in PZT can negatively affect human health and the environment [2]. To mitigate these effects, restrictions on the amount of lead permissible in electronic devices have been applied through the RoHS and WEEE regulations from the European Union and similar legislation from various countries [2,7,9]. Therefore, the discovery of new lead-free materials with piezoelectric properties that are comparable to PZT is urgently required. Many efforts from researchers to look for and discover new material systems have been in progress. Many methods were proposed to improve the piezoelectric properties of well-known lead-free systems by making binary or ternary solid solutions, doping or fabrication of single crystals [2,3,10–21].

Sodium Bismuth Titanate, $(Na_{1/2}Bi_{1/2})TiO_3$ (NBT), is a relaxor ferroelectric material with high coercive electric field that makes it difficult to pole [2,22]. Below $255\, ^{\circ}\text{C}$, NBT is rhombohedral. The space group is generally considered to be $R3c$ [23,24], although a monoclinic structure (space group $Cc$) is also possible [25]. Rhombohedral to tetragonal ($P4bm$) and tetragonal to cubic ($Pm\bar{3}m$) phase transitions take place at $\sim 255\, ^{\circ}\text{C}$ and $\sim 540\, ^{\circ}\text{C}$, respectively [24,26–28]. The rhombohedral and tetragonal phases co-exist between $255$–$400\, ^{\circ}\text{C}$, while the tetragonal and cubic phases co-exist between $500$–$540\, ^{\circ}\text{C}$ [24]. To improve the electrical properties, SrTiO$_3$ (ST) was combined with NBT; the Sr$^{2+}$ ion is dispersed in the NBT crystal lattice to make a solid solution [11,29]. The coercive electric field is decreased, which assists poling [30]. Addition of ST to NBT causes the NBT rhombohedral structure to change to a pseudocubic structure as ST concentration increases, with a morphotropic phase boundary (MPB) existing between rhombohedral and pseudocubic phases at $x \approx 0.25$ [11,31,32]. At compositions near the MPB the piezoelectric properties can be improved, at the cost of a reduction in the depolarization temperature $T_d$ and the rhombohedral to tetragonal phase transition temperature $T_{R-T}$ [29–32]. Hiruma et al. studied the (100-x)NBT-xST system and found that compositions near the MPB with $x = 26$–28 mol % had improved inverse piezoelectric properties with a strain of 0.29% and a normalized strain $S_{\text{max}}/E_{\text{max}}$ of 488 pm/V [11]. Acosta et al. found that 75 mol % $(Na_{1/2}$

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\begin{supplementary}
\textsuperscript{a} English language editing provided by the ELD editorial team. \textsuperscript{b} Supplemental data for this article can be accessed here.
\end{supplementary}
B_{1/2}TiO_3 – 25 mol % SrTiO_3 (NBT-25ST) ceramics, which have a composition close to the MPB, showed a normalized strain S_{max}/E_{max} of 600–700 pm/V at a relatively low electric field of 4 kV/mm [3].

Single crystals of NBT-based compositions generally have improved properties relative to their ceramic counterparts [33,34]. Some NBT-BT single crystals with compositions near to the morphotropic phase boundary between rhombohedral and tetragonal phases exhibit a high S_{max}/E_{max} and free strain such as 0.945(Na_{1/2}Bi_{1/2}TiO_3-0.055BaTiO_3, with S_{max}/E_{max} ≈ 1420 pm/V and 0.44% strain, and Na_{1/2}Bi_{1/2}TiO_3-Ba(Ti,Zr)O_3, with S_{max}/E_{max} ≈ 2000 pm/V and 0.45% strain [35–37]. Single crystals of (Na_{1/2}Bi_{1/2}TiO_3)-BaTiO_3-(K_0.5N_0.5)NbO_3 (NBT-BT-KNN) compositions showed a giant strain of 0.57% and S_{max}/E_{max} of 950 pm/V [38] and a giant strain of 0.83% at an electric field of 28 kV/cm [39]. Single crystals of NBT-25ST may also have improved piezoelectric properties, but as of yet only limited work on single crystal growth in this system has been reported and the electrical properties have not been measured [13].

In the present work, the solid state crystal growth technique is used to grow single crystals [40,41]. In this technique, a piece of single crystal (the seed crystal) is buried inside the polycrystalline powder of the composition to be grown, pressed into a pellet and then sintered. A single crystal with the same composition as the powder grows epitaxially on the seed crystal. The relatively low processing temperature (lower than the melting point of the compound to be grown) helps the single crystal preserve its stoichiometry and chemical homogeneity. Solid state crystal growth has been used to grow single crystals with properties comparable to those of conventionally-grown single crystal. Single crystals of (Na_{1/2}Bi_{1/2}TiO_3)-BaTiO_3, (Na_{1/2}Bi_{1/2}TiO_3)-Ba(Ti,Zr)O_3, (Na_{1/2}Bi_{1/2}TiO_3)-CaTiO_3, (Na_{1/2}Bi_{1/2}TiO_3)-SrTiO_3 and (Na_{1/2}Bi_{1/2}TiO_3)-BaTiO_3-(K_0.5N_0.5)NbO_3 have been grown by this technique [13,15,33,38,42–45]. In the present work, single crystals of 75 mol % (Na_{1/2}Bi_{1/2}TiO_3 – 25 mol % SrTiO_3 (NBT-25ST) are grown by solid state crystal growth and the microstructure and electrical properties of the grown single crystals are studied. Single crystals of NBT-25ST are found to have significantly improved inverse piezoelectric properties over their ceramic counterparts.

2. Experimental

The NBT-25ST powder is synthesized from Na_2CO_3 (ACROS organics, 99.5%), Bi_2O_3 (Alfa Aesar, 99.9%), TiO_2 (Alfa Aesar, 99.8%) and SrCO_3 (Aldrich, ≥ 99.9%) starting materials by solid state reaction. For further details, see reference [13]. SrTiO_3 single crystal seeds (MTI Corp., CA) with (110) orientation and dimensions of 5 mm × 5 mm × 0.5 mm are buried in 0.5 g of powder in a 10 mm steel die which is then pressed by hand into pellets, followed by cold isostatic pressing at 1500 kg cm^{-2} (~147 MPa). The pellets are sintered at 1250°C for 5 h with heating and cooling rates of 5°C.min^{-1}. To reduce volatilization of Na and Bi during sintering, the pellets are buried in a 2 wt% Na_2CO_3 ~ 2 wt% Bi_2O_3 ~ 96 wt% NBT-25ST packing powder in double alumina crucibles with lids. A schematic diagram of the experiment is shown in Figure S 1(a).

To study the microstructure, samples are vertically sectioned, polished to a 1 μm finish with diamond suspension and thermally etched at 1200°C for 1 h. The etched samples are Pt-coated and observed by Scanning Electron Microscopy (SEM, Hitachi S-4700, Tokyo, Japan) with attached Energy Dispersive X-ray spectrometer (EDS, EMAX energy EX-200, Horiba, Kyoto, Japan). The mean matrix grain size and matrix grain size distribution are analyzed from the SEM micrographs using imageJ v1.50a image analysis software (National Institute of Mental Health, Bethesda, MD). To analyze the mean matrix grain size and grain size distribution, the equivalent 2D radii of at least 200 grains are analyzed. For EDS analysis, a polished and un-etched sample was used.

To study the structure, a single crystal sample is polished with SiC paper up to grade #4000 to expose NBT-25ST single crystal faces with (110) orientation on both sides. The sample is analyzed by X-ray diffraction (XRD, X’Pert PRO, PANalytical, Almelo, the Netherlands) using CuKα radiation, a scan range of 20–90° 2θ and a scan speed of 3°.min^{-1}. Kα peak removal was carried out using MDI Jade 6.5 (Materials Data Inc., CA). For micro-Raman scattering, a single crystal sample is removed from the matrix and polished to a 1 μm finish with diamond suspension to expose the (110)-oriented NBT-25ST single crystal face on one side. To remove strains generated during polishing, the sample is annealed at 400°C for 1 h and cooled at a rate of 1°C. min^{-1}. Micro-Raman scattering is carried out with a 514 nm Ar⁺ ion laser and output power of 10 mW (LabRam HR800 UV Raman microscope, Horiba Jobin-Yvon, France). The Raman spectrum is recorded at room temperature in back scattering geometry with a resolution of ~0.5 cm⁻¹. The diameter of the laser spot on the sample is 1–2 μm. Peak fitting of Gaussian peaks is carried out using fit2k 0.9.8 peak fitting software [46].

To carry out impedance spectroscopy, the single crystal sample that had been prepared for XRD analysis is used. Both (110) faces of the single crystal are coated with Pt-paste and the sample is annealed at 900°C for 30 min with heating and cooling rates of 5°C.min^{-1} to prepare Pt electrodes. An impedance analyzer (HP4284A, Hewlett-Packard, Kobe, Japan) is used to record the electrical properties of the sample at different temperatures and frequencies. The sample is measured in a furnace in the temperature range of 30 to 800°C in oxygen with heating and cooling rates of 1°C.min⁻¹. The AC voltage was set at 0.1 V and the
frequency range from 1000 kHz to 39.8 Hz. For comparison, a ceramic NBT-25ST sample is prepared by sintering a 0.3 g pellet (without seed crystal) at 1250°C for 1 h, with heating and cooling rates of 5°C.min⁻¹ and its electrical properties measured in the same way.

As will be seen, the single crystals of NBT-25ST grown by solid state crystal growth are limited in thickness. In order to prepare larger NBT-25ST single crystals for measurement of the inverse piezoelectric properties, top-seeded solid state crystal growth experiments are carried out [47]. Details of these experiments, as well as details of the SEM and XRD analyses, are provided in the supplemental material. Single crystal samples with (110) and (001) major faces are prepared for electrical property measurements (Figure 5.2). For polarization and strain hysteresis measurements, silver paste electrodes are applied on the (110) or (001) major faces of the samples. The external electric field (E) dependencies of polarization (P) and strain (S) hysteresis are measured in a commercial apparatus, aixPES (aixACCT system GmbH, Aachen, Germany) using a bipolar electric field profile at 1 Hz. To carry out impedance spectroscopy, Pt paste electrodes are applied as before. Samples are measured in the temperature range of 70 to 800°C in oxygen with heating and cooling rates of 1°C.min⁻¹. The AC voltage was set at 1 V and the frequency range from 1000 kHz to 39.8 Hz.

3. Results

An SEM micrograph of a sample are shown in Figure 1. An NBT-25ST single crystal has grown epitaxially on the SrTiO₃ seed crystal. At a sintering temperature of 1250°C, a grown single crystal thickness of ~315 μm was obtained after sintering for 5 h. In the matrix, coarse grains are predominant (Figure 3.3(a)). Porosity is visible in both the single crystal and the matrix grains. Micro-faceting of the grains is visible as steps on the grain boundaries. Some examples are marked with arrows in Figure 3(b). The matrix grain size distribution shows that the matrix grains have a bimodal size distribution with the largest grain reaching to ~85 μm in radius as shown in Figure 3(b). The mean size and standard deviation of the matrix grains is 21 ± 16 μm.

Energy Dispersive X-ray Spectroscopy (EDS) results are shown in Table 1. EDS was taken on ten points on the single crystal and ten points on the matrix grains. The results show the mean and standard deviation. The NBT-25ST single crystal is slightly deficient in Na and has an excess of Bi. The matrix grains show similar behavior but the Na loss is less pronounced and the Bi excess is slightly more pronounced.

The NBT-25ST single crystal sample shows two peaks in the XRD pattern (Figure 2), which can be indexed as 110 and 220 peaks using pseudocubic indices. The top and bottom faces of the single crystal sample show identical XRD patterns, showing that the sample is single crystalline throughout its thickness. An XRD pattern of a (110) oriented SrTiO₃ single crystal substrate is also shown for comparison. The positions and δ-spacings of the 110 peaks for the NBT-25ST and SrTiO₃ single crystals are given in Table 1. The XRD results show that the NBT-25ST single crystal has epitaxially grown on the SrTiO₃ seed crystal. However, the peak positions and lattice parameters of the substrate and grown single crystal are slightly different, so the grown single crystal has some mismatch with the seed sample.

![Figure 1. SEM micrograph of an NBT-25ST single crystal grown by solid state crystal growth.](image1)

![Figure 2. X-ray diffraction patterns of a single crystal NBT-25ST sample grown by solid state crystal growth and a SrTiO₃ seed crystal.](image2)

### Table 1. EDS analysis results of an NBT-25ST single crystal grown by solid state crystal growth and its surrounding matrix grains.

| Element | Single crystal (at. %) | Matrix grains (at. %) | Nominal value (at. %) |
|---------|------------------------|-----------------------|-----------------------|
| O       | 38.3 ± 2.5             | 57.4 ± 3.1            | 60                    |
| Na      | 7.0 ± 0.9              | 7.4 ± 1.4             | 7.5                   |
| Ti      | 20.1 ± 1.8             | 21.0 ± 1.9            | 20                    |
| Sr      | 5.7 ± 0.6              | 5.3 ± 0.7             | 5                     |
| Bi      | 8.6 ± 0.7              | 8.9 ± 0.7             | 7.5                   |
crystal. A Raman spectrum of the NBT-25ST single crystal is shown in Figure 3. The black curve is the experimental data, the blue curves are the fitted peaks and the red curve is the sum of the fitted peaks. Gaussian peaks were fitted as this peak shape is more suitable for fitting the spectra of solids [48]. Wavenumber regions corresponding to the different types of vibrations (described in the Discussion) are indicated.

The impedance spectroscopy results of the NBT-25ST single crystal and polycrystalline samples are presented in Figure 4. The numbers in the legends are the logarithmic values of the measurement frequency. The curved arrows show the directions of increasing measurement frequency. The plots of the real part of the relative permittivity $\varepsilon'$, vs. temperature show broad peaks with a maximum at $\sim 190^\circ$C (Figure 4(a,d)). At temperatures below the peak temperature, the value of $\varepsilon'$ decreases as measurement frequency increases. At temperatures close to and above the peak temperature, $\varepsilon'$ does not show much dispersion with frequency. A shoulder is visible in the $\varepsilon'$ vs. temperature curves of the single crystal sample at $\sim 135^\circ$C. A corresponding shoulder is hardly visible in the polycrystalline sample. In the curves for the polycrystalline sample, peaks are visible at temperatures $> 500^\circ$C, becoming smaller as measurement frequency increases. These peaks are due to polarization effects at the electrodes. In the plots of loss tangent vs. temperature, peaks corresponding to the $\varepsilon''$ shoulder at $\sim 135^\circ$C are clearly visible, both in the single crystal and polycrystalline samples (Figure 4(b,e)). The peaks move to higher temperature and larger value of loss tangent with increasing measurement frequency. Loss tangent minima, corresponding to the peaks in $\varepsilon''$, are visible at lower measurement frequencies. The low frequency data for $\varepsilon''$ and loss tangent are not shown as it is very noisy. As previously reported [15,43,49–51], from the AC conductivity curves (Figure 4(c,f)), activation energies of 1.65 eV and 1.19 eV above $\sim 600^\circ$C at the low frequency limit can be estimated for the single crystal and polycrystalline samples respectively (calculated from the data measured at 39.8 Hz) [52,53].

An SEM micrograph of an NBT-25ST single crystal grown by top-seeded solid state crystal growth is shown in Figure 5. A single crystal of NBT-25ST has grown $\sim 1,200 \mu$m in the [110] direction. The interfacial region between the single crystal and the matrix grains

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**Figure 3.** Raman spectrum of an NBT-25ST single crystal grown by solid state crystal growth. The black curve is the experimental data, the blue curves are the fitted Gaussian peaks and the red curve is the sum of the fitted peaks. Wavenumber regions corresponding to the different types of vibrations are indicated.

**Figure 4.** Real part of the relative permittivity, loss tangent and conductivity as functions of temperature measured in the temperature range from 30 to 800°C on (a) – (c) an NBT-25ST single crystal grown by solid state crystal growth and (d) – (f) an NBT-25ST polycrystalline sample. The numbers in the legends are the logarithmic values of the measurement frequency.
is shown in Figure 5. A secondary phase can be seen at the matrix grain boundaries and in the single crystal. EDS analysis of the secondary phase in the matrix shows it to be TiO₂. The secondary phase in the single crystal may be an artifact caused by thermal etching [15,42]. The matrix grain size distribution of this sample is shown in Figure 5. The mean and standard deviation of the matrix grain size is 14 ± 6 μm. EDS analysis results are shown in Table 2. Each value is the mean and standard deviation of five measurement points. Both the single crystal and the matrix grains have excess Na and Bi compared to the nominal values.

Figure 5 shows the NBT-25ST single crystals oriented in the [100] and [110] directions with their dimensions. Figure 5 shows XRD patterns of the single crystals. The peaks are again indexed using pseudocubic indices. The peaks of the (001)-oriented single crystal show shoulders on the low angle side. These may be caused by a skin layer on the sample [54]. The Rietveld refinement results of the annealed powder sample prepared from a polycrystalline NBT-25ST ceramic are given in Table 5. Refinement was carried out using rhombohedral (R3c), tetragonal (P4bm), cubic (Pm3m) and coexisting rhombohedral + tetragonal, rhombohedral + cubic and tetragonal + cubic phases. Coexisting rhombohedral and cubic phases provide the best fit to the data. The XRD pattern, Rietveld refinement and difference plot of the annealed polycrystalline NBT-25ST powder sample is shown in Figure 5. The pattern was fitted with coexisting rhombohedral (R3c) and cubic (Pm3m) phases. The sample contains ~76 vol. % rhombohedral phase and ~24 vol. % cubic phase.

The polarization-electric field (PE) and bipolar strain-electric field (SE) hysteresis loops of the (001)- and (110)-oriented NBT-25ST single crystal samples are shown in Figure 6. For comparison, polarization and strain hysteresis curves of a polycrystalline sample (sintered at 1250°C for 1 h) are also shown. The properties of the samples are given in Table 3. The (001)-oriented NBT-25ST single crystal sample has a narrow, pinched PE loop and a sprout-shaped SE bipolar loop with almost remanent and negative strain (Figure 6(a,b)). The polycrystalline NBT-25ST sample also has a narrow, pinched PE loop and a sprout-shaped SE bipolar loop (Figure 6(e,f)). The properties of the polycrystalline NBT-25ST sample are comparable to those previously measured [3,11]. Compared with the polycrystalline sample, the (001)-oriented single crystal shows lower coercivity E₀, increased saturation polarization Pₛ, remnant polarization P₀, and maximum strain Sₘₐₓ an increase in Sₘₐₓ/E₀ of 41% and a reduced strain hysteresis ΔS/Sₘₐₓ of 18%, where ΔS is the difference in strain between the upper and lower parts of the curve when E = maximum electric field Eₘₐₓ/2 [38]. The Sₘₐₓ/Eₘₐₓ value of the (001)-oriented NBT-25ST single crystal sample is comparable to those of (Na₁/₂Bi₁/₂)TiO₃-BaTiO₃-(K₀.₅N₀.₅)NbO₃ single crystals [38,44].

The behavior of the (110)-oriented NBT-25ST single crystal is quite different (Figure 6(c,d)). The PE hysteresis loops are slim but do not have a pinched appearance. The PE loops are also not well saturated with relatively low Pₛ. The bipolar SE loops are also slim with almost zero remanent and negative strain, but the shape is slightly different to that of the (001)-oriented NBT-25ST single crystal and also that of the polycrystalline sample. Sₘₐₓ is also greatly reduced.

The impedance spectroscopy results of the (001) and (110)-oriented NBT-25ST single crystals are presented in Figure 6. The results appear similar to those in Figure 4. However, the temperature of maximum ε', increases to ~215°C and the values of loss tangent in the temperature range 400–600°C are larger than those of the single crystal in Figure 4. The plots of ε' vs. temperature for both orientations have a shoulder at ~135°C. The values of ε' for the (001)-oriented single crystal are larger than those of the (110)-oriented single crystal. In the plots of loss tangent vs. temperature, the drop in loss tangent corresponding to the shoulder in ε' is more clearly defined for the (001)-oriented sample.

### Table 2. EDS analysis results of an NBT-25ST single crystal grown by top seeded solid state crystal growth and its surrounding matrix grains.

| Element | Single crystal (at. %) | Matrix grains (at. %) | Nominal value (at. %) |
|---------|-----------------------|-----------------------|-----------------------|
| O       | 59.3 ± 2.8            | 58.4 ± 4.8            | 60                    |
| Na      | 8.3 ± 1.2             | 7.7 ± 2.3             | 7.5                   |
| Ti      | 18.7 ± 1.3            | 19.6 ± 2.0            | 20                    |
| Sr      | 5.2 ± 1.0             | 5.1 ± 0.4             | 5                     |
| Bi      | 8.6 ± 0.4             | 9.2 ± 0.8             | 7.5                   |

### 4. Discussion

In the solid state crystal growth technique, the seed crystal acts as a rapidly growing abnormal grain and consumes the surrounding matrix grains, causing a single crystal of the matrix composition to grow epitaxially onto the seed [41,55]. For single crystal growth to take place, the grain boundaries must be
ordered [41,56], as was found in previous work on NBT-based ceramics [13,57,58] and as indicated by the presence of micro-facets at the grain boundaries (Figure S 3(a)) [59]. The broad matrix grain size distribution (Figure S 3(b)) shows that abnormal grain growth has occurred, where abnormal grains are defined as grains with a radius greater than three times the mean grain radius [58].

As the single crystal’s driving force for growth decreases as mean matrix grain size increases [41], retarding grain growth in the matrix (especially abnormal grain growth) is important in order to grow a large
crystal. The NBT-25ST system suffers from abnormal grain growth, as can be seen in Figure S 3, which restricts growth of the single crystal. In the single crystals grown by top-seeded solid state crystal growth, the single crystal growth distance is larger and the matrix grains are smaller than in the sample grown by solid state crystal growth (Figure 5 and Figure S 4(a)). Also, the grain size distribution is narrower (Figure S 4(b)). During the pre-sintering step at 900°C some matrix grain growth will take place. This will lower the driving force for growth of the matrix grains in the subsequent annealing step at 1250°C [60], reducing their growth rate and delaying the onset of abnormal grain growth. The smaller matrix grain size means an increased driving force for single crystal growth, leading to increased single crystal growth. The EDS results also show the matrix grains in the sample grown by top-seeded solid state crystal growth to be slightly more Bi-excess (Table 2), which may also affect the growth behavior. Bi-excess was found to reduce grain growth in NBT [61].

From the EDS results (Table 1), it is seen that the single crystals grown by solid state crystal growth at 1250°C for 5 h are Na-deficient due to volatilization of Na₂O during sintering, as also found in our previous work [13]. Compared to the previous work, which used a packing powder without excess Na₂CO₃ and Bi₂O₃, the use of a packing powder with excess Na₂CO₃ in the present work could reduce the amount of Na volatilization. From the EDS results of the single crystal grown by top-seeded solid state crystal growth (Table 2), it appears that surrounding the sample with compacted NBT-25ST powder and NBT-25ST packing powder is effective in preventing Na and Bi losses by evaporation.

Raman spectra of NBT-based materials are generally separated into three regions. Modes between 100–150 cm⁻¹ are associated with A₁-symmetry Na-O vibrations or vibrations of other A-site cations [29,62]. The mode at ~75 cm⁻¹ may correspond to Bi-O vibrations [63]. Modes at 200–450 cm⁻¹ are associated with A₁-symmetry Ti-O vibrations, while modes in the region 450–700 cm⁻¹ are associated with vibrations of the TiO₆ octahedra [29]. A₁(LO) and E(LO) overlapping bands are probably the cause of modes in the region between 700–900 cm⁻¹ [64]. The shapes of the peaks in the different spectral regions are sensitive to the phase or phases present in the material [63,65–67]. For rhombohedral NBT, the peak at ~270 cm⁻¹ is relatively narrow and can often be fitted with a single mode. The peaks in the region 450–700 cm⁻¹ are merged together and are not well defined. For tetragonal NBT, the peak at ~270 cm⁻¹ becomes broader and may be fitted with two modes [65–68]. A shoulder on the high wavenumber side may appear. The peaks in the region 450–700 cm⁻¹ begin to separate and become more clearly defined. The Raman spectrum of the NBT-25ST single crystal is in an intermediate state (Figure 3). The peak at ~270 cm⁻¹ is broad enough to be fitted with two modes, but the shoulder at the high wavenumber side has not appeared. Likewise the peaks in the region 450–700 cm⁻¹ are beginning to separate. The overall appearance of the spectrum is similar to that of (Na₁₉Bi₁₇)TiO₃-BaTiO₃ ceramics in the MPB region between rhombohedral and tetragonal phases [63,65–67], indicating that the NBT-25ST single crystal contains both rhombohedral and tetragonal regions. From the XRD and Rietveld refinement results (Figure S 5 and Table S2), the NBT-25ST structure appears to consist of coexisting rhombohedral and cubic phases. The fact that the NBT-25ST structure in the present work is not perfectly cubic is also evident from the presence of remanent polarization (Figure 6). This is consistent with the study by Rout et al., which found an MPB between rhombohedral and pseudocubic (tetragonal) phases at x ≈ 0.25 [29]. Likewise, Sayyed et al. found an MPB between rhombohedral and pseudocubic phases at x = 0.25–0.26 [32]. However, Tong et al. found that their 0.74(Na₁₉/Bi₁₇)TiO₃-0.265SrTiO₃ ceramics contained coexisting pseudocubic and tetragonal phases [69]. The present work also differs from previous work on the 0.75(Na₁₉/Bi₁₇)TiO₃-0.25SrTiO₃ composition by Acosta et al., in which a pseudocubic structure was reported [3]. It is difficult to determine the structure of NBT-based materials using XRD, as the rhombohedral and tetragonal distortions are very small and the average structure often appears cubic [70,71]. This may explain why the XRD results indicate coexisting rhombohedral and cubic phases whereas the Raman scattering results indicate coexisting rhombohedral and tetragonal phases. The NBT-25ST structure may contain a tetragonal phase whose correlation length is too short to be detected by XRD, but which can be detected at the unit cell level by Raman scattering [72]. The reduction in the rhombohedral to tetragonal phase transition temperature Tₓₐₜ toward room temperature with increasing SrTiO₃ concentration may also account for the presence of a tetragonal phase [11]. Further study on the phase composition of this material needs to be carried out to account for the conflicting experimental results of different authors.

The plots of ε’, and loss tangent vs. temperature (Figure 4) are similar to those measured by previous workers on this composition and show behavior typical of NBT relaxor ferroelectric materials [3,30,73]. The broad peaks with a maximum at ~190°C do not correspond to the Curie temperature but are associated with the thermal evolution of polar nanoregions [74,75] or a transition between polar and nonpolar tetragonal phases [76]. The nature of the shoulders at ~135°C is not yet certain. They may correspond to the transition from the rhombohedral phase to the mixed rhombohedral and tetragonal phases [24,77–79],
thermal evolution of mixed rhombohedral and tetragonal polar nanoregions [75], a transition from a non-ergodic to ergodic relaxor [80] or from a ferroelectric to relaxor state [74]. The plots of $\varepsilon'$, and loss tangent vs. temperature of the single crystals prepared by top-seeded solid state crystal growth show differences in behavior to those of the single crystal prepared by solid state crystal growth. These differences may be due to the different sample preparation conditions leading to differences in composition (Tables 1 and 2) [61,81]. The $\varepsilon'$, values of the single crystals vary with crystallographic orientation (Figure S 6). A similar variation in values of relative permittivity with crystallographic orientation has also been found in single crystals of NBT-BaTiO$_3$ [82,83].

The activation energy values of 1.65 eV and 1.19 eV estimated from the AC conductivity curves (Figure 4(c, f)) are considered to represent the electronic conductivity. The activation energy of 1.65 eV observed for the single crystal sample appears to be close to half of the band gap value of NBT-based materials [84–86]. The smaller activation energy of 1.19 eV and high conductivity values observed in the polycrystalline sample may be ascribed to the extrinsic effects induced by the presence of the grain boundaries, e.g. facilitated oxidation/reduction reactions. It is notable that the AC conductivity plots of the polycrystalline sample indicate another Arrhenius behavior of activation energy $\sim$ 0.70 eV. As the high temperature extrapolation of this lower activation energy trace does not determine the high temperature conductivity behavior, the feature could not be explained by the brick-layer model in the presence of blocking grain boundaries. Therefore it is suggested that the trace of activation energy 0.70 eV may represent the ionic conduction mechanism in perovskites. Oxide ion conductivity or alkali ion conductivity has been discussed to explain high DC loss and electrode polarization in ferroelectric perovskites but few conclusive investigations have been reported yet [52,53,87–89]. It is notable that the traces of activation energies of 1.19 eV and 0.70 eV are also indicated in the single crystal sample in Figure 4(c) (the thin black lines), in addition to a trace (the dashed line) of a line parallel to that of the 1.65 eV trace for the DC limit conductivity. This trace has conductivity values about 2.3 times higher than the DC limit conductivity, similar to the current constriction effects due to the grain boundaries of ionic conductors [90–92]. The origin of such current constriction effects in a nominally single crystalline sample should also be understood in future work together with the other traces related to the mixed conduction effects.

The narrow, pinched PE loops and sprout-shaped SE bipolar loops of the (001)-oriented NBT-25ST single crystal sample (Figure 6(a,b)) and polycrystalline sample (Figure 6(e,f)) are characteristic of an electric-field induced transformation from an ergodic relaxor phase to a ferroelectric phase [3,7,70,75,79,93–95]. The difference in shape of the PE and SE loops of the (110)-oriented NBT-25ST single crystal sample (Figure 6(c,d)) shows that the ferroelectric and inverse piezoelectric behavior of NBT-25ST depends on the crystallographic orientation. The PE loops of the (110)-oriented NBT-25ST single crystal sample also appear unsaturated, possibly due to the low value of the applied electric field. The NBT-25ST single crystals have relatively high conductivity, which makes applying higher electric fields difficult.

Similar variation of piezoelectric properties with crystallographic orientation has been found in other NBT-based single crystals [44,79,82,83,96,97] and is generally the case for single crystals e.g. BaTiO$_3$ [98], KNbO$_3$ [99,100] and relaxor-PbTiO$_3$ [101,102]. This dependence of piezoelectric properties on crystallographic orientation is due to the different types of ferroelectric domain structure that form during poling (domain engineering) [82,83,102], different electric field induced phase transitions [103–105], polarization extension [79,106] and polarization rotation [106] (although polarization rotation does not take place in NBT-based materials [79]). For NBT-based compositions, application of an electric field along different crystallographic directions causes different electric field induced phase transitions to take place. Luo et al. studied the behavior of (Na$_{1/2}$Bi$_{1/2}$)TiO$_3$-5.6% BaTiO$_3$ single crystals under electric fields applied along the pseudocubic [001] and [111] directions using XRD and unipolar strain hysteresis measurements [95]. At temperatures close to $T_\text{c}$, application of an electric field along [001] caused a phase transition from pseudocubic to tetragonal phases with a large strain. Application of an electric field along [111] caused a pseudocubic – rhombohedral phase transition with a lower resultant strain. Chen et al. used electric field-dependant Raman scattering and XRD to study the orientation-dependant behavior in single crystals of 0.92(Na$_{1/2}$Bi$_{1/2}$)TiO$_3$-0.06BaTiO$_3$-0.02(K$_{0.3}$Na$_{0.7}$)NbO$_3$ [97]. They found that their (001)-oriented single crystal underwent an electric-field induced pseudocubic to tetragonal phase transition with a large resultant strain, whereas their (111)-oriented single crystal underwent a partial pseudocubic to rhombohedral phase transition with a small resultant strain. Similar behavior may also be happening in the NBT-25ST single crystals in the present work. This could also explain the increase in strain for the NBT-25ST single crystal sample oriented in the [001] direction compared to the polycrystalline sample at electric fields of $\geq$3 kV/mm. The single crystal can be oriented with its [001] direction parallel to the electric field, thus maximizing the electric-field induced pseudocubic to tetragonal phase transition. The polycrystalline ceramic will have grains randomly oriented to the electric field, limiting the degree of pseudocubic to tetragonal phase transition that can take place [79]. The NBT-25ST single crystals have inverse piezoelectric properties superior to those of PZT i.e. $S_{\text{max}}/E_{\text{max}} \approx$ 625–750 pm/V for a soft
PZT at an electric field of 4 kV/mm vs. 1042 pm/V for the NBT-25ST single crystal [2,8]. The reduced strain hysteresis of the NBT-25ST single crystal compared to the NBT-25ST ceramic means that less energy will be wasted as heat during operation, which will improve temperature stability. With further development, single crystals of NBT-25ST could be possible replacements for PZT in actuator applications.

5. Conclusions
Single crystals of 0.75(Na$_{1/2}$Bi$_{1/2}$)TiO$_3$-0.25SrTiO$_3$ were grown by the solid state and top-seeded solid state crystal growth techniques using (110)-oriented SrTiO$_3$ seed crystals and their electrical properties studied for the first time. Raman scattering indicated that the crystal structure has coexisting rhombohedral and tetragonal phases, whereas X-ray diffraction and Rietveld refinement of a polycrystalline sample indicated coexisting rhombohedral and cubic phases. Both the single crystal and polycrystalline samples showed relaxor behavior typical of (Na$_{1/2}$Bi$_{1/2}$)TiO$_3$-based materials. AC conductivity measurements over a wide temperature range revealed directly the Arrhenius behavior with activation energies of 1.65, 1.19, and 0.70 eV in the paraelectric region, which are attributed to mixed ionic and electronic conduction mechanisms. The polarization and bipolar strain hysteresis loops of the (001)-oriented NBT-25ST single crystal indicate an electric-field driven ergodic relaxor to ferroelectric phase transition. Ferroelectric and inverse piezoelectric properties are superior in the (001)-oriented single crystal compared to the (110)-oriented single crystal and the ceramic sample. The inverse piezoelectric constant of the (001)-oriented NBT-25ST single crystal is improved by 41% compared to that of the NBT-25ST ceramic ($S_{\text{max}}/E_{\text{max}} = 1042$ pm/V vs. 739 pm/V) and strain hysteresis is reduced by 18%.

Acknowledgments
The authors would like to thank Kyeong-Kap Jeong (Chonnam Centre for Research Facilities, Chonnam National University) for operating the XRD, Hey-Jeong Kim (Centre for Development of Fine Chemicals, Chonnam National University) for operating the SEM, and Dr. Sang-Hun Jeong (Korea Basic Science Institute, Gwangju centre) for carrying out the Raman scattering experiment.

Disclosure statement
No potential conflict of interest was reported by the authors.

Funding
This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Education under Grant numbers [2015R1D1A1A01057060 and 2017R1D1A1B03033918].

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