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### Growth of tungsten bronze phase out of niobate perovskite

## phase for opto-ferroelectric applications

Yang Bai<sup>1\*</sup>, Constantin Prucker<sup>2</sup> and Neamul H. Khansur<sup>2</sup>

<sup>1</sup>Microelectronics Research Unit, Faculty of Information Technology and Electrical Engineering,

University of Oulu, 90014 Oulu, Finland

<sup>2</sup>Institute of Glass and Ceramics, Department of Materials Science and Engineering, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

\*Corresponding author: yang.bai@oulu.fi

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#### Abstract

Engineering the optical bandgaps of classic ferroelectrics from the typical UV-range down to the visible range is an emerging methodology of developing the next-generation optoelectric and opto-ferroelectric devices including ferroelectric solar cells, light-driven transistors and modulators, and multi-sensors/energy harvesters. Recently, a material interface comprised of a pseudo-morphotropic phase boundary between the tungsten bronze and perovskite phases of the KNBNNO  $[(K,Na,Ba)_x(Ni,Nb)_yO_z]$  has been reported to be an effective approach for bandgap engineering whilst retaining excellent ferroelectricity and piezoelectricity of the perovskite phased KNBNNO. However, this approach requires the compositions of the materials to be determined at the synthesis stage, leaving little room for any further modification of the microstructure and functional properties at the post-processing stage. This paper presents a post-processing method, *i.e.*, atmospheric annealing in N<sub>2</sub> and O<sub>2</sub>, to grow the necessary tungsten bronze phase out of the perovskite phase in the KNBNNO. This method is advantageous over the previously reported because it enables to grow the tungsten bronze-perovskite interface region independent of the initial composition. The distinctive electrical properties and the giant tunability of photoconductivity of the tungsten bronze phase, the perovskite phase, and the interface are characterized in detail in this paper, supporting the exploitation of fabricating opto-ferroelectric devices using the reported method which is compatible and comparable with some of the post-processing methods applied in the silicon industry.

#### 1. Introduction

After more than 100 years' research, ferroelectric and piezoelectric materials have shown reliable and attractive capabilities of electro-mechanical and/or electro-thermal coupling widely used in sensors, actuators, transducers, and energy harvesters<sup>1, 2</sup>. Conventional research on ferroelectrics and piezoelectrics does not necessarily involve the interaction of microstructure (*e.g.*, domain wall motion) and functional properties with light. This is because most of such materials have wide optical bandgaps in the violet- or UV-range, making the absorption of visible-range photon energy and the associated influence of the photo-excited charge carriers on the material properties negligible<sup>3</sup>.

However, a potentially tunable bandgap, especially when extending deep into the visible light range, will expand the application perspectives of photo-responsive ferroelectrics and piezoelectrics. For instance, previous works showed that the incident light which can excite charge carriers is able to drive or stimulate the ferroelectric domain switching<sup>4-6</sup>. This provides opportunities to use light as a virtual gate in ferroelectric field-effect transistors and thus to develop non-volatile memories and artificial synapses for neuromorphic computing with writing/reading functions by light<sup>7, 8</sup>. The photo-assisted domain switching may also be used in opto-electrical dual-source actuators for remote and precise control of micromachines and medical operations<sup>3, 9,</sup> <sup>10</sup>. Meanwhile, the intrinsic spontaneous polarization is believed to be able to assist the separation of photo-excited charge carriers<sup>11</sup>. This offers possibilities to develop either standalone ferroelectric solar cells free from electron- and hole-transporters or an additional layer in conventional semiconductor solar cells to help reduce the recombination and improve the photovoltaic energy conversion efficiency<sup>12–14</sup>. Furthermore, the visible-light photovoltaic effect co-existing with the piezoelectric and pyroelectric effects in narrow bandgap ferroelectrics enables truly integrated, multi-functional sensors and multi-source energy harvesters (converting optical, mechanical, and thermal energies simultaneously into electricity) made from single materials<sup>15, 16</sup>. This helps to solve the issue of miniaturization for hybrid and multi-functional systems<sup>17</sup>.

A recently developed bandgap engineering method for oxide perovskite (ABO<sub>3</sub> structure) ferroelectrics is the B-site doping, *i.e.*, the use of non- $d^0$  metal ions to partially substitute the  $d^0$  transition metal ions. For instance, it has been reported that by replacing 1 mol.% of the Nb<sup>5+</sup> with Ni<sup>2+</sup>, and meanwhile creating corresponding oxygen vacancies ( $V_{O}$ ), the bandgap of the parental KNN [(K<sub>0.5</sub>Na<sub>0.5</sub>)NbO<sub>3</sub>] could be reduced from > 3.5 eV to as low as 1.6 eV with the retention of > 50 % of the original remanent polarization (~11 µC cm<sup>-2</sup> after doping) and 100 % of the original piezoelectric coefficient (d<sub>33</sub> ≈ 100 pC N<sup>-1</sup>)<sup>18</sup>. The bandgap reduction was due to the eased charge transfer from/to the Ni 3*d* states in the introduced Ni<sup>2+</sup>- $V_{O}$  defect dipoles<sup>19</sup>. In practice, the Ni<sup>2+</sup>- $V_{O}$  defect dipoles were introduced by doping BNNO [Ba(Ni<sub>0.5</sub>Nb<sub>0.5</sub>)O<sub>3-8</sub>] in the air atmosphere. Works of bandgap engineering using similar mechanisms have also been reported for other KNN-based compositions and BNT-BT [(Bi,Na)TiO<sub>3</sub>-BaTiO<sub>3</sub>] with promising multi-functional properties<sup>20</sup>.

In addition, co-doping using equally higher- and lower-valanced cations on the B-sites is a more recently reported alternative for bandgap engineering. For instance, partially replacing the Nb<sup>5+</sup> with equal concentrations of Ti<sup>4+</sup> and Mo<sup>6+</sup> (*i.e.*, 5 mol.% by Ti<sup>4+</sup> and 5 mol.% by Mo<sup>6+</sup>) could reduce the bandgap of the KNbO<sub>3</sub> from > 3 eV to approximately 2.2 eV<sup>22</sup>. The bandgap reduction was due to the presence of coupled Ti<sup>4+</sup>/Mo<sup>6+</sup> cations triggering the dipole-allowed O-2*p* to metal-4*d* across-the-gap excitation. Meanwhile, the high distortion ability of the Ti<sup>4+</sup> and Mo<sup>6+</sup> preserved the *d*<sup>0</sup> nature of the B-cation sublattice and thus helped to retain > 60 % of the original remanent polarization<sup>22</sup>. A similar phenomenon has also been reported with the Mn<sup>3+</sup>/Nb<sup>5+</sup> co-doping by replacing Ti<sup>4+</sup> in BaTiO<sub>3</sub><sup>23</sup>.

However, both the reported methods require precise control of the dopant concentration since both of them modify the B-site thus the distortion of the  $BO_6$  octahedra. The dopant

concentration must be at a perfect balance between (a) being large enough to have sufficient energy states that can noticeably ease the band-band transition and reduce the bandgap significantly and (b) being small enough to minimize the influence on the lattice distortion and thus to retain the spontaneous polarization. The challenge is a "landslide" phenomenon shown by experimental evidence, meaning that even a slight shift away from the perfectly balanced point would lead to either an ineffective bandgap reduction or disappearance of useful ferroelectricity<sup>18, 24, 25</sup>. This makes it complicated to replicate the materials in practice, not only because of the potential errors in the weighing procedure of the starting reactants before the synthesis but also due to possibly arduous diffusion of the dopants into the matrix perovskite unit cells during the synthesis, which may cause off-stoichiometry in the synthesized perovskite structure and hence the "landslide" effect<sup>25</sup>.

Such a difficulty has been partially solved in a recently reported work by designing a composition at the pseudo-MPB (morphotropic phase boundary) between the tungsten bronze and perovskite phases of the composition KNBNNO  $[(K_i,Na_j,Ba_k)_x(Ni_l,Nb_m)_yO_z]^{25}$ . By intentionally introducing 5-15 mol.% A-site deficit in the starting reactants of the nominal composition (K,Na,Ba)(Ni,Nb)O<sub>3-8</sub>, self-assembly of the polar tungsten bronze phase and the ferroelectric perovskite phase was observed. Different from classic MPB, the pseudo-MPB plays a role equivalent to a heterojunction within which the band structure, polar symmetry and electrical properties may change significantly<sup>26</sup>. The formed pseudo-MPB interface region (*i.e.*, a monolithic material rather than a true interface between two materials), instead of either individual phase, boosted the remanent polarization and piezoelectric coefficient by up to 3-5 times and reduce the bandgap by 1-2 eV<sup>25</sup>. The tungsten bronze component provided a higher solubility to the Ni<sup>2+</sup>, whereas the perovskite phase helped in retaining the necessary ferroelectric distortion of the unit

cells. Such an approach was proved to be much more flexible in terms of the requirement for the stoichiometry of the starting reactants and the synthesized compounds, ensuring replicability of the materials and desired properties.

Nevertheless, the A-site deficit pseudo-MPB strategy still required the chemical compositions to be determined before the synthesis stage. Ideally, for device applications, post-processing such as thermal and chemical treatments (*e.g.*, those used in the Si industry) should be allowed to modify the microstructure and functional properties of the fabricated materials further. This paper reports and highlights the atmospheric condition-dependent heat-treatment of the air-sintered samples as the way to overcome the limitations of the previously reported methods for the bandgap engineered KNBNNO. It is found that the previously reported pseudo-MPB regions and the interfaces between the tungsten bronze and perovskite phases that were randomly distributed in the samples can now be intentionally grown to a region adjacent to the sample surface. The distinctive electrical properties such as photoconductivity and domain switching can then be individually characterized. These results open doors to optoelectric and opto-ferroelectric devices that may be more compatible than classic ferroelectric counterparts with the widely adopted Si-based electronics.

#### 2. Materials and Methods

#### 2.1. Fabrication of the ceramic samples

Two compositions designed with 10-15 mol.% and < 5 mol.% A-site deficiency in the nominal formulas (*i.e.*, the mixture of the starting reactants) were synthesized in this work. The nominal

formulas of Composition I and Composition II were  $K_{0.45}Na_{0.35}Ba_{0.05}Ni_{0.02}Nb_{0.98}O_{2.92}$  and  $K_{0.50}Na_{0.44}Ba_{0.04}Ni_{0.02}Nb_{0.98}O_{2.98}$ , respectively. Starting reactants of  $K_2CO_3$  ( $\geq$  99 %, J.T.Baker, USA), Na<sub>2</sub>CO<sub>3</sub> ( $\geq$  99 %, Sigma-Aldrich, USA), BaCO<sub>3</sub> (99.98 %, Aldrich Chemistry, USA), NiO (99.999 %, Aldrich Chemistry, USA), and Nb<sub>2</sub>O<sub>5</sub> (99.9 %, Aldrich Chemistry, USA) powders were precisely weighed according to the stoichiometries and then mixed on a ball milling machine using 3 mm ZrO<sub>2</sub> beads and ethanol as the milling media. The dried mixture was subject to one-step calcination at 825 °C for 4 hours and a further ball milling step. Green bodies were obtained with a uniaxial press under 90 MPa pressure and were subsequently sintered in a powder bed of the same composition in question at 1150 °C for 2 hours in the air atmosphere. Details of the compositional designs can be found in the previous work<sup>25</sup>. The nominal formulas examined by XRF (X-ray fluorescence, ASX S4 Pioneer, Bruker, USA) of the two compositions (Composition I and Composition II) used in this work are listed in Table 1. For the nominal formulas, the concentrations of the cations were designed while those of the oxygen were calculated.

#### 2.2. Atmospheric annealing

The sintered ceramic samples were polished with P1200 silicon carbide abrasive paper to reach the thickness of 500-600  $\mu$ m. Each polished sample was cut into several 4 mm × 4 mm square-shaped pieces using a diamond wire saw. The samples were then heat-treated at 500 °C, *i.e.*, above the Curie temperatures to remove possible residual stress caused by the cutting process. Atmospheric condition-dependent annealing was performed at 1000 °C for 2 hours with a heating and cooling rate of 5 °C/minute in N<sub>2</sub> or O<sub>2</sub>. The atmospheric gas flow was maintained at ~500 cm<sup>3</sup>/min using the mass flow controller. The surface tungsten bronze phase was formed naturally after the atmospheric annealing.

#### 2.3. Characterizations

Structural and elemental analyses of the sintered and atmospherically annealed samples were carried out with XRD (X-ray diffraction, Bruker D8 Advance eco diffractometer with Cu Ka  $(\lambda = 1.5406 \text{ Å})$  source, Germany), SEM (scanning electron microscopy, Quanta 200, FEI Co., USA), and EPMA (electron probe micro-analysis, JXA-8530FPlus, Joel, Japan). The XRD patterns were collected with a step size of 0.02° for 20. Some samples were coated with Pt electrodes on both surfaces and were then subject to temperature-dependent dielectric and room-temperature ferroelectric measurements with an LCR meter (E4980AL, Keysight, USA) and a ferroelectric evaluation system (TF2000, aixACCT, Germany), respectively. The heating and cooling rates were 2 °C/minute during the temperature-dependent dielectric measurements. Some other samples were further polished to achieve 50-60 nm surface roughness using a polishing plate and diamond suspension (grain size 1 µm, MD-Nap and DiaPro Nap B, respectively, Struers, USA). The finely polished surfaces were coated with interdigitated Au electrodes having 7 pairs of finger electrodes and ~150 µm gaps between the fingers. J-E (current density-electric field) curves were measured with a source meter (Model 2450, Keithley, USA) in the dark and under illumination at room temperature. Monochromatic lasers with wavelengths of 405 nm, 552 nm and 660 nm (OBIS LX/LS series, Coherent, USA) were used as the light sources. The J-E curve was measured with both the unpoled and poled (at 4 kV mm<sup>-1</sup> in the dark at room temperature) samples. It should be noted that the "domain switching current" and possibly other interfering signals were excluded before collecting the data in the J-E curves. Details can be found at the end of Section 3.2.

#### 3. Results and discussions

#### 3.1. Influence of annealing atmosphere on microstructure

Figure 1 shows the XRD data of the unannealed and atmospherically annealed Composition I and Composition II ceramic samples. The primary reflections for the perovskite and tungsten bronze phases are marked correspondingly<sup>25</sup>. In Figure 1(a), the unannealed Composition I sample formed a major perovskite phase and a minor tungsten bronze phase. In Figure 1(c), the unannealed Composition II sample formed a single perovskite phase. These are consistent with those previously reported<sup>25</sup>. The quantitative analysis results of the XRD Rietveld refinement and the EMPA, *i.e.*, the concentrations and actual chemical formulas of the phases, are listed in Table 1. The residual NiO is negligible in these compositions and hence is not marked in Figure 1. Further details of the unannealed samples can be found in the previous work<sup>25</sup>.

In Figure 1(a) and (b), the minor tungsten bronze phase in the unannealed sample grew slightly after being annealed in N<sub>2</sub> and became the major phase after being annealed in O<sub>2</sub>, as evident by the increasing reflections assigned to the tungsten bronze phase. The XRD patterns of the surface tungsten bronze phases could be modelled using tetragonal symmetry with the *P4bm* space group, highlighting the existence of a single tungsten bronze phase with the composition of  $(K_{0.25}Na_{0.11}Ba_{0.18}Ni_{0.03}Nb_{0.97}O_{2.82})^{25}$  at the surface after the O<sub>2</sub> annealing. For the unannealed ceramics, it has been reported that when the nominal chemical formula of the starting reactants was designed with a 5-15 mol.% A-site deficiency, mass transfer of K and Na might occur to ensure the formation of the preferred perovskite phase in which the A-site was relatively fully occupied regardless of the substantial deficiency in the starting reactants (also see Table 1)<sup>25</sup>. The rest of the starting reactants was "forced" to form the tungsten bronze phase because the ratio of

the A-site to B-site elements was insufficient for the requirement (*i.e.*, 1:1) of the formation of perovskite phase. From this observation, it can be stated that the growth of the tungsten bronze phase in the Composition I sample after the N<sub>2</sub>- and O<sub>2</sub>-annealing might be attributed to the further loss of K and/or Na. Obviously, the K and/or Na were escaping from the perovskite phase at a significantly faster rate in O<sub>2</sub> compared to that in N<sub>2</sub>. The data presented in Figure 1(a)-(b) highlight that the pre-existing minor tungsten bronze phase in the unannealed sample could act as the "seed" for further growth during the atmospheric annealing.

Interestingly, in Figure 1(c) the tungsten bronze phase also grew in a "seed-free" scenario. The tungsten bronze phase was formed out of the single perovskite phase after being annealed in N<sub>2</sub> and O<sub>2</sub> with a similar phenomenon as shown in Figure 1(a) that the growth was much faster in O<sub>2</sub> atmosphere. The tungsten bronze phases grown in the Composition I and Composition II samples can be confirmed identical in Figure 1(d). Figure 2 shows the appearances of the unannealed Composition II sample, N2-annealed Composition II sample, and O2-annealed Composition II sample. The transparency of the N<sub>2</sub>- and O<sub>2</sub>-annealed samples changed in the same way with the samples containing increasing concentrations of the tungsten bronze phase, as reported previously<sup>25</sup>. This evidence supports the above-mentioned prediction that the formation of the tungsten bronze phase was due to the loss of K and/or Na during the annealing process. The reaction with O<sub>2</sub> of the alkaline elements in the perovskite phase and then escaping from the structure in the form of K<sub>2</sub>O or Na<sub>2</sub>O was likely the primary reason for the elemental loss. However, other reasons such as possibly unidentified reactions between the alkaline elements and N<sub>2</sub> or the alkaline elements escaping the structure alone at high temperatures might also contribute to the loss in N<sub>2</sub>, which requires further in situ elemental analyses. The elemental volatilization during sintering and atmospheric annealing has also been widely observed in other alkaline and Zn-containing compounds<sup>27–30</sup>.

Empirically, the loss of the alkaline elements would only happen at well above 800 °C<sup>24</sup>. Figures S1 and S2 in the supporting information compare the XRD patterns of the unannealed Composition I and Composition II samples with their O<sub>2</sub>-annealed counterparts but at much lower temperatures (600-700 °C) and for a much longer period (10 hours). No evidence of the significant growth of the tungsten bronze phase was found when the samples were annealed in O<sub>2</sub> at 600-700 °C for 10 hours (Figures S1 and S2). Such a statement is also supported by Figure S3 in the supporting information, where the dielectric properties were also compared. Below the Curie temperature, the permittivity of the unannealed and annealed (in O<sub>2</sub> at 600 °C for 10 hours) Composition I samples was identical, implying no formation of additional tungsten bronze phase occurred during the annealing. As such, it can be stated that the temperature above the empirical value, 800 °C, was critical for triggering the growth of the tungsten bronze phase, *i.e.*, the loss of the alkaline elements.

Figure 3 shows the cross-sections of the  $O_2$ -annealed Composition I and Composition II samples observed under SEM. As reported previously<sup>25</sup>, the tungsten bronze phase was randomly distributed among the perovskite phase of the unannealed Composition I sample. It can be noticed (Figure 3(a)) that the growth of the tungsten bronze phase only occurred from the sample surface while the bulk microstructure remained as the unannealed sample. The phenomenon can also be seen in Figure 3(b), where no tungsten bronze phase was formed in the bulk of the sample whilst the surface part of the perovskite phase changed to tungsten bronze phase after the annealing. This reflects the fact that the XRD patterns in Figure 1 were obtained only for the surface region of the samples, namely the majority for the tungsten bronze phase for the O<sub>2</sub>-annealed samples. The surface morphologies of the unannealed and annealed samples are shown in Figure S4 in the supporting information. The shapes of the grains of the tungsten bronze phase are revealed in Figure 3(b) and Figure S4(b) and (d), consistent with the lattice parameters (*i.e.*, significantly larger a or b and smaller c)<sup>25</sup>.

Figure 4 compares the unannealed Composition I sample, O<sub>2</sub>-annealed Composition I sample, and the O<sub>2</sub>-annealed Composition I sample after the tungsten bronze surface was removed by polishing. Distinguishing that shown in Figure S4(b), the surface morphology (Figure 4(a)) of the tungsten bronze removed surface similar to that of the unannealed sample (Figure S4(a)). This is also confirmed in Figure 4(b) that the XRD pattern after surface removal was identical to that of the unannealed sample. The influence of the surface layer is also evident from evolution of dielectric behaviors, as shown in Figure 4(c). The O<sub>2</sub>-annealed sample exhibited generally smaller relative permittivity and higher dielectric loss than those of the unannealed sample, indicating an influence of the atmospheric condition-dependent growth of the tungsten bronze phase. The surface-removed sample showed similar dielectric properties to those of the unannealed sample, especially at < 300 °C. With the increase of the temperature, the relative permittivity and dielectric loss of the surface-removed sample started to decrease and increase, respectively, compared to those of the unannealed sample. This was likely due to the minor growth of the tungsten bronze phase in the bulk during the O<sub>2</sub>-annealing (Figure 4(a)). Nevertheless, it can be concluded that the growth of the tungsten bronze phase progressed dominantly from the sample surface.

The growth behaviour initiated from the sample surface makes it feasible to fabricate the favoured pseudo-MPB region on the desired surface region to manipulate the in-plane electrical properties. It should be noted that micro-cracks appeared on the surface of the tungsten bronze phase after the  $O_2$  annealing (Figure S4(b) and (c)), possibly due to the thermal expansion

mismatch between the two phases considering their vastly different lattice parameters<sup>25</sup>. For macro-scale applications, it needs further improvement, such as heating/cooling rate optimization to minimize the surface cracks, but for microelectronics and nano-electronics, the reported atmospheric annealing method should be widely applicable for the material or device fabrication.

# **3.2.** Electrical and photoconductive properties of the individual perovskite and tungsten bronze phases and the pseudo-MPB regions

The dielectric and ferroelectric properties of the unannealed and annealed Composition I samples are shown in Figure 5. The data support the above discussions that the slight growth of the tungsten bronze phase increased the dielectric loss (Figure 5(c)) while the extensive growth of the tungsten bronze phase significantly increased the dielectric loss and decreased the relative permittivity (Figure 5(e)), compared to the situation before annealing (Figure 5(a)). Consistent with previously reported<sup>25</sup>, the unannealed sample exhibited a well saturated P-E (polarization-electric field) loop with the excellent maximum and remanent polarizations of  $\sim 30 \ \mu C \ cm^{-2}$  and  $> 20 \ \mu C \ cm^{-2}$ . respectively (Figure 5(b)), thanks to the proper concentration of the tungsten bronze phase thus the overall area of the pseudo-MPB regions. The N<sub>2</sub>-annealed sample showed similar ferroelectric properties with slightly decreased maximum and remanent polarizations (Figure 5(d)) due to the growth of the tungsten bronze phase which degraded the overall ferroelectric properties and overshadowed the improvement achieved by the pseudo-MPB regions. This is evident in literature<sup>25</sup> as well as in Figure 5(f), where a lossy P-E loop was obtained due to the grown tungsten bronze surface layers (Figure 3(a)). The maximum strains in the S-E (strain-electric field) loops also gradually decreased with the growth of the tungsten bronze phase (Figure 5(b), (d) and (f)).

In Figure 5(b), (d) and (f), the electric field values corresponding to the minimum strain points are not coincident with the coercive fields. This was possibly caused by the dual-phase microstructure. The pure perovskite KNBNNO phase tended to show smaller coercive fields compared to the perovskite-tungsten bronze composites<sup>25</sup>. As both the phases were polar and ferroelectric, the mismatch between the coercive fields and the strain behaviours of the two phases was likely to cause a frustration and thus an overall inconsistency.

However, as the growth of the tungsten bronze phase was layered as discussed in Section 3.1, the "plate capacitor" electrode configuration used in the measurements of Figure 5 could not reveal the true electrical properties of different individual phases and the pseudo-MPB regions. As such, the surface electrical properties were characterized with the interdigitated electrode configuration (see Section 2.3). The complete results of the J-E curves for the unannealed and annealed Composition I and Composition II samples (all unpoled) are shown in Figures S5 and S6 in the supporting information. Most samples started to develop a photoconduction with the 1.88 eV incident photon energy (660 nm laser), consistent with those previously reported<sup>25</sup>.

Figure 6 shows the sheet resistance of the unannealed and annealed Composition I and Composition II samples (unpoled) when subject to different photon energy (0 eV represents the dark condition). The dark resistivity of the unannealed Composition I sample was smaller than that of the unannealed Composition II sample (Figure 6(a)-(b) and Figures S5-S6) due to the existence of the pseudo-MPB in the former, consistent with that previously reported<sup>25</sup>. In the meantime, the growth of the tungsten bronze phase significantly increased the dark resistivity and, in general, decreased the photoconductivity under photon energy of 1.88-3.06 eV (660 nm - 405nm lasers, Figure 6(a)-(b) and Figures S5-S6). This implies that the individual tungsten bronze phase tended

to be less conductive than the individual perovskite phase, but the pseudo-MPB region could be more conductive than both phases, which is consistent with the previously reported<sup>25</sup>.

However, when all the sheet resistance values in the dark were normalized to 1, it can be seen that the growth of the tungsten bronze phase thus the pseudo-MPB region made the samples to be more responsive to lower photon energy, *i.e.*, 1.88 eV and 1.88-2.25 eV for the Composition I and Composition II samples, respectively (Figure 6(c)-(d) and Figures S5-S6). This again signifies that the pseudo-MPB region, rather than either individual phase, facilitated to reduce and tune the bandgap, supporting the previously reported data<sup>25</sup>.

Figure 7 and Figure S7 (supporting information) show the J-E curves of the poled samples and reveal the influence of the pseudo-MPB region on the small-signal behaviour. By comparing Figure 7 and Figures S5-S7, it can be found that the dark conductivity and photoconductivity at the poled state were approximately twice the corresponding values at the unpoled state for the unannealed and N<sub>2</sub>-annealed Composition I samples as well as for the N<sub>2</sub>- and O<sub>2</sub>-annealed Composition II samples. The O<sub>2</sub>-annealed Composition I and unannealed Composition II samples did not show a similar phenomenon. It is known that the unannealed Composition I sample exhibited larger spontaneous and remanent polarizations than those of the unannealed Composition II sample<sup>25</sup>, implying the former yielded a more active domain wall mobility. Considering that (the alignment of) the domain walls may play an important role in the conductivity<sup>31, 32</sup>, it can be estimated that the pseudo-MPB region and its growth during the annealing helped to develop higher domain wall mobility. An exception was in the O<sub>2</sub>-annealed Composition I sample, where the overgrowth of the tungsten bronze phase leading to the deterioration of the electrical properties (Figure 6(a)) overshadowed the effect of the pseudo-MPB regions. Furthermore, by properly developing higher domain wall mobility through the growth of the pseudo-MPB region, hysteretic J-E curves typically observed with ferroelectrics appeared under the dark and 1.88-2.25 eV laser illumination conditions (Figure 7(b) and (d) ccompared to Figure 7(a) and (c), respectively). The hysteresis also implies active domain switching even at the poled state. This provides an opportunity to develop opto-ferroelectric memory or communication devices that can read and/or write by numerous combinations of electric fields and incident lights<sup>8</sup>.

In addition, the poled J-E curves of the O<sub>2</sub>-annealed Composition II sample in the dark and under the 1.88 eV laser showed asymmetry (Figure 7(d)) compared to the corresponding symmetric ones of the unannealed sample (Figure 7(c)). This phenomenon has been studied and discussed in detail elsewhere<sup>7</sup>. However, it is interesting that in the same sample, because of the presence of an appropriate amount of the pseudo-MPB region, the electrical properties may change from a diode feature (dark and 1.88 eV) to ferroelectric (2.25 eV) and then semiconducting (3.06 eV) ones when subject to different lighting conditions (Figure 7(c)). Despite this exceptional case, the pseudo-MPB region may show at least two electrical statuses, ferroelectric and semiconducting, with the help of different photon energy (Figure 7(b)). This feature establishes the basis of the multifunctionality, i.e., the simultaneous applications of piezoelectric, ferroelectric, pyroelectric, photoelectric, photovoltaic, and semiconducting properties of photoferroelectric materials like the KNBNNO tungsten bronze-perovskite pseudo-MPB composites.

It should be noted that the dynamic J-E curve measurement of ferroelectrics would be severely interfered by the widely known "domain switching current"<sup>33</sup> if the moments for adding voltages and collecting data were not carefully controlled or selected. Figure S8 in the supporting information explains the interfering signals in the measurement process and the data collection

points for the J-E curves. Therefore, truly stabilized current signals are shown in Figure 7 and Figures S5-S7, and the reliability of the reached conclusions related to the J-E curves are ensured.

#### 4. Conclusions

By annealing the KNBNNO photoferroelectric ceramics at 1000 °C in N2 or O2 atmosphere, a tungsten bronze phase can be grown from the perovskite phase on the surface. The growth either initiates from the tungsten bronze phase "seed" that may have been formed in the pristine KNBNNO ceramics or from a "seed-free" state due to the alkaline element loss. However, the growth rate of the surface tungsten bronze phase significantly varies depending on the "seed" or "seed-free' state of the pristine sample. Neither the individual perovskite phase nor the tungsten bronze phase but the interfacial region where a pseudo-MPB between the two phases exists enables a significant tunability of the dark conductivity and photoconductivity consecutively from an insulator level to a semiconductor level. The resultant electrical properties can also be manipulated by applying different photon energy to change the behaviour seamlessly from a diode-like to ferroelectric and semiconducting materials within the same pseudo-MPB regions. These results open doors to multi-functional and multi-state ferroelectric-semiconducting components. As such, these results may stimulate the development of opto-ferroelectric devices, including multi-task artificial synapses, multi-level/state writable/readable memories, multi-sensors and multi-source energy harvesters.

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#### **Captions of figures and tables**

Figure 1. XRD patterns of the unannealed, N<sub>2</sub>-annealed, and O<sub>2</sub>-annealed ceramic samples for
(a) Composition I and (c) Composition II. (b) Magnified 2θ range between 42-57° showing the variation in the crystal structure as a function of annealing condition for Composition I.
(d) Comparison of the XRD patterns of O<sub>2</sub>-annealed Composition I and Composition II samples.

Figure 2. Pictures of the unannealed and annealed Composition II samples.

Figure 3. Cross-sectional SEM micrographs of the (a) Composition I and (b) Composition II samples annealed in  $O_2$  at 1000 °C for 2 hours.

Figure 4. (a) Surface micrograph of the  $O_2$ -annealed Composition I sample but with the tungsten bronze surface removed; (b) XRD patterns and (c) Dependence of relative permittivity and dielectric loss (tan $\delta$ ) on temperature (measured at 1 kHz during heating) for the unannealed and  $O_2$ -annealed Composition I samples and the  $O_2$ -annealed sample but with the tungsten bronze surface removed.

Figure 5. (a)(c)(e) Dependence of relative permittivity and dielectric loss (tan $\delta$ ) on temperature measured during heating and (b)(d)(f) dependence of polarization and strain on electric field (P-E

and S-E loops, respectively) measured at 0.5 Hz for (a)(b) unannealed, (c)(d) N<sub>2</sub>-annealed and (e)(f) O<sub>2</sub>-annealed Composition I samples. Please note the difference in the left Y-axis in (f).

Figure 6. Variations of the (a)(b) sheet resistance and (c)(d) normalized sheet resistance with different incident photon energy for the unannealed, N<sub>2</sub>-annealed and O<sub>2</sub>-annealed Composition I (a and c) and Composition II (b and d) samples. In (c) and (d) the dark (0 eV) sheet resistance values are normalized to 1. All samples were unpoled.

Figure 7. Dependence of current density on electric field (J-E curves) for the (a) unannealed and
(b) N<sub>2</sub>-annealed Composition I and (c) unannealed and (d) O<sub>2</sub>-annealed Composition II samples.
All samples were poled. The arrows indicate the sweeping direction of the applied electric field.

Table 1. Nominal chemical formulas of the starting reactants and actual chemical formulas (perovskite and tungsten bronze phases) of the sintered ceramics for the Composition I and Composition II samples.