Vacancy-Induced Niobate Perovskite-Tungsten Bronze Composite for Synergetic Tuning of Ferroelectricity and Band Gaps

Yang Bai, Andrey A. Kistanov, Wei Cao, and Jari Juuti

1. INTRODUCTION

Ferroelectrics, among polar dielectrics with switchable spontaneous polarizations (namely, ferroelectricity) in unit cells and domains, are widely used in electro-mechano-thermal coupling components like memories, detectors, and transducers. Although most ferroelectrics are considered as insulators or semiconductors with wide optical band gaps beyond the majority of photon energy of visible light (e.g., >2.7 eV), their band gaps can be engineered as small as 1.1 eV (same as that of Si). Ferroelectrics may also exhibit a photovoltaic effect and, given proper conditions, they are able to deliver above band gap, ultra-high photovoltages and a photovoltaic energy conversion efficiency that breaks the physical (Shockley–Queisser) limit predicted for conventional semiconductor solar cells.

Most high-performance ferroelectrics have ABO$_3$ perovskite structures. The d$^0$ transition metals on the B-sites possess necessary electronic structures for the second-order Jahn–Teller distortion, driving the B-site cations to displace from the center positions in the O-octahedra and thus giving rise to ferroelectricity. However, the large electronegativity difference between the two ends of the B–O bonds leads to a high charge transfer energy from O 2p states to the B-site metal d states, resulting in a large band gap. Pioneering studies suggested that by properly introducing non-d$^0$ metal states into the B-sites as well as pairing them with O vacancies (V$_{O}\$), the large band gap in ABO$_3$ ferroelectric perovskites could be effectively reduced. For instance, KNbO$_3$ has been doped with 10–40 mol % Ba(Ni$_{0.5}$Nb$_{0.5}$)$_{0.3}$O$_{1.3}$ (BNNO), which could naturally provide both Ni$^{2+}$ and V$_{O}\$. The Ni$^{2+}$-V$_{O}\$ defect dipoles significantly eased the charge transfer (band–band transition) and impressively reduced the band gap of KNbO$_3$ by up to 2.7 eV (from 3.8 to 1.1 eV). Although polarizations were suppressed to a negligible level at room temperature in the KNbO$_3$-BNNO, a follow-up work has proven that by precisely controlling and limiting the BNNO dopant to 2 mol % and by introducing Na+ on the A-site to help increase unit cell distortion, the doped (K$_{0.3}$Na$_{0.7}$)NbO$_3$ reduced the band gap by up to 2.4 eV (from 4 to 1.6 eV) and simultaneously retained the remanent polarization at 11 $\mu$C cm$^{-2}$ (55% of that of the undoped (K$_{0.5}$Na$_{0.5}$)NbO$_3$).

Nevertheless, in the research community, using Ni doping to reduce band gaps of niobate perovskites is under debate. It is questionable how effective is the Ni$^{2+}$-V$_{O}\$ doping strategy, especially when being transferred to other fabrication routes or compositions. For instance, standalone NiO was found in both ceramic samples made via solid-state reaction and nanoparticles synthesized by the sol–gel method for the KNbO$_3$-BNNO and (K$_{0.5}$Na$_{0.5}$)NbO$_3$-BNNO compositions. Meanwhile, in ceramic samples of BaTiO$_3$ doped with BNNO, a Ni-V$_{O}\$-rich composition at grain boundaries was observed to be favored while only a small amount of Ni was...
diffused into the grains where it was expected to be.\textsuperscript{11} These pieces of evidence indicate that it is difficult to form a single perovskite phase with the desired Ni concentration on the B-site of the unit cells, probably due to different radii of Ni\textsuperscript{2+} and Nb\textsuperscript{5+} ions.\textsuperscript{9} Furthermore, when being adopted to compositions like (Na\textsubscript{0.5}Bi\textsubscript{0.5})TiO\textsubscript{3}-BaTiO\textsubscript{3} and (K\textsubscript{0.5}Na\textsubscript{0.5})TiO\textsubscript{3}-CaZrO\textsubscript{3}, the Ni\textsuperscript{2+}-VO doping caused multiple absorption peaks, which was thought to be attributed to the in-gap states created by Ni between the conduction band minimum formed by Nb 4d states and valence band maximum formed by O 2p states.\textsuperscript{12,13}

In other words, the Ni\textsuperscript{2+}-VO in fact did not ease the band transition and thus did not reduce the actual band gap, in contrast to that observed in KNbO\textsubscript{3}-BNNO and (K\textsubscript{0.5}Na\textsubscript{0.5})-NbO\textsubscript{3}-BNNO.\textsuperscript{3,8} The discrepancy implies that the Ni\textsuperscript{2+}-VO doping strategy is considerably composition-dependent, thus imposing obstacles to developing a universal strategy for band gap engineering for ferroelectric perovskites.

In this paper, an alternative route of simultaneously tuning ferroelectricity and band gaps is presented. During the research of the Ni\textsuperscript{2+}-VO doping in (K\textsubscript{0.5}Na\textsubscript{0.5})NbO\textsubscript{3}, the authors accidentally found a perovskite-tungsten bronze composite, which also showed surprisingly an effective reduction of the band gap and increase of spontaneous and remanent polarizations compared to the single perovskite phase counterpart. After implementing a comprehensive and systematic investigation, the phenomenon observed in the new composite is confirmed. The composite shares the same fabrication method with the previously reported single-phase perovskite, but instead of having stoichiometric starting reactants, different concentrations of A-site deficits are intentionally introduced into the nominal chemical formula of the starting reactants. Within a certain window of the A-site deficit concentration, a composite containing a perovskite phase and a tungsten bronze phase having the same types of elements but different molecular ratios between the elements and microstructures is grown from the homogeneously mixed starting reactants. Neither the perovskite nor the tungsten bronze phase is able to individually reach the optimum ferroelectricity and narrowest band gap (measured in this research), but the composite as a whole can achieve this. With studies of the ferroelectric hysteresis loop and photoconductivity on both the phases, the interface between them is concluded to be responsible for the rise of polarizations and ease of charge transfer. Band bending and/or misalignment at the phase interface region are suggested to be the reasons supported by density functional theory (DFT) calculations. The approach of the perovskite-tungsten bronze composite in this paper may provide hints for potential further work on other compositions such as KNbO\textsubscript{3}-BaTiO\textsubscript{3}, (Bi\textsubscript{0.5}Na\textsubscript{0.5})TiO\textsubscript{3} and their families to optimize their photoferroelectric properties.

**2. EXPERIMENTAL SECTION**

**2.1. Sample Fabrication.** Ceramic samples were fabricated via the solid-state route. The concentrations of the starting reactants were calculated based on the nominal chemical formula (K\textsubscript{0.5}Na\textsubscript{0.5}Ba\textsubscript{x})(Nb\textsubscript{1-x}Ni\textsubscript{x})O\textsubscript{3-δ} (KBNBNO). In this formula, the B-site (value of $l + m$) was normalized to 1 while the A-site (value of $x = i + j + k$) varied from 1.05 (5 mol % extra compared to the stoichiometric one) to 0.8 (20 mol % in deficit). This consideration was made based on the fact that each Ba\textsuperscript{2+} may replace one or two K\textsuperscript{+} (or Na\textsuperscript{+}) in reality, which could not be controlled during high-temperature reaction.\textsuperscript{14} The value of $3 - \delta$ was calculated by neutralizing the net chemical valence, i.e., $3 - \delta = (i + j + 2k + l + 2m)/2$. Figure 1 shows the distribution maps of $x$ and $3 - \delta$ values in this research. Figures S1 and S2 in the Supporting Information details the distributions of $i$, $j$, $k$, $l$, and $m$ values as well as their ratios. Tables S1 and S2 in the Supporting Information list the actual weighed concentrations and amounts of the starting reactants. Table 1 summarizes the nominal chemical formulae of the four types of starting reactant mixtures marked in Figure 1. A detailed description of the fabrication procedures is given in the Supporting Information (Section 1 — Detailed experimental procedures). In brief, the weighed starting reactants were mixed, calcined at 825 °C for 4 h in air, shaped into disc green bodies, and sintered at 1150 °C for 2 h in a buried and sealed environment. The synthesis conditions were kept identical to all samples.

It should be noted that the values in Figure 1 and Figure S1 were determined with XRF (X-ray fluorescence, ASX S4 Pioneer, Bruker, USA) for the 11 mixtures of starting reactants. For each mixture sample (20 g for each mixture), five random batches of the mixed reactant powders (1 g for each batch) were subjected to XRF tests. The values shown in Figure 1 and Figure S1 were the averages with deviations of less than 5%. This indicates that the mixing process (see Section 1 of the Supporting Information) was effective and the starting reactants were evenly present in each mixture. Although the ratios between $i$, $j$, $k$, $l$, and $m$ varied across the 11 mixtures as can be seen in Figure S2 (Supporting Information), the types of samples (Type A, Type B, Type C, and Type D) were mainly classified by $x$ and $3 - \delta$ values as shown in Figure 1. The ratios between $i$, $j$, $k$, $l$, and $m$ had only a negligible influence on the microstructure and properties of the finally sintered ceramics. Such results will be shown and discussed in the following parts of this paper.

In these complex compounds, the practical weighing procedure (see Section 1 of the Supporting Information) required special attention. The reactants were first weighed targeting to the desired concentrations and mixed followed by validation under XRF. Due to the daily change of humidity in air, the relatively more hygroscopic $K_2CO_3$ and Na\textsubscript{2}CO\textsubscript{3} (compared to other reactants) could cause an increased level of deviation from the desired concentrations during weighing. If this happened and was detected by XRF, a minor adjustment (i.e., an increase or decrease of certain concentration in the
opposite direction to the detected deviation) was introduced and the weighing process was repeated immediately on the same day until the desired concentrations were reached in XRF tests as shown in Figure 1 and Figures S1 and S2.

2.2. Characterization. XRD (X-ray diffraction, D8 Discover, Bruker, USA) was used to identify phase structures. A UV−vis−NIR spectrophotometer (Cary 500 Scan, Varian, USA) was used to characterize the absorption behavior. FESEM (field emission scanning electron microscope, ULTRA plus, Zeiss, Germany) and EPMA (electron probe micro-analyzer, JXA-8530FP Plus, JEOL, Japan) were used to analyze the microstructures and elements. Ferroelectric hysteresis loops (1 Hz) and piezoelectric coefficients were measured using a ferroelectric evaluation system (Precision LCII, Radiant Technologies Inc., USA) and a Berlincourt piezoelectric meter (YE2730A, APC International Ltd., USA), respectively. Large-signal conductivity was measured with the same ferroelectric evaluation system. Small-signal conductivity was measured using a four-terminal method with a SourceMeter (model 2450, Keithley, USA). Light sources were provided by three lasers (OBIS LX/LS series, Coherent, USA) with wavelengths of 405, 552, and 660 nm. Detailed characterization methods are described in the Supporting Information (Section 1—Detailed experimental procedures). It should be noted that in both the conductivity measurements, no matter which phase was illuminated, the conductivity was measured for the entire surface area covered by electrodes.

3. RESULTS

3.1. Materials and Structures. All sintered ceramic samples had densities of 4.5−4.6 g cm−3 (equivalent to >98% relative density). Figure 2 shows the appearances and microstructures (backscattered electron image obtained with EPMA) of the ceramic samples (finely polished, see Section 1 in the Supporting Information) made from the four types of powder mixtures (as shown in Figure 1 and Figures S1 and S2). In Figure 2a−c, the rainbow-like background helps to indicate the transparency where the samples had the same thickness of about 400 μm (see Section 1 in the Supporting Information). It can be seen in Figure 2a that the Type A ceramics were rather transparent with an antique bronze color. Figure 2f shows that a single perovskite phase (identified later with XRD) was formed in the Type A ceramics with roughly 1 μm-sized residual NiO particles that can be clearly seen on the surface. The residual NiO did not diffuse into the unit cells as expected, reflecting observations in the literature.8,10

Comparison Figure 2a,b, the transparency difference between Type A and Type B samples was hard to distinguish. However, in Figure 2g, a secondary phase, which was later identified as a tungsten bronze phase, was formed in the perovskite phase matrix. A significant decrease of transparency from Type B to Type C samples can be noticed by comparing Figure 2b,c. Correspondingly, the size of the tungsten bronze phase increased from <1 μm in Figure 2g to 1−3 μm in Figure 2h. The Type D samples shown in Figure 2d,e formed an extended amount of tungsten bronze phase, which could even be easily seen by eyes. This resulted in the majority part shown in Figure 2i to be the tungsten bronze phase surrounding the perovskite phase, which is opposite to the situation in Figure 2h where the tungsten bronze phase was surrounded by the perovskite phase. Although the samples shown in Figure 2e had the same values of x and 3−δ, the difference between their Ba concentrations (see Figures S1−S2 in the Supporting Information) caused the sample in Figure 2d to form a distributed, smaller tungsten bronze phase while the one in Figure 2e formed a larger tungsten bronze phase. This difference will be discussed in Section 4 of this paper.

As mentioned above, the perovskite and tungsten bronze phases were identified with XRD patterns shown in Figure 3. Table S3 in the Supporting Information gives full lists of peak positions, d-spaces, and peak intensities extracted from the raw data collected from the XRD scans (Figure 3) for the four

![Figure 2](https://example.com/figure2.png)

![Figure 3](https://example.com/figure3.png)

1. Table 1. Nominal Chemical Formulae of the Mixtures of Starting Reactants

| sample type | nominal chemical formula |
|-------------|--------------------------|
| A           | (K₂₂₀·₉₆Ba₄₂·₂₂(Nb₂·₇₇Ti₂·₃₅O₄·₆₂·₅₂)O₂·₉₈±₀·₂) |
| B           | (K₂·₂₄Ba₄₂·₂₂(Nb₂·₇₇Ti₂·₃₅O₄·₆₂·₅₂)O₂·₉₈±₀·₂) |
| C           | (K₂·₅₄Ba₄₂·₂₂(Nb₂·₇₇Ti₂·₃₅O₄·₆₂·₅₂)O₂·₉₈±₀·₂) |
| D           | (K₂·₄₂Ba₄₂·₂₂(Nb₂·₇₇Ti₂·₃₅O₄·₆₂·₅₂)O₂·₉₈±₀·₂) |
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Table 2. Chemical Formulae and Lattice Parameters of the Perovskite Phase and Tungsten Bronze Phase

| phase               | chemical formula     | space group |
|---------------------|----------------------|-------------|
| perovskite          | (K_{0.537 ± 0.012}Na_{0.374 ± 0.012}Ba_{0.085 ± 0.003})(Nb_{0.996 ± 0.004}Ni_{0.003 ± 0.001})O_{2.877 ± 0.007} | Amm2, orthorhombic |
| tungsten bronze     | (K_{0.251 ± 0.001}Na_{0.007 ± 0.001}Ba_{0.190 ± 0.001})(Nb_{0.975 ± 0.001}Ni_{0.005 ± 0.001})O_{2.815 ± 0.001} | P4bm, tetragonal |

Table 3. Concentrations of the Perovskite and Tungsten Bronze Phases in Each of the Four Types of Ceramics

| sample type | perovskite phase (mol %) | tungsten bronze phase (mol %) |
|-------------|--------------------------|-------------------------------|
| A           | 100                      | 0                             |
| B           | 92.5 ± 0.5               | 7.5 ± 0.5                     |
| C           | 82.7 ± 7.7               | 17.3 ± 7.7                    |
| D           | 57.4 ± 16.9              | 42.6 ± 16.9                   |

Figure 4. Dependence of (a) transmittance and (b) (\(\sigma h\nu\))\(^2\) on (a) wavelength and (b) photon energy (\(h\nu\)) of incident light for the Type A, Type B, and Type C samples, where \(\sigma\) is the absorption coefficient. The concentrations of the tungsten bronze phase (mol %) for the Type B and Type C samples are indicated.

The tungsten bronze phase were first calculated by refinement but with a nominal chemical formula of \((K,N_{0.537 ± 0.012}Na_{0.374 ± 0.012}Ba_{0.085 ± 0.003})(Nb_{0.996 ± 0.004}Ni_{0.003 ± 0.001})O_{2.877 ± 0.007}\). In Tables 2–3 and Figure S4, the chemical formulae of both the phases were normalized to Ni + Nb (B-site) = 1 for easier comparison. Therefore, the indicative concentrations listed in Table 3 and elsewhere throughout this paper were obtained from the values calculated from the refinements and then multiplying a factor of 5.4. NiO was ignored in Table 3 because the analysis was inaccurate (<0.5 mol%). The indexes of each individual phase are provided in Table S4 in the Supporting Information. The phase structures are also supplied as CIF files in the Supporting Information 2 and 3. Detailed EPMA results are provided in Figure S4 in the Supporting Information.

As the size of the tungsten bronze phase in Type B samples was smaller than the EPMA spot size (as presented above), the elemental analyses on Type B samples exhibited an increased level of deviations in Figure S4. However, such deviations were proven to be analysis errors caused by the large EPMA spot size through a series of tests at the phase boundary area on a Type C sample, as shown in Figure S5 in the Supporting Information.

3.2. Optical and Electrical Properties. Figure 4 shows the transmittance and absorption coefficients of the Type A, Type B, and Type C ceramic samples. The Type D samples were too opaque for the light sources of the spectrophotometer (light intensities were not high enough) used in this research to penetrate through the samples. As a result, the collected transmittance and absorbance data were like white noises varying around 0. Therefore, the data obtained from the Type D samples were not able to make meaningful assessment and thus are not shown here. The Type C ceramics exhibited a clearly different behavior from those of the Type A and Type B samples. As shown in Figure 4a, the transmittances of the Type A and Type B samples started to increase at an incident light wavelength of about 400 nm, compared to 600 nm for the Type C. Similarly, in Figure 4b, the band gaps of the Type A and Type B samples defined by the Tauc fitting were 2.4–2.6 eV while that of the Type C was about 2.1 eV. Figure S6 in the Supporting Information shows the grains of the ceramic samples imaged under FESEM. As can be seen in Figure S6, the grain sizes of the perovskite phases in Type A and those of the Type B and Type C samples were similar. Therefore, the changes of transmittance and absorption observed in Figure 4 were likely to be due to the expansion of the tungsten bronze phase. Figure S7 in the Supporting Information plots the square roots of the absorption coefficients, which, together
Figure 5. Dependence of conductivity on the photon energy of the incident laser beam for the four types of ceramics. The data points at 0 eV were collected in darkness. The concentrations of the tungsten bronze phase (mol %) for the Type B, Type C, and Type D samples are marked.

Figure 6. Ferroelectric hysteresis loops and $d_{33}$ values measured in darkness for the four types of ceramics.

Four types of ceramics. Similar to that shown in Figure 5, the Type D sample with a 59 mol % tungsten bronze phase (Figure 2e) in Figure 6 was measured by applying an electric field only on the tungsten bronze phase. The remanent polarization and $d_{33}$ values increased with the increase of the tungsten bronze phase concentration in the sample until approximately 24 mol % and then decreased. Figure 6 indicates that neither individual perovskite nor tungsten bronze phase alone was able to maximize the ferroelectric and piezoelectric properties but the cumulative effect of both phases was needed.

To summarize the relationships between the material structures and properties, Figure 7 plots $E_g^*$, $P_{33}$, $P_{r}$ and $d_{33}$ as a function of the tungsten bronze phase concentration, where $P_{33}$ and $P_{r}$ are the polarization at the maximum electric field and the remanent polarization (extracted from Figure 6), respectively. $E_g^*$ represents the photon energy needed to increase the sample’s conductivity by an order of magnitude (extracted from Figure 5). Here, $E_g^*$ is used as an alternative method to effectively reflect the band gap. Clearly, $E_g^*$ started to decrease with the increase of the tungsten bronze concentration from the 8–10 mol% point and reached a minimum of about 2 eV with an approximately 20 mol % tungsten bronze phase. After the 20 mol % point, $E_g^*$ increased rapidly beyond the visible light range. The trends for $P_{33}$, $P_{r}$ and $d_{33}$ were inverse compared to that of $E_g^*$, where the maxima were reached with an approximately 25 mol % tungsten bronze phase. A jump and a plunge in the $d_{33}$ curve
In these A-site deficient starting reactant mixtures, a KNBNNO perovskite phase was still preferred to be first formed during the solid-state reaction because the tungsten bronze phase expanded only with the A-site deficiency (Figures 1–2 and Table 3). Although there were A-site deficits (>5 mol %) in the starting reactants, a consistent, stoichiometric KNBNNO perovskite phase could always be formed with >95 mol % of the A-sites occupied, which was the same situation as in the Type A ceramics (Figure S4). This also happened independent of specific ratios between K, Na, and Ba concentrations (Figures S1, S2, and S4). These results imply that during the solid-state reaction, the elements diffused actively to prioritize the formation of the stoichiometric KNBNNO perovskite phase, leading to increased levels of A-site deficit in the unreacted regions of the starting reactant mixtures. This forced the rest of the reactants to form a KNBNNO tungsten bronze phase.

Surprisingly, the unit cells of the KNBNNO tungsten bronze phase could easily host 3 mol % (compared to only 0.5 mol % in the perovskite phase) Ni on the B-sites (Table 2). This left much less residual NiO particles in the Type B, Type C, and Type D ceramics. Compared to the perovskite phase, the tungsten bronze phase contained significantly less K and Na but more Ba (Table 2 and Figure S4). As one Ba$^{2+}$ could replace two K$^+$ (or Na$^+$), the high concentration of Ba in the tungsten bronze phase was likely to leave enough space and tolerance in the unit cell to host more Ni (radius larger than that of Nb). It was also possible that Ni had a higher diffusion rate in the tungsten bronze phase.

Furthermore, the ratio between K (or Na) and Ba in the starting reactants was likely to be a crucial factor for the formation of the tungsten bronze phase. In one of the Type D samples (starting reactant mixture ID 10 in Figures S1–S2), the K/Ba ratio (i.e., $i/k$ value) was about 9 (Na/Ba or $j/k$ value was about 8) while the other Type D sample (mixture ID 11) had an $i/k$ ($j/k$) value of about 11 (9) (Figure S2). This difference resulted in two different ceramics as shown in Figure 2d,e where the sample in Figure 2d had a smaller amount and distributed tungsten bronze phase compared to that in Figure 2e with a larger amount and area of the tungsten bronze. In mixtures 10 and 11, the K/Na ratios ($i/k$) and K + Na concentrations ($i + j$) were similar (Figure S2). This implies that, given the same and high level of A-site deficit (>15 mol %, Figure 1) in the starting reactants, a relatively smaller concentration of Ba promoted the formation of the large area tungsten bronze phase. A relatively higher Nb concentration (Figure S2) in the starting reactants seemed to have the same effect. It can then be concluded that the 15 mol % A-site deficit in the KNBNNO starting reactants was the boundary beyond which the formation of the tungsten bronze phase became favored.

4.2. Correlation of the Perovskite-Tungsten Bronze Phase Interface and Band Gap/Ferroelectric Properties.

In Section 3.2, it has been proven that neither of the individual phases was able to reach the optimum ferroelectric/piezoelectric properties, and could not diffuse into the perovskite unit cells was forced to stay as standalone NiO particles (Figures 2 and 3). However, Ni showed a much better diffusion into the KNBNNO tungsten bronze phase formed in the Type B, Type C, and Type D ceramics. These samples had corresponding types of starting reactants with increased A-site deficit (>5 mol %). A reaction and phase formation route can be proposed here:

An input electric field was slightly higher than the coercive field for large-signal measurements was chosen in order to minimize the influence of mobile trapped charges/charged defects and leakage current surge during domain wall motion on the conductivity.15–17 However, in order to validate the conductivity results, small-signal measurements (see Section 1 in the Supporting Information) were also carried out. Figure S9 shows the results of a Type C sample (10 mol % tungsten bronze phase) measured in darkness and under illuminations. The photon energy needed to reach an order of magnitude increase of the conductivity was about 8 eV for the same sample, consistent with the corresponding results shown in Figure 5. This proves the validity of the large-signal measurements used in this paper.

4. DISCUSSION

4.1. Relationship between A-Site Deficits in the Starting Reactants and Phases in the Sintered Ceramics.

Formation of the tungsten bronze phase in KNN perovskite ceramics has been well presented in the literature. From the evidence shown in Section 3.1 above, it can be concluded that in KNBNNO ceramics, a single perovskite phase would be formed with a maximum 5 mol % A-site deficit in the starting reactants (Figure 1). This was independent of the specific ratios between K, Na, and Ba concentrations (Figures S1, S2, and S4). However, although the Ni concentration was about 2 mol % of the B-site atoms in the starting reactants (Table 1), only 0.5 mol % Ni (of B-site atoms) could finally diffuse into the perovskite phase to form integrated KNBNNO unit cells (Table 2). With relatively fully occupied A-sites (like Type A ceramics), the extra Ni that
electric properties and the narrowest achievable band gap. Therefore, a hypothesis is proposed here to explain the cumulative effect of both the perovskite and tungsten bronze phases.

It is known that for the same ferroelectric composition, a larger remanent polarization usually induces a larger piezoelectric coefficient. The change of $d_{33}$ followed the trend of the remanent polarization in Figure 6, indicating a variation of true remanent polarization in the measurements. Meanwhile, ferroelectric hysteresis loops were obtained individually with the single perovskite phase (Type A sample) and mainly tungsten bronze phase (Type D 59 mol %), proving that both the phases contained switchable domains and mobile domain walls. For the tungsten bronze phase, a nonpolar space group, $P4/mnbm$, and a polar equivalent, $P4/nbm$, could both be identified during the refinements. The difference between the two symmetries was negligible for XRD reflections, especially when those intensities of the tungsten bronze phase were rather small. However, the polar $P4/nbm$ was believed to be a preferred ground state of the tungsten bronze phase according to the hysteresis loop measured as well as to some similar examples predicted by calculations.\textsuperscript{19–21}

Since the perovskite and tungsten bronze phases had orthorhombic and tetragonal structures, respectively, a pseudo-morphotropic phase boundary could be formed at the interface regions between the phases where the adjacent unit cells gradually evolved from one structure to the other (Figure S5). Formation of morphotropic phase boundaries has been well proven to be an effective approach to optimize ferroelectric and piezoelectric properties in KNN-based compositions.\textsuperscript{22} In this paper, the interface regions between the perovskite and tungsten bronze phases were thought to be responsible for the increased ferroelectric and piezoelectric properties by enhancing the domain wall mobility at the pseudo-morphotropic phase regions. In such regions, all the unit cells were in a transition status and tended to both the orthorhombic perovskite and tetragonal tungsten bronze phases. More possibilities were given to the polarization directions when switching the domains compared to the situations in the individual phases. Particularly, a giant leap of the polarizations and $d_{33}$ was observed at the tungsten bronze phase concentration of approximately 10 mol % (Figure 7). This implies that when the tungsten bronze phase was less than 10 mol %, the phase interface area was not large enough to induce a significant increase of ferroelectric and piezoelectric properties.

Figure 8 proposes a mechanism of the band gap reduction at the phase interface. According to Figures 4, 5, and 7, the band gaps of individual perovskite and tungsten bronze phases were likely to be 2.5–3 and >4 eV, respectively, as shown in Figure 8 where the valence band may be contributed by O 2p states and/or trapped charges at $V_0$ that could become mobile under illumination and/or electric field and the conduction band may be contributed by Ni 3d and/or Nb 4d states.\textsuperscript{3,16,23} In the KNBNNO perovskite-tungsten bronze composites fabricated in this research, the conduction and valence bands were possibly bent and/or misaligned at the phase interface in two ways as shown in Figure 8. Such a bent and/or misaligned band structure at the interface allowed the electrons in the valence band of the perovskite phase to be excited to the conduction band of the tungsten bronze phase with photon energy larger than 1.5–2 eV (Possibility 1 in Figure 8) or the other way round (Possibility 2 in Figure 8), resulting in largely reduced $E_g^*$ values of 1.5–2 eV compared to those of individual phases as shown in Figures 5 and 7. The overlaps of the conduction band minimum and valence band maximum of different phases in Figure 8 are presented to visualize the possible band extensions toward each individual structure in the unit cells of the interface regions that may be in a mixed/transition status. The real situation of the conduction and valence bands should be expressed by a proper band structure calculation.

To confirm the proposed hypothesis, the band structures of perovskite KNBO$_3$, tungsten bronze K$_2$Nb$_2$O$_7$, and their interfaces were studied by DFT calculations. Details of the calculation methods can be found in the Supporting Information (Section 3 – Simulation). Due to the complexity of the unit cells of KNBNNO perovskite and tungsten bronze structures, the models were simplified to be a KNBO$_3$/K$_2$Nb$_2$O$_7$ interface. Figures S10–S13 in the Supporting Information show the atomic structures, band structures, and local densities of states (LDOS) of the perovskite KNBO$_3$, tungsten bronze K$_2$Nb$_2$O$_7$, and two kinds of possible interfaces between the phases. According to the results of the calculations, KNBO$_3$ (Figure S10) and K$_2$Nb$_2$O$_7$ (Figure S11) had band gaps of 2.46 and 1.75 eV (0.25 eV with states of 1.5 eV below the Fermi level), respectively. Meanwhile, the LDOS plots in Figures S10 and S11 indicate that the valence bands of KNBO$_3$ and K$_2$Nb$_2$O$_7$ mainly consisted of O 2p states while their conduction bands mainly consisted of Nb 4d states. Analyses of band structures and LDOS at the two kinds of KNBO$_3$/K$_2$Nb$_2$O$_7$ interfaces, as shown in Figures S12 and S13, suggest the O and Nb originating states were strongly mixed. Consequently, the conduction and valence bands at the interfaces were bent and misaligned, resulting in a decrease or vanishing of the band gap of the KNBO$_3$/K$_2$Nb$_2$O$_7$ composite. The obvious change of the band’s alignment at the perovskite–tungsten bronze interface revealed in the DFT calculations confirmed the hypothesis shown in Figure 8.

5. Conclusions

By intentionally designing 5–15 mol % A-site deficit in the starting reactants, composites containing a roughly 80–90 mol \% perovskite phase (nominal chemical formula (K$_{0.54}$Na$_{0.37}$Ba$_{0.09}$)(Nb$_{0.996}$Ni$_{0.004}$)O$_{2.979}$) and 10–20 mol \% tungsten bronze phase (nominal chemical formula (K$_{0.25}$Na$_{0.10}$Ba$_{0.09}$)(Nb$_{0.97}$Ni$_{0.03}$)O$_{2.82}$) have been fabricated via solid-state reaction. The perovskite and tungsten bronze phases have obtained orthorhombic and tetragonal structures, respectively, likely to form a pseudo-morphotropic phase boundary at the phase interfaces. The phase boundary has boosted the remanent polarization and piezoelectric coefficient by up to 3 and 5 times, respectively, compared to those of the individual phases. The possible band bending and misalignment at the interfaces have also reduced the band gap by...
approximately 1–2 eV compared to the individual phases. This research offers a new, alternative route to simultaneously tune (optimize) ferroelectric/piezoelectric properties and band gaps in inorganic photoferroelectric materials, especially for alkaline niobates.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c01845.

Detailed experimental procedures, supplementary data, and simulation (PDF)

CIF file for \((\text{K}_{0.54}\text{Na}_{0.47}\text{Ba}_{0.03})(\text{Li}_{0.95}\text{K}_{0.05})\text{O}_{2.97}\) (CIF)

CIF file for \((\text{K}_{0.23}\text{Na}_{0.10}\text{Ba}_{0.19})(\text{Li}_{0.85}\text{K}_{0.15})\text{O}_{2.82}\) (CIF)

### AUTHOR INFORMATION

#### Corresponding Author

Yang Bai — Microelectronics Research Unit, Faculty of Information Technology and Electrical Engineering, University of Oulu, FI-90014 Oulu, Finland; orcid.org/0000-0002-0861-2410; Email: yang.bai@oulu.fi

**Authors**

Andrey A. Kistanov — Nano and Molecular Systems Research Unit, Faculty of Science, University of Oulu, FI-90014 Oulu, Finland; orcid.org/0000-0001-6175-5296

Wei Cao — Nano and Molecular Systems Research Unit, Faculty of Science, University of Oulu, FI-90014 Oulu, Finland; orcid.org/0000-0003-3139-1780

Jari Juuti — Microelectronics Research Unit, Faculty of Information Technology and Electrical Engineering, University of Oulu, FI-90014 Oulu, Finland

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acs.jpcc.1c01845

#### Notes

The authors declare the following competing financial interest(s): The results of this manuscript are also included in a patent application (pending): Application number PCT/FL2020/050810.

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