Junctionless thin-film ferroelectric oxides for photovoltaic energy production

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ABSTRACT

Streaming Process for Electrode-less Electrochemical Deposition (SPEED) method is used to create complex thin-film structures, such as KBNNO, in a single step, in contrast to hydrothermal approaches with separate nanoparticle growth and deposition processes. This new ferroelectric oxide $[KNbO_3]_{1-x}[BaNi_{1/2}Nb_{1/2}O_{3-\delta}]_x$ or "KBNNO" has an alloy-tunable band gap as low as 1.1 eV, so that its absorption can be tailored to match the solar spectrum. At the same time, it has a reasonably large polarization allowing for charge separation across the bulk, sizeable photocurrents, and open-circuit voltages V_{oc} that exceed the band gap, potentially leading to efficiencies that exceed those possible for standard pn-junction cells. Physical characterization of KBNNO films demonstrate the microstructure and stoichiometry of SPEED-produced thin-films, ratio of elements needed to achieve an ideal band gap of ~1.39 eV, the effect on film chemistry, microstructure, and band gap of annealing, the practical separation of excited carriers at room temperature, the maximum achievable polarization and its temperature dependence, and the conditions for ideal poling. Photovoltaic characterization of KBNNO cells will determine the efficiency, the relative strengths of dark and photo currents, the open circuit voltage, the short circuit current, and cell fill factor (FF).

Keywords: Bulk photovoltaics, Perovskite oxide, Ferroelectric thin-film, KBNNO, Solar cell, SPEED deposition.

1. INTRODUCTION

Ferroelectric materials have recently attracted a lot of attention due to their light-absorbing properties [1-3]. Although photovoltaic effect observed in ferroelectric perovskite thin films is very promising [4], most well-studied perovskite oxides (i.e., $(Pb,La)(Zr,Ti)O_3$, $BaTiO_3$, $BiFeO_3$ and $PbTiO_3$) have wide bandgaps in the UV [5-9] which allow the use of only 20 percent of the solar spectrum. Recent efforts have emphasized electronic structure modification of ferroelectric oxides to engineer band-gaps that span the solar spectrum [1]. Fig. 1 (left) presents a plot of experimentally achieved band-gaps versus dielectric polarization for some well-known ferroelectrics (open symbols), whose band gaps generally exceed 3 eV [4]. This is undesirable for solar cells, where the optimum gap is about 1 eV.

Among all the different ferroelectric materials, $[KNbO_3]_{1-x}[BaNi_{1/2}Nb_{1/2}O_{3-\delta}]_x$ (KBNNO) is the most promising candidate in BPVE applications, since its bandgap can be engineered into the near IR. This creates opportunities for innovation in photovoltaic cells and state of the art optoelectronic devices. The best-measured polarization of KBNNO material to date is ~0.2 C/m^2 (Fig. 1). It exceeds that, and its gap is lower than, the next best material indicated in Fig. 1 SbSI. The polarization value indicated for KBNNO is thought to be limited by ferroelectric domain motion in sintered pellets, and it is not considered a fundamental limit for the actual bulk value [1], which has yet to be determined.

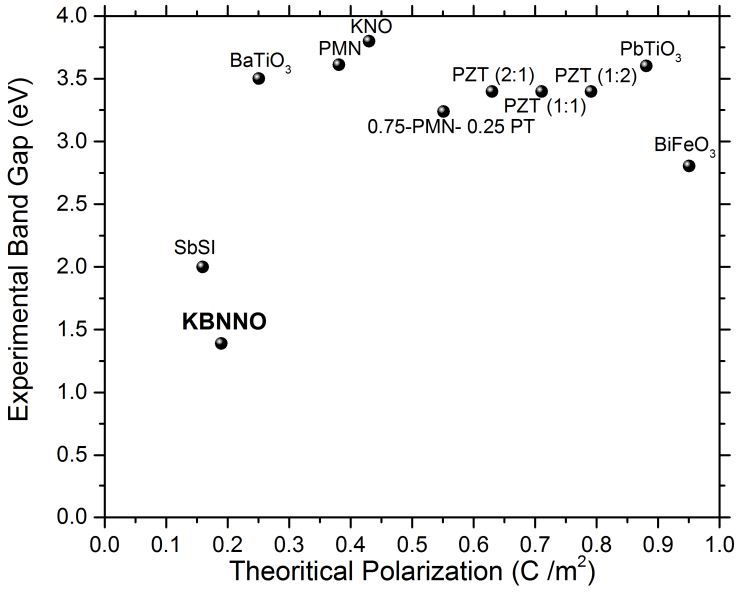


Figure 1. Bandgap and polarization in common ferroelectric oxides.

Ferroelectric perovskites (with ABO_3 composition) typically possess a direct bandgap higher than 3 eV due to their metallic bonds to oxygen atoms [10]. Consequently, substituting the B site of KNO ($KNbO_3$) perovskite oxide with elements whose bonds with oxygen are less ionic (i.e. BNNO) can lead to the reduced bandgap of the final mixed oxide. CdTe and Si with 1.5 and 1.2 eV bandgaps, respectively, are known solar cell materials with lab cell efficiency between 15 to 20%. KBNNO with 1.39 eV bandgap has potentially better efficiency, according to published predictions. Grinberg et al. [1] mixed the perovskite ferroelectric oxides $KNbO_3$ (KNO) with $BaNi_{0.5}Nb_{0.5}O_{3-\delta}$ (BNNO) to introduce Ni cations to the B site and oxygen vacancies, which gave a band gap in the resulting KBNNO material of 1.39 eV.

2. DEPOSITION PROCESS

KBNNO is deposited by SISOM's proprietary SPEED deposition method on stainless steel or quartz glass substrates. We target the composition $K_{0.9}Ni_{0.05}Ba_{0.1}Nb_{0.95}O_3$, which has been shown [1] to have a bandgap of 1.39 eV. The ratio of Nb to K, Ni, Ba, and O sources in the precursor that lead to the target final film composition will be determined by experiment. Post deposition annealing is carried out in air or Ar ambient at temperatures ranging from 400 to 700 ^oC to determine the optimum conditions that give film with the best photovoltaic properties.

SISOM's "SPEED", aqueous-based deposition process deposits self-assembled nanomaterial inorganic thin films over large areas, without a vacuum. Published literature documents the use of SPEED to produce operational II-VI semiconductor p-n junction solar cells with efficiency exceeding 10% [11]. Additionally we have fabricated bio-sensors [12] and solid-state electrolyte for batteries [13] by SPEED. Growth rates are up to 1 µm/min at relatively low temperatures on hydrophilic stiff or flexible substrates. SISOM has three existing SPEED deposition methodologies:

• Liquid-Phase SPEED (LPSPEED), where the heated substrate is immersed in liquid precursor with controlled replenishment and recirculation. LPSPEED growth rates range from 10 to 100 nanometers per minute.

• Vapor-Phase SPEED (VPSPEED), where precursor droplets with 10 - 20 µm diameters impinge on the heated substrate. VPSPEED provides growth rates exceeding 100 nanometers per minute.

• Gel Phase SPEED (GPSPEED), where precursor-impregnated gel is cast on a heated substrate. GPSPEED growth rate exceeds 1,000 nanometers per minute.

Precursor System: Deionized water is the preferred growth medium. The aqueous solution of water-soluble compounds contains engineered complexing agents that discourage unwanted homogeneous reactions so that growth occurs only by heterogeneous reaction on the substrate.

Substrate: The substrate must be hydrophilic to enable the controlled attachment of hydroxyl ions (OH^-) from the precursor solution. Nanoparticle-based films are directly deposited onto metallic, glass, or plastic substrates. Conducting sub-layers may be deposited first on insulating substrates to provide electrical contact.

Film Growth: The OH^- ions attached to the substrate in a high-density monolayer ($>10^{12}$ sites/cm^2) are the reaction nucleation sites. The heterogeneous reactions that form the molecules of interest occur only if the substrate temperature supplies at least the activation energy of reaction, usually in the range 125 – 300 ^oC. The lateral growth of grains on the substrate is short lived and self-limited because there are millions of grains nucleating and growing simultaneously until the surface area is consumed. Upon reaction, the OH^- ions are liberated and repopulate the active sites of the newly created film.

Film Quality: The films consist of densely packed grains with sizes in the range 50 to 100 nm. Recrystallization is accomplished by post-growth annealing. We use VPSPEED for this project. A water based precursor is nebulized into 10 - 20 µm droplets and made to impinge on the heated substrate, which is maintained at 200 - 300 ^oC. Such heating increases the growth rate, increases the number of materials that can be grown, provides energy needed for the heterogeneous reaction, and volatilizes the reaction by-products. Fig. 2 (left) shows our VPSPEED set up, which currently provides 100 mm x 100 mm growth area.

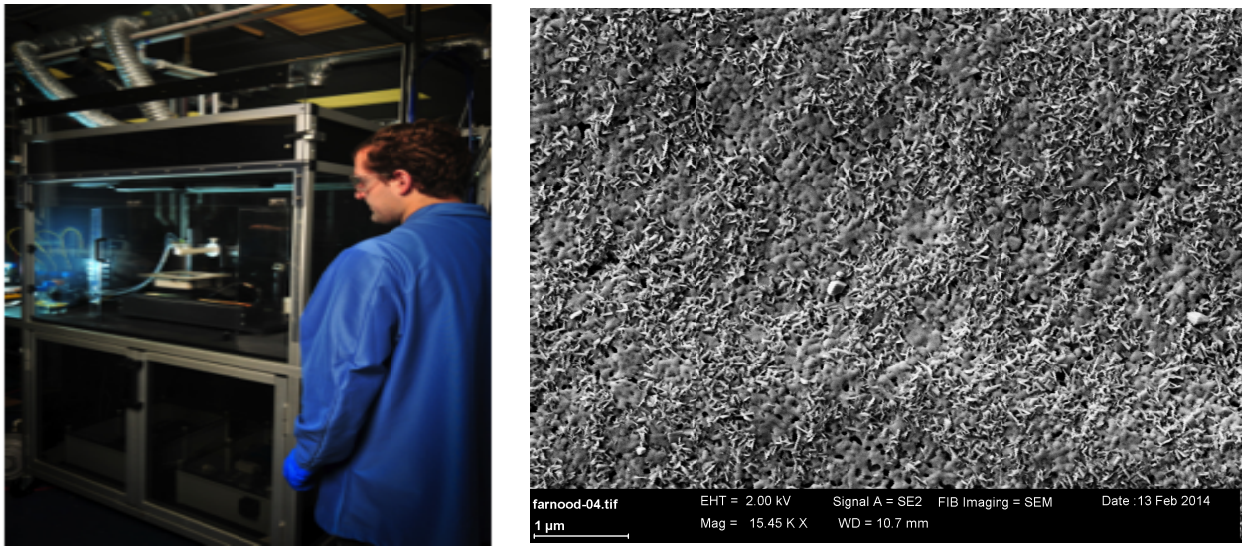


Figure. 2. (left) Laboratory VPSPEED capable of growing 100 mm x 100 mm films. (right) SEM image of a KBNNO film grown by SPEED.

3. EXPERIMENTAL RESULTS

Characterization of thin-films is performed by a number of advanced methods available at University of Central Florida. Scanning electron microscopy (SEM) of fabricated thin-films reveals information about the film morphology at nanometer and micrometer length scales. Fig. 2 (right) presents an SEM image of a first KBNNO film fabricated by SISOM's SPEED method. The thin-film is grown on a stainless steel substrate. Outstanding adhesion has been achieved

by annealing the KBNNO sample at 650 °C. The microstructure of the films is better than that of the sintered pellets that have been reported previously [1]. The roughness evident in the SEM image for the several-µm-thick film will be eliminated by growing thinner films on a strain-relieving conducting sub-layer. Optical measurements indicate that films need not exceed 1 µm thickness.

Energy-dispersive X-ray spectroscopy (EDS) of the scanning electron microscope reveals the film composition. EDS results for the thin-film in Fig. 2 (right) confirms the expected atomic abundances in the targeted $K_{0.9}Ni_{0.05}Ba_{0.1}Nb_{0.95}O_3$ compound, as shown in Table 1.

Table 1. Atomic composition of KBNNO as targeted and as measured by EDS in a SPEED grown film.

Element	Calculated ratio of elements in KBNNO with x = 0.1	EDS ratio of elements in preliminary SISOM KBNNO film
K	18	15.6
Ni	1	2.6
Ba	2	2.0
Nb	19	22.3
O	60	57.5

Raman and micro-Raman spectra reveals characteristic spectral signatures of the ferroelectric phase. Fig. 3 shows that SISOM's thin film has a matching spectrum with previous work [1] in 100-600 cm^{-1} range.

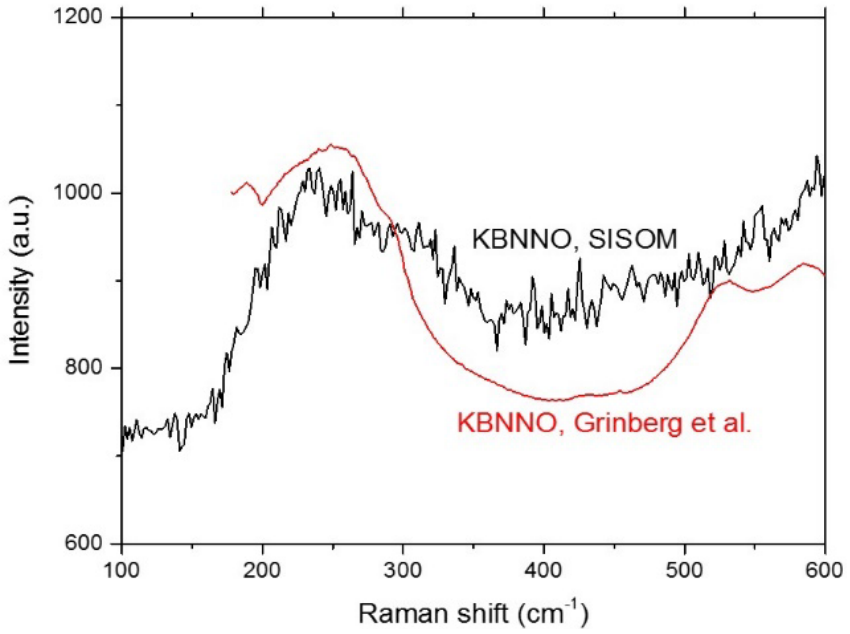


Figure. 3. Raman shift of fabricated KBNNO film by SPEED is compared to Grinberg et al. results [1].

UV-Visible spectroscopy determines the optical band gap and absorption coefficient from the transmission spectrum of the grown film. Fig. 4 presents a measurement on a first KBNNO film grown on quartz and compares the absorption to the solar emission spectrum. The characteristic thickness for absorption is already just 830 nm at a wavelength of 0.8 µm. Thus, films of just ~ 1 µm thickness should suffice very well.

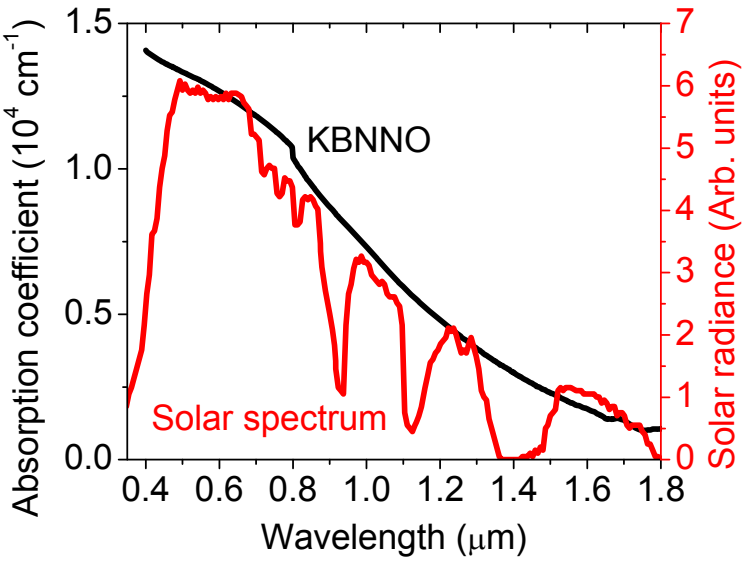


Figure. 4. Transmission spectrum of preliminary SISOM-grown 3-μm-thick KBNNO thin-film on quartz substrate compared with solar spectrum.

Ferroelectric hysteresis (Polarization P vs. electric field E) is measured by the Sawyer-Tower method [14], which is shown schematically in Fig. 5 (left). A sense capacitor C is chosen much greater than the sample capacitance C_s, so that most of the supply voltage V_0 drops across the sample. The electric field in the sample is then $E = V_0/d$, where d is the film thickness and V_0 is determined from the voltage divider output V_R. Then according to the component values shown, $E = 11\ V_R/d$. The sample permittivity is expected to be large, so that most of the electric induction $D = Q/A_s$ in the sample of area A_s is due to the polarization P. Thus $P = Q/A_s$. Here charge Q on the sample capacitor is the same as that on the sense capacitor $Q = C\ V_c$. Thus, $P = (C/A_s)\ V_c$. A plot of V_c vs V_R then directly gives the P vs E hysteresis curve when the axes are appropriately scaled.

Fig. 5 (right) presents our preliminary ferroelectric hysteresis curves for SPEED-grown KBNNO film. It differs in a number of ways from published data [1]. Namely, the data are asymmetric about zero polarization (Q axis), and the maximum polarization achieved is higher though the applied electric (poling) field is smaller. Considering out 2 mm contact diameter, the maximum polarization achieved ($Q/\pi r^2$) is 0.3 C/m^2. This is in good agreement with, and even a little larger than, the value 0.2 C/m^2 reported in [1], which was considered a lower limit on the bulk value due to domain-wall motion in sintered pellets. Measurements on microscale samples extracted from the sintered samples show stronger switching-loop behavior [1], which is a promising indication for our proposed films. The saturated value of polarization is important to photo-carrier separation and photo-current, and we believe it will be larger in SPEED grown films due to superior microstructure.

A large hysteresis indicates a desirably strong polarization reversal field (coercive field) and large remnant polarization. Published accounts indicate a coercive field for KBNNO of ~5 V/μm. Fig. 5 (right) shows a coercive voltage of about 5-10 V for a 1 micron sample [1], or 5-10 V/μm, which is in good agreement. These field values inform our Sawyer-Tower experiment by showing that for our expected ~1 μm thicknesses, only modest (~10 V) poling voltages are required. These may be supplied by a simple DC power supply, though higher voltage supplies are available if needed.

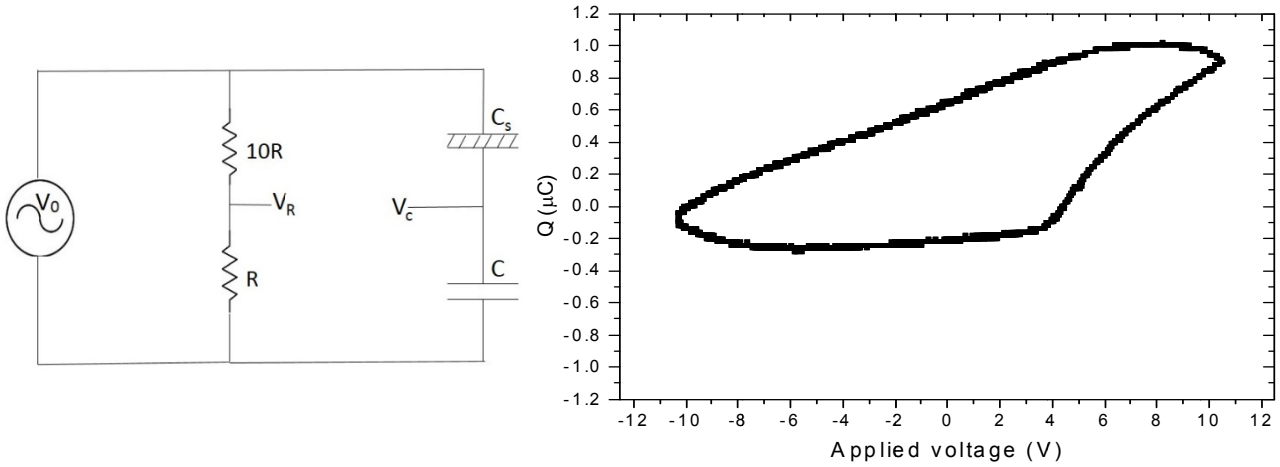
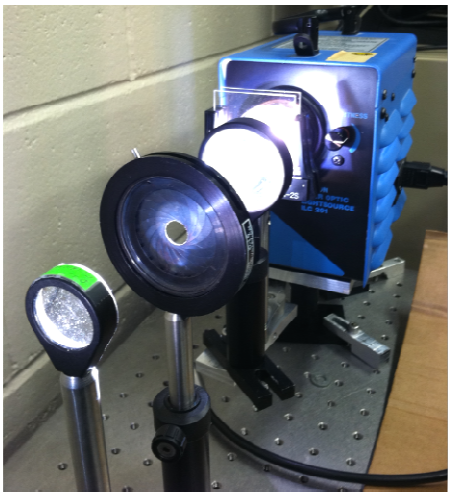


Figure. 5 (left) Sawyer-Tower circuit. (right) Dielectric hysteresis loop of SPEED-grown KBNNO film.

A "metal foil/KBNNO/SnO_2:F" cell structure has been fabricated as a prototype solar cell. The KBNNO film thickness is ~1 μm. I-V measurements to determine solar-cell figures of merit on poled films have are incomplete as of this writing. Characterization of the photovoltaic properties uses a Keithley SourceMeter, filtered Xenon arc lamp to give solar spectrum, and LabView for data acquisition and control. Efficiency is a figure of merit (FOM) determined by the ratio of the maximum power point (MPP) to the input power of the incident radiation, which is determined using a calibrated detector. The MPP is where the output power of the solar cell is maximal, which occurs at the knee of the I-V curve. Our characterization setup (Fig. 6) includes a 150 W Xenon lamp equipped with two filters (AM 0 and AM 1.5), which provides ~13% of the power of the sun.



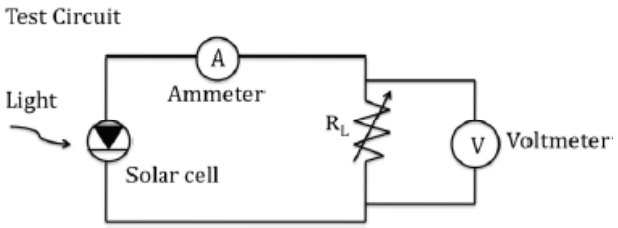


Figure 6. Xe lamp with filters as solar simulator. Optics produce uniform illumination across the area of the 100 mm square cell. (right) Test circuit for electrical measurements.

The electrical characterization of solar cells, shown schematically in Fig. 6 (right), produces a characteristic I-V curve. As an example, we have used this set up to characterize a commercial amorphous silicon thin-film solar cell [15]. We will evaluate figures of merit including open circuit voltage V_{oc}, short circuit current I_{sc} , and maximum power point MPP, cell efficiency, and the cell fill factor FF = I_{MPP} V_{MPP}/ V_{oc} I_{sc}.

4. SUMMARY

A low-cost water-based SPEED deposition method has been successfully applied to grow thin ferroelectric films of KBNNO. KBNNO has a relatively large polarization and could possibly produce high open-circuit voltages exceeding its bandgap. Preliminarily KBNNO films have shown high absorption in the visible range with a good match with the solar spectrum. Fabricated KBNNO films also possess excellent adhesion to the substrate surface and are stable under wide range of chemical, mechanical and thermal conditions, which makes them desirables in solar cell applications.

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