

Investigation of electrical, optical and mechanical control of ferroelectric domains using scanning probe microscopy

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Investigation of electrical, optical and mechanical control of ferroelectric domains using scanning probe microscopy

GAURAV VATS

A thesis submitted for the fulfillment of requirements for the degree of

Doctor of Philosophy



School of Materials Science and Engineering,

University of New South Wales, Sydney

March, 2020

Dedicated to

my Teachers

and

Family



Surname/Family Name: Vats Given Name/s: Gaurav Abbreviation for the degree as given in the University calendar: Ph.D. Faculty: Science School: Materials Science and Engineering Thesis Title: Investigation of electrical, optical and mechanical control of ferroelectric domains using scanning probe microscopy

Abstract 350 words maximum: (PLEASE TYPE)

This thesis compiles the applications and nanoscale understanding of electrical, optical and mechanical manipulation of ferroelectric domains in (($K_{0.5}Na_{0.5}$)NbO₃–2 mol% Ba(Ni_{0.5}Nb_{0.5})O₃– δ) (KNBNNO). KNBNNO is a novel bandgap (1.6 eV) engineered ferroelectric with an excellent piezo-response (100 pm/V). This made it interesting for light-dependent nanoscale investigations using scanning probe microscopy. The light is found to work analogous to an applied electric field and the charge carriers generated by the presence of light are found to be compensated by the movement of ferroelectric domains. The domain wall velocities achieved by the exposure to the light source are of the order of 0.01 nm/s. To make KNBNNO viable for practical applications, the domain wall velocities were further enhanced to 30,000 nm/s by the cumulative effect of light and low electric fields (< 4 kV/mm). The light illumination on this material is found to tune the material's electrical conductivity by orders of magnitude and the charge injection due to illumination is governed by the ferroelectric photovoltaic effect. KNBNNO is also found to illustrate mechanical switching under atomic-force microscopy (AFM) tip pressure (> 0.4 µN). It is found that tip pressures higher than 3 µN can cause permanent deformation of the sample surface. The optical response of the materials is found to be influenced under the mechanical loading via an atomic force microscope tip.

The presence of multiple domain switching mechanisms in KNBNNO makes it interesting for an ample spectrum of applications (neuromorphic computing and solid-state energy conversion) and to develop a fundamental understanding of more complex possible mechanisms. Based on the understanding gained, the phenomenon of electro-optic control of ferroelectric domains is utilized to modulate photo- and pyro-currents. Using this, a prototype monolithic light-effect transistor is presented. This could be a potential solution to the scaling limit of three-terminal transistors. In addition, two novel energy conversion cycles (Opto-electric and thermo-opto-electric) are proposed. Finally, the study is concluded with a hope to motivate the scientific community for utilizing the cumulative effect of light, electric field and mechanical force for novel devices and applications.

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Table of contents

Acknowledgements	i
Preamble	iii
List of publications	
List of figures	vii
1. Introduction	
1.1. Fundamental background	2
1.1.1. Introduction to ferroelectrics	2
1.1.2. Pyroelectricity	5
1.1.3. Piezoelectricity	6
1.1.4. Charge transport properties of ferroelectrics	7
1.1.5. Dielectric/semi-conducting properties	8
1.1.6. Depolarization field	9
1.1.7. Interface and domain wall effects	9
1.1.8. Ferroelectric photovoltaic effect	10
1.2. Material selection and literature	11
1.3. Instruments and methods	15
1.3.1. Scanning probe microscopy	15
1.3.2. Kelvin probe force microscopy	16
1.3.3. Piezoresponse force microscopy	18
2. Optical control of ferroelectric domains	20-40
2.1. Motivation	21
2.2. Experimental details	23
2.3. Results and discussion	24
2.4. Conclusions	39

3.	3. Opto-electric control of ferroelectric domains 4	
	3.1. Motivation	42
	3.2. Experimental details	43
	3.3. Analogy in optical and electrical behavior	44
	3.4. Light as a virtual electrode	46
	3.5. Light-assisted electrical poling	50
	3.6. Application	55
	3.7. Conclusions	59
4.	Opto-mechanical control of ferroelectric domains	60-72
	4.1. Literature and motivation	61
	4.2. Experimental details	62
	4.3. Mechanical control of domains	63
	4.4. Opto-mechanical control of domains	69
	4.5. Conclusions	71
5. Thermo-electro-optic effects		73-84
	5.1. Motivation	74
	5.2. Experimental details	75
	5.3. Electrical modulation of photo- and pyro-current	76
	5.4. Novel electro-optic and thermo-electro-optic energy conversion cycles	79
	5.5. Comparison of cyclic energy harvesting capability	82
	5.6. Conclusions	84
6.	Summary and conclusions	85-87
Vi	Vistas ahead	
References 8		89-97

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Gaurav Vats

Preamble

This thesis compiles the applications and nanoscale understanding of electrical, optical and mechanical manipulation of ferroelectric domains in $((K_{0.5}Na_{0.5})NbO_3-2 \text{ mol}\% Ba(Ni_{0.5}Nb_{0.5})O_{3-\delta})$ (KNBNNO). The thesis work is organized and summarised as follows:

Chapter 1: Introduction - This chapter provides insights into the basics of semiconducting ferroelectrics for multifunctional devices and explains the area of interest. Recent advancements have highlighted the potential of these materials for photovoltaic applications. The intrinsic polar properties of these materials, such as ferroelectricity, provide additional possible mechanisms such as the piezoelectric effect and pyroelectric effect. The performance of these ferroelectric features depends on various intrinsic characteristics of ferroelectrics such as non-centrosymmetry, polarization, depolarization field, interface and domain walls. Therefore, the work is primarily focused on the investigation of ferroelectric domains in a novel member of the semiconducting ferroelectric community _ (K_{0.5}Na_{0.5})NbO₃-2mol.% Ba(Ni_{0.5}Nb_{0.5})O_{3- δ} (KNBNNO). KNBNNO has been chosen due to low bandgap and excellent piezoresponse. The thesis is based on the nanoscale investigation of ferroelectric domains in KNBNNO using piezoresponse force microscopy (PFM) and Kelvin probe force microscopy (KPFM) as well as macroscopic applications of KNBNNO. A brief idea about the nanoscale measurements (PFM and KPFM) employed in completing the work presented in this chapter.

Chapter 2: Optical control of ferroelectric domains - This chapter explains the optical control of ferroelectric domains in a novel bandgap (1.6 eV) engineered

ferroelectric (KNBNNO) which also exhibits an excellent piezo-response (100 pm/V). The light is found to work analogous to an applied electric field and the charge carriers generated by the presence of light are found to be compensated by the movement of ferroelectric domains. The domain wall velocities achieved by the exposure to the light source are of the order of 0.01 nm/s.

Chapter 3: Electro-optic control of ferroelectric domains - In order to make KNBNNO viable for practical application the domain wall velocities were further enhanced to 30,000 nm/s by utilizing the cumulative effect of light and low electric fields (< 4 kV/mm). The light illumination on this material is found to tune the material's electrical conductivity by 3 orders of magnitude and the charge injection due to illumination is governed by the ferroelectric photovoltaic effect. The developed understanding is used to demonstrate a prototype ferroelectric light-effect transistor which could be a potential solution to the scaling limit of three-terminal transistors.

Chapter 4: Mechanical control of ferroelectric domains - This chapter provides a nanoscale insight into mechanical as well as opto-mechanical control of ferroelectric domains in KNBNNO ((K_{0.5}Na_{0.5})NbO₃-2mol.% Ba(Ni_{0.5}Nb_{0.5})O_{3- δ}). KNBNNO is found to exhibit domain switching under atomic force microscopy (AFM) tip-induced mechanical force of 0.4 µN. Higher mechanical forces (> 3µN) are found to cause permanent deformation of the sample surface. Therefore, opto-mechanical manipulation of ferroelectric domains is studied under mechanical forces less than 1 µN. The optical, as well as mechanical changes in ferroelectric domains, are found to be fully reversible. However, opto-mechanical changes in ferroelectric domains for the same laser exposure time and energy are found to vary significantly with the mechanical pressure. This helped in concluding that it is possible to achieve a

different state of polarization by using the cumulative effect of light and mechanical forces. This provides a nanoscale explanation of the piezoelectric photovoltaic effect in ferroelectrics.

Chapter 5: Thermo-opto-electric effects in KNBNNO - This work dedicates towards the realization of this multi-source energy conversion, and thus provides an understanding of electric field-assisted modulation of photo-current and pyro-current in KNBNNO. Thereafter, electrical modulation under simultaneous photovoltaic and pyroelectric inputs is utilized to achieve several orders of an increase in the electrical output. This is attributed to a light-assisted increase in the material's electrical conductivity and ferroelectric photovoltaic effect. The phenomena of electro-optic and thermo-electro-optic modulations are further employed to propose two novel energy conversion cycles. The performance of both the proposed energy conversion cycles is compared to that of Olsen cycle (well-known for pyroelectric energy harvesting and capable of offering ~39000 higher current output than the pyroelectric effect using KNBNNO) in the operating temperature range of 20 °C to 200 °C, with a rhombohedral to tetragonal transition at ~ 170 °C, for the applied electric field range of 0-5 kV cm⁻¹, and illumination from dark to 405 nm wavelength. The electro-optic and thermo-electro-optic cycles are found to harvest 7 and 10 times more energy than the Olsen cycle, respectively. Moreover, both novel energy conversion cycles offer broader flexibility and ease in operating conditions thus paving a way towards the practice of multi-source energy harvesting with a single material for enhanced energy conversion capability and device/system compactness.

Chapter 6: Conclusions and future work – A summary of all conclusions made through this work is provided in this chapter.

List of publications

The following publications are largely based on the studies conducted as a part of the research work reported in this thesis.

- Gaurav Vats* et al., Mechanical control of piezo-photovoltaic effect, (To be submitted - 2020)
- 2. Gaurav Vats* *et al.*, Coalition of ferroelectric thermo-optical output for enhanced energy conversion, (To be submitted 2020)
- **3.** Gaurav Vats* *et al.*, A ferroelectric light-effect transistor by opto-electric control of domains, (Submitted 2020)
- 4. Gaurav Vats* et al., Optical control of ferroelectric domains: Nanoscale insight into macroscopic observations, Adv. Opt. Mater. (2019); 1800858, 1-8
- Richa Pandey[#], Gaurav Vats^{*,#}, et al, Mutual insight on ferroelectrics and hybrid halide perovskites: A platform for future multifunctional energy conversion, Adv. Mater. (2019); 31 (43), 1807376
- 6. Yang Bai, Gaurav Vats, et al, Boosting photovoltaic output of ferroelectric ceramics by optoelectric control of domains, *Adv. Mater.* (2018); 30(43), 1803821, 1-7
- Gaurav Vats*, Yang Bai, Jan Seidel, Light-assisted ferroelectric poling for ultralarge domain switching, IEEE-UFFC International Symposium on Applications of Ferroelectrics (ISAF), Switzerland, July 2019
- Gaurav Vats*, Yang Bai, Jan Seidel, Fundamental insight on optical control of ferroelectric domains, International Conference on Emerging Advanced Nanomaterials (ICEAN), Newcastle, Australia, November 2018
- *Corresponding/presenting author; [#]Equal contribution

List of Figures

Figure 1.1. (a) Perovskite structure with symmetric and (b) non-centrosymmetric
arrangements. (b)-(c) tuning of the degree of non-centrosymmetry by means of an
external stimulus
Figure 1.2. Relationships between perovskite, piezoelectric, pyroelectric and
ferroelectric materials
Figure 1.3. Classification of perovskites for multifunctional energy harvesting using a
single engineered material
Figure 1.4. Schematic of the pyroelectric effect where time-dependent thermal
fluctuations cause the displacement of the central atom in a non-centrosymmetric
perovskite and result in an output voltage
Figure 1.5. Schematic of (a) 33 and (b) 31 piezoelectric generator modes
Figure 1.6. (a) XRD pattern of the sintered KNBNNO pellets. (b) The optical band
gap determined from absorption and reflection spectra. (c) Frequency dependence of
ferroelectric hysteresis loops of bulk (black line) and $\sim 100~\mu m$ thick ceramic film and
converse piezoelectric coefficient with respect to the applied electric field (shown in
blue circles). (d) Pyroelectric response for temperature fluctuations between 40 0 C to
50 °C
Figure 1.7. (a) Photocurrent obtained from KNBNNO using Halogen and Deuterium
lamps (b) I-V characteristics of sintered KNBNNO pellets under 20 W white light
source
Figure 1.8. (a) Schematic of AFM components working and (b) Force-tip sample
separation plot showing the governing forces for measurement using contact and non-
contact AFM16

Figure 1.9. Schematic of two-pass KPFM used for measuring the contact potential
difference between the sample and the AFM tip17
Figure 1.10. Block diagram of the set-up used by Gruverman et al. ¹¹⁹ for mapping of
ferroelectric domains using AFM18
Figure 2.1. PFM images showing the change in piezoresponse with exposure to light
(monitored for 100 minutes of continuous laser exposure)
Figure 2.2. PFM images showing the change in piezoresponse after the laser was
turned off (monitored for 100 minutes after the laser was turned off)25
Figure 2.3. Light-dependent out of plane piezoresponse force microscopy (PFM)27
Figure 2.4. Light-induced changes in ferroelectric response. 29
Figure 2.5. Temperature-dependent ferroelectric hysteresis (<i>P-E</i>) loops of KNBNNO.
Figure 2.6. Out-of-plane phase (a) in dark condition, (b) after poling the whole area
with -6V bias and (c) 60 minutes post poling. Out-of-plane amplitude (d) in dark
condition, (e) after poling the whole area with -6V and (f) 60 minutes post poling32
Figure 2.7. Variation of photo- and electric- current. 32
Figure 2.8. Short-circuit photocurrent density measured macroscopically with Au
electrode on one side and ITO electrode on the other side for wavelengths (a) 660 nm
and (b) 552 nm, respectively. The light was shaded on the ITO electrode side of the
sample
Figure 2.9. Surface potential changes with light illumination
Figure 3.1. Comparison of electrical and optical response45

Figure 3.3. Material properties under the application of positive and negative electric
fields
Figure 3.4. In-plane light and dark current corresponding to applied voltages of 0.5
V, 1 V, 2 V, 3 V and 4 V measured on an un-poled sample with an inter-electrode gap
of 140 μ m. Inset shows the comparison of dark current for applied positive and
negative bias
Figure 3.5. The cumulative effect of light and applied electric field
Figure 3.6. Reproducibility of light assisted electric field poling with +4V at another
location
Figure 3.7. Reversibility of opto-electrically poled domains
Figure 3.8. Reproducibility of light assisted electric field poling with -4V at another
location53
Figure 3.9. Electrical control of the poled area
Figure 3.10. Controlling of the poled area by laser spot size
Figure 3.11. (Stability test at location 2) Irreversibility of opto-electrically poled
domains
Figure 3.12. (Stability test at location 3) Irreversibility of opto-electrically poled
domains
Figure 3.13. Modulation of photocurrent and electrical current
Figure 3.14. Photocurrent and modulation of electrical current corresponding to two
different states of polarizations
Figure 3.15. Modulation of photocurrent and electrical current
Figure 4.1. Mechanical switching in KNBNNO. 63
Figure 4.2. Figure 4.2. Change in area of up domains' and PFM amplitude as a

function of the applied mechanical force via AFM tip: (a) Area of up domains
(red-colored) and normalized maximum PFM amplitude depicted from the data shown
in Figure 4.1. (b) Force dependent variation in the area of up domains (red-colored)
and normalized maximum PFM amplitude obtained from the data shown in Figure 4.3
and 4.4. Note: The normalization factor for data shown in Figures (a) and (b) is
different to provide an overview of the force-dependent variation of the PFM
amplitude for the respective set
Figure 4.3. Determination of mechanical switching threshold
Figure 4.3. Determination of mechanical switching threshold and variation in
localized piezoresponse
Figure 4.5. Reversibility of mechanical force-induced changes
Figure 4.6. Optomechanical manipulation of ferroelectric domains and reversibility.
Figure 4.7. Photocurrent in KNBNNO: a) Nanoscale photocurrent measurement with
different AFM tip pressure of 0.07 uN and 1 uN. In this measurement tungsten-
carbide, AFM tip acted as the top electrode while the bottom was electrode Au-Cr. (b)
Macroscopic photocurrent measurement of the same KNBNNO sample with ITO
electrodes on both sides under different states of polarization
Figure 5.1. Electrical modulation of the photocurrent. 76
Figure 5.2. Electrical modulation of the pyro-current. 78
Figure 5.3. Electro-optic modulation of the pyro-current. 79
Figure 5.4. Novel electro-optic energy conversion cycle. 81
Figure 5.5. Temperature-dependent photocurrent measurement in the absence of
applied electric field

Figure 5.6. Temperature-dependent *I-V* measurement in (a) dark and (b) in light. ...82 Figure 5.7. Comparison of the energy harvested using the Olsen cycle (operating temperature range 20 0 C - 200 0 C), novel electro-optic cycle (operated at 20 0 C between dark and 405 nm laser wavelength), and thermo-electro-optic cycle (operating temperature range 20 0 C - 200 0 C; wavelength range: Dark to 405 nm). .83

CHAPTER 1 INTRODUCTION

This chapter provides background information about semiconducting ferroelectrics for multifunctional devices and explains the area of interest. Recent advancements have highlighted the potential of these materials for photovoltaic applications. The intrinsic polar properties of these materials, such as ferroelectricity, provide additional possible mechanisms such as the piezoelectric effect and pyroelectric effect. The performance of these ferroelectric features depends on various intrinsic characteristics of ferroelectrics such as non-centrosymmetry, polarization, depolarization field, interface and domain walls. Therefore, the work is primarily focused on the investigation of ferroelectric domains in a novel member of the semiconducting ferroelectric community - $(K_{0.5}Na_{0.5})NbO_3-2mol.\% Ba(Ni_{0.5}Nb_{0.5})O_{3-\delta}$ (KNBNNO).

KNBNNO has been chosen due to low bandgap and excellent piezoresponse. An overview of KNBNNO with reasons for studying this material is provided in Section 1.2. The thesis is based on the nanoscale investigation of ferroelectric domains in KNBNNO using piezoresponse force microscopy (PFM) and Kelvin probe force microscopy (KPFM). An overview of these techniques is provided in section 1.3 so as to provide a brief idea about the nanoscale measurements employed in completing the work presented in this thesis.

Parts of this chapter appear in "*R Pandey*[#], <u>*G Vats***</sub>[#], *J Yun, CR Bowen, AWY Ho-Baillie, J Seidel**, *KT Butler, and SI Seok**, *Advanced Materials 31, 1807376 (2019)*" ([#]Equal contribution; *Corresponding author)</u>

Contribution details: GV planned this review article, prepared outline, collected data/permissions, prepared figures and wrote 60% of this review paper. JS and CRB wrote about ferroelectric photovoltaics and pyroelectric energy harvesting, respectively. Also, both helped in improving discussion on ferroelectrics while JY, AWYHB, KTB, SIS worked on the hybrid halide perovskites (not included in this chapter/thesis).

1.1. Fundamental background

1.1.1. Introduction to ferroelectrics

'A ferroelectric is a material that exhibits, over some range of temperature, a spontaneous electric polarization that can be reversed or reoriented by application of an electric field.'¹ In general, ferroelectrics have ABX₃ type perovskite structure where A and B are cations of different atomic radii that occupy the corner and center of the unit cell, respectively, whereas X is an anion which is coordinated with B located at the face of the unit cell to form BX₆ octahedra; see Figure 1.1. (a) and (b). The coordination number of the cation A in an undistorted perovskite is 12, which is an alluring feature of the perovskite structure. Perovskites can be classified based on their band gap as conductors and insulators/dielectrics. Dielectrics with a bandgap less than 3eV are termed *semiconductors*. These can also be classified as centrosymmetric, asymmetric and non-centrosymmetric based on their symmetry. Several non-centrosymmetric perovskites are also ferroelectric in nature.



Figure 1.1. (a) Perovskite structure with symmetric and (b) non-centrosymmetric arrangements. (b)-(c) tuning of the degree of non-centrosymmetry by means of an external stimulus. Reproduced from refrence²

The definition suggests that ferroelectrics exhibit reversible spontaneous electric polarization (see the movement of the central atom in Figure 1.1. (b)-(c)).¹ However, the spontaneous polarization of several ferroelectrics can also be reversibly switched by application of stress¹, uniform heating/cooling¹ or light³⁻⁵. The phenomenon of achieving an electric charge by means of uniform heating or cooling is known as the '*pvroelectric*' effect' while an electrical change obtained by exposure to light and stress in a ferroelectric is termed the 'photoferroic effect' and 'piezoelectric effect' respectively. It is to be noted that all ferroelectrics are both pyroelectric and piezoelectric in nature, while the reverse is not true. At the same time, there exists a group of perovskites (semiconducting perovskites) which may or may not be non-centrosymmetric but have appealing charge generation and transport properties which lead to a significant 'photovoltaic' response; namely the effect of obtaining an electrical output on exposure to light. Figure 1.2. provides an insight into the relationship between these materials and suggests that a single material could have both ferroelectric and semiconducting nature. The coexistence of these features could be utilized for enhanced energy conversion and storage as well as next-generation opto-electric devices. Thus, it will be of interest to explore the possibilities of simultaneously utilizing these mechanisms a single ferroelectric perovskite material.

Ferroelectrics are well known for piezoelectric, and pyroelectric properties⁶⁻³², and are also gaining interest in photovoltaic and optoelectronic applications³³⁻⁴⁶. Therefore, a fundamental understanding of multiple inputs in a single ferroelectric material is worthy of consideration. Figure 1.3 indicates the classification scheme for perovskites and highlights the area of interest. The chosen area of interest aims to motivate the scientific community towards semi-conducting ferroelectrics. A detailed discussion of the key characteristics is provided in the following sections.



Figure 1.2. Relationships between perovskite, piezoelectric, pyroelectric and ferroelectric

materials. Reproduced from²



Figure 1.3. Classification of perovskites for multifunctional energy harvesting using a single engineered material. Reproduced from²



Figure 1.4. Schematic of the pyroelectric effect where time-dependent thermal fluctuations cause the displacement of the central atom in a non-centrosymmetric perovskite and results in an output voltage. Reproduced from²

1.1.2. Pyroelectricity

The ability to achieve a temporary voltage as a result of thermal fluctuation is known as the *pyroelectric effect*^{24, 30, 47, 48}. In ferroelectrics, a temperature change causes a change in the state of polarization and this change in polarization could further be utilized to obtain an electrical current through an external circuit. Figure 1.4 shows the schematic of time-dependent thermal fluctuations that lead to a displacement of the central ion in a non-centrosymmetric perovskite and results in a change in output voltage. It is to be noted that the mechanisms (in addition to non-centrosymmetric distortion) explained in the previous section could also lead to a pyroelectric effect in perovskites. This can be used to supply an electrical current using a resistive load. The change in polarization (ΔP_i) with temperature change (ΔT) is given as⁴⁹:

$$\Delta P_i = p \Delta T \tag{1.1}$$

where *p* is the pyroelectric coefficient perpendicular to the direction of the electrodes (i.e. in the polarization direction). Further, for a given surface area *A*, the induced short circuit current (I_P) for a given rate of temperature change (dT/dt) is^{49,50}

$$I_P = Ap \frac{dT}{dt} \tag{1.2}$$

1.1.3. Piezoelectricity

Piezoelectricity can be defined as the linear coupling between stress and electric charge¹⁴. Ferroelectric materials undergo a polarization change when mechanical stresses are applied and this change of polarization leads to an induced charge, which could further be extracted in the form of electrical current through an external circuit.¹⁴ The potential energy (QV) per unit charge generation (Q) due to stress-induced dipole movement can be expressed as the generated potential difference (V). Therefore, a piezoelectric element can generate both charge and potential difference. Ferroelectrics have a well-defined spontaneous polarization based on crystal orientation. The polar axis is denoted by direction '3'. The in-plane directions at the right angle to the polar axis could be considered the same and marked as '1'. In most commonly used piezoelectric device configurations the stress is applied either parallel (d_{33} mode) or perpendicular (d_{31} mode) to the polar axis, as shown in Figure 1.5.14 The maximum energy obtained from a piezoelectric element per cycle can be expressed as $\frac{c}{ab}d_{33}g_{33}F^2$ (for 33 mode) and $\frac{1}{a}d_{31}g_{31}F^2$ (for 31 mode). Here, d_{33} and d_{31} are piezoelectric charge coefficients (charge per unit force) while g_{33} and g_{31} are piezoelectric voltage coefficients (electric field per unit stress) in 33 and 31 directions respectively. These two configurations cover the most scenarios for practical piezoelectric energy harvesters. In addition, shear modes (such as

 d_{15}) have also been explored⁵¹ and should be noted that there exist several other configurations that become more complex in the systems with lower symmetry.⁵²



Figure 1.5. Schematic of (a) *33* and (b) *31* piezoelectric generator modes. Reproduced from reference¹⁴.

1.1.4. Charge transport properties of ferroelectrics

The charge transport properties of perovskites are controlled by mobilities, diffusion lengths, effective masses and lifetime of the charge carriers.^{53, 54} Ferroelectric oxides typically have short carrier diffusion lengths and lifetimes due to their high band gap⁵⁴ and hence have poor charge transport properties in contrast to well-known semiconductors.^{53, 54} However, the presence of dipoles, domains and boundaries facilitates charge separation.⁵⁵ The presence of surface charges, ions, dipoles, and electrons make it difficult to conclude the actual conduction mechanism in ferroelectrics. However, in general, the charge transport in ferroelectrics stems either from or a combination of bulk (Poole–Frenkel emission, Ohmic conduction, charge carrier hopping, space charge conduction) or/and interface (Schottky emission and Fowler–Nordheim tunneling) effects.^{53, 56} Additionally, charge screening at domain walls and conduction through domains plays an important role in governing the charge transport properties,

especially in ferroelectric thin films.⁵⁷⁻⁵⁹ Diffusion of oxygen vacancies and change in the oxidation state of central atoms due to the presence of oxygen vacancies have also been reported as the assisting mechanisms for better transport properties in ferroelectric oxides^{45, 46, 60, 61} and have been discussed in the context of small polaron hopping. The transport properties in ferroelectrics could further be tuned by heat-treatment and strain engineering which eventually leads to defect induced conduction.⁶²

1.1.5. Dielectric/semi-conducting properties

The dielectric property of a material is a result of the surface charge (P_{SC}) , dipolar (P_{dp}) , ionic (P_{ionic}) and electronic $(P_{electronic})$ polarizations. These polarizations are frequency-dependent and can be easily distinguished by relaxation on increasing the frequency in the following order: PSC, Pdp, Pionic, Pelectronic. Relaxation occurs due to a variation in the effective masses of the charge carriers associated with these polarizations. The dielectric constant of any material can also be expressed as a combination (ε' -i ε'') of real (ε') and imaginary (ε'') parts, where the real part represents the energy storage capability while the imaginary part denotes the associated energy losses. In general, an increase in the imaginary part (losses) on exposure to an external stimulus indicates a semiconducting behavior whereas an increase in the real part denotes a dielectric response. Therefore, an increase in the imaginary part or a decrease in the real part of the dielectric constant on exposure to light at high frequencies is a clear indication of lightinduced charge carriers (electrons and holes) and can be considered as a technique to reveal charge transport properties⁶³. However, it is to be noted that the dielectric behavior is also influenced by several other factors such as temperature dependence due to proximity to a phase, de-trapping trapped charges on light exposure, Rayleigh-like behavior associated with larger amplitude electric fields in ferroelectric materials.

1.1.6. Depolarization field

Ferroelectric materials possess a spontaneous polarization, i.e. electric dipoles are formed within the material. Ideally, if the ferroelectric is sandwiched between electrodes with the same work-function then the built-in voltage due to the presence of dipoles must be balanced by the presence of charges at the electrodes. However, in practice, the free charges at the electrodes are not able to completely cancel the space and polarization charges which gives rise to internal fields in the opposite direction of polarization⁶⁴. The cumulative internal field developed by these unscreened charges accumulated at the ferroelectric-metal interface is known as a *depolarization field* ^{53, 65}. It has been shown that the depolarization field is capable of changing the overall magnitude of the polarization, transition temperature, coercive field and the order of the phase transitions⁶⁶, ⁶⁷, which can further affect the charge transport characteristics⁶⁸. Interestingly, the depolarization field is dependent on the material as well as electrode thickness and the area of contact^{66, 67}. The depolarization field is negligible for a large inter-electrode distance in bulk ferroelectrics but is likely to increase with a reduction in inter-electrode distance, as in thin films^{64, 66, 67, 69}. This eventually makes it a governing factor for a number of applications in thin films as they significantly influence both the screening of spontaneous polarization and the separation charge carriers⁷⁰⁻⁷³.

1.1.7. Interface and domain wall effects

Domain walls in complex oxides have been the focus of intense research over recent years. The fact that domain walls can be electrically conducting opens new pathways for a number of applications.⁷⁴⁻⁷⁸ Recently anomalous photovoltaic effects related to domain walls in ferroelectric materials have been reported.^{33, 75, 79-85} Interestingly, electric-field control over the domain structure of a material allows the photovoltaic effect to be

reversed in polarity or even to be turned off. The band structure and local bandgap of domain walls in ferroelectrics have also been studied.⁸⁶⁻⁸⁹ In addition, photo-induced electrochemical effects at domain walls are a further interesting route in applications in water splitting⁹⁰ or for domain wall decoration (see⁹¹ and references therein). The spatial and temporal evolution of photo-induced charge generation and carrier separation in heteroepitaxial BiFeO3 thin films was measured using the Kelvin probe and piezoresponse force microscopy.⁹² Contributions from the self-poled and ferroelectric polarization charge were identified from the time evolution of the correlated surface potential and ferroelectric polarization in both, films as-grown and after poling, and at different stages and intensities of optical illumination. Variations in the surface potential with bias voltage, switching history, and illumination intensity were investigated. It was shown that both bulk ferroelectric photovoltaic and the domain wall offset potential mechanisms contribute to the photo-generated charge. Polycrystalline⁷⁰, 2-D interfaces⁹³⁻ ⁹⁶ and 1-D ferroelectric nanostructures have also been explored for enhanced photovoltaic responses^{97, 98,} in addition to nanoscale enhancements of ferroelectric photovoltaic effects at metal nano-tips.⁹⁹

1.1.8. Ferroelectric photovoltaic effect

The dipole moment in ferroelectrics could be triggered by light-induced localized heating, a fluctuation in the internal field and interface band bending. This facilitates the generation and separation of charge carriers at the material-electrode interface. In the early 1970s, a *bulk* or *anomalous photoferroic/ photovoltaic* effect was discovered in non-centrosymmetric crystals; this is also known as the *galvanic effect* or *non-linear photonics*^{36, 44}. This effect in ferroelectric and multi-ferroic materials refers to the phenomena of obtaining a steady-state current in the short circuit condition or a high

output photovoltage in the open-circuit condition in the direction of polarization of the materials on exposure to continuous illumination^{35, 40}. Initial investigations focused on bulk materials, but it was later observed and studied at the nanoscale, which became a reason for the effect to be described as a *'bulk'* photovoltaic effect (BPVE); while the term *'anomalous'* photovoltaic effect (APVE) was used due to experimental observations of photovoltages 10³ to 10⁴ times higher at open circuit in contrast to the bandgap of the material^{35, 39}. Not all ferroelectrics exhibit an APVE, as it is dependent on the polarization magnitude¹⁰⁰, direction of polarization^{34, 41, 101}, light intensity¹⁰², electrode spacing^{69, 103}, electrical conductivity³⁹ and the crystallography of the material^{69, 104, 105}, in addition to the nature of domain walls^{33, 34} and material/electrode interfaces¹⁰⁶. Its dependence on so many factors often leads to difficulty in reproducing the APVE, even in the same material^{54, 107}. Therefore, several models have been proposed to explain the distinct type and nature of photoferroic effects. These include Schottky-junction effects, depolarization field effects, and interface and domain wall effects^{33, 34}

1.2. Material selection and literature

Section 1.1 helps us understand that non-centrosymmetry and polarization plays a crucial role in governing the ferroelectric properties. On the other hand, the understanding of how ferroelectricity helps to achieve an enhanced photo-response is an open question¹⁰⁸. Moreover, from the photovoltaics view-point, there is a strong requirement of developing new ferroelectrics with a narrow bandgap and improved conductivity. Beyond this, other important considerations are the presence of piezo- and pyro-electricity in ferroelectrics as these effects along with photovoltaic effect can help in achieving a higher electrical output. One such attempt has been made by Rappe and co-workers where they tuned the bandgap of a ferroelectric oxide to 1.1-1.38 eV.⁴⁶ Inspired by this,

Yang *et. al.* recently illustrated an enhanced electrical output by simultaneously employing the pyroelectric and photovoltaic effect in a novel lead-free ferroelectric ceramic - $(K_{0.5}Na_{0.5})NbO_3-2mol.\%$ Ba $(Ni_{0.5}Nb_{0.5})O_{3-\delta}$ (KNBNNO).⁴⁵ The KNBNNO exhibit a bandgap of 1.65 eV with an excellent piezoresponse ($d_{33} = 100$ pm/V).



Figure 1.6. (a) XRD pattern of the sintered KNBNNO pellets. (b) The optical band gap determined from absorption and reflection spectra. (c) Frequency dependence of ferroelectric hysteresis loops of bulk (black line) and $\sim 100 \ \mu m$ thick ceramic film and

converse piezoelectric coefficient with respect to the applied electric field (shown in blue circles). (d) Pyroelectric response for temperature fluctuations between 40 $^{\circ}$ C to 50 $^{\circ}$ C. Reproduced from reference⁴⁵



Figure 1.7. (a) Photocurrent obtained from KNBNNO using Halogen and Deuterium lamps (b) *I-V* characteristics of sintered KNBNNO pellets under 20 W white light source. Reproduced from reference⁴⁵

Figure 1.6 (a) shows XRD pattern of the sintered KNBNNO pellets and helps in confirmation of the single-phase in the newly developed KNBNNO ceramics. Figure 1.6 (b) confirms the optical bandgap of 1.6eV from absorption and reflection spectra while the frequency dependence response and piezoelectric properties could be visualized in Figure 1.6 (c). Figure 1.6 (d) provides an overview of KNBNNO's pyroelectric response for temperature fluctuations between 40 °C to 50 °C. Yang *et. al.* found that KNBNNO exhibits above bandgap photovoltages and is sensitive to the full visible spectrum (see Figure 1.7).⁴⁵ However, there is no report on the investigation of ferroelectric domains in KNBNNO. The KNBNNO has been chosen for the work presented in this thesis due to it's excellent ferroelectric and semiconducting features and lack of understanding of the domain wall behavior. The same quality samples were provided by Yang Bai for our investigation. The procedure for sample fabrication is as follows:

Sample fabrication: (K_{0.49}Na_{0.49}Ba_{0.02})(Nb_{0.99}Ni_{0.01})O_{2.995} (KNN-BNNO) ceramics were fabricated by conventional solid-state reaction method, from the starting reactants of $K_2CO_3 (\ge 99 \%, J. T. Baker, USA)$, $Na_2CO_3 (\ge 99 \%, Sigma-Aldrich, USA)$, $BaCO_3$ (99.98 %, Aldrich Chemistry, USA), NiO (99.999 %, Aldrich Chemistry, USA) and Nb₂O₅ (99.9 %, Aldrich Chemistry, USA). As the reactants are hygroscopic, they were dried at 220 °C for over 4 hours before weighing, in order to ensure the correct stoichiometry. The precise weighing was carried out with an electronic balance of 0.01 mg readability and 1 mg accuracy (ES 225SM-DR, Precisa, Dietikon, Switzerland). The weighed reactants were mixed in a ZrO₂ jar on a planetary ball mill (Pulverisette 6, Fritsch, Idar-Oberstein, Germany). ZrO₂ balls (3 mm diameter) and ethanol were used as the milling media. The mixing went for 6 hours, followed by drying at 80 °C. The onestep calcination was carried out at 850 °C for 4 hours in the air. The calcined powder was milled again for 12 hours with the same procedure presented above. After drying at 80 °C, 8.8 wt.% of the binder (3.3 wt.% polyvinyl alcohol dissolved in deionized water) was added and mixed with the powder. The mixture was uniaxially pressed at 62 MPa into 14.5 mm diameter discs. Following burning off the binders at 500 °C for 10 hours with a slow ramping rate of 1 °C min⁻¹, the discs were subsequently sintered at 1165 °C for 2 hours on Pt foil. During sintering, the samples were placed in a covered alumina crucible and buried by the sacrificial powder of the same composition to help inhibit the volatilization of potassium. After sintering samples were polished with P1200 silicon carbide abrasive paper (Eco-Wet, KWH Mirka Ltd., Finland) cooled by ethanol on a 3 µm grain-sized plate (MD Dur, Struers, Denmark) with diamond suspension (DiaPro Mol B3, Struers, Denmark), and on a 1 µm grain-sized plate (MD Nap, Struers, Denmark) with diamond suspension (DiaPro Nap B1, Struers, Denmark). An average surface roughness of 50-60 nm was obtained. The samples were finally 100-150 µm thick. In

addition, a 200 nm thick ITO (indium tin oxide) electrode was coated on one side of each sample whilst a 220 nm thick metal (20 nm Cr and 200 nm Au, Au on top) electrode was put on the other side.

1.3. Instruments and methods

1.3.1. Scanning Probe Microscopy

Scanning probe microscopy (SPM) is a powerful tool for imaging material topography and atomic-scale interactions. The research in this direction was sped up with the discovery of the scanning tunneling microscope.^{109, 110} Following the pioneering work by Binnig and Rohrer^{109, 110}, Williams and Wickramasinghe developed non-contact modes for studying localized interactions.¹¹¹ SPM modes can be classified as contact, tapping, and non-contact mode. Most of the SPM techniques require a cantilever with a tip attached to the end. If the tip is in direct contact with the sample then it is known as the contact mode. On the other hand, a vibrating tip is used to gently touch the sample in the tapping mode and is kept in close proximity to the sample in the non-contact mode. The deflection of the tip due to various forces (mechanical, electrostatic, Van der Waals, Casimir or chemical interactions) is used to prepare a false-color image of the respective interactions and the surface topography. One of the most prominently used types of SPM is Atomic Force Microscopy (AFM) or Scanning Force Microscopy (SFM). AFM uses sharp tips with a reflective coating on the backside of the cantilever. In this technique, a photodiode detector is used to map the movement of the AFM tip as shown in Figure 1.8 (a). Figure 1.8 (b) shows the attractive and repulsive forces as a function of tip-sample separation. In the non-contact or tapping mode, the tip is balanced against these attractive and repulsive forces using a combination of AC and DC bias applied to the tip with the help of a feedback system. The feedback loop helps in creating an estimate of the nanoscale forces exerted on the AFM tip due to the sample. The resolution obtained by AFM depends on the tip radius, cantilever quality factor, environment conditions (vacuum, the high vacuum of ultra-high vacuum), the force exerted by the cantilever on the surface of the sample, applied electric field, and the scanning speed during the measurement.



Figure 1.8. (a) Schematic of AFM components working and (b) Force-tip sample separation plot showing the governing forces for measurement using contact and non-contact AFM. Reproduced from reference¹¹²

1.3.2. Kelvin Probe Force Microscopy

Kelvin Probe Force Microscopy (KPFM) or Scanning Maxwell Stress Microscopy is a non-contact technique that was introduced by Nonnenmacher and Wickramasinghe.¹¹³ It is used to measure the contact potential difference (CPD) between the conductive AFM tip and the sample surface and hence allows collecting information about the surface charges.^{3, 114-116} The surface potential in this method is measured by having dual-pass over the sample surface. In the first pass, the sample topography is imaged while in the second pass, the tip is lifted at a constant height and is oscillated using the AC bias $V_{ac}Cos\omega t$ as shown in Figure 1.9 below:


Figure 1.9. Schematic of two-pass KPFM used for measuring the contact potential difference between the sample and the AFM tip. Adapted from reference¹¹⁷

The electrostatic contact potential difference between the tip and the sample is defined as $(\Delta V = V_{tip} - V_{sample} + V_{ac} Cos\omega t; \Delta V = \Delta V_{dc} + V_{ac} Cos\omega t)$ and the electrostatic energy can be obtained by the following expression:

$$U = \frac{CV^2}{2} \tag{1.2}$$

The force of attraction can further be defined by $F = -\frac{\partial U}{\partial z} = -\frac{1}{2}\frac{\partial C}{\partial z}(\Delta V)^2$. Substituting all values in this expression, we can have the following equation for all interacting forces during the measurement:

$$F = -\frac{1}{2}\frac{\partial C}{\partial z}\left((\Delta V_{dc})^2 + \frac{1}{2}V_{ac}^2\right) - \frac{\partial C}{\partial z}\Delta V_{dc}V_{ac}\sin(\omega t + \phi) + \frac{1}{4}\frac{\partial C}{\partial z}\cos(2\omega t + 2\phi)$$
(1.3)

The static deflection of the tip can be modeled by the DC term $\left(-\frac{1}{2}\frac{\partial C}{\partial z}\left((\Delta V_{dc})^2\right)\right)$ while the ΔV_{dc} in the first harmonic term $\left(-\frac{\partial C}{\partial z}\Delta V_{dc}V_{ac}\sin(\omega t + \varphi)\right)$ represents the CPD. In order to nullify the CPD, a DC bias is applied to the tip for maintaining a constant height in the second pass. The filtered signal is imaged as the CPD using KPFM. The third term $\left(\frac{1}{4}\frac{\partial C}{\partial z}\cos(2\omega t + 2\varphi)\right)$ in the equation is known as the second harmonic term and can be used to depict the dielectric constant of the material by suitably modeling of the capacitance.



Figure 1.10. Block diagram of the set-up used by Gruverman *et al.*¹¹⁸ for mapping of ferroelectric domains using AFM. Reproduced from reference¹¹⁸

1.3.3. Piezoresponse Force Microscopy

Piezoresponse Force Microscopy (PFM) is a contact mode technique based on the inverse piezoelectric effect discussed in previous sections. It has been widely employed to image and study ferroelectric domains since the early 1990s.¹¹⁸⁻¹²³ Figure 1.10 shows the block diagram of one of the first set-ups used to perform PFM on ferroelectric materials.¹¹⁸ In this method, a voltage (V_{tip} - V_{dc} + $V_{ac}Cos\omega t$) is applied to the sample. This applied voltage causes a localized change in the sample height (z= z_{dc} + $A(V_{dc}, V_{ac}, \omega t)V_{ac}$ $cos(\omega t + \phi)$) due to the piezoelectric effect. The change in the sample height is measured by the vertical deflection of the cantilever. The cantilever response is resolved by the Lock-in amplifier to visualize the structure of ferroelectric domains. The PFM amplitude provides information about the piezoresponse of the material while the phase signal helps in distinguishing the areas with different states of polarization/domains. The magnified view of the SFM tip and sample interactions in Figure 1.10 shows that the areas with opposite polarization directions will vibrate with a phase difference of 180⁰.

In our experiments, we used a customized AIST-NT Smart SPM system and an additional Fianium Whitelase supercontinuum laser source for shining light of different wavelengths (405 nm, 500 nm, 600 nm, and 700 nm) on the sample surface. The maximum intensity corresponding to a wavelength of 405 was 8.1 Wcm⁻². The switching voltages were initially determined by the electrical poling experiments. An AC bias of 5 kVm⁻¹ was found to be able to cause partial domain switching in the samples. Therefore, an optimized AC bias of 2 kVm⁻¹ was applied between the bottom Cr-Au electrode and the conductive AFM tip in all PFM experiments.

CHAPTER 2

OPTICAL CONTROL OF FERROELECTRIC DOMAINS

Domain wall nanoelectronics constitutes a potential paradigm shift for nextgeneration energy conversion and von-Newman devices.¹²⁴ In this context, attempts have been made to achieve energy-efficient control over ferromagnetic^{125, 126}, ferroelectric^{127, 128} and ferroelastic¹²⁹ domain walls through electric and magnetic fields or applied stress. However, optical control of ferroic domains offers an additional degree of freedom and significant advantages of reduced hysteresis and Joule heating losses by eliminating the physical contacts. Therefore, optically controlled domain walls create novel opportunities in the regime of nano-electronics and photonics.

In this chapter, reversible optical control of domains in lead-free ferroelectric ceramic $(K_{0.5}Na_{0.5})NbO_3$ -2mol.% Ba $(Ni_{0.5}Nb_{0.5})O_{3-\delta}$ (KNBNNO) is demonstrated. The light generated charge carriers are transported towards domain walls or electrodes due to a nonzero field in the samples causing a change in the internal electric field influencing the nanoscale state of polarization, which could also be interesting for other ferroelectrics if the voltage generated by light is in the range of the switching voltages. This work establishes a relationship between light-induced macroscopic observations and nanoscale changes in the ferroelectric response, providing fundamental insight and facilitating research into ferroelectric photovoltaics and optoelectronics.

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Contribution details: GV performed all nanoscale experiments (in the supervision of JS), visualized the results and wrote the manuscript. YB prepared the samples and performed macroscopic measurements. DZ helped in preparing figures and discussion of the results. All co-authors discussed the results and provided inputs for finalizing the manuscript.

2.1. Motivation

As discussed in the previous chapter, ferroelectric materials possess a spontaneous polarization that can be reversibly switched using external electrical fields. Warren et. al. manifested that it is also possible to tune the state of spontaneous polarization merely by the exposure of light.¹³⁰ Fundamental understanding of this mechanism is likely to offer new device prospects especially in optoelectronics and information storage.^{5, 128, 131-133} It is to be noted that the photovoltaic effect in ferroelectrics is well known since the 1960s³⁵, ^{37, 134-138} and has been investigated for the optical reading of ferroelectric random-access memories^{139, 140}, photodiodes¹⁴¹ and photovoltaic^{40, 80, 131, 142-146} applications. Current research is focused on developing band-gap tuned ferroelectric materials as their performance is restricted by low mobility of charge carriers and short diffusion lengths.^{46,} ^{147, 148} Bandgap tuned ferroelectric materials are capable of hosting multiple functionalities (due to ferroelectricity and semiconducting features) which suggest the possibilities of multiple energy conversions (piezoelectric, pyroelectric and photovoltaic) simultaneously. In this context, Bai et. al. synthesized a novel band-gap (1.6 eV down from > 4 eV) engineered lead-free ferroelectric composition ($(K_{0.5}Na_{0.5})NbO_3-2 mol.\%$ Ba(Ni_{0.5}Nb_{0.5})O_{3- δ} (KNBNNO, or KNN-BNNO)) and demonstrated multiple functionalities (piezoelectric, pyroelectric and photovoltaic effects) and their cumulative effect using this single material.45, 149, 150 (K0.5Na0.5)NbO3 (KNN) supports off-center distortion and is responsible for the ferroelectric nature of KNBNNO while Ba(Ni_{0.5}Nb_{0.5})O_{3- δ} (BNNO) controls the electronic states in the gap of the parent (K_{0.5}Na_{0.5})NbO₃ using oxygen vacancies and Ni⁺² ions.⁴⁶ The simultaneous presence of ferroelectric and semiconducting features makes this composition alluring for photovoltaic applications. In addition, it also provides an opportunity to understand how ferroelectric properties in semiconductors could help in improving the photovoltaic

response and vice-versa. In this context, the present study aims to provide an insight into light-induced changes in the ferroelectric behavior of KNN-BNNO. The recent demonstration of light-driven switching of nano-domains in $(K_{0.5}Na_{0.5})NbO_3$ also makes it interesting to further explore KNN-BNNO¹⁵¹.

Light-induced changes in ferroelectrics could persist due to a number of reasons such as (i) localized heating assisted diffusion of alkali element (as in LiNbO₃) and oxygen vacancies¹⁵², (ii) change in oxidation state of the central atom (e.g. in $BaTiO_3$)¹⁵³ and (iii) Jahn Teller distortions due to light-induced pyroelectric current or charge injection in the conduction band (as in SbSI)^{134, 138}. Warren et. al. suggested that similar to electrical and thermal fluctuations, exposure to light involves "locking domains by electronic charge trapping at domain boundaries".¹³⁰ Any change in the macroscopic behavior could be attributed to nanoscale changes in the ferroelectric domains. Moreover, it is interesting to know which of the three mechanisms is responsible for the optical behavior of KNN-BNNO. Hence, light-dependent nanoscale changes are investigated in KNN-BNNO using a homemade photoelectric atomic force microscopy (see the Method section for details). In this study, Piezo-response Force Microscopy (PFM) and Kelvin Probe Force Microscopy (KPFM) measurements have been performed and the obtained results have been correlated with the macroscopic observations. The same results have been used to confirm the achievement of additional control over ferroelectric behavior by the exposure of light. An understanding thus attained would be helpful in developing semiconducting ferroelectrics based optoelectronic devices with additional functionalities. Moreover, it will stimulate the development of novel device mechanisms to achieve optical control over ferroelectricity and ferroelectric domain walls by effective utilization of the associated semiconducting material characteristics.

2.2.Experimental details

Macroscopic characterization: A ferroelectric test system (Precision LCII, Radiant Technologies, Inc., USA) was used to measure ferroelectric hysteresis (*P-E*) loops. The temperature was controlled by silicone oil heated on a hot plate. The d_{33} values were measured with the Berlincourt piezoelectric meter (YE2730A, APC International Ltd., USA). A source meter (2450, Keithley, USA) was used to measure photocurrents. Lasers (OBIS LX/LS series, Coherent, USA) with different wavelengths were used as the light sources. The wavelength/maximum power/beam diameter at $1/e^2$ were 405 nm/50 mW/0.8±0.1 mm, 552 nm/20 mW/0.7±0.05 mm and 660 nm/100 mW/0.9±0.1 mm, respectively. A 14 W white light energy-saving fluorescent lamp which illuminated the entire sample surface with an intensity of ~12.5 mW cm⁻² was used to test light-induced poling. The intensity of the white light was measured with an S120C silicon photodiode detector integrated with a PM100D optical power and energy meter (Thorlabs, Germany). The incident light was shaded on the ITO electrodes.

Nanoscale measurements: A Cr-Au electrode was deposited on one side of the sample while the other surface was left uncoated and was then further polished using a 0.25 µm diamond suspension (DiaPro Nap 1/4, Struers, Denmark). The peak-to-peak surface roughness was reduced to 5-10 nm. The disc samples were laser-cut into 5 mm x 5 mm square samples for the convenience of nanoscale measurements. AFM (Atomic Force Microscopy), PFM (Piezoresponse Force Microscopy) and KPFM (Kelvin-probe Force Microscopy) measurements were performed in the dark using a customized AIST-NT Smart SPM system and a Fianium Whitelase supercontinuum laser. The light source with variable wavelengths (405 nm, 500 nm, 600 nm, and 700 nm) was used to illuminate the samples. The maximum intensity corresponding to a wavelength of 405 was 8.1 Wcm⁻². The switching voltages were initially determined by the electrical poling experiments. An

AC bias of 5 kVm⁻¹ was found to be able to cause partial domain switching in the samples. Therefore, an optimized AC bias of 2 kVm⁻¹ was applied between the bottom Cr-Au electrode and the conductive AFM tip (Platinum coated NSC35/PT probes from MikroMasch) when carrying out the light-induced temporal PFM measurements. A noncontact mode with a lift height of 10 nm was chosen for the KPFM measurements. All KPFM measurements were performed on the same area (1000 nm x 500 nm) with a lift height of 10 nm. The scan direction was fixed from the bottom left corner to the top. Images in Figure 2.9 (a) and (b) of the main text were captured with a scanning speed of 1 Hz while the images and data corresponding to Figure 2.9 (c) and (d) were captured with a scanning speed of 0.5 Hz. Consequently, the time to acquire the image of Figure 2.9 (c) and the number of data points were increased. The sample was allowed sufficient time (1 hr for each measurement) to reach a fully relaxed state in dark condition before performing the measurement. The scan started in the dark and then the sample was exposed to laser light of wavelength 405 nm till 200 s. Thereafter, the laser was turned off and the decay in surface potential was measured. Similarly, measurements were performed for other wavelengths as well in the same area under similar conditions. Finally, the extracted line profile of all images is plotted in Figure 2.9 (d).

2.3.Results and discussion

Firstly, light-dependent temporal PFM was performed to understand the nanoscale effects of light on KNN-BNNO. Out-of-plane phase images and PFM amplitude were acquired every 10 minutes for 100 minutes of continuous exposure to a monochromatic DC laser source of wavelength 405 nm (see Figure 2.1). Afterward, the laser was turned off and the PFM signal was recorded for another 100 minutes in dark (shown in Figure 2.2). Figure 2.3 (a)-(f) presents the nanoscale movement of domains and domain walls

with continuous exposure to light and the reversal on turning the light off. The changes are highlighted by the dotted white boxes. Interestingly, most of the domains returned to their original position with a few exceptions. These exceptions could be attributed to the difference in the potential energy of the unrecoverable domain walls from those of the recoverable.¹⁵⁴ For these unrecoverable domain walls, the exposure of light might have given enough energy to fully overcome the potential between out-of-plane and in-plane domain walls or defects. When the light was turned off, these stable domain walls could not fully reverse to the initial status, because they had to overcome the same potential, but no extra energy was obtained and allowed them to do so.



Figure 2.1. PFM images showing the change in piezoresponse with exposure to light (monitored for 100 minutes of continuous laser exposure).



Figure 2.2. PFM images showing the change in piezoresponse after the laser was turned off (monitored for 100 minutes after the laser was turned off).

Another intriguing observation is the change in contrast of domains shown in Figure 2.3 (a) and (b). This can be more clearly observed in Figures 2.1 and 2.2 which signify a change in the phase difference of the domains with up and down polarizations. In order to elucidate this, PFM amplitude of domains with outward polarization are plotted in Figure 2.3 (g) and the fractional change in domain area (calculated from out-of-plane bright domains) is unfolded in Figure 2.3 (h) (shaded area represents the time corresponding to the laser exposure). Both trends complement each other. It can be established that exposure to a laser source leads to the increase in piezo-response of the domains to a maximum value followed by domain relaxation at a point with higher piezo-response in contrast to the dark condition. Such behavior can be interpreted as light-induced ferroelectric poling. Furthermore, it is found that the area fraction decreases on exposure to the laser source in comparison to the dark condition followed by a sudden jump corresponding to the maximum PFM amplitude and finally leading to the minimal domain area of the relaxed condition (Figure 2.3 (h)). It is to be noted that the piezoresponse amplitude of the first image acquired in dark conditions is significantly different from the image acquired after 100 minutes of turning the laser off. This is because the sample is very sensitive to the full spectrum of the visible light including the white light in the room and was not at a fully relaxed condition at the beginning of the experiment. To confirm this, similar experiments were carried out at several locations with different pre-experiment dark resting time, but it was difficult to estimate the actual dark condition response.

The confirmation of the optical poling of ferroelectric domains was also performed macroscopically by exposing an unpoled sample with negligible piezoelectric constant to white light for 8 hours. Post-exposure piezo-response (piezoelectric charge coefficient d_{33}) of the sample raised to 4 pC/N, which also confirms the optical control of the

polarization state of the ferroelectric domains. It is to be noted that the optical poling of ferroelectric domains depends on the intensity of incident radiation and the exposure time. In the present case, the illumination source only helped in partial and reversible poling of the sample, not a complete poling of the sample, which could lead to very high d_{33} (200 pC/N)⁴⁵ values. The light-induced change in polarization state was also confirmed by the difference in the piezo-response of the samples electrically poled in dark and light (405 nm) conditions for the same time (30 mins) and applied electric field (1 MVm⁻¹). The sample poled in dark showed a piezo-response of 25 pC/N while the sample poled in light illustrated 37 pC/N. Both these d_{33} values were measured in dark. Since the d_{33} is dependent on the polarization of the material, it can be concluded macroscopically as well as at the nanoscale that light can be used to achieve optical control over ferroelectric polarization in KNN-BNNO.



Figure 2.3. Light-dependent out of plane piezoresponse force microscopy (PFM): Phase images acquired (a) under dark, after (b) 20 minutes and (c) 30 minutes of

continuous exposure to a laser source of 405 nm wavelength. Images acquired after (d) 10 minutes, (e) 20 minutes and (f) 30 minutes of laser off, respectively. Change in the color contrast indicates the localized change in piezoresponse. Light-induced change in PFM amplitude is highlighted in (g) while the average fraction change in domain area is plotted in (h). (i)-(k) show the magnified view of domain wall motion corresponding to dark, laser exposure and post-laser exposure state. (Note: the notation of up and down domains is different for Figure (a)-(f) and (i)-(k) just to have better presentation).

In addition to the results shown above, reversible control over domain walls is unveiled in Figure 2.3 (i)-(k). A clear reversible and fully reproducible collapse and splitting of two domain walls can be observed on exposure to laser and on turning it off, respectively. The understanding attained so far concludes optical control of domain walls and light assisted electrical poling. However, it is difficult to measure the exact difference in the domain and domain wall velocities on exposure to light as it is a dynamic process and is continuously occurring during the PFM scans. This could be clearly observed from the squared areas in Figure 2.1. From our measurements, domain walls velocities as high as 1 nm/minute have been observed (e.g. seen in Fig. 2.3 (i-k)). In principle, a constantly applied DC bias will lead to the state of maximum polarisation until an equilibrium is achieved. Afterward, the macroscopic polarisation, which is a resultant of the interaction between polarisations, becomes constant. Nevertheless, this constant change in macroscopic observation does not guarantee an equilibrium at the nanoscale. The lightinduced maximum polarisation in two adjacent domains may keep on interacting with each other for very long times in contrast to the macroscopic equilibrium time (see the fluctuation in the encircled domain in Figure 2.1). On the contrary, the change in macroscopic polarisation with light (shown in Figure 2.4 (a)) was found to be

instantaneous and stable over long periods of time (no change was observed even after 1 hr). This means that the light-induced nanoscale changes instantaneously provide the most significant macroscopic fluctuation in polarisation. Thereafter, longer exposure times (~8 hrs) lead to partial poling of the sample which supports the argument of continuous long-term interaction of domains until a state of equilibrium is achieved. Intriguingly, this also suggests that light-dependent nanoscale and macroscopic changes could be utilized separately for distinct device applications. An understanding of the physics behind this phenomena could help to achieve precise control over domain walls that can be used to prepare an optically controlled ferroelectric counterpart of spin-polarized race-track memories¹⁵⁵ and many other advanced optoelectronic devices.



Figure 2.4. Light-induced changes in ferroelectric response: (a) Ferroelectric hysteresis (P-E) loops (measured at 1 Hz), (b) frequency dependence of relative permittivity, (c) dielectric losses as a function of log frequency and (d) the relative change

in relative permittivity measured in dark and illuminated conditions.



Figure 2.5. Temperature-dependent ferroelectric hysteresis (P-E) loops of KNBNNO.

The aforementioned observations in KNN-BNNO could be distinguished from localized heating and pyroelectric effect by temperature-dependent *P-E* loops displayed in Figure 2.5. A nominal change ($< 2\mu$ C/cm²) in polarization over the broad temperature range (20^oC to 155^oC) ruled out the possibility of localized heating and pyroelectric effect. All of the nanoscale experiments were performed at room temperature and the localized temperature change corresponding to the wavelength of 405 nm was found to be 0.5^oC (direct measurement using a thermocouple). Furthermore, nanoscale electrical poling experiments were performed to have an insight into the light-dependent behavior. It is found that the sample is quite sensitive to the electrical poling and even small voltages (both AC and DC) of 5 kVm⁻¹ are sufficient to cause a change in ferroelectric domains. Therefore, a significantly higher DC bias of -60 kVm⁻¹ was chosen for the electrical poling experiment while PFM was performed with an AC bias of 2 kVm⁻¹. The experiments were performed under the same parameters as during optical poling in full

dark conditions. Post-poling PFM images acquired at constant intervals for 60 minutes suggest that the electrical poling using negative bias behaved analogous to the optical poling (see results depicted in Figure 2.6). The domains returned to their original position in around 30 minutes and attained stability afterward. This means that the light is acting as a constant current source for the material as all experiments were performed in the short circuit conditions. The same phenomenon was confirmed using light-dependent $(\lambda = 405 \text{ nm})$ short circuit current measurement as shown in Figure 2.7. Figure 2.7 (a) shows the photocurrent measured macroscopically with Cr-Au and ITO electrodes. The sample is behaving as a photo-transistor/photo-detector – a device where merely by switching the light on and off a remarkable change in short circuit current density could be observed. Similar behavior was observed in the full visible light range but with a comparatively lower photocurrent density (See Figure 2.8). The photocurrent was also observed at the nanoscale (Figure 2.7 (b)) with Cr-Au electrode on one side of the sample and AFM tip acting as the electrode on the other side. However, a small AC bias of 2 kVm⁻¹ was applied for nanoscale photocurrent measurement for the following two reasons:

- (i) The photocurrent values fall below the detection range of the instrument as the electrode size (AFM tip contact ~ 10 nm) is very small and, therefore, it becomes difficult to detect the short-circuit photocurrent corresponding to λ =405 nm. The photocurrent for wavelengths >405 nm is even smaller and therefore the nanoscale photocurrents corresponding to them were not recorded.
- (ii) All PFM measurements were performed with an AC bias of 2 kVm⁻¹. So, it becomes essential to understand the photocurrent behavior under the same conditions.



Figure 2.6. Out-of-plane phase (a) in dark condition, (b) after poling the whole area with -6V bias and (c) 60 minutes post poling. Out-of-plane amplitude (d) in dark condition, (e) after poling the whole area with -6V and (f) 60 minutes post poling.



Figure 2.7. Variation of photo- and electric- current: (a) Short circuit photocurrent

density measured macroscopically with Au electrode on one side and ITO electrode on the other side. (b) Photocurrent density measured using the AFM tip as one electrode while the Au electrode on the other side of the sample. The laser spot was larger than the AFM tip, so the size of the AFM tip can be considered as an effective area of contact. An AC bias of 2 kV/m was applied for photocurrent measurement using AFM while no bias was applied for macroscopic measurement. Change in current density with an applied bias of (c) + 10 kV/m and (d) -10 kV/m for the under the same conditions in which light was shined on the sample. Note the difference in the direction of an increase in current density with light, positive bias, and negative bias. Photo-response works analogously to applied negative bias.

Analogous to macroscopic photocurrent density a significant difference in the nanoscale photocurrent density was observed merely by changing the light intensity. This means that the small-applied AC voltage only helped in scaling the photocurrent density and tuning the sensitivity of the instrument. The nanoscale photocurrent measurement clearly shows that there is a huge difference in rising and decay times of the photocurrent that can be estimated using exponential fitting ($I = I_0 + A_1 e^{\pm (t-t_0)/\tau}$). τ is the photocurrent rise and decay constant, found to be 12 s and 72 s, respectively. This difference in rise and decay time explicates why the domain movement on exposure is faster in contrast to the reversal in dark (note that the maximum nanoscale change is observed in the first 10 minutes of exposure (see 2.1 (a)-(b)) while a significant reversal is observed in the first 30 minutes after turning the laser off (See Figure 2.2 (a)-(d)). In addition to this, the change in current density was also recorded for positive (Figure 2.7 (c)) and negative (Figure 2.7 (d)) bias of 10 kVm⁻¹ which was chosen to show a significant difference in the current density with the least possible influence of the

switching current. Similar trends of change in current density were observed at different locations on the sample when measured (AFM tip was placed) at up and down domains and their interfaces. Intriguingly, the direction of the increase in current density for applied negative bias is found to be the same as of the photocurrent and is opposite to the direction of increase in the current density for applied + 10 kVm⁻¹. This helps in establishing the fact that the sample supports a particular type of charge carrier, which is obvious for any semi-conducting material. Having established this fact, an understanding of the shrinking of bright (up) and the expansion of dark (down) domains on exposure to illumination could be made. The orientation/polarisation of domains is due to the specific alignment of dipoles in a region. Change in concentration of charge carriers in the material influences the orientation of the dipoles and hence the state of polarisation. That is why up domains are favored under illumination and a reduction in charge carrier concentration in dark condition leads to the reversal of optically polarised domains.



Figure 2.8. Short-circuit photocurrent density measured macroscopically with Au electrode on one side and ITO electrode on the other side for wavelengths (a) 660 nm and (b) 552 nm, respectively. The light was shaded on the ITO electrode side of the sample.

Importantly, it has been reported that a change in short-circuit current can cause charge injection leading to the tuning of the coercive field.⁴ The maximum electric field

associated with an induced current injection can be calculated using the following equation^{4, 156, 157}:

$$E_{max} = 0.4 \left(\frac{I_{SC}}{\pi \theta \mu \varepsilon_0 \varepsilon_r}\right)^{1/2} \left(\frac{1}{r}\right)^{1/2}$$
(2.1)

 E_{max} is the electric field associated with the current injection (short circuit current (I_{SC}) in this case). r is the electrode area, θ is a parameter for trapping effects in the shallow bandgap regions, ε_0 and ε_r are the vacuum and relative permittivity of the material. The equation could be rearranged as follows to estimate the change in the electric field with variation in short circuit current:

$$\frac{E_{Dark}}{E_{\lambda}} = \left(\frac{\varepsilon_{\lambda}I_{SC,Dark}}{\varepsilon_{Dark}I_{SC,\lambda}}\right)^{1/2}$$
(2.2)

$$\frac{E_{Dark}}{\left(\frac{\varepsilon_{\lambda}I_{SC,Dark}}{\varepsilon_{Dark}I_{SC,\lambda}}\right)^{1/2}} = E_{\lambda}$$
(2.3)

Here, it is to be noted that the change in relative permittivity for KNN-BNNO at higher frequencies (600-900 kHz) is 70%, as shown in Figure 2 (d). The PFM measurements were also carried out in the same frequency range. This relation suggests that in the present case $E_{\lambda=405} \sim 5E_{Dark}$. θ is assumed to be constant but is likely to change under experimental conditions, so the value may vary. The change in relative permittivity (shown in Figure 2.4 (b)) can be explained through the following relationship:

$$P = \varepsilon_r \chi E \tag{2.4}$$

here, P= polarization; χ = dielectric susceptibility; E= applied electric field. Light-induced non-linear reduction in the real part of dielectric constant at low frequencies (see Figure 2.4 (b) and (d)) means a small increase in polarization in contrast to the net applied field (a combination of the applied electric field ($E_{Applied}$) and light-induced enhanced electric field (E_{λ});P/E= $P/(E_{Applied} + E_{\lambda}) = \varepsilon_r \chi$) whereas, χ governs the frequency dependence of this behavior. A cumulative effect of light-induced electric and depolarization field will thus govern the material behavior and optical control over ferroelectric behavior.



Figure 2.9. Surface potential changes with light illumination: (a) The topography of the KNN-BNNO surface. (b) KPFM image captured with different wavelengths of light superimposed on the contact potential difference (CPD) of the line profile highlighted in (a). (c) KPFM mapping of the CPD starting from the dark condition followed by the exposure to light of a particular wavelength (405nm, 500nm, 600nm, 700nm (only one at a time)) and CPD reversal on turning the light off. (d) Comparison of CPD rise and decay for different wavelengths corresponding to the line profile highlighted in (c). The shaded area in (d) denotes the period when the sample was exposed to the laser source. (I) and (II) indicates the sudden and slow decay zones.

Similar to nanoscale experiments, illumination during the macroscopic measurements cause charge injection. Due to this charge injection, a change in the state of polarization is expected as noticed in P-E loop data (measured at 1 Hz) shown in

Figure 2.4 (a). Nominal change in dielectric losses at low frequencies (<100 kHz) shows that the increase in polarization and a corresponding decrease in dielectric constant at low frequencies must primarily originate from the optical poling of the ferroelectric domains. The same is also supported by the nanoscale and piezoelectric measurements. However, the dielectric losses under the cumulative effect of light and applied electric field will be different. Therefore, the increase in polarization at all other points except E=0 must be a combination of light assisted polarization of the material and the leakage current induced by the cumulative effect of applied electric field and photocurrent due to the nature of the measurement process. Nevertheless, it is difficult to distinguish between the two based on the macroscopic measurements, the fact that the sample is polarized under light can be unambiguously accepted. Interestingly, the light-dependent increase in remnant polarization in KNN-BNNO is analogous to observations in a few recent studies^{5, 147, 148} but is not commonly observed in ferroelectrics¹³⁰. Remnant polarization decreases on exposure to ultraviolet light in classical ferroelectrics such as (Pb,La)(Zr,Ti)O₃.¹³⁰ This difference could again be explained using equation 2.4 and the optical behavior of ferroelectrics can be classified as type (i) or type (ii) (as introduced above) similar to the temperature-dependent changes (decrease or increase) in polarization.¹³

Another method to confirm the light-induced change in surface potential (or induced electric field) is Kelvin Probe Force Microscopy (KPFM). In our experiments, the tip was maintained at a constant height of 10 nm from the surface of the sample and KPFM was performed. Figure 2.9 (a) shows the topography of the area under investigation. The sample was initially (first 200 nm distance in the x-direction) maintained at the full dark condition and was then consecutively exposed to the light of wavelengths 700nm, 600nm, 500nm and 405nm for equal scanning areas. The contact potential difference (CPD) of the line shown in Figure 2.9 (a) is plotted in Figure 2.9 (b)

(white line with circular symbols) while the background shows the KPFM mapping of the area in Figure 2.9 (a). Figure 2.9 (b) clearly illustrates that light corresponding to 405 nm creates the maximum difference in the surface potential of KNN-BNNO while the CPD for other wavelengths is significantly low. This is in line with the macroscopic photocurrent measurement. Further, to elucidate the potential rise and decay time of the surface potential, KPFM was performed on the same area but with different parameters (for longer scanning time and more data points) to observe time-dependent variation in CPD (see the experimental section for details). Figure 2.9 (c) shows the KPFM mapping of the sample area while the CPD profiles corresponding to the line marked in Figure 2.9 (c) are drawn in Figure 2.9 (d). A sharp increase in CPD could be clearly observed for all wavelengths while the time for decay is relatively quite high. The decay could further be categorized in sudden (zone (I)) and slow decay (zone (II)) zones. This shows the ability of KNN-BNNO to allow and maintain charge traps for a longer time than the light-induced poling in unpoled samples. Such ability is a prerequisite for the non-contact optical reader of a ferroelectric RAM^{19,20}.

The KPFM and photocurrent measurements can help us conclude that the light induces charge carriers on the surface of the material. The semiconducting nature of KNN-BNNO further helps in the migration of these charge carriers towards the bottom electrode and finally, a constant potential is maintained across the two electrodes. This potentially influences the state of polarization in the material, which leads to the movement of the domains and domain walls. Consequently, it must result in some structural changes in the material such as migration of oxygen vacancies or a tetragonal or octahedral shift along with the increased dielectric losses in the material (See Figure 2.4 (c) for dielectric losses). It is to be noted that the light-dependent *P-E* loops were captures at low frequencies (1 Hz) where the losses are quite low in contrast to the losses

at the higher frequencies (> 600kHz) which were used while performing PFM. Therefore, there is a good possibility that the increase in polarization is a cumulative effect of changes induced in domains (which are fundamentally related to the structure of the material) and the losses. The same is also supported for the macroscopic d_{33} measurements. However, it is difficult to distinguish between the two as all ferroelectric characterizations involve either electrical contacts or a light/energy source. Undoubtedly, the light-induced surface charge is compensated by the movement of the domain walls and change in the state of polarization of domains at least within the Debye length which means that there must be some structural changes and thus, the increase in polarization can not be merely an artifact. Quantitative measurement of the contribution of lightinduced structural changes and losses towards polarization is an open-ended question but irrespective of this, both the light-induced dielectric losses and the structural changes can be utilized to achieve optical control of ferroelectric domains.

2.4.Conclusions

Experiments described above suggest that the exposure to light changes the surface potential of the sample as the light acts as a constant current source in short circuit condition. The charge carriers injected through the surface of the material polarize the dipoles similar to an applied electric field. The material is behaving as a phototransistor; therefore, it is likely that the charges are distributed throughout the sample thickness, which is also confirmed by the macroscopic piezoresponse noticed after 8 hours of exposure to the white light. The same can also be conceived from the light-dependent increase in remnant polarization. However, the possibility of diffusion of oxygen vacancies or current channeling through defects leading to a macroscopic change in polarization can not be completely ruled out. The effect is likely to be irreversible or dynamically slow if only ionic defects such as oxygen vacancies are responsible for this kind of behavior. Since $(K_{0.5}Na_{0.5})NbO_3$ supports off-center distortion and Ba $(Ni_{0.5}Nb_{0.5})O_{3-\delta}$ controls the electronic states in the gap of parent $(K_{0.5}Na_{0.5})NbO_3$ using oxygen vacancies and Ni⁺² ions, it could be concluded that the light affects the number of charge carriers in Ba $(Ni_{0.5}Nb_{0.5})O_{3-\delta}$ which eventually leads to structural changes in KNN-BNNO. Thus, the light-induced reversible poling of ferroelectric domains and domain walls' movement in KNN-BNNO are due to a combined effect of fluctuations in the semiconducting response aided by the non-centrosymmetric distortion caused by the light. Our main finding is that light behaves as a virtual current/voltage source through the photovoltaic effect. If the switching voltages of the sample are in the range of the electric field induced by the incident light, then it could be possible to achieve optical control over domains and domain walls in several ferroelectric materials. We hope that the understanding gained here will help the creation of novel photonic and optoelectronic devices based on ferroelectrics.

CHAPTER 3

OPTO-ELECTRIC CONTROL OF FERROELECTRIC DOMAINS

This chapter presents understanding of the combined effect of light and lowvoltage bias for opto-electric control of ferroelectric domains in KNBNNO $((K_{0.5}Na_{0.5})NbO_3-2mol.\% Ba(Ni_{0.5}Nb_{0.5})O_{3-\delta})$ to achieve two orders of magnitude amplification in electrical response, asymmetric AC modulation, and domain velocities of 30,000 nm s⁻¹ with ultra-large domain switching areas of over 30 um in fractions of a second. The switched areas are found to be controlled by the applied voltage and laser spot size. Light illumination on this material is found to act as a virtual electrode and the charge injection/modulation is governed by the ferroelectric photovoltaic effect and optical tuning of the material conductivity. The same phenomena are verified macroscopically and the modulation of the photocurrent as well as electrical current is demonstrated. Besides, a prototype of a monolithic light-effect transistor based on this material, which could be a potential solution to the scaling limit of three-terminal transistors.

Parts of this chapter will appear in "<u>*G Vats*</u>", J Peräntie, J Palosaari, J Juuti, J Seidel* and Y Bai*, A ferroelectric light-effect transistor for current modulation by opto-electric control of domains (Submitted 2020)"

Contribution details: GV performed all nanoscale experiments (in the supervision of JS), planned macroscopic measurements, visualized the results, prepared figures and wrote the manuscript. YB prepared the samples. JP performed the laser cutting and prepared electrical contacts for macroscopic measurements. YB and JP performed macroscopic measurements. All co-authors discussed the results and provided inputs for finalizing the manuscript.

3.1. Motivation

The renaissance of photo-ferroelectrics has attracted significant research interest in recent years^{2, 53, 55, 107} due to advancement in the understanding of underlying mechanisms^{33, 146, 158-160}. This has resulted in renewed research interests towards ferroelectric for photovoltaic energy conversion with high efficiency¹⁶¹ and the development of new concepts such as domain wall photovoltaics^{33, 146}, tip-enhanced photovoltaic effects⁹⁹, and shift current models¹⁵⁸⁻¹⁶⁰. Parallel ongoing investigations of the possibility of utilizing optical control of ferroelectric domains^{3-5, 128} for the tuning of capacitance/resistive states^{150, 162, 163}, multiferroic states¹⁶⁴ and macroscopic polarization^{3,} ⁵ have also opened new pathways for the creation of next-generation neuromorphic devices such as photo-detectors¹⁶⁵, optical modulators¹⁶⁶, ferroelectric diodes¹⁶⁷, memristors¹⁶³, solaristors¹⁶⁸, optoelectric tunnel junctions^{169, 170} and photo-ferroelectric generators². Some commercial devices for optoelectronic applications of ferroelectrics are based on LiNbO3, with other materials being less explored.¹⁷¹⁻¹⁷⁷ Here, we present a costeffect and easy to fabricate polycrystalline bulk ferroelectric (KNBNNO: $((K_{0.5}Na_{0.5})NbO_3-2 \text{ mol.}\% Ba(Ni_{0.5}Nb_{0.5})O_{3-\delta}))^{3, 45, 150}$ that has a 60% lower electro-optic poling energy requirement than LiNbO₃ crystals¹⁷¹⁻¹⁷⁷.

As discussed in previous chapters, KNBNNO is a bandgap engineered ($E_g = 1.6 \text{ eV}$) ferroelectric ceramic that has been reported as a monolithic multifunctional energy conversion material with above bandgap photovoltages.^{45, 149} These alluring features make it intriguing for several electronic and energy harvesting devices.^{2, 124} and nanoscale optoelectric investigations¹⁴⁴. The material has been documented for reversible optical control of ferroelectric domains with domain velocities of the order of 0.01 nm s⁻¹, corresponding to domain wall displacements of ~20 nm in 15 minutes under the influence of a continuous laser source (wavelength: 405 nm; intensity: 8.3 W cm⁻²).³ To be viable

for practical applications the optical switching time, domain wall velocities and the traveled distance need to be increased significantly. To address this, we utilized the cumulative effect of light and low electric fields by establishing a correlation in electrical and optical behavior and developing an understanding of the mechanism of optoelectric control of ferroelectric domains. Guided by this, the applications of fast ultra-large domain switching, a ferroelectric function generator, DC amplification, asymmetric modulation of AC and a monolithic solaristor¹⁶⁸/photo-transistor¹⁶⁸/photo field-effect transistor¹⁷⁸ (FET)/photo-switch¹⁷⁹ or a light-effect transistor¹⁸⁰ (a device with two-electrical terminals and light acting as a virtual gate) are finally presented.

3.2.Experimental details

Macroscopic measurements: Two sample and electrode configurations were prepared. Configuration 1: The fabricated samples were coated with 200 nm thick ITO electrodes on both sides. The coated samples were then laser-cut into small rectangular (1-2 mm length and width) and round (1-2 mm diameter) samples. This configuration was used for out-of-plane measurement. Configuration 2: Small-sized rectangular (1-2 mm length and width) silver electrodes (DT 1402, Heraeus, fired at 600 °C for 20 minutes) were deposited on the same surface of the sample through masked doctor blading. The gaps between the electrodes ranged from 100 μ m to 200 μ m. This configuration was used for in-plane measurements. The high-field poling process was carried out with a poling station consisting of a voltage amplifier (Ultravolt, USA) and a data acquisition card (USB-6211, National Instruments, USA). During the high field (60 kV cm⁻¹) poling, each sample was immersed in silicone oil at room temperature with the poling voltage on for 30 minutes in dark. The photocurrent was measured and the external electric field was provided by the SourceMeter (2450, Keithley, USA) connected with a probe station. The light source was 405 nm, 50 mW laser (OBIS LX/LS Series, Coherent, USA), of which the beam spot size was 0.8 ± 0.1 mm in diameter at $1/e^2$. The transmittance was measured with a UV-Vis-NIR spectrophotometer (Cary 500 Scan, Varian, USA).

Nanoscale measurements: The parameters for the nanoscale measurements are the same as described in the experimental section of chapter 2.

3.3. Analogy in optical and electrical behavior

Firstly, an understanding of the analogies between electrical and optical behavior of KNBNNO was developed at the nanoscale on an un-poled sample. Figure 3.1 (a)-(c) shows the PFM (piezoresponse force microscopy) out-of-plane phase images of ferroelectric domains at three different locations captured in dark. Figure 3.1 (d) displays the post optical poling (with zero DC electric bias) domain structure of KNBNNO, which was acquired after 15 min of continuous laser exposure showing that the bright domains (up polarization) have shrunken due to laser exposure. Figure 3.2 confirms the reversibility of the process, i.e. bright domain regions tend to recover after turning off the laser. The optical measurements were performed with a laser source of 405 nm wavelength (laser spot size: 0.06 mm²; power: 5 mW; intensity: 8.3 W cm⁻²). Figure 3.1 (e) and (f) reveal the post electrical poling (both performed in dark) behavior with -4V (electric field -40 V mm⁻¹) and +4V (electric field +40 V mm⁻¹), respectively. A shrinkage of bright domains within the negatively poled area is observed (Figure 3.1 (e)) while the bright domains were expanded due to positive poling as shown in Figure 3.1 (f). This indicates that the light and negative bias are working in an analogous manner and support the switching of ferroelectric domains in an identical fashion. The phenomenon was further confirmed by ruling out the effect of temperature change due to laser exposure³ and by comparing the photocurrent and electrical current (in dark)³ measured

using a conductive AFM tip of 30 nm tip radius. Figure 2.7 (b) of chapter 2 shows the growth (100 s) and decay (250 s) of the photocurrent. The dark electrical current responses to the voltages of -1 V (electric field -10 V mm⁻¹) and +1V (electric field +10 V mm⁻¹) are presented in Figure 2.7 (c) and (d), respectively. Though the growth and decay time for the photocurrent and electric current (1 s each) are different, the same direction of photocurrent and electrical current with -1V supports the argument of analogy in the photo-response and applied negative bias on the sample. The variation in the magnitude of electrical response for +1V (18 mA cm⁻²) and -1V (-28 mA cm⁻²) indicates an asymmetry in the device configuration. This induced asymmetry could be due to the difference in electrode area or the work-function difference between the two electrodes (30 nm Pt AFM tip on one side while 4 x 4 mm Au-Cr electrode on the other side).



Figure 3.1. Comparison of electrical and optical response: (a)-(c) PFM out-of-plane phase images of ferroelectric domains at three different locations in dark condition. PFM images of ferroelectric domains post (d) optical poling with a laser source of 405 nm

wavelength with no electrical bias, electrical poling with (e) -4V (electric field -40 V mm⁻¹) in dark and (f) +4V (electric field +40 V mm⁻¹) in dark. All images were acquired on an unpoled sample. The sample was kept in dark for over 2 hours before each measurement to avoid the effect of partial poling due to ambient white light exposure.



Figure 3.2. Reversible optical control of ferroelectric domains: PFM phase images $(1x1 \ \mu m)$ acquired (a) in dark, (b) after 30 minutes of continuous exposure to a laser of 405 nm wavelength and (c) after 30 minutes of turning laser off, respectively.

3.4.Light as a virtual electrode

It is important to note that any asymmetry in the state of polarization leads to a builtin field in the material. The applied electric field will either be supported or opposed by this built-in field which will govern the magnitude of the indicated net applied electric field (E_{Net}) shown in Figure 3.3 (a)-(c). It is evident that above bandgap photo-voltages in ferroelectrics are due to band-to-band or intraband excitations and are explained using ballistic and/or shift current models.^{2, 55, 158, 161, 181} The applied electric field in addition to the resultant built-in field due to laser exposure leads to modification of the Fermi-level and hence results in enhanced/modulated photocurrent (see schematic Figure 3.3 (d)-(e)). We note that there is a negligible difference in the transmittance spectra of unpoled and poled samples (Figure 3.4 (f)) corresponding to 405 nm wavelength. Following this, a two

orders of magnitude modulation of the sample conductivity was observed as a function of laser intensity (laser spot size: 0.5 mm²) when measured macroscopically on an indium tin oxide (ITO) and Cr-Au coated sample (Figure 3.4 (g)). Additionally, light-dependent (laser spot size: 0.5 mm²; power: 50 mW; intensity: 10 W cm⁻²) modulation of in-plane conductivity corresponding to applied voltages (+ 0.5 V to + 4 V) over a wide interelectrode gap (140 µm) was measured (Figure 3.4 (h)). The results indicate that the light acts as a virtual electrode for KNBNNO. Although the ratio of light and dark conductivities is remarkably high corresponding to all applied voltages, the in-plane current (Figure 3.4) is significantly low. However, out-of-plane current (not shown here) was comparatively high in the same un-poled sample. In order to enhance the out-ofplane current output, the sample asymmetry was enhanced by poling the sample for 30 min in an electric field of 60 kV cm⁻¹. Though poling didn't have much impact on inplane conductivities, the observed light to dark conductivity ratio is significantly high (Figure 3.3 (i)) in the poled sample. This suggests that poled KNBNNO is an ideal material candidate for a monolithic two-terminal photo-transistor/solaristor¹⁶⁸. Furthermore, light to dark conductivity ratios ($\sigma_{\text{Light}}/\sigma_{\text{Dark}}$; Figure 3.3 (i)) under applied voltages help in determining the voltage thresholds for opto-electric applications such as asymmetric rectification of AC bias ($\sigma_{\text{Light}}/\sigma_{\text{Dark}} < 1$), and for the use as a gating material for a ferroelectric field-effect transistors ($\sigma_{Light}/\sigma_{Dark} < 1$) and photodetectors ($\sigma_{Light}/\sigma_{Dark}$ >1). In addition, the same mechanism helps in understanding light assisted ferroelectric poling. Since light acts as a virtual electrode with enhanced surface conductivity, the applied electric field modulates the photocurrent resulting in a high charge injection over a broad area. This charge injection leads to a fast and ultra-large domain switching area (much larger than the electrical contact of the AFM tip) which could further be controlled by laser spot size and the applied electric field.



Figure 3.3. Material properties under the application of positive and negative electric fields: (a) Built-in field (E_{B-in}) due to the polarization of the material. Effect on external bias applied (E_{App}) in the (b) same and (c) opposite direction of the built-in field. Schematic of charge migration from the valence to the conduction band in the presence of (d) light only and (e) under the cumulative effect of light and electric field. (f) Transmission spectra of un-poled, positively poled and negatively poled samples with ITO electrodes on both surfaces. (g) Change in sample conductivity along with the sample thickness as a function of laser intensity. The ratio of the light and dark electrical conductivities measured as a function of applied DC bias (from ±0.5 V to ±4 V) along (h) in-plane direction in an unpoled sample and (i) out-of-plane direction in a poled sample.



Figure 3.4. In-plane light and dark current corresponding to applied voltages of 0.5 V, 1 V, 2 V, 3 V and 4 V measured on a un-poled sample with an inter-electrode gap of 140 μ m. Inset shows the comparison of dark current for applied positive and negative bias.



Figure 3.5. The cumulative effect of light and applied electric field: (a) and (d) PFM phase images captured in dark condition. Changes in the domain structure of pristine area

after cumulative poling under light (incident on a large sample area) and electric bias of (b) +4 V and (e) -4 V applied at a single point (marked in (a) and (d)) with 30 nm AFM tip. (f) Large area scan to show the full switched area under cumulative action of light and -4 V for 40 s (White shaded area indicates light illumination area on the sample). Charge injection due to light assisted electrical poling with a bias of (c) +4 V and (g) -4 V.

3.5.Light-assisted electrical poling

Figure 3.5 (a)-(c) reveals the effect of light-triggered positive poling with +4 V while the effect of light assisted negative poling with -4 V is displayed in Figure 3.5 (d)-(g). The reproducibility of the results at different locations is illustrated in Figure 3.6 (lightassisted positive poling) and 3.8 (light-assisted negative poling). Initially, the laser was turned on for 40 s followed by application of +4 V (Figure 3.5 (c)) or -4 V (Figure 3.5 (g)) for 40 s at the center of the area (shown by a circle in Figure 3.5 (a) and (d)) using a 30 nm AFM tip. Interestingly, the out-of-plane photocurrent was modulated in the opposite direction with nearly the same magnitude using +4 V while the negative bias led to a modulation of two orders of magnitude in the same direction (Figure 3.5 (c) and (g)). The growth time for 8000% modulation with negative bias was ~1 s while the fullmodulation of 16000 % was achieved in around 100 s which is similar to the photocurrent rise time in the absence of applied electric field as shown in Figure 2.7 (b). This indicates that a combination of laser intensity and AC bias can be used to obtain asymmetric halfwave rectification which was demonstrated macroscopically (Figure 3.13 and discussions below). The post-poling shrinkage of the out-of-plane bright domains in Figure 3.5 (b) was found to be fully reversible by the application of -4 V for 10s at the same spot in dark (See Figure 3.7). It shows that the charge injected by the cumulative action of light and electric field can be reversed by applying an electric field alone in the opposite direction

through the AFM tip placed at the same spot. The reversal of domains (Figure 3.7) leads to the possibility of the creation of connected charged channels across the domain walls⁷⁴ due to light-triggered single point electrical poling. The same channels could be utilized for the domain reversal if a higher current than the modulated photocurrent is applied in an opposite direction. The same is true for light-assisted negative poling but it was only confirmed macroscopically (Figure 3.13) due to the limitation of our AFM system. In addition, it was revealed that light-assisted positive poling could lead to optoelectric domain wall velocities of 72 nm s⁻¹ which could further be increased to 30,000 nm s⁻¹ using light assisted negative poling (as reflected in Figure 3.5 (e)-(f)). Light assisted negative poling also results in ultra-large domain area switching (450,000 times in contrast to the electrode (AFM tip) area) which could further be controlled by an applied voltage (Figure 3.9) and laser spot size (Figure 3.10). Figure 3.9 shows that the switched area was extended equally in all directions due to an increase in applied voltage. A similar extension of the switched area with increasing applied voltage (in dark) has been reported for several other ferroelectrics and is attributed to the pinning potential and domain wall creep.^{182, 183} The domain wall velocity in such a scenario is given by $(v) \sim v_0 e^{\left[-\frac{E_a}{E}\right]\mu}$; where E_a is the activation field and E is the applied electric field.^{182, 184} μ is an exponent governing the nature of the pinning potential and dimensionality of the wall.^{182, 184} Lou et al. suggested a statistical model that explains the same phenomena in bulk ferroelectrics.¹⁸⁵ Opto-electrically tuned in-plane conductivity and corresponding charge migration (Figure 3.3 (h)) modulates the pinning potential resulting in fast domain wall moment for low applied electric fields in KNBNNO in comparison to the reported higher electric fields in several well-known ferroelectrics such as Pb(Zr_{0.2}Ti_{0.8})O₃¹⁸², poly(vinylidene-fluoride-trifluorethylene)¹⁸⁶, and BaTiO₃¹⁸⁴. Post-poling stability of the switched domains was studied at two different locations (locations 2 and 3) for 60 and

120 minutes (Figures 3.11 and 3.12). No changes were observed in opto-electrically poled domains, whereas, only optically poled domains return to their original position in 17 minutes³. The robustness of opto-electrically poled domains makes them ideal for opto-electric modulators.



Figure 3.6. Reproducibility of light assisted electric field poling with +4V at another location: Out-of-plane phase and amplitude before ((a), (b)) and after ((e), (f)) poling with light and +4 V. In-plane phase and amplitude before ((c), (d)) and after ((d), (h)) poling with light and +4 V. 30 nm AFM tip is placed at the center of the image for applying electric field of 40 kV/m (+4 V) while the shown area was fully illuminated.



Figure 3.7. Reversibility of opto-electrically poled domains: Out-of-plane phase images (a) before and (b) after poling with +4 V and light. (c) Out-of-plane phase image acquired after poling with -4 V in dark at the center of the image with an AFM tip.


Figure 3.8. Reproducibility of light assisted electric field poling with -4V at another location: Out-of-plane phase, out-of-plane amplitude, in-plane phase and in-plane amplitude images acquired in dark ((a)-(d)) and after poling with light and -4 V ((e)-(f)). (i)-(k) shows the large area scan on the same location after poling with light and -4 V. 30 nm AFM tip was placed at the center of the image for applying an electric field of - 40kV/m (-4 V) while the switched area highlights the laser spot size.



Figure 3.9. Electrical control of the poled area: Out-of-plane phase images before ((a),

(c), (e) and (g)) and after ((b), (d), (f) and (h)) poling with light and -2 V, -3 V, -4 V and -5 V respectively. Note: 30 nm AFM tip was placed at the center of the image for applying the electric field while the switched area highlights the laser spot size.



Figure 3.10. Controlling of the poled area by laser spot size: Out-of-plane phase images after poling with -4 V and light with different spot sizes. Note: 30 nm AFM tip was placed at the center of the image for applying the electric field while the switched area highlights the laser spot size.



Figure 3.11. (Stability test at location 2) Irreversibility of opto-electrically poled domains: Out-of-plane phase images after poling with -4 V and light obtained (a) immediately after poling and (b) 60 min post-poling.



Figure 3.12. (Stability test at location 3) Irreversibility of opto-electrically poled domains: Out-of-plane phase images obtained after poling with -4 V and light obtained

(a) immediately, (b) 60 min, (c) 90 min and (d) 120 min post poling.

3.6. Application

To demonstrate the potential applications of KNBNNO, a device was prepared using 120 um thick KNBNNO sandwiched between two 200 nm thick ITO electrodes. The sample was poled electrically (60 kVcm⁻¹ for 30 minutes) to achieve higher asymmetry and built-in fields. It is to be noted that the sample is very sensitive to light and its polarization changes even in ambient lighting conditions. The specific state of polarization can to some extent be ascertained by the magnitude of the measured photocurrent. A comparison of photocurrent (in absence of external electric field) and electrical currents corresponding to applied positive and negative bias (measured in dark) is presented in Figure 3.13 (a)-(c), respectively. The same sample is used to illustrate the modulation of electrical current (Figure 3.13 (d)) and photocurrent (Figure 3.13 (e)) by shining light and applying an electric field, respectively. Interestingly, the electrical current corresponding to + 0.5 V is suppressed by the presence of light while the current corresponding to + 1 V and higher voltages is enhanced in the positive direction as depicted in Figure 3.13 (d). In principle, the resultant current should be the cumulative result of electrical (+0.7 nA) and photocurrent (-1.8 nA), which is not the case here. The resultant of the applied electric field and built-in field helps in controlling the direction of the photocurrent. The sample's asymmetry directs the photocurrent in a negative direction while the applied positive bias guides it in a positive direction. The outcome is governed by the equilibrium state of ferroelectric domains (as also found at the nanoscale in Figure 3.5 (a)-(b)). With a higher applied voltage of +1 V, the photocurrent is also modulated in a positive direction, and the resultant electrical current is enhanced. This could also be complemented with the out-of-plane light to dark conductivity ratio (< 1) corresponding

to +0.5 V for the poled sample (see Figure 3.5 (i)). The suppression of electrical current corresponding to +0.5 V due to light illumination was confirmed for two different states of polarization, where the obtained photocurrents with the same sample were different (Figure 3.14) In both conditions, a voltage of + 0.5 V results in an increase in the electrical current in a positive direction. However, the electrical current decreases to + 0.2 nA and + 0.5 nA corresponding to the states of polarization upon light illumination of the sample (Figure 3.14 (a) and (b)). On the contrary, the electrical current with higher voltages is increased in the respective directions by the presence of light. Due to this reason, a bias of 0.5 V was chosen to demonstrate asymmetric AC modulation of the dark current (Figure 3.13 (f)). The AC dark current for an applied voltage of 1 V (peak to peak) can be modeled by fitting Equation 3.1 (shown by a black line in Figure 3.13 (e)). The modulated photocurrent for the same applied voltage is modeled using Equation 3.2 (shown by a red line). Similarly, several other functions could be designed to obtain the desired output using the presented photo-ferroelectric function generator.



Figure 3.13. Modulation of photocurrent and electrical current: (a) Photocurrent (without electric field) and electrical current corresponding to applied (b) positive and (c)

negative bias (measured in dark) on a bulk poled KNBNNO sample. Modulation of electrical current with light due to applied (d) positive bias of ± 0.5 V and ± 1 V. (e) Modulation of photocurrent by applied negative and positive biases of ± 0.5 V and ± 1 V. (f) Demonstration of asymmetric AC photo-ferroelectric rectification behavior.



Figure 3.14. Photocurrent and modulation of electrical current corresponding to two different states of polarizations. Obtained photocurrents in KNBNNO samples poled with 60 kV cm⁻¹ for (a) 30 minutes and (b) 60 minutes. Modulation of the electrical current (with +0.5 V and +1 V) by using light in samples poled with 60 kV cm⁻¹ for (c) 30 minutes and (d) 60 minutes.

$$y=y_0+Asin(\pi(x-x_c)/w)$$
 (3.1)

$$y = y_0 + A(sin(\pi(x-x_c)/w))^2$$
 (3.2)

Interestingly, the cumulative action of light and electric field for voltages higher than 0.5 V modulates the individually obtained current. The difference in the modulated magnitude for applied positive and negative bias can be explained on the basis of E_{Net} due to the built-in field. The same is also supported by the dark and light conductivity ratio. The current modulation was found to be consistent and reproducible irrespective of the process (voltage applied before turning the laser on; laser turned on before applying voltage: Figure 3.15). This voltage-dependent modulation of the photocurrent makes KNBNNO suitable for a photodetector or self-powered two-terminal photo-transistor. In addition, several orders magnitude change in photocurrent by application of small voltages suggest that KNBNNO's photovoltaic performance can be significantly tuned by applying small voltages. The understanding developed through this work and the presented scope of ferroelectrics for a monolithic photo-ferroelectric function generator/modulator, asymmetric AC rectifier and self-powered transistor can be utilized to develop improved opto-electronic devices for next-generation applications.



Figure 3.15. Modulation of photocurrent and electrical current: (a) Photocurrent (without electric field) and electrical current corresponding to applied (b) positive and (c) negative bias (measured in dark) on a bulk poled sample. Modulation of (d) negative (-

0.5V, -1V, -2V, -3V and -4V) and (e) positive (+2V, +3V and +4V) electrical current with light. (e) Modulation of photocurrent by applied voltages of ± 0.5 V, ± 1 V, ± 2 V, ± 3 V and ± 4 V.

3.7.Conclusions

The work presented in this chapter helps us understand that in optically active ferroelectrics light exposure can tune the material conductivity by several orders of magnitude. The application of small electric fields on the illuminated area can further cause a significant variation in the charge transport properties and hence confirms that the light is acting as a virtual electrode. The magnitude of the applied voltage and laser spot size provides additional control over this phenomenon. The charge injection and current modulation are governed by the ferroelectric photovoltaic effect and optical tuning of the material conductivity. The demonstrated optoelectric effect leads to a fast (< 1s) and ultra-large (> 30um) switching of ferroelectric domains. This phenomenon can be used to modulate photocurrent using small electric fields or electrical current by the presence of light makes optoelectric control of ferroelectric domains a promising method for several optoelectronic applications such as photo-detectors and electrical function generator. Based on the understanding developed, a prototype of a monolithic light-effect transistor using KNBNNO is presented. It is a two-terminal device in which laser exposure acts as the virtual transistor gate. This could be a potential solution to the scaling limit of threeterminal transistors.

CHAPTER 4

OPTO-MECHANICAL CONTROL OF DOMAINS

The piezo-photovoltaic effect has been recently demonstrated for boosting the photovoltaic performance of ferroelectrics under applied uniaxial mechanical loads.¹⁸⁷ The impact of the piezo-photovoltaic effect on ferroelectric domains is not yet studied. In this context, this chapter provides a nanoscale insight into mechanical as well as optomechanical control of domains in a novel bandgap engineered (1.6eV) ferroelectric namely - KNBNNO ((K_{0.5}Na_{0.5})NbO₃-2mol.% Ba(Ni_{0.5}Nb_{0.5})O_{3-δ}). Atomic force microscopy (AFM) tip-induced mechanical forces higher than 3 μ N are found to cause permanent deformation of the sample surface. The ferroelectric domain switching mechanical force threshold is found to be 0.4 µN. The optical, as well as the mechanical movement of the ferroelectric domains, are found to be fully reversible. However, the applied mechanical force of 1 µN evinces a 67% amplification in piezo-response to that of measured using 0.07 μ N. Even on removing mechanical load the domains retain 33% higher piezo-response than the pristine state. The opto-mechanical piezoresponse of ferroelectric domains for identical laser exposure time and energy are found to vary with the mechanical force. This helped in concluding that applied mechanical stress polarizes the material and thus enhance the photovoltaic charge screening. This provides a nanoscale explanation of the piezo-photovoltaic effect in ferroelectrics.

Parts of this chapter will appear in "<u>*G Vats*</u>", Y Bai and J Seidel^{*}, Opto-mechanical control of ferroelectric domains: Nanoscale understanding of the piezo-photovoltaic effect (2020)"

Contribution details: GV performed all nanoscale experiments (in the supervision of JS), planned macroscopic measurements, visualized the results, prepared figures and wrote the manuscript. YB prepared the samples. All co-authors discussed the results and provided inputs for finalizing the manuscript.

4.1.Literature and motivation

The ferroelectric photovoltaic effect has attracted significant attention in recent years^{65, 76}. A quest to further enhance the photovoltaic performance of ferroelectrics is currently ongoing^{40, 150, 158}. One of the proposed solutions is to boost the photovoltaic output by using multiple inputs.^{2, 188} In this context, mechanical pressure-induced escalation of the ferroelectric photovoltaic output is recently reported.^{45, 187, 189} Yang *et al.* induced mechanical strains in centrosymmetric crystals by the aid of an atomic force microscopy (AFM) tip and a nano-indentor for the realization of a hike in photocurrent and named it as the flexo-photovoltaic effect.¹⁸⁹ This work was further extended to ferroelectrics by Nadupalli et al.¹⁸⁷ They applied uniaxial pressure on Fe-doped LiNbO₃ single crystals and found that the increase in photovoltaic output maintains a linear relationship with the applied mechanical force. Mechanical force-induced manipulation of ferroelectric domains has been independently extensively studied in ferroelectric single crystals^{190, 191} and thin films¹⁹²⁻²⁰⁴. It has been suggested that the mechanical switching in ferroelectric domains could either occur individually or by the cumulative effect of (a) pure mechanical loading²⁰⁵, (b) flexoelectric effect¹⁹⁵, and (c) triboelectric effect²⁰⁶. The mechanical loading in ferroelectrics has been found to cause structural changes or chemical modifications²⁰⁷ (e.g. diffusion of oxygen vacancies or alkali elements²⁰⁸). This can further lead to electrostatic or Vegard strains.²⁰⁵ Most of the studies involve scanning probe-based techniques for understanding the nanoscale mechanical response of ferroelectric domains^{195, 209} and more attention is paid to the mechanical writing and electrical erasing ferroelectric domains and vice-versa.^{195, 205, 210} This is expected to lead to novel domain wall mechano-electric devices.¹²⁴ However, to the best of the author's knowledge, no report provides a nanoscale opto-mechanical or flexo-photovoltaic mapping of ferroelectric domains. In this context, ferroelectric domains in the bandgap

engineered KNBNNO ((K_{0.5}Na_{0.5})NbO₃-2mol.% Ba(Ni_{0.5}Nb_{0.5})O_{3-δ}) are studied using a customized piezoresponse force microscopy (PFM). KNBNNO is an optically active material with a good piezoresponse.⁴⁵ It has been reported for optical^{3, 150} and optoelectric²¹¹ control of ferroelectric domains. This makes it an ideal candidate for studying mechanical and opto-mechanical control of ferroelectric domains. A nanoscale insight into the variation of the photovoltaic output due to opto-mechnical manipulation of ferroelectric domains is likely to pave new opportunities in the regime of ferroelectric photovoltaics. We performed AFM tip induced mechanical strain mapping of ferroelectric domains and topography in KNBNNO followed by opto-mechanical manipulation of ferroelectric domains. The developed understanding is finally used to explain mechanical force-induced amplification of the photocurrent.

4.2. Experimental details

The nanoscale experiments were performed on room-temperature AIST-NT Smart SPM 1000 AFM system with a Fianium Whitelase supercontinuum laser. HA_HR W2C ETALON series tips from NT-MDT (spring constant = 17 to 40 N/m) were used for the mechanical switching and PFM measurements. Resonance PFM was performed using an AC PFM amplitude of 0.5 V (peak-to-peak) with frequencies in the range of 800 to 1600 kHz. Macroscopic d_{33} values of partially and fully poled sample were measured with a Berlincourt piezoelectric meter (YE2730A, APC International Ltd., USA). A source meter (2450, Keithley, USA) was used to measure photocurrents. Lasers (OBIS LX/LS series, Coherent, USA) with different wavelengths were used as the light sources. The wavelength/maximum power/beam diameter at $1/e^2$ was 405 nm/50 mW/0.8±0.1 mm. The intensity of the white light was measured with S120C silicon photodiode detector integrated with PM100D optical power and energy meter (Thorlabs, Germany).

4.3. Mechanical control of domains in KNBNNO



Figure 4.1. Mechanical switching in KNBNNO: (a)-(f)Topography, (g)-(l) Out-of-plane phase and (m)-(r) out-of-plane PFM amplitude of images acquired at 0.1 μ N and post mechanical poling on central 1x1 μ m area (highlighted with white box) with 1-5 μ N respectively. Note the impression impinged due to mechanical force in Figure (e) and (f). (Scale in Figure (a) = 500 nm)

The mechanical switching measurements were performed firstly by calibrating (using the in-built software tool provided by the AIST-NT Smart system) the AFM tip for the applied mechanical force on the sample. The force threshold was initially investigated under pure mechanical loading. In this context, a large area (3x3 um) was selected (Figure 4.1 (a)) and imaged with an intentional low AFM tip force (0.1 µN) to avoid domain manipulation while performing PFM. Thereafter, a small area (1x1 um; see the white box in Figure 4.1) was poled under pure mechanical loading $(1 \mu N)$ with the AFM tip (PFM driving voltage and all other electronics were set zero). The area was re-imaged with AFM tip force 0.1 µN to depict the change in piezoresponse caused by the mechanical force of 1 µN. The topography, out-of-plane phase, and amplitude are shown in Figure 4.1 (b), (h) and (n), respectively. Though the phase signal shows a small/negligible variation in the mechanically poled area, remarkable changes can be observed in the phase signal in the vicinity (see the nearby area outside the white boxes) of the mechanically poled area (compare Figure 4.1 (g)-(h)). The out-of-plane PFM amplitude, when compared with the pristine state, shows the significant variation confirming localized mechanical poling of the sample (compare Figure 4.1 (m) and (n)). Similar observations could be noticed for the data acquired after mechanical poling with higher forces (2 to 5 µN). Intriguingly, no or almost negligible changes are noticed in the sample topography till 3 μ N force (see the area in the white box Figure 4.1 (a)-(d)). However, the sample surface starts deforming under mechanical loads of 4 µN (note the deformation of topography and appearance of a light square in Figure 4.1 (e) corresponding to the white boxes shown in Figure 4.1 (a)-(d)). The change in topography can be more clearly observed in Figure 4.1 (f). These measurements suggest that the threshold mechanical force for causing deformation in KNBNNO surface is 3 µN. The changes in the sample phase and amplitude below this threshold are due to pure mechanical poling. No changes in the topography of mechanically poled areas corresponding to 1 μ N were observed but the changes in the phase and PFM amplitude signal in the poled as well as nearby area indicate interactions with the adjacent domains. To have a better understanding, the area of up domains and normalized maximum PFM amplitude for the data illustrated in Figure 4.1 are plotted in Figure 4.2 (a). A clear fall in the area of red/up domains from 0.1 μ N - 3 μ N and corresponding fluctuations in the PFM amplitude complement each other. A sudden jump in the amplitude and increase in the area of up domains for 4 μ N could be attributed to the mechanical deformation of the sample surface. To further elucidate the mechanical switching threshold of ferroelectric domains, PFM was performed on a different location for incremental mechanical forces from 0.04 to 1 μ N.



Figure 4.2. Change in area of up domains' and PFM amplitude as a function of the applied mechanical force via AFM tip: (a) Area of up domains (red-colored) and normalized maximum PFM amplitude depicted from the data shown in Figure 4.1. (b) Force dependent variation in the area of up domains (red-colored) and normalized maximum PFM amplitude obtained from the data shown in Figures 4.3 and 4.4. Note: The normalization factor for data shown in Figures (a) and (b) is different to provide an overview of the force-dependent variation of the PFM amplitude for the respective set.

The PFM out-of-plane phase (Figure 4.3) and amplitude (Figure 4.4) images acquired with mechanical loading (0.04 µN to 1 µN) using AFM tip suggest that mechanical poling starts at nearly 0.40 µN (note the change in color (Figure 4.3 (f)-(h)) and the area covered by the up/red color domains in Figure 4.4; major changes are highlighted using white boxes). The same is also revealed by the analysis of the area of up-domains and PFM amplitude disclosed in Figure 4.2 (b). An abrupt decline in the domain area from 0.3 µN to 0.4 µN is conclusive evidence for depicting the mechanical threshold for ferroelectric domains switching as 0.4 μ N. The changes in the area of updomains are not alluring for forces higher than 0.4 µN while the variation in PFM amplitude becomes more prominent for the aforementioned force range. Interestingly, even within the same domain, the piezoresponse of the material varies drastically and is confirmed by the variation in PFM out-of-plane amplitude data as manifested in Figure 4.4. The domains with lower piezoresponse (highlighted with the white boxes in Figure 4.3 and 4.4) are the first ones to exhibit a change in the domain shape. The piezoresponse of all domains sinks with the change in domain area till 0.4 μ N (note the difference in PFM amplitude scale color in Figure 4.4; yellow to red for mechanical forces 0.04 to 0.4 μ N). The mechanical threshold of 0.4 μ N acts as an equilibrium state for the movement of domain walls and on further raising the force (0.5 to 0.6 µN) the PFM amplitude proliferate (see Figure 4.2 (b)). The area of the up domain further drops corresponding to the applied mechanical force of 0.6 to 0.9 µN with nominal fluctuation in amplitude but an elevation at 1 µN leads to a reduction in piezoresponse/PFM amplitude. This helps in generalizing the trend of up domains with PFM amplitude for the forces below the threshold for the mechanical deformation of the sample. Also, it can be concluded that the maximum possible domain wall speed due to the mechanical loading is equivalent to the dimension of the adjacent domains with a lower state of polarisation/piezoresponse.

Following this, the reversibility of the mechanical loading was tested and is illustrated in Figure 4.5. To test the reversibility of mechanically poled domains, PFM was performed with a tip force of 0.07 μ N at the pristine state (Figure 4.5 (a) and (d)), with the mechanical load of 1 μ N (Figure 4.5 (c) and (f)) and post-mechanical poling with PFM tip force 0.07 µN (Figure 4.5 (b) and (e)). A clear reversal of domain area can be observed (Figure 4.5 (g)) through the phase images with a 67% increase in the PFM amplitude signal due to mechanical loading with 1 µN (see the normalized PFM amplitude (0.6 to 1 arbitrary unit in Figure 4.5 (g); percentage increase : (1.0-(0.6)X100/0.6)). After removing the mechanical load even through the domains fully return to their original position, a 33% higher PFM amplitude is achieved in contrast to the pristine state. The same can be cross verified by the color contrast of Figure 4.5 (d)-(f). The reversal of ferroelectric domains with divergence PFM in amplitude/piezoresponse for forces $< 1 \mu N$, makes it interesting to investigate the optomechanical control of ferroelectric domains in this regime.



Figure 4.3. Determination of mechanical switching threshold: Out-of-plane phase

images of the area poled with mechanical loads 0.04 μ N – 1 μ N. (Scale = 200 nm). Significant changes in the PFM phase are noticed for force higher than 0.5 μ N. White boxes show the change in phase signal with variation in tip-pressure.



Figure 4.4. Determination of mechanical switching threshold and variation in localized piezoresponse: Out-of-amplitude phase images of the area poled with mechanical loads 0.04 μ N to 1 μ N (Scale = 200 nm). White boxes show the change in the piezoresponse with variation in tip-pressure. Scales of (k)-(o) are different on purpose.



Figure 4.5. Reversibility of mechanical force-induced domain area: (a)-(c) Out-ofplane phase and (d)-(f) amplitude of images acquired under mechanical loads of 0.07 μ N

(pristine), 1 μ N and 0.07 μ N (post-mechanical poling). (g) Normalized area and amplitude obtained from the analysis of data shown in Figures 3 (a)-(f). (Scale = 500 nm)



Figure 4.6. Opto-mechanical manipulation of ferroelectric domain area and reversibility: Out-of-plane phase images acquired in (a) Dark, (b) post optical poling and (c) after turning the laser off at the mechanical force of 0.07 μ N. The phase images of the same area acquired in (d) Dark, (e) post optical poling and (f) after turning the laser off at a mechanical force of 1 μ N. (g) Area of the up (red) domains obtained from the analysis of data shown in Figures 4.6 (a)-(f). (Scale = 500 nm)

4.4.Opto-mechanical control of domains

To study the opto-mechanical manipulation of ferroelectric domains firstly a PFM out-of-plane phase image was procured corresponding to the mechanical force of 0.07 μ N (Figure 4.6 (a)) and 1 μ N (Figure 4.6 (d)). The sample was then poled optically and the corresponding phase illustrated in Figure 4.6 (b) and (e) (See Figure S3 for the corresponding amplitude images). Figure 4.6 (c) and (f) shows the reversibility of domains after turning the laser off under mechanical lodes of 0.07 μ N and 1 μ N, respectively. Comparing Figure 4.6 (a) and (d) changes due to mechanical loading can be observed. Similarly, a comparison of Figure 4.6 (a) with (b) and (c) confirms light-

induced changes and their reversal on turning the light off at 0.07 µN. The same observations can be made by comparing Figures 4.6 (d)-(f). Interestingly, the comparison of opto-mechanically manipulated domains (Figure 4.6 (b) and (e)) show differences in the domain size. The same is also highlighted in Figure 4.6 (g). The changes in the area of the up domains with respect to different mechanical forces are higher in dark (0.07 μ N: 2.57 μ m² and 1 μ N: 2.34 μ m² in the pristine state; 0.07 μ N: 2.62 μ m² and 1 μ N: 2.29 μ m² after turning the laser off) than due to optical poling (0.07 μ N: 1.90 μ m² and 1 μ N: 1.86 μ m²). Through Figure 4.2 (b) it is already established that for a nominal change in the domain area due to an external stimulus a significant change in the PFM amplitude is expected. A higher PFM amplitude/piezoresponse of mechanically as well as optomechanically manipulated domains at 1 µN is an indication of a higher state of polarisation (note the difference in the color of Figure 4.4 (e) and (k)) and thus is expected to provide a higher photocurrent by enhanced charge screening due to ferroelectric photovoltaic effect. This was also tested by measuring photocurrent under the same conditions in which PFM measurements were performed (PFM driving amplitude 0.5 V and tip force of 0.07 μ N and 1 μ N). An increase in the photocurrent at higher mechanical force (Figure 4.7 (a)) helps in interpreting that the opto-mechanical effect or piezo-photovoltaic effect¹⁸⁷ is helping in achieving a higher state of polarisation with amplified piezoresponse due to which a hike in photocurrent can be observed. Though no changes in the sample topography were observed for AFM tip forces less than $3 \mu N$, the possibility of an increase in the tip contact area due to applied force can not be denied.²¹² Since KNBNNO is very sensitive to light, electric field, mechanical vibrations, and thermal fluctuation⁴⁵, we established that the state of polarisation of KNBNNO can be defined using the piezoelectric constant (d_{33}) of the sample.³ Moreover, in a macroscopic measurement unpoled samples were found to show no or negligible (in the

noise range of the source meter) photocurrent. Therefore, we further performed macroscopic photocurrent measurements on a sample that was electrically poled (60 kV cm⁻¹) for different time (Figure 4.7 (b)). A variation in the photocurrent of the sample with different d_{33} helps in understanding that a variation in polarisation state due to any stimulus (optical, mechanical or thermal) should also lead to a change in photocurrent. This supports the argument of having enhanced photovoltaic output due to the optomechanical manipulation of ferroelectric domains and explains the piezo-photovoltaic effect at the nanoscale.



Figure 4.7. Photocurrent in KNBNNO: (a) Nanoscale photocurrent measurement with AFM tip force of 0.07 μ N and 1 μ N. In this measurement tungsten-carbide, AFM tip acted as the top electrode while the bottom was electrode Au-Cr. (b) Macroscopic photocurrent measurement of the same KNBNNO sample with ITO electrodes on both sides under different states of polarization.

4.5.Conclusions

In conclusion, the mechanical control of ferroelectric domains is confirmed in KNBNNO. It is demonstrated that the ferroelectric domains in KNBNNO can be controlled with the mechanical forces, light and under the cumulative effect of light and mechanical force applied using an AFM tip. The minimum force required to manipulate the ferroelectric domains is 0.4 μ N. Interestingly, it is found that forces higher than 3 μ N can induce a change in the sample surface. The applied forces are found to be further supported by the optical manipulation of ferroelectric domains in KNBNNO. This could lead to the poling of the sample and help in achieving an improved photo-response as expected by the piezo-photovoltaic effect. The observations presented in this work thus broaden the nanoscale understanding of the opto-mechanical response of ferroelectrics.

CHAPTER 5

THERMO-ELECTRO-OPTIC EFFECTS

The concept of multi-source energy harvesting (of light, kinetic and thermal energy) using a single material has recently been proposed. This work discusses the realization of this novel concept, and thus provides insight into electric field-assisted modulation of photo-current and pyro-current in a bandgap engineered ferroelectric KNBNNO ((K_{0.5}Na_{0.5})NbO₃-2 mol.% Ba(Ni_{0.5}Nb_{0.5})O_{3-δ}). Thereafter, DC (direct current) electrical modulation under simultaneous inputs of light and thermal changes for photovoltaic and pyroelectric effects, respectively, is utilized to achieve several orders of increase in the output current density. This is attributed to a light-assisted increase in the material's electrical conductivity and ferroelectric photovoltaic effect. The phenomena of electrooptic and thermo-electro-optic DC modulations are further employed to propose two novel energy conversion cycles. The performance of both the proposed energy conversion cycles is compared to that of the Olsen cycle. The electro-optic and thermo-electro-optic cycles are found to harvest 7 and 10 times more energy than the Olsen cycle alone, respectively. Moreover, both energy conversion cycles offer broader flexibility and ease in operating conditions thus paving a way towards the practical applications of multisource energy harvesting with a single material for enhanced energy conversion capability and device/system compactness.

Parts of this chapter will appear in "<u>G Vats</u>*, J Peräntie, J Juuti, J Seidel* and Y Bai*, Coalition of thermo-opto-electric effects in ferroelectrics for enhanced cyclic multi-energy conversion (Submitted 2020)"

Contribution details: GV planned and performed all nanoscale experiments with help of JP and YB, visualized the results, prepared figures and wrote the manuscript. YB prepared the samples. All co-authors discussed the results and provided inputs for finalizing the manuscript.

5.1. Motivation

One of the prime reasons for global warming involves the solutions we employ to satisfy our power needs. Either we are dependent on conventional sources of energy (such as burning coal, petroleum products) or renewable sources of energy such as sunlight, hydropower plants and wind. All these have associated pros and cons followed by fundamental energy conversion limits of physics. Moreover, the storage from either source of energy requires batteries, which further leads to environmental pollution and an increased carbon footprint.^{2, 188} The problem becomes severe in the case of consumer electronics where almost 70% of the energy is stored using batteries.¹⁸⁸ Therefore, there is an utmost need for self-sustaining consumer electronics.^{2, 188} An ideal solution to these aforementioned problems could be a synergized energy harvesting approach from multiple forms of energy (light (photovoltaic effect), mechanical vibrations (piezoelectric effect) or thermal fluctuations (pyroelectric effect)) using a device made of a single material.^{2, 45, 149, 150, 188} One of such ideas is using the pyroelectric effect (charge generation due to thermal fluctuations) to support the photovoltaic performance in several materials.²¹³⁻²¹⁵ Recently, light illumination is also reported for tuning piezoelectric²¹⁶, pyroelectric and dielectric properties.^{147, 217} The same is further supported by suggestions of improving pyroelectric^{12, 19} and/or photovoltaic performance^{12, 189} using the piezoelectric effect. In addition, the phenomenon of pyroelectric photodetection is used to develop ultra-fast photodetectors.²¹⁸ The energy conversion capability could further be enhanced if the synergized multiple energy conversion mechanisms are used in a cyclic manner. Such cycles are documented to enhance the energy conversion using the pyroelectric effect (the Olsen cycle)^{6-10, 13}, pyro-magnetic effect²¹⁹⁻²²¹, and mechanical confinement^{11, 19, 21}. However, the operating ranges of these cycles are constrained due to the involvement of slow thermal, mechanical and magnetic changes. In this context, we propose two novel energy conversion cycles by exploring a novel monolithic multifunctional material - KNBNNO $((K_{0.5}Na_{0.5})NbO_3-2 \text{ mol.}\% Ba(Ni_{0.5}Nb_{0.5})O_{3-\delta}))^{3, 45, 149, 150}$

KNBNNO being a bandgap engineered (1.6 eV) ferroelectric with a good piezo- and pyro-response is capable of simultaneously utilizing inputs from an external electric field, stress, thermal fluctuation, and light.^{3, 45, 149, 150} It has been reported to demonstrate optical control of ferroelectric domains³ and material conductivity^{45, 150}. In this chapter, we first study the electrical modulation of photocurrent and pyro-current to develop a basic understanding of the material. Thereafter, the cumulative of the electric field, pyroelectric effect, and light illumination are explored. The developed understanding is thus utilized to propose two novel energy conversion cycles based on *electro-optic* and *thermo-electro-optic* effects in KNBNNO. The energy conversion performance is finally compared to the Olsen cycle^{6-10, 13} which is well-known for cyclic energy harvesting using the pyroelectric effect.

5.2.Experimental details

All measurements were performed on 100 um samples with 200 nm thick ITO electrodes coated on both sides. A high-field electrical poling of the samples was carried out with a poling station consisting of a voltage amplifier (Ultravolt, USA) and a data acquisition card (USB-6211, National Instruments, USA). During the high field (60 kV cm⁻¹) poling, each sample was immersed in silicone oil at room temperature with the poling voltage on for 30 minutes in dark. The photocurrent was measured and the external electric field was provided by the SourceMeter (2450, Keithley, USA) connected with a probe station. The light source was 405 nm, 50 mW laser (OBIS LX/LS Series, Coherent, USA), of which the beam spot size was 0.8±0.1 mm in diameter at 1/e². The temperature

fluctuation was applied through the LTS 350 stage which was precisely controlled with the software.



Figure 5.1. Electrical modulation of the photocurrent: Electrical current obtained due to applied (a) positive (grey shading) and (b) negative (violet shading) 1 V, 2 V, 3 V and 4 V (measured in dark). (c) Photocurrent measured (sky blue shading) in the absence of an applied electric field. (d) electrical modulation of photocurrent due to applied voltages of \pm 1 V, 2V, 3V, and 4V.

5.3. Electrical modulation of photo- and pyro-current

Firstly, the macroscopic modulation of photocurrent is studied under the influence of applied electric fields. Figure 5.1 shows the electrical output under applied (a) positive and (b) negative electric fields of \pm 1 to 4 V. Figure 5.1 (c) shows the photocurrent obtained from KNBNNO corresponding to a laser source of wavelength 405 nm. The

photocurrent modulates by several orders of magnitude by applying small electric fields (Figure 5.1 (d)). This occurs due to light-assisted tuning of the material conductivity and charges injection due to the ferroelectric photovoltaic effect.³ The increase in the negative direction is higher in comparison to the positive direction. This asymmetry is due to the poled state of the material as aligned dipoles favor charge collection in one direction but create as an internal electric field in the opposite direction resulting in relatively less charge collection.²¹¹ This effect can be used to have a multi-level ferroelectric memory^{222, 223} or a photo-detector with a high on-off ratio²¹⁸.

In the next step, pyro-current (Figure 5.2 (a)) was measured for temperature fluctuations of +5 ⁰C at 42 ⁰C (see the temperature profile in Figure 5.2 (a)). Thereafter, electrical modulation of the pyro-current is investigated and is illustrated in Figure 5.2 for (b) + 1V(c) + 2V and (d) + 3V. The material was allowed to relax in the absence of the electric field for one cycle after every measurement so as to avoid modulation due to delay in relaxation of electric field modulated pyro-current. Grey shaded areas correspond to the time when a positive DC bias was applied while the negative bias is indicated using the violet shaded area. Though the output of the pyroelectric effect is analogous to an applied AC electric field, the applied positive and negative DC voltages caused a respective linear electrical offset in the pyro-current. Similar results could be obtained using a function generator by a combination of AC and DC electric fields. Following this, the cumulative effect of the electric field and light on pyro-current is investigated. Figure 5.3 shows the modulation of pyro-current with +4 V (a) in dark and (b) in light. After this, the light and electric field were turned off and the material was allowed to relax merely under temperature fluctuations. A bias of -4V was applied after 150 s of relaxation and a modulation in the pyro-current was noticed (Figure 5.3 (c)). Here, instead of an offset in pyro-current, a continuous decrease in the output is observed. The possible reason envisaged for this was a lack of relaxation time before performing the measurement. But this was ruled out by repetitive measurements on two different samples by allowing materials to have relaxation time of more than 30 minutes. Even after a relaxation time of more than 24 hours, the material demonstrated similar behavior. Therefore, this could only be explained on the basis of a change in the overall state of polarisation due to thermo-electro-optic effect with +4 V and light. Therefore, in the shown measurement the material was again allowed to relax for one cycle before obtaining pyro-electro-optic modulation with -4V and light. Two orders of increase in the pyro-current suggest that the process can be used to have enhanced energy conversion or electrical output.



Figure 5.2. Electrical modulation of the pyro-current: (a) Pyro-current and the temperature profile for which the pyro-current is measured. Modulation of the pyro-current due to applied (b) ± 1 V, (c) ± 2 V and (d) ± 3 V.(grey shaded area correspond to applied positive bias; violet shaded area correspond to the applied negative field)



Figure 5.3. Electro-optic modulation of the pyro-current: (a) Modulation of the pyrocurrent due to applied (a) + 4V in dark and (b) in light. (c) Modulation of the pyro-current due to applied (c) - 4 V in dark and (d) in light.

5.4. Novel electro-optic and thermo-electro-optic energy conversion cycles

Literature suggests that there exists a method to obtain enhanced energy conversion using the pyroelectric effect. The method was introduced by R.B. Olsen in 1980s²²⁴⁻²³¹ and has recently attracted huge attention^{6-8, 11, 12, 17, 20, 22, 232, 233} after Vats *et al.*^{10, 13} introduced the generalized version of this method for all pyroelectric materials. It is suggested that the material should first be polarised isothermally (at low temperature) and then allowed to exchange heat iso-electrically.^{10, 13} The material can then be depolarised isothermally at a higher temperature followed by iso-electric cooling to bring the material at its initial state and to complete the cycle. ^{10, 13} On a similar platform, here

we propose an 'electro-optic cycle' (Figure 5.4 (a)), the isothermal polarisation (process 1-2) of the material followed by isoelectric polarisation by the cumulative effect of applied electric field and laser exposure (process 2-3). Henceforth, the material can be depolarised in presence of light (process 3-4; iso-illumination) and iso-electric removal of the illumination (process 4-1) to complete the cycle. The proposed cycle provides an advantage over the Olsen cycle as light-induced changes are fast and comparatively easy to have. It becomes more important for optically active ferroelectrics like KNBNNO where only a small or nominal change in polarisation occurs over a vast temperature range (Figure 5.4 (b)) whereas, the light-dependent polarisation changes are more significant.³ Moreover, a temperature change could be induced during iso-electric exposure and removal of illumination to further enhance the electrical output and this could be termed as 'thermo-electro-optic cycle'. However, the thermo-electro-optic cycle should be used with caution because the temperature change can induce joule heating which might also cause an increase in the material's resistance and will, therefore, reduce the overall energy conversion. To provide a better understanding of this we performed temperature-dependent photocurrent measurements on KNBNNO, as shown in Figure 5.5 (a). The photocurrent density in KNBNNO at 20 °C was nearly 400 nA cm⁻². This increased linearly with an increase in temperature till 150 °C (700 nA cm⁻²) while start falling down for the temperatures higher than 150 °C (Figure 5.5 (b)). Interestingly the photocurrent density at 220 °C (350 nA cm⁻²) is less than the values obtained at 20 °C. It is to be noted that the material was maintained at the measured temperature for nearly 30 minutes before performing the photocurrent measurement so as to avoid any contribution due to the pyroelectric effect. The trend of temperature dependance of photocurrent could simply be explained on the basis of change in fermi-level due to the thermalization of the charge carriers as there are no structural transitions associated with the investigated

temperature range (20 0 C to 150 0 C). However, there is a structural rhombohedral to tetragonal structural transition at 170 0 C with a nominal change in the lattice parameter.⁴⁵ Besides this, no change in the trend for photocurrent was observed at 170 0 C (See Figure 5(b)).



Figure 5.4. Novel electro-optic energy conversion cycle: (a) Schematic of the novel electro-optic energy conversion cycle with exaggerated change in polarisation with laser exposure (only for indicative purpose). (b) Temperature-dependent *P-E* loops to provide an estimate of the energy harvesting using the Olsen cycle.



Figure 5.5. (a) Temperature-dependent photocurrent measurement in the absence of applied electric field (b) Average value of the maximum photo-current obtained from Figure 5 (a) as a function of temperature.

5.5. Comparison of cyclic energy harvesting capability

A systematic comparison of cyclic energy conversion using the Olsen cycle, and novel *electro-optic*, as well as *thermo-electro-optic* cycles, is performed by measuring temperature-dependent current-voltage (I-V) characteristics of KNBNNO in dark (Figure 5.6 (a)) and under illumination with a laser source of wavelength 405 nm (Figure 5.6 (b)). These provide a good estimate of the electrical output that could be obtained during isothermal, iso-illumination and iso-electric processes. It also helped in understanding that the difference in electrical output obtained during polarization and depolarisation process is the net work done on the system. From the *I-V* measurements, one can also understand that the energy conversion in the last step of iso-electric cooling or photocurrent decay is usually negligible if there is no significant difference in the remanent polarization of the material at position 4 and 1 in Figure 5.4 (a). Therefore, in all energy conversion cycles under investigation, the most important step is 2-3 (iso-electric heating or illumination). From the *I-V* curves depicted in Figure 5.6, we estimated the electrical current output from the Olsen (operating temperature range 20 °C - 200 °C), and novel electro-optic (operated at 20 °C; Wavelength range: Dark to 405 nm), as well as thermo-electro-optic cycles (operating temperature range 20 °C - 200 °C; Wavelength range: Dark to 405 nm) and plotted it as a function of the applied electric field in Figure 5.7.



Figure 5.6. Temperature-dependent *I-V* measurement in (a) dark and (b) in light.



Figure 5.7. Comparison of the energy harvested using the Olsen cycle (operating temperature range 20 0 C - 200 0 C), novel electro-optic cycle (operated at 20 0 C between dark and 405 nm laser wavelength), and thermo-electro-optic cycle (operating temperature range 20 0 C - 200 0 C; wavelength range: Dark to 405 nm).

A comparison of the harvested electrical energy from the three energy conversion cycles help in interpreting that in the absence of structural transitions, an optically active ferroelectric can perform much better than the Olsen cycle. The maximum energy conversion for the Olsen cycle corresponding to 0-5 kVcm⁻¹ and the operating temperature range 20 0 C - 200 0 C was 39000 nAcm⁻². On the other hand, the novel thermo-electro-optic under the same operating range with a wavelength variation of dark to 405 nm resulted in 407000 nAcm⁻² which is more than 10 times higher when compared to the Olsen cycle. Moreover, the energy conversion using the electro-optic energy conversion cycle corresponding to the same operating electric field range was 303000 nAcm⁻² (~ 8 times higher than the Olsen cycle). The highest energy conversion efficiency of the thermo-electro-optic cycle among all three cycles suggests that using a laser source can also improve the performance of the Olsen cycle by several orders. Interestingly, the harvested energy using the Olsen cycle for KNBNNO is already ~36000 times higher than the pyro-current (Compare Figure 5.7 with Figure 5.2). As the Olsen cycle is well

known to have a high energy conversion if there are any structural transitions occurring in the operating temperature range then its performance is likely to increase further by using laser illumination. Importantly, the novel electro-optic energy conversion cycle offers ease of operation as having fast thermal fluctuations are much difficult to achieve in contrast to illumination. Since the maximum output in the novel electro-optic is obtained during the process 2-3, it is wise to maintain material at this step for constant high electrical energy output. In short, this process of obtaining higher photoresponse by applying small electric fields could be a potential solution for improving the photovoltaic performance of ferroelectrics. We hope that the proposed energy conversion cycles will motivate the scientific community to develop better materials for more significant cyclic energy output under multiple inputs.

5.6.Conclusions

In conclusion, two novel energy conversion cycles (electro-optic and thermo-electrooptic energy conversion cycles) for optically active ferroelectrics are proposed. Both energy conversion cycles are found to be capable of providing several times higher energy conversion efficiency in contrast to the well-known pyroelectric energy harvesting Olsen cycle, which is likely to increase more in the presence of structural transitions. In addition, the proposed energy conversion cycles provide advantages of more flexibility in operating conditions than the Olsen cycle. Also, electrical modulation of photocurrent and pyro-current followed by electro-photo-pyroelectric modulations in KNBNNO are presented. The temperature-dependent photoresponse of KNBNNO is attributed to changes in the electronic structure of the material. The presented understanding through this work is expected to motivate the ferroelectric community for cyclic energy harvesting by the combined effect of photovoltaic and pyroelectric effects.

CHAPTER 6

SUMMARY AND CONCLUSIONS

I sum up my study with summaries of conclusions as detailed below:

Experiments described in this thesis suggest that the exposure to light changes the surface potential of the KNBNNO as the light acts as a constant current source in short circuit condition. The charge carriers injected through the surface of the material polarize the dipoles similar to an applied electric field. The material is behaving as a phototransistor; therefore, it is likely that the charges are distributed throughout the sample thickness. This is also confirmed by the macroscopic piezoresponse noticed after 8 hours of exposure to the white light. The same can also be conceived from the lightdependent increase in remnant polarization. However, the possibility of diffusion of oxygen vacancies or current channeling through defects leading to a macroscopic change in polarization can not be completely ruled out. The effect is likely to be irreversible or dynamically slow if only ionic defects such as oxygen vacancies are responsible for this Since (K_{0.5}Na_{0.5})NbO₃ supports off-center distortion and kind of behavior. Ba(Ni_{0.5}Nb_{0.5})O_{3-δ} controls the electronic states in the gap of the parent (K_{0.5}Na_{0.5})NbO₃ using oxygen vacancies and Ni⁺² ions, it could be concluded that the light affects the number of charge carriers in Ba(Ni0.5Nb0.5)O3-8 which eventually leads to structural changes in KNBNNO. Thus, the light-induced reversible poling of ferroelectric domains and domain walls' movement in KNBNNO are due to a combined effect of fluctuations in the semiconducting response aided by the non-centrosymmetric distortion caused by the light. The main finding of this work is that light behaves as a virtual current/voltage source through the photovoltaic effect. If the switching voltages of the sample are in the range of the electric field induced by the incident light, then it could be possible to

achieve optical control over domains and domain walls in several ferroelectric materials.

Chapter 3 helps us understand that in optically active ferroelectrics light exposure can tune the material conductivity by several orders of magnitude. The application of small electric fields on the illuminated area can further cause a significant variation in the charge transport properties and hence confirms that the light is acting as a virtual electrode. The magnitude of the applied voltage and laser spot size provides additional control over this phenomenon. The charge injection and current modulation are governed by the ferroelectric photovoltaic effect and optical tuning of the material conductivity. The demonstrated optoelectric effect leads to a fast (< 1s) and ultra-large (> 30 um) switching of ferroelectric domains. This phenomenon can be used to modulate photocurrent using small electric fields or electrical current by the presence of light makes optoelectric control of ferroelectric domains a promising method for several optoelectronic applications such as photo-detectors and electrical function generator. Based on the understanding developed, a prototype of a monolithic light-effect transistor using KNBNNO is presented. It is a two-terminal device in which laser exposure acts as the virtual transistor gate. This could be a potential solution to the scaling limit of threeterminal transistors.

Chapter 4 provides insight into the mechanical control of ferroelectric domains is confirmed in KNBNNO. It is demonstrated that the ferroelectric domains in KNBNNO can be controlled with the mechanical forces, light and under the cumulative effect of light and mechanical force applied using an AFM tip. The minimum force required to manipulate the ferroelectric domains is $0.4 \ \mu$ N. Interestingly, it is found that forces higher than 3 μ N can induce a change in the sample surface. The applied forces are found to be further supported by the optical manipulation of ferroelectric domains in KNBNNO. This could lead to an improved photoresponse as expected by the piezoelectric photovoltaic effect. The observations presented in this work are thus expected to broaden the nanoscale understanding of the opto-mechanical response of ferroelectrics.

In chapter 5 two novel energy conversion cycles (electro-optic and thermoelectro-optic energy conversion cycles) for optically active ferroelectrics like KNBNNO are proposed. The performance of these novel cycles is compared with the well-known pyroelectric energy harvesting Olsen cycle. Both energy conversion cycles are found to be capable of providing several times higher energy conversion efficiency in contrast to the Olsen cycle, which is likely to increase more in the presence of structural transitions. Besides, the proposed energy conversion cycles provide advantages of ease in operation and relatively more flexibility in operating conditions than the Olsen cycle. The work also provides insight into the electrical modulation of photocurrent and pyro-current followed by electro-photo-pyroelectric modulations in KNBNNO. The KNBNNO is also found to demonstrate temperature-dependent variation in the photoresponse which is attributed to changes in the electronic structure of the material. The presented understanding through this chapter is expected to motivate the ferroelectric community for cyclic energy harvesting by the combined effect of photovoltaic and pyroelectric effects.

I hope that the understanding gained here will help the creation of novel photonic and optoelectronic devices based on semiconducting ferroelectrics.

This thesis provides an understanding of electrical, optical and mechanical control of ferroelectric domains in (K_{0.5}Na_{0.5})NbO₃-2mol.% Ba(Ni_{0.5}Nb_{0.5})O_{3-δ}) (KNBNNO). In addition, the cumulative effect of electro-optical and optomechanical manipulation of ferroelectric domains is investigated. The interesting extension of the presented work would be to study the domain wall behavior and dynamics under joint electrical, optical and mechanical inputs. Moreover, the effect of temperature on the ferroelectric domain is also worth studying. Importantly, the performance of the ferroelectric light-effect transistor under different mechanical loads and over different temperatures could also be potentially interesting extensions of this work. From a more fundamental viewpoint, it would be interesting to explore the structural transformation under due to laser illumination which could further be stretched by inputs from multiple stimuli. However, this kind of work will require special setups and neutron or synchrotron sources. The work presented in the thesis is mostly focused on electrical outputs. However, the changes in the optical properties of KNBNNO by electrical, optical, thermal and mechanical inputs will be entirely a new regime of research interests. A less explored part of this thesis, identification of prospective applications and device designs. The presence of all possible kinds of energy conversion mechanisms on KNBNNO makes it an ideal candidate for an ample spectrum of monolithic devices, especially in designing hardware support for next-generation neuromorphic computing. All suggested future work were out-of-scope of the present thesis due to limitation of time and research focus on advanced scanning probe microscopy techniques.
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