Investigations of electrocaloric effect in ferroelectric thin-films, single crystals and devices

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INVESTIGATIONS OF ELECTROCALORIC EFFECT IN
FERROELECTRIC THIN-FILMS, SINGLE CRYSTALS AND DEVICES

By

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Abstract

An electrocaloric (EC) effect is the temperature change accompanied by the change in electric field intensity of a thermally isolated system. The EC effect is relatively new and a challenging research topic in the field of ferroelectric materials. In principle, the EC effect is analogous to magnetocaloric effect, and the latter utilizes magnetic fields to cool. A notable advantage of EC effect is the ease in generating large electric fields compared to magnetic fields. The EC refrigeration of ferroelectric materials is gaining much interest recently in solid-state cooling applications. The cooling method is often described as a clean, robust and efficient process due to its intriguingly simple design and operation. Moreover, an EC cooling device can be more suitable for special needs in medical appliances, hot spot cooling in integrated circuits due to its compactness and low noise performances.

The first EC effect was observed in Rochelle salt in the early 1930s. Over the years, extensive research in ceramic materials has produced interesting EC results for broad range of scientific and technological applications. Among them, a highly ordered $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$ material demonstrating an EC temperature change of $\Delta T = 2.3 \text{ K}$ at $T_c \sim 18^\circ\text{C}$, has been claimed to be the most promising ceramic materials found to date. The practical applications of EC based cooling restricted to very few systems to until 2006. This was because most identified ceramic materials were exhibiting either low ΔT ($\sim 1\text{-}2 \text{ K}$) values or because engineering their functional properties to meet the practical considerations was difficult. The resurgence of EC cooling was spotlighted only after the discoveries of giant EC temperature changes of 12 K in $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ and poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] ferroelectric thin-films. Recent results in thin-films show almost six times higher

cooling values than the better cooling values found in ceramics. On the bright side, with every two folds increase in ΔT values of EC materials, the operating costs of the refrigeration devices will also be reduced by half. Though the results are very fascinating, thin-film materials suffer from other difficulties such as dominating substrate effects and low heat fluxes. A lot of work must be focused in this direction to realize the EC based cooling which is comparable to other solid-state cooling technologies.

In this dissertation, we systematically investigated the EC properties of ferroelectric thin-films, single crystals and devices with a focus on smart engineering materials. The magnitudes of EC coefficients were initially computed by phenomenological theory and later verified with experimental results. Our experimental works focused on the synthesis of high quality thin-films followed by structural and electrical characterizations of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin-films, $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ thin-films, $0.7\text{Pb}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$ - 0.3PbTiO_3 and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.06PbTiO_3 single crystals. The EC properties of thin-films and single crystals were analyzed for their structure-property relationships and their dependencies on film thickness, substrate and working temperatures. Results revealed large adiabatic cooling figures of $\Delta T \sim 260$ nm PZT films (11 K in 15 V), 200 μm thick 0.7PMN-0.3PT single crystals (2.7 K in 240 V) and 300 μm thick PZN-0.06PT single crystals (0.45 K in 330 V) at Curie temperatures and secondary cooling peaks near critical points.

Analytical modeling of EC cooling elements was also performed using a 2D solid-state device model to predict the cooling efficiencies in Carnot, Brayton and Ericsson refrigeration cycles. Using a comprehensive model for coupled thermal, electrical interactions in ferroelectric 0.7PMN-0.3PT single crystals, we demonstrated Carnot, Ericsson and Brayton efficiencies under thermodynamic cooling cycles. We also explained the intricacies involved in device

design, fabrication and testing of a solid-state EC cooler. The bulk EC cooling effects of 0.7PMN-0.3PT single crystals were exposed with the help of a prototype device to demonstrate EC based cooling. The cooling device was tested on a simulated microchip test section and results reported 7.2°C/min additional cooling rates under optimized test conditions. Besides the high ΔT requirements of working elements, we also explained the significances of electric pulse width and frequency in EC based cooling.

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Symbols

T_{ad}	Adiabatic temperature (K)
C	Capacitance (F)
T_{crit}	Critical point temperature (K)
T_c	Curie temperature (K)
I	Current (amps)
ρ	Density (kg/m ³)
ε	Dielectric constant
$\tan \delta$	Dielectric loss tangent
η	Efficiency
E	Electric field (kV/cm)
S	Entropy (J/m ³ K)
G	Free energy (J/m ³)
C_E	Heat capacity (J/kgK)
Q	Heat flux (W/m ²)
U	Internal energy (J/m ³)
T_{max}	Maximum temperature (K)
P	Polarization (C/m ²)
A	Surface area (m ²)
T	Temperature (K)
k	Thermal conductivity (W/mK)
t	Time (s)
W	Work done (J)
V	Voltage (volts)

Abbreviations

AFE	Anti-ferroelectric
AFM	Atomic Force Microscope
COP	Coefficient of performance
EC	Electrocaloric
ECE	Electrocaloric Effect
ECC	Electrocaloric Cooling
EPMA	Electron Probe Micro Analyzer
FE	Ferroelectric
MCE	Magnetocaloric Effect
M_c	Monoclinic phase
MPB	Morphotropic Phase Boundary
O	Orthorhombic phase
PE	Paraelectric
Pt	Platinum
PLD	Pulsed Laser Deposition
RSM	Reciprocal Space Mapping
RC	Refrigeration capacity
RTD	Resistance Temperature Detector
R	Rhombohedral phase
T	Tetragonal phase
TE	Thermoelectric
XRD	X-Ray Diffraction
ZFC	Zero Field Cooling
ZFH	Zero Field Heating

Chapter 1:

INTRODUCTION

1. Introduction

Refrigeration is a process of transporting heat from heat source to heat sink. Conventional refrigeration for many years have been provided by vapor compression based systems. Although modern compressors are relatively efficient, they are now approaching their theoretical and technological limits [1]. In addition to the efficiency plateau, vapor compression technology has some environmental issues. For example, volatile refrigerants such as hydrochlorofluorocarbons or halofluorocarbons are significant sources of greenhouse gas emissions. Global warming potential for these volatile refrigerants are as high as 1000 times that of CO₂ [2, 3]. In order to protect the environment from destruction of ozonosphere and high concentrations of greenhouse gases generated from refrigeration systems, usage of volatile fluids should be abolished.

There are urgent needs to develop new and affordable cooling technologies, to enhance overall energy efficiencies, and to reduce greenhouse gas emissions. Most cooling technologies over years go hand in hand into improving products, energy efficient methods and environmental performances. For example, solid-state refrigeration technologies claim no moving parts and use no volatile fluids could possibly be the promising alternatives. Solid-state heat pumps offer high efficiency, are compact in size, less weight, and have easy device integration benefits relative to conventional vapor-compression systems [4].

Moreover, demands for solid-state technologies in electronic industries with the recent developments in through silicon via (TSV) technologies have grown and the trends of increasing circuit densities within ICs and packagings have led to higher heat densities. More importantly, thermal management is a key element in the mechanical design of today's advanced electronics. According to Moore's law, the densities of chips in microprocessors double every two years. With these increasing densities and functionalities of the current

chips, the amount of heat generated by these chips is also drastically increasing [5]. If the same trend continues over the next decade with no major improvements in power management methods, high performance computing devices will surpass the industry's ability to cool them economically.

In general, heat transformers can be classified into two types based on cyclic or non-cyclic refrigeration modes and the type of work done to drive heat from heat source to heat sink. During the refrigeration process, heat is removed from a low temperature object and rejected to a high temperature heat sink with the help of external work. A non-cyclic refrigerator uses simple cooling methods like melting ice or dry ice to cool the objects; in most cases, this method is used to cool small scale objects. Vapor-compression based heat pumps and solid-state devices are good examples of cyclic refrigeration systems. Depending on the type of external work used, the new classes of solid-state coolers are classified as magnetocaloric (magnetic field), thermoelectric & electrocaloric (electric field) and thermoacoustic (sound waves) heat pumps.

Among the solid-state heat pumps, magnetocaloric and thermoelectric coolers have been well studied, and common in commercial applications [6], whereas electrocaloric (EC) coolers are the latest interest in the solid-state community. The field of EC research has gained increasing popularity after the discoveries of giant EC effects in thin-films. From the thermodynamic perspective, electrocaloric effect is analogous to magnetocaloric effect. The two cooling methods have their own pros and cons in practical usage. Magnetocaloric coolers are powerful and can be used as direct replacements to vapor-compression systems in commercial refrigeration due to their large cooling capacities [7]. On the other hand, electrocaloric coolers are compact in size, robust and easy to use for small objects cooling. Furthermore, EC coolers are highly compatible for miniaturized refrigeration applications

such as in electronics or automobile cooling. Also they have a distinct advantage over magnetocaloric devices, as their electric fields are easier to apply compared to magnetic fields, which generally require a huge space to fix electromagnets around the device.

In addition to the above advantages, electrocaloric coolers also boast of high theoretical cooling efficiencies compared to other solid-state based devices [8]. The thin-film based cooling technologies have also pronounced some fascinating applications such as modern jackets for defense applications (where the body temperatures can be modulated by application of small voltages with help of a portable battery) and in medical appliances. However, the bottle necks in the current stage of EC technology is in the identification of materials with large temperature changes and smart device engineering.

1.1. Background Information

An electrocaloric cooler works in a similar fashion to vapor-compression system and it undergoes four stages of reversible thermodynamic cooling cycle during the refrigeration process. The spontaneous heat flow direction is defined by the second law of thermodynamics [postulated by Carnot in 1824] and heat always flows from high temperature heat source to low temperature heat source. Refrigeration is the process of transferring heat from low temperature source to the high temperature source and the process is against the natural flow of heat. Hence, some work must be spent to enable this process of reverse heat transfer. This work is traditionally provided either by mechanical, magnetic, electric, heat or sound forces.

It is easy to understand the underlying physics and working principle of a solid-state cooling device by simply comparing it with a conventional vapor based refrigerator as shown in Figure 1.1.

Figure 1.1: Schematic of (a) vapor-compression refrigerator[9] and (b) solid-state cooling device.

The essential elements of any refrigeration system consist of at least a heat source, a heat sink and a working medium. The working medium collects heat from the heat source and rejects it to heat sink. The refrigeration process takes place against the natural flow of heat and must be supported by external work. An ideal cooling method must follow the reversible Carnot cycle in order to pump the extra heat to the heat sink each time.

In general, the refrigeration cycle consists of four stages of thermodynamic operations, two isothermal and two adiabatic steps.

The vapor-compression cycle uses mechanical work to drive heat against the heat sink. The working medium of a conventional refrigerator comprises of various components, the condenser, compressor, evaporator, thermostat and a highly volatile fluid such as Freon gas. The vapor-compression cooling cycle can be analyzed with the help of a diagram as shown in Figure 1.1 [a]. Initially, a circulating refrigerant in the form of vapor enters the compressor and the vapor is compressed adiabatically. During the process the refrigerant gas

exits the compressor in a superheated form. The superheated vapor travels through the condenser which is connected to the heat sink, resulting in cooling the gas by removal of extra heat. Then, the super cooled vapor is transformed into liquid form by losing the additional heat to the heat sink at a constant pressure and temperature condition. The next step is the circulation of liquid refrigerant through the expansion valve. The pressure decreases abruptly causing flash evaporation and then it passes through the evaporator where the refrigeration happens and takes heat from the heat source. The cycle is repeated several times until the required cooling is achieved. Overall, the cooling process repeats several reversible Carnot cycles by undergoing through constant entropy and constant temperature stages.

The EC refrigeration process comprises similar cooling cycles such as vapor-compression systems, i.e. a four stage reversible Carnot cycle as shown in Figure 1.2. Electrocaloric heating occurs in an adiabatic environment when the electric field is applied to a working medium (usually a ferroelectric material) and the cooling happens when the field is removed. Thermodynamic refrigeration cycles are employed to isolate the heating and cooling stages in the EC materials, and engage them in solid-state coolers.

As shown in Figure 1.2, compression and evaporations cycles are directly compared with electric field applied and breakdown steps from stage 1 to 4. During stage 1, electric field is applied under adiabatic environment to the working element. The temperature of the materials rises as a result of increase in lattice entropy to compensate for the drop in dipolar entropy while the electric field is on. The excess heat is removed in stage 2 by connecting the working medium to a heat sink with the help of the heat switch. In stage 3, the field is removed adiabatically so that dipolar entropy reaches its original state to result in reducing the temperature of the working medium. Finally, the heat source placed in contact with the

working medium in stage 4 to cool the final object of interest. The cycle is repeated reversibly to achieve the solid-state refrigeration through electrocaloric cooling.

Figure 1.2: Schematic of refrigeration cycles directly compared in electrocaloric working material (left side) with vapor-compression system. Stage 1 and 3 are corresponding to adiabatic operations and stage 2 and 4 corresponding to isothermal steps in Carnot refrigeration cycle. The figure is adapted from M. Valant [8].

Solid-state cooling technologies have their own advantages and appeal in terms of simplicity in device operations compared to systems that must compress and expand a two phase (gas/liquid) working fluid [10]. With recent progress in smart materials engineering of EC working elements, electrocaloric coolers have shown great potential towards the

designing of energy efficient devices. The niche of the current project lies in acquiring in-depth knowledge of the working elements and their performance under different working environments. Details and discussions on the issues are presented in the following sections.

1.2. Theory

EC cooling is defined as the ability of a material to change its body temperature upon application or withdrawal of an electric field. The EC coolant material works on the principle of electric field constrains the orientation of electric dipoles in polar materials, and the overall energy of systems that can be tuned by the variation of electric field strength. The EC material is able to change its temperature by changing its lattice entropy caused by movements of electric dipoles in the controlled fields. A large EC effect is a direct result of large entropy change associated with the dipoles movements/polarization changes in solid materials. The EC material must be capable of generating large polarization changes or adiabatic entropies. Change in entropy is a measure of unusable energy in the dipolar materials after the use of an electric field, and it causes the change in internal energy and there by the temperature difference.

The working elements used in electrocaloric cooling devices are highly polar dielectrics [11]. Polar dielectrics have the potential to achieve large EC effects near order-disorder phase transitions due to large changes in polarization induced by the applied electric field and causes large lattice entropy changes. This is because of the unique capability as working elements in solid state cooling devices.

Ferroelectrics are a special class of polar materials, which exhibit spontaneous polarization or electric dipole moment even in the absence of an external field. In the absence

of an electric field, ferroelectric materials contain entropy in the form of spin entropy plus lattice entropy. When the electric field is applied, the spin entropy decreases by adjusting the alignment of dipoles to the external field. The energy involved during the process of random spin orientation changes has to go somewhere and it finally get transferred into lattice entropy [12]. Thermodynamically speaking, this dipole ordering lowers the lattice entropy, so the system is compensated by increasing its body temperature as a consequence of energy total conservation under adiabatic conditions. When the field is removed, the dipoles tend to go back to their normal state by reducing the material body temperature through consuming its internal energy. In ferroelectric materials, ferroelectric – paraelectric transition is characterized by sudden polarization change induced by polar to non-polar transition. In order to achieve large EC coefficients, it is always advantageous to consider ferroelectric materials near the FE-PE transformation temperatures [13-15].

The EC effects in ferroelectric materials are originally postulated from Maxwell's relations [16]. It is a well realized fact that absolute measurements of entropy changes in any system are impractical and equivalent polarization changes measurements under isofield conditions are considered as alternative solution [17]. Any specific system under thermodynamic equilibrium can be defined by a set of intensive and extensive variables which are related to one another through a unique set of rigidities or compliances. For the case of a deformable polarizable solid, the intensive variables are the electric field (E_i), temperature (T) and mechanical stress (X_{ij}) and the corresponding extensive variables are electric displacement (D_i), entropy (S) and strain (x_{ij}).

$$dD_i = [\partial D_i / \partial T]_{X,E} dT + [\partial D_i / \partial E_i]_{X,T} dE_i + [\partial D_i / \partial X_{ij}]_{E,T} dX_{ij} \quad \text{Equation (1.1)}$$

$$dx_i = [\partial x_i / \partial T]_{X,E} dT + [\partial x_i / \partial E_k]_{X,T} dE_k + [\partial x_{ij} / \partial X_{kl}]_{E,T} dX_{kl} \quad \text{Equation (1.2)}$$

$$dS_i = [\partial S / \partial T]_{X,E} dT + [\partial S / \partial E_i]_{X,T} dE_i + [\partial S / \partial X_{ij}]_{E,T} dX_{ij} \quad \text{Equation (1.3)}$$

Compliances of particular interest to us are the electrocaloric coefficient ($\partial S/\partial E$), the pyroelectric coefficient ($\partial D/\partial T$) and the dielectric permittivity ($\partial D/\partial E$). The electrocaloric and pyroelectric properties of a dielectric material are converse effects and are related by **Maxwell's equation**, $(\partial S/\partial E)_T = (\partial D/\partial T)_E$, whereas the electric displacement (**D**) includes both charges associated with polarization of the material (P_i) and charges created by the polarization free space ($\epsilon_0 E_i$). i.e. $D_i = \epsilon_0 E_i + P_i$.

The relationship between adiabatic temperature changes corresponding to the entropy changes in polar materials at any specific temperature is given by the Second law of Thermodynamics. In practice, the EC effect is difficult to measure directly and is often described with the help of Maxwell relations.

The thermodynamic free energy (G) of materials in terms of system entropy (S), induced polarization (P) in an electric field (E) is given in the following relation;

$$\delta G = -S dT + P \delta E \quad \text{Equation (1.4)}$$

From here, it can be determined that

$$S = -\left[\frac{\partial G}{\partial T}\right]_E \quad \text{and} \quad P = \left[\frac{\partial G}{\partial E}\right]_T \quad \text{Equation (1.5)}$$

From Maxwell relations, it can be derived that electrocaloric coefficient is equivalent to pyroelectric coefficient under constant temperature.

$$-\left[\frac{\partial P}{\partial T}\right]_E = \left[\frac{\partial S}{\partial E}\right]_T \quad \text{Equation (1.6)}$$

Isothermal entropy ΔS and reversible adiabatic temperature change ΔT due to the applied electric field E , for a material of density ρ with heat capacity C , are given by

$$\Delta S = - \int_{E_1}^{E_2} \left(\frac{\partial P}{\partial T} \right)_E dE \quad \text{Equation (1.7)}$$

and

$$\Delta T = - \frac{1}{\rho} \int_{E_1}^{E_2} \frac{T}{C} \left(\frac{\partial P}{\partial T} \right)_E dE \quad \text{Equation (1.8)}$$

Values of electrocaloric coefficient $p = \left[\frac{\partial S}{\partial E} \right]_T$ can be obtained from electrical hysteresis measurements which are carried out in a range of temperatures.

In general, ferroelectric materials show total polarization (P) as spontaneous polarization plus field induced polarization component in external electric fields. The path of polarity change due to cation movements follows hysteresis loop as shown in Figure 1.3[a]. A comparison was drawn between the total polarization changes with electric field in ferroelectric materials to the entropy changes with temperatures in thermodynamic operations.

Figure 1.3: (a) A typical P-E loop of a dielectric and (b) Carnot cycle given T Vs S. Figure is adapted from [18].

The hysteresis path ABCD is nearly a reversible process in ferroelectrics and at initial point A, where no dipole movement in zero-fields exists. When the electric field is slowly

raised from A to B, polarization also changes because of the addition of field induced component to the spontaneous polarization. Once the field is brought back to zero, part of P still exists as remnant polarization due to hysteresis. The polarization along B to C aligns in the applied field direction represent an ordered state. Intrinsic polarization changes are directly compared to the adiabatic entropy changes in Figure 1.3 [b]. When the field is modulated by introducing constant time steps at E_1 and E_2 in hysteresis loops, it corresponds to the four stages of Carnot cycle.

When moving from A to B in Figure 1.3 [b], the material experiences a rise in adiabatic temperature from T_c to T_h due to the drop in entropy values. A constant field stage introduced along B to C for a short period can be used to reject heat to the heat sink at T_h . When the electric field is reversed along C to D, the material regains its entropy from S_c to S_h , resulting in the adiabatic cooling step. The material loses polar-ordering by receiving heat from the heat source. By further reducing the applied electric field from D to A, i.e. E_2 to E_1 equivalents on the left side of the figure, the material will be brought back to its original state.

1.3. Literature

Electrocaloric studies in ferroelectric ceramics were the focus of significant scientific interest in early 1960s and 1970s. The first discovery of ECE was reported in Rochelle salt in 1930 by Kobeko and Kurtschatov [2]. Subsequently it was reexamined experimentally in the same material by Wiseman [11] in 1963 who measured $\Delta T = 0.0036^\circ\text{C}$ at 22.2°C . The adiabatic temperature changes were too small to consider them for practical applications. Another significant effort was seen from E Hegenbarath in 1961 in ferroelectric ceramics at cryogenic temperatures [9]. During the next couple of decades, intensive research had

focused on identifying high ΔT values in ferroelectric ceramics, inorganic dipolar materials as well as in single crystals [11, 19-25].

The quest for new EC materials bestowed some interesting results in KH_2PO_4 crystal [26], SrTiO_3 ceramics [4], $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$ ceramics [5], and $\text{Pb}_{0.98}\text{Nb}_{0.02}(\text{Zr}_{0.75}\text{Sn}_{0.20}\text{Ti}_{0.05})_{0.98}\text{O}_3$ ceramics [15, 27]. For KH_2PO_4 crystal, $\Delta T = 1^\circ\text{C}$ under 11 kV/cm electric field at -150°C was deduced from the Maxwell relation and an entropy change of $2.31 \times 10^3 \text{ J}/(\text{m}^3\text{K})$ (or $0.99 \text{ J}/(\text{kgK})$) was reported [24]. For SrTiO_3 ceramics, $\Delta T = 1^\circ\text{C}$ and $\Delta S = 34.63 \text{ J}/(\text{m}^3\text{K})$ ($6.75 \times 10^{-3} \text{ J}/(\text{kgK})$) under 5.42 kV/cm electric field at a temperature of -269°C was deduced from the Maxwell relation. For $\text{Pb}_{0.98}\text{Nb}_{0.02}(\text{Zr}_{0.75}\text{Sn}_{0.20}\text{Ti}_{0.05})_{0.98}\text{O}_3$ ceramics, $\Delta T = 2.5^\circ\text{C}$ and $\Delta S = 1.73 \times 10^4 \text{ J}/(\text{m}^3\text{K})$ ($2.88 \text{ J}/(\text{kgK})$) at 30 kV/cm and 161°C was deduced [20]. Futtzzo *et al.* claimed that the ECE was permitted only above Curie temperature (T_c) in ferroelectric materials and it vanished below T_c [1]. A completely contrasting explanation to the above claims was made by Mitsui *et al.*; the ECE is negligible above T_c and is only significant below T_c [3]. Unfortunately, it created ambiguity in the fundamental understanding of ECE until 1980s between different research teams. Later the problem was addressed by Scott J.F., who explained the assumptions and misinterpretations made in calculations of EC coefficients with indirect methods [28, 29]. Scott pointed out that the problem with Mitsui *et al.* was that they implicitly assumed in their equations that the ferroelectric phase transitions were second order; whereas first order phase transitions permit a wide range of temperatures above the transition temperature, at which an applied field (in BTO) can still induce a spontaneous polarization. In this range, the ECE is usually at its maximum. However, for second order phase transitions (considered by Mitsui *et al.*), the ECE is often nearly zero. Li *et al* [30] recently supported Scott's argument by showing that changing the order of the phase transition near tricritical point greatly reduces the ECE in PVDF films.

High electric fields can induce large ΔT and ΔS values in EC materials, but this is limited by the electrical breakdown strengths. A drawback with the majority of EC ceramic materials for using them in practical applications is their low ΔT (~ 1 -2 K) values. Tuttle & Payne emphasized on possibilities of obtaining high ECEs in lead zirconate titanate (PZT) materials family [30, 31]. The research on ECE of Pb based ferroelectrics soon recorded much higher values on broad working temperature ranges [32-36]. The maximum EC temperature changes identified [2.3 K] in highly ordered $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$ [37] at T_c 18°C was one of the promising materials for practical usage but the materials choice was limited to only a few systems.

Major breakthroughs in ECE materials were seen after the two notable discoveries of giant EC effects in $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ thin-films in 2006 [16], followed by technologically promising polymer thick-film materials in 2008 [38]. Mischenko *et al.* (2006) reported a giant ECE in PZT 350 nm thin-films prepared by sol-gel method (0.48 kelvin per volt near its $T_c \sim 222^\circ\text{C}$). The reasons behind such large ΔT values were given as high electric field sustaining capabilities of the thin film near the F-P transition. In August 2008, a team from Pennstate developed a ferroelectric polymer with isothermal entropy change of more than 55 J/Kg/K and adiabatic temperature change of 12 K. They also showed that the relaxor ferroelectric polymer thick films resulted in the same level of ECE near room temperature in P(VDF-TrFE-chlorofluoroethylene) [38]. Phenomenological investigations were carried to understand the effects of misfit strain, film thickness and mechanical boundary conditions on electrocaloric coefficients [17, 39-45].

Two noteworthy *Science* works revitalized the hunt for EC materials in a new direction and produced some fascinating results in organic[18], inorganic[46] and relaxor ferroelectric thin-films[47-49]. Organic ferroelectrics are regarded as the most promising

commercial materials so far for their large cooling per volt values and easy scalability characteristics [47, 50, 51]. Also relaxor ferroelectrics such as 0.9PMN-0.1PT films [52, 53] showed relatively high refrigeration capacities that are comparable to organic ferroelectrics [54]. Despite the progressive developments in new materials, direct temperature measurement of ECE still stood as one of the toughest challenges to accomplish. Kar-Naryan *et al.* first demonstrated direct temperature measurements on BaTiO₃ commercial multilayer capacitors [55]. Modified differential scanning calorimetry method was used by Bai Y *et al* to reexamine the commercially available MLCs [56]. Separation of heat lost to the substrate in thin-film EC measurements by careful calibration methods was first proposed by Rozic B *et al.* in P(VDF-TrFE) polymer films [49, 57]. A recent study by Sebald *et al.* compared strengths of both measurement techniques[58]. Modeling of EC cooling device has been tried to study the possibilities of using these materials in solid-state devices [59-64].

Similar to the electrocaloric effect in ferroelectric materials, the magnetocaloric effect (MCE) show high cooling values when operating near the ferromagnetic-paramagnetic transition in magnetoelectric materials. For instance, an impressive entropy change of 18 J/kg/K was induced with a magnetic field of 5 T at near room temperature in MnFeP_{0.45}As_{0.55} [65]. Similar values near room temperature were also demonstrated in MnAs_{1-x}Sb_x where a magnetic field change of 5 T resulted in an entropy change of 30 J/kg/K and temperature change of 13 K, resulting in a refrigerant capacity of 390 J/kg [66]. While the values above were calculated based on the Maxwell relations, a direct measurement of 10 K temperature change with a magnetic field of 7 T at about 7°C was reported in Gd₅Si₂Ge₂ [67]. A detailed review of near room temperature magnetocaloric materials was given by V Franco *et al* [68]. Due to the greater cooling effects detected in MCE materials as opposed to ECE materials, more work was focused on developing cooling devices based on the MCE materials, but the technology has not been widely commercialized.

1.4 Applications

The new technology based on EC cooling elements offer low noise performance and high precision control, and is ideal for medical appliances. There is great potential for this kind of technology to significantly lower the cost of refrigeration. The charge/discharge cycling is very efficient in EC devices. The devices can be as small as a few millimeters in thickness by top-down and bottom-up approaches, which are highly suitable for the next generation of nanoelectronics.

The solid-state device is ecologically clean, and is thus very attractive for cooling of transistors and interconnects in laptops. Integration of these devices can be achieved easily in portable electronic gadgets, and with further development in the thin-film technology by suppressing substrate effects, many smart applications can be foreseen. The state of the art technology lies in the development of new materials with high electrocaloric coefficients and in identification of appropriate heat switches to control the cooling cycles.

1.5 Motivation

The field of ECE is resurging not only because of the exciting findings reported in **Science** recently, but also because of the high theoretical efficiencies of EC devices compared to thermoelectric cooling systems based on Seebeck and Peltier effects [69-71]. On the other hand, EC working elements can easily overreach magnetocaloric based cooling in cost and performance, as electric fields are much cheaper and easier to apply compared with those using magnetic fields. Some motivating factors are considered from the literature to acknowledge the importance of current research.

- a. Since feasibility to get large ECE has been demonstrated in sol-gel thin-films [72], the limitation of 4-15 K in cooling can be further enhanced via epitaxial deposition by

changing mechanical boundary conditions such as de-clamping by forming high aspect ratio islands, stripes and scaling down to nanosizes. Systematic analysis of the dependencies of ECE on the film/substrate misfit, aspect ratio of structure, film thicknesses and orientations can be checked.

Epitaxial thin-films allow high applied electric fields & thus much higher ECE never reported before in bulk materials is applicable. The fabrication of ferroelectric (FE) – based thin-films is also compatible with current Si Technology. Some characteristics & advantages of our ECE-based thin-films & devices are shown as:

- (i) Fast switching: The operation of conventional cooling device, which usually takes a long time, is made possible by certain thermodynamic cycles. In the ECE design, a natural cycle in ac mode, which was never tried in epitaxial thin- films is allowed. In addition, the ECE is controlled by switching ferroelectric polarization, which can be very fast near pico-second level.
- (ii) Low power consumption: Conventional device requires constant gate bias to maintain “on” state. Leakage current through the gate dielectrics contributes to power consumption. The FE-based EC device only needs a voltage pulse to switch the ferroelectric polarization. There is no leakage current contributing to high power consumption. It also reduces power cost compared with conventional magnetocaloric effect where a magnetic field is applied [28, 29].
- (iii) Nonvolatile: The state of the device can be retained even if the power is switched off due to the nonvolatile nature of the ferroelectric polarization. The system immediately goes to its previous state once the power is on. There is no need to reload any programs.
- (iv) Scalability: Since the electrocaloric device is an electric field-controlled device, the lateral scalability is only limited by lithographic capabilities; furthermore, it has

been demonstrated that ferroelectric polarization can exist in thin-films of only a few nanometer [73, 74].

- b. So far investigations on electrocaloric materials pertained to understandings of the origin of electrocaloric effect in various materials. On careful observation of all previous experimental and theoretical results, we conceive that the materials with compositions having critical points in their phase diagrams produces more electrocaloric effects than others. Here we propose the famous piezoelectric material $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ from PZT family (which processes two tricritical transition points at MPB composition), $0.7\text{Pb}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$ - 0.3PbTiO_3 and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.06PbTiO_3 materials for our investigations.
- c. Few attempts have been reported on direct measurements of EC effects in thin-films so far. Most EC coefficients were computed via entropy change through the results obtained from P-E loops under different temperatures. It is necessary to design and test an ECE test section to observe the direct temperature changes in thin-films. Also, it is important to choose realistic thermodynamic cycles in devices to calculate the EC efficiency and have a direct evaluation towards ECE.
- d. The common thermodynamic cycles in any working devices are Carnot, Stirling and Ericsson cycles [69]. Carnot cycle is the easiest in principle but difficult to implement in practice because of its hard control over successive adiabatic and isothermal conditions. One can easily choose between Ericsson cycle (two constant electric field paths and two isothermal paths) and Stirling cycle (two constant electric induction paths and two isothermal paths) and compare the figures of merit of both cycles for different materials/devices. The advantages with the latter cooling cycles are,
 - (i) Natural ac mode as well as dc mode is proposed in Sterling and Ericsson cycles in the capacitor structures.

- (ii) Both the methods use regular cycles for cooling and reverse cycles for energy harvesting from the same EC device.

1.6 Problems Statement

The studies of EC effect in ferroelectric materials are quite challenging, because EC materials pose orthogonal difficulties in terms of dimensionalities [75, 76]. In bulk materials, the observed EC effects are relatively small and also struggle with low thermal responses against ultrafast heat transfer requirements. The EC effect is directly proportional to the magnitude of overall field used; usually bulk materials require large voltages to generate the same magnitudes compared to thin-films and arcing is a major issue in generating them. On the other hand, thin-films are predicted to show large EC effects but cannot pump significant heat due to insignificant masses compared to their bulk counterparts and also the properties are thermally anchored by substrates.

At present, the challenges involved within EC studies are classified into two sections as depicted in the flow chart above. There is an immediate requirement to identify materials with large ΔT values near room temperatures to address the refrigeration tasks. Though, several EC materials have been identified till now, a clear connection and interpretations between the existing materials is seriously lacking. A proper criterion must be established to understand the intrinsic properties and materials selections for different applications.

Moreover, effective cooling over wide temperatures is a coveted property of any coolant material for efficient cooling process. For practical cooling, the EC materials must possess large ΔS values along with large ΔT values to achieve high uniform cooling throughout the working temperatures.

1.7 Summary of the Thesis

In this section, a brief summary of the dissertation and significant findings are presented. We started the project with aims of investigating new class of materials with high ΔT values near room temperature and smart engineer the materials properties suitable for practical EC cooling applications. We also aimed to demonstrate the EC device by proof of concept method. The overall project was carried out in three different work modules; phenomenological studies, experimental investigations and prototype device design & testing.

Our primary investigations were focused on studies of EC effects in epitaxial thin-films, which is a new concept to pursue the topic at the beginning of the project. Before quickly jump into experimental works, we tried to assimilate the EC properties of well-known ferroelectric materials, barium titanate (BT), barium strontium titanate (BST) and lead

zirconium titanate (PZT) films by phenomenological modeling to resonate on materials selection. Followed by it, we conducted experiments to deposit high quality PZT thin-films by sol-gel (polycrystalline films) and pulsed laser deposition (epitaxial films) methods. The EC coefficients of BST and PZT materials were derived by indirect methods and the results were compared with phenomenological data to predict the structure-property correlations. Based on the knowledge acquired by thus far, we derived a hypothesis on materials at morphotropic phase boundaries (MPB) for smart engineering of EC properties. Also, we conducted experimental works to prove the universality of the hypothesis in PZT epitaxial thin-films, PMN-PT and PZN-PT single crystals (planner samples of single crystals were obtained from commercial sources). Though, the PZT films showed giant cooling values (of 11.2 K at 577 kV/cm), thin-film structures were found to be difficult to test as EC cooling elements. Single crystal wafers were proposed as alternative materials to overcome the challenges involved and to obtain effective cooling figures over wide operating temperatures.

In our final work module, we tested the cooling performances of PMN-PT crystals with the help of a prototype device. The test section was designed to verify the bulk cooling values that are possible when the EC elements attached to cool a simulated heating surface such as a microchip. Thermodynamic parameters of different cooling cycles were modeled using 2D geometries by solving transient heat equations of with Comsol Multiphysics commercial software. We investigated cooling efficiencies of Ericsson and Brayton cycles, which are considered to be more practical solid-state EC cooling methods. Also our test device results demonstrated interesting aspect of EC cooling such as the EC device performance is highly dependent on frequency of applied electric field besides high ΔT values in EC materials.

Chapter 2:

OBJECTIVES

2. Objectives

The crux of this project lies in identifying materials with large EC effects in thin-films, free-standing thick films, and single crystals, in conducting EC measurements under adiabatic conditions and test them by controlling of the polarization switching cycles with appropriate heat switches and in optimizing test parameters to perform the thermodynamic cooling in EC devices. Another challenge involves is proving solid-state EC cooling by a proof of concept method.

The primary objectives of the dissertation are to:

1. Identify near room temperature EC materials with large ΔT values over broad working temperatures.
2. Establish proper criteria for materials selections for various application requirements.
3. Design a proof of concept device with the potential to be scaled down to nanosize.

2.1. Challenges

- Designing a physical system that is close to instability to carry out direct temperature change measurements in thin-films so that small external perturbations from electric fields or thermal excitations will tip the system into a new ground state.
- To realize the reversible electrocaloric cycle, it is essential to apply a pulsed electric field to the working medium, and also to periodically make and break the thermal connections between the working medium, heat receiver and heat source at quick intervals.
- Some practical considerations to be considered are
 - Fast and sensitive temperature sensors

- Stable and precisely controllable heat bath
- High performance thermal diodes
- A solid-state powerful heat sink.
- Implementation of apt thermodynamic cycles to predict the efficiency of the cooling device.

2.2 Detailed Methodology

An overview of the proposed methodology is given in Figure 2.1 below and detailed discussions are presented in subsequent paragraphs. The project tasks are split into three work modules. Work modules 1 & 3 deal with both theoretical and experimental investigations and work module 2 is experimental.

Figure 2.1: Outline of the proposed work plans.

Work Module 1: Initial theoretical studies are carried out based on phenomenological theory to identify ferroelectric materials with near room temperature EC cooling values (chapter 3). In later stages, the experimental works are aimed at synthesis, characterization and structure-property evaluation of electrocaloric materials (chapter 4) in several stages as elaborated below,

- a. Identification of suitable compositions from PZT & BST families in strained thin-film form on various substrates and electrodes. Optimization of materials geometries by single crystal relaxer ferroelectric compounds of PMN-PT and PZN-PT at MPBs.
- b. Ferroelectric-based films are the single active elements, prepared as EC working materials. The polarization switching behavior under different working temperatures can be used to determine the device performances. Pulsed laser deposition (PLD) has been an extensively used technique for preparing high quality epitaxial oxide films. PLD and chemical solution deposition methods are employed for materials synthesis, since they can produce ferroelectric films with epitaxial and polycrystalline properties suitable for structure functionality comparisons.
- c. The ferroelectric thin-films prepared by PLD are characterized by XRD and TEM for their structures and interface details. Topographies of thin-films are analyzed by AFM and SEM. Electrical properties under different temperatures are studied using ferroelectric tester and SPM-based microscopy.
- d. Systematic analysis of dependences of ECE on the film/substrate misfit, film thicknesses and orientations are crucial to get high ECE. The scaling of device size will be conducted with individually addressable ECE capacitors.

Work Module 2: In this work module, we carried out experimental work on different materials in order to prove the universal nature of the proposed hypothesis. Single crystal

wafers are studied as alternative materials to overcome the challenges involved with thin-films and to obtain effective cooling figures over operating temperatures close to RT (Chapters 5 and 6).

Work Module 3: Analytical models are used to solve 2D heat equations to predict the EC device parameter and cooling efficiencies in solid-state device models. We aimed at design, fabrication and testing of electrocaloric working elements for solid state cooling devices (more details of it are provided in Chapter 7).

2.3 Novelty of the Approaches

- ECE in epitaxial thin-films is a relatively new method for studying intrinsic properties; we initiated the idea by measuring the intrinsic EC effects in epitaxial thin-films and compared the results with polycrystalline films. Epitaxial thin-films can provide better control of EC properties and enhance the ECE. High quality thin-films can pave the way for scaling down the nanosize addressable devices using both bottom-up and top-down approaches.
- Cooling temperatures of EC materials can be tuned by optimization of intrinsic parameters such as film composition, substrate, orientation, thickness, misfit and other mechanical boundary conditions. Materials compositions play a key role and are very important to consider for spreading the applications domain of EC cooling. Our approach of MPB dependent ECE studies can be a key contribution.
- More pragmatic methods of Sterling and Ericsson cooling cycles are tested with modulation of electric pulse cycles. A prototype device can be used to demonstrate EC based cooling for practical applications.

Chapter 3:

PHENOMENOLOGICAL DESCRIPTION

3. Phenomenological Approach

Electrocaloric effects of ferroelectric bulk materials and thin-films are studied using phenomenological calculations in order to identify possible new materials systems with high cooling values near room temperature. It is important to understand the effects of film thickness, strain, chemical composition and field induced components on EC coefficients. Thermodynamic relations are used to describe the relationships between polarization (P), electric field (E) and induced electrocaloric temperatures (T). Later, the adiabatic temperature (ΔT_{ad}) values are compared with experimental results for validation.

A thermodynamic analysis of the EC effect based on Landau-Ginsburg-Devonshire theory was employed to study FE-based thin-films with the motive of understanding various materials behavior under different mechanical boundary conditions & compositions [17, 42, 43, 77]. The aim of the study is also to identify materials with large electrocaloric effects near room temperature and to study their intrinsic effects. The phenomenological theory was successfully used to compute macroscopic EC properties of ferroelectric materials. For the ferroelectric to paraelectric phase transition, free energy change can be written as;

$$G = G_0 + \alpha_1 P^2 + \alpha_{11} P^4 + \alpha_{111} P^6 + \dots - E P \quad \text{Equation (3.1)}$$

Where α_1 , α_{11} and α_{111} are Landau coefficients and G_0 is the energy of paraelectric phase. The quadratic coefficient is given by the Curie-Weiss law, $\alpha_1(T) = (T - T_C) / (2C\epsilon_0)$, where T_C is the Curie temperature, C the Curie constant, and ϵ_0 the dielectric permittivity of vacuum.

Dependence of polarization on temperature and applied electric field are calculated from the equilibrium conditions, i.e. at $\partial G / \partial P = 0$. As an example, the temperature dependence of polarization $P(T)$, computed at different electric fields in $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin-films is shown

in Figure 3.1. The substitution of $P(T)$ values in Equation 3.1 transform the equilibrium energy in terms of $G(T)$ and this can be used to solve the temperature dependent parameters.

Figure 3.1: Polarization (P) plotted against sample temperature (T) for different electric field values.

The excess entropy (S_E) and specific heat of the phase transition (ΔC_E) can be derived with the following relations,

$$S_E = -T \left(\frac{\partial G}{\partial T} \right)_E \quad \text{Equation (3.2)}$$

$$\Delta C_E = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_E \quad \text{Equation (3.3)}$$

When the electric field is varied from E_1 to E_2 , the polarization of materials changes and it also induces changes in adiabatic entropy. The P changes are always maximum at the ferroelectric to paraelectric transition, which is called Curie temperature, T_c . The final adiabatic temperatures changes (as a result of electric field, dE), polarization/entropy changes are computed by using Maxwell equations. The relationship between pyroelectric and

electrocaloric coefficients is defined as $(\partial S/\partial E)_T = (\partial P/\partial T)_E$. The magnitude of the adiabatic temperature change is given by:

$$\Delta T(T) = -\frac{T}{C_E(T)} \left(\frac{\partial P}{\partial T} \right)_E dE \quad \text{-- Equation (3.4)}$$

The EC properties of Barium Titanate (BaTiO_3), Barium Strontium Titanate ($\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ and $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$) and Lead Zirconate Titanate ($\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$) materials were predicted by using phenomenological equations. The Landau coefficients used for the calculations were obtained from literature and are shown in Table 3.1. BaTiO_3 (BTO) is well known ferroelectric material with Curie temperature $T_c \sim 393$ K. Single crystals of SrTiO_3 (STO) show a structural phase transition from ferroelectric to paraelectric at $T_c \sim 105$ K. The doping of Strontium (Sr) on A sites of BTO decreases the T_c due to its paraelectric stabilizing nature.

It can be inferred from the above results that with the help of chemical substations, T_c of electrocaloric materials can be tuned to the desired temperature ranges. The basis for obtaining high ΔT values near room temperature electrocaloric materials can be framed as identification of paraelectric to ferroelectric transition within the working temperatures. From literature, it is also identified that Pb-based materials show high adiabatic temperature changes. For the same reason, we also computed the ΔT values in PZT thin-films with intentions to investigate the dependency behavior of EC effects on chemical compositions.

Table 3.1: Thermodynamic potentials of elastic and electromechanical coefficients of BTO [78, 79], BST [31, 80, 81] and PZT [82-84] materials listed.

	BaTiO₃	Ba_{0.6}Sr_{0.4}TiO₃	Ba_{0.7}Sr_{0.3}TiO₃	PbZr_{0.5}Ti_{0.5}O₃
T_c (°C)	133	-29.2	8.1	392.6
C (10⁵ °C)	2.74	1.34	1.43	4.247
α_1 (10⁷ m/F)	4.124	7.90	8.58	-4.887
α_{11} (10⁷ m⁵/C²F)	2.56	2.16	2.52	4.764
α_{12} (10⁸ m⁵/C²F)	5.97	4.13	3.987	1.735
α_{111} (10⁸ m⁹/C⁴F)	1.294	3.69	4.62	1.336
Q₁₁ (10⁻² m⁴/C²)	-1.950	0.0843	0.0907	9.660
Q₁₂ (10⁻² m⁴/C²)	5.970	-0.0324	-0.0356	-4.600

The electrocaloric properties of BTO, BST (70/30) and BST (60/40) films are presented in Figure 3.2. The ΔT values shown are computed at similar electric field values, $dE = 10, 50$ and 100 kV/cm in all three compositions. It is more evident from the results that the peak adiabatic temperatures always appear near Curie temperatures, T_c . As one move away from T_c , the drop in ΔT values is more significant in all materials. The magnitude of applied field change (dE) has less effect on ΔT values below and above FE-PE transition temperatures but shows very strong influence near T_c . So, it is always advantageous to design material with compositions which can sustain high electric fields, and thereby generate high adiabatic temperature changes. From this perspective, thin-films have their own merits compared to bulk materials, which are able to produce large electric fields without generating any sparks.

As the Sr content doped more onto A sites of BTO lattice in Figure 3.2 [b] to (c), T_c gradually shifts towards lower temperatures. It is also found that a gradual reduction of overall ΔT values at higher doping levels and sharp drop of $\Delta T_{\max}$ values under similar fields.

This is due to Sr acting as paraelectric phase stabilizer at high temperatures to keep the overall free energy to minimum.

Figure 3.2: Adiabatic change of temperatures as a function of working temperatures shown for [a] BTO [b] BST (70/30) and [c] BST (60/40) thin-films. Effect of chemical doping on T_c and ΔT are compared at $dE = 50$ kV/cm in [d].

Figure 3.2 [d] depicts a close comparison of EC effects between BTO, BST (70/30) and BST (60/40) films at $dE = 50$ kV/cm. The BTO films show nearly six fold higher cooling values compared to BST thin-films. Though the T_c of BTO has been brought close to room temperature by chemical doping, the results were accomplished at the cost of ΔT values. On

the other hand, the BST films show nearly flat cooling curves compared to BTO, which are highly desirable in solid-state cooling devices.

The PZT thin-films are one of the widely studied materials in microelectronics as sensors, actuators and MEMs. The material synthesis procedures are well practiced and it is easy to obtain good quality thin-films by sol-gel and physical vapor deposition techniques. The PZT thin-films show giant adiabatic temperature changes of as high as $\Delta T \sim 16$ K at 675 K in the fields of $dE = 100$ kV/cm in Figure 3.3 [b]. As shown in Figure 3.3 [a], the slopes of $P(T)$ data derived from $P(E)$ curves obtained at various temperatures were used to estimate $\Delta T(T)$ values at different electric fields.

Figure 3.3: [a] $P(T)$ data computed for $PbZr_{0.5}Ti_{0.5}O_3$ thin-films and [b] the adiabatic temperatures plotted as a function of T . Very high values of $\Delta T \sim 16$ K near T_c observed at $dE = 100$ kV/cm.

By considering the giant adiabatic cooling values in $PbZr_{0.5}Ti_{0.5}O_3$ materials, the PZT thin-films close to morphotropic phase boundary (MPB) are proposed as promising candidate materials for our further experimental investigations. From the above results, it can also be seen that at MPB, the temperature changes are relatively high even in small applied electric fields due to phase instability induced entropy changes.

Figure 3.4: [a] The EC properties of BTO bulk and thin-film structures are compared, also [b] the electric field dependent behavior of $\Delta T(T)$ shown for BTO thin-films.

The adiabatic temperature changes of BTO bulk and thin-films were computed in similar procedures as above and the results were compared in Figure 3.4 [a]. Under the same fields, BTO thin-films show less ΔT values compared to bulk systems due to mechanical clamping effects aroused from the substrates. So, it is very important to choose a substrate material with close lattice mismatch to thin-film material in order to minimize the clamping effects from misfit strains.

The results of Figure 3.4 [b] show that as the electric field increases, the transition temperatures shift from first order to second order type. This is a significant phenomenon to be noticed in order to achieve broad ΔT values in the working regions but the $\Delta T_{\max}$ values are compromised. Effective cooling over wide temperatures is a coveted property of any coolant material for efficient cooling process. For practical cooling devices, the EC materials must possess large ΔS values along with large ΔT values to achieve high uniform cooling throughout the working temperatures. It is well realized that the materials with discontinuous phase transition exhibit higher ΔT values than those with continuous phase transitions. First order phase transition is always preferred for obtaining maximum temperature changes but

second transition is attractive when we consider broad uniform cooling temperatures. This suggests that one needs to look for optimum values between sharp and broad phase transitions in order to achieve high temperature changes along with high device efficiencies.

Summary

Chemical doping of transition elements on both A and B sites in perovskite structures significantly influences the EC properties. For instance, by doping Sr into BTO structure, the T_c of electrocaloric materials can be designed near to room temperature to suit any specific application. Also flat cooling curves of BST thin-films are highly appealing as high refrigeration capacity working elements in cooling devices. The maximum cooling temperatures are always seen near FE-PE phase transition temperatures and the transition temperatures can also be shifted to lower working temperatures also by inducing lattice strains.

The PZT films near MPB composition showed giant adiabatic cooling figures at very low voltages used. By today's state of art methods for PZT materials processing, the thin-film cooling elements can be integrated easily with current Si based technologies for various solid-state applications. With every two folds increase in ΔT values of EC materials, the operating costs of the refrigeration devices will be cut close to half.

Inferences

It is well conceived from the phenomenological results that near T_c , materials exhibit possible maximum ΔS values. For practical cooling devices, the EC materials must possess large ΔS values along with large ΔT values to achieve high uniform cooling throughout the working temperatures. In search of new EC materials with high ΔS and ΔT values, one must

identify continuous $(\partial P/\partial T)_E$ over wide working temperatures. Recent investigations of V. Shvartsman et. al. and H. Kabelka et.al. [4–6] reported very large dielectric and piezoelectric properties at MPB composition due to the triple point phase transition contributions at 450 K [85]. We inferred from the above conclusions that triple points and ferroelectric to ferroelectric (FE-FE) phase transitions at MPBs can contribute to excess ΔS values by considering the variations in $P(T)$ over other compositions. It is well realized that the materials with discontinuous phase transition exhibit higher ΔT values than those with continuous phase transitions, which is due to the abrupt changes in total polarization/entropy values at T_c . Besides, some earlier works suggest that the change of order phase transition from first order to second order greatly reduces the temperature dependence of ΔT at a cost of its peak cooling values (ΔT_{max}). Even though the first-order phase transition is preferred (while considering ΔT_{max}) to the second-order transition, the latter offers consistent cooling over wide working temperatures due to its minimal temperature dependence. This led us to frame an important hypothesis over materials selection for further studies.

Materials Selection Criteria Used in Further Studies

The $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ materials are proposed for investigation as candidate materials for near room temperature EC cooling applications due to their flat ΔT values around 298 K. Also the deposition of BST thin-films by pulsed laser method is a well-established technique for obtaining high quality epitaxial structures to study intrinsic properties.

Among the other ferroelectric materials, PZT thin-films are widely investigated in microelectronics because of their high chemical stability and remarkable ferroelectric properties. Theoretical investigations revealed that it is possible to observe giant EC coefficients near T_c in Pb rich compositions. The existence of triple point phase transition

along with MPB at $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ composition is highly appealing to consider the material as the second candidate for experimental investigations.

Figure 3.5: Equilibrium phase diagrams of [a] PZT, [b] PZN-PT and [c] PMN-PT shown. Figure is adapted from B. Noheda *et al* [86].

We aimed to study the EC properties of two other Pb based systems with MPB compositions to verify that the proposed hypothesis is valid universally. The presence of MPBs over wide compositional ranges in $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ -6% PbTiO_3 (PZN-PT), $\text{PbMg}_{2/3}\text{Nb}_{1/3}\text{O}_3$ -PbTiO₃ (PMN-PT) materials suggest that there a huge scope for the existence of broad EC temperatures between the critical transition points. It is also proposed to investigate 0.7PMN-0.3PT and PZN-0.06PT single crystals for accessing materials with heat fluxes much higher compared to thin-film structures.

Chapter 4:

EXPERIMENTAL

4. Experimental Methods

Based on phenomenological study results, $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) and $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ (BST) materials were undertaken for the EC experimental investigations of thin-film structures. Thin-films of BST & PZT were deposited by pulsed laser deposition (PLD) technique to obtain epitaxial quality. For the deposition of PZT materials, sol-gel technique is the most widely used because of its low cost and ease of fabrication. However, PLD was able to produce close stoichiometric PZT compositions in thin-films.

The PZT thin-films deposited by sol-gel method and PLD were investigated using piezoresponse force microscopy (PFM) for microscopic EC characteristics of materials. Electrical properties including dielectric, ferroelectric and piezoelectric were characterized to determine the ferroelectric functionalities of PZT and BST systems. The PFM scanned images represented topography, amplitude and phase information along in-plane and out-of-plane directions, and also included details of domain orientations.

4.1. *Sol-Gel Method*

Sol-gel method is a simple and well-studied technique for the deposition of PZT polycrystalline thin-films [13]. The method has several advantages over vacuum based thin-film deposition methods such as flash, electron beam evaporation, rf sputtering and ion beam deposition techniques [14-17]. Its advantages include minimal processing temperature, low cost, short fabrication cycle, and good control over thickness & materials compositions.

Precursors from Sigma-Aldrich were used to prepare the PZT sols. $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ sol was dissolved in methanol and refluxed for 2 hours at 120°C . The Pb and Zr/Ti based

solutions were mixed with 20% excess Pb to compensate for its losses during sintering. The thin-films of PZT were prepared by spin-coating of sol at 1500 rpm for 30s on Pt(111)/SiO₂/Si(100) substrates, which were cleaned thoroughly with acetone and ethanol after each layer of deposition during the process. Layers of ~35 nm were obtained by pre-firing in air on a hotplate at 350°C for 60 s, at 500°C for another 60 s, and then further annealed at 700°C for 10 minutes. The procedure was repeated twelve times to obtain ~400 nm thick films. Step by step details of deposition process are summarized in the flowchart below.

Figure 4.1: Flow chart of Sol-Gel deposition of PbZr_{0.52}Ti_{0.48}O₃ thin-films

4.2. Pulsed Laser Deposition (PLD)

In a PLD thin-film growth process, the target material is evaporated by targeting a high energy laser beam in a vacuum chamber. Substrate materials used for the process are usually single crystals placed parallel to target at a fixed distance. Thin-film deposition takes place through a gas phase and the working of principle of PLD is shown in Figure 4.2. A high frequency intense laser beam was used to ablate the solid target material into vapor phase. The evaporation process was carried out in a vacuum chamber under high vacuum condition or in a controlled environment. When the laser beam of high power density was focused onto

the target, it was partially absorbed by the solid material and the remaining material was removed in the form of an ejected luminous plume. Then the plume was allowed to settle on a substrate, where film growth takes place slowly. High quality epitaxial films require laborious optimization of deposition parameters including temperature, oxygen pressure, laser energy density, laser frequency, and target-to-substrate distance.

Figure 4.2: Schematic diagram of a pulsed-laser deposition system.

A KrF excimer laser of wavelength 248nm was used in our experiments for ablation. Before begin the deposition process, the substrates were cleaned ultrasonically in acetone and ethanol each time and then transferred into the deposition chamber. A good thermal contact between the substrate and sample holder is very important to maintain stable temperatures and silver paste is used for the job. The deposition chamber is usually pumped down to a base pressure of 10^{-7} ~ 10^{-6} Torr to avoid contamination. During the film deposition, the substrate was heated and maintained at high temperature and low oxygen pressure condition. The ablated ferroelectric material then set to deposit on the heated substrate, which was placed opposite the target. The main advantage of the PLD process is the direct composition transfer of target to the film in the stoichiometry.

Post processing of the thin-films was followed by preparation of electrodes using photolithography. The Pt bottom electrode was exposed by performing chemical etching on part of the sol-gel PZT thin film using dilute HF solution. For the BST and PZT thin-films deposited by PLD, SrRuO₃ (SRO) buffer layer of thickness 30-50 nm was deposited with PLD at 700°C and 100 mTorr oxygen pressure acted as the bottom electrode. Platinum was sputtered on top of the films through a photo-lithography mask to design top electrodes.

4.3. Characterization Methods

4.3.1 Structure Analysis: XRD

In 1912, Bragg recognized that x-ray diffraction in crystals obeys particular geometric restrictions related to inter-planar crystal spacing. Later, this relationship was designated as Bragg's Law that states $n\lambda = 2d \sin\theta$; where λ is the x-ray wavelength, d is the crystal plane spacing, and θ is the x-ray incident angle. This forms the basis for the interpretation of XRD results. The XRD system used in this thesis was Rigaku thin-film diffractometer, which is the basic platform for a wide variety of applications in analytical x-ray diffraction. This system was used in my thesis to perform (i) high-resolution lattice parameter measurements, both at room temperature and as a function of temperature up to 600°C, and (ii) ω -2 θ scans to characterize the structures of the films.

4.3.2 Electric Measurements: RT6000, PFM

The ferroelectric properties (including hysteresis loop, pulsed polarization, polarization retention and fatigue, and resistivity) were measured using a commercially available Radiant Technology Precision 6000 system. The dielectric constant was measured using a HP impedance analyzer.

A standard photolithography technique was used to define the pattern upon which small capacitors are made. First, photoresist was spin coated onto the surface of the sample, which was then baked at 110°C for 10 minutes. The next step was to align the selected mask pattern with the sample and expose it to UV radiation for crosslinking. After developing, the right pattern for the top Pt-electrode was achieved. Since the big capacitor has a much larger capacitance, the voltage can be treated as though it has been applied solely to the small capacitor. The polarization was then determined by integrating the current flow,

$$P = \frac{Q}{A} = \frac{1}{A} \int I dt$$

where A is the small capacitor area. The same setup was used for other electrical characterizations such as leakage, pulsed polarization and dielectric constant measurements.

Piezoelectric analysis, domain imaging were performed using a scanning force microscope (SFM). This technique has been used to characterize PZT thin-films. It is based on detection of the vibration of a ferroelectric sample, which is induced by an external ac voltage. The voltage with a frequency ω was applied through the tip, which causes the sample area under the electric field to vibrate at the same frequency due to the converse piezoelectric effect. This vibration then forced the SFM tip to oscillate, and the modulated deflection signal was detected using the lock-in amplifier.

In the imaging mode, the conducting tip is in direct contact with the sample surface. The electric field underneath the tip measures local domain orientation information. By scanning along the sample surface, the domain configuration of the sample can be mapped out. The resolution of the domain features depends on the sharpness of the tip.

4.3.3 Characterization of Thin-films

The films deposited by the PLD and Sol-gel methods, analyzed for crystal structure and crystalline quality using high resolution X-ray diffractometer (Rigaku Thin-film XRD). The surface roughness of the films scanned with atomic force microscope (AFM), was used to provide feedback for growing high quality films by the PLD method. Chemical compositions of both the thin-films and target materials were verified by scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) [JSM-6360], while thicknesses of the films were determined by stylus profilometry techniques. Top electrodes of 40 μ m square Pt were patterned via a standard photolithography process. Electrical measurements were carried out on thin-film capacitors using Presicion LC test system (Radiant Technologies). Piezoresponse of the films was measured with the help of Research MFP-3D system using Pt/Ir coated tips.

Ferroelectric hysteresis loops over heating and cooling cycles were measured at 1 kHz frequency using a Radiant Technologies Precision Premier workstation and a high temperature probe station. The temperature of the samples was controlled via feedback from a thermocouple in contact with the samples to an accuracy of $\pm 0.3^\circ\text{C}$.

Capacitance and dielectric loss were measured using a Hewlett Packard 4192A Impedance Analyzer with an a.c. signal of 100 mV amplitude and 100 kHz frequency across the sample. Dielectric constant (ϵ_r) values were then calculated using the equation 4.1 below.

$$C_E = \frac{\epsilon_r \epsilon_0 A}{d} \quad \text{Equation (4.1)}$$

Where C_E is the capacitance of the film in Farads

ϵ_r is the dielectric constant

ϵ_0 is the permittivity of space

A is the cross-sectional area of top electrode

d is the thickness of film

Leakage current in ferroelectric materials is defined as the inherent flow of current between the ferroelectric and metal electrode that flows when the ideal current is zero.

4.4. Results & Discussions

The thin-films deposited by pulsed laser deposition as well as sol-gel methods were analyzed to understand the structure-property relationships of EC materials. Our preliminary experimental results in this section are discussed to resolve the major challenges encountered while carrying out the experimental works and they also pave the path for exploring the actual goals of the project in later chapters. The ferroelectric thin-films of BST and PZT materials with large electrocaloric effects have been identified and the detailed discussions are classified in the subsections that follow.

4.4.1. Electrocaloric Effects of BST thin-films

The BST thin-films were grown on STO (001) substrates by PLD (Lambda Physik) using a 248 nm KrF excimer laser with a repetition rate of 5Hz. The laser beam with a fluence rate of 1.1 J/cm^2 was used for the film depositions. The substrate to target distance was fixed at 6 cm during the deposition. A buffer layer of SRO (~40 nm) deposited initially on a clean substrate and was used as the bottom electrode for electrical measurements. ~290 nm, $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin-films were prepared at 750°C substrate temperature and 1 Pa oxygen pressure. Post annealing was carried out at 4×10^5 Pa, oxygen pressure in the same chamber after deposition.

Figure 4.3: Thin-films of BST prepared by PLD method show [a] no impurities and near epitaxial quality. [b] Representative ferroelectric hysteresis loops plotted at different temperatures. The P vs E data can be drawn as a function of temperature is used to obtain $(\partial P/\partial T)_E$ with 5th order polynomial fits as shown in [c]. [d] Adiabatic temperatures derived by indirect measurements plotted against sample temperature.

The θ - 2θ scans in Figure 4.3 [a] show (00l) reflections aroused from the STO substrate and STO film, without any detectable secondary phases. The $P(T)$ data was obtained from hysteresis loops at different electric field conditions, while the films were cooled very slowly (0.1°C/min) from 390 K to 300 K. The slope of the curves $P(T)$ in Figure 4.3 [c] at different field conditions was used to estimate the ΔT values using Equation 3.2. The experimental data was compared with phenomenological results obtained from the earlier section.

Figure 4.4: Comparison of ΔT vs T data obtained from experiments and phenomenological calculations shown in BST (70/30) thin-films.

The experimental data of ECE in BST thin-films in Figure 4.4 show a close match to the theoretical values. A maximum temperature change of $\Delta T_{\max} = 0.48$ K was observed at $\Delta E = 100$ kV/cm.

PZT Phase Diagram (B. Noheda *et al* [86])

Figure 3.5 [a] is presented again as references to the next section of discussions.

4.4.2. Sol-Gel Deposited PZT films

Piezoresponse force microscopy (PFM) was used to investigate ferroelectric domain switching and mapping on the nanoscale to produce topography, piezoresponse amplitude and phase images of the domains within the thin-film samples. A 10 kHz ac voltage with amplitude of 5 V was applied to the tip to obtain PFM phase images and shown in Figure 4.5.

Figure 4.5: [a] Topography, [b] amplitude, [c] phase contrast of out-of-plane and in-plane PFM images of sol-gel deposited PZT thin-films are shown.

The phase reference angle for the lock-in amplifier was set at 0° which means that in the acquired PFM images, c- ferroelectric domains appeared as bright spots (a 180° difference from the reference) and c+ domains appeared as dark region (in phase with the reference).

The thin-films deposited by sol-gel method shown on the left side of Figure 4.5 displayed an island-like texture. This could be explained by the pyrochlore to perovskite phase transformation during the annealing process. As the sol layer was first pyrolyzed at low temperature, a non-piezoelectric pyrochlore phase was formed. As the films were then annealed at higher temperature, the pyrochlore phase then transformed into the piezoelectric perovskite phase [20]. The resulting perovskite phase growth stems from nucleation sites and spread throughout the pyrochlore phase. Grain boundaries were then formed between the interfaces of these two growth regions. The results provide a better understanding of the localized surface morphology, ferroelectric and piezoelectric properties of the PZT thin-films in the nanoscale range.

Next, electrical hysteresis measurements were conducted to estimate $P(E)$ data at regular intervals of cooling temperature stages. The cooling cycle was chosen to minimize fatigue reductions of P values. The $P(T)$ data were obtained from $P(E)$ measurements and $(\partial P/\partial T)$ data calculated by polynomial fits of $P(T)$. Other parameters such as ρ and C were taken from literature for the given PZT composition. Finally, the EC temperature changes were calculated by using Equation 3.4 and the results are shown in the following page.

Figure 4.6: [a] Representative P-V loops shown at different temperatures and [b] I-V data obtained in similar conditions. [c] Dielectric constant (ϵ) and Loss tangent ($\tan \delta$), measured at 100 kHz. [d] $P(T)$ data extracted from $P(E)$ values and [e] Electrocaloric temperature change, ΔT due to applied electric field, ΔE plotted.

Figure 4.6 [a] represents P-E loops measured in a temperatures range from 30 - 400°C in PZT sol-gel films. The I-V and C-V measurements were carried out simultaneously on the same capacitors. It can be seen that as the temperature increased, the total polarization was reduced. At high temperatures leakage-currents (up to 10^{-2} amps at 400°C) dominated the total polarization and the values become erroneous. Below 240°C, the leakage currents were under allowable limits ($<10^{-7}$ amps). For the reason, the P(T) measurements were shown from room temperature to 240°C.

The real parts of the dielectric constant (ϵ) and loss tangent ($\tan \delta$) were measured at 100 kHz shown in Figure 4.6 [c]. A sharp peak of ϵ curves at $T = 387^\circ\text{C}$ indicate phase-transition between FE-PE phases called Curie temperature, T_c of PZT films. Extrapolation of the low-temperature $1/\epsilon$ data gives exact value of $T_c = 382^\circ\text{C}$. A gradual change in the slope of loss tangent was resolved at 175°C . This suggests that at lower temperature a secondary phase transformation occurred between FE-FE phases for the chosen composition of PZT material. It also appears to confirm that the sol-gel deposited films cross MPB composition lines.

A hump in adiabatic temperature curves in Figure 4.6 [e] was seen at 172°C , which was close to the tricritical phase transition of PZT films. The critical point between triclinic, rhombohedral and tetragonal phases produced an EC temperature change of 4.2°C as result of the FE-FE phase transition [87]. These results strengthen the argument that EC effect is high near phase transitions and critical points in multiphase systems. The results are highly appealing and show possibilities of achieving high ΔT values over wide working temperatures at MPB composition in PZT system. Later experiments were carried out to minimize the leakage currents of PZT material at high temperatures (up to 400°C) by

depositing epitaxial thin-films. The temperature swings were measured up to the breakdown fields of the capacitors.

4.4.3. Characterization of PLD deposited PZT thin-films

Epitaxial films of ~450 nm thick PZT samples are prepared on single crystal SrTiO₃ [001] substrates by pulsed laser deposition (Lambda Physik) while SrRuO₃ (SRO) was used as a buffer layer. A 248 nm KrF excimer laser with energy density of 1.1 J cm⁻² and repetition rate of 5 Hz were used as optimized parameters. Later the samples annealed in oxygen rich (5x10⁴ Pa) environment.

Table 4.1

	Temp, °C	O ₂ Partial Pressure, Pa	Laser Frequency, Hz	Target- Sample Distance, cm	Laser Energy, mJ	Film Thickness, nm
S1	700	13	5	6	55	~360
S 2	600	13	10	7	50	~450

Crystal structure and film crystallinity were determined by Shimadzu X-ray diffractometer using Cu K α radiation. The θ -2 θ scans corresponded to a polycrystalline perovskite phase with no preferred orientations, and no traces of impurities. Pt top electrodes of diameter 50 μ m were sputtered through a photo-litho mask, and the bottom electrode of thickness 30-50 nm was SrRuO₃ deposited with PLD at 700°C and 100mTorr oxygen pressure.

Figure 4.7: XRD patterns of PZT films deposited on STO substrate shown for different thicknesses.

Composition Analysis

Compositions of thin-films were analyzed by the electron probe microanalyses (EPMA) method. It is important to make sure that the grown films are free from impurities and stand on the aimed compositions to obtain morphotropic phases.

Wt. %	Avg	Std Dev	% Std Dev
Pb	64.33	0.28374725	0.44108075
Zr	14.40118	0.20005881	1.38918383
Ti	6.886471	0.07516159	1.09143849
O	14.61824	0.07152231	0.48926776
At. %			
Pb	20.34941	0.14350395	0.70519948
Zr	10.34529	0.11034705	1.06664001
Ti	9.421765	0.09664596	1.02577342
O	59.88412	0.0480961	0.08031529

The results show atomic ratios of PZO: PTO is 52:48, which confirms MPB compositions in PZT thin-films.

The dielectric constant and loss tangent were measured at 100 kHz and 100 mV ac amplitude. Hysteresis measurements during heating were taken at 1 kHz and representative loops shown in Figure 4.8 [a]. Leakage currents were measured on the same workstation under a maximum applied voltage of 50 V ($E = 1250$ kV/cm).

Figure 4.8: The real part of the effective dielectric constant measured at 100 kHz shows a single peak at the bulk transition temperature $T_c = 387^\circ\text{C}$. Inset: Representative hysteresis loops measured at 10 kHz in PZT thin-films at 80°C .

Figure 4.9: C-V characteristics of PLD thin film with respect to increasing temperature along the dielectric lines shown.

Capacitance-voltage (C-V) characteristics of PLD thin-films were studied using a.c. fields of 100 mV amplitude and 100 kHz frequency across the sample while the d.c. field was swept from positive bias to negative bias. The C-V measurements were taken during increasing temperature from 20°C to 400°C. The results in Figure 4.9 at temperatures 40°C and 240°C display the typical “butterfly” shapes, which are linked to the DC dependence of the polarization of ferroelectric thin-films. It was also observed that permittivity and capacitance show an increasing trend with increasing temperatures in PLD films. The C-V characteristics measured below Curie temperature were also noted to be asymmetrical in shape. This difference in peak capacitance values may be attributed to space charge regions developed from dc biasing during the measurements [19]. As temperature rises to the Curie temperature of PZT at 380°C, the peak-to-peak capacitance values were also observed to be

decreasing. This could be due to the phase transition from ferroelectric T phase to paraelectric C phase within in PZT thin-films.

Summary:

High quality single phase thin-films of BST and PZT were successfully deposited on STO substrates by PLD method and characterized for ECE analysis. Structural properties of the films revealed that there were no impurities present and also the leakage currents were under allowable limits ($< 10^{-7}$ Amps). Compositions of PZT films from EPMA studies revealed that the materials were processed close to MPB composition on the phase diagram. In addition to epitaxial films from PLD, PZT films were also synthesized from sol-gel methods and characterized for relative properties of ECE. Though, the leakage currents of thin-films showed very low in sol-gel films at lower temperatures, it progressively became difficult to measure the intrinsic polarization values at high temperatures, close to T_c .

The ECE measured in PZT thin-films at MPB composition revealed a secondary ΔT peak near lower critical phase transition points, i.e. from FE-FE. The results supported our basic hypothesis derived from phenomenological results and prompted us to verify its universality at other MPB compositions. In this direction, we selected more compounds for investigating ECE properties at MPB compositions such as $0.7\text{Pb}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$ - 0.3PbTiO_3 and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.06PbTiO_3 . In later Chapters, we discussed detailed experimental studies of EC properties in epitaxial thin-films at high temperatures and in single crystal wafers. We had chosen to study single crystals in place of thin-films, to solve some practical issues involved such as to eliminate substrate effects in direct ΔT measurements and also to obtain high RCs by considering more mass of crystals compared to thin-film structures.

Chapter 5:

ELECTROCALORIC STUDIES

5. Electrocaloric Measurements at MPBs

Electrocaloric (EC) refrigeration of ferroelectric materials is of high interest for solid-state cooling applications. The cooling method is often described as a clean, robust and efficient process due to its intriguingly simple design and operation. Despite its technical advantages, the developments were relatively slow compared to other solid-state techniques such as magnetocaloric refrigeration[88] or thermoelectric cooling[89]. The resurgence of EC cooling is spotlighted only after the notable findings of adiabatic temperature changes (ΔT) in $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ and poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] ferroelectric thin-films[16, 38]. The discoveries revealed that the giant ΔT values in thin-films are due to the large isothermal entropy changes (ΔS) near ferroelectric-paraelectric (FE-PE) phase transitions. The sharp rise in EC effects are attributed to the improved breakdown strengths of the materials in thin-films form compared to their bulk counter parts. Later, the field of research is quickly animated by several groups with the addition of various thin film systems with huge cooling capabilities to the materials treasure [56, 90-94]. This has revived the possibilities of materials selection over a range of working temperatures for solid-state cooling applications. However, despite the progressive developments in materials; very few studies were devoted to the implementation of the EC materials into practical cooling devices [55, 57, 95]. The hitches in device designs are; being thin-film structures, the materials are capable of imbibing only small portions of huge heat fluxes from the loads and secondly, the maximum ΔT values are mostly confined to Curie temperatures (T_c) alone. These are some serious limitations to achieve high refrigeration capacities (RCs) in materials with sharp and narrow cooling peaks [96].

Effective cooling over wide temperatures is a coveted property of any coolant material for efficient cooling process. For practical cooling devices, the EC materials must

possess large ΔS values along with large ΔT values to achieve high uniform cooling throughout the working temperatures. It is well realized that the materials with discontinuous phase transition exhibit higher ΔT values than those with continuous phase transitions,^{3,8} which is due to the abrupt changes in total polarization/entropy values at T_c . Besides, some earlier works suggest that the change of order phase transition from first order to second order greatly reduces the temperature dependence of ΔT at a cost of its peak cooling values (ΔT_{max})[17]. For instance, in recent works of Li *et al* described that by changing the nature of the phase transition from first-order to second-order in P(VDF-TrFE) polymers, ΔS is reduced nearly to half of its original value[30]. Even though the first-order phase transition is preferred (while considering ΔT_{max}) to the second-order transition, the latter offers consistent cooling over wide working temperatures due to its minimal temperature dependence. This poses some orthogonal difficulties to attain high ΔS and ΔT values at the same time.

Here, we established a hypothesis to improve the cooling capacities of ferroelectric capacitors by improving the ΔS values at lower temperatures without sacrificing ΔT_{max} at FE-PE phase transition. It is believed that the phase boundaries act as potential sources of high ΔS values due to lattice entropy changes induced by phase transitions in stimulated electric fields (ΔE). The existence of continuous phase boundaries along the entire cooling line below T_c (e.g. morphotropic phase boundary (MPB), where two or more phases co-existence with each other) originate high entropy changes more than any single phase does under the same ΔE . This may yield high ΔS values in ferroelectrics below T_c at MPB and contribute to uniform cooling even at lower temperatures without losing ΔT_{max} (because the same order-disorder transition exists at Curie point). To validate the postulations, we studied PZT [001] oriented epitaxial films and 0.7PMN-0.3PT single crystals with [111] orientations at MPBs and demonstrated the enhanced intrinsic ECE both in thin-films and bulk materials. The results showed large $\Delta T = 2.7$ K in 200 μm single crystal 0.7PMN-0.3PT samples under an

applied field 12 kV cm^{-1} at its Curie temperature ($T_c = 127^\circ\text{C}$) and a minor hump of $\Delta T = 2.2 \text{ K}$ at ($T = 90^\circ\text{C}$) its critical point temperature. It explains that the ΔT values induced by critical points and FE-FE phase boundaries were equally effective as FE-PE transition and stretch the cooling range to near uniform values by extending the high ΔS values further down to low temperatures ($T_{crit} \leftarrow T_c$). A similar ECE trend was also seen in 260 nm epitaxial PZT thin-films ($\Delta T = 11.1 \text{ K}$ at $T_c = 387^\circ\text{C}$ and a secondary peak, $\Delta T = 1.4 \text{ K}$ at 195°C). This further reinforces the hypothesis and complies with the universal behavior of ferroelectric materials at MPBs.

5.1. Electrocaloric Properties of PMN-PT Single Crystals

Single crystals of 0.7PMN-0.3PT used in this study are finely polished [111] oriented wafers, coated with Pt electrodes on both sides. The dielectric measurements were performed using a HP 4192A Impedance Analyzer in both zero field heating (ZFH) and zero field cooling (ZFC) approaches. Hysteresis measurements were carried out at 1 kHz frequency using Radiant Technologies Precision workstation at every 5°C interval of cooling from 160°C to room temperature. Temperatures of the samples were precisely controlled to near equilibrium states via feedback from Pt100 RTD sensors, accurate to $\sim 0.2^\circ\text{C}$, in contact with the sample.

Figure 5.1: [a] Representative hysteresis loops of 0.7PMN-0.3PT single crystals measured at 1 kHz in cooling temperatures. [b] Temperature dependence of dielectric constant during ZFH and ZFC and frequency dependent relaxor behavior (in inset) are shown. [c] Polarization variation induced by temperature changes $P(T)$ data are extracted from the series of P - E hysteresis loops and fit to 7th order polynomials. [d] The EC temperature changes as a function of sample temperature from 40 to 160 °C at an applied field 12 kV cm⁻¹. The $\Delta T_{max} = 2.7$ K occur at $T_c = 127^{\circ}\text{C}$ and the secondary peak $\Delta T_{critl} = 2.2$ K appear at $T_{critl} = 93^{\circ}\text{C}$ due to critical phase transitions. Figure adapted from ref. [48].

Figure 5.1 [a] depicts representative plots of 0.7PMN-0.3PT single crystal hysteresis loops measured at different temperatures during the cooling process to minimize reductions in total polarization (P) values due to fatigue. Typical hysteresis characteristics of single crystals were seen as the temperature descended. The temperature dependence of polarization, $P(T)$ at different electric fields is presented in Figure 5.1 [c]. We observed an anomalous behavior of $P(T)$ in 0.7PMN-0.3PT single crystals poled along [111] direction. The deviations in $P(T)$ data near critical point temperature ($T_{crit} \sim 93^\circ\text{C}$) were identified in a similar way to Kutnjak *et al.* reports[97-99] and the irregularities are attributed to the result of multiphase transitions between tetragonal (**T**) and rhombohedral (**R**) ferroelectric states in applied bias. The dielectric measurements shown in Figure 5.1 [b] also display similar anomaly at T_{crit} and the results cross-confirm the crossover of multiphase transitions during heating and cooling cycles. The real part of the dielectric constant ε measured during ZFH and ZFC shows maximum at 127°C , which is claimed as Curie temperature, T_c in our studies. The strong frequency dependence of T_c (inset) indicates the relaxor-ferroelectric behavior of 0.7PMN-0.3PT single crystals. Also the T_c displays phase transition degradation during ZFC, which in turn is due to the reorientation of nanopolar-domains during structural transitions at MPB [38, 100]. The existence of broad phase transition at lower temperatures and the T dependence of ε are the push to achieve large ΔS and ΔT values in relaxor-ferroelectrics at MPBs.

The $(\partial P/\partial T)_E$ data was derived from 7th order polynomial fits to $P(T)$ to closely account for the P variations near T_{crit} at different fields. The adiabatic temperature change, isothermal entropy change and refrigeration capacity of the materials were determined using Maxwell's relations:

$$\Delta T = -\frac{1}{\rho} \int_{E1}^{E2} \frac{T}{C} \left(\frac{\partial P}{\partial T} \right)_E dE$$

$$\Delta S = -\frac{1}{\rho} \int_{E1}^{E2} \left(\frac{\partial P}{\partial T} \right)_E dE$$

$$RC = \int_{T1}^{T2} \Delta S dT$$

Equation (5.1)

where $C = 0.34 \text{ (J g}^{-1}\text{K}^{-1}\text{)}$, is the specific heat capacity and $\rho = 8.01 \text{ g cm}^{-3}$, the mass density of 0.7PMN-0.3PT single crystals is assumed to be constant values[101] in the testing temperature range. The EC temperature changes obtained from Equation 1.8 along the working temperatures are presented in Figure 5.1 [d]. The maximum temperature change, $\Delta T_{max} = 2.7 \text{ K}$ was detected at $T_c = 127^\circ\text{C}$ when $\Delta E = 12 \text{ kV cm}^{-1}$ is applied. It is also interesting to notice very high cooling values throughout the working temperatures from 125 to 75°C ($> 2 \text{ K}$ up to 75°C). The ΔS values derived using Equation 1.7 at FE-PE transition, $\Delta S_{max} = 2.3 \text{ J Kg}^{-1}\text{K}^{-1}$ and at critical point transition, $\Delta S_{critl} = 2.04 \text{ J Kg}^{-1}\text{K}^{-1}$ claim that the critical points are equally effective as FE-PE transitions in PMN-PT crystals at MPB compositions. Even though the FE-FE phase boundary is considered inferior to FE-PE boundaries, the presence of orthorhombic (**O**), monoclinic (**M_B**, **M_C**) phases between **R** and **T** transitions at the critical point according to Kutnjak *et al* [97] makes the lattice more frustrated and causes huge ΔS values even in small applied fields. The $RC = 206 \text{ J Kg}^{-1}$ estimated (from equation 5.1) in the limits of 40 to 160°C at an applied field 12 kV cm^{-1} and the ΔT_{max} observed was larger than the previous best reported results in PMN-PT ceramics[33, 102].

5.2. Electrocaloric Properties of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ Thin-films

Furthermore, we carried out similar studies in PZT thin-films to verify the EC properties of ferroelectric systems at MPB compositions for confirming its universality. Electrical hysteresis measurements made at 10 kHz by varying the external temperature every 10°C and the representative plot $P(E)$ are shown in Figure 4.8.

The relative permittivity ϵ and loss tangent, $\tan \delta$ of epitaxial films measured at 100 kHz and the results have been discussed in Chapter 4, Figure 4.9. The Curie transition temperature, $T_c = 387^\circ\text{C}$ derived from extrapolation of $1/\epsilon$ data was consistent with the bulk transition results reported at MPB composition [86]. A change in the slope of dielectric constant and loss tangent resolved between 145 and 220°C suggested phase transition induced anomalies during the heating process. To verify the results, differential scanning calorimetry (DSC) measurements were conducted at a ramp rate of $1^\circ\text{C}/\text{min}$ (inset Figure 5.2 [a]) during heating cycle in N_2 atmosphere. The exothermic peak observed at 195.7°C confirmed the crystallographic transformation in PZT. According to earlier reports, the phase transition was described as the tricritical point transition between **R**, **M_A** and **T** phases [86, 87]. The specific heat capacity ($C = 0.37 \text{ J g}^{-1}\text{K}^{-1}$) was deduced from DSC data of PZT thin-films and density ($\rho = 7.8 \text{ g cm}^{-3}$) values used to calculate ΔT from Equation 1.8. The $(\partial P/\partial T)_E$ data was derived from the 6th order polynomial fits of $P(T)$.

Figure 5.2: [a] The isothermal entropy changes ΔS as a function of sample temperature in PZT thin-films. Upper inset: DSC data shows an exothermic peak at 195°C during heating at a ramp rate 1°C/min corresponds to tricritical transition point. [b] The adiabatic temperature changes ΔT in applied bias ΔE . The peak $\Delta T_{max} = 11.1$ K occurs at Curie point 387° C and a secondary peak $\Delta T_{critl} = 1.4$ K at $\Delta E = 577$ kV cm⁻¹. Lower Inset: Polarization as function temperature $P(T)$ at different electric fields fit to 6th order polynomials. The figure was adapted from ref. [48].

The results showed in Figure 5.2, exhibit similar EC characteristics as 0.7PMN-0.3PT single crystals. The peak adiabatic temperature $\Delta T_{max} = 11.1$ K was detected at $T_c = 387^\circ\text{C}$ and a secondary cooling peak $\Delta T_{critl} = 1.4$ K was at tricritical temperature, $T_{critl} = 195^\circ\text{C}$ in $\Delta E = 577$ kV cm⁻¹ (Figure 5.2 [b]). The ΔT_{max} observed in our measurements exceeds the earlier reports in PZT thin-films at any other compositions [102, 103] but surprisingly the secondary cooling peaks originated from tricritical phase transitions showed less pronounced effects compared to relaxor-ferroelectric single crystals. The adiabatic cooling line exhibits a non-linear behavior between T_{critl} and T_c and $\Delta T = 0.75$ K pointed out at $T = 285^\circ\text{C}$ in $\Delta E = 577$ kV cm⁻¹. This is due to the slim boundary and higher degree of ordering between **R** and **T** phases in PZT along MPB line. Inclusion of unsymmetrical phases such as **M_A** to **T** and **R** transitions at lower temperatures enhances ΔS values, minimizes the temperature dependence of ΔT and broadens the cooling ranges. The isothermal entropy changes derived from Equation 1.7 are represented in Figure 5.2 [a]. The critical isothermal entropy, $\Delta S_{critl} = 1.1$ J Kg⁻¹K⁻¹, and the $\Delta S = 0.49$ J Kg⁻¹K⁻¹ at $T = 285^\circ\text{C}$ are substantially less than the $\Delta S_{max} = 6.17$ J Kg⁻¹K⁻¹ at T_c . The RC estimated in the limits of 100 to 420°C at an applied field of 577 kV cm⁻¹ is given as 688 J Kg⁻¹. But when we look at the refrigeration capacity contributions from major and minor peaks independently, $RC = 474$ J Kg⁻¹ in the temperature range 285 to 420°C and $RC = 213$ J Kg⁻¹ in 100 to 285°C were observed. Even though the ΔT values differed significantly at T_c and T_{critl} , the secondary cooling peak still contributed ~ 30 % to the total RC . It is thus highlighted that the critical points are equally important as FE-PE transformations in ferroelectrics to achieve large refrigeration capacities.

Overall, the results presented in both 0.7PMN-0.3PT single crystals and PZT thin-films indicate the potential to achieve large ΔS and ΔT values at the same time in ferroelectric

materials at MPBs. The single crystal relaxor-ferroelectrics exhibit more prominent cooling figures than the ferroelectric thin-films at MPB. This is because the excess lattice entropy generated from the field induced nanopolar-to-polar transitions in relaxor-ferroelectrics⁴ contributed to the overall ΔS values and thereby ΔT values. It is also inferred that when phase symmetries are highly irregular, even small perturbations in neighboring phases can produce huge lattice entropy changes at MPB.

5.3. Electrocaloric Properties of PZN-PT Single Crystals

Single crystal wafers of PZN-6% PT were grown by improved flux method. Crystal orientations were carefully controlled by means of Laue back-reflection technique. Specimen samples of (001), (011) and (111) orientations were cut into $10 \times 10 \times 0.3 \text{ mm}^3$ dimensions and finely polished. Dielectric measurements were performed using a HP 4192A Impedance Analyzer in both zero field heating (ZFH) and zero field cooling (ZFC) conditions. The polished wafers spray coated with platinum electrodes on planar faces, were used in electrical measurements. Hysteresis measurements were carried out at 10 kHz frequency using Radiant Technologies Precision workstation between 180°C to room temperature at every 10°C interval of cooling. The temperatures of samples were precisely controlled to near equilibrium states via feedback from Pt100 resistance temperature detector (RTD) temperature sensors, which are accurate to 0.2°C, in contact with the sample.

Figure 5.3: [a] Representative hysteresis loops of PZN-0.06PT single crystals measured at 1 kHz in cooling temperatures. [b] Temperature dependence of dielectric constant during ZFH and ZFC and frequency dependant relaxor behavior (in inset) are shown. [c] Polarization variation induced by temperature changes $P(T)$ data are extracted from the series of P - E hysteresis loops and fit to 6th order polynomials. [d] The EC temperature changes as a function of sample temperature from 40 to 180°C shown.

In summary, we investigated EC properties of PZT thin-films, 0.7PMN-0.3PT and PZN-0.06PT single crystals with the aim of accessing materials with broad working temperature ranges below T_c . The relaxor-ferroelectric single crystals exhibiting large ΔT s and RC s are very attractive for high performance solid-state cooling devices. It is possible to engineer the effective cooling values of ferroelectrics down to lower temperatures by

selecting the materials, which involve in more number of evenly spaced critical points at MPBs. Though the PZN-PT single crystals exhibit relatively small ΔT values[104] compared to other ferroelectrics, they have distinct advantages. Single crystals of PZN-PT are easy to control and grow in different orientations. Their nearly flat cooling curves allow us to use them as cooling elements over wide working temperatures, where the cooling ranges are more suitable for chip cooling applications. Our work provides a new recipe for tailoring the EC properties of both bulk and thin film materials for possible cooling applications.

With a careful selection of crystal orientations, it is possible to obtain either high cooling temperatures or high cooling capacities in the same material. The role of FE-FE phase transitions in PZN-PT single crystals and their contributions to ΔT values at low temperatures is emphasized in the next chapter. It is also possible to engineer the materials by considering single crystals to tune electrocaloric coefficients by considering orientation dependent factors. In order to achieve high refrigeration capacities, materials with multiple phase transition in close temperature ranges need to be selected.

Chapter 6:

ORIENTATION DEPENDENCE STUDIES

6. Dependence of EC Coefficients on Crystal Orientation

The dependencies of EC effects on principal polarization and electric field orientations near ferroelectric-ferroelectric phase transition regions in $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ single crystals were thoroughly investigated. Samples of (001), (011) and (111) orientations at morphotropic phase boundary composition were analyzed to study their FE-FE phase transition induced entropy contributions to the electrocaloric coefficients. It was observed that (111) oriented samples exhibited higher cooling figures near lower critical phase transitions from rhombohedral (R) to tetragonal (T) phase compared to (001) and (011) samples. Though (111) samples showed higher cooling values, (011) samples showed better cooling capacities due to their easy switchable characteristics between R and T phases. The results provided an important conclusion that by careful selection of applied electric field direction with respect to the principal crystal orientation, it is possible to obtain high cooling temperatures or high cooling powers in the same material.

In this chapter, we attempted to explain the role of crystal orientation and symmetry differences between neighboring phases on total isothermal entropy (ΔS)/polarization (ΔP) changes. The change in isothermal entropy (ΔS) in ferroelectric systems is directly proportional to the change in polarization (ΔP) under the application of an external electric field, a result based on the coupling of electric dipoles with the electric field. From the second law of thermodynamics, large ΔS results in high values of temperatures changes (ΔT) during the EC process. High ΔS values in ferroelectric materials can be achieved by two possible ways, either by the application of high electric fields or by inducing anisotropic phase transitions in EC materials.¹³ Very high electric fields can be applied to materials in thin-film form but the amount of applied electric field is often limited by electrical break-down strengths of the materials. So the other feasible way to tune ΔS values was by inducing phase

changes by subjecting the ferroelectric system to slow heating/cooling process. The most common phase transitions observed in ferroelectric systems were antiferroelectric to ferroelectric (AFE-FE), ferroelectric to ferroelectric (FE-FE) and ferroelectric to paraelectric (FE-PE) phase transitions. Each of these phase transitions was characterized by magnitudes of change in polarization values. The magnitude of ΔS varies in proportional to ΔP , which in turn depends on differences in crystal symmetry and phase coherencies.

There are some reports in the literature describing the effect of phase changes on ΔS and ΔT values. So far, the FE-PE transition has been reported to be the dominant phase transition in defining maximum ΔT values in ferroelectric materials.[18] The AFE-FE transition shows less significant effects in PbZrTiO_3 compounds [16, 36, 105, 106] and also an abnormal electrocaloric effect in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-BaTiO}_3$ ceramics [107]. Several other studies have demonstrated notable contributions arising from FE-FE transitions to ΔS and hence ΔT [48, 61, 108-110]. Our earlier work showed that coupling of the PE-FE phase transition with FE-FE phase transition could possibly extend ΔT range over wide working temperatures and attain high refrigeration capacities. In this study, we investigated the orientation dependent effects of relaxor ferroelectric single crystals at FE-FE phase transitions.

Figure 6.1 represents a schematic of principal polarization axes of rhombohedral (R), orthorhombic (O) and tetragonal (T) phases along (111), (011) and (001) directions, respectively. During the phase transitions, the polarization will align in the direction of applied field by extension and rotation along principal polarization directions of R to O, O to T and vice versa.

Figure 6.1: Schematic of principal polarization directions $[001]$, $[011]$ and $[111]$ shown in T, orthorhombic (O) and R phases respectively.

Polarization switching characteristics between the phases during the phase transitions can influence the shape of the electrocaloric cooling curves. Smooth polarization switching during phase transitions results in a broad temperature peaks whereas, complex polarization rotation paths show sharp ΔS and ΔT peaks [111]. Our experimental investigations provided useful knowledge in materials selection methods with suitable orientations to obtain high cooling values in a broader temperature ranges or acute cooling peaks in narrow temperature zones depending on application requirements.

Dielectric measurements were carried out for all samples under variable frequency conditions under zero applied fields, with $\pm 10^\circ\text{C}$ step sizes in heating and cooling cycles between 40°C to 190°C . As shown in Figure 6.2[a], dielectric constant, ϵ depicts a typical frequency dependent relaxor ferroelectric behavior. The Curie temperature (T_c) of PZN-PT single crystal was determined to be around 154°C , which was in consistent with previous reports [112]. In addition, a low temperature anomaly was observed at a temperature, $T_a \sim 90^\circ\text{C}$. The non-linearity in dielectric behavior could be attributed to the crossover of R to T

phase near MPB region and the variation of the dielectric constant with temperature representing the proportion of phase mixtures (R+T) in each of the orientations [97].

Figure 6.2: [a] Dielectric measurements carried out for (001) samples at varying frequencies, show a non-linear transition around 90°C and Curie temperature at $T_c = 154^\circ\text{C}$ [b] orientation dependant dielectric behavior found in PZN-6%PT samples at FE-FE phase transition temperatures.

The non-linear behavior was consistently seen in all the samples around the same temperature (as shown Figure 6.2 [b]). At lower temperatures, R phase was stable and above the upper critical transition line T phase was found to be stable until T_c . Above T_c , paraelectric phase such as cubic phase appeared.

Field dependent polarization P-E hysteresis loops were measured for PZN-PT samples in three different orientations in the temperature range of 40 – 190°C during cooling and are shown in Figure. 6.3(a)-(c). From the P-E loops temperature dependent polarization $P_r(T)$ values were derived and are shown in figure. 6.3 (d). The remnant polarization, P_r plotted against the sample temperature depicted non-linear dependence of $P(T)$ curves. The polarization values exhibited a variation from 25 $\mu\text{C.cm}^{-2}$ to 44 $\mu\text{C.cm}^{-2}$ in $\langle 001 \rangle$ and $\langle 111 \rangle$ at 40°C under 11 kV.cm^{-2} , respectively. It was observed that anomalous behavior exhibited by polarization around T_a is consistent with the dielectric data. The differences in the P values are mainly because of the changes in the alignment of the principal polarization axes during the phase transitions. A maximum polarization value could be achieved when the electric field is in the direction of the principal polarization axis. The change in slopes of $P(T)$ data were fitted to a 5th order polynomial, which was further used in the calculation of ΔT values.

When the electric field, E acts in the same direction as the principal polarization direction of stable phase at a specific T, it generates possible maximum P values. The remnant polarization, P_r plotted against sample temperature depicts non-linear P dependence of T. Similar anomalous behavior around T_a inconsistent with dielectric data was observed. The change in slopes of $P(T)$ data were fitted to a 5th order polynomial, which was further used in the calculation of ΔT values.

Figure 6.3: Representative hysteresis loops of PZN-0.06PT single crystals measured at 10 kHz for [a] (001), [b] (011) and [c] (111) samples during cooling temperatures. [d] Remnant polarization, Pr plotted for all three samples against temperature changes.

During phase transition, the principal polarization direction of R phases switched from [111] to that of a T phase, i.e [001] direction and vice versa. The switching of polarization direction of R phase to T phase in PZN-PT samples was accompanied by intermediate crystallographic reorientation to [011] direction. The polarization direction situated at certain angle to the applied field direction in (011) samples was assisted by finding its new axis along [011] and resulted in smooth switching. As in the case of other orientations, polarization pinning was observed due to multiple reorientation steps of the

principal polarization axis towards the applied field direction. Continuity in slopes of hysteresis loops in (011) samples indicated easy rotation of polarization axis between R and T phases along the principal orientations during phase transitions. Irrespective of the direction of applied field, (011) samples show more or less the same values of ΔP , whereas R and T phases strongly depended on field directions (shown in Figure 6.3[d]).

Figure 6.4: Polarization vs electric field data plotted over MPB region in [a] (001), [b] (011) and [c] (111) samples. The anomalies observed in the hysteresis curves are due to polarization pinning near transition from R phase to T phase.

The anomalies in all samples near MPB regions could be closely seen in Figure 6.4. During phase transition, the principal polarization direction of R phase switched from [001] to T phase [111] direction and vice versa. The polarization switching of R to T in PZN-0.06PT samples was accompanied by intermediate crystallographic reorientation to [011]

direction. The polarization direction situated at a certain angle to the applied field direction in (011) samples assisted by finding its new axis along [011] and this resulted in smooth switching. While in other orientations, polarization pinning was observed because of the multiple reorientation steps of the principal polarization towards the applied field direction. Slim hysteresis loops in (011) samples indicated the easy rotation of polarization axis between R and T phases along the principal orientations during phase transitions. Irrespective of applied field directions, (011) samples showed more or less the same ΔP values, whereas R and T phases were strongly dependent on field directions (shown in Figure 6.3 [d]).

It is also important to determine proximities of phase transition zones, order of transitions at MPB in different orientations and their contributions to final ΔS and ΔT values. Lengths of phase transition regions were studied carefully by using the high resolution diffraction technique and reciprocal space mappings (RSMs). The RSMs of HL-plane, KL-plane and HHL-plane scans were obtained with incident x-ray beam energy of 8 keV for (001), (011) and (111) samples shown in Figure 6.5. The samples maintained at near equilibrium conditions while conducting measurements. A series of HHL-plane mesh scans were measured using ω scans at different 2θ angles.

Figure 6.5: Reciprocal space mappings are plotted for [a] (001), [b] (011) and [c] (111) samples near MPB phase transition regions.

High resolution diffraction peak intensities vs temperatures plotted for fixed 2θ values in Figure 6.6. It was observed that the lengths of transition from R to T phases were significantly differing between different orientations. Splitting in diffraction peaks data in

Figure 6.6 [a], [c] and [d] indicate the range of existence of R and T phases over temperature zones in different orientations. The gradual shifts in peak intensities were used to estimate the length of phase transition regions. Figure 6.6 [b] elaborates on details of lattice constants and lattice reflection changes during phase transformation from complete R to T in (001) oriented samples. Lattice constant and lattice reflection values vary abruptly in two phase regions and are used to determine length of phase transition boundaries precisely. The same information was also used to identify lower critical temperature, where T phase initially appeared and upper critical temperature, where R phase completely disappeared while heating the samples.

Figure 6.6: High resolution diffraction peaks are plotted against temperature rise in [a] (001) oriented sample along with [b] lattice constant and lattice reflection changes, in [c] (011) oriented sample and in [d] (111) samples.

Intensities of high resolution diffraction peaks vs test temperatures were plotted for fixed 2θ values as shown in Figure 6.6. The lengths of phase transition boundaries were determined from the diffraction data. It was observed that lengths of transition from R to T phases were considerably different between different orientations under constant applied fields (11 kV/cm). The dual peaks of diffraction data in Figure 6.6 [a], [c] and [d] indicate the temperature range over which R and T phases co-existed in different orientations. For instance, the position of the intensity of the major peak in Figure 6.6 [c], correspond to the R phase and that of the minor peak correspond to T. During the heating process, intensities of the peaks were gradually switched indicating R to T transformation at high temperatures. The gradual shifts in peak intensities were used to estimate the length of phase transition regions in each of the samples. Figure 6.4[b] elaborates details of change in lattice constants and lattice angle (α) during phase transformation in (001) oriented samples. Values of lattice constant vary abruptly in two phase regions and were used to determine length of phase transition boundaries precisely. The same information can also be used for identification of lower and upper critical temperatures.

It was observed that (011) samples showed coexistence between the two phases over a wide temperature region followed by (001) and (111) oriented samples. The (011) samples showed the co-existence of phases throughout the temperature scale. This could be due to easily switchable characteristics of [011] polarization axis between principal polarization directions of [001] and [111] in R and T phases. All samples showed diffused phase transitions from R to T phase and the width of diffusion regions were different in different orientations. This leads to a conclusion that the nature of phase transitions in PZN- PT samples is second order at MPBs.

Figure 6.7: The EC temperature changes plotted as a function of sample temperature at an applied field 11 kV cm⁻¹. The $\Delta T_{max}=0.42$ K found at $T_{max}=155^{\circ}\text{C}$ and the secondary peak appeared at $T_a \sim 90^{\circ}\text{C}$ due to FE-FE phase transitions.

Electrocaloric coefficients in the samples were determined by indirect measurements. The $(\partial P/\partial T)_E$ data were interpolated from the polynomial fits to $P(T)$ values. The adiabatic change in temperature of the materials was calculated by Maxwell's relation,

$$\Delta T = -\frac{1}{\rho} \int_{E1}^{E2} \frac{T}{C} \left(\frac{\partial P}{\partial T} \right)_E dE$$

The maximum adiabatic change in temperature of $\Delta T_{max} = 0.42$ K was detected at $T_c = 154^{\circ}\text{C}$ and a secondary cooling peak $\Delta T = 0.27$ K at FE-FE transition temperatures at, $T_a = 87^{\circ}\text{C}$ in (111) oriented samples under the applied fields of $\Delta E = 11$ kV cm⁻¹. The FE-FE phase

transition temperature, T_a values were taken from differential scanning calorimetric scans (Figure 6.7, inset) and the heat capacity values (C) were derived for each of the samples. The $\Delta T_{\max}$ values for all samples shown in Figure 6.7 were found to be in close range and seemed to be less dependent on orientation of the crystal at T_c in PZN-PT. On the other hand, ΔT values induced by the FE-FE phase transition were highly dependent on orientation of the crystal and directions of applied field. Samples oriented in (111) direction featured sharp ΔT peaks and those oriented in (011) exhibited broad cooling peaks near the FE-FE phase transitions. The responses of ΔT values showed similar resemblance to ΔP variations in these samples with different orientations. Thus, depending on a smooth or pinning type of phase transitions in ferroelectrics materials, it is possible to obtain broad or sharp EC peaks, respectively. Though PZN-0.06PT single crystals showed small ΔT values compared to other ferroelectric systems in literature [8], the cooling curves were nearly uniform over wide working temperatures. It emphasizes on other important factors such as orientation effects on materials selection methods.

In conclusion, the electrocaloric effect for (001), (011) and (111) oriented single crystals has been thoroughly investigated to study the ferroelectric-ferroelectric (FE-FE) phase transition induced isothermal entropy changes in $0.94\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--}0.06\text{PbTiO}_3$ (PZN-PT) material. The results show that PZN-PT crystals oriented in (111) direction exhibited $\sim 38\%$ higher cooling values near lower critical phase transition, from rhombohedral (R) to tetragonal (T) phase, compared to those oriented in (011) direction. Though (111) samples displayed higher cooling values, (011) samples showed broader cooling curves due to their easily switchable characteristics between R and T phases.

Chapter 7:

ELECTROCALORIC DEVICE

7. Modelling of Electrocaloric Cooling Device

Electrocaloric working elements are modeled by a 2D geometry and the thermodynamic efficiencies of Carnot, Ericsson and Brayton cycles were investigated in a solid-state electrocaloric cooling device. Using a comprehensive model for coupled thermal, electrical interactions in ferroelectric PMN-0.3PT single crystals, we demonstrated high Carnot efficiencies followed by Ericsson and Brayton cycles respectively. We also developed a physical model based on cascade systems to improve the device efficiency of Ericsson.

New approaches to thermal management of electronic components are of general interest. Ferroelectric materials with large electrocaloric (EC) coefficients have attracted a great deal of interest in recent solid-state cooling applications. Solid-state heat pumps are robust and offer more efficiency, compact in size, less weight, and device integration benefits relative to conventional vapor compression systems. This research area became a center of attention because of its promising potential in the construction of EC based solid-state refrigerators.

In general, the EC device comprises of at least one heat transforming medium or working medium (i.e. EC material), heat source (the object of interest to cool) and a heat sink. The three elements are connected through a pair of heat switches, either movables (e.g. MEMs) or immovables (e.g. Thermoelectric devices, thermal diodes etc), placed on top and bottom surfaces of the working medium to control the on and off states of the cooling device. The system is allowed to transfer heat from either source to working medium or working medium to heat sink in isothermal cycles and isolates the EC elements in adiabatic cycles. During the thermal isolation process, an electric field is applied to regulate the body temperature of the working medium. The temperature of the working element increases when the electric field is applied and cools down when the field is removed. While the working

element is at lower temperature, it is allowed to keep in contact with the heat source and when the material absorbs heat and becomes hot, it is placed close to the heat sink. In an ideal electrocaloric cooling, the cooling device operates under two isothermal and two adiabatic cycles to attain maximum efficiency by Carnot, and the process is totally reversible. In principle the efficiency for EC device in Carnot cycle is higher than any other solid-state cooling cycles such as Ericsson or Brayton cycles. Even though Carnot efficiency is higher, Ericsson and Brayton cycles in solid-state devices are more viable practically because of their easier operating isofield cycles. Ericsson cycle is conducted under two isofield and two isothermal stages, whereas Brayton cycle is carried out under two isofield and two adiabatic cycles. Still the major issues in today's state of art of EC technologies are effective implementation of right refrigeration cycles of ferroelectric refrigerants based on its specific applications. For example, although the Ericsson cycle has been well identified as the best refrigeration cycle in solid-state cooling devices its complex and expensive heat switches makes them practically hard to implement in electronic cloning systems.

Recently, Yang *et al.*[113] showed at near room temperature in a magnetic refrigerator, a regenerative cycle is more efficient than the Carnot, Ericsson or Stirling cycles[114]. A Carnot cycle hypothetically has more thermodynamic efficiency with two isothermal and two isentropic processes. The overall cycle capacity for a given T_{hot} and T_{cold} is confined mainly by the allowable safe magnetic fields limits in actual devices [59, 115]. So it can always be assumed that it is possible to achieve nearly close theoretical efficiencies with apt understanding on thermodynamic cooling cycles. The main focus of this study is devoted to investigating the solid-state heat transforming medium based on the two-dimensional device model. The final objective is to complete the picture of the electrocaloric parameters in ferroelectric materials and to prove their interconnections with the material

properties and external conditions by carrying out the detailed analysis of the theoretical foundations. Such information is invaluable for the development of nanoelectronics for energy harvesting and chip cooling.

7.1. Modeling of EC Device

In order to investigate the cooling process in the EC device involving in thermal and electrical phenomena, the fundamental principles of conservation of energy from the first law of thermodynamics were applied [116]. However, internal energy, U or free energy, and G are rather inconvenient quantities to measure and use in simulations.

Figure 7.1: A 2-D geometrical model is used to simulate EC cooling device here. [a] Heat source (object of interest to cool) and heat sink are connected through the EC working medium (cross sectional view of the device is shown). The device is isolated from ambient atmosphere and [b] PMN-0.3PT single crystal of $1 \times 1 \times 0.2 \text{ cm}^3$ wafer used as working element. [c] Variation of electric field (E) during device operation is controlled by four steps as depicted (Figure [c] adapted from[59]). Figure adapted from [61].

We developed a 2-D theoretical model to investigate the cooling efficiencies of ferroelectric based heat transforming EC device. Numerical simulations were performed using finite difference methods used to solve 2-D transient heat equations. To evaluate the thermodynamic efficiencies of EC cooling line in terms of Carnot, Ericsson or Brayton cycles, cascade systems were considered. The designing of a physical system as shown in the Figure 7.1 is close to instability so that small external perturbations from electric fields or thermal excitation will tip the system into a new ground state.

The Heat Equation

In order to determine the thermal field $T(x, y, t)$, the 2-D transient heat equation was considered. The theoretical thermodynamic cycles of Carnot, Ericsson and Brayton are depicted in Figure 7.2.

Transient heat conduction by electrocaloric heat elements is given in the equation below:

$$\frac{dQ}{dt} = -k \oint \nabla T \cdot \overrightarrow{dA} \quad \text{Equation (7.1)}$$

A surface area (m^2)

Cp heat capacity (J/Kg/K)

k thermal conductivity (W/m/K)

Q heat flux (W/m^2)

T temperature (K)

P polarization (C/m^2)

Figure 7.2: [a] Thermodynamic cycles of Carnot and Ericsson stages represented in black and red color plots. The numbers 1, 2, 3 and 4 indicates the time steps of each cycle corresponding to applied field modulations in Figure 7.1 [c]. [b] Similarly Brayton cycles are compared with Carnot cycles and it can be inferred that the work done is more in case of Brayton geometries. Figure is adapted from [61].

From the second law of thermodynamics,

$$dQ = \rho C_p dT + T \left(\frac{\partial P}{\partial T} \right)_E dE \quad \text{Equation (7.2)}$$

To address the practical device performance, the time duration of thermal and electrical pulse fronts were incorporated. From Equations 7.1 and 7.2,

$$-k \oint \nabla T \cdot d\vec{A} = \rho C_p \frac{dT}{dt}(x, y, t) + T \left(\frac{\partial P}{\partial T} \right)_E \frac{dE}{dt}$$

$$\rho C_p \frac{dT}{dt}(x, y, t) + k \left(\frac{\partial^2 T}{\partial x^2}(x, y, t) + \frac{\partial^2 T}{\partial y^2}(x, y, t) \right) = -T \left(\frac{\partial P}{\partial T} \right)_E \frac{dE}{dt} \quad \text{Equation (7.3)}$$

Where $Q(x, y, t) = -T \left(\frac{\partial P}{\partial T} \right)_E \frac{dE}{dt}$, is the quantity of heat absorbed or released during EC cooling cycles.

$$Q_C(x, y, t) = \rho C_p \frac{dT_C}{dt}(x, y, t) + k \left(\frac{\partial^2 T_C}{\partial x^2}(x, y, t) + \frac{\partial^2 T_C}{\partial y^2}(x, y, t) \right) \quad \text{Equation (7.4)}$$

$$Q_H(x, y, t) = \rho C_p \frac{dT_H}{dt}(x, y, t) + k \left(\frac{\partial^2 T_H}{\partial x^2}(x, y, t) + \frac{\partial^2 T_H}{\partial y^2}(x, y, t) \right) \quad \text{Equation (7.5)}$$

Equations 7.4 and 7.5 represent the heat absorbed, Q_C from heat source and heat transferred, Q_H to the heat sink by the EC working medium.

Considering a rectangular EC working materials (Figure 7.1 [b]) with dimensions bounded by $x = 0$, $x = h$, $y = 0$ and $y = k$; boundary conditions, $T(x, 0, t) = T(0, y, t) = T(x, k, t) = T(h, y, t)$, $T_C(x, y, 0) = T$, $T_H(x, y, 0) = T_0$ assuming an infinite heat sink and is always maintained at T_0 temperature.

The Second boundary is given as $\frac{dT}{dx dy}(h, k, t) = \frac{dT(t)}{dx dy}$

From the first law of thermodynamics, $W_{in} = Q_H - Q_C$

Carnot efficiency is given by, $\eta_{Carnot} = \frac{T_C}{T_H - T_C}$ Equation (7.6)

Coefficient of performance, $COE = \frac{Q_C^{in}}{W_{in}}$ Equation (7.7)

During the Ericsson and Bryton cycles, the total work determined by each segments of the cycles are depicted in Figure 7.2.

$$\delta W_{Ericsson} = -(T_H - T_C) \int_{E_1}^{E_2} P dE \quad \eta_{Ericsson} = \frac{Q_C^{in}}{\delta W_{Ericsson}}$$

$$\delta W_{Brayton} = (S_C - S_H) \int_{T_C}^{T_H} E dT \quad \eta_{Brayton} = \frac{Q_C^{in}}{\delta W_{Brayton}}$$

Results and Discussions

Our earlier works in Chapters 5 and 6 have been focused on experimental measurements of electrocaloric properties in relaxor ferroelectric single crystal wafers to analyze its intrinsic effects. The EC values of $[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]$ -30% $[\text{PbTiO}_3]$ (PMN-0.3PT) capacitors[48] were measured to demonstrate temperature swings of up to 2.7 K near its T_c and ~ 2 K values over wide temperature ranges as shown in Figure 7.3. The single crystal wafers of outer dimensions $1 \times 1 \times 0.2 \text{ cm}^3$ were used for the measurements. Even though these materials are very bad conductors of heat, the thickness of in out of plane orientation is considerably less to treat them as 2-D slabs in our model[75].

Figure 7.3: Adiabatic temperature changes in PMN-0.3 PT single crystal wafers are measured by indirect estimates using Maxwell relation and plotted with respect to sample temperature. Figure adapted from [61].

The difference between non-linear heat transfer of Q_C and Q_H was calculated from adiabatic temperatures ΔT from Figure 7.3. Carnot efficiency and COP were derived from

Equations 7.6 and 7.7 for the given material. At an operating temperature of 400 K, the efficiency was 0.33 Carnot, which is considerably higher than other solid state technologies like thermoelectric. Also $\eta_{Ericsson}$ and $\eta_{Brayton}$ were estimated from above relations and the results compared. It is more evident from the schematic of Figure 7.2 that the total work functions in both the cycles exceeds Carnot, which results in lower efficiency values correspondingly $0.61\eta_{Carnot}$ and $0.48\eta_{Carnot}$ respectively. We also investigated a method of controlling cascade systems to reduce isothermal and isofield cycles by placing two working elements connected to a heat sink operated at very low temperatures. Relaxor ferroelectric systems such as PMN-0.3PT possess a great advantage in terms of their wide range of uniform adiabatic temperatures and they can be used in solid-state electronic cooling devices like micro-chip cooling.

7.2. *Prototype Device Design and Testing*

The electrocaloric effects of ferroelectric materials are hard to measure by direct means with today's state-of-the-art technologies. A solid-state cooling device prototype is designed to demonstrate electrocaloric effects of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ 70/30 single crystals as active cooling elements. The test section is designed to carefully measure the possible bulk cooling figures of PMN-0.3PT electrocaloric working materials under repeated on/off cycles of electric fields. Despite the materials low adiabatic temperature changes (predicted by indirect methods), the single crystal materials showed high cooling rates under optimized device parameters and working environment. It is identified that the pulse width and frequency of applied field play a vital role in achieving possible high cooling efficiencies of the device prototype.

In recent years, there has been significant interest in developing alternative active cooling technologies to liquid coolants for high power electronics. Solid-state thermoelectric coolers are proposed as one of the promising technologies for this purpose because of their compact structures, quick cooling responses, high reliability and absence of no moving parts [117]. Though the technology appears attractive in many ways, the coefficients of performance (COP) of thermoelectric devices are mainly limited by figure of merits of the materials available today [118].

It is an extremely challenging task to measure the adiabatic temperature changes (ΔT) precisely in EC materials because of their ultrafast response of ΔT values in thin-films and considerably small temperature changes in bulk forms. Significant research has been devoted to this field to predict absolute cooling figures of various organic and inorganic oxide materials by direct and indirect methods [46, 49, 60, 119]. So far, several research groups have been successful in reporting the EC coefficients of different materials systems and some

have even been able to compare their results with directly measured values and showed close agreements with them [53, 58]. However, despite the progressive developments, real cooling devices are yet to be seen in practice. Here, we try to demonstrate possible bulk cooling effects that can be generated in EC working materials under repeated cycles of electric fields. A prototype device has been designed to explain the active cooling concepts of EC cooling elements in solid-state devices and their significant results by engineering of device operating parameters.

Though the ECE of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin-films show adiabatic cooling temperatures of $\Delta T = \sim 0.45$ K at 100 kV/cm (as shown in Figure 4.3 [b]), our 1-D model showed that it is possible to attain high cooling values of ~ 2.5 K by modulating the operating parameters such as frequency of the electric field, during 25 sec of continuous device operation.

Figure 7.4: Frequency dependence of EC behavior in BST thin-films plotted working temperature against device operating time (inset represent material parameters used in 1-D modeling).

Thus smart engineering of the materials is essential to achieve the realistic approach of ECC in practical devices.

Description of Test Section

Solid-state cooling devices are well known for their compact designs and minimal or no moving physical parts to avoid any complications during device operations. In principle, the EC cooling elements are convenient to assemble due to their simple geometries and design configurations. A typical EC cooling device (schematic is shown in Figure 7.5) consists of active cooling/working material sandwiched between heat source and heat sink. The EC working elements are electrically extended to connect to a power supply unit. In order to ensure unidirectional heat flow from heat source to heat sink, thermal diodes are required to interface between heat source and working material and similarly between working material and heat sink. All the interfaces are assembled with high thermal conductive interface materials such as thermal grease or ceramic tape to avoid any contact resistances. To monitor the temperature changes on heat source and working element during device operations, highly sensitive thermocouples are attached onto the surfaces.

Figure 7.5: A solid-state electrocaloric model is shown (Figure scale adjusted to the details).

The experimental test section was originally designed by using a 10 W thick film resistor of $15 \times 15 \text{ mm}^2$ planar heating element as heat source, a solid copper block as heat sink, a couple of peltier cells as thermal diodes and a $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.3\text{PbTiO}_3$ (PMN-0.3PT) single crystal of $10 \times 10 \times 0.2 \text{ mm}^3$ wafer as EC working material. The electrocaloric cooling profiles of PMN-0.3PT crystals were measured and reported in chapter 5. All the components were carefully assembled as shown in Figure 7.5 by using Al_2O_3 ceramic tape as thermal interface materials to maintain good thermal contact between the interfaces. The entire setup was placed in a closed transparent enclosure to prevent any quick heat losses to the environment. All the electrical and temperature sensor connections were extended

through side walls of the insulation box, and firmly sealed to the walls to avoid any misalignments in testing stages. 4-wire Pt 100 resistance temperature detector (RTD) thin-film sensors used to detect the quick temperature changes on the heat source as well as on the working material. Temperature profiles on the heat source and EC working material were continuously recorded into an electronic storage device using Hioki LR8401-20 HiLogger (30Ch) and the data plotted in later stages.

The entire test assembly was then fitted into a closed frame of thermally isolated transparent container. The isolated container was helpful to stabilize the device environment and also the transparent case allowed monitoring of the test assembly in case of any irregularities during the device testing. The heat source was designed with a planner heating element, to heat the entire stage steadily to the desired maximum test temperature and then the power was disconnected from its source to allow natural cooling of the test section in closed environment. Proper care had to be taken between the test runs to bring back the ambiance to initial conditions each time. The test section was calibrated thoroughly to reproduce similar heating and cooling profiles when the working elements were at inactive state. The tasks were repeated several times to ensure that the test section stabilized over a period of trials. Thermocouples were connected externally to a digital data-logger, which allowed temperature recording online and were later transferred to the computer.

Figure 7.6: [a] a prototype EC device was designed to test the cooling capabilities of single crystal ferroelectric cooling elements. [b] 2D sectional view of device test assembly. Temperature profiles of [c] heat source and [d] EC cooling element calibrated in controlled working environment.

The prototype device was calibrated precisely in a controlled environment with all device connections firmly built. Temperature profiles of heat source and working element were recorded during several runs of repeated calibration procedures and the heating-cooling trends were plotted as shown in Figure 7.6. The entire test setup was calibrated when the heat source raised its temperature from room temperature to 140°C at a heating rate of 14°C/min and then allowed to cool to room temperature slowly at a cooling rate of 4.5°C/min. With placement of the Peltier device between heat source and working element, it created a variable heat profile on its faces. It generated a maximum temperature of 85°C on the face connected to EC working element. Also it was found that the heating and cooling rates of EC

working element during calibration were $7.2^{\circ}\text{C}/\text{min}$ and $2.3^{\circ}\text{C}/\text{min}$ respectively. Mere replication of temperature profiles with consistent magnitude differences in temperature values between heat source and working element suggested that good thermal contacts were established throughout the device structure.

Figure 7.7: Adiabatic temperature changes in PMN-0.3PT single crystals plotted against sample temperatures.

Single crystal wafer of PMN-0.3PT, spray coated with platinum electrodes on both planar faces were used in the EC test measurements. The ΔT value of the test element at any working temperature as shown in Figure 7.7 is a representation of the temperature changes obtained in alternative cycles of two isothermal and two adiabatic operations. The advantage of using PMN-0.3PT material as cooling elements is that it demonstrates nearly uniform temperature swings ($\sim 2 \text{ K}$) compared to any other materials near the device testing temperatures designed.

Thermodynamically estimated cooling figures of EC cooling elements can be reproduced only when the device operates close to ideal adiabatic operating cycles at discrete temperature points. In practice, the exploitation of adiabatic environment around the cooling element is a highly difficult feat to achieve, especially when the device contains non-moving sections. In this study, we focused mainly on the measurement of bulk cooling properties in PMN-0.3PT crystals instead of local ΔT values at some specific points. Besides having high ΔT values in cooling elements, several other important parameters had to be considered to estimate the overall cooling capacities of the EC materials especially the applied electric field configuration which determines the shape of thermodynamic cycles. We thoroughly investigated the effects of pulse width (w) and pulse repetition rate (as shown in inset Figure 7.7) on EC device cooling.

Figure 7.8 [a] controlled pulses of electric field applied to device to modulate the cooling process [b] the voltage changes (ΔV) in Peltier cell cross-confirm the cooling produced by EC working material in active state at different field cycles.

Cooling performances of the test material as a result of application of controlled electric pulses in terms of temperature and voltage changes at different pulse rates are shown in Figure 7.8. The bulk cooling values of EC working elements were estimated by comparing the relative cooling rates of the test section under calibrated cooling conditions to active cooling states. The calibrated cooling curve, representing the sample temperature when allowed to cool under free cooling condition took ~ 1450 sec to reach the ambient temperature. Active cooling states of the device were introduced by application of electric field cycles to the EC working material continuously in the cooling range from 85°C to until 25°C . A gradual shift of total cooling time towards the left hand side or faster cooling of the device with increase of pulse repetition rate up to a certain point was observed. There are several key parameters which determine the cooling rates of solid-state device such as electric pulse width (W) or pulse repetition rate $[(W+g)/\text{pulse}]$, heat fluxes and contact resistance between the surfaces.

Electric pulse width or pulse repetition rate signifies the total time required to accomplish the ideal isothermal and adiabatic cycles close to Carnot conditions during on/off cycles of the electric field. The prototype device was tested by varying electric pulse repetition time and optimized conditions were obtained (as shown in Figure 7.8 [a]) by considering other parameters such as device geometry, device environment and power of the heat sink unchanged. The overall cooling time of the device was reduced to nearly half of its original cooling time when the device operated at an optimum pulse repetition rate of 2.4 sec/pulse under 12 kV/cm fields. The estimated cooling rate at an applied field frequencies of 2.4 sec/pulse was observed to be $5.4^{\circ}\text{C}/\text{min}$ compared to normal calibrated cooling rate of $2.3^{\circ}\text{C}/\text{min}$. Any pulse frequencies below 2.4 sec/pulse rate take longer cooling times due to insufficient time allowed for heat transfer in specific directions. The device cooling rates

could be improved by employing a powerful heat sink close to ideal heat sink conditions and also by establishing very good thermal contacts between the test sections.

On the other hand, bigger W values tend to stabilize the working elements close to device environment during adiabatic cycles of the field applied. The cooling data was also complemented by the voltage changes recorded on the Peltier cell during device testing (Figure 7.8 [b]). In the given test section, the heating profiles on the working element simulated close to working temperatures of a microchip, so that we could observe the direct application of EC materials as active cooling elements in hot spot cooling technologies.

In summary, the bulk EC cooling effects of 0.7PMN-0.3PT single crystals were successfully demonstrated with the help of a prototype device. The testing was carried out on a simulated test section and large bulk cooling values with optimized device operating parameters were reported. It was identified that the pulse width and frequency of applied field play a vital role in achieving possible high cooling rates. It was estimated that the cooling rates of the prototype device was drastically improved from $2.3^{\circ}\text{C}/\text{min}$ at normal cooling condition to $5.4^{\circ}\text{C}/\text{min}$ when the EC cooling element was at activate state (under 2.4 sec/pulse applied field frequencies).

Chapter 8:

CONCLUSIONS

8. Conclusions & Recommendations

1. the electrocaloric effects of four different ferroelectric systems were thoroughly investigated and high ΔT values in thin-films and single crystals over wide working temperatures were reported.

Figure: Summary of EC materials investigated over wide range of working temperatures.

2. The electrocaloric properties of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ epitaxial films, $0.7\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.3PbTiO_3 and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.06PbTiO_3 single crystals were measured and they demonstrated enhanced low temperature refrigeration at morphotropic phase boundary compositions. The results revealed large adiabatic cooling figures in ~ 260 nm PZT films (11 K in 15 V), 200 μm thick 0.7PMN-0.3PT single crystals (2.7 K in 240 V) and 300 μm thick PZN-0.06PT single crystals (0.45 K in 330 V) at their Curie transition temperatures and secondary cooling peaks at lower temperatures, near critical points. This is a very useful aspect of ferroelectric cooling elements to extend the cooling range over broad working temperatures in solid-state devices.

3. Dependence of electrocaloric effects on principal polarization and electric field orientations, near ferroelectric-ferroelectric phase transition regions in PZN–6%PT single crystals were thoroughly investigated. By careful selection of crystal orientations and electric field directions, it is possible to obtain either high cooling temperatures or high cooling capacities in same material. It is also emphasized that the role FE-FE phase transitions in PZN-6%PT single crystals and their contributions to ΔT values at low temperatures. In order to achieve high refrigeration capacities, materials need to be selected with multiple phase transition in close temperature ranges.
4. The EC working elements modeled by 2-D geometry and the thermodynamic efficiencies of Carnot, Ericsson and Brayton cycles were investigated in a solid-state electrocaloric cooling device. Using a comprehensive model for coupled thermal, electrical interactions in ferroelectric 0.7PMN-0.3PT single crystals, we demonstrated high Carnot efficiencies followed by Ericsson and Brayton cycles respectively.
5. A solid-state cooling device prototype was designed to test the electrocaloric effects of single crystals as active cooling elements. The bulk EC cooling effects of 0.7PMN-0.3PT crystals were successfully demonstrated with the help of a prototype device. The testing was carried out on a simulated test section and reported large bulk cooling values with optimized device operating parameters. It was identified that the pulse width and frequency of applied field could play a vital role in achieving possible high cooling rates.

Future Work

Direct Measurements of ECE in Thin-films

Focus of future work will be devoted to direct measurements of electrocaloric effects in thin-films. A major challenge in direct measurements is that the ultra fast dipole switching (typically in picoseconds) in ferroelectrics drives quick surface heat transfer on thin-films. The rate of heat transfer is very high even in oxide films ranging from few microseconds to milliseconds and pose difficulty over the control of thermodynamic cycles. Thus ultra fast temperature sensors with high sensitivities to measure the changes are recommended. A review of recent direct measurements of the giant electrocaloric effect in polymeric and inorganic ferroelectrics has been given [120]. Among the techniques, scanning thermal microscopy (SThM) could be a more accurate and versatile method to carryout the measurements under Ericson cycles. By calibration of heat losses/contributions arising from substrate materials, it is highly possible to implement this technique for direct ECE measurements in thin-films as well as single crystal substances.

Proof of Concept Study

On-chip cooling has become one of the most active and challenging research areas in thermal management of electronic devices and packaging. Many technologies are focused on improving cooling performances and efficiency issues. However, despite many novel approaches to develop alternative cooling methods, there is a more urgent need for improved techniques. Our prototype device studies demonstrated the possibility of using EC devices for mass cooling purposes. In principle, the new reliable active EC solid-state device without moving parts, can offer some advantages over the common approaches for microchip cooling.

Figure A.1: Schematic illustration of thin-film EC device mounted onto a hot chip.

We plan to examine a method of controlling a cooling system with thin-film working elements for transferring heat from a heat source (chip) to a heat sink (ambience). Ferroelectric thin-films or single crystal wafers with possible large electrocaloric effects will be used as working elements to cool the microchips. The device comprises of at least two heat switches; one, to receive heat from the heat source, and the other to pass heat to the heat sink; at least one electrocaloric element between the two heat switches and a heat source (Silicon Chip) and a heat sink.

The device efficiency and cooling power depend on the time required to fill each stage of a refrigeration cycle. The time of polarization/depolarization of an EC element is difficult to estimate because of its dependence on the electrical capacitance of an EC element and circuit resistivity. To make an effective refrigeration system, various effective heat switches need to be explored. These include heat switches that have a make/break physical contact or unidirectional heat transport systems like thermal diode or TE coolers.

Further, we propose to investigate novel thin-films and structures using electrocaloric effect (ECE) for energy harvesting and chip cooling. It aims not only at understanding the mechanism of ECE, but also its efficiency in comparison with thermoelectric and other mechanisms. Our future interests include getting large ECE for various working temperatures, implementing ECE in real devices with potential to be scaled down to nanosize and to be individually addressable.

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Appendix

A. Temperature measurement set-up

The ΔT measurements in the ferroelectric samples require special set up for temperature detection, because of the ultrafast switching of ferroelectric polarizations and their induced temperature changes which proven to be difficult to detect in a quick time. The stability and repeatability of the sensors over a long time are vital in order to respond to the minute temperature modulations. For each sample, the duration of the test run is at least 8 hours, thus the test section has to be attached a proper heat to compensate for fluctuations. Also the connections should not be altered throughout the process of the experiment so that the results are stable and comparisons can be done appropriately.

In order to minimize heat loss from the samples, the experiments were conducted in a near adiabatic environment to prevent excessive heat loss from the heating platform. Because of the heat transmitted from the heating platform to the samples, the channels between the heating platform and the samples are vital. Thus, the PMN-PT crystal has to be mounted on a wafer, using silver conductive adhesive paste, to fix the samples so that they do not shift in positions. The layer of silver paste has to be flat, so that the PMN-PT surface will be horizontal to the heating platform.

The PT100 sensors have to be placed on the PMN-PT flat surface with a tight-fit, but not at compressive stance. If compressive force is applied, it causes self-induced pressure which will trigger detection of an increase in temperature. This will cause deviations from the actual temperatures that are induced from the electric field. In instances when the PT100 is unable to stay attached to the working element, DuPont Kapton™ tape that can withstand

high temperature applications is used to secure the attachments. This creates an environment where the heat transmitted from the sample will be directly detected by the PT100 sensors that have an accuracy of $\pm 0.25\text{K}$. The data logger is able to sense temperatures with 10ms accuracy.

Secondly, an electric pulse is applied through the sample and the corresponding temperature changes were being recorded by the HIOKI Memory HiLogger. Both systems must operate concurrently so that the comparisons between the cause and consequence can be compared directly. The electric pulse is customized so that the step-up and step-down of the electric pulse effects on the temperature variation can be observed. From this variation, the electrocaloric changes can be determined. This is conducted at 1 Hz for 1 waveform for 100 s.

B. Sample Calibration Procedure

The sample was set on a heating platform and the temperature was increased gradually from room temperature to 180°C at 10°C intervals. The temperature on the film and the stage platform were recorded. There is slight deviation between the 2 PT100 RTD sensors, with the sensor on the film detecting a higher temperature. This could be due to the fact that heat is trapped between the sensor and the film with a smaller surface area, as compared to the stage with a much larger surface area for heat to escape.

Figure B.1: Pt100 RTD sensors calibrated [a] under equilibrium heating conditions and [b] the sensitivities measured.

Secondly, the results obtained coincide with theoretical explanation that thermocouple has a lower sensitivity and has a longer response time than PT100 RTD sensors. It also shows higher stability when data was being recorded. During the experimental stage, the PT100 RTDs sensors were able to record a steady reading within 10s whereas a thermocouple requires about 20s before the reading stabilizes. This confirms that the PT100 RTD sensors to be used in the later stages. The readings from this test are used as calibration for later experiments. The temperature detected on the film will be determined as the film temperature, with the equation.

List of Publications

Published:

1. **Rami Chukka**, Suresh Vandarngi, Lu You, Santirajan Shannigrahi and Lang Chen, “Orientation dependence of electrocaloric coefficients in $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{-PbTiO}_3$ single crystals”, AIP Advances **3**, 072118 (2013).
2. V. Suresh Kumar, **Rami Chukka**, Zuhuang Chen, Ping Yang and Lang Chen, “Substrate induced strain dependent magnetocaloric effect in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ thin-films”, AIP Advances **3**, 052127 (2013).
3. **Rami Chukka**, Santirajan Shannigrahi and Lang Chen, “Electrocaloric Cooling Efficiencies of Ferroelectric Working Elements”, Integrated Ferroelectrics **133**:3-8, 2012.
4. **Rami Chukka**, Jun Wie Cheah, Zuhuang Chen, Ping Yang, Santirajan Shannigrahi, Junling Wang and Lang Chen, “Enhanced Cooling Capacities of Ferroelectric Materials at Morphotropic Phase Boundaries”, Appl. Phys. Lett. **98**, 242902(2011).
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6. V. Swaminadhan, Steven S. Pramana, T. J. White, L. Chen, **Rami Chukka** and R. J. Ramanujan, “Microwave Synthesis of Noncentrosymmetric BaTiO_3 Truncated Nanocubes for Charge Storage Applications”, Mater Interfaces **2**(11):3037-42 (2010).
7. **Rami N Chukka**, Suresh Telu, Bhargava NRM and Lang Chen, “A Novel Method of Reducing Melting Temperatures in SnAg and SnCu Solder Alloys”, Journal of Materials Science: Materials in Electronics: Volume 22, Number 3, 281-285 (2010).

Conferences Attended:

1. **Rami N Chukka**, Santiranjana Shannigrahi and Lang Chen, “Investigations of Electrocaloric Cooling Efficiencies in Ferroelectric Thin-films by Solid State Model”, International Symposium on Integrated Functionalities, Cambridge, England, July 31 – Aug 4, 2011 (oral presentation).
2. **Rami Naidu Chukka**, Yang Wang and Lang Chen, “Towards Room Temperature Ferroelectricity and Ferromagnetism in BiMnO_3 ”, International Conference on Materials for Advanced Technologies, Suntec, Singapore, 26 June – 1 July, 2011 (oral presentation).
3. **Rami Naidu Chukka**, Santiranjana Shannigrahi and Lang Chen, “Solid-state Model to Investigate Electrocaloric Efficiencies in Ferroelectric Thin-films”, International Conference on Materials for Advanced Technologies, Suntec, Singapore, 26 June – 1 July, 2011 (Poster).
4. **Rami Chukka** and Lang Chen, “Enhanced Refrigeration Capacities in Ferroelectric Thin-films”, International Symposium on Integrated Functionalities, San Juan, Puerto Rico, 13-16 June, 2010 (Invited Talk).
5. **Rami Chukka**, Santiranjana Shannigrahi and Lang Chen, “Solid-state Electrocaloric Cooling Devices and Methods”, 4th MRS-S Conference on Advanced Materials, IMRE, Singapore, 17-19, March 2010 (Poster).