Proceedings of the Sixth IASTED International Conference
EUROPEAN POWER AND ENERGY SYSTEMS
June 26–28, 2006, Rhodes, Greece

HIGH PERFORMANCE PYROELECTRIC CONVERTER

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ABSTRACT

Pyroelectric conversion can produce high voltage DC from low-grade waste heat. Our pyroelectric converter uses 60%/40% P(VDF-TrFE) copolymer. Previously we encountered substantial power losses due to internal leakage at high temperature and voltage. In order to increase the power output, we examined the polymer purification using solvent extraction. After copolymer purification, we compared the electrical properties of the purified copolymer with these of the unpurified. Although we removed only 0.4 wt % of the copolymer impurities by solvent extraction, the electrical resistivity of purified copolymer was 35% higher than that of unpurified copolymer. We also observed that thin films produced using purified copolymer were able to withstand 50% higher electric field before they were ruined by electrical short-circuit. Subsequently, we conducted pyroelectric conversion using single 25 :m thick 60%-40% P(VF$_2$-TrFE) copolymer films. Copolymer purification resulted in a three-fold increase in net power output. Net power output per unit volume of unpurified copolymer was 95 J/L but increased to 279 J/L for purified copolymer.

KEY WORDS

Pyroelectric, Waste heat, Poling, Resistivity, P(VDF-TrFE**).**

1. Introduction

Many industrial processes emit large amounts of waste heat. However, due to the high cost of energy recovery and the lack of promising technologies, low-grade heat is normally discharged to the environment. Large amounts of low-grade heat are wasted at pulp and paper mills, steel works, petrochemical plants, glass manufacturers and electric power stations. When the temperature of heat source is low, the amount of available heat for useful work is also low, i.e., inherently limited Carnot cycle efficiency. Further, equipment for improved heat utilization becomes bulky and the cost of installation prohibitive. Nevertheless, the opportunity exists for converting waste heat to high-value electricity. Existing technologies such as the organic Rankine cycle cannot function well below 80^{o}C [1]. Pyroelectric conversion technology could meet this challenge.

Poly (vinylidene fluoride) (PVDF) is known for its piezoelectric and pyroelectric behaviour. These properties originate from its molecular structure which could be represented as (-CH$_2$ -CF$_2$-)$_n$ for an ideal defect free material [2]. Fluorocarbons are highly appropriate monomers to yield piezoelectric polymer crystals. The stereochemical manner in which monomers are linked together defines polymer's chain configuration. In the melt or in the solution, polymer chains have randomly coiled shapes (conformations), which configurationally disordered macromolecules are, to a grate extent, forced to retain in their solid state as well; however, chains free from configurational defects can crystallize into regular conformations when cooled from the melt. This is accomplished by rotation about single bonds in a manner that minimizes the potential energy of the chains arising from internal steric and electrostatic interactions. The most favorable torsional bond arrangements have substituents at 180^o to each other (called trans *t*) or at + 60^o (gauche g+) or – 60^o (gauche g $^-$); The three conformations of PVDF are all-trans, tg$^+$ tg$^-$, and tttg$^+$ tttg $^-$. The first two conformations are by far the most common and important ones. Because of the alignment of all its dipoles in the same direction normal to the chain axis, the all trans is the most highly polar conformation in PVDF. The tg$^+$ and tg $^-$ conformation is also polar, but because of the inclination of dipoles to the molecular axis, it has components of the net moment both perpendicular and parallel to the chain; approximately the same values also characterize the tttg$^+$ tttg $^-$ conformation. PVDF exhibits at least four crystalline phases (α, β, γ and δ) [3].

The electroactive properties of PVDF are associated with the polar β-phase, which is not usually produced from the melt, but obtained upon stretching several times their original length, and subsequent poling under a high electrical field. Stretching induces transformation of the non-polar α- phase, the most commonly observed structure, into the polar β-phase [4]. Electrical poling accomplished by applying an electric field across the thickness of the polymer. The chain conformation, packing and macroscopic electric response can change significantly in the presence of an electric field. All of these structural changes directly influence the overall electrical properties of VDF polymers [5]. An electric field on the order of 50MV/m is typically sufficient to effect crystalline orientation. Polymer poling can be accomplished using a direct contact method or a corona discharge [6]. The formation of β phase in common PVDF was a main technical issue in earlier days [7].

The introduction of TrFE monomer into the VDF chain stabilizes the trans conformation, shortens the regular VDF sequence, increases the disorder along the chain direction within the crystal region, and reduces the effective dipole moment of trans chain. That is to say, TrFE unit plays an essential role in determining the transitional behaviour of copolymers. The β-phase of the copolymer is formed directly on crystallization from the melt without any further stretching, and shows higher piezoelectricity than PVDF [5].

P(VDF-TrFE) exhibit a clear Ferroelectric to-paraelectric transition at a temperature Tc (Curie). Tc is below the melting temperature and its value increases with the VDF mol % [4, 8, 9,10]. We used a 60/40% P(VDF-TrFE) copolymer which has a transition temperature of 65^{o}C at zero electric field.

The pyroelectric conversion cycle developed by Olsen et al. utilizes the charge - voltage characteristics (displacement versus applied electric field) of pyroelectric materials at different temperature and voltage to achieve a power conversion cycle. It was observed earlier that when commercial P(VDF-TrFE) copolymer was used for power conversion, substantial power losses occurred due to internal leakage at high temperature and high voltage, resulting in increased internal conduction losses during pyroelectric conversion[1,11]. The only known solution for minimizing the leakage current is to reduce the electric field on the copolymer. However, reducing the electric field seriously limits the final net power output by restricting a voltage differential needed during power conversion. Many works have been devoted to improving the piezoelectric properties in ferroelectric polymers [10,12,13,14,15,16], but very little has been reported on the improvement of pyroelectric properties in ferroelectric polymers. Olsen at al. stated that the "bake-out" of residual monomer and other impurities at 140^{o}C for an extended duration (12 h plus) and under vacuum (50 mTorr) improved both the dielectric strength and the resistivity of P (VDF-TrFE) [11]. We examined the use of solvent extraction to purify commercial 60/40 P(VDF-TrFE) copolymer and the impact it has on the performance of pyroelectric conversion.

2. Experimental

In order to address the above problems we used solvent extraction to purify commercial pyroelectric copolymer. Pellets 60%-40% P(VDF-TrFE) were dissolved in methyl ethyl ketone (MEK, 99.5%, supplied by Aldrich Chemical Company, Inc.) to produce a 4 wt % solution. After the pellets were completely dissolved in MEK, anhydrous ethanol (EtOH, Commercial Alcohols Inc.) was added to the solution. This resulted in copolymer precipitation as gel. The gel was separated from the solvent mixture (MEK/EtOH) by filtration using Whatman paper filter No.42. Subsequently the gel was washed with anhydrous ethanol. It has been found that this purification procedure removes approximately 0.4% of un-identifiable "impurities". Differential scanning calorimeter (DSC) was used to compare purified and unpurified materials. The unpurified P(VDF-TrFE) appears to have plural peaks whereas the purified P(VDF-TrFE) has only one phase transition peak, at about 78^{o}C. Further, the purified P (VDF-TrFE) has a transition temperature approximately 10^{o}C higher than that of the unpurified material. It seems the solvent extraction was able to reduce non-polar phase in unpurified materials. According to Kim and Kim ferroelectrics having the higher Curie transition points have more trans sequences and less gauche defects, closer packing order, shorter intermolecular spacing and larger thickness of the crystalline along the chain axis [14]. These changes improve the pyroelectric properties of the material. The increase in the polar phase domain corresponds to the increase in capacitance, i.e., ability to hold electric charge.

Purification of P(VDF-TrFE) substantially enhanced electrical and pyroelectric properties. The electrical resistivity of the purified copolymer is approximately 35% higher than that of the unpurified copolymer. Subsequently we observed that the instances of short-circuiting in purified material under an intense electric field were reduced and preconditioning (pre-polarizing) process becomes easier. The pyroelectric conversion can therefore be operated at a significantly higher voltage and at a higher temperature without developing a large leakage current.

Figure 1 shows the copolymer resistivity as a function of pre-polarization time. It shows that the time required to achieve 'good' resistivity is easier for the purified copolymer than the unpurified (as received) copolymer.

We also investigated the effect of annealing on purified P(VDF-TrFE). These samples were annealed at 125^{o}C for 17 h in an oven. DSC showed that the annealing does not significantly affect melting temperatures of the purified material.

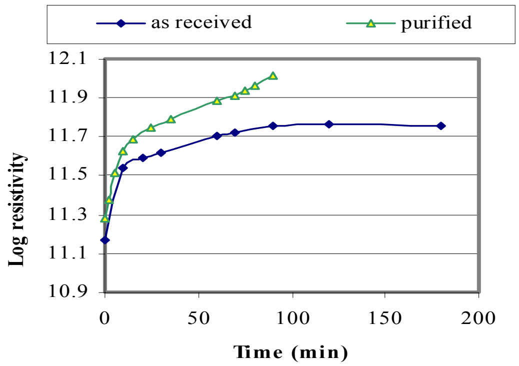


Fig. 1 - Pre-polarization time vs. Log (Δ_f) at constant 25 MV/m

Table 1 summarizes enthalpies and entropies at phase transition temperatures and melting temperatures for these Samples

3. Measuring Circuit

Figure 2 illustrates the measuring circuit used for pyroelectric conversion. A data acquisition system includes LabVIEW, Plug-in DAQ (Model AT-MIO-16F 5) and Signal Conditional Modules (SCXI-1000, 1100 and 1124) from National Instruments Corporation. It measures voltage on the pyroelectric film and the electric current that responds to change in temperature and control voltage. We measured output and input current to the pyroelectric film using R_1 and the applied voltage on the film using R_2. Resistors R_D and R_L serve as voltage dividers to scale down current signals in order to match the input limits of the measurement instruments. Applied voltage and current were monitored continuously. R_1, R_2, R_3 and R_4 were 10 kΣ, 200 Σ, 1 MΣ and 8 Σ respectively.

4. Expected Output

The overall heat absorbed by the copolymer near phase transition is used in two parts - lattice vibration and dipole change and we need to separate them. The lattice entropy change ΔS_L during the phase transition is given by $\Delta S_L = m\, C_p \ln(T_2/T_1)$, where m is the mass, C_p is the specific heat, T_2 and T_1 represent the end and the start of the transition temperatures respectively. The specific heat of 60/40 P(VDF-TrFE) determined away from the phase transition was 1.50 J/gK. We also determined by using DSC that the phase transition of the purified copolymer under zero electric field begins at 68°C and ends at 84°C. Thus, we estimate lattice entropy change $\Delta S_L = 0.0688$ J/g K. Assuming we operate the Olsen cycle at a temperature span of $\Delta T = 40^{o}C\text{-}97^{o}C$, we estimate the contribution from lattice vibration $\Delta Q_L = \Delta S_L \cdot \Delta T = 3.92$ J/g. entropy change $\Delta S_L = 0.0688$ J/g K. Assuming we operate the Olsen cycle at a temperature span of $\Delta T = 40^{o}C\text{-}97^{o}C$, we estimate the contribution from lattice vibration $\Delta Q_L = \Delta S_L \cdot \Delta T = 3.92$ J/g.

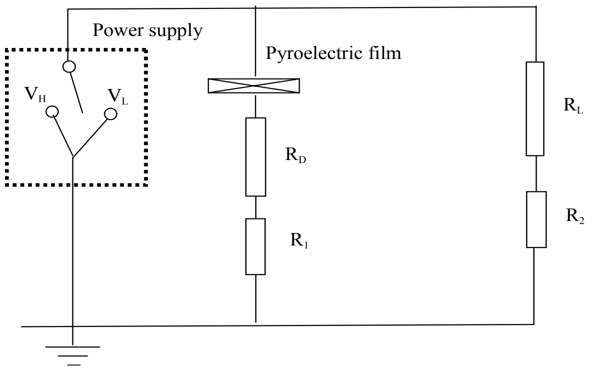


Fig.2- Latest measuring circuit

Table 1 - Thermodynamic properties of as received, as received but annealed, purified, and purified and annealed P (VDF-TrFE)

Sample	Transition			Melting			Reference
	Temperature (K)	Enthalpy (J/g) ΔH_T	Entropy (J/gK) ΔS_D	Temperature (K)	Enthalpy (J/g) ΔHm	Entropy (J/gK) ΔSm	
As received	343	3.87	0.011	417	18.9	0.45	*
	347	10.01	0.029	427	25.1	0.06	[13]
			0.031				[14]
As received, annealed	340	4.59	0.014	421	22.1	0.52	*
Purified	348	5.07	0.015	417	17.7	0.04	*
Purified, annealed	340	7.08	0.021	417	20.8	0.05	*

* present work

Dipole entropy change ΔS_D near the phase transition is given by $\Delta S_D = \Delta H_T/T_c$. This was obtained from the DSC measurement of the purified material as shown in Table l. ΔH_T is the additional heat flow into the sample above the lattice contribution near the phase transition and T_c the average Curie temperature (348 K).

The heat used for dipole change is given by $\Delta Q_D = \Delta S_D{\cdot}\Delta T$, where the entropy change ΔS_D during ferroelectric to paraelectric transition is 0.015 J/g K as reported in Table 1 and with a phase transition span of 16^oC, $\Delta Q_D = \Delta S_D{\cdot}\Delta T = 0.24$ J/g.

Therefore, the total heat input to the copolymer near the phase transition is $\Delta Q_T = 4.16$ J/g. This shows that if we run pyroelectric conversion with a 57^oC temperature span, to include the phase transition, then the pyroelectric conversion efficiency η in a single cycle is estimated as $\eta = (\Delta Q_D/\Delta Q_T) = 5.77\%$. This value corresponds to 37.5% of the Carnot efficiency of a heat engine that operates between 97^oC and 40^oC. In reality, we will configure a pyroelectric converter to utilize a well-known heat regeneration technique and thus we should be able to achieve even higher overall energy conversion efficiency. We can calculate net output energy density N from a single cycle per unit volume of the pyroelectric film using $N = (\Delta Q_D/V)/t$, where V is volume of the copolymer film and t is cycle time. Assuming P(VDF-TrFE) density is 1.93 g/cm^3 [17] and the cycle time 1.4 s, we estimate N is equal to 456 J/L (0.326 kW/L of copolymer used).

5. Measured Net Output

From Table 1, we can conclude that purified, not annealedMaterial has a higher transition temperature and consequently better pyroelectric properties. Purified P(VDF-TrFE) films were pre-conditioned by applying 45-48 MV/m electric field and used for pyroelectric conversion. The same electric field was used for preconditioning unpurified films in previous work [1]. We observed that the purification resulted in less electrical sparks (short circuits) during preconditioning and instances of film failure caused by the lead detachment from the aluminum electrode were significantly less.

The Olsen cycle was performed after the purified film was prepolarized at 85^oC and 500V (20 MV/m) for 90 min in order to achieve maximum film resistivity. Film dimensions were 2 cm by 5 cm by 25 µm thick. We compared the power output of the purified and unpurified materials (Fig. 3). V_{low} and V_{high} were 7 MV/m (175 V/25 µm) and 34.8 MV/m (870V/25 µm) respectively for both cases.

The average peak power for the purified film was 60 mW, which is about 33% more than that for the unpurified film(40 mW). Figure 4 compares integrated pyroelectric output from "as received" and "purified" copolymer. According to Figure 4, for the unpurified material the power output is very low due to the large leakage current.

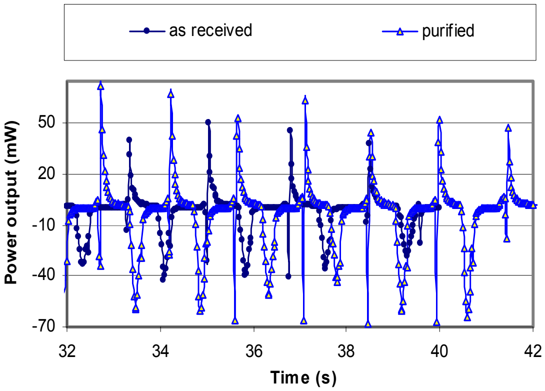
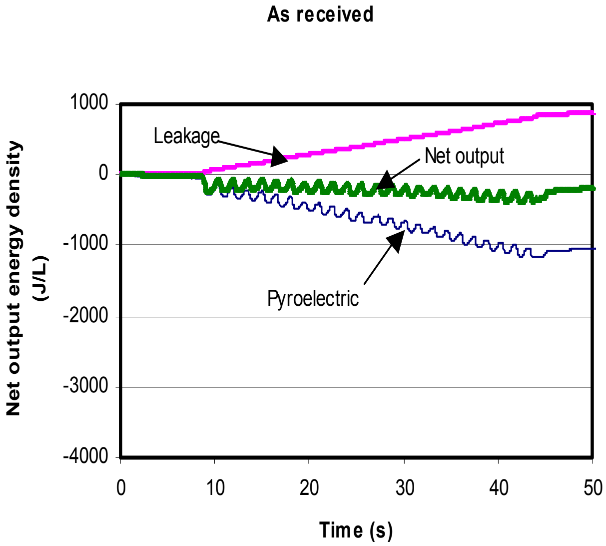


Fig. 3 - Comparison of power output


As received

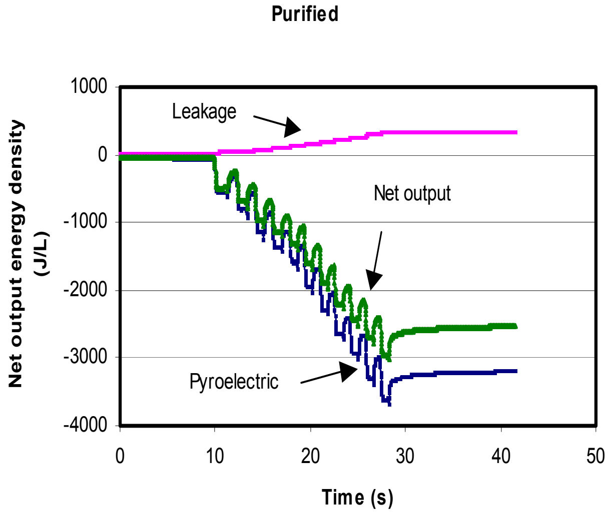

Purified

Fig. 4 - Integrated output at 40 ^oC-97^oC and applied voltage 400V-800V

The unpurified film was effective up to 24 MV/m (600 V/25 µm) and the purified film 34 MV/m (850 V/25 µm) above which the internal leakage current became detrimental to the net power output. We were able to increase the differential voltage on the purified film as high as 28 MV/m, above which internal leakage current became noticeable. The highest net output energy density at this V is 279 J/L (Fig.5).

This corresponds to 61% of the theoretical value (456 J/L of copolymer used) as estimated from the thermodynamic data for the purified P (VDF-TrFE) as presented in this paper.

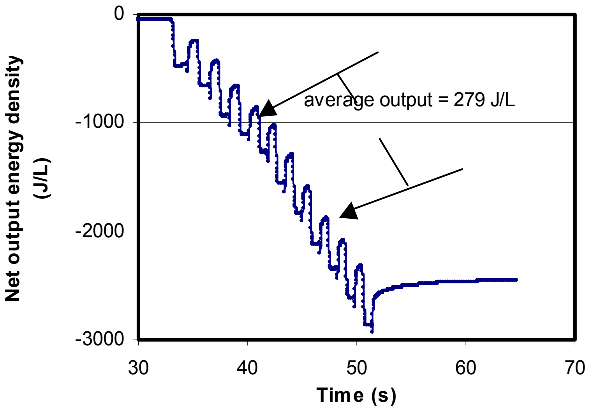


Fig. 5 - Cumulative net power output as a function of time for the Olsen cycle for purified (not annealed) material

6. Effect of Operating Conditions on Phase Transition Interval

According to previous studies by Date [18] and Ikura and Yu [1], the phase transition of P(VDF-TrFE) shifted to near 90°C to 100°C under a high electrical field and it becomes difficult to capture the whole phase transition when heat source temperature is limited to 100°C or less. We explored the effect of capturing the shifted phase transition temperature. This was done by plunging a prepolarized film at room temperature and high voltage into hot water near 100°C. As the film's ability to hold electrical charge near its phase transition temperature diminishes, the charge is released as a current. Figure 6 presents instantaneous pyroelectric power output. The phase transition temperature T_p was determined as the temperature at which highest pyroelectric output occurred. When the applied voltage increased, so did power output and phase transition. When the applied voltage was less than 36.4 MV/m, the power output still increased and the phase transition was at less than 100°C. But when the applied voltage V_{high} is equal to 36.4 MV/m, the power output decreases because of the increased leakage current at high temperature and voltage. At this voltage the phase transition temperature

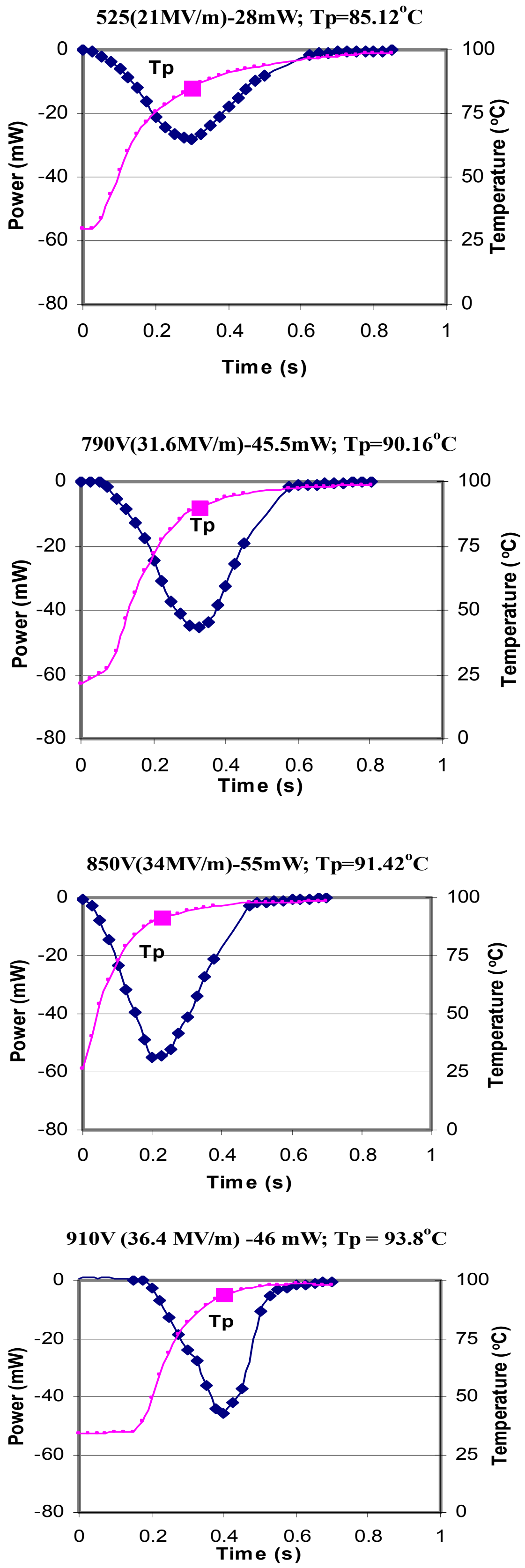


Fig. 6 – Pyroelectric power output and phase transition temperature (pT) at different electric field

still remained under 100 ^{o}C. Because of the increasing leakage current, it was not possible to study the effect of capturing the shifted phase transition temperature at higher voltages at this point of investigation. The electrical and pyroelectric properties of ferroelectric material still need to be improved if we were to use this method for phase transition determination.

7. Conclusion

We were able to purify commercial 60%/40% P (VDF-TrFE) copolymer to increase the resistivity of the material by about 35%. This allowed us to operate pyroelectric. We were able to purify commercial 60%/40% P (VDF-TrFE) copolymer to increase the resistivity of the material by about 35%. This allowed us to operate pyroelectric conversion at significantly higher voltage and at high film temperature. We were able to use the high limiting voltage (V_{high}) as high as 34 MV/m without developing large internal leakage. This V_{high} is 33% higher than what was possible with unpurified film (24 MV/m) and increased the net power output nearly three-fold from 95 J/L of unpurified copolymer to 279 J/L of purified copolymer. Proper prepolarization and high resistivity are key factors for superior pyroelectric materials that achieve high pyroelectric conversion efficiency. Further improvement of the electrical and pyroelectric properties of the material and changing the operation parameters, for example increasing T_{high}, will increase the pyroelectric conversion even higher by capturing the entire phase transition as it shifts to about 90^{o}C-100^{o}C under a high electric field.

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