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Elastocaloric and barocaloric effects in polyvinylidene di-fluoride-based polymers

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Polyvinylidene di-fluoride-based polymers were investigated for elastocaloric and barocaloric effects. Bulk samples were subjected to uniaxial tensile and hydrostatic loading. Resulting strain profile (function of temperature) was used to predict the temperature change. A peak elastocaloric effect of 1.8 K was observed at 298 K (15 MPa). Alternately, a large barocaloric effect of ~ 6 K was observed at 300 K (200 MPa). This was further improved to an astounding ~ 19 K near 368 K (200 MPa). The results of this study are expected to greatly benefit the field of ferroelectric solid-state refrigeration and open another horizon for future exploration of multicaloric effects in ferroelectric polymers. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4942000>]

Micro/nano scale refrigerators are posed to be the next generation cooling/heat pump devices.^{1–4} Conventional mechanical refrigeration systems suffer from severe performance degradation upon downscaling from macro-scale.^{5,6} Foremost, compressors cannot be scaled down to nano/micro scales. Therefore, there is a dire need to develop suitable alternatives for integrated cooling. Solid state refrigeration could be a prominent solution for on-board cooling as these are compressor free systems.^{1,4–6} These work on material's entropy change under an external field. Thermal response is registered in a material (heating/cooling) when subjected to a sudden change of an external field (electric, mechanical, magnetic). This phenomenon is known as the caloric effect (electrocaloric (EC), elastocaloric (eC), magnetocaloric (MC)).^{4–6} Some of these techniques (such as MC and thermoelectric) have been well explored by researchers and various designs have been proposed for specialized commercial applications.⁷ However, devices based on thermoelectric/magnetocaloric effects have relatively poor coefficient of performance (COP).^{1,2,5,6} In order to improve their performance, researchers are now interested in novel materials/efficient design phenomenon which possess either a high COP or the ability to demonstrate multiple or coupled caloric effects to enhance the cooling capacity. In this direction, materials which can demonstrate more than one caloric effect are expected to perform with higher COP when individual caloric effects can be coupled or are made to operate in a crossover.^{2,4–6} Multicaloric effect entails coupling of EC, MC, eC, and barocaloric (BC) effects. These caloric effects have been extensively investigated (except BC) in their respective class of materials.^{1,6–9} At the forefront of this field, shape-memory alloys have been used to demonstrate eC and MC effects in separate instances.^{8–13} However, other classes of materials have not been well explored for multicaloric effects. Recently, few interesting articles have attempted demonstration of eC effects in ferroelectric

materials, conventionally reported for EC effects.^{8,14–18} In this regards, ceramics such as PbTiO_3 ,¹⁵ BaTiO_3 ,¹⁶ $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$,¹⁴ $(\text{Ba}_x\text{Ca}_{1-x})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ (BCZTO),^{18–20} and $x\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – $1-x\text{PbTiO}_3$ ¹⁷ have been studied for stress driven caloric effects. This has sparked interest in the field of ferroelectric solid-state refrigeration through enhanced cooling of coupled caloric effects. However, research in this field is still at its preliminary stage and possibility exists for obtaining rapid improvement in terms of multicaloric cooling capacity. We have previously demonstrated that some classes of ferroelectric materials produce significantly larger temperature drops when subjected to ferroelastic depolarization.^{17,18} This effect can easily surpass even the maximum EC cooling capacity within the same material,¹⁸ hence suggesting the existence of large untapped potential of ferroelectric materials for eC cooling applications.

Polyvinylidene di-fluoride (PVDF) and its co-polymers are another important ferroelectric materials reported for giant EC in a wide temperature range.³ Additionally, PVDF has other advantages such as ease of fabrication (shape), low cost, and low processing temperatures.^{3,21} Further, PVDF being a cross-linked polymer (with high crystallinity) promises high potential for eC and BC refrigeration applications. Through this study, we have made an attempt to demonstrate eC and BC effects in PVDF. Such studies have not been reported so far. At this point, it becomes imperative to mention that BC effect has not been thoroughly examined for many material classes. BC effect has an analogy similar to vapor compression cycle, where heating and cooling effects are obtained using fluid compression and expansion. Giant barocaloric effect has been reported in various classes of magnetic materials including shape memory alloys and in one instance for BaTiO_3 single crystal.^{8–12,22} By general extension, other ferroelectric materials are also anticipated to produce significant BC effect due to polarization change, which is the major component in material's entropy change.^{15,22} However, there is a lack of any additional literature reported. Hence, present study also tries to account for estimation of BC cooling effect in ferroelectric PVDF.

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Some modern calorimeters exist which allow simultaneous measurement of thermal parameters under the influence of external stimuli.^{3,5,6} This allows for direct and *in situ* measurement of the caloric effects. However, such systems are few, and most predictions are based on results derived from either mean-field theory or Maxwell's relations.^{3,5,6} The choice of method for predicting the caloric effects is generally decided by considering two factors: (a) nature of material and (b) availability of experimental data.²³ Indirect assessment has been corroborated with those obtained directly and found to be in good agreement.²³ A few anomalies as recorded resulted often due to incorporation of an hysteretic second order phase transition. Hence in this study, we proceed by using Maxwell's relations as their use is justifiable. Magnitude of eC effect produced can be determined by using the Maxwell's relation for entropy change in ferroelastic (ΔS_{eC}) materials as follows:^{16,24}

$$\Delta S_{eC} = -\frac{1}{\rho} \int_{\sigma_1}^{\sigma_2} \left(\frac{\partial \epsilon}{\partial T} \right)_{\sigma} d\sigma. \quad (1)$$

Here, the symbols σ , ϵ , and ρ represent the conventional values of stress, strain, and density, respectively. By determining the isothermal entropy change of the material at any given temperature, the equivalent adiabatic temperature change obtainable (at the said temperature) can be determined by modifying Equation (1)^{16,24}

$$\Delta T_{eC} = -\frac{T}{\rho * c_p} \int_{\sigma_1}^{\sigma_2} \left(\frac{\partial \epsilon}{\partial T} \right)_{\sigma} d\sigma, \quad (2)$$

where the symbols T and c_p are used to denote the material's initial temperature and heat capacity, respectively. Equation (2) indicates that a material possessing a large strain gradient with respect to temperature will exhibit a large eC effect. Indeed, some of the largest eC effects have been demonstrated in ferroelastic materials including shape memory alloys and other cross-linked polymers.^{2,4,10} The theory behind the origin for eC effects in ferroelectric and other classes of materials has been well reported in the literature.^{2,4,16–19,24} Polarization and structural transitions are closely coupled in ferroelectric materials, and hence, it is to be expected that ferroelectric materials will possess elastocaloric effect.^{2,4,17,18} On the other hand, reports concerning BC abilities of different material classes are far and few. The Maxwell's relation for estimating BC temperature change in a given material is described as^{15,16}

$$\Delta T_{BC} = -\frac{T}{\rho * c_p} \int_{\sigma_1}^{\sigma_2} \left(\frac{\partial \epsilon_v}{\partial T} \right)_{\sigma} d\sigma_v. \quad (3)$$

In Equation (3), all symbols carry their usual meanings and the subscript v stands for volumetric parameters. Most reports concerning BC effects have been documented for magnetic shape memory alloys only,^{8–13} with the exception of BaTiO₃ single crystal²² and PbTiO₃.²⁵ However, preliminary results have yielded promising results indicating high cooling capacity near room temperature. This study aims to expand such study to include cooling capacity for PVDF.

In order to prepare the PVDF for mechanical testing, the PVDF granules (MW 530000) supplied by Sigma Aldrich

were melt mixed in Brabender plasticorder (Model: PLE 331) for 15 min at 448 K and then hot pressed at this temperature to obtain a sheet of area 150 mm² with 0.3 mm thickness. Hounsfield tensile testing machine (50KN) was used to load the films and obtain the necessary stress-strain data. Temperature was varied using an integrated cryo-chamber. The results for the same are plotted in Figure 1 (0–35 MPa and 298–373 K). To obtain the necessary data for eC measurement, strain was plotted as a function of temperature and tensile stress (0–15 MPa), represented as inset in Figure 1. 15 MPa was selected as the upper limit for the strain data corresponding to the highest elastic limit of the material under the selected parameters. XRD patterns of the PVDF polymer before and after load application are shown in Figure 2(a).

Figure 2(b) describes the strain gradient ($\frac{\partial \epsilon}{\partial T}$) as a function of stress and operating temperature. It can be clearly depicted from the figure that there exists an abrupt change in strain gradient at a temperature of 323 K. This phenomenon is seemingly unaffected by the loading conditions and is common to all stress values. The plot of specific heat as a function of temperature is shown in inset of Fig. 2(b) and has been adopted from a previous publication as reported by Roland *et al.*²⁶ These data were used in conjunction with Equation (2) to evaluate the eC temperature change profile and the same is depicted in Figure 2(c), while the corresponding entropy change is depicted in Figure 2(d). The ΔT_{eC} appears to increase with the intensity of loading. As the applied stress moves from 7.5 MPa to 15 MPa, the amount of cooling produced more than doubled from 0.7 K to 1.8 K, at 298 K. This stress induced large temperature change is due to significant entropy variation. In PVDF polymer, there could be a number of factors which could contribute towards entropy changes. PVDF can be elastically stretched to several percent which could be a major factor in contributing entropy change due to orientation of polymeric chains. Such a phenomenon is reported in natural rubber where significant elastocaloric effect is reported.²⁷ It is well documented that PVDF commonly crystallizes in non-polar crystalline α and γ phase²⁶ which is also evident from Figure 2(a). However, polar phase (β phase) is responsible for ferroelectric behavior. β phase can be induced via mechanical stretching of polymer as depicted in Figure 2(a). From Figure 2(a), it is clear that β phase is formed (along with small fraction of α phase) after elongation. In present study, tensile stretching will be responsible for orientation of polymeric chains and α to β phase transformation. Hence, elastocaloric effect in PVDF is due to change in free volume and structural transformation as well. However, their contribution is not quantified in this study. It is important to note that structural transformation (α/γ to β) can only contribute in caloric applications when it is a reversible transformation. It is only possible when this transformation occurs in the elastic region of PVDF polymer. The cooling capacity decreases with increase in operating temperature and a drastic reduction is observed at the phase transition temperature of 323 K. The prediction is in accordance to the original stress strain curves where this temperature marks a stark decrease in the mechanical strength of the polymer. The reported values are indicative of a large improvement in terms of cooling efficiency of bulk ferroelectric materials. Not only is the

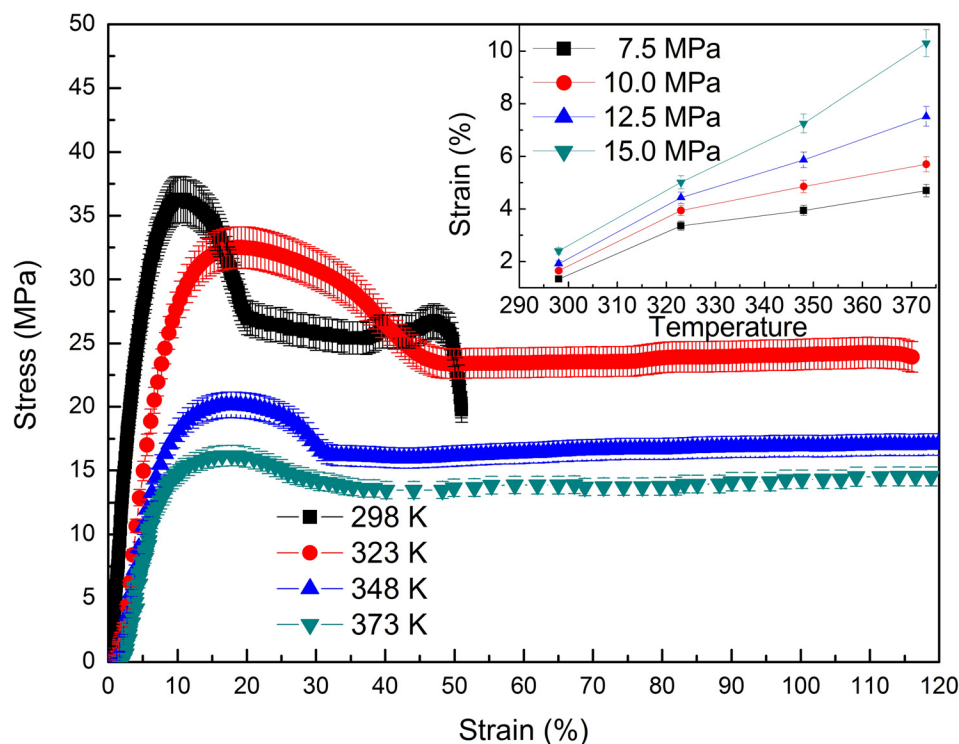


FIG. 1. Stress-strain for PVDF at different temperature. Inset shows strain versus temperature plots.

temperature drop (1.8 K) among the largest eC ever reported in bulk ferroelectric materials, but it has been obtained at a substantially lower value of applied stress (15 MPa) as opposed to 1.5 K reported for BCZTO composition for an applied stress of 250 MPa.¹⁸ Further, the peak temperature change has been achieved closer to room temperature and is relatively insensitive to temperature variation (albeit in a small window of operation). All these results are indicative of a substantial improvement in performance and would help expedite the realization of a practical multicaloric cooling system based on ferroelectric materials. As the value of

stress required is small, relatively smaller loading cells can be readily deployed for the purpose. Further, this combined with the already enhanced EC cooling capacity of the polymer will give it definitive edge over other contending materials.

In order to further evaluate the mechanical cooling capacity of PVDF-TrFE-CTFE (trifluoroethylene-chlorotrifluoroethylene), the volumetric stress-strain data were also utilized. Data for the same have been adopted from a previous publication as reported by Roland *et al.*²⁶ The volumetric strain as a function of stress and temperature so acquired has

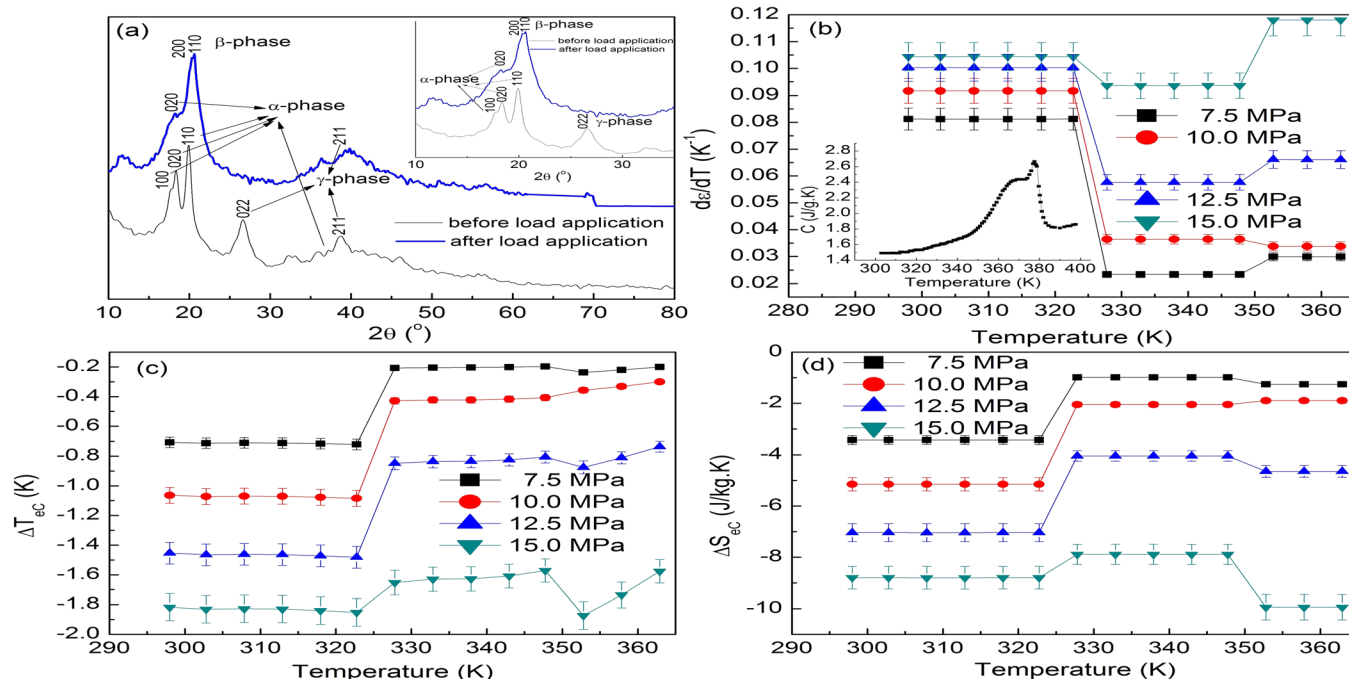


FIG. 2. (a) XRD, (b) $d\epsilon/dT$ (inset shows heat capacity c_p), (c) elastocaloric (ΔT_{ec}), and (d) corresponding entropy change (ΔS_{ec}) as a function of temperature at different loading.

been depicted in Figure 3(a). It can be clearly understood from the figure that thermal expansion acts to counter the volumetric strain resulting from hydrostatic pressure. The relationship between the two appears to be approximately linear, as is expected. Further, a small peak is observed between the pressure-volume graphs corresponding to the pressure induced α to β phase change, as documented by Roland *et al.*²⁶ A maximum volumetric strain of 0.03 could be obtained for an applied pressure of 200 MPa at 298 K. The mass specific heat capacity of the sample has been depicted in Figure 2(b). These data were used to estimate ΔT_{BC} by utilizing Equation (3) and the same is reported in Figure 3(b) and the corresponding entropy change is plotted in Figure 3(c). From Figures 3(a) and 3(b), it can be observed that a small peak corresponding to a large temperature change is observed near the phase transformation for the respective applied pressures. The phase transition corresponds to a drastic change in the mechanical properties and crystallinity of the polymer, and hence, this sudden increment in ΔT_{BC} is expected. Further, the temperature drop increases with increasing pressure, corresponding to the enhanced upper limit of the pressure in Equation (3). While the maximum temperature change for 10 MPa pressure is a significant 1.8 K, the highlight of the result lies at the staggeringly high temperature drop of ~ 19 K expected near 368 K for an applied pressure of 200 MPa. This value represents an order of magnitude improvement over the other results reported for bulk ferroelectric samples till date. Furthermore, mass specific entropy change also receives a corresponding increment. Even if the peak temperature change is excluded, the polymer, under 200 MPa pressure, can still boast of a substantial temperature drop of 6 K near 300 K (room temperature). Roland *et al.* have reported pressure induced phase transformation (α to β) in PVDF-TrFE-CTFE polymer.²⁶ It has been documented that hydrostatic pressure can drastically

influence PVDF-TrFE-CTFE structure like uniaxial tensile loading which will ultimately boost entropy change. This value is further improved as the temperature rises indicating the much desired self-adjusted cooling performance under enhanced thermal loading. Additionally, the overall BC performance of the polymer is fairly invariant of operating temperature. All these properties combined boast of a superior caloric performance which could propel PVDF-TrFE-CTFE for development of ferroelectric based solid-state refrigerators. In order to highlight the ramifications of the result, Table I has been provided with a list of some of the best known eC and BC materials reported till date along with their operating conditions, input normalized performance parameters, and the maximum temperature drop reported. Table I contains data for bulk materials only. It is clear that the values reported in this study are at par with some of the best reported materials till date, indicating the huge untapped potential of ferroelectric polymers for multicaloric effects. This study is also aimed to trigger extensive research in the field of eC and BC potential of other ferroelectric polymers displaying large recoverable strain.

Thus in summary, we have experimentally (indirectly) demonstrated eC and BC effects in PVDF-based polymers. Remarkably large elastocaloric response (ΔT_{eC} of 1.8 K) was observed under a tensile loading of 15 MPa at room temperature (298 K). Alternately, a large BC temperature change of ~ 6 K was observed near room temperature for an applied hydrostatic pressure of 200 MPa. This value was improved by an order of magnitude to an astounding ~ 19 K near the phase transition temperature of 368 K. The results of this study are expected to benefit greatly the field of ferroelectric solid-state refrigeration and open another horizon for future exploration of the regime of multicaloric effects in ferroelectric polymers.

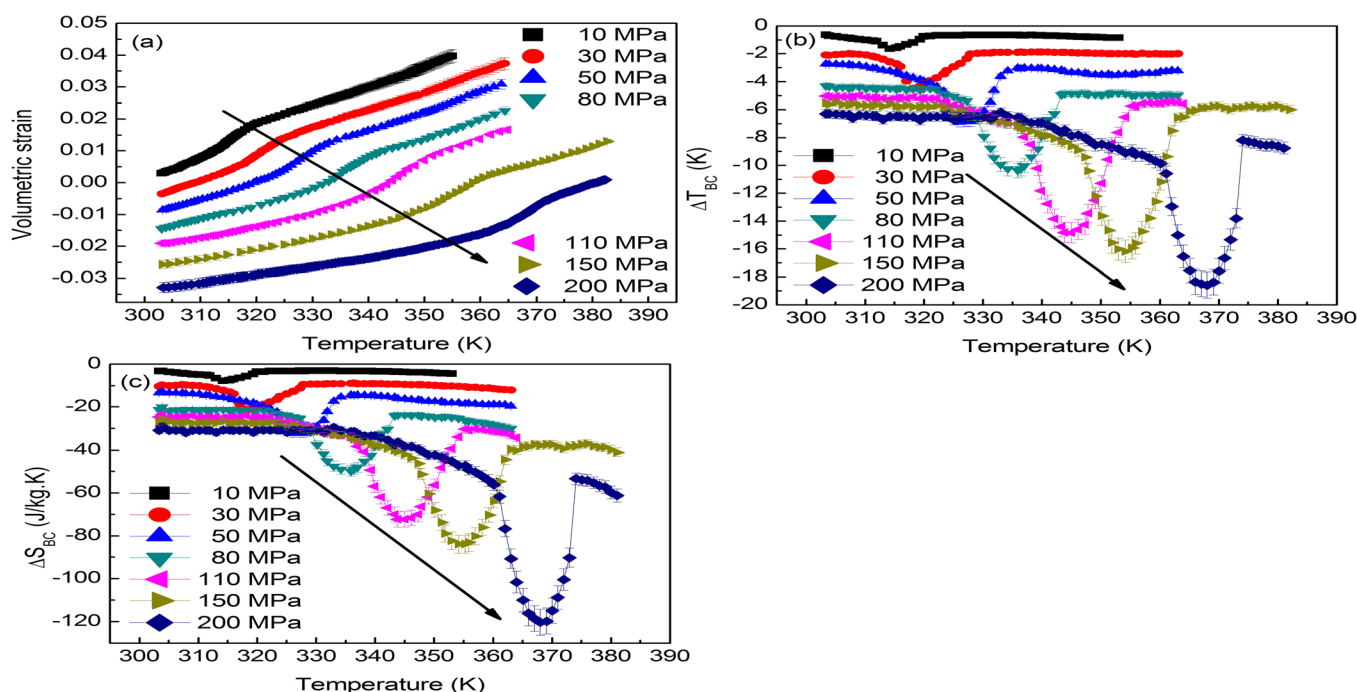


FIG. 3. (a) Volumetric strain, (b) barocaloric (ΔT_{BC}), and (c) corresponding entropy change (ΔS_{BC}) as a function of temperature under different hydrostatic pressure level.

TABLE I. Comparison of elastocaloric (eC) and barocaloric (BC) properties for various class of materials.

Compound	T (K)	ΔT (K)	σ/p(σ _v) (MPa)	(ΔT/dσ)/(ΔT/dp) (mK MPa ⁻¹)	References
eC					
Ba _{0.5} Sr _{0.5} TiO ₃	250	9	1000	9	14
PVDF	298	~1.8	15	120	Present work
PMN-32PT	323	0.36	28	12.8	17
BaTiO ₃	401	3.2	200	16	16
PbTiO ₃	750	20	1000	20	15
(Ba _{0.85} Ca _{0.15})(Zr _{0.1} Ti _{0.9})O ₃ (at 2MV m ⁻¹)	340	1.5	250	6	18
(Ba _{0.865} Ca _{0.135} Zr _{0.1089} Ti _{0.8811} Fe _{0.01})O ₃	298	1.4	200	7	19
(Ba _{0.865} Ca _{0.135} Zr _{0.1078} Ti _{0.8722} Fe _{0.01} Nb _{0.01})O ₃	298	1.17	200	5.85	20
BC					
Rb ₂ KMoO ₃ F ₃	200	16	500	32.00	12
La-Fe-Co-Si	230	2.2	210	10.48	9
Gd ₅ Si ₂ Ge ₂	267	1.2	200	6.00	13
Ni-Mn-In	291	4.5	260	17.31	10
MnAs (at 1 T)	300	20	150	133.33	11
Li(Fe _{0.89} Si _{0.11}) ₁₃	150	16	450	35.56	8
Li(Fe _{0.89} Si _{0.11}) ₁₃ (at 5 T)	170	13.8	450	30.67	8
Ni-Mn-In	350	3-4	250	14.00	28
BaTiO ₃	305	3	2000	1.50	22
La _{0.7} Pb _{0.3} MnO ₃	339	1.1	400	2.75	29
PVDF-TrFE-CTFE	368	~18.6	200	93	Present work
PbTiO ₃	758	2.2	30	73.33	25

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ERRATUM | SEPTEMBER 06 2018

Erratum: “Elastocaloric and barocaloric effects in polyvinylidene di-fluoride-based polymers” [Appl. Phys. Lett. 108, 072903 (2016)] **FREE**

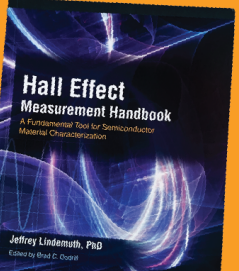
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Erratum: “Elastocaloric and barocaloric effects in polyvinylidene di-fluoride-based polymers” [Appl. Phys. Lett. 108, 072903 (2016)]

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The original paper⁶ reports on the elastocaloric and barocaloric effects in polyvinylidene di-fluoride-based polymers. Predictions were made based on original and previously reported experimental data in conjunction with Maxwell's relations. However, upon comparing the data with recently reported direct measurements, several discrepancies were identified. Most notably, the nature of temperature change was observed to carry an opposite sign (inverse) to those reported directly. In this erratum, we attribute this discrepancy to a sign error in the formulas used to calculate the change in entropy as a function of stress, in the published manuscript.

Hence, the following corrections need to be made in the original article:

1. Equation (1) in the original article should not carry negative sign and hence must be replaced by¹

$$\Delta S_{eC} = \frac{1}{\rho} \int_{\sigma_1}^{\sigma_2} \left(\frac{\partial \epsilon}{\partial T} \right)_{\sigma} d\sigma. \quad (1)$$

2. Extending the same analogy to hydrostatic systems, we arrive at the corresponding Maxwell equation^{2,3}

$$\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_p, \quad (2)$$

where p is the applied hydrostatic pressure and v represents the change in volume. Using Eq. (2), the new relationship for barocaloric entropy and temperature change (per unit volume) can be expressed as follows:

$$\Delta S_{BC} = - \frac{1}{\rho} \int_{\sigma_1}^{\sigma_2} \left(\frac{\partial \epsilon_v}{\partial T} \right)_{\sigma} d\sigma_v, \quad (3)$$

$$\Delta T_{BC} = \frac{T}{\rho * c_p} \int_{\sigma_1}^{\sigma_2} \left(\frac{\partial \epsilon_v}{\partial T} \right)_{\sigma} d\sigma_v. \quad (4)$$

In both Eqs. (3) and (4), the expressions σ_v and ϵ_v are used to represent volumetric stress (through applied hydrostatic pressure) and the corresponding volumetric strain produced in the material, respectively. Note that the new Eq. (4) for ΔT_{BC} does not carry a negative sign and must replace Eq. (3) in the original article.

3. On additional note, the term (c_p) should be replaced by (c_{σ}) which is heat capacity under constant stress. Indeed, for a high reliability prediction, the material parameters including specific heat capacity, strain and density must all be measured under similar loading conditions. However, the present work assumed specific heat capacities (c_{σ} or c_p) were essentially the same, adopting the approach of previously reported experiments.⁴ Therefore, all results and conclusion in the paper are not affected. The authors agree that this is a strong approximation as there is invariably a non-negligible component of specific heat that changes in the presence of stress. Furthermore, ideally dynamic values corresponding to the limits of integration must be employed. However, direct measurement of these parameters under external loading conditions is an experimentally challenging task. Hence, it is not uncommon to utilize a static value of specific heat capacity and density for the purpose of simplification.^{3,5}

Finally, as a result of the sign errors, the values represented on y-axis in Figs. 2(c) and 2(d) (original article) should be taken to be the absolute values of $|\Delta T_{eC}|$ and $|\Delta S_{eC}|$. Similarly, please read the values as $|\Delta T_{BC}|$ and $|\Delta S_{BC}|$ for Figs. 3(a) and 3(b) and corresponding $|\Delta T|$ in Table I.

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