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## Direct characterization of the electrocaloric effects in thin films supported on substrates

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We report a direct characterization of the electrocaloric (EC) effect in thin films clamped on substrates using micro-thermometers integrated onto the substrates. The measured temporal temperature profiles are analyzed using a 3D heat diffusion model to extract the adiabatic temperature changes. Thin-film thermometers with very different temperature coefficients of resistance are used to verify that experimental errors due to electric or electromagnetic coupling are negligible. Our approach captured asymmetry between the electrocaloric heating and cooling due to hysteresis and yielded adiabatic temperature changes that are consistent with the existing data on free-standing ter- and co-polymer films of similar compositions. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4816333>]

The electrocaloric (EC) effects represent changes in the entropy and hence the thermal state of a polarizable dielectric material in response to a change in an applied electric field. A number of recent studies explored the electrocaloric effects in organic and inorganic materials, especially their thin films, with potential applications in solid-state refrigeration.<sup>1,2</sup>

The large EC effects reported in thin films were often quantified using the “indirect method,” which involves an analysis of temperature-dependent polarization data using the Maxwell relations, or using calorimetric measurements.<sup>3</sup> Previous studies of the EC effects in relaxor ter-polymer films suggested a failure of Maxwell’s relations in samples exhibiting non-ergodic behavior.<sup>4</sup> Calorimetric characterization of the EC effects requires a separate measurement of the specific heat of an electrocaloric material, which is often assumed to be independent of the electric field due to experimental difficulties.

Synthesis of EC films very often require rigid and thermally stable substrates. Direct measurement of the EC effects in thin films supported on such substrates, however, is very challenging because the thermal mass of the films is much smaller than that of the substrate. Some previous studies used small-bead thermistors to measure the adiabatic temperature changes in free-standing foils of polymeric materials or multi-layer capacitor structures.<sup>5–7</sup> Although a direct characterization of the electrocaloric effects in thin ceramic films supported on substrates were reported in a previous study, no actual temporal temperature profiles or detailed thermal analysis were presented to help establish the validity and accuracy of the reported values.

A more recent study<sup>8</sup> used a scanning thermal microscopy probe and an infrared imager to directly measure the adiabatic temperature changes in multi-layer capacitor structures. Although one recognizes an intriguing potential of applying such approaches directly to thin films as prepared on substrates, they may find limited use due to the relatively poor temporal resolution of infrared imaging and the economic barrier of scanning thermal microscopy.

In the present article, we report a characterization approach for the electrocaloric effects (both heating and cooling) in thin EC films as prepared and/or clamped on an insulating substrate. Thin-film resistance thermometers, which double as bottom electrodes, are integrated directly onto the substrate to monitor transient temperature changes in response to the application or removal of electric fields across the EC thin films. Such thin-film thermometers can be readily prepared using a single lithography or shadow mask. The temporal temperature profiles were analyzed using 3D numerical simulations of heat diffusion to help establish the validity of our measurement approach. Metal films with very different temperature coefficients of resistance (TCR) were used as resistance thermometers to further verify that the measured resistance changes were not artifacts of electric or electromagnetic coupling.

Figure 1(a) schematically illustrates the cross section of our test structure. A serpentine thin-film thermometer (20 nm Ti/200 nm Au or W) of the overall width of 5 mm was first lithographically defined on a 0.5 mm-thick glass substrate. The thermometer also serves as the bottom electrodes for electrical biasing of an EC thin film deposited on it.

Thin films of a poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) (P(VDF-TrFE-CFE) 56.2:36.3:7.5 mol.%) terpolymer and a poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE) 55/45 mol.%) co-polymer were prepared using a solution-cast method. These polymer types were chosen in part because of the availability of extensive work on similar ter- or co-polymers in the literature<sup>1,6,9</sup> and, for the former, in part because of wider temperature ranges accessible to relaxor ferroelectric materials for solid-state EC refrigeration than typical ferroelectric materials. Powders of the ter- or co-polymer were first dissolved in methyl ethyl ketone (MEK) and stirred at 60 °C until the powders were completely dissolved. The polymer solution was then filtered using a 0.45 μm-pore size filter and spin coated at 500 rpm on the glass substrates with the prefabricated thin-film thermometers. The samples were subsequently annealed in a vacuum oven at 140–145 °C overnight to evaporate any residual solvent and volatile impurities. Dielectric properties of the films prepared

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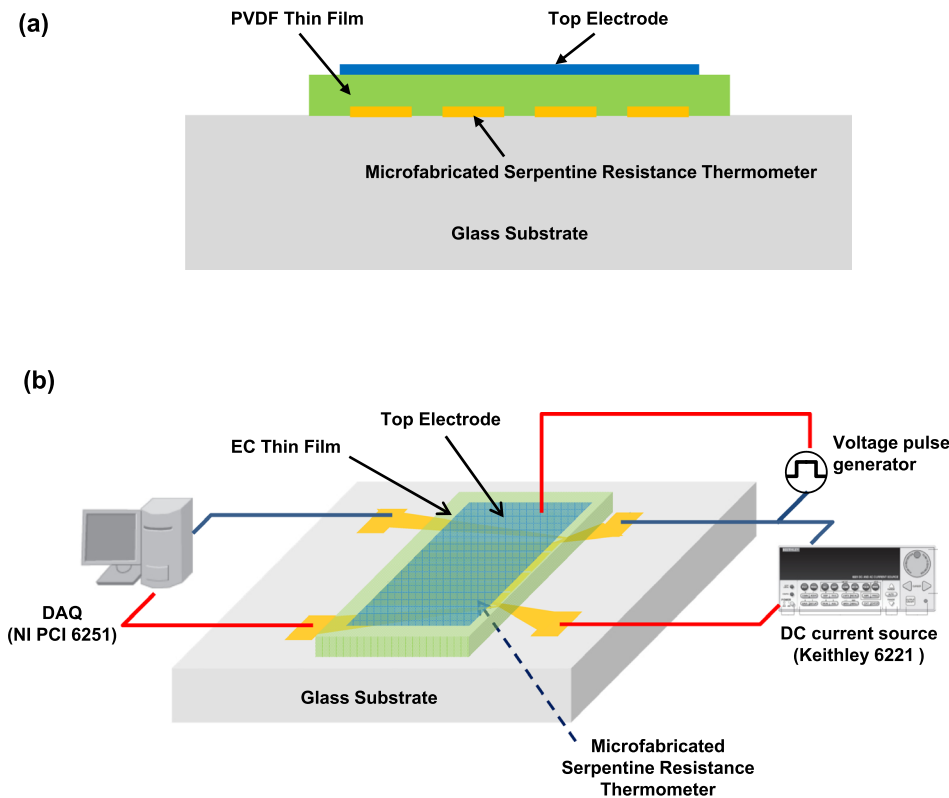


FIG. 1. (a) Cross section of a sample and (b) experimental setup for the characterization of the electrocaloric effects in thin films.

using a similar procedure were characterized and reported in multiple prior publications. The final film thickness was approximately  $5\ \mu\text{m}$ . A top electrode was formed last by depositing a 200-nm-thick aluminum film through a shadow mask.

Figure 1 also shows an experimental setup used in the present study. A current source (Keithley 6221) was used to apply a DC current of a fixed amplitude to the thin-film resistance thermometer. The resulting voltage drop was monitored using a PC-based analog-to-digital converter (PCI-6251, National Instruments) to determine the electrical resistance of the thermometer as a function of time. Finite Joule heating in the resistance thermometer also allows a fine control of the temperature of the EC films. The temperature coefficient of resistances of the thermometers was predetermined in separate calibration experiments. The voltage drop across the resistance thermometer was kept below 5 V, approximately two orders of magnitude smaller than the bias voltages applied across the EC films (200–500 V).

To induce EC heating or cooling, rectangular voltage pulses of varying magnitudes were applied to the top electrode. The rise and fall time of the voltage pulse were measured to be approximately 0.1 ms for all the cases reported in the present article. We note that non-rectangular (trapezoidal, triangular, sinusoidal, etc.) electric “pulses” may also be used with our technique. The magnitude of temperature changes and its interpretation, however, are different for different pulse shapes due in part to finite hysteresis in the electric field-polarization relations and in part to a finite timescale associated with thermal diffusion in the substrate.

In the present experiment, the duration of the voltage pulses was fixed at 100 ms, which is much longer than the voltage rise/fall time but is of the same order as the

characteristic time for heat diffusion into the substrate. We did not observe any significant change in the temporal temperature profiles even when the pulse duration was increased to 1 s.

Figure 2 shows a representative temporal temperature profile obtained in a single voltage pulse sequence using a resistance thermometer made of Au ( $\text{TCR} = 0.003\ \text{K}^{-1}$ ). The EC film first experienced rapid heating and then gradually cooled down to the initial set temperature due to heat diffusion into the substrate. We note that the EC film was maintained under a quasi-isothermal condition because heat diffusion into the substrate of a much larger thermal mass render the apparent temperature changes in the film much

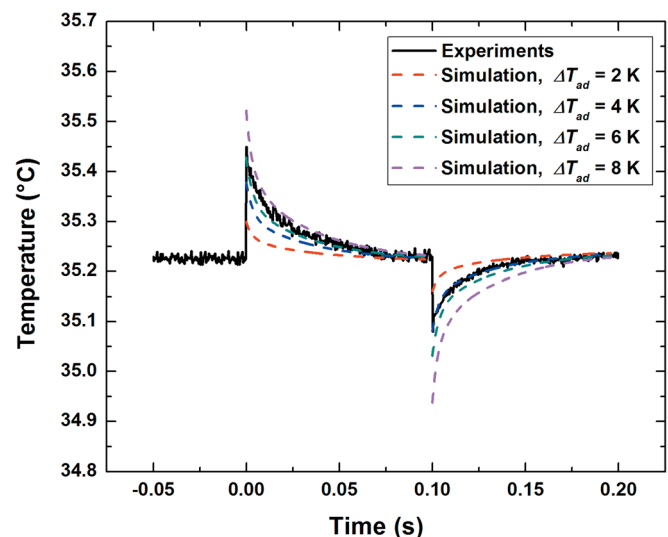


FIG. 2. Representative experimentally measured and numerically simulated temporal temperature profiles. A voltage pulse was applied between 0 and 0.1 s to apply an electric field of 80 MV/m across the EC film.

smaller than the true adiabatic values. No significant extra Joule heating caused by a leakage current across the EC film was observed for electric fields up to 110 MV/m. Repeated application of fields greater than that value resulted in irreversible degradation or breakdown of our films. When the bias voltage was removed, the EC film experienced rapid cooling and then gradually warmed up to the initial set temperature.

We solved the 3D transient heat diffusion equation using a finite element method to analyze the temporal temperature profiles acquired. The electrocaloric effects were modeled using a uniform volumetric heat source or sink in these simulations. The relevant thermophysical properties of the substrate (thermal conductivity = 1.0 W/m K, heat capacity per unit volume = 1.9 MJ/m<sup>3</sup> K) were independently characterized using the hot disk/wire techniques. The thermal diffusivity ( $1 \times 10^{-7}$  m<sup>2</sup>/s) of the EC film has a relatively small effect because heat diffusion time across the polymer film, approximately 0.25 ms, is much smaller than the characteristic time associated with heat diffusion into the substrate. Figure 2 shows results from the finite element simulations for different prescribed values of the adiabatic heating or cooling temperature changes  $\Delta T_{ad}$ . The best fit value is considered to represent  $\Delta T_{ad}$  of the film at that electric field. The simulated temperature profiles qualitatively reproduce the measured profiles very well, strongly suggesting that they indeed represent a thermal phenomenon and not an electrical artifact.

The peak EC heating temperature exceeds the peak EC cooling temperature, resulting in an asymmetric temporal temperature profile around the two switching transitions (field switched on or off). Such “hysteric” behavior was also observed in a calorimetric characterization of P(VDF-TrFE-CFE) terpolymer samples<sup>9</sup> and a direct characterization of BaTiO<sub>3</sub> single crystals.<sup>10</sup> This hysteresis decreases with the increasing temperature but at the expense of reduced absolute values of  $\Delta T_{ad}$  for a given electric field.

To further verify that the measured temperature profiles reflect real thermal phenomena and not experimental artifacts due to electric or electromagnetic coupling, we repeated the measurements using a resistance thermometer made of tungsten with TCR approximately 20 times smaller than that of Au. Figure 3 shows the normalized voltage changes obtained from the two different resistance thermometers. The measured normalized voltage changes (and therefore the relative change in the electrical resistance) scale directly with the measured TCR values. This confirms that an experimental error due to electric or electromagnetic coupling can be made negligible even in the presence of large swings in the electric field applied across EC thin films.

Figure 4 shows the extracted adiabatic cooling temperatures as a function of the electric field amplitude for the terpolymer films at 35 °C. Also plotted for comparison are the values reported in independent previous studies<sup>4,9</sup> of terpolymer films of similar compositions, which had to be removed from their original substrates for direct or semi-direct characterization. The present data are consistent with the existing data obtained using a direct method or a calorimetry-based semi-direct method but deviate substantially from the values

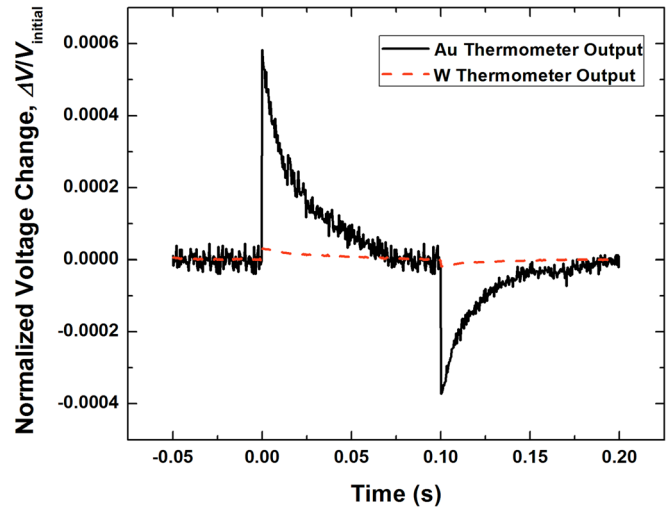


FIG. 3. Normalized voltage changes measured across the two different resistance thermometers with different temperature coefficients of resistance (Au and W). In the absence of any appreciable electric or electromagnetic coupling, the normalized voltage change is proportional to the electrical resistance, which is in turn proportional to the temperature change.

deduced from the pyroelectric coefficient using Maxwell’s relations. The use of Maxwell’s relations is known to be problematic for relaxor ferroelectric materials that exhibit non-ergodic behavior.

Previous modeling studies, as summarized by Valant,<sup>1</sup> suggested the impact of mechanical boundary conditions, thermal stress, and misfit strains on the EC effect in thin films. For free-standing films, a previous approximate phenomenological model for uniaxial ferroelectrics<sup>11</sup> yielded an expression for the EC-induced entropy change per unit volume,

$$ds^{FS} = -[\beta/2 + \alpha\beta(T - T_c)/2 + 3\alpha\gamma P^2/4]P^2, \quad (1)$$

where  $\beta$  and  $\gamma$  are the coefficients in the Landau-Devonshire phenomenological expansion of the Gibbs free energy and  $\alpha$

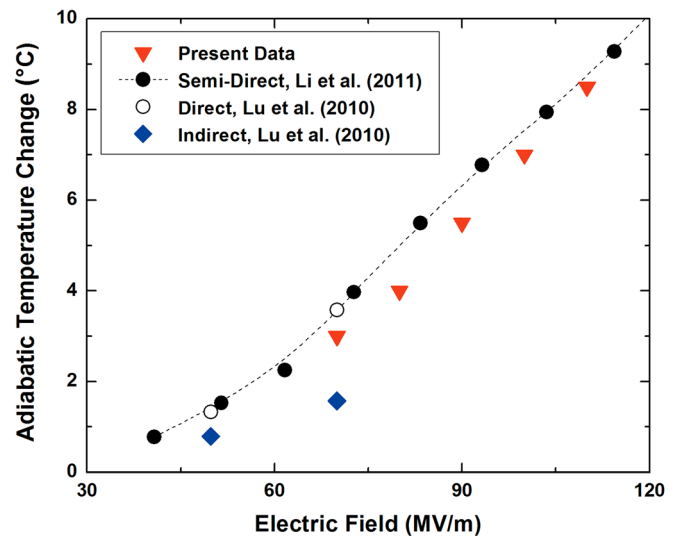


FIG. 4. Adiabatic EC temperature changes in response to the removal (cooling) of an electric field across the EC terpolymer thin film as a function of the electric field amplitude. The values extracted by analyzing the temporal temperature profiles using the 3D heat diffusion analyses are shown as the inverted triangles. Also shown for reference are the values reported in the literature for terpolymer films of similar compositions.



is the thermal expansion coefficient. The second and the third term represent the secondary electrocaloric effects due to interactions among the thermal expansion, strain, and polarization. These last two terms for the free standing P(VDF-TrFE) samples are estimated to be relatively small, accounting for approximately 25% of the total electrocaloric effect.<sup>11</sup>

Similarly, the entropy change for clamped uniaxial ferroelectric films may be approximated as

$$ds^{CF} = -[\beta/2 + 2\alpha Q_{12}P^2/(s_{11} + s_{12})]P^2, \quad (2)$$

where  $Q$  is the electrostrictive coefficient and  $s$  is the compliance tensor. The second term in the bracket represents the secondary EC effect for clamped quasi-isothermal samples, reflecting the interplay between thermal expansion and electrostriction to reduce the in-plane strain to zero. The second term is estimated to be approximately 10% of the total EC effect for the co-polymer samples. The adiabatic temperature changes measured previously from free-standing co-polymer films and those measured from our present experiments agreed also within  $\sim 20\%$ , consistent with the above estimates of the secondary EC effects.

In summary, the present work reports a direct thermal characterization of EC thin films clamped on a substrate. Microfabricated resistance thermometers are directly integrated onto the substrate to capture changes in the temperature of EC thin films at high temporal resolution as they are subjected to time-varying electric fields. The approach was validated by analyzing the measured temporal temperature profiles using full heat diffusion modeling and by using resistance thermometers made of materials with very different temperature coefficients of resistance. Our experiments captured asymmetry between the electrocaloric heating and cooling due to hysteresis and adiabatic temperature changes that are consistent with the results from independent previous studies on free-standing samples.

The present work establishes a versatile and efficient experimental technique to help rapidly screen EC thin films as grown on rigid and thermally stable substrates and also allow

further studies of the impact of mechanical conditions on the EC effects in thin films.

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