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Effect of inactive volume on thermocouple measurements of electrocaloric temperature change in multilayer capacitors of $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$

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Abstract

On increasing the active/total volume ratio of $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ multilayer capacitors (MLCs), the electrocaloric temperature change measured using a thermocouple near the centre increases, until saturating to reveal the nominally adiabatic limit ($|\Delta T| \sim 2.7$ K for rapid field changes of $|\Delta E| = 28.8$ V μm^{-1}). For all MLCs that we studied, the practice of multiplying the measured temperature change by the total/active heat capacity ratio causes the adiabatic temperature change to be overestimated by a small numerical factor. These findings highlight the challenge associated with quantifying electrocaloric effects in MLCs of the type that are currently being used as working bodies in prototype cooling devices.

Keywords: electrocaloric effect, ferroelectric ceramic, multilayer capacitor

S Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

Electrocaloric (EC) effects are reversible thermal changes that arise due to changes of electric field E, and tend to peak near ferroelectric phase transitions [1]. Bulk EC materials tend to display limited EC effects due to relatively small breakdown fields, but they have nevertheless been exploited in three [2–4] of the eight EC prototype coolers [2–9] that have now been demonstrated. Current activity in electrocalorics was stimulated by reports of giant EC effects in films of ceramic [10, 11] and polymer [12] materials, but a single film cannot generate significant cooling power. However, the technology for fabricating an assembly of ceramic films in the form of an MLC is well established, and EC effects have been demonstrated in commercial [13] and bespoke [5, 14–19] MLCs. Such MLCs possess a suitable geometry for EC applications [20], and have been exploited as the working body in the majority of EC prototype coolers [5–9].

While developing MLCs that show larger EC effects, accurate parameterization can be challenging because of heat exchange between active EC regions and the surrounding inactive regions (figure 1(a)). In particular, it can be difficult to establish values of adiabatic temperature change ΔT, even though this is perhaps the most important parameter for an EC working body because it drives heat flow, just as a voltage drives electrical current. For MLCs manufactured by the fully automated commercial process, the inactive volume fraction can be small, permitting good correspondence between direct measurements of MLC temperature change and indirect measurements of the active region [13]. However, MLCs under

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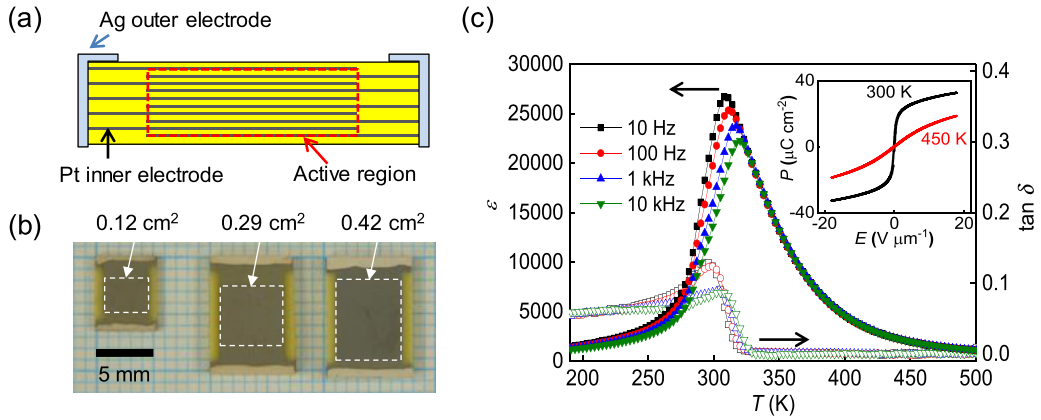

Figure 1. MLCs based on PMN–PT. (a) Schematic cross-section of MLC structure. (b) Photograph of three MLCs with an active area per layer of 0.12, 0.29 and 0.42 cm^2 within dashed lines. (c) For the 19-layer MLC with an active area per layer of 0.29 cm^2, we show the temperature and frequency dependences of relative dielectric constant ε and loss tangent tan δ, and (inset) electrical polarization P versus electric field E measured at 5 Hz, at 300 K and 450 K.

development are fabricated manually or by a semi-automatic process, resulting in inactive regions that form a relatively large fraction of the total MLC volume.

Here we investigate how thermocouple measurements of EC temperature change are influenced by the active/total volume ratio, using MLCs of $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PMN–PT, $x \sim 0.1$), which is known to be a good EC material based on studies of thin films [11], bulk samples [21–23] and MLCs [17–19]. We find that rapidly driven EC effects are highly adiabatic if measured near MLC face centres that lie sufficiently far from the inactive EC material. Specifically, the measured temperature jump ΔT_j tends towards adiabatic change ΔT if the active/total volume ratio is sufficiently large, such that there is no significant thermalisation within the MLC on the time scale during which ΔT_j is measured. We identify this limit to be adiabatic in spite of the (electrically insulated) Cu heater stage used to vary the starting temperature[4], given that suspending MLCs on their voltage leads has no discernible influence on (room-temperature) measurements of ΔT_j at the top surface.

As described in supplementary material[4], MLCs fabrication was based on solid-state reaction, and x-ray diffraction confirmed that the PMN–PT ceramic contained just a few percent of a parasitic pyrochlore phase. The cross-sectional schematic (figure 1(a)) shows the Ag outer electrodes, the Pt inner electrodes, and the active EC region (within red dashed line) where the applied electric field is strong. We will ignore fringing fields near the floating ends of inner electrodes, such that the surrounding material is considered inactive. However, when calculating inactive volume, we will not include the distant outer electrodes, and we will not take into account the thermal mass of the measurement set up (supplementary figure 2)[4]. Photographs of three MLCs appear in figure 1(b).

All MLCs had PMN–PT layers of thickness ~35–39 μm, and inner electrodes of thickness ~2 μm. However, as summarized in table 1, different MLCs possessed different numbers of active layers (9, 14 or 19), different active areas per layer (0.12, 0.29 or 0.42 cm^2), and different inactive volumes, yielding different active/total volume ratios. By comparing different MLCs in figure 3(b) we will show that the active/total volume ratio for the 19-layer MLC with an active area per layer of 0.29 cm^2 was large enough to permit highly adiabatic thermocouple measurements of temperature change at the face centre. All other figures in this paper show data for that MLC alone.

Dielectric and ferroelectric properties were measured by using an impedance analyzer (Novocontrol technologies, Broadband Dielectric Spectrometer) and a ferroelectric tester (Radiant Technologies, Precision Premier II Ferroelectric Tester). The measurement temperature was controlled by placing the MLCs on a Cu heater stage via a 0.2 mm-thick sheet of PTFE (supplementary figure 2)[4], and controlling the temperature of the heater stage using a RIKO controller. High voltages of up to 1000 V were applied to the MLCs using an ultra-high resistance meter (ADVANTEST, R8340A). EC temperature change was measured using a K-type thermocouple (diameter 0.05 mm) that was attached to the centre of each MLC face using adhesive kapton tape, and read using a Keithley 2000 digital multimeter. These measurements of EC temperature change were corroborated using an infrared (IR) camera (Optris, PI200) with low temperature resolution. All values of EC temperature change presented in this paper represent measured data that has not undergone any form of correction.

The 19-layer MLC with an active area per layer of 0.29 cm^2 was characterized by observing (1) a peak in relative permittivity that shifted to higher temperatures with increasing measurement frequency (figure 1(c)), (2) ferroelectricity with a saturation polarization in excess of 30 $\mu C\ cm^{-2}$ at 300 K (black data, inset of figure 1(c)), and (3) the nearly complete loss of ferroelectricity at 450 K (red data, inset of figure 1(c)). These properties are very similar with respect to previous reports [24], evidencing the good quality of PMN–PT in our MLCs.

[4] See supplementary material at stacks.iop.org/JPhysD/50/424002/mmedia regarding MLC fabrication and characterization, the measurement set-up, and the dependence of EC effects on active volume alone and inactive volume alone.

Table 1. Details of MLC geometry. For all MLCs, inner electrode thickness ~2 μm, PMN–PT layer thickness ~35–39 μm, and the inactive volume does not include the outer electrodes. The volume ratio given in the last column is used as 'correction' factor α in the inset of figure 3(b).

Number of layer	Active area per layer (cm^2)	Total active area (cm^2)	Active volume (mm^3)	Inactive volume (mm^3)	Volume ratio (total/active)
9	0.12	1.1	3.5	8.8	3.57
19	0.12	2.3	7.4	16	3.13
9	0.29	2.8	9.0	16	2.78
14	0.29	4.4	14	23	2.63
19	0.29	6.0	23	34	2.50
19	0.42	8.0	30	27	1.89

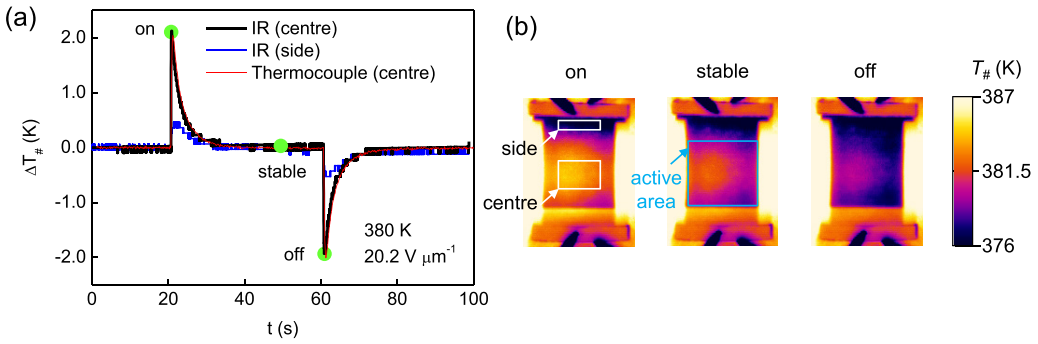

Figure 2. IR camera measurements of EC effects in the 19-layer MLC with an active area per layer of 0.29 cm^2, at starting temperature = 380 K. (a) EC temperature change $\Delta T_{\#}(t)$ averaged over the centre area (lower white rectangle in (b)) that lies within the active area (blue rectangle in (b)), and the side area (upper white rectangle in (b)), when 20.2 V μm^{-1} was applied at time $t \sim 20$ s and removed at $t \sim 60$ s. Data measured with the thermocouple at the centre are included for comparison. (b) Maps of MLC temperature $T_{\#}$ at three representative times (green dots in (a)).

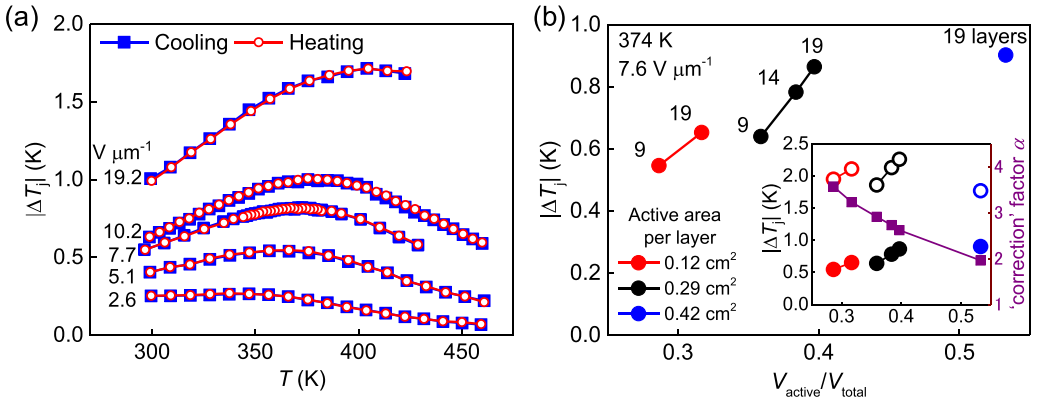

Figure 3. Variation of EC temperature change with field change, starting temperature, and MLC geometry. (a) For the MLC of figure 2, we plot cooling-jump magnitude $|\Delta T_j|$ versus the starting temperature T achieved on heating and cooling, for the field changes indicated. (b) For MLCs identified via the number of active layers and the active area per layer, field changes of 7.6 V μm^{-1} at starting temperature 374 K produce cooling jumps whose magnitude $|\Delta T_j|$ varies with V_{active}/V_{total}. Inset: $|\Delta T_j|$ data from the main panel are replotted, and multiplied by 'correction' factor α, to yield incorrect values of $|\Delta T_j|$ (open circles). All data were measured in the centre areas of the MLCs using the thermocouple.

For the same 19-layer MLC with an active area per layer of 0.29 cm^2, we used both the thermocouple and IR camera to measure EC temperature change $\Delta T_{\#}$ versus time t, due to field changes of 20.2 V μm^{-1} at a starting temperature of 380 K (figure 2). The thermocouple at the face centre recorded $\Delta T_j \sim 2.1$ K on field application, a subsequent return to the starting temperature that implies negligible Joule heating, and $\Delta T_j \sim -2.1$ K on field removal (red data, figure 2(a)). These values of ΔT_j are very similar to the nominally adiabatic values of ΔT (black data, figure 2(a)) that were identified by averaging data obtained from the IR camera for the MLC centre area, which lies within the active area. These IR data were obtained from a series of images, three of which show how the centre area becomes hot, returns to near the starting temperature, and then becomes cold (figure 2(b)). We observed considerably smaller changes of temperature in the MLC side area

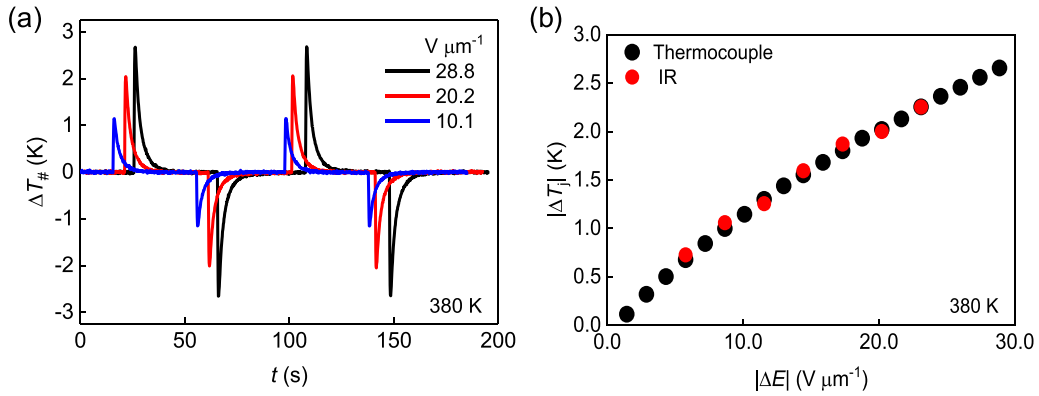

Figure 4. Variation of EC temperature change with field change. (a) For the MLC of figure 2 at starting temperature 380 K, we plot EC temperature change $\Delta T_{\#}$ versus time t for selected fields that were alternately applied and removed at ~40 s intervals before increasing the magnitude. Hence (b) the magnitude of the cooling jump $|\Delta T_j|$ versus field change $|\Delta E|$. Data in (a) and (b) were measured using the thermocouple at the centre of the MLC. Data measured in the centre area of the MLC using the IR camera are included in (b) for comparison.

that lies outside the active area (figure 2(b)), for which $|\Delta T_j|$ ~ 0.5 K (blue data, figure 2(a)). These EC effects just outside the active area arise due to heat exchange with the active area.

The 19-layer MLC with an active area per layer of 0.29 cm^2 was also studied using the thermocouple to measure $|\Delta T_j|$ in the face centre while varying the starting temperature and the magnitude of the field change (figure 3(a)). Values of cooling-jump magnitude $|\Delta T_j|$ measured while increasing and decreasing the starting temperature were very similar, and showed a peak at higher starting temperatures when using higher fields due to the field-induced growth of polar nano-regions [23]. The largest value of $|\Delta T_j|$ ~ 1.7 K was obtained near 400 K using the maximum field change of 19.2 V μm^{-1}, implying an EC strength of $|\Delta T_j|/|\Delta E|$ ~ 0.089 K $\mu m\ V^{-1}$. This highly adiabatic temperature change measured at the face of a suitable MLC represents an improvement with respect to non-adiabatic measurements of a single 38 μm-thick layer of PMN–PT on a substrate, where scanning thermal microscopy recorded $|\Delta T_j|$ ~ 0.23 K for $|\Delta E|$ ~ 10.5 V μm^{-1} [25], such that $|\Delta T_j|/|\Delta E|$ ~ 0.02 K $\mu m\ V^{-1}$ was four times smaller than the value recorded here with many such EC layers and no substrate.

Our key result is that the EC temperature change $|\Delta T_j|$ measured with the thermocouple at MLC face centres only saturates near the adiabatic limit ($|\Delta T|$ ~ 0.9 K for the modest field change $|\Delta E| = 7.6$ V μm^{-1} starting at 374 K) provided that the active volume is large enough with respect to the total volume (figure 3(b)), as demonstrated using six geometrically different MLCs based on ~35–39 μm-thick layers of PMN–PT (table 1). When the active volume is too small with respect to the total volume, the observed suppression of $|\Delta T_j|$ arises primarily because heat exchange between the active and inactive regions compromises the intended heat exchange between the active regions and the thermocouple. Heat exchange between the active regions and the Cu heater stage is not relevant given that MLCs show equivalent values of $|\Delta T_j|$ when suspended. Having established that both of our 19-layer MLCs with active areas per layer of 0.29 cm^2 and 0.42 cm^2 show highly adiabatic changes of temperature (figure 3(b)), either could have been used to generate the other figures in this paper, but we selected the MLC with the smaller area as it is less prone to breakdown.

The reader may note that the heat exchange between active and inactive regions would be irrelevant when measuring at the face centre of an MLC with sufficiently large area, but $|\Delta T_j|$ would probably be suppressed by a reduced breakdown field, such that our observed variation of $|\Delta T_j|$ with active/total volume ratio may hold true a little more generally than we have shown here. The reader may also note that the correlation between active and inactive volumes permits the possibility of a non-monotonic increase of $|\Delta T_j|$ with increasing active volume (supplementary figure 3(a))[4], and explains the counter-intuitive tendency for $|\Delta T_j|$ to increase with increasing inactive volume (supplementary figure 3(b))[4].

If we attempt to follow the approach adopted elsewhere [19] and correct the measured values of $|\Delta T_j|$ (figure 3(b)) by assuming that the MLC has thermalized prior to measurement, then we would multiply our measured values by a 'correction' factor $\alpha = C_{total}/C_{active}$ to attempt to obtain adiabatic temperature change $|\Delta T|$ for the active region. Assuming that this total/active heat capacity ratio is given by the total/active volume ratio of our six MLCs (table 1), we find 'corrected' values that exceed the adiabatic limit ($|\Delta T|$ ~ 0.9 K for 7.6 V μm^{-1} starting at 374 K) by a small numerical factor (inset, figure 3(b)). Therefore no such correction factor is valid here.

In our final experiment on the 19-layer MLC with an active area per layer of 0.29 cm^2, we used the thermocouple at the face centre to measure EC temperature change $\Delta T_{\#}$ versus time t at a starting temperature of 380 K, while increasing the value of the field change until breakdown (figure 4(a)). Our highest field change of $|\Delta E| = 28.8$ V μm^{-1} resulted in ΔT_j ~ 2.7 K on field application, a subsequent return to the starting temperature that implies negligible Joule heating, and ΔT_j ~ −2.7 K on field removal (black data, figure 4(a)). The variation of the nominally adiabatic cooling-jump magnitude $|\Delta T_j|$ with $|\Delta E|$ was slightly sublinear, as confirmed using the IR camera (figure 4(b)), and as seen for single layers of PMN–PT prepared similarly [25]. Using the heat capacity and density

Table 2. EC temperature change $|\Delta T|$ for MLCs and bulk samples of 0.9PMN–0.1PT (0.92PMN–0.08PT in [18]). Line 1 presents our largest value of $|\Delta T|$, while lines 2–3 demonstrate the equivalence of our two measurement techniques.

Sample type	$\|\Delta T\|$ (K)	$\|\Delta E\|$ (V μm^{-1})	Breakdown field (V μm^{-1})	Measurement	Reference
MLC	2.7	28.8	>28.8	Thermocouple	This work
MLC	2.3	23.1	>28.8	Thermocouple	This work
MLC	2.3	23.1	>28.8	IR camera	This work
MLC	0.17	2	~10	Thermocouple	[18]
MLC	2.3[a]	10	~10	Thermistor	[19]
Bulk	3.5	16	~16	Thermistor	[26]
Bulk	1.2	5	—	Thermocouple	[23]

[a] Denotes data obtained after multiplying the measured temperature change by a 'correction' factor of 2.86.

values that we reported previously [25], the maximum value of $|\Delta T_j| \sim 2.7$ K corresponds to an isothermal heat of ~0.19 J, or 918 J kg^{-1} when normalized by the mass of the active region.

The EC properties of our MLCs compare favourably with respect to the EC properties of PMN–PT layers of similar or greater thickness, as found in MLCs [18, 19] and bulk samples [4], respectively (table 2). Detailed comparison with these other MLCs is not straightforward due to differences in MLC structure, but our maximum values of $|\Delta T_j| \sim 2.7$ K and $|\Delta E| = 28.8$ V μm^{-1} exceed the values recorded for these other MLCs. Our high breakdown strength comes primarily from the high quality of the ceramic material in our MLCs, and may also arise in part because mechanical stress associated with piezoelectricity in the active regions is suppressed by clamping from the inactive regions.

In summary, we have shown that one may achieve good adiabaticity when using a thermocouple to measure rapidly driven EC effects in MLCs, provided that the active MLC volume is sufficiently large with respect to the inactive volume. Therefore adiabatic temperature change can be accurately determined for EC materials at high field by using a thermocouple to measure MLCs that are constructed in a suitable geometry for both measurement and applications. Our 19-layer MLC with an active area per layer of 0.29 cm^2 possesses a high breakdown strength of 28.8 V μm^{-1} at a starting temperature of 380 K, permitting large and highly adiabatic EC effects of $|\Delta T_j| \sim 2.7$ K. These EC effects are large enough to be exploited in prototype EC coolers, given that they are larger than the EC effects arising in the MLCs used previously for this purpose [5–9]. Increasing the active volume may reduce the large breakdown field, so one should construct prototypes that exploit many MLCs in parallel, such that the failure of an individual MLC can be tolerated, as seen with LEDs in modern UK traffic lights. In future, it would be desirable to better understand heat flow in MLCs and their surroundings by using high-resolution IR imaging and finite element analysis.

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References

[1] Moya X, Kar-Narayan S and Mathur N D 2014 Caloric materials near ferroic phase transitions *Nat. Mater.* **13** 439
[2] Sinyavsky Y V, Pashkov N D, Gorovoy Y M and Lugansky G E 1989 The optical ferroelectric ceramic as working body for electrocaloric refrigeration *Ferroelectrics* **90** 213
[3] Sinyavsky Yu and Brodyansky V M 1992 Experimental testing of electrocaloric cooling with transparent ferroelectric ceramic as working body *Ferroelectrics* **131** 321
[4] Plaznik U, Kitanovski A, Rožic B, Malic B, Uršic H, Drnovšek S, Cilenšek J, Vrabelj M, Poredoš A and Kutnjak Z 2015 Bulk relaxor ferroelectric ceramics as a working body for an electrocaloric cooling device *Appl. Phys. Lett.* **106** 043903
[5] Gu H, Qian X, Li X, Craven B, Zhu W, Cheng A, Yao S C and Zhang Q M 2013 A chip scale electrocaloric effect based cooling device *Appl. Phys. Lett.* **102** 122904
[6] Jia Y and Ju S 2012 A solid-state refrigerator based on the electrocaloric effect *Appl. Phys. Lett.* **100** 242901
[7] Wang Y D, Smullin S J, Sheridan M J, Wang Q, Eldershaw C and Schwartz D E 2015 A heat-switch-based electrocaloric cooler *Appl. Phys. Lett.* **107** 134103
[8] Sette D, Asseman A, Gérard M, Strozyk H, Faye R and Defay E 2016 Electrocaloric cooler combining ceramic multi-layer capacitors and fluid *APL Mater.* **4** 091101
[9] Blumenthal P, Molin C, Gebhardt S and Raatz A 2016 Active electrocaloric demonstrator for direct comparison of PMN–PT bulk and multilayer samples *Ferroelectrics* **497** 1
[10] Mischenko A S, Zhang Q, Scott J F, Whatmore R W and Mathur N D 2006 Giant electrocaloric effect in thin-film $PbZr_{0.95}Ti_{0.05}O_3$ *Science* **311** 1270
[11] Mischenko A S, Zhang Q, Whatmore R W, Scott J F and Mathur N D 2006 Giant electrocaloric effect in the thin film relaxor ferroelectric 0.9 $PbMg_{1/3}Nb_{2/3}O_3$–0.1 $PbTiO_3$ near room temperature *Appl. Phys. Lett.* **89** 242912
[12] Neese B, Chu B, Lu S-G, Wang Y, Furman E and Zhang Q M 2008 Electrocaloric effect in ferroelectric polymers near room temperature *Science* **321** 821
[13] Kar-Narayan S and Mathur N D 2010 Direct and indirect electrocaloric measurements using multilayer capacitors *J. Phys. D: Appl. Phys.* **43** 032002
[14] Lawless W N and Clark C F 1987 Dielectric and electrothermal measurements on $(Cd_{0.83}Pb_{0.17})_2Nb_2O_7$ at liquid-nitrogen temperatures *Phys. Rev.* B **36** 459

[15] Shebanovs L, Borman K, Lawless W N and Kalvane A 2002 Electrocaloric effect in some perovskite ferroelectric ceramics and multilayer capacitors *Ferroelectrics* **273** 137
[16] Bai Y, Zheng G and Shi S 2010 Direct measurement of giant electrocaloric effect in $BaTiO_3$ multilayer thick film structure beyond theoretical prediction *Appl. Phys. Lett.* **96** 192902
[17] Hirose S, Usui T, Crossley S, Nair B, Ando A, Moya X and Mathur N D 2016 Progress on electrocaloric multilayer ceramic capacitor development *APL Mater.* **4** 064105
[18] Molin C and Gebhardt S 2016 PMN–8PT device structures for electrocaloric cooling applications *Ferroelectrics* **498** 111
[19] Fulanovic L, Drnovšek S, Uršic H, Vrabelj M, Kuščer D, Makarovic K, Bobnar V, Kutnjak Z and Malic B 2017 Multilayer $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ elements for electrocaloric cooling *J. Eur. Ceram. Soc.* **37** 599
[20] Kar-Narayan S and Mathur N D 2009 Predicted cooling powers for multilayer capacitors based on various electrocaloric and electrode materials *Appl. Phys. Lett.* **95** 242903
[21] Xiao D Q, Wang Y C, Zhang R L, Peng S Q, Zhu J G and Yang B 1998 Electrocaloric properties of $(1 - x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ ferroelectric ceramics near room temperature *Mater. Chem. Phys.* **57** 182
[22] Hagberg J, Uusimäki A and Jantunen H 2008 Electrocaloric characteristics in reactive sintered 0.87 $Pb(Mg_{1/3}Nb_{2/3})O_3$–0.13 $PbTiO_3$ *Appl. Phys. Lett.* **92** 132909
[23] Peräntie J, Tailor H N, Hagberg J, Jantunen H and Ye Z-G 2013 Electrocaloric properties in relaxor ferroelectric $(1 - x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ system *J. Appl. Phys.* **114** 174105
[24] Swartz S L, Shrout T R, Schulze W A and Cross L E 1984 Dielectric properties of lead-magnesium niobate ceramics *J. Am. Ceram. Soc.* **67** 311
[25] Crossley S, Usui T, Nair B, Kar-Narayan S, Moya X, Hirose S, Ando A and Mathur N D 2016 Direct electrocaloric measurement of $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ films using scanning thermal microscopy *Appl. Phys. Lett.* **108** 032902
[26] Vrabelj M, Uršic H, Kutnjak Z, Rožic B, Drnovšek S, Bencan A, Bobnar V, Fulanovic L and Malic B 2016 Large electrocaloric effect in grain-size-engineered $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ *J. Eur. Ceram. Soc.* **36** 75