

反铁电材料中负电卡效应的研究进展

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摘要: 电卡效应是指电介质材料中施加或去除电场导致材料温度变化的现象, 包括正电卡效应和负电卡效应两种类型。电卡效应作为一种高效率、无噪声、环境友好的制冷效应, 在固态制冷特别是集成电路制冷领域显示出广阔的应用前景, 在过去的几十年中吸引了科研人员广泛的研究兴趣。研究表明, 通过结合正负电卡效应, 可以显著提高电卡效应的制冷能力。与正电卡效应不同, 负电卡效应因其独特的物理起源, 调控手段极为有限。本文以负电卡效应为中心, 重点介绍反铁电材料中负电卡效应的最新研究进展, 具体内容包括以下四个部分: 首先, 从电卡效应的研究历史出发, 介绍了电卡效应的制冷原理, 介绍了一个典型的能将正、负电卡效应结合的双制冷循环; 其次, 介绍了基于 Maxwell 关系的负电卡效应间接测试方法, 以及几种负电卡效应直接测试方法, 并讨论了不同方法的适用条件和优缺点; 再次, 以典型的负电卡效应材料——反铁电材料为例, 着重介绍了负电卡效应的物理起源, 综述了反铁电薄膜和反铁电块体材料中的负电卡效应, 并对其它铁电材料中的负电卡效应做了简要介绍; 最后, 对负电卡效应的研究进行了总结和展望。

关键词: 负电卡效应; 反铁电体; PbZrO₃; 综述

中图分类号: TB64 文献标志码: A

Negative Electrocaloric Effects in Antiferroelectric Materials: a Review

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Abstract: The electrocaloric effect refers to the phenomenon of the temperature change of a material caused by the application or removal of an electric field, and includes two types, positive electrocaloric effect and negative electrocaloric effect. As a high-efficiency, noise-free and environment-friendly refrigeration effect, the electrocaloric effect shows promising application in the field of solid-state refrigeration, especially in integrated circuit refrigeration, and has attracted extensive research interests over the past decades. It is reported that the cooling capacity of the electrocaloric effect can be significantly improved by combining the positive and negative electrocaloric effects. However, different from the widely studied positive electrocaloric effect, the research on negative electrocaloric effect is relatively rare due to its complex physical origin. This article focuses on the latest research progress of the negative

收稿日期: 2021-07-05; 收到修改稿日期: 2021-08-09; 网络出版日期: 2021-11-01

基金项目: 陕西省自然科学基金基础研究计划项目(2021JQ-042); 国家自然科学基金(51772238)

Shaanxi Provincial Natural Science Foundation Research Project (2021JQ-042); National Natural Science Foundation of China (51772238)

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electrocaloric effect in antiferroelectric materials. The specific content includes the following four parts. Firstly, starting from the research history of the electrocaloric effect, the principle of refrigeration of the electrocaloric effect is introduced, as well as a typical dual refrigeration cycle that can combine positive and negative electrocaloric effect. Secondly, the indirect measurement method of negative electrocaloric effect based on Maxwell relationship, several direct measurement methods of negative electrocaloric effect, and the suitable applying conditions as well as the advantages and disadvantages of different methods are discussed. Thirdly, taking antiferroelectric which is a typical negative electrocaloric effect material as an example, the physical origin of negative electrocaloric effect is narrated. Then the recent progress of negative electrocaloric effect in the antiferroelectric film and antiferroelectric bulk materials is reviewed. In addition, the negative electrocaloric effect in some other ferroelectric materials is also briefly introduced. Finally, a summary and prospect of the research on the negative electrocaloric effect are put forward.

Key words: negative electrocaloric effect; antiferroelectric; PbZrO_3 ; review

19世纪初,英国科学家 Michael Faraday 发现液态氨在蒸发时会导致周围空气温度降低,由此打开了压缩制冷技术的先河。随着经济社会的发展,基于机械压缩的制冷技术已在日常生活、工业生产和科学研究中发挥越来越重要的作用。经过近两个世纪的研究,机械压缩制冷技术已得到充分优化,然而其能源利用效率依旧低于 50%^[1]。此外,氢氟烃气体作为一种常用的机械压缩冷媒介质,具有很强的温室效应。氢氟烃气体的使用和泄漏加剧了全球气候的异常变化,已被世界上超过 150 个国家禁用。在这一背景下,以电卡效应、磁卡效应和热电效应为代表的新一代制冷技术吸引了科学界和工业界的广泛关注。电卡制冷效应由于理论效率高(60%~70%)、无噪声、环境友好、易于操作等优点,成为下一代制冷技术的有力竞争者^[1-2]。

电卡效应是指电介质材料在外加电场施加或去除的过程中,由熵变而导致的材料温度变化的现象^[1,3-5]。19世纪30年代, Kobeko 和 Kurchatov 首先在罗息盐(即酒石酸钾钠, $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, 是一种典型的铁电材料)中观察到了电卡效应^[2]。2006年, Mischenko 等^[6]利用溶胶-凝胶法制备了 $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})$ 铁电薄膜,并在其中发现了高达 12 K 的巨大温度变化,由此掀起了电卡效应研究的热潮。2019年, Nair 等^[5]在 $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$ 多层铁电陶瓷电容器中发现了宽温区大电卡效应(在 294~470 K 的温度区间内温度变化超过 3 K),并指明该多层陶瓷电容器具有优于磁卡制冷设备中永磁材料的制冷性能,从而能够显著减小固态制冷设备的体积并降低生产和运行成本。

铁电材料中的电卡效应起源于自发极化在外加电场作用下的翻转,其制冷循环如图 1 所示。在外

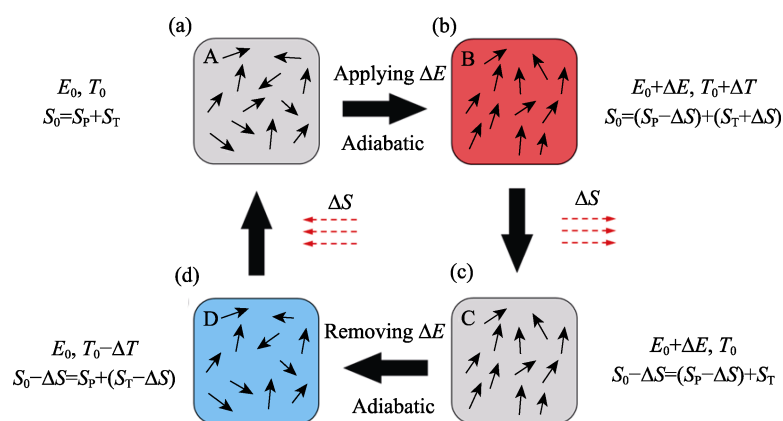


图 1 电卡效应冷却循环中的极化翻转、温度变化和熵变示意图

Fig. 1 Schematic of polarization switching, temperature change and entropy change during cooling cycle of electrocaloric effect

(a) In virgin state, the ferroelectric polarization is randomly distributed; (b) With the application of electric field, the ferroelectric polarization is aligned, and the temperature of the ferroelectric materials is increased; (c) After an isothermal process, the temperature of the ferroelectric materials decreases to the environment temperature; (d) After removal of the electric field, the ferroelectric polarization recovers random distribution, the temperature of the ferroelectric materials decreases

加电场为 E_0 (通常 $E_0=0$)、环境温度为 T_0 的条件下, 铁电材料的自发极化随机分布(图 1(a)). 此时铁电材料的总熵为 S_0 , 包括来自于晶格振动的热熵 S_T 和来自于铁电极化随机排布的极化熵 S_P . 若在绝热条件下增加作用于铁电材料上的外加电场($E_0+\Delta E$), 铁电极化的排列变得更为有序, 如图 1(b)所示. 此时极化熵($S_P-\Delta S$)减小, 而系统总熵 S_0 不变(系统与外界无热交换), 铁电材料的热熵($S_T+\Delta S$)增加, 铁电材料温度($T_0+\Delta T$)上升. 图 1(b, c)说明了恒电场条件下铁电材料的等温过程. 在此过程中, 铁电材料的温度恢复至环境温度(T_0), 热熵恢复为 S_T , 系统熵($S_0-\Delta S$)减小. 当在绝热条件下去掉外加电场 ΔE , 铁电极化会恢复至随机排列状态, 如图 1(d)所示, 铁电极化熵也相应恢复至 S_P . 而由于绝热条件下系统熵($S_0-\Delta S$)保持不变, 材料热熵($S_T-\Delta S$)减小, 材料温度降低为 $T_0-\Delta T$. 在图 1(d)至图 1(a)的过程中, 铁电材料从外界热源吸热, 并恢复至起始状态.

负电卡效应(Negative electrocaloric effect)是一种特殊的电卡效应, 也被称之为异常电卡效应(Abnormal electrocaloric effect)或逆电卡效应(Inverse electrocaloric effect). 与电卡效应相反, 在负电卡效应中, 施加外加电场会降低材料温度, 而去除外加电场则会升高材料温度(将在 2.1 节中详细讨论). 负电卡效应广泛见于反铁电材料、含缺陷铁电材料、多层铁电薄膜、弛豫铁电材料和具有不同铁电相的铁电材料等材料体系中, 它与电卡效应既可以同时存在于同一种材料中, 也可以分别存在于不同材料中. 研究人员发现, 将电卡效应和负电卡效应结合, 可有效提高电卡效应的制冷能力^[7-9]. 北京科技大学白洋课题组^[10]在 $\langle 001 \rangle$ 取向的 $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.7}\text{Ti}_{0.3}\text{O}_3$ (PMN-PT) 单晶中巧妙设计了一个双制冷循环, 显著提升了电卡效应制冷能力. PMN-PT 单晶在低温下表现为稳定的铁电三方相(R 相), 在高温下表现为铁电四方相(T 相). 在温度和电场的共同作用下, PMN-PT 单晶发生 R-T 相变, 且相变温度取决于外加电场的大小. 利用该特性, Li 等^[11]将 PMN-PT 单晶中由极化有序-极化无序诱导的电卡效应和 R-T 相变诱导的负电卡效应相结合(图 2(a)), 使电卡效应制冷能力提升了 150%. 此外, 图 2(b)表明, 该双制冷循环的制冷能力可通过调节外加电场的大小和时间间隔得到进一步优化. 注意到该双制冷循环的工作温度为 85 °C(图 2(b)), 不利于室温下的制冷应用. 白洋课题组^[10]进一步开发了 $\text{PbMg}_{0.5}\text{W}_{0.5}\text{O}_3$ 电卡制冷材料, 该材料在 36 °C 表现出温度变化为 1.79 K 的正电卡效应, 而在 34 °C 表现出

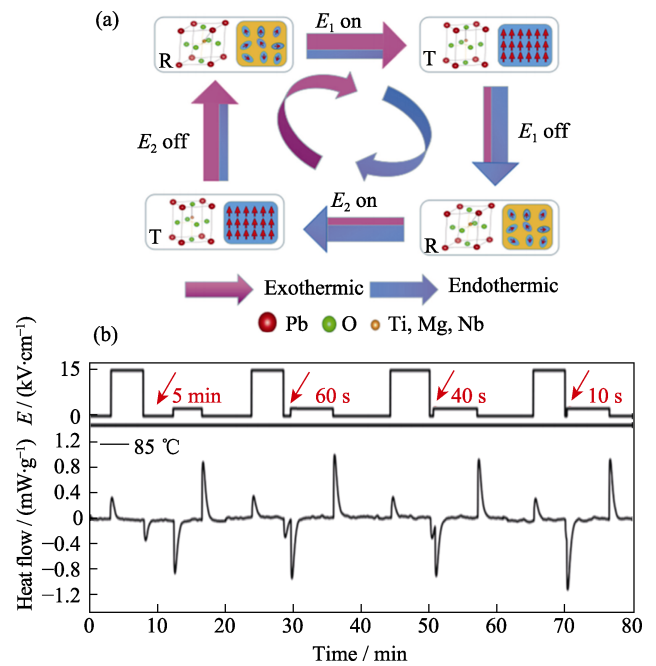


图 2 基于正负电卡效应共存的制冷循环^[10]

Fig. 2 Feasible combination of positive and negative electrocaloric effect^[10]
(a) Schematic of the cooling cycle; (b) Heat flow of the dual cooling cycle measured by DSC

温度变化为 2.02 K 的负电卡效应. 这些工作对基于双制冷循环的室温制冷器件设计具有重要意义.

电卡效应是铁电材料研究领域的热点问题之一, 近年来介绍电卡效应的文献也比较丰富^[12-13], 然而针对负电卡效应的相关介绍却较少. 本文以负电卡效应为中心, 立足典型的负电卡效应材料体系——反铁电材料, 回顾了负电卡效应的最新研究进展, 并对负电卡效应的未来发展方向做出展望.

1 负电卡效应的测量方法

电卡效应引起的介质材料温度变化既可以由电场诱导的极化变化间接推算, 也可以通过监测材料的温度或热流变化进行直接测量.

1.1 基于麦克斯韦关系的间接测量法

在各种间接方法中, 基于麦克斯韦关系的方法应用最为广泛. 电场诱导的熵变大小(即极化翻转的程度)直接决定了电卡效应引起的电介质材料温度变化的大小. 要直接测量电场所导致的熵变非常困难, 只能通过麦克斯韦关系式进行间接估算^[1-2,6,14].

$$\left(\frac{\partial S}{\partial E_i}\right)_{T,x} = \left(\frac{\partial P_i}{\partial T}\right)_{E,x} \quad (1)$$

其中 $\left(\frac{\partial S}{\partial E_i}\right)_{T,x}$ 是恒定温度、恒定压力条件下的单位

电场所导致的熵变, $\left(\frac{\partial P}{\partial T}\right)_{E,x}$ 是恒定电场、恒定压力

条件下的单位温度所导致的极化变化(也即热释电系数)。基于吉布斯自由能展开, 电介质材料中由电场引起的熵变(ΔS)和温度变化(ΔT)可以通过以下公式来估算:

$$\Delta S = \int_{E_1}^{E_2} \left(\frac{\partial P}{\partial T}\right)_E dE \quad (2)$$

$$\Delta T = -\frac{T}{\rho} \int_{E_1}^{E_2} \frac{1}{C_E} \left(\frac{\partial P}{\partial T}\right)_E dE \quad (3)$$

式中, E_1 是施加于电介质材料的起始电场(通常是 0), E_2 是终止电场, P 是极化, T 是温度, ρ 是电荷密度, C_E 是比热容。熵变 ΔS 和温变 ΔT 是评价材料电卡效应的最重要参数。

根据麦克斯韦关系, 通过测量电介质材料在不同温度下的极化强度并绘制极化-温度曲线(称为 P - T 曲线), 可以很容易地估算电卡效应。该方法加速了铁电材料中电卡效应的研究。在某些情况下, 温度升高会导致材料漏电流增大, 此时麦克斯韦方法会计算出假的负电卡效应^[14]。使用麦克斯韦方法估算电卡效应, 特别是估算负电卡效应时, 应特别重视测试高温条件下漏电流, 以避免假的负电卡效应。值得注意的是, 麦克斯韦方法在二级相变材料体系中能够给出较为准确的电卡效应估算, 而在一阶相变和弛豫铁电相变中, 麦克斯韦方法估算的温度变化低于实际情况。

1.2 直接测量法

电卡效应也可以通过监测温度或热流的变化直接测量, 典型方法包括热电偶法(图 3(a))^[15]、扫描热显微镜法(图 3(b))^[16]、红外相机法(图 3(c))^[17]和差示扫描量热法(图 3(d))^[18]。

在图 3(a)所示的结构中, 研究人员在 PVDF 薄膜和玻璃衬底之间制备了一个嵌入式的温度计, 通过该温度计可直接监测 PVDF 薄膜温度^[15]。该方法能够实现对电卡效应导致薄膜温度变化的直接监测, 且易于实现。值得注意的是, 薄膜与衬底之间的热扩散无法避免, 电卡效应的绝热过程与等温过程耦合在一起, 实际测试得到的温度变化往往小于理论值。

温度变化也可以由扫描热显微镜 (Scanning thermal microscope, SthM) 测量^[16]。扫描热显微镜的本质是原子力显微镜, 区别在于, 它以热敏电阻作为探针扫描样品, 并以该热敏电阻作为惠斯通电桥的一臂, 如图 3(b)所示。当电介质材料的温度因电卡效应而改变时, 热敏电阻的阻值也相应发生改变。通过读取惠斯通电桥的参数, 就能得到样品的温度。扫描热显微镜方法的优点在于可以实现高精度的样品温度空间分布测量, 且温度分辨率可达 8 mK。扫描热显微镜的温度测量是通过逐点扫描实现的, 高空间分辨率的温度分布扫描往往需要较长时间。

图 3(c)所示的红外相机是另一种可实现温度空间分布测量的装置^[17]。它利用红外光子探测器或热释电晶体感知材料发射的红外辐射, 从而得到材料的温度。相对于扫描热显微镜而言, 红外相机可在

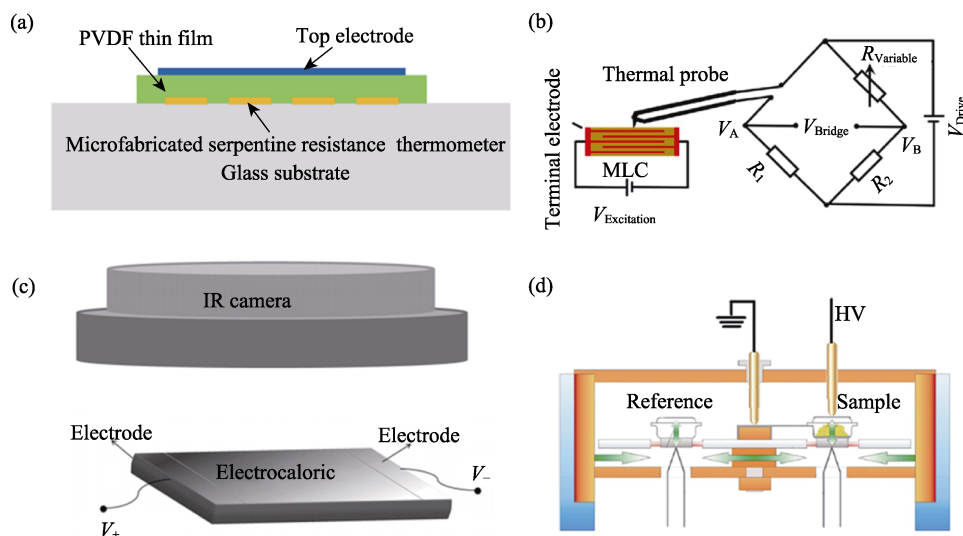


图 3 电卡效应直接测量法

Fig. 3 Direct measurements of electrocaloric effect

(a) Thermocouple or thermometer^[15]; (b) Scanning thermal microscopy^[16]; (c) Infrared camera^[17]; (d) Modified differential scanning calorimetry^[18]

数十毫秒内拍摄到样品的温度分布图像,能够较准确地反映样品中由电卡效应导致的温度变化。红外相机的缺点在于它对样品表面光洁度的要求较高,粗糙表面造成的红外光漫反射会降低红外相机测温的精度。

差示扫描量热法(Differential scanning calorimetry, DSC, 图 3(d))被广泛应用于测量铁电陶瓷电卡效应,基本原理是监控样品中热流的变化^[18-20]。该方法基于差示扫描量热仪,可同时记录来自参照物和样品的热流。在恒定温度下,若对样品施加或去除电场,则样品的热流会发生变化。通过对热流积分,就可以计算出样品的电卡效应。相对于其它方法而言,差示扫描量热法具有较好的绝热条件,因此精度较高。

直接法的精确度依赖于温度测量过程中的绝热条件^[17],否则直接法的结果会被低估。从这个角度来看,对于沉积在衬底上的铁电薄膜而言,想要直接、准确地测量电卡效应是相当困难的。薄膜和衬底之间的热扩散相当迅速且很难避免。对于厚度通常为数百纳米的铁电薄膜而言,其热容相对于衬底来说可以忽略不计。因此薄膜中由电卡效应导致的温度变化将很快被衬底平衡,难以准确检测。

2 反铁电材料中的负电卡效应

2.1 反铁电体中负电卡效应的成因

负电卡效应在反铁电材料^[21]、含点缺陷铁电材

料^[22-23]、R-T 相变铁电材料^[10,24]以及多层铁电薄膜材料^[25-26]等材料中被广泛报道。在不同类型的负电卡效应材料中,以 PbZrO_3 为代表的反铁电材料体系激发了人们极大的研究兴趣。

反铁电材料的特征在于,未施加外电场时,相邻电畴极化方向反向平行(图 4(a))^[27]。在电场的作用下,反向平行于电场的极化强度将被翻转至与电场方向相同(图 4(b))。相应地,所测试的 $P-E$ 曲线呈现典型的双电滞回线特征,如图 4(c)所示。双电滞回线起源于反铁电材料中的反铁电-铁电相变, E_F (图 4(c))表示从反铁电相到铁电相的相变矫顽电场,而 E_A (图 4(c))表示从铁电相到反铁电相的相变电场。

反铁电材料中的负电卡效应起源于反铁电-铁电相变,如图 4(d)所示^[27]。在不施加电场时(图 4(d1)),极化反向平行有序排列,此时材料的极化熵较低。在外加电场的情况下,与外加电场反向的极化发生翻转,垂直于电场方向的极化熵分量将增加,而沿电场方向的极化熵分量几乎保持不变(图 4(d2)),此时材料具有较高的极化熵,材料的温度会降低,即材料中产生负电卡效应。不难发现,反铁电材料中的负电卡效应起源于外加电场与极化的非共线,而这一理论也适用于上述其它体系的负电卡效应材料^[28]。

从图 4(a, b)中可以看出,反铁电材料处于反铁电相或铁电相时,极化都是有序排列的,此时材料的极化熵处于较低状态。外加电场导致反铁电材料极化熵增加的过程仅出现在其发生反铁电-铁电相

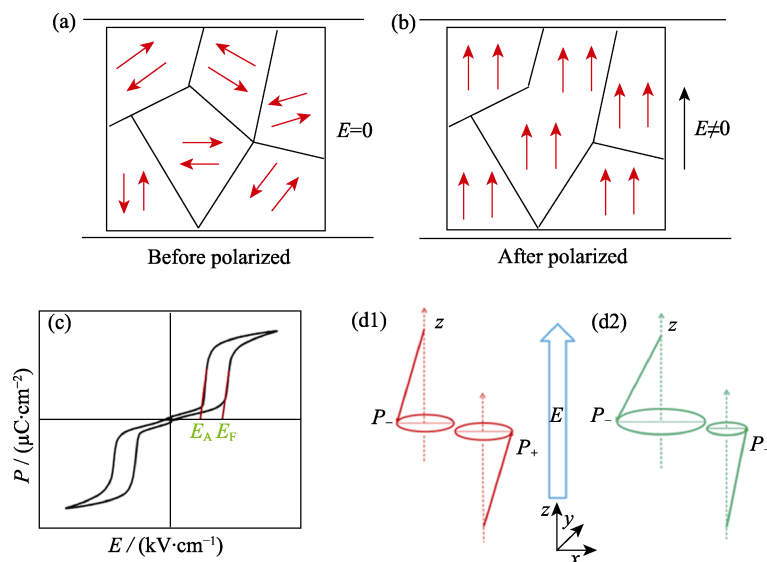


图 4 反铁电材料中的电畴、电滞回线和产生负电卡效应的可能机制示意图^[27]

Fig. 4 Electric domain and representative hysteresis loop of antiferroelectrics, schematic of a possible mechanism of negative electrocaloric effect in antiferroelectrics^[27]

Electric domain of antiferroelectrics (a) before and (b) after being polarized; (c) Representative hysteresis loop of antiferroelectrics; Schematic of a possible mechanism of negative ECE in antiferroelectrics (d1) without any electric field and (d2) under a modest electric field

变的过程。从麦克斯韦方法出发, 提高电卡效应的理论基础在于提高材料的热释电系数和增大材料的外加电场。在反铁电材料中, 负电卡效应的提升方法在于利用不同手段调控其反铁电-铁电相变, 增大热释电系数, 以及增大反铁电-铁电相变矫顽电场^[29]。

2.2 PbZrO₃ 基反铁电薄膜中的负电卡效应

早期反铁电材料中的负电卡效应主要发现于块体材料(包括单晶和陶瓷)中, 由负电卡效应导致的温度变化 $|\Delta T|$ 通常小于 2 K^[30-31]。2015 年, Geng 等^[21]在(Pb_{0.97}La_{0.02})(Zr_{0.95}Ti_{0.05})O₃(PLZT)反铁电薄膜中首次报道了 $|\Delta T|$ 超过 5 K 的显著负电卡效应。他们采用溶胶-凝胶法在 Pt(111)/Ti/SiO₂/Si 衬底上制备了厚度为 650 nm 的 PLZT 薄膜, 并利用 XRD 验证了薄膜的正交反铁电钙钛矿结构和(100)方向的择优取向生

长。图 5(a)展示了该薄膜在不同电场下(0~615 kV/cm)的极化曲线(P - T 曲线)随温度的变化关系。在较高电场下($E \geq 415$ kV/cm), 薄膜的极化强度随温度升高而减小, 薄膜表现为电场诱导的铁电相特征。当电场低于 415 kV/cm 时, P - T 曲线随温度升高先增大后减小。且随着外加电场增大, P - T 曲线的峰位向低温方向移动。这是反铁电材料在电场-温度耦合作用下发生反铁电-铁电相变的结果。基于 P - T 曲线, 利用麦克斯韦关系计算的薄膜电卡效应结果如图 5(b)所示。可以看出, PLZT 薄膜在较低的温度范围内(即对应反铁电-铁电相变过程)主要表现为负电卡效应, 而在较高的温度下则主要表现为正电卡效应, 对应铁电-顺电相变。在 59 °C 时, 薄膜中由负电卡效应导致的最大温度变化 $|\Delta T|$ 为 5.76 K。

Ye 等^[32]利用类似的方法分别制备了 Eu 和 Yb

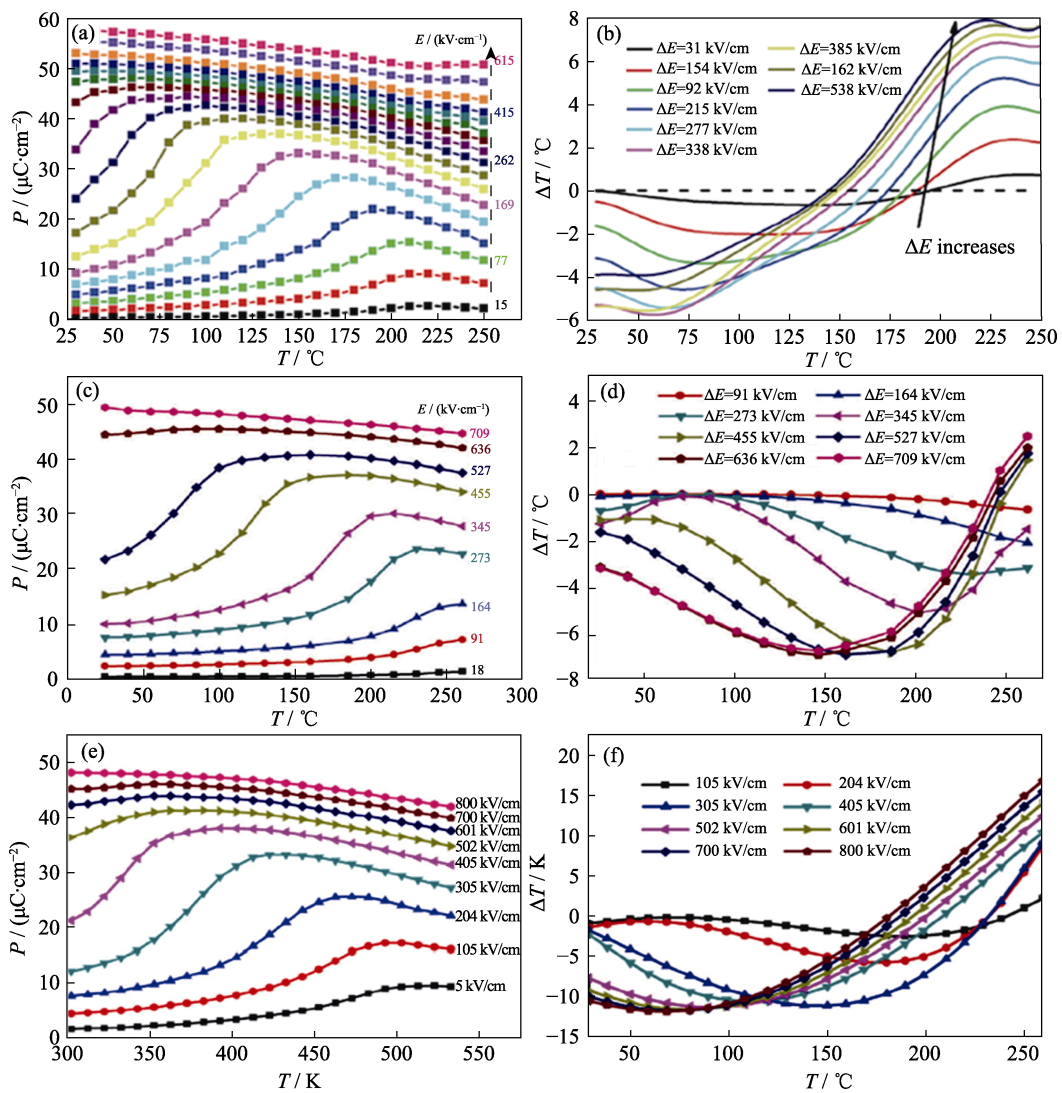


图 5 PbZrO₃ 基反铁电薄膜中的负电卡效应

Fig. 5 Negative electrocaloric effect in PbZrO₃-based antiferroelectric thin films

(a) P - T curves and (b) temperature change of (Pb_{0.97}, La_{0.02})(Zr_{0.95}, Ti_{0.05})O₃ thin film^[21]; (c) P - T curves and (d) temperature change of 4% (molar ratio) Eu doped PbZrO₃ thin film^[32]; (e) P - T curves and (f) temperature change of 1% Yb (molar ratio) doped PbZrO₃ thin film^[33]

掺杂的 PbZrO_3 薄膜并研究了薄膜的电卡效应, 如图 5(c~f)所示。研究发现, Eu 、 Yb 掺杂导致的最大负电卡效应温度变化 $|\Delta T|$ 分别为 6.6, 12.01 K^[33]。Eu 和 Yb 的掺杂能够显著提高 PbZrO_3 的反铁电-铁电相变能垒, 增强反铁电-铁电相变矫顽场, 从而实现负电卡效应显著提升。

反铁电-铁电相变的势垒也可以通过界面缺陷来增大, 如图 6 所示^[29]。在该工作中, Wu 等^[29]利用

溶胶-凝胶法制备了 PbZrO_3 薄膜, 并利用多孔电极在电极-薄膜界面引入了缺陷。界面缺陷在电场循环过程中能够钉扎极化的翻转(钉扎过程如图 6(a)), 并在无外电场的情况下暂时稳定瞬态铁电相。瞬态铁电相的出现使 PbZrO_3 薄膜的反铁电-铁电相变矫顽场从 400 kV/cm 增大到 800 kV/cm 左右(图 6(b))。估算界面缺陷调节的 PbZrO_3 薄膜中的负电卡效应, $|\Delta T|$ 为 18.5 K, 这是室温范围内所报道的最大值, 如

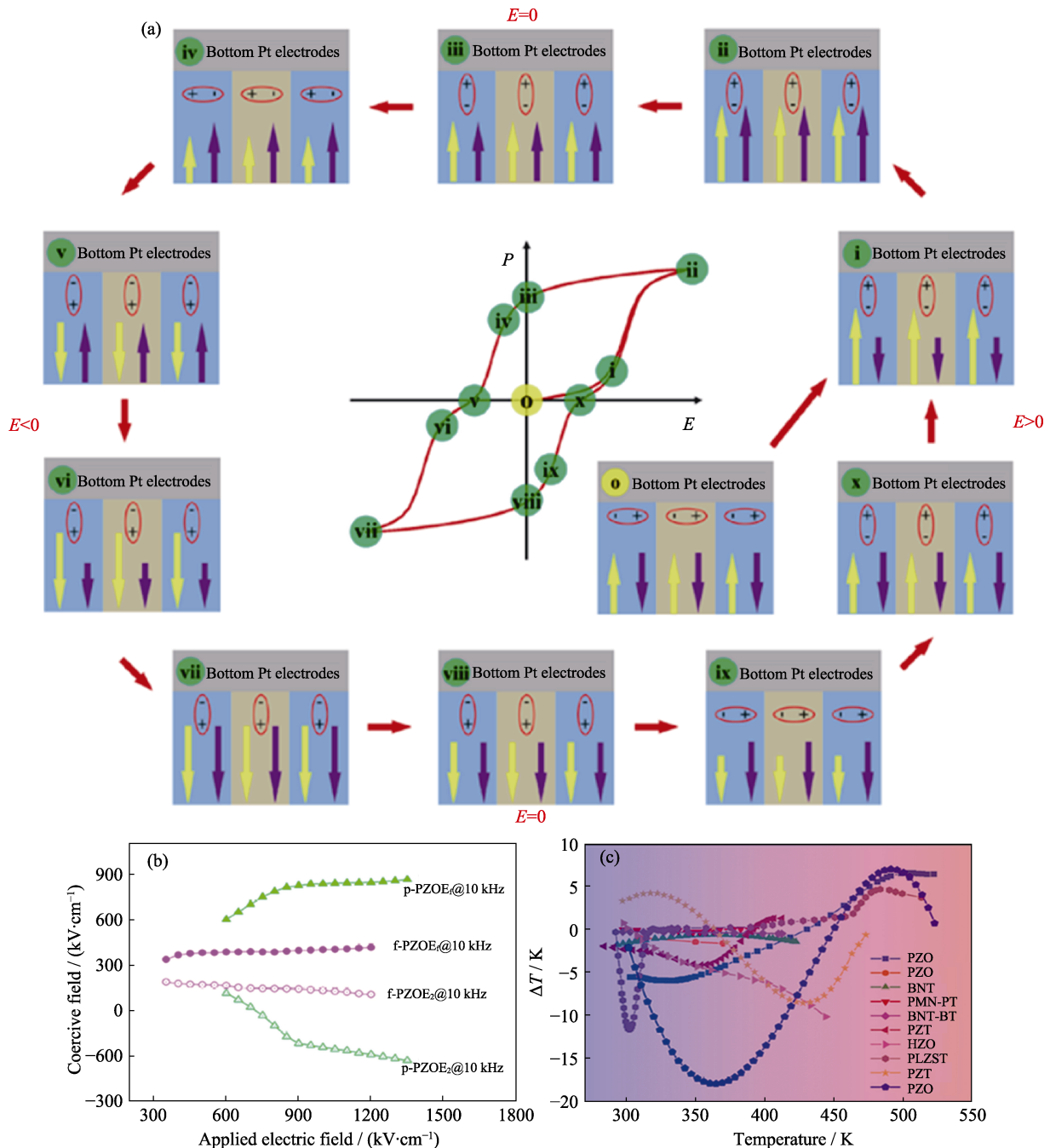


图 6 PbZrO_3 薄膜中利用界面缺陷增强负电卡效应^[29]

Fig. 6 Interface-defect-enhanced negative electrocaloric effect in PbZrO_3 thin films^[29]

(a) Mechanism of the defect-dipole-suppressed antiferroelectric-ferroelectric phase transition during electric cycling; (b) Antiferroelectric-ferroelectric phase transition field of the PbZrO_3 thin films with interface defect (p-PZO) and without interface defect (f-PZO); (c) Comparison of negative ECE in different materials

Colorful figures are available on website

图6(c)所示。

2.3 反铁电块体材料中的负电卡效应

反铁电块体材料工作体积比薄膜高出几个数量级,在短时间内可视为绝热系统,这为直接测量反铁电材料中的负电卡效应提供了基础。直接测量法需要较高分辨率的温度计或是热流检测设备,对反铁电块体材料负电卡效应的研究也以基于麦克斯韦关系的间接法居多。

Pirc 等^[34]首次使用特制的高分辨率热量计测试了 PbZrO_3 陶瓷中的负电卡效应,发现在低于反铁电相变温度的较宽温度范围内,负电卡效应导致的温度变化 $|\Delta T|$ 可高达 1.6 K,如图 7(a)所示。元素掺杂可以进一步提高 PbZrO_3 陶瓷的负电卡效应。Zhao 等^[35]通过 La 和 Ti 的共掺制备了 $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ 陶瓷,并用间接法测量了其负电卡效应,发现 50 kV/cm 的电场引起的最大温度变化 $|\Delta T|$ 为 7.47 K,如图 7(b)所示。Niu 等^[36]发现,非化学计量比对 $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ 陶瓷的负电卡效应也有积极的影响,合成了 $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.95}\text{Ti}_{0.05})_{1+y}\text{O}_3$ 陶瓷 ($y = -0.03, -0.01, 0.01, 0.03$),并用间接法测试了负电卡效应,发现当 $y = -0.01$ 时,所得负电卡效应温度变化最大,为 12.45 K,如图 7(c)所示。

Xu 等^[37]研究了相变顺序对 $\text{Pb}(\text{Nb}, \text{Zr}, \text{Sn}, \text{Ti})\text{O}_3$ 陶瓷电卡效应的影响,制备了 $\text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.85}\text{Sn}_{0.13}\text{Ti}_{0.02})_{0.98}\text{O}_3$ (PNZST13/2/2) 陶瓷和 $\text{Pb}_{0.99}\text{Nb}_{0.02}[(\text{Zr}_{0.57}\text{Sn}_{0.43})_{0.92}\text{Ti}_{0.08}]_{0.98}\text{O}_3$ (PNZST43/8/2) 陶瓷,这两种陶瓷在加热过程中分别具有反铁电-铁电-顺电相变顺序(图 8(a))和铁电-反铁电-顺电相变顺序(图 8(b))。两种陶瓷中基于间接法测试的负电卡效应结果如图 8(c~h)所示,可以看出,具有反铁电-铁电-顺电相变顺序的 PNZST13/2/2 陶瓷主要表现为负电卡效应,如图 8(c~e)所示;而具有铁电-反铁电-顺电相变顺序的 PNZST43/8/2 陶瓷主要表现

为正电卡效应,如图 8(f~h)所示。此外,PNZST13/2/2 陶瓷的最大负电卡效应温度变化 ($|\Delta T|$ 为 4 K) 在 82 °C 附近出现,与 130 kV 电场作用下材料的反铁电-铁电相变温度相符。以上结果再次证明,反铁电材料所展现的负电卡效应,是材料发生反铁电-铁电相变的结果。

Zhuo 等^[9, 38-40]主要研究了 $(\text{Pb}, \text{La})(\text{Zr}, \text{Sn}, \text{Ti})\text{O}_3$ 块体材料的负电卡效应,用熔剂法制备了 $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.66}\text{Sn}_{0.23}\text{Ti}_{0.11})\text{O}_3$ (PLZST66/23/11) 单晶^[9]。PLZST66/23/11 单晶在室温下表现为反铁电相,但在 1.8 kV/mm 的临界电场下可以被极化为铁电相。电场诱导的铁电相处于亚稳态,当温度升高到退极化温度 (70~100 °C) 以上时,亚稳态铁电相又会恢复到反铁电相。该单晶材料在不同温度下的电滞回线如图 9(a)所示,用间接法测试的负电卡效应如图 9(b)所示。结果表明,在居里温度以下时,材料主要表现为正电卡效应,此时负电卡效应相对较小,室温下的负电卡效应温度变化 $|\Delta T|$ 为 0.054 K, 125 °C 下的负电卡效应温度变化 $|\Delta T|$ 为 0.12 K。通过改变 Sn/Ti 的比值,研究人员进一步合成了 $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.66}\text{Sn}_{0.27}\text{Ti}_{0.07})\text{O}_3$ (PLZST66/27/7) 单晶^[40]。PLZST66/27/7 单晶在加热过程中表现出从正交反铁电相到四方反铁电相再到立方顺电相的相变顺序,这与 PLZST66/23/11 单晶有很大的不同。PLZST66/27/7 单晶在不同温度下的电滞回线如图 9(c)所示,用间接方法测试的负电卡效应结果如图 9(d)所示,该单晶在 125 °C 表现出温度变化为 3.6 K 的显著负电卡效应。在 $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_x\text{Sn}_{0.94-x}\text{Ti}_{0.06})\text{O}_3$ ($x = 0.90, 0.85, 0.80, 0.75$) 陶瓷中,研究人员进一步优化了 $(\text{Pb}, \text{La})(\text{Zr}, \text{Sn}, \text{Ti})\text{O}_3$ 块体材料的负电卡效应^[39]。当 $x = 0.8$ 时, $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.80}\text{Sn}_{0.14}\text{Ti}_{0.06})\text{O}_3$ 陶瓷在 30 °C 附近表现出显著的负电卡效应,温变 $|\Delta T|$ 为 11.5 K (图 9(e)), 满足了中、大规模固态制冷应用的大多数关键制冷指标要求。此外,与其它负电卡效应

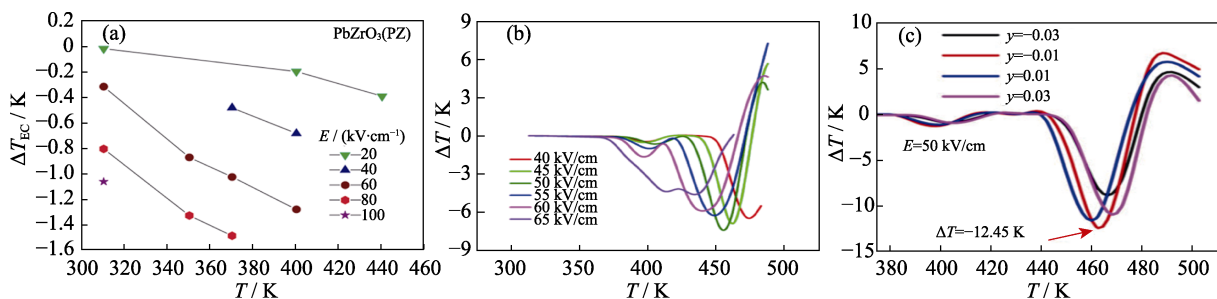


图7 不同电场下 PbZrO_3 、 $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ 和 B 位非化学计量比 $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.95}\text{Ti}_{0.05})_{1+y}\text{O}_3$ ($y = -0.03, -0.01, 0.01, 0.03$) 陶瓷的负电卡效应

Fig. 7 Negative electrocaloric effects of PbZrO_3 , $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ and B-site nonstoichiometric $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.95}\text{Ti}_{0.05})_{1+y}\text{O}_3$ ($y = -0.03, -0.01, 0.01, 0.03$) ceramics under different electric fields (a) PbZrO_3 ^[34]; (b) $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ ^[35]; (c) B-site nonstoichiometric $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.95}\text{Ti}_{0.05})_{1+y}\text{O}_3$ ($y = -0.03, -0.01, 0.01, 0.03$)^[36] Colorful figures are available on website

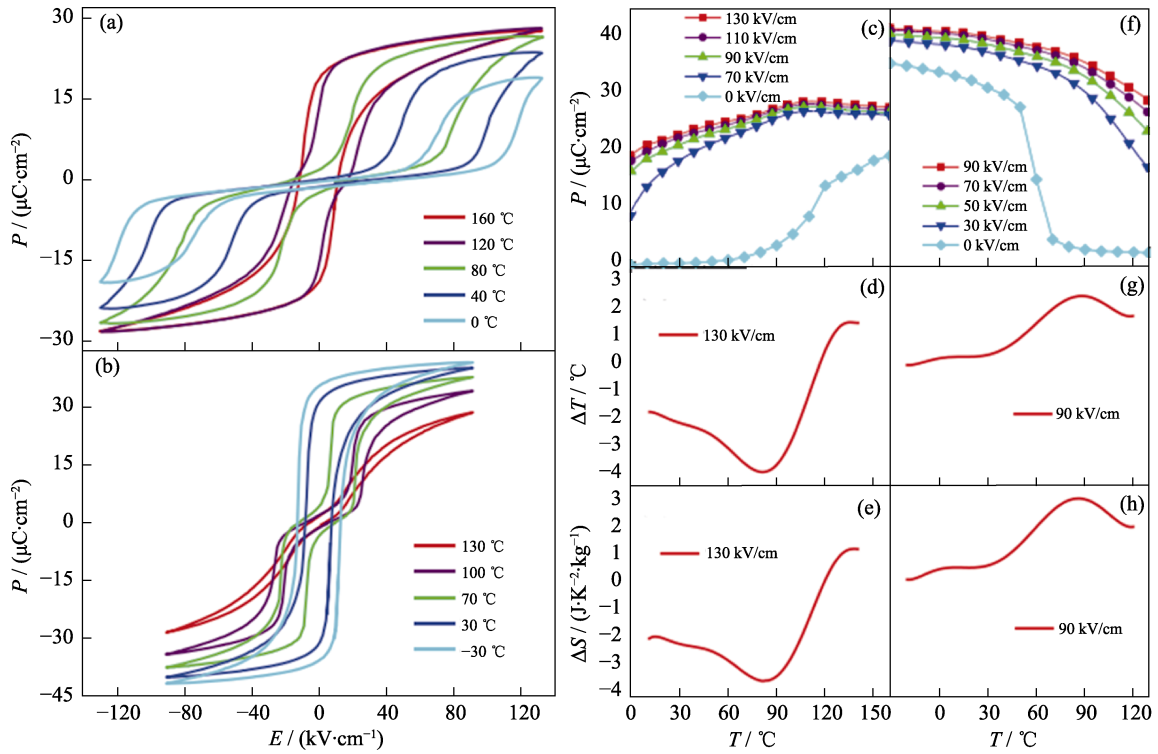


图 8 两种 PNZST 陶瓷在不同温度下测试的电滞回线以及两种陶瓷的 $P-T$ 曲线、温度变化 ΔT 和熵变 ΔS ^[37]
 Fig. 8 Hysteresis loops of PNZST13/2/2 and PNZST43/8/2 under different temperatures, $P-T$ curves, temperature change ΔT and entropy change ΔS of PNZST13/2/2 and PNZST43/8/2^[37]
 (a) Hysteresis loops of PNZST13/2/2; (b) Hysteresis loops of PNZST43/8/2; (c–e) $P-T$ curves, temperature change ΔT and entropy change ΔS of PNZST13/2/2; (f–h) $P-T$ curves, temperature change ΔT and entropy change ΔS of PNZST43/8/2
 Colorful figures are available on website

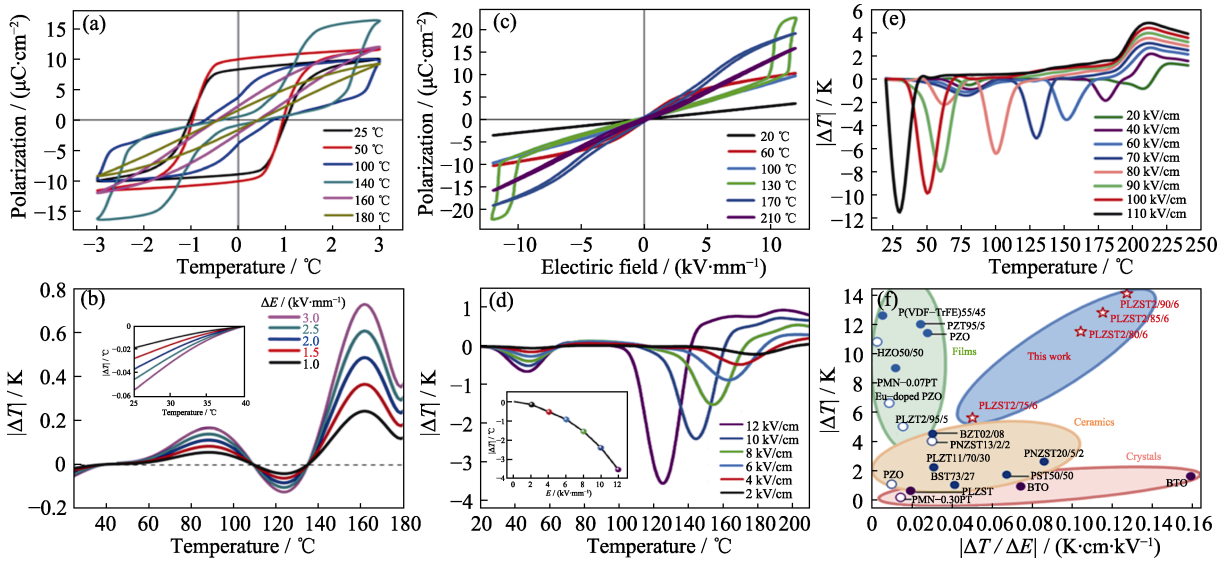


图 9 $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.66}\text{Sn}_{0.23}\text{Ti}_{0.11})\text{O}_3$ 单晶、 $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.66}\text{Sn}_{0.27}\text{Ti}_{0.07})\text{O}_3$ 单晶、 $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.80}\text{Sn}_{0.14}\text{Ti}_{0.06})\text{O}_3$ 陶瓷和 $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_x\text{Sn}_{0.94-x}\text{Ti}_{0.06})\text{O}_3$ 陶瓷的电卡效应
 Fig. 9 Electrocaloric effect of $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.66}\text{Sn}_{0.23}\text{Ti}_{0.11})\text{O}_3$ single crystal, $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.66}\text{Sn}_{0.27}\text{Ti}_{0.07})\text{O}_3$ single crystal, $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.80}\text{Sn}_{0.14}\text{Ti}_{0.06})\text{O}_3$ ceramics, and $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_x\text{Sn}_{0.94-x}\text{Ti}_{0.06})\text{O}_3$ ceramics
 (a, b) Hysteresis loops and temperature change ΔT of the $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.66}\text{Sn}_{0.23}\text{Ti}_{0.11})\text{O}_3$ single crystal^[9]; (c, d) Hysteresis loops and temperature change ΔT of the $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.66}\text{Sn}_{0.27}\text{Ti}_{0.07})\text{O}_3$ single crystal^[40]; (e) Temperature change ΔT of the $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.80}\text{Sn}_{0.14}\text{Ti}_{0.06})\text{O}_3$ ceramics^[39]; (f) Comparison of the temperature change in $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_x\text{Sn}_{0.94-x}\text{Ti}_{0.06})\text{O}_3$ ceramics with other dielectric materials^[39]
 Colorful figures are available on website

材料相比, $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_x\text{Sn}_{0.94-x}\text{Ti}_{0.06})\text{O}_3$ 陶瓷同时兼具了较高的温度变化和较好的电卡效应效率

($|\Delta T|/\Delta E$, 也就是电卡效应的能量效率), 如图 9(f) 所示, 表明该材料具有非常好的制冷应用前景。

2.4 其它铁电材料的负电卡效应

除反铁电材料之外,负电卡效应在许多其它铁电材料体系中也广泛报道。Park等^[8]利用原子层沉积(ALD)方法制备了9.2 nm厚的 $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ 薄膜,并在3.26 MV/cm的电场下发现了 $|\Delta T|$ 为10.5 K的负电卡效应;Chen等^[41]在 $\text{Bi}_{0.5}(\text{K}_{0.15}\text{Na}_{0.85})_{0.5}\text{TiO}_3$ 弛豫铁电薄膜中发现了 $|\Delta T|$ 为16.55 K的负电卡效应;Ma等^[22]利用蒙特卡罗方法研究了 BaTiO_3 中由缺陷偶极子诱导负电卡效应的可能。

3 总结与展望

本文介绍了负电卡效应的定义、测量方法和起源机制,综述了反铁电薄膜和块体材料中负电卡效应的研究进展。关于反铁电材料中负电卡效应的研究还可以从如下几个方面展开:

1)研究反铁电厚膜的负电卡效应

有关负电卡效应的研究大多集中在薄膜和块体材料上,关于厚膜报道很少。相对于薄膜和块体材料来说,厚膜能够实现工作体积和击穿电场的兼具,具有更好的制冷性能。从这个角度来看,厚膜在集成电路的固态制冷中具有更好的应用前景。

2)优化 $(\text{Pb,L a})(\text{Zr,S n,T i})\text{O}_3$ 材料的负电卡效应

$(\text{Pb,L a})(\text{Zr,S n,T i})\text{O}_3$ 陶瓷所呈现的最大负电卡效应温度变化 $|\Delta T|$ 超过10 K,几乎是已报道的块体材料的最高值,远高于最近报道的 $\text{Pb}(\text{S c}_{0.05}\text{T a}_{0.05})\text{O}_3$ 陶瓷的温度变化^[5]。 $(\text{Pb,L a})(\text{Zr,S n,T i})\text{O}_3$ 陶瓷的工作温度范围相对较窄。通过调控陶瓷成分进一步优化 $(\text{Pb,L a})(\text{Zr,S n,T i})\text{O}_3$ 陶瓷的负电卡效应,拓宽其工作温度范围,将使得该材料更具应用价值。

3)开发基于负电卡效应的固态制冷样机

目前,研究人员已经设计了几种基于正电卡效应的制冷样机,基于负电卡效应的制冷样机并不多见。在正负电卡效应结合的基础上设计更多的制冷循环,也能显著提高电卡效应的制冷能力和制冷效率。

除此之外,负电卡效应在低温区间的工作潜力还有待更深入的挖掘^[42],负电卡效应材料的电疲劳性能也有待研究。

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