

高熵铁电体研究进展

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摘 要: 铁电材料因其换能、储能等功能性而被广泛应用于各类电子功能材料和器件, 这主要取决于铁电材料晶体结构基因——极化构型。传统构建相界策略对极化构型调控不够灵活, 性能增幅有限, 已越来越无法满足器件微型化和集成化的需求。近期, 研究者将高熵策略引入到铁电化合物中并系统研究了其对局域极化构型的调控机制。结果表明, 在保留传统高熵效应的同时, 高熵策略还可充分发挥原子铁电活性、半径等综合因素用于铁电功能基元(局域极化构型与氧八面体倾斜)的定向设计, 有效提升外场响应的灵活度, 进而大幅度提升铁电化合物的相关电学性能。该类兼具高化学无序度和高铁电功能基元无序度的材料称之为“高熵铁电体”。采用高熵策略在铁电体中开展了一系列研究工作, 研究者们分别设计出高熵压电、高熵电致伸缩、高熵储能等材料。本文通过总结高熵铁电体方面的研究工作, 将高熵铁电体的发展历程、设计策略、性能优化、结构机理进行梳理, 以期设计下一代高性能铁电材料提供指导。

关键词: 高熵; 铁电材料; 极化构型; 储能; 钙钛矿

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1 铁电材料与极化功能基元

对于一些介电材料晶体, 晶胞的低对称性结构使正负电荷中心不重合而出现电偶极子, 产生电极化强度, 即晶体产生了自发极化。铁电体的自发极化方向会由于外电场的变化而改变, 当施加外电场时, 可以改变电偶极矩方向, 铁电体的自发极化和电畴都会发生改变和翻转; 当没有外电场时, 多晶铁电体样品则呈各向同性, 各个电畴互补以实现材料整体处于较低能量的稳定状态, 此时极化强度可近似为零, 晶体的这种性质被称为铁电性^[1-2], 而电偶极子的排列方式不同构成了多种多样的极化构型^[3-7], 因此极化构型可以理解为介电材料中电偶极子的排列和取向状态。

图 1 为极化功能基元作为媒介实现铁电体电学性能调控。由图 1 可见, 极化构型作为实现铁电材料物理性质多样性的核心功能基元, 设计新型可控的极化构型有利于发现具有优异性能的新材料。

薄膜和陶瓷材料中的极化构型主要分为共线和非共线 2 种类型。对于铁电体和反铁电体材料, 共线构型较为常见, 例如, PbTiO_3 晶体中的平行排列偶极子, 沿 c 轴排列的偶极子使其具有四方极性, 其可以与其它化合物结合形成固溶体, 例如 $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) 和 $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) 等体系。为了改善陶瓷的性能, 通常对材料的晶粒、电畴、准同型相界与多晶型相界进行调控与优化, 然而这些对材料电学性能的提升通常较为有限, 为了更大幅度提高材料的性能, 人们尝试对局域结构进行设计。

有研究利用分子动力学模拟在弛豫铁电体 PMN-PT 单晶中发现了沙冰极性结构, 通过这种极性结构组成的无非极性基体的小尺寸畴(2~10 nm)解释了畴壁的微观结构特征, 这为寻找新型高性能弛豫铁电体提供了新思路^[5]。由于阳离子位移和氧八面体倾斜的共存, 由钙钛矿型晶体结构构建的反铁电超晶胞在成分、电场、温度等方面表现出很强

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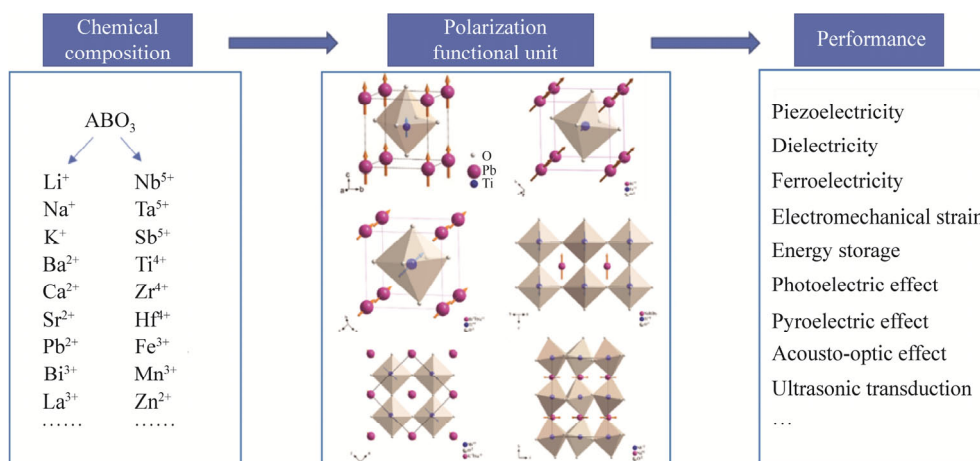


图 1 极化功能基元作为媒介实现铁电体电学性能调控

Fig. 1 Polarization functional units serve as mediators to modulate ferroelectric electrical properties in materials

的可调性,通过化学改性得到的 PbZrO_3 基陶瓷内部的极化构型不再严格地反平行。近期一些研究工作在 PbZrO_3 基反铁电体中发现了新的极化构型,例如混合的 Ising 型和 Néel 型^[8],倾斜的反铁电结构^[6],反铁电体与铁电体之间极化不平衡的中间态^[7],电偶极子的螺旋排列和 Polar-skyrmions 结构,这些研究发现大大丰富了铁电体的各种极化构型^[3-4]。极化构型会影响材料压电、储能等性质,因此,设计极化构型对于制备高性能材料是至关重要的。

在钙钛矿压电材料中,无论是铅基还是无铅压电,最常用的极化功能基元调控策略即为构建相共存的相界。在铅基材料中,构建准同型相界是提高性能的常用方法,在准同型相界的组分中,菱方和四方相共存,进而表现出更多的极化方向,平坦的自由能分布促进了畴的重新定向,多种因素的共同作用导致了优异的电学性能^[9-10]。但是对于不同的准同型相界的组分,材料的性能也不尽相同,因此,有待进一步研究晶体结构,探索准同型相界与材料性能之间的关系。有关低对称性单斜相的研究为解释准同型相界导致高性能的原因提供了思路,单斜相的极化位于 $(110)_{\text{PC}}$ 平面中作为多相的过渡。 M_A 相被定义为 $[001]_{\text{PC}}$ (T) 和 $[111]_{\text{PC}}$ (R) 方向之间角度变化较大的极化矢量, M_B 相是 $[111]_{\text{PC}}$ (R) 和 $[110]_{\text{PC}}$ (O) 之间角度变化较小的极化矢量^[11]。LIU 等^[11]报道了一些具有单斜相的压电体系在电场下的连续极化旋转,这通常指的是材料中电偶极矩方向随着外部电场方向的变化而旋转的现象。研究表明,由于连续的极化旋转, M_A 和 M_B 相与 R 或 T 相的固定极化方向相比具有更高的压电性能,这说明极化旋转对于获得较高压电性能是有利的,其关系体现为电场诱发的极化旋转速率越大,材料的压电系数越高。

为了改进材料性能,有研究者们提出了引入可逆相变和局域异质结构的方法^[12-13]。通过研究多个 Pb/Bi 基压电陶瓷在准同型相界附近包含四方相和新相共存的电场驱动相变,根据总结过去工作提出的相变趋势 (dT/dE) 与压电系数之间的经验关系^[12]可以得知。相变可以导致非 180° 畴翻转,从而驱使极化沿着电场的方向排列,优化后的极化排列和激活后的“死畴”使得压电性得以提高^[12]。再加上准同型相界的低对称度极化构型,进一步引入弛豫行为打破了长程极化有序进入局域异质结构,这进一步增强了材料的压电性。LI 等^[13-14]将大半径稀土 Sm^{3+} 引入 PMN-PT 系统,并通过引入局域结构异质性获得了显著提高的压电性能(d_{33} 约为 $1\,500\text{ pC/N}$)和介电性能(ϵ 约为 $113\,000$)。通过原子分辨率扫描透射电子显微镜(STEM)照片可以很好地观察到由局域结构异质性形成的极化构型。在其它铅基系统中也有研究验证了局域多样的极化构型具有提升压电性能的作用^[15-16]。

无铅压电陶瓷中也存在相界,不同的是 BaTiO_3 基和 KNN 基压电陶瓷中的相界是通过移动多晶相变温度来实现的,被称为多晶型相界,其由组分和温度共同决定^[17]。2009 年,LIU 等^[18]在 $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ 系统中构建了立方相 C-R-T 三相点,得到了较高的压电系数(d_{33} 约为 620 pC/N),极化的各向异性在三相点处减弱,这也导致了能垒降低进而促进极化旋转,从而使 $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ 体系能够获得十分优异的性能。YAO 等^[19]研究表明,准四极点 (C-T-O-R 共存)能够进一步增强了 $\text{Ba}(\text{Ti},\text{Sn})\text{O}_3$ 体系中的压电(d_{33} 约为 697 pC/N)和介电性能(ϵ_r 约为 $75\,000$),这得益于各相间能垒降低和自由能曲线的

平坦化。ZHAO 等^[20]利用多相共存在 $\text{Ba}(\text{Ti},\text{Sn})\text{O}_3$ – $(\text{Ba},\text{Ca})\text{TiO}_3$ 体系中设计了 1 个宽组分区域,在该区域内几种组分的压电性能可达 $d_{33}\sim 700\text{ pC/N}$ 。通过像差校正 STEM 和相场模拟,确认局域极化构型包括共存的铁电纳米相(T+O+R)和连续极化旋转^[20]。WANG 等^[21]将局域结构异质性的极化构型与多相共存结合,在无铅 $\text{Ba}(\text{Ti},\text{Sn})\text{O}_3$ 体系中得到了超高压电性能($d_{33}\sim 1\,120\text{ pC/N}$),这也是目前无铅系统中最高的压电性能,是原本钛酸钡基陶瓷压电系数(d_{33} 约为 190 pC/N)的 6 倍左右^[9]。对于 KNN 压电陶瓷,随着温度升高经历 3 个相变: $123\text{ }^\circ\text{C}$ 时由 R 相转变为 O 相; $210\text{ }^\circ\text{C}$ 时由 O 相转变为 T 相; $410\text{ }^\circ\text{C}$ 时由 T 相转化为 C 相^[22]。KNN 体系具有多种相变和相界,这也导致了其具有更加多样化的极化构型调控方式,例如通过化学改性将 $T_{\text{R-O}}$ 或 $T_{\text{O-T}}$ 的相变温度转移到室温,或形成新的 R–T 相界^[23–28]。

TAO 等^[29]曾设计了具有纳米级多相共存(R–O–T)的沙冰极性状态,将压电性提升至 d_{33} 约为 650 pC/N 。引入模板晶粒的生长方法,可以在 KNN 体系的织构化陶瓷中得到 d_{33} 约为 700 pC/N 的高压电性,也是目前 KNN 达到的最高压电系数值^[30]。

综上所述,极化功能基元的调控在实现无铅和铅基系统的高性能方面发挥着至关重要的作用,特别是在具有局域无序异质结构的复杂极化构型的情况下。压电材料中极化构型的调节策略分为 2 大类: 1) 长程有序极化对称性调控,包括相界构造、极化旋转、单斜相和电致相变; 2) 局域极化调控,涉及局域结构不均匀性、纳米级多相共存等。调节局域极化使铁电和压电材料能够在纳米尺度上进行精确的微观结构设计,有助于实现更高的电学性能。随着现代设备对性能要求的不断提高,局域极化构型的调节成为研究人员青睐的材料设计方法。

2 高熵材料与高熵铁电

高熵策略最早于 2004 年在高熵合金(HEAs)中被提出^[31–32],由于高熵策略特殊的设计理念,高熵合金具备许多特殊性能,因此,高熵策略逐渐成为人们研究的热点。受到高熵合金的启发,陶瓷、聚合物和复合材料等领域均已引入高熵的概念^[33–40]。目前,高熵的概念有 2 个主要定义:一是基于熵值定义,即根据熵值大小来判断;二是基于化合物的组成定义,由元素的浓度和数量来定义^[39–40]。根据熵值定义,构型熵(S)是系统无序性的量度,影响固溶体的 Gibbs 自由能。根据热力学公式,定义构型

熵^[41–42]:

$$\Delta S = -R \sum x_i \ln x_i$$

其中: R 为理想气体常数; x_i 为元素的摩尔浓度。当各元素的摩尔浓度相等时,构型熵达到最大值。随着元素数目的增加,构型熵增加,如图 2 所示。由图 2a 可见,材料根据熵的大小分为 3 类材料:低熵材料: $\Delta S < R$; 中熵材料, $R < \Delta S < 1.5R$; 高熵材料: $\Delta S > 1.5R$ ^[34,40,43]。根据组成定义高熵材料,需要含有 5 种或 5 种以上的主要元素,且每种元素所占的摩尔分数在 5% 和 35% 之间^[31,39–40],限制了元素的含量。上述的高熵合金作为第一代高熵材料,均具有单相及等摩尔数的特性,如图 2b 所示^[43]。随着人们对高熵材料的研究,组成的限制逐渐被打破,二代高熵材料的主要成分数量从 5 个主要组分减少到 4 个,同时可以具备双相和复相以及非等摩尔的元素含量。

对比常规合金,由于设计理念的差异,高熵合金中的 4 个核心效应(即高熵效应)导致了异于传统材料的性能: 1) 热力学的高熵效应,扩大了元素之间的溶解度界限,为随机固溶体的形成提供了稳定性; 2) 结构的晶格畸变效应,晶格畸变严重,材料获得强化硬化; 3) 动力学的迟滞扩散效应,阻止第二相颗粒生长; 4) 鸡尾酒效应,混合多种元素后可能产生意外的性能^[40]。受到高熵合金的启发,高熵策略也逐渐被应用于陶瓷材料,人们对高熵陶瓷的研究也逐渐成为热点^[41,44]。高熵陶瓷被定义为占据同一亚晶格的元素数量为 5 种或更多,同时以接近或相等的摩尔数的形式出现,构型熵($\Delta S > 1.5R$),如图 2c 所示。固溶体中元素的数量与熵值的大小呈正相关的关系,多种元素会导致固溶体较大的构型熵。高熵陶瓷有多种高熵氧化物、碳化物、氮化物、磷酸盐等^[41],它们被广泛应用于各个领域,例如电池、热电、催化剂等^[45]。高熵陶瓷自被提出以来,就受到了人们的广泛关注,一系列相关综述被报道^[33,41,46–48],后来有研究将高熵概念进一步引入到铁电材料中,一系列高熵铁电材料包含钙钛矿型及铋层状结构氧化物^[49–50]、钙钛矿层状结构及烧绿石结构等^[51–52]被报道。以结构简单的钙钛矿型结构为例来对高熵铁电体进行介绍,如图 2d 和图 2e 所示。由于钙钛矿型结构具有结构简单,容易掺杂改性等特点,其具有丰富的可调性以及较大的固溶度,可以产生多种极化构型。对于高熵铁电,首先从组成和熵的角度,其与传统高熵陶瓷/合金类似,需要满足 $\Delta S > 1.5R$ 且具有多个主元素的条件^[53]。然而传统高熵策

略只考虑了异质原子的种类和含量,对于功能材料,功能性的调控需要以功能基元为媒介,这是传统高熵效应中没有包含的。例如,铁电材料中的功能基元主要包含阳离子偏心位移引起的极化、缺陷偶极子带来的缺陷极化、氧八面体倾斜等。因此,高熵功能材料不仅仅是指具有化学构型熵很高,同时也要求功能基元结构在局域尺度上具有高无序度,从而带来功能性的提升,如图 3 所示。在高熵铁电体中,可以在提升化学无序度的同时考虑基体对称性和引入元素的特性,使得极化强度和极化方向(或/和氧八面体倾斜)在局域尺度上具有很高的无序度,这也是高熵铁电体区别于甚至优于传统弛豫铁电体之处。若不考虑功能基元的调控作用,在无穷多的化学成分中寻找高性能高熵功能组分将变得非常盲目和困难。虽然很多高熵铁电体也表现出了介电弛豫特性和极性纳米微区,其中的极化构型应与在传统弛豫铁电体中观察到的极性纳米区域(短程共线极化)不同,因为高熵铁电体需要具有高极化熵,即极化角度和强度都表现出明显的无序度,从而利于实现更高的物理性质。

尽管高熵材料具有特殊的性质与优异的性能,但是对于其更深层次的机理以及更系统的总结仍然较为匮乏。由于铁电体的极化构型调控对于材料的电学性能影响重大,针对这一方面,高熵策略能够对极化构型进行调节,从而改善高熵铁电体的性能。有研究通过第一性原理计算证实了高熵策略通过弥散极化幅值和角度的分布,产生了更为灵活的极化构型,这也有利于设计高性能的材料。在后文中将对高熵策略控制极化构型从而获得较优异的性能进行论述,同时研究高熵策略对场效应机理和性能的影响。

3 压电性能

一系列研究致力于提高材料的压电性能以拓宽压电材料的应用领域,目前已经取得了许多成果,例如通过构造准同型相界、单斜相、局域结构异质性、多相共存等方式提高材料性能。根据研究表明在铁电材料中增加极化构型的无序性有利于改善材料压电性能,而通过高熵策略设计铁电材料高无序度极化构型为产生高压电性提供了基础。

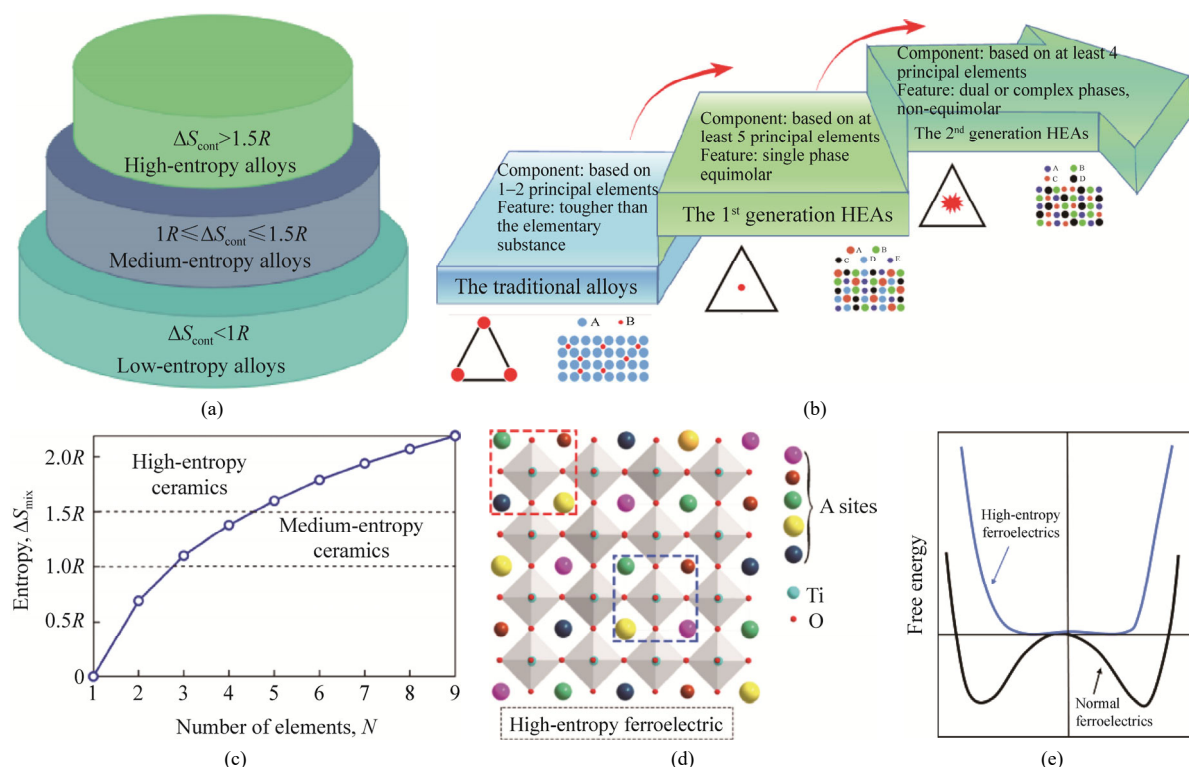


图 2 高熵合金、高熵陶瓷与高熵铁电材料 (a) 基于构型熵的合金分类^[43] (b) 高熵合金的发展^[43] (c) 陶瓷基于构型熵和元素数量的分类^[41] (d) 钙钛矿型高熵铁电材料的结构图^[54] (e) 高熵铁电材料和普通铁电材料的自由能对比^[54]

Fig. 2 High-entropy alloys, high-entropy ceramics, and high-entropy ferroelectric materials. (a) Alloy classification based on configurational entropy^[43], (b) Development of high-entropy alloys^[43], (c) Classification of ceramics based on configurational entropy and the number of elements^[41], (d) Structure diagram of perovskite-type high-entropy ferroelectric materials^[54], (e) Free energy comparison between high-entropy ferroelectric materials and conventional ferroelectric materials^[54]

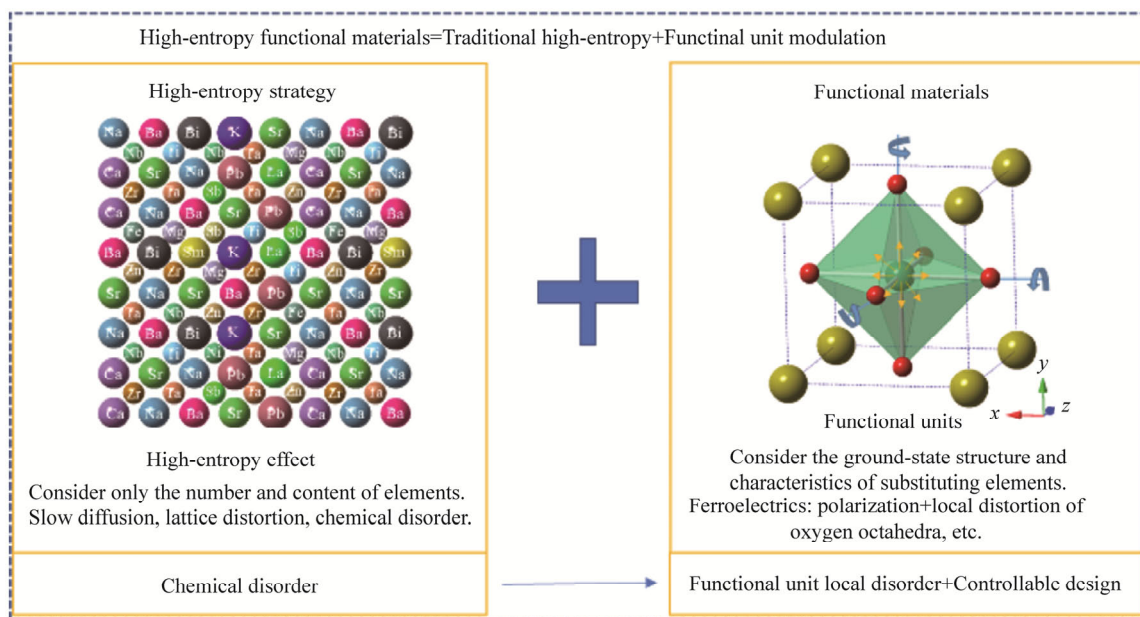


图3 高熵功能材料设计策略

Fig. 3 High-entropy functional material design strategy

有研究尝试通过在铅基化合物的B位引入不同半径和价态的离子来实现熵值调控^[53,55–56],在B位掺杂,5种不同的元素占据同一个晶格位置,最终获得了具有极高压电系数的 $\text{Pb}(\text{Ni}_{0.173}\text{In}_{0.07}\text{Zr}_{0.034}\text{Ti}_{0.306}\text{Nb}_{0.417})\text{O}_3$ 陶瓷($d_{33} \sim 1\,200\text{ pC/N}$),在B位引入这些不同元素后,由于离子半径和价态的差异引起了局域结构畸变,形成了与传统铁电体中均匀单一的R或T相不同的特殊的极性分布,如图4a所示^[53]。经过对极化角的研究,发现在 $0^\circ \sim 45^\circ$ 之间存在均匀的角度分布,有利于产生极化旋转,并且具有更大的极化灵活性,如图4b所示,有利于产生高的压电性能。在 $\text{Pb}(\text{Ni}_{0.153}\text{In}_{0.115}\text{Nb}_{0.422}\text{Ti}_{0.31})\text{O}_3$ 体系中也观察到了类似的现象(d_{33} 约为 920 pC/N)。多个局域极性对称(R–M–T)的共存降低了自由能垒和极化各向异性,呈现出准各向同性局域极化分布,如图4c和图4d所示,从R到M再到T的连续极化跃迁和丰富的单斜相增加了电场作用下极化旋转的灵活性,从而获得较高的压电性能^[55]。

高熵策略除了对钙钛矿型陶瓷中实现了对性能的改善,在其它结构中也有相关案例,例如有研究在铋层状结构氧化物陶瓷中就引入高熵策略。铋层状结构氧化物陶瓷具备较高的Curie温度和机械性能^[49–50],但是低压电性和高矫顽场使得其应用受到限制,针对铋层状陶瓷的特点,高熵概念的引入可以优化其微观结构。ZHANG等^[50]设计了A位掺杂的多种元素的单相 $\text{BaBi}_2\text{Nb}_2\text{O}_9$ 基高熵弛豫铁电陶

瓷,其压电性能的增强可以归因于长程有序的微畴和纳米畴共存的多畴结构,并且纳米畴在电场下不可逆地转变为微畴,这种特殊的多畴结构有利于降低矫顽场,提高压电性。除此之外,ZHANG等^[49]还制备了具有正交相的4层Aurivillius结构 $(\text{Ca}_{0.2}\text{Sr}_{0.2}\text{Ba}_{0.2}\text{Pb}_{0.2}\text{Nd}_{0.1}\text{Na}_{0.1})\text{Bi}_4\text{Ti}_4\text{O}_{15}$ 高熵铋层状陶瓷,其呈现出极性纳米微区与复杂的铁电行为,Curie温度可达 557°C ,这为设计高性能高熵压电陶瓷提供了新思路。

4 电致伸缩

电致伸缩效应起因于阳离子从平衡位置偏移以产生极化引起的晶格参数的变化^[57–60]。与普通的压电材料相比,电致伸缩材料由于无滞后、对电场快速响应、良好的温度稳定性、抗疲劳性以及无需极化处理的优良特性而在诸如双稳态光学器件等高精度位移致动器的应用中得到广泛关注^[57–59,61–62]。电致伸缩效应可以定义为极化(P)或电场(E)的平方,如下关系所示:

$$S_{33} = Q_{33}, P_3^2 = M_{33}E^2 \quad (1)$$

其中: Q_{33} 和 M_{33} 均为电致伸缩系数,大的电致伸缩需要较大的应变位移与小的驱动电场或极化。

最近,有研究提出了通过在具有局域异质极化的基体中引入分散的纳米共格析出沉淀相来调节极化构型以实现高熵弛豫铁电体中的大电致伸缩系数,如图5所示^[60]。 $\text{Sm–Pb}(\text{Ni}, \text{In}, \text{Zr}, \text{Ti}, \text{Nb})\text{O}_3$ 高

熵体系在 8 kV/mm 的电场下表现出 0.18% 几乎无滞后的大应变。通过计算不同应变下的电致伸缩系数可以得到高熵体系的电致伸缩性能优于其它体系的结论, 这也表明该高熵体系可以在较小的电场下被驱动。优异的电致伸缩性能可以归因于特殊的极化构型, 如图 5b~图 5g 所示。其结构由大面积的基体和 $5\sim 10 \text{ nm}$ 的局域异质的极性纳米微区(PNR)和纳米共格析出相共存组成。首先, 如图 5c 所示, 基体呈现了 R-T-C 共存局域结构, 促进极化翻转和晶格应变, 并诱导宏观大应变的产生; 另一方面, 共格纳米颗粒的表现出非极性状态, 这与 Sm^{3+} 的偏析

以及相应的非铁活性阳离子在 B 位点的富集有关, 如图 5d~图 5f 所示。即使施加非常高的电场, 纳米析出相的内部也不能被极化, 这为系统提供恢复力^[60]。当陶瓷在电场下产生大应变响应后, 纳米析出相可以帮助陶瓷在放电过程中快速恢复至非极化状态, 从而减少应变滞后的发生, 极化构型如示意图如图 5g 所示, 其中, 大应变和无滞后的极化特性共同导致了较大的电致伸缩效应。这种特殊极化构型的大晶格应变和无滞后响应也可以通过使用原位电场同步辐射(XRD)结果得到验证, 如图 5h 和图 5i 所示。

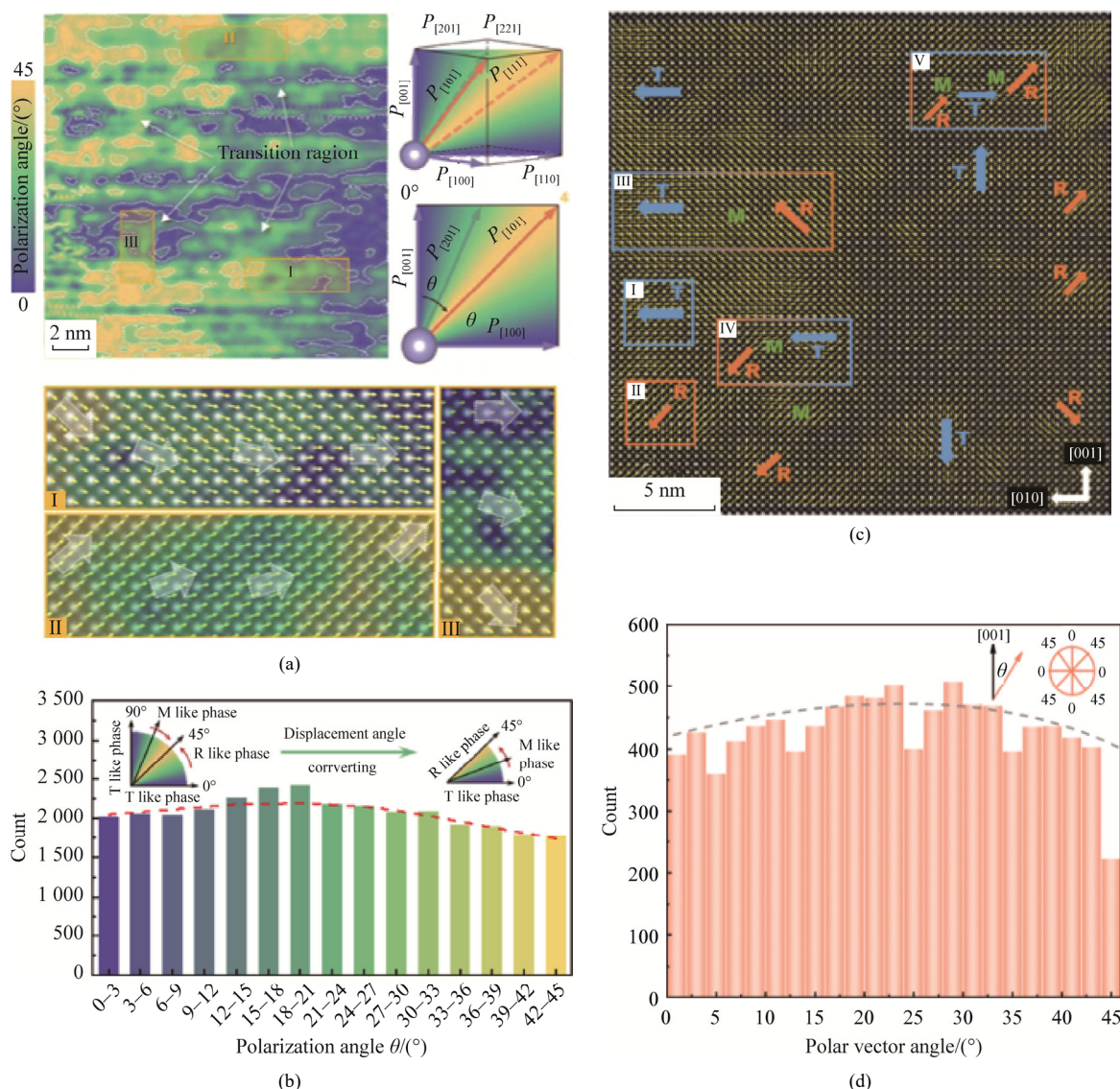


图 4 高熵系统的高压电性能和局域极化分布 (a)、(b)高熵 $\text{Pb}(\text{Ni}_{0.173}\text{In}_{0.07}\text{Zr}_{0.034}\text{Ti}_{0.306}\text{Nb}_{0.417})\text{O}_3$ 系统的原子分辨率极化图和极化角度统计分布^[53] (c)、(d) $\text{Pb}(\text{Ni}_{0.153}\text{In}_{0.115}\text{Nb}_{0.422}\text{Ti}_{0.31})\text{O}_3$ 系统的极化矢量图和极化矢量角度^[55]

Fig. 4 Depicts the high piezoelectric performance and local polarization distribution in high-entropy systems.(a), (b) Atomic-resolution polarization maps and statistical distribution of polarization angles for the high-entropy $\text{Pb}(\text{Ni}_{0.173}\text{In}_{0.07}\text{Zr}_{0.034}\text{Ti}_{0.306}\text{Nb}_{0.417})\text{O}_3$ system^[53], (c), (d) Polarization vector maps and polarization vector angle distributions for the $\text{Pb}(\text{Ni}_{0.153}\text{In}_{0.115}\text{Nb}_{0.422}\text{Ti}_{0.31})\text{O}_3$ system^[55]

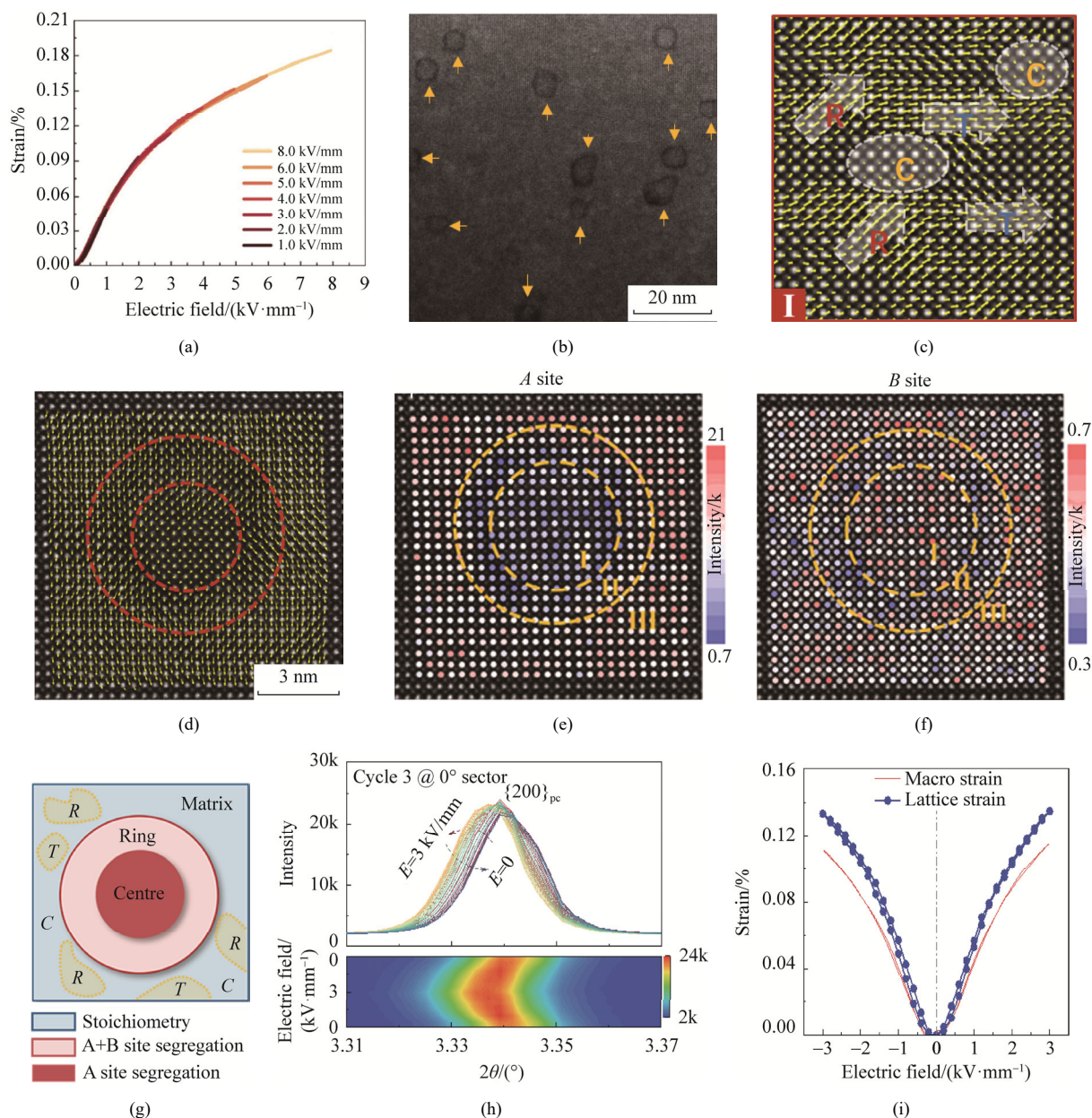


图5 Sm-Pb(Ni, In, Zr, Ti, Nb)O₃ 陶瓷的大电致伸缩系数(M_{33})、内生纳米沉淀物的新极化构型和在电场下的结构变化^[60] (a) 不同电场下的单极应变(b)域结构的 HAADF-STEM 照片 (c)基体的原子尺度极化矢量图 (d)内生纳米沉淀物的原子尺度极化矢量图 (e) A 位点原子柱的极化强度分布 (f) B 位点原子柱的极化强度分布 (g)内生纳米沉淀物结构的示意图 (h) $\{200\}_{pc}$ 峰值在 0° 区域内随电场变化而变化 (i)内在晶格应变和测量宏观应变的比较

Fig. 5 Illustrates the large electrostrictive coefficient (M_{33}), new polarization configurations of intrinsic nanoprecipitates, and structural changes under an electric field in Sm-Pb(Ni,In,Zr,Ti,Nb)O₃ ceramics^[60] (a) Unipolar strain under different electric fields, (b) Domain structure HAADF-STEM images, (c) Atomic-scale polarization vector map of the matrix, (d) Atomic-scale polarization vector map of intrinsic nanoscale precipitates, (e) Polarization intensity distribution of A-site atomic columns, (f) Polarization intensity distribution of B-site atomic columns, (g) Schematic representation of the structure of intrinsic nanoscale precipitates, (h) Variation of $\{200\}_{pc}$ peak in the 0° sector with electric field in the structure of intrinsic nanoscale precipitates, (i) Comparison between intrinsic lattice strain and measured macroscopic strain

5 电介质储能

随着科学技术的发展,人们对高效能源利用的需求逐步提高,也逐渐从煤、石油等不可再生能源转为使用清洁的可再生能源,因此能源的高效运输

与存储也受到人们的广泛关注。近年来,电介质储能相关的研究得到了人们的广泛关注,介质电容器对比其它储能模式,其具有较高的功率密度以及较快的充放电响应,这也让其在电路、通信、车辆等多种领域得到了广泛应用^[63–65]。随着人们对能源行

业的应用需求逐渐扩大, 电介质电容器因此也成为了人们研究的热点。尽管电介质电容器具备显著的优势, 但是对比燃料电池较低的能量密度限制了其在人们实际生产生活中的应用。高储能性能一直是人们研究的目标, 总储能密度(W_t)、能量密度(W_{rec})、储能效率(η)主要与最大极化强度(P_{max})、剩余极化强度(P_r)、以及击穿场强(E_b)为 3 个参数相关。根据下式^[66-67]:

$$W_t = \int_0^{P_{max}} E dP, W_{rec} = \int_{P_r}^{P_{max}} E dP, \eta = \frac{W_{rec}}{W_t} \times 100\% \quad (2)$$

根据能量存储的定义, 获得具有高 W_{rec} 的材料需要大的极化差($\Delta P = P_m - P_r$), 即大 P_m 、小 P_r 、高击穿强度和延迟极化饱和, 而通常情况下, 难以同时获得高的能量密度和储能效率。目前, 用于储能的介电电容器材料主要为弛豫铁电材料和弛豫反铁电材料^[68-82]。弛豫反铁电材料在高电场下会经历从反铁电体到铁电体的转变, 从而提供高 W_{rec} , 但是由于相变的滞后效应, 储能效率较低, 例如, 基于 NaNbO_3 的弛豫反铁电系统, 其中报告了超高的能量密度(W_{rec} 约为 12.2 J/cm^3 , η 约为 69%)以及(W_{rec} 约为 18.5 J/cm^3 , η 约为 78.7%)^[68-69, 83-88]。而在弛豫铁电材料中, 不同离子占据 A/B 位点晶格引起随机场的生成破坏了长程铁电域, 使其形成了极性纳米微区, 产生了细长的 $P-E$ 回线, 可以实现高储能效率^[89-93]。为了提高介电常数, 需要降低极化滞后, 减少能量损失, 解决储能密度和效率之间的限制关系的问题, 目前可以通过传统的畴工程, 化学掺杂改性以及相变来对电容器的性能进行优化^[68-71, 75, 83-85, 88]。

高熵策略的引入为提高介质电容器的性能提供了全新思路, 其通过形成局域多样性极化、超顺电态、无序结构、抑制晶粒粗化和提高能带间隙等方面进行多角度协同调控, 能够有效地获得高极化响应、极低的剩余极化强度、快速放电响应、延迟极化饱和、高击穿强度以及机械性能等, 如图 6 所示^[94-96]。由图 6 可见, 通过高熵策略调整局域极化构型以满足较高的综合储能性能的参数要求。例如在钙钛矿体系中, 通过使用多个异质原子进行 A 位掺杂可以增加局域极化的无序程度, 获得 $(\text{Na}_{0.2}\text{Bi}_{0.2}\text{Ba}_{0.2}\text{Sr}_{0.2}\text{Ca}_{0.2})\text{TiO}_3$ ^[54, 67, 97-98]、 $(\text{NaBaBi})_x(\text{SrCa})_{(1-3x)/2}\text{TiO}_3$ ^[99]和 $(\text{La}, \text{Li})_x[(\text{Bi}, \text{Na})\text{BaSrCa}]_{1-x}\text{TiO}_3$ 陶瓷^[100]。研究者在 $(\text{Bi}_{0.3}\text{Na}_{0.3}\text{Ba}_{0.4})(\text{Fe}_{0.2}\text{Ti}_{0.6}\text{Nb}_{0.2})\text{O}_3$ 高熵陶瓷中发现了动态极性纳米微区, 如图 6a 所示, 高活性的极性纳米微区为获得高储能性能提供了基础。为了揭示构型熵对储能性能的影响, 对 $(\text{Bi}_{0.5}\text{Na}_{0.5})(\text{Ti}_{1-2x}\text{Fe}_x$

$\text{Nb}_x)\text{O}_3$ (即 $(1-2x)\text{BNT}-x\text{BF}-x\text{NN}$ 三元体系)陶瓷的构型熵与电学性能间关系进行了系统的研究, 结果表明, W_{rec} 和 η 都随着 ΔS 的增加而单调增加, 在 $(\text{Bi}_{0.5}\text{Na}_{0.5})(\text{Ti}_{1/3}\text{Fe}_{1/3}\text{Nb}_{1/3})\text{O}_3$ 高熵组分中分别达到最大值 13.8 J/cm^3 和 82.4%, 如图 6b 所示^[101]。高熵组分中得到优异的储能性能应当归因于随机场的增强、纳米微区尺寸的减小、局域变形以及击穿电场的增强。在 $\text{BT}-\text{BNT}-\text{NN}$ 三元体系中也发现了随着 ΔS 增加而增强的储能性能^[94], 相应的设计方法和局域极化构型如图 6c 所示。如图 6c₁ 所示, 根据 Landau-Devonshire 理论计算得到的 Gibbs 自由能分布, 具有多种极化结构(T-C、R-T、O-T、R-O-T-C)晶体的自由能分布变平坦, 极化不稳定性增强。 $\text{NN}-\text{BT}$ 和 $\text{NN}-\text{BNT}$ 中熵陶瓷由于分别受到较快极化饱和与大滞后的限制, 因而难以同时达到高 W_{rec} 和 η 。为了解决 W_{rec} 和 η 之间的相互制约关系, 研究者们选择了在电场下具有近似线性极化响应的超顺电体, 如图 6c₂、6c₃ 所示, 和一种新的局域分极化, 如图 6c₄ 所示。结合 BNT 的高 P_s 基因和 NN 的宽带隙(E_g), 制备了 $1/3\text{BT}-1/3\text{BNT}-1/3\text{NN}$ 高熵超顺电陶瓷, 室温下得到了优秀的储能性能, W_{rec} 约为 10.59 J/cm^3 , η 为 87.6%, 具有良好的热稳定性和频率稳定性。

大多数钙钛矿都表现出氧八面体倾斜, 氧八面体倾斜程度较大会阻碍电场作用下的极化重新取向过程, 因此, 氧八面体倾斜的引入可能有利于减缓极化饱和的过程, 如图 7a 所示。许多具有不同离子半径和价态的离子被引入到 $\text{K}_{0.2}\text{Na}_{0.8}\text{NbO}_3$ 晶格中, 将其中表现出复杂氧八面体倾斜的 R、O、T、C 相将多晶相边界移到室温附近, 同时形成弛豫的特性^[95]。在 $[(\text{K}_{0.2}\text{Na}_{0.8})_{0.8}\text{Li}_{0.08}\text{Ba}_{0.02}\text{Bi}_{0.1}](\text{Nb}_{0.68}\text{Sc}_{0.02}\text{Hf}_{0.08}\text{Zr}_{0.1}\text{Ta}_{0.08}\text{Sb}_{0.04})\text{O}_3$ (KNN-H)高熵陶瓷中产生的新型极化构型被称为“局域多重无序畸变”, 包含 R-O-T-C 多相纳米团簇和随机氧八面体倾斜, 其产生了 10.06 J/cm^3 的高能量密度以及 90.8% 的超高储能效率, 具备优异的综合性能, 如图 7b 和图 7c 所示。

既往的研究表明高熵铁电陶瓷具有大 W_{rec} 与高 η , 较好的机械性能, 优秀的温度、频率稳定性, 以及优异的充放电性能, 综合储能性能十分优秀, 具有较大的潜力。这些优异性能可以通过高熵策略设计的具有局域多重无序畸变的特殊极化构型产生的超高 E_b 、大的 ΔP 、延迟极化饱和和温度、频率稳定的介电响应来实现^[95]。

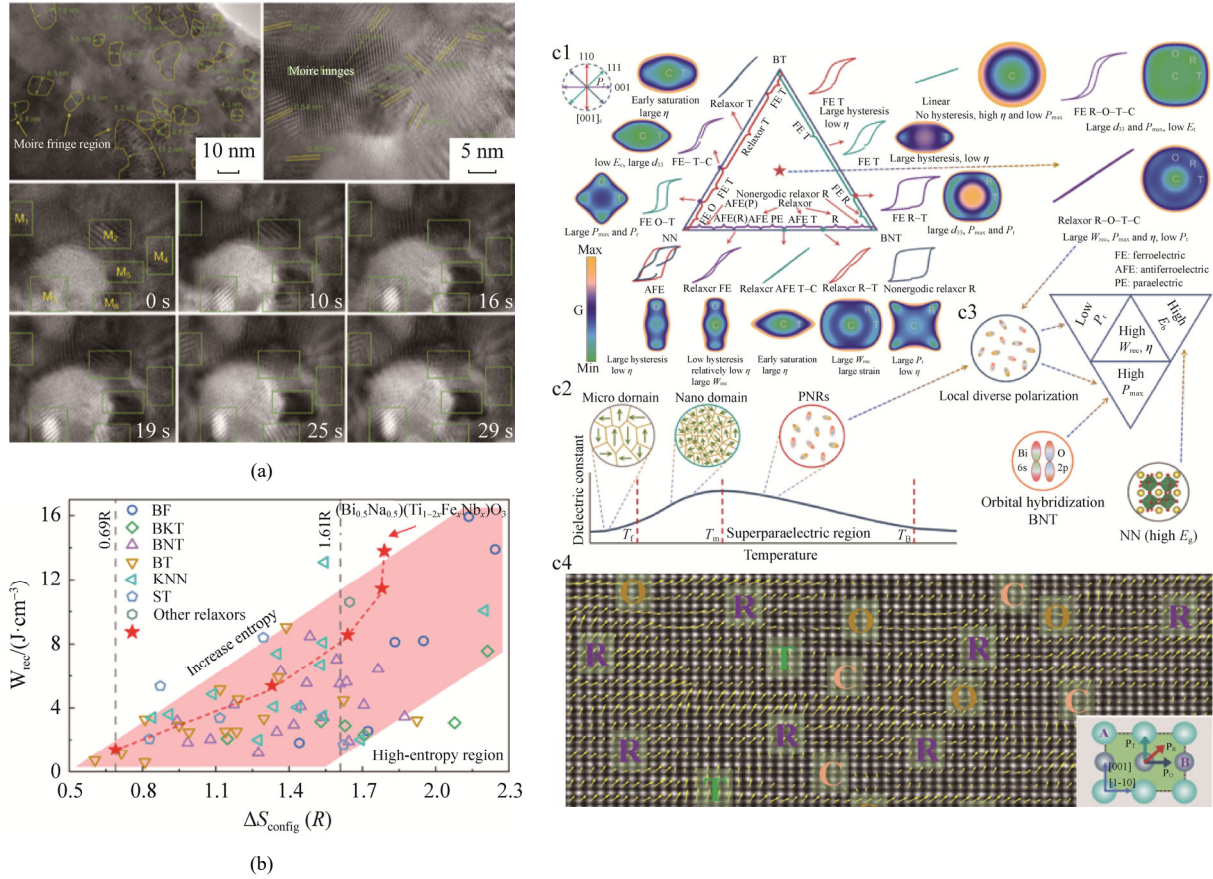


图 6 具有优异能量储存性能的铁电陶瓷的高熵设计 (a) $(\text{Bi}_{0.3}\text{Na}_{0.3}\text{Ba}_{0.4})(\text{Fe}_{0.2}\text{Ti}_{0.6}\text{Nb}_{0.2})\text{O}_3$ 高熵陶瓷中的动态极性纳米微区^[102] (b) 具有不同构型熵 ΔS 的弛豫铁电陶瓷的 W_{rec} 以及 $(\text{Bi}_{0.5}\text{Na}_{0.5})(\text{Ti}_{1-2x}\text{Fe}_x\text{Nb}_x)\text{O}_3$ 陶瓷的 W_{rec} 与 ΔS 之间的正相关关系^[101] (c) 优化 BT–BNT–NN 三元高熵超电容材料的综合能量存储性能的区域多样化极化构型示意图^[94]: (c₁) BT–BNT–NN 的三元相图示意图, 以及使用 Landau–Devonshire 理论得出的相应 P – E 回线和 Gibbs 自由能图; (c₂) 弛豫铁电材料在不同温度区域的局域结构变化; (c₃) 结合轨道杂化和高 E_g 特性, 建立局域多样化极化以实现高 W_{rec} 和 η ; (c₄) 在 1/3BT–1/3BNT–1/3NN 高熵铁电陶瓷中观察到的局域多样化的极化构型

Fig. 6 Presents high-entropy design of ferroelectric ceramics with outstanding energy storage performance (a) Dynamic polar nanoregions in $(\text{Bi}_{0.3}\text{Na}_{0.3}\text{Ba}_{0.4})(\text{Fe}_{0.2}\text{Ti}_{0.6}\text{Nb}_{0.2})\text{O}_3$ high-entropy ceramics^[102], (b) Correlation between W_{rec} (energy recovered) of relaxor ferroelectric ceramics with different configurational entropy (S) and the positive correlation between W_{rec} and S in $(\text{Bi}_{0.5}\text{Na}_{0.5})(\text{Ti}_{1-2x}\text{Fe}_x\text{Nb}_x)\text{O}_3$ ceramics^[101], (c) Schematic representation of diverse local polarization configurations for optimized high-entropy super capacitor materials BT–BNT–NN^[94]: (c₁) Ternary phase diagram of BT–BNT–NN, along with corresponding P – E hysteresis loops and Gibbs free energy diagram obtained using Landau–Devonshire theory, (c₂) Local structural changes in relaxor ferroelectric materials in different temperature regions, (c₃) Establishing diverse local polarization configurations for high W_{rec} and η , combining orbital hybridization and high E_g characteristics, (c₄) Observation of diverse local polarization configurations in 1/3BT–1/3BNT–1/3NN high-entropy ferroelectric ceramics

首先, 可以通过熵增来提高 E_b 。通过引入多种元素来设计体系的高熵, 特别是在异质原子中选择助烧剂, 可以活化晶格, 降低烧结温度, 从而优化烧结后的机械和电学性能。同时, 抑制晶粒粗化, 形成具有均匀元素分布的细晶结构, 从而导致相对密度增加, 介电损耗降低^[33]。位错的运动受阻、高电阻晶界的比例增加, 大大增强了 E_b 。此外, 选择的高带隙原子设计组分也将有利于提高 E_b 。

对于 ΔP , 在高熵铁电体中可以设计较大 P_{max} 和几近为零的 P_r 从而得到更大的 ΔP 。局域尺度上

不同对称性共存的无序晶格畸变使极化在电场下发生重新取向, 增强了电场方向的极化的织构化程度, 有利于产生较大的 P_{max} ; 高熵效应使得材料在强电场作用下表现出延迟极化饱和, 这是由于 PNR 之间的弱关联性, 这也是高熵晶体显现出优异储能性能的重要原因之一; 额外引入随机分布的氧八面体倾斜的结构也会在形成长程有序铁电体的过程中消耗一些能量, 导致具有接近线性 P – E 回线的延迟极化饱和; 高熵陶瓷的超高硬度应归功于具有致密微观结构的超细晶粒的 Hall–Petch 强化^[103]; 此外, 由高

熵策略设计引起的质量无序和固溶体硬化可以承受由表面电荷的静电吸引产生的压缩力和由电致伸缩效应产生的应力, 将会降低电场击穿的可能性; 通过熵增引起的介电弛豫和扩散相变过程有利于材料的温度和频率稳定性, 氧八面体倾斜体系也显示出良好的温度稳定性, PNR 之间的弱关联性使它们能够在电场下发挥快速响应, 导致优异的频率稳定性。由于尺寸效应的影响, 薄膜对比陶瓷的击穿场强大大提高, 因此薄膜用于储能时能量密度也更大。根据延迟极化饱和的原理, 通常选择介电常数相对较低的介质作为候选材料, 如顺电体、超顺电体和一些非铁电体氧化物。目前, 已经有研究报道了超顺电钙钛矿薄膜中得到的超高储能密度^[104-106]。而非钙钛矿材料较弱的铁电性导致相对较低的极化响应与固溶度, 不利于获得较高储能密度^[104,107-109]。

有研究报道了通过高熵策略来改进非钙钛矿材料的性能, 例如引入等比例的阳离子取代 $\text{Bi}_2\text{Ti}_2\text{O}_7$,

利用 Zr、Hf、Sn 取代 Ti 位点, La 取代 Bi 位点, 随着熵值增加, 烧绿石相的 Gibbs 自由能会降低, 因此有利于获得稳定的高熵薄膜^[110]。对于立方 $\text{Bi}_2\text{Ti}_2\text{O}_7$ 的结构, Bi 和 Ti 阳离子应当位于高对称性的晶格位置, 然而高熵 $(\text{Bi}_{3.25}\text{La}_{0.75})(\text{Ti}_{1.8}\text{Zr}_{0.4}\text{Hf}_{0.4}\text{Sn}_{0.4})\text{O}_{12}$ 薄膜中的阳离子对比原本的位置发生了位移, 如图 8a 和图 8b 所示。位移量和角度呈现不规则的无序分布, 这也导致了无规则的晶格畸变。晶格畸变引起晶粒细化大幅增加了结晶的能量, 导致了与高熵系统中较高结晶能量相关的无序非晶相的出现, 这也通过 STEM 检测得到了证明。如图 8c 和图 8d 中所示的方法, 稳定的微结构有利于获得优异的储能性能, 结果显示了材料的击穿场强增加, 极化滞后减小。在铋层状结构薄膜中, 通过熵增的策略提升钙钛矿层中局域极化的无序度, 如图 8e 和图 8f 所示, 也能获得优异的储能性能^[111]。

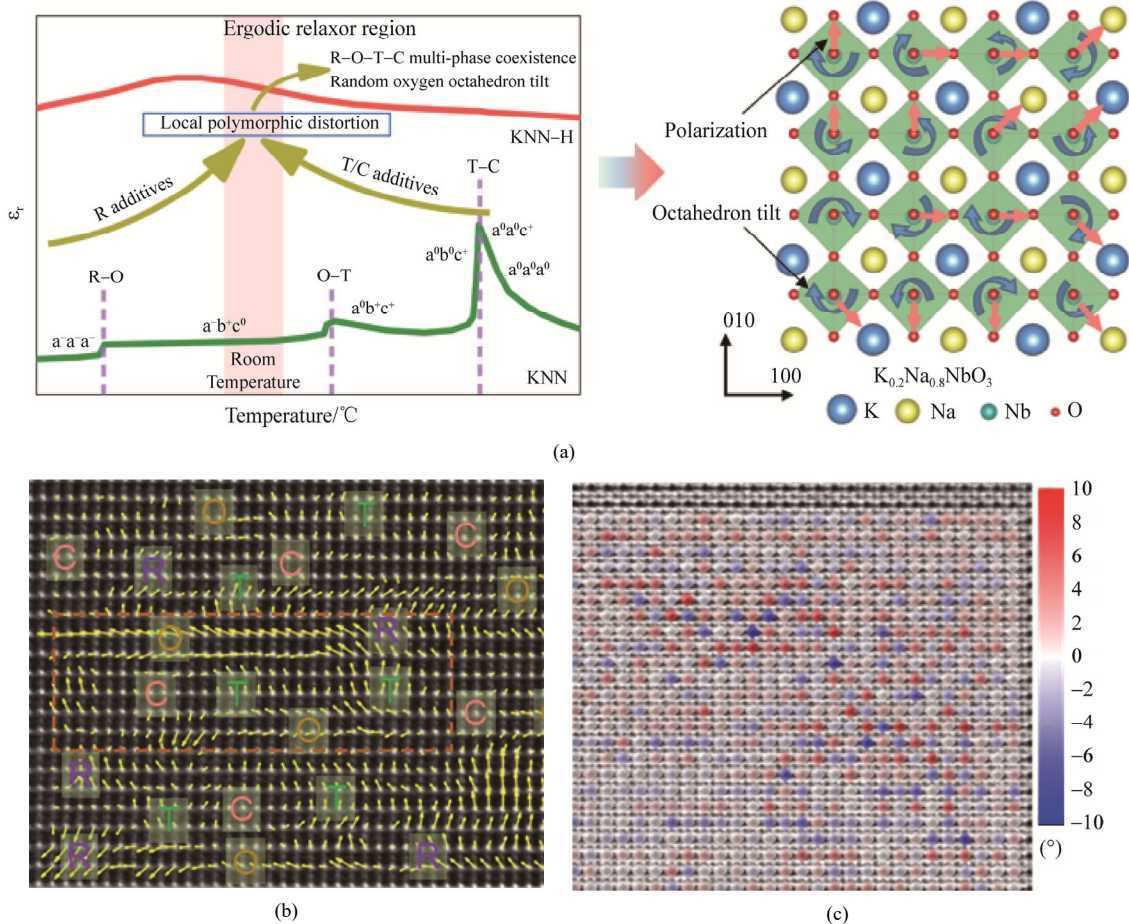


图 7 基于高熵设计的 KNN 基无铅陶瓷中的局域多形形变和优秀的能量存储性能^[95] (a)极化构型设计的高熵策略示意图 (b)、(c) KNN-H 高熵陶瓷的原子尺度 HAADF-STEM 极化矢量图和氧八面体倾斜信息

Fig. 7 Demonstrates local multiphase deformations and excellent energy storage performance in lead-free KNN-based high-entropy ceramics^[95] (a) Schematic diagram of high-entropy strategy for polarization configuration design, (b) and (c) Atomic-scale HAADF-STEM polarization vector maps and octahedral tilt information of KNN-H high-entropy ceramics

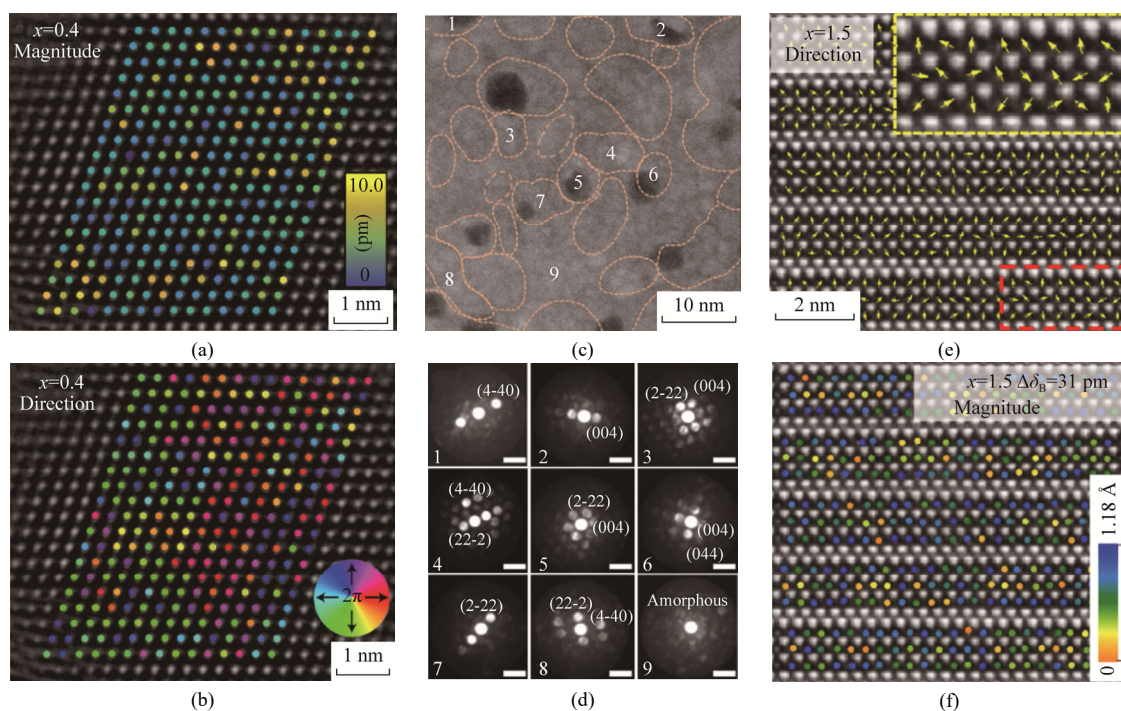


图8 高熵薄膜中的晶格畸变、纳米晶粒和非晶态相以及它们的能量存储性能^[110], 晶格畸变通过 $(\text{Bi}_{3.25}\text{La}_{0.75})(\text{Ti}_{1.8}\text{Zr}_{0.4}\text{Hf}_{0.4}\text{Sn}_{0.4})\text{O}_{12}$ 薄膜中阳离子位移的幅度(a)和方向(b)映射来说明(c)低放大度的 HAADF 图像显示 $(\text{Bi}_{3.25}\text{La}_{0.75})(\text{Ti}_{1.8}\text{Zr}_{0.4}\text{Hf}_{0.4}\text{Sn}_{0.4})\text{O}_{12}$ 薄膜中纳米晶粒(标号 1–8)和非晶态相的共存 (d) 纳米晶粒和非晶态相的 nano-beam 电子衍射图案, 由(c)中标号为 1–9 的标记; $\text{Bi}_{2.5}(\text{La}_{0.325}\text{Pr}_{0.325}\text{Nd}_{0.325}\text{Sm}_{0.325})\text{Ti}_3\text{O}_{12}$ 中熵薄膜中 Ti 位置 (e)极化分布图 (f)极化强度分布^[111]

Fig. 8 Illustrates lattice distortion, nanocrystalline grains, and amorphous phases in high-entropy thin films along with their energy storage performance^[110]. Lattice distortion is explained through the amplitude (a) and direction (b) mapping of cationic displacements in $(\text{Bi}_{3.25}\text{La}_{0.75})(\text{Ti}_{1.8}\text{Zr}_{0.4}\text{Hf}_{0.4}\text{Sn}_{0.4})\text{O}_{12}$ films, (c) Low-magnification HAADF image shows the coexistence of nanocrystalline grains (labeled 1–8) and amorphous phases in $(\text{Bi}_{3.25}\text{La}_{0.75})(\text{Ti}_{1.8}\text{Zr}_{0.4}\text{Hf}_{0.4}\text{Sn}_{0.4})\text{O}_{12}$ films. (d) Nano-beam electron diffraction patterns of nanocrystalline grains and amorphous phases, labeled 1–9 in (c), Ti positions in the entropy thin film of $\text{Bi}_{2.5}(\text{La}_{0.325}\text{Pr}_{0.325}\text{Nd}_{0.325}\text{Sm}_{0.325})\text{Ti}_3\text{O}_{12}$ are shown with (e) polarization distribution and (f) polarization intensity distribution^[111]

6 高熵电卡制冷

除了压电和储能等性能, 近年来基于电卡效应的固态制冷技术受到了人们的广泛关注^[112–118]。当极化电场变化时, 场致熵变可以引起铁电体产生明显的温度变化, 这也被称为电卡效应。通过增加铁电体的构型熵, 在弛豫铁电体有序与无序转变过程中, 可能产生较大的熵变。此外, 无序成分的弥散相变有利于提高材料的热稳定性, 例如在高熵陶瓷中发现其具有的优异的电卡效应与温度稳定性以及较大的等温熵变, 以及在低电场下的较大的电卡效应等^[119–121]。

由于薄膜具备较高的击穿场强, 因此有望在高熵薄膜中获得更高的温度变化, 有研究制备了 $\text{Ba}(\text{Ti}_{0.2}\text{Sn}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2})\text{O}_3$ 高熵薄膜, 可以检测到尺寸约为 2~6 nm 的纳米畴, 施加电场后呈现出较大的熵变, 同时伴随双 $P-E$ 电滞回线^[122]。由于弥散相变和高电场, $\text{Pb}(\text{Hf}_{0.2}\text{Zr}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2}\text{Al}_{0.2})\text{O}_3$ 高熵

膜在 200 K 以上的宽温度范围内可以实现大的电热效应, 如图 9a 所示^[123]。为了获得更大的电卡效应, QIAN 等^[36]将极性氯氟乙烯基团的少量共价双键转化为增强聚合物的极性熵的共价双键, 从而形成了高熵状态, 表现出超高电卡熵变, 以及 50 MV/m 低电场下大约 7.5 K 的温度变化, 如图 9b 所示。

7 结论与展望

尽管高熵策略在调节各类材料的性能方面展现出无与伦比的潜力, 然而掺杂了多种基体组分之外的离子, 它们自身的特性以及其对于基体的影响机理尚不明确, 而且大量的高熵组分并没有表现出明显的性能提升。因此, 设计高熵功能材料不能直接沿用传统结构材料中的高熵策略, 需在考虑化学无序的同时利用高度可调的化学成分来设计功能基元结构无序, 即为了在材料中获取优秀的功能性, 需要满足化学无序、结构无序以及功能基元的无序, 如图 10 所示, 这也是设计新型高熵功能材料的核心。

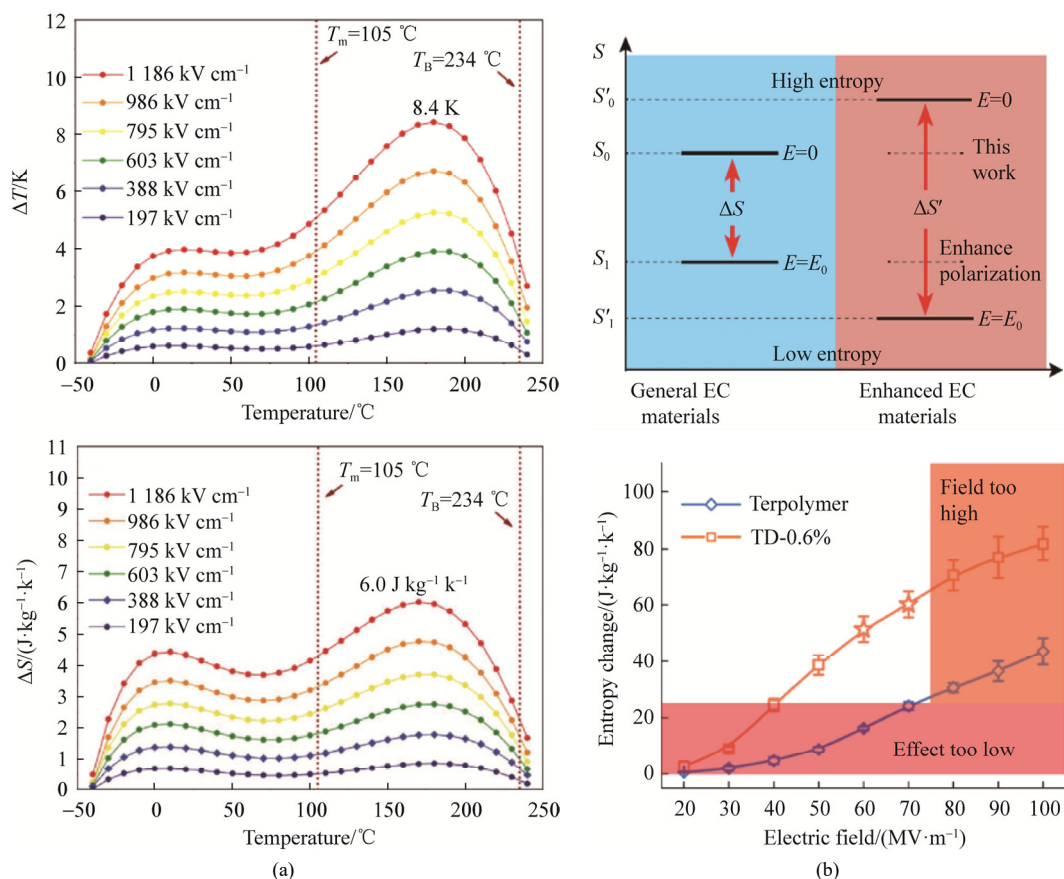


图 9 (a) $\text{Pb}(\text{Hf}_{0.2}\text{Zr}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2}\text{Mn}_{0.2})\text{O}_3$ 高熵薄膜的点卡温度变化和相应的熵变化^[123] (b) 在 TD-0.6% 聚合物中实现在特定电场下更大 ECE 和增强的熵变的原理图^[36]

Fig. 9 (a) Curie temperature variation and corresponding entropy change of $\text{Pb}(\text{Hf}_{0.2}\text{Zr}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2}\text{Mn}_{0.2})\text{O}_3$ high-entropy thin films^[123], (b) Schematic diagram illustrating the enhanced electrocaloric effect (ECE) and increased entropy change achieved in TD-0.6% polymer under specific electric fields^[36]

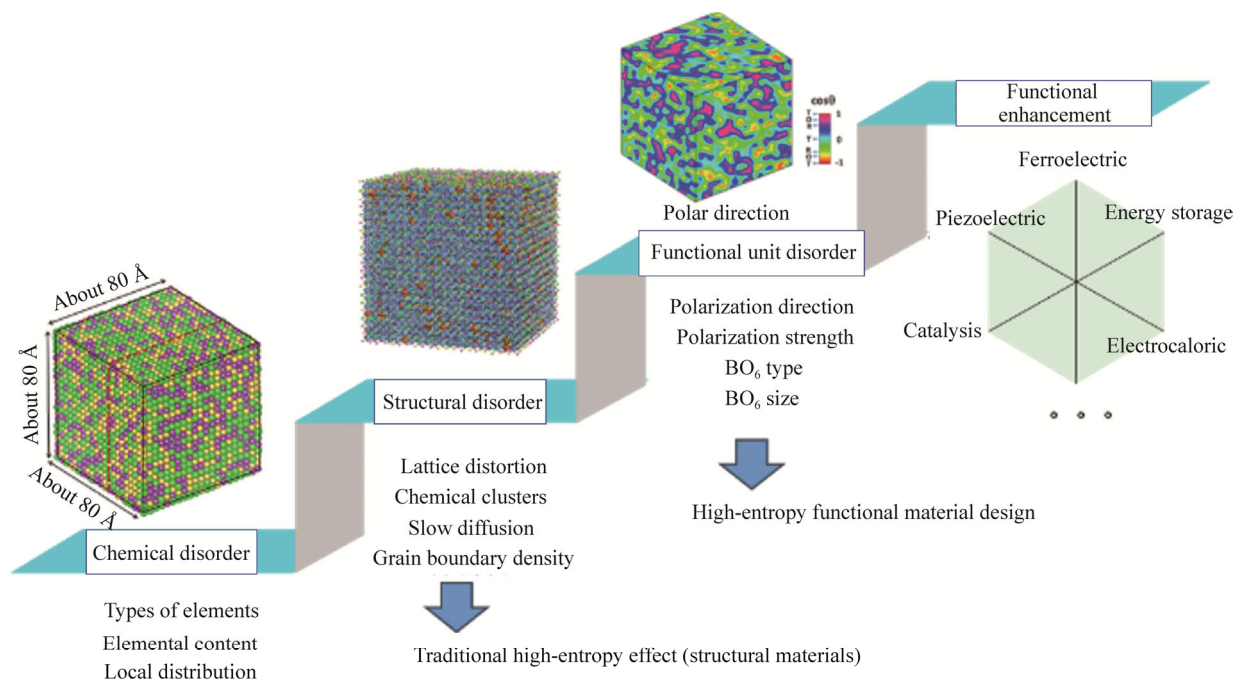


图 10 从化学无序到结构无序到功能基于无序设计策略获取优异功能性

Fig. 10 From chemical disorder to structural disorder, employing a strategy of designing functionality based on disorder to achieve superior functional properties

而极化构型的设计对于改善铁电材料性能是至关重要的, 很多研究报道了通过设计特殊的极化构型, 以获得优异的材料电学性能^[4,7,8,124–128]。高熵铁电体由于其特殊性质与结构, 在极化构型的设计方面也显得更加多样化, 另外高熵策略有利于晶粒细化, 增强机械性能和熵稳定效应^[33,41–43,129]。为深入揭示化学无序对极化无序的调控机理, 研究者采用中子/同步辐射全散射技术结合反向蒙特卡洛方法实现了原子级三维结构重构, 定量解析了亚纳米离子团簇及其形成强极化波动极化构型的内在机制, 该方法为认识化学无序与结构功能基元无序间关系提供桥梁。另外, 一些新技术例如机器学习^[130–134]和相场模拟^[135–137]等, 有助于在诸多高熵组分中预测其中的高性能材料, 而高通量实验方法可以提高探索具有新型极化构型组成的效率。在未来有望对高熵铁电体进一步研究, 设计更多新型的极化构型, 获得更加优异的性能, 从而使得高熵铁电体得到更加广泛的应用。

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Research and Development of High Entropy Ferroelectrics

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Extended Abstract

Ferroelectric materials are widely used in various electronic functional materials and devices due to their excellent energy conversion and storage functions, which mainly depends on the crystal structure gene of ferroelectric materials, named as polarization configuration. Traditional phase boundary construction strategies were not flexible enough in regulating polarization configuration, and the improvement on the electrical properties of materials was also limited for the requirements of miniaturization and integration of next-generation devices.

Recently, researchers introduced the high-entropy strategy into ferroelectric materials and systematically studied the regulation mechanism of local polarization configuration. Theoretical and experimental results showed that, when retaining the traditional high-entropy effect, the high-entropy strategy could also fully utilize the comprehensive factors of atomic ferroactivity and radius for the directional design of ferroelectric functional elements (local polarization configuration and oxygen octahedron tilt), effectively improved the flexibility of external field response, and then significantly improved the related electrical properties. Materials with both high chemical disorder and high ferroelectric functional element disorder can be called “high-entropy FEs”. A series of researches have been carried on the ferroelectrics via the high-entropy strategy, and varieties of high-performance functional materials were designed and prepared.

In this paper, the polarization configuration, acted as the core functional unit, is firstly introduced to achieve the diversity of physical properties in ferroelectric materials and the crucial role in regulating material's properties. Then the mechanism of improving the performance of high-entropy FEs by adjusting the polarization configuration through the high-entropy strategy is discussed; Finally, the research on controlling the polarization configuration of ferroelectrics using the high-entropy strategy to enhance their performance is summarized and categorized, which demonstrated that the high-entropy strategy could improve the performance of ferroelectric materials in a feasibility and broad prospects. Finally, four directions of high-entropy strategy for enhancing material performance, including piezoelectric performance, large electrostriction, excellent energy storage, and refrigeration with large electrocaloric effect are introduced.

Summary and Prospects Previous researches clearly showed the large potential of high-entropy strategy on the adjustment of multiple properties in FEs materials, However, the high configuration entropy only implied the substitution of a high ratio of multiple exotic atoms, and the characteristic of these atoms as well as their influence on the structure of the final compositions were not revealed clearly, even though a large number of high-entropy FEs did not exhibit outstanding performance. Therefore, designing high-entropy FE materials did not involve directly adopting the high-entropy strategy used in traditional structural materials. Instead, it entailed ensuring chemical disorder while utilizing highly adjustable chemical compositions to design functional unit disorder. To achieve functional materials with excellent performance, it is necessary to simultaneously satisfy chemical disorder, structural disorder, and functional unit disorder, it is also the core principle behind designing new high-entropy functional materials. Polarization configuration design is the core for achieving excellent physical properties in FE materials, many special polarization configurations have been reported to show unique electrical properties in many studies. The high-entropy strategy shows strong operability on polarization configuration design because of the unique properties and structure of high-entropy FEs. Furthermore, the high-entropy strategy would also benefit the grain refinement, mechanical property enhancement, and entropy stabilization effects. To elucidate the regulatory mechanism of chemical disorder on polarization disorder, researchers utilized neutron/synchrotron total scattering techniques combined with reverse Monte Carlo methods to achieve atomic-level three-dimensional structure reconstruction. They quantitatively analyzed the intrinsic mechanisms of sub-nanometer ion clusters and the formation of strong polarization fluctuation polarization configurations, it served as a bridge for understanding the relationship between chemical disorder and structural functional unit disorder. Some new technologies, such as machine learning and phase field simulation, could be used for assisting the prediction of high-performance materials among endless high-entropy compositions, and high throughput experiment method can also greatly improve efficiency for exploring new compositions with novel polarization configurations. In the future, further research on high-entropy FEs should focus on the design of more novel polarization configurations to attain better performance of this kinds of materials, thereby to facilitate the application of high-entropy FEs in a wide field.

Keywords high entropy; ferroelectrics; polarization configuration; energy storage; perovskite