

信息功能陶瓷研究的几个热点

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信息功能陶瓷是具有电、磁、声、光、热、力、化学或生物等不同性能之间相互转化和耦合效应的一类无机非金属功能材料, 亦称为功能陶瓷或电子陶瓷, 主要包括介电、铁电、压电、热释电、半导体、电光、磁性、高温超导等多种功能的新型高技术陶瓷。基于各种功能效应的新一代电子元器件如: MLCC 电容器、片式电感器、电阻器、PTC 和 NTC 热敏电阻、变阻器、晶界层电容器、滤波器、谐振器、压电换能器、驱动器、微位移器等等, 它们是计算机、集成电路、移动通信、能源技术和军工电子等领域的重要基础材料与元器件。随着高新技术的快速发展, 功能陶瓷材料的发展趋势是多层化、低维化、复相化、织构化以及高均匀性、低成本、低温合成、环境协调; 新型元器件则朝着片式化、微型化、模块化、低功耗、高频化、智能化、绿色化、大功率以及在极端条件下服役的高可靠性方向发展。

近几年来, 随着人们环境保护意识的日益增强, 经济发展对能源需求的快速增长以及环境污染问题的日益突出, 环境友好型的无铅压电陶瓷、储能介质与高性能电容器、巨电卡效应成为功能陶瓷研究的三大热点。

1 $d_{33} > 400$ pC/N 的铌酸钾钠基无铅压电陶瓷

目前, 无铅压电陶瓷主要有 BaTiO_3 、 $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ 和 $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN)三大体系, 其中 BaTiO_3 和 $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ 的压电性能和居里温度相对较低, 主要用于超声探测器; KNN 的烧结温度较低、居里温度高、压电系数高, 有望成为 PZT 的替代材料^[1-2]。

当 $\text{K}/\text{Na}=47/53$ 时, KNN 体系中存在两种正交相的相界, 此处的压电性能最优^[3]。从高温降低的过程中, KNN 体系经历立方 \rightarrow 四方 \rightarrow 正交 \rightarrow 三方等系列相变。三个介电峰位于 690、480 和 158 K, 分别对应 C-T、T-O 和 O-R 三个相变。通过元素的掺杂取代可以改变 KNN 中的相变温度, 提高其铁电和压电性能。等价掺杂中 A 位通常掺杂一价的 Li^+ 或 Ag^+ , B 位掺杂五价的 Ta^{5+} 或 Sb^{5+} ; 不等价掺杂时, A 位可以掺杂 Ca^{2+} 、 Sr^{2+} 或 Ba^{2+} , 甚至可以共掺 $(\text{Bi}_{0.5}\text{Li}_{0.5})^{2+}$ 、 $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ 或 $(\text{Bi}_{0.5}\text{K}_{0.5})^{2+}$, 此时 B 位可以有 Ti^{4+} 和 Zr^{4+} 。

研究发现 Li^+ 是唯一能够提高 T_c 的掺杂元素, 价态不匹配会导致 T_c 的迅速下降^[4]。T-O 和 O-R 相变受到 B 位离子的强烈支配。B 位 Ti^{4+} 离子取代时会导致 T-O 和 O-R 相变温度降低^[5]。当 B 位被 Zr^{4+} 取代时, T-O 相变温度同样下降, 尽管随组成下降略缓, 相反的是 O-R 相变温度升高, 8% 的 Zr^{4+} 取代就能将 R 相移到室温; Sb^{5+} 的取代同样能够提高 O-R 相变温度, 9% 的 Sb^{5+} 取代将 O-R 相变温度提升到室温; Ta^{5+} 取代会引起居里温度的下降, 并降低 T-O 相变温度^[4, 6]。从这些离子取代对 O-R 的影响规律上看, O-R 相变的决定因素不仅仅是由 B 位离子半径引起的化学应力, 化学键的强弱也可能是影响因素。总之, 通过 MPB 和 PPT 相界组成的优化, 在 $0.90(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3-x\text{BaZrO}_3-(0.10-x)(\text{Bi}_{0.5}\text{Li}_{0.5})\text{TiO}_3$ 体系中, 当 $x=0.7\sim 0.8$ 时, $d_{33}=230\sim 265$ pC/N, $k_p=40.6\%\sim 41.9\%$ 。当组成为 $0.92(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3-0.06\text{BaZrO}_3-0.02(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3-0.25\text{wt}\%\text{MnO}_2$ 时, $d_{33}=420$ pC/N, $k_p=56\%$, $T_c=243^\circ\text{C}$ ^[7-9], 其室温压电性能与 PZT-4 陶瓷接近, 但是其温度稳定性和长期工作的可靠性还有待进一步研究和考验, 因此, 关于“垂直相界的研究”将是今后的重要研究内容之一^[10]。

不同离子取代时 KNN 中不同相变调控规律, 其机理仍需要进一步探讨。对复杂的 KNN 固溶体中相界和相变的系统实验和理论研究有可能是实现无铅压电陶瓷实际应用的最有希望的突破口。

2 高性能陶瓷储能介质的研究

储能电容器具有储能密度高、充放电速度快、抗循环老化、高温和高压等极端环境下性能稳定等优点,

在电动汽车、功率电子器件、脉冲功率电源、高能量密度武器、新能源及智能电网系统等基础科研和工程应用领域有着广阔的应用前景^[11]。

美国 EESstor 公司在静电介质超级电容器方面申请了多项专利^[12], 如“采用陶瓷介质和集成电路技术的电能存储单元(EESU)取代电化学电池”的专利技术在学术界和产业界产生了强烈反响, 对纯电动汽车来说, 无疑是一个重大突破, 但相关的技术细节、验证和实施还需要大量的研究工作。

章启明等^[13]在有机介质电容器中实现了高密度储能的新途径($>17 \text{ J/cm}^3$), 引起人们对介质超级电容器储能系统的广泛重视。最近, 刘芸等^[14]报道在(Nb/In)共掺杂的金红石 TiO_2 陶瓷中形成缺陷偶极子团簇, 在宽温区获得巨介电常数($>10^4$)的同时具有较小的介质损耗(<0.05)。

当前, 正在开展的研究工作还有陶瓷晶粒包裹玻璃层、在玻璃之中析出极性区域以及 BaTiO_3 表面包覆一层 $\text{Al}(\text{OH})_x$ 离子介质层可能形成电化学赝电容等方法^[15], 这种通过引入离子导电性晶界使电化学赝电容与静电电容共存的概念, 为陶瓷储能电容器研究开启了新的思路。同时, 在双电层电容器中也在尝试引入电介质层来提高其工作电压。各种技术优势的相互渗透和交融大大激发了新概念、新机理电容器的研究, 无疑会促进电容器储能技术和应用的发展。

3 巨电卡效应

电卡效应是指在极性材料中因外电场的改变导致极化状态发生改变而产生的绝热温度或等温熵的变化。上个世纪 30 年代就有电卡效应的报道, 只是由于陶瓷材料的工作场强低, 得到绝热温度的变化都小于 1°C 。近年来, 相关研究取得飞速发展, 为此, 本专辑特邀鲁圣国教授撰写相关综述论文, 以飨读者。

2006 年, Mischenko 等^[16]报道了在溶胶-凝胶法制备的 $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ 反铁电薄膜的电卡效应, 薄膜厚度为 350 nm, 工作电场为 48 MV/m, 得到了绝热温变为 12°C , 熵变 $\Delta S = 8 \text{ J/(kg}\cdot\text{K)}$ 。随后, 章启明等^[17]在铁电共聚物(P(VDF-TrFE, 68/32 mol%))中获得大的铁电-顺电相变热为 $2.1 \times 10^4 \text{ J/kg}$, 熵变 $\Delta S = 56.0 \text{ J/(kg}\cdot\text{K)}$, 为巨电卡效应和新材料研究开启了新的大门。

鲁圣国等^[18]在 PLZT8/65/35 薄膜中观察到绝热温变达 40 K, 等温熵变达 $50 \text{ J/(kg}\cdot\text{K)}$ 的现象。最近, 樊慧庆等^[19]在 $\text{Pb}_{0.8}\text{Ba}_{0.2}\text{ZrO}_3$ 薄膜中, 也发现存在室温巨电卡效应, 在工作电场为 598 kV/cm 时, 电卡效应的最佳值为 $\Delta T = 45.3 \text{ K}$, $\Delta S = 46.9 \text{ J/(kg}\cdot\text{K)}$ 。

上述这些研究结果预示着一一种新的制冷技术实现变革的可能性, 利用固态电卡制冷原理取代传统卡诺制冷压缩机的超小体积、高效节能和环保无制冷剂的新一代冰箱、空调等将成为功能陶瓷研究新热点。

Some Hot Topics in Electroceramics Research

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Information functional ceramics is a class of ceramic materials which have unique electrical, magnetic, acoustic, optical, thermal, mechanical, chemical and biological properties which convert one to another, generate coupling effects. The ceramic materials used primarily for their electrical properties are generally called electroceramics or functional ceramics. They have become of increasing importance in many key technologies including computers, wireless communication, automotive and industrial control systems. The developments in the various subclasses of electroceramics have paralleled the growth of new technologies. Examples include ferroelectrics-MLCC, FeRAM; ferrites-filters, resonators; solid electrolytes-energy storage and conversion; piezoelectrics-sonar, transducers, actuators; semiconducting oxides PTC & NTC-environmental monitoring. The trend of electroceramics are thin films, low-dimensional materials, multiphase, multi-functional, textured, single crystal and high uniformity, low-cost, LTCC, environmental friendly. The new components and devices are to be miniaturized, low power consumption, microwave, high-power, intelligent and high reliability under extreme conditions.

Recently, as the increasing awareness of environmental protection, the rapid growth in demand for energy

and its impact on air-pollution have become increasingly prominent. Therefore, the studies on lead-free piezoceramics, high-performance dielectric for energy storage capacitors, as well as giant electrocaloric effect become three hot topics on the research of functional ceramics.

1 KNN based lead-free piezoceramics with $d_{33} > 400$ pC/N

There are three main lead-free piezoelectric materials, *e.g.* BaTiO₃, Na_{0.5}Bi_{0.5}TiO₃ and K_{0.5}Na_{0.5}NbO₃, among which the KNN is the most promising candidate for substitute of PZT-based ceramics^[1-2].

It is reported that there is a phase boundary between two orthorhombic phases near the composition K/Na = 47/53 which resulting in superior piezoelectric properties^[3]. The pure KNN undergoes a series of phase transitions at 690 K (T_{C-T}), 480 K (T_{T-O}) and 158 K (T_{O-R}). Ion substitution can change the phase transition temperature thus may improve the ferroelectric and piezoelectric properties. The A-site is usually substituted with Li⁺, Ag⁺ ions, and Ta⁵⁺, Sb⁵⁺ ions are in the B-site. While in unbalanced situation, the A-site is doped with Ca²⁺, Sr²⁺, Ba²⁺, even co-doped with (Bi_{0.5}Li_{0.5})²⁺, (Bi_{0.5}Na_{0.5})²⁺, (Bi_{0.5}K_{0.5})²⁺, and Ti⁴⁺, Zr⁴⁺ in the B-site.

Li⁺ is the only dopant ion that can increase the T_C of KNN. It was studied that the valence mismatch could cause the T_C to rapidly decrease^[4]. T-O and O-R phase transitions are strongly dominated by B-site ions. Both T_{T-O} and T_{O-R} decrease by substituting of Ti⁴⁺ substitution in B-site and almost independent of A-site ions^[5]. Zr⁴⁺ ion also decreases T_{T-O} but increases T_{O-R} , 8% Zr⁴⁺ addition will stabilize the rhombohedral phase to room temperature. Sb⁵⁺ can also increase the T_{O-R} , and 9% content Sb⁵⁺ substitution increases T_{O-R} to room temperature. Ta⁵⁺ substitution decreases the T_{C-T} and T_{T-O} at the same time. It is noted that 40% Ta⁵⁺ addition decreases the T_{T-O} to room temperature^[4,6]. It could concluded that the T_{O-R} may not merely affected by the chemical pressure introduced by different B-site ionic radii but also the chemical bond strength. In short, through the optimization of MPB, in 0.90(Na_{0.5}K_{0.5})NbO₃- x BaZrO₃-(0.10- x)(Bi_{0.5}Li_{0.5})TiO₃ system, when $x = 0.7-0.8$, $d_{33} = 230-265$ pC / N, $k_p = 40.6\%-41.9\%$ could be obtained. For the ceramic with a composition of 0.92(Na_{0.5}K_{0.5})NbO₃-0.06BaZrO₃-0.02(Bi_{0.5}K_{0.5})TiO₃-0.25wt% MnO₂, $d_{33} = 420$ pC/N, $k_p = 56\%$, $T_c = 243^\circ\text{C}$ were achieved^[7-9]. These piezoelectric properties at room temperature are very close to that of PZT-4 ceramics. However, the temperature stability and long-term reliability remains questionable and to be tested further. The recent study on the "vertical MPB" has become an important issue^[10].

The phase transitions (MPB, PPT) of KNN-based ceramics with different ions substitution still need to be explored. KNN-based ceramics seems to be the most promising substitution of PZT for devices applications.

2 High-performance ceramic dielectrics for energy storage

Dielectric capacitors possess advantages of high energy density, fast charge and discharge, anti-aging cycle under extreme environmental conditions. It is highly demanded for electric vehicles, power electronics, pulse power systems, high energy density weapons, renewable energy and smart grid systems^[11].

EEStor Inc. of US filed a number of patents on dielectric ultracapacitors, *e.g.* "Electrical-energy-storage unit (EESU) utilizing ceramic and integrated-circuit technologies for replacement of electrochemical batteries"^[12]. EEStor reports a large relative permittivity (19818) at an unusually high electric field strength of 350 MV/m, giving 10^4 J/cm³ in the dielectric. The capacitor can store more energy than lithium-ion batteries used in portable devices for cheaper than the low-cost lead-acid batteries used in gasoline powered cars. Its claims, if true, would radically change the electric car industry. However, the technology still has not publicly demonstrated.

Zhang, *et al*^[13] reported dielectric polymers with high dipole density have the potential to achieve a very high energy density (> 17 J/cm³, > 575 MV/m) with fast discharge speed and low loss, by using defect modified poly(vinylidene fluoride) polymers. Recently, Liu, *et al*^[14] reported high-performance colossal permittivity material of (Nb/In) co-doped rutile TiO₂ ceramics, due to the formation of electron-pinned defect-dipoles (defect-dipole clusters). The new high-performance dielectric materials, exhibiting temperature- and frequency-stable, with a giant dielectric constant ($> 10^4$) and a small dielectric loss (< 0.05).

Currently, the research work on the glass coated grains, glass with nano-polar region, as *et al.* well as BaTiO₃ coated with Al(OH)_x ionic layer, which may form electrochemical pseudo-capacitance. Randall, *et al*^[15] invented

a new type of capacitor that combines electrochemical pseudo-capacitor with ceramic capacitor energy storage. The ionically conducting dielectric materials may have heterogeneously distributed conductivity that may generate barrier layer effects. The Ionic-Based-Barrier-Layer (IBBL) effect may generate an effective barrier layer capacitance. Meanwhile, a dielectric layer is also introduced the electric double layer capacitor to improve its working voltage. New concepts and mechanism of dielectric capacitors will greatly stimulate the studies and applications of capacitor energy storage technologies.

3 Giant electrocaloric effect

The electrocaloric effect (ECE) is a change in temperature (ΔT) in a polarable material by virtue of the change in entropy (ΔS) upon the application of or withdrawing of an electric field under adiabatic conditions. The ECE occurs in both ferroelectric and paraelectric phases, and the effect is larger in the paraelectric phase just above the F-P transition.

In 2006, Mischenko, *et al*^[16] reported that “giant” ECEs were found in ferroelectric ceramic $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ thin films by Sol-Gel preparation at temperatures near and above the F-P transition. The film with a thickness of 350 nm, working at 48 MV/m, showed an adiabatic temperature change (ΔT) of 12 °C, the entropy change $\Delta S = 8 \text{ J}/(\text{kg}\cdot\text{K})$. Shortly thereafter, Zhang, *et al*^[17] reported that in the ferroelectric copolymer (P(VDF-TrFE), 68/32 mol%) large ferroelectric-paraelectric phase transition heat of $2.1 \times 10^4 \text{ J/kg}$, the entropy change $\Delta S = 56.0 \text{ J}/(\text{kg}\cdot\text{K})$ were obtained, which draw great attention to use the solid-state electrocaloric effects to developed new model of cooling system.

Lu, *et al*^[18] revealed that giant ECEs can be obtained in the high energy electron irradiated poly (vinylidene fluoride-trifluoroethylene) relaxor copolymer and in the La-doped $\text{Pb}(\text{ZrTi})\text{O}_3$ relaxor ceramic thin films, which are much larger than that from the normal ferroelectric counterparts. The adiabatic temperature change of 40 K and isothermal entropy change of 50 J/(kg·K) were achieved. Recently, Huiqing Fan, *et al*^[19] found that a giant electrocaloric effect ($\Delta T = 45.3 \text{ K}$ and $\Delta S = 46.9 \text{ J}/(\text{kg}\cdot\text{K})$) at 598 kV/cm) was obtained in nanoscale antiferroelectric and ferroelectric phases coexisting in a relaxor $\text{Pb}_{0.8}\text{Ba}_{0.2}\text{ZrO}_3$ thin films at room temperature.

The above exited results of these studies indicate a new refrigeration technology to achieve the possibility of change, the use of solid-state electronic cards to replace the traditional principle of Carnot refrigeration compressor refrigeration ultra-small size, energy efficient, environmentally friendly and without refrigerants. A new generation of refrigerators, air conditioners become a new functional ceramics research focus.

The ECE may provide an efficient means to realize solid-state cooling technology. New refrigeration based on the ECE approach is more environmentally friendly and hence may also provide an alternative to the existing vapor-compression approach.

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