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Electrocaloric Effect in $Pb_{0.3}Ca_xSr_{0.7-x}TiO_3$ Ceramics Near Room Temperature

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Abstract: The electrocaloric (EC) effect is strongly related to interaction of polarization and temperature changes, showing great potential in high-efficient solid state refrigeration. This work focuses on the $Pb_{0.3}Ca_xSr_{0.7-x}TiO_3$ (PCST(x), x = 0.00, 0.05, 0.10, 0.15) ceramics in which the influence of Ca content on dielectric and ferroelectric property under electric field was studied, and the EC temperature change was calculated through indirect method. Substitution of Ca largely modifies the diffused phase transition behaviors of PCST ceramics, which the diffusion exponent of PCST(0.05) increases with electric field up, indicating a promising wide temperature range of large electrocaloric effect. Thus, the largest adiabatic temperature change (1.71 K) is obtained near the room temperature in PCST(0.05) by indirect method. With an electric field of 8 kV/mm, PCST(0.05) ceramic shows good EC effect in a wide temperature range that the adiabatic temperature change is larger than 1 K from 5 ℃ to 70 ℃.

Key words: electrocaloric effect; ferroelectrics ceramics; diffused phase transition

When an electric field is applied or removed, there is a reversible temperature change in dielectric materials that can be exploited as promising solid-state refrigeration candidates to replace vapor-compression systems[1-3]. In 2006, the giant EC response with an adiabatic temperature change (ΔT) of 12 K was demonstrated in $Pb(Zr_{0.95}Ti_{0.05})O_3$ (PZT) antiferroelectric films near the Curie temperature (T_C) for a huge polarization change[4]. From then on, a booming development of EC effect started, and many advancements have been achieved[3,5-7].

The pyroelectric and EC effects of ferroelectrics are strongly correlated with each other. The EC effect is the thermodynamically reverse process of pyroelectric effect due to Maxwell relationship. Thus many pyroelectrics can also be good EC materials for solid-state refrigeration, such as PZT, $Ba_xSr_{1-x}TiO_3$ (BST) and $PbSc_{1/2}Ta_{1/2}O_3$ (PScT)[5, 8-11]. Much attention has been especially paid on BST and PScT for its large pyroelectric effect near the room temperature[5, 8, 10-11]. Recently, $Pb_{0.3}Ca_xSr_{0.7-x}TiO_3$ [PCST(x), x = 0.00, 0.05, 0.10, 0.15] was reported to show high pyroelectric coefficient near room temperature[12], and the maximum of pyroelectric coefficient is obtained under a very low electric field of 200 V/mm. The diffused phase transitions occur in PCST(x) ceramics, which may lead to a wide EC temperature span. The enhanced pyroelectric properties and the low induced-electric-field of PCST(x) ceramics predict high EC effect in PCST(x) ceramics, indicating great potential in electrocaloric solid-state refrigeration devices.

This work focuses on the EC effect of $Pb_{0.3}Ca_xSr_{0.7-x}TiO_3$ (PCST(x), x=0.00, 0.05, 0.10, 0.15) ceramics. The PCST(x) ceramics experience typical diffused phase transition, thus good EC effects were observed in a wide temperature span. The optimized EC effect was obtained in 0.05 Ca-doped ceramic, and the indirect EC method was carried out to verify ΔT values.

1 Experimental

The $Pb_{0.3}Ca_xSr_{0.7-x}TiO_3$ (x = 0.00, 0.05, 0.10 and 0.15) ceramics were fabricated by conventional solid-state reaction. The raw materials, Pb_3O_4 (99.26%), $SrCO_3$ (99%), TiO_2 (99.38%), and $CaCO_3$ (99%) with 0.5wt% excess of Pb_3O_4 to compensate for Pb volatilization, were well mixed by sufficient ball-milling. Then the mixed raw materials were calcined at 900 ℃ for 2 h. The calcined PCST(x) powders were shaped into ϕ15 mm green compact and sintered at 1280 ℃ for 2 h. The temperature

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dependence of dielectric constant was measured by a Hewlett Packard LCR meter at 1 kHz during heating (2 K/min). The polarization versus electric field (*P-E*) hysteresis loops from 5 ℃ to 90 ℃ were measured with aixACCT TF Analyzer 2000 at 1 Hz. The densities of the samples were measured using the Archimedes method. The specific heat used in this work is approximated from the specific heat value of PST from Ref.[6, 13-14]. In the EC effect calculation, six fold polynomial fitting was used to calculated the $\left(\frac{\partial P}{\partial T}\right)_E$.

2 Results and Discussion

2.1 Dielectric properties

The temperature dependence of dielectric permittivity for PCST(x) ceramics is given in Fig. 1(a). The ferroelectric-paraelectric phase transition of PCST(x) ceramics happens near the room temperature. The electric field is believed to stabilize the ferroelectric phase when the temperature is higher than T_C. Thus the peak value of dielectric permittivity is suppressed with an electric field of 0.5 kV/mm. To reveal it clearly, the diffusion exponent of the phase transition can be characterized by[8] Eq(1):

$$\frac{1}{\varepsilon_r}-\frac{1}{\varepsilon_{max}}=\frac{(T-T_C)\gamma}{2\varepsilon_{max}\sigma^2} \quad (1)$$

where ε_{max} and T_C are the peak value of dielectric constant and the corresponding temperature, γ the diffusion exponent, and σ the variance. The diffusion exponent of samples with electric field were given in Fig. 1(b). As it was reported, the phase transition of PCST(x≤0.10) is second-order transition, while the phase transition order is first order in PCST(0.15)[12]. In general, γ increases with electric field when a second order phase transition occurred (x≤0.10). For x=0.15, where the first order phase transition happened, γ firstly decreases then increases with electric field up. The diffusion exponent of PCST(0.05) rises from 1.36 to 1.68 with an electric field changing from 0 to 0.5 kV/mm, indicating an enhanced diffused transition happened with electric field increasing. These diffusion behaviors under electric field give us expectation for a temperature-broadened EC effect in PCST(x) ceramics with application of large electric field[13-14].

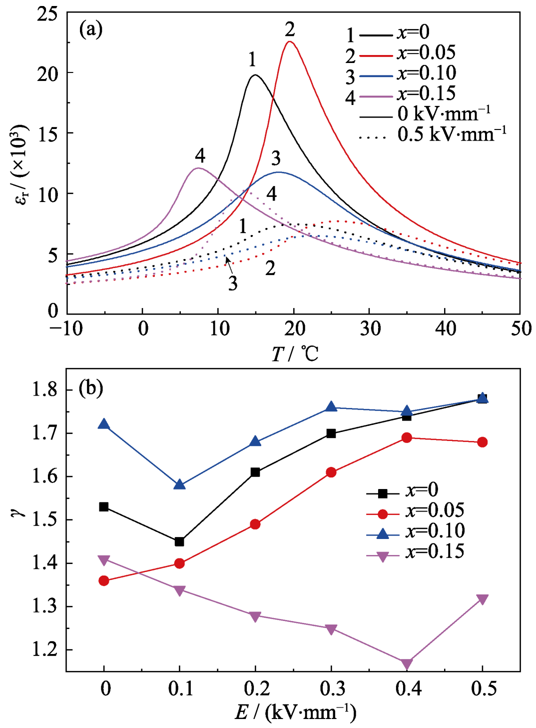

Fig. 1 (a) Temperature dependence of dielectric permittivity for PCST(x) ceramics with and without electric field, and (b) diffusion exponent *versus* electric field curves of PCST(x) ceramics

2.2 Ferroelectric properties

Fig. 2 shows the *P-E* loops of PCST(x) ceramics at 5 ℃, and inset shows the composition-dependent T_C in PCST(x) ceramics. The samples show the similar slim ferroelectric hysteresis loops with small coercive field. The maximums of the polarization (P_{max}) of samples are different and peak at x=0.05.

2.3 Electrocaloric properties

Fig. 3(a) shows the *P-E* loops of PCST(0.05) ceramic with an electric field of 8 kV/mm at different temperatures, and the inset illustrates the temperature dependence of the polarization under different electric fields. It is seen that the polarization decreases sharply just above T_C under low electric fields but decreases slowly under high electric field. Based on the Maxwell relationship[15], the adiabatic temperature change (ΔT) of EC effect can be calculated by,

$$\Delta T=-\frac{T}{c\rho}\int_{E_1}^{E_2}\left(\frac{\partial P}{\partial T}\right)_E \mathrm{d}E \quad (2)$$

Where ρ is the density and c is the specific heat (426 J/(kg·K)).

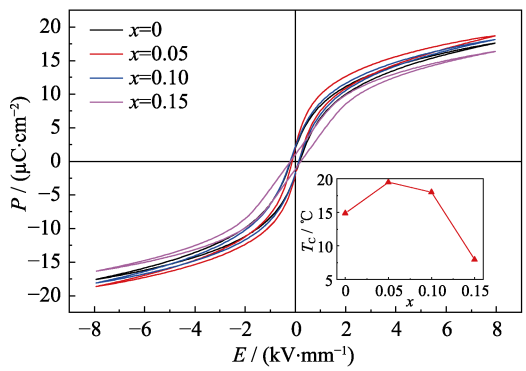

Fig. 2 *P-E* loops of PCST(x) ceramics at 5 ℃ with inset showing the composition dependence of Curie temperature in PCST(x) ceramics

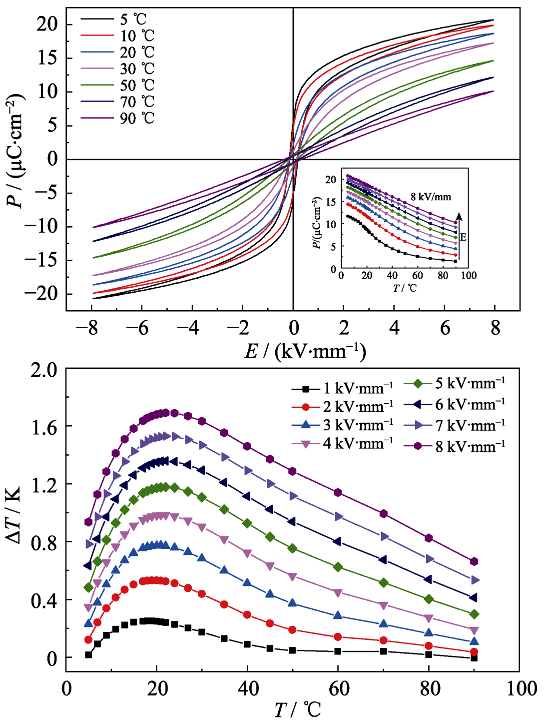

Fig. 3　(a) *P-E* loops under different temperatures, and (b) calculated ΔT-T curves under different electric fields of PCST(0.05) sample

The temperature dependence of the ΔT for PCST(0.05) under different electric fields is given in Fig. 3(b). The maximum ΔT is obtained at the temperature slightly higher than T_C and increases gradually with the increase of the electric field.

The indirect ΔT as a function of temperature in PCST(x) ceramics is shown in Fig. 4. The maximum of ΔT reaches 1.71 K under an electric field of 8 kV/mm in PCST(0.05) ceramic at 22 ℃, and the diffused phase transition contributes to a wide temperature range, where the ΔT of PCST (0.05) ceramic is higher than 1 K even at 70 ℃. The span from 5 to 70 ℃ is the main operating temperature range for many devices, as well for cooling applications.

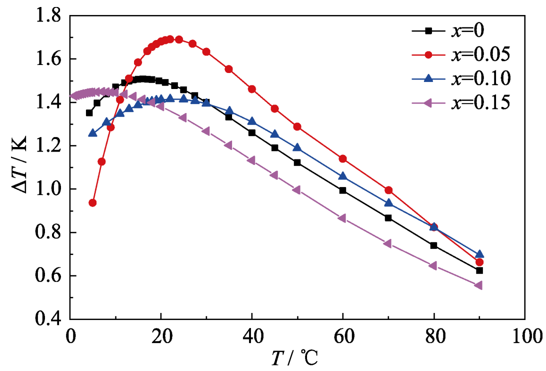

Fig. 4　Calculated ΔT-T curves of PCST(x) ceramics

In Table 1, the EC properties of PCST(x) are listed, and other EC materials that show good EC effect are given for comparison. Since the practical cooling devices work at room temperature to a large extent, PCST(0.05) ceramic exhibits good performance at room temperature compared to other EC materials. Meanwhile, the ΔT of PCST(0.05) ceramic larger than 1 K from 5 ℃ to 70 ℃. All these superior performances demonstrate that PCST (0.05) is a good EC material with high cooling efficiency.

3　Conclusions

In summary, the dielectric diffusion behaviors of PCST(x) ceramics under electric field were systematically studied, all samples show the increasing diffusion exponent with high electric field applied. When Ca substitution is 0.05, the sample shows the largest P_{max}. The enhanced EC effect near the room temperature with the broadened range is obtained by the indirect method based on the Maxwell relationship. The EC response of PCST(0.05) reaches 1.71 K at 20 ℃ , and it is larger than 1 K in a wide temperature range from 5 ℃ to 70 ℃. Therefore the EC effect near the room temperature with the wide range exhibits great potential for practical cooling applications.

Table 1　Comparison of EC properties of common reported materials

Material	Form	T_C/℃	ΔT/K	ΔE/(kV·mm^{-1})	$(\Delta T/\Delta E)/(\times10^{-6}$, K·m·V$^{-1})$	Method	Ref.
PCST(0.00)	Ceramic	14.9	1.52	8.0	0.19	Indirect	This work
PCST(0.05)	Ceramic	19.5	1.71	8.0	0.21	Indirect	This work
PCST(0.10)	Ceramic	18.0	1.43	8.0	0.18	Indirect	This work
PCST(0.15)	Ceramic	8.0	1.49	8.0	0.19	Indirect	This work
$PbZr_{0.95}Ti_{0.05}O_3$	Film	226.0	12.00	77.6	0.15	Indirect	[4]
$PbMg_{1/3}Nb_{2/3}O_3$	Ceramic	67.0	2.50	9.0	0.27	Direct	[16]
0.75PMN-0.25PT	Single crystal	110.0	0.66	2.5	0.26	Direct	[17]
PMN-30PT	Ceramic	145.0	2.60	9.0	0.29	Direct	[16]
$Ba_{0.94}Dy_{0.04}TiO_3$	Ceramic	138.0	1.04	3.0	0.35	Direct	[18]
$BaZr_{0.2}Ti_{0.8}O_3$	Ceramic	39.0	4.50	14.5	0.31	Direct	[19]
$BaTiO_3$	Single crystal	129.0	0.90	1.2	0.75	Direct	[7]

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$Pb_{0.3}Ca_xSr_{0.7-x}TiO_3$ 陶瓷的室温电卡效应

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摘 要: 电卡效应是极性材料中极化强度和温度的相互作用, 具有电卡效应的铁电陶瓷材料在高效固态制冷领域有很好的应用前景。本研究以 $Pb_{0.3}Ca_xSr_{0.7-x}TiO_3$ [PCST(x), x = 0.00, 0.05, 0.10, 0.15]陶瓷为对象, 系统研究了在电场作用下 Ca 含量对材料介电性能和铁电性能的影响, 并通过间接法计算了不同温度下材料的电卡温变。研究结果显示: Ca 含量可显著调控 PCST 陶瓷的弥散相变特性, PCST(0.05)的相变弥散因子随外加电场的增大而增大, 可利用弥散相变在较宽温度区间内获得较大的电卡效应。经计算可得: PCST(0.05)在室温下可产生 1.71 K 的温变。当电场为 8 kV/mm 时, PCST(0.05)陶瓷在 5~70 ℃的温度范围内, 绝热温变均大于 1 K, 表现出优异的电卡效应。

关 键 词: 电卡效应; 铁电陶瓷; 弥散相变

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