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# Electrocaloric Effect in $\text{Pb}_{0.3}\text{Ca}_x\text{Sr}_{0.7-x}\text{TiO}_3$ 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  $\text{Pb}_{0.3}\text{Ca}_x\text{Sr}_{0.7-x}\text{TiO}_3$  (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 °C to 70 °C.

**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<sup>[1-3]</sup>. In 2006, the giant EC response with an adiabatic temperature change ( $\Delta T$ ) of 12 K was demonstrated in  $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$  (PZT) antiferroelectric films near the Curie temperature ( $T_C$ ) for a huge polarization change<sup>[4]</sup>. From then on, a booming development of EC effect started, and many advancements have been achieved<sup>[3,5-7]</sup>.

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,  $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$  (BST) and  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  (PScT)<sup>[5, 8-11]</sup>. Much attention has been especially paid on BST and PScT for its large pyroelectric effect near the room temperature<sup>[5, 8, 10-11]</sup>. Recently,  $\text{Pb}_{0.3}\text{Ca}_x\text{Sr}_{0.7-x}\text{TiO}_3$  [PCST( $x$ ),  $x = 0.00, 0.05, 0.10, 0.15$ ] was reported to show high pyroelectric coefficient near room temperature<sup>[12]</sup>, 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  $\text{Pb}_{0.3}\text{Ca}_x\text{Sr}_{0.7-x}\text{TiO}_3$  (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  $\Delta T$  values.

## 1 Experimental

The  $\text{Pb}_{0.3}\text{Ca}_x\text{Sr}_{0.7-x}\text{TiO}_3$  ( $x = 0.00, 0.05, 0.10$  and  $0.15$ ) ceramics were fabricated by conventional solid-state reaction. The raw materials,  $\text{Pb}_3\text{O}_4$  (99.26%),  $\text{SrCO}_3$  (99%),  $\text{TiO}_2$  (99.38%), and  $\text{CaCO}_3$  (99%) with 0.5wt% excess of  $\text{Pb}_3\text{O}_4$  to compensate for Pb volatilization, were well mixed by sufficient ball-milling. Then the mixed raw materials were calcined at 900 °C for 2 h. The calcined PCST( $x$ ) powders were shaped into  $\phi 15$  mm green compact and sintered at 1280 °C for 2 h. The temperature

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 °C to 90 °C 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 calculate 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<sup>[8]</sup> Eq(1):

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

where  $\varepsilon_{\max}$  and  $T_C$  are the peak value of dielectric constant

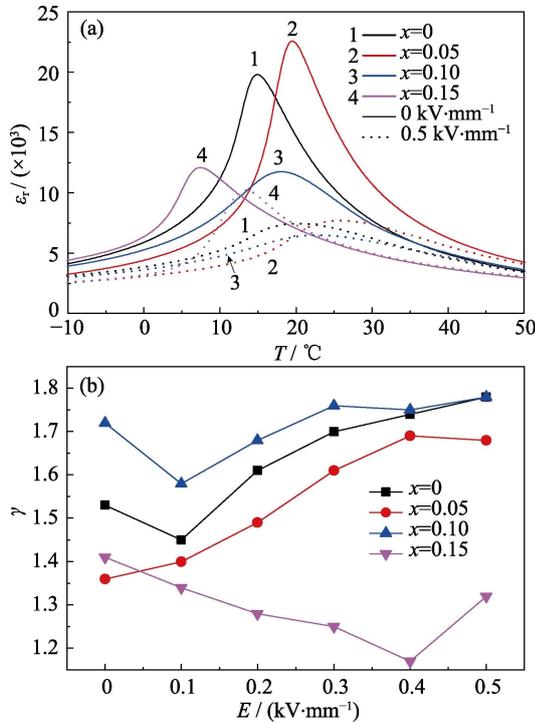


Fig. 1 (a) Temperature dependence of dielectric permittivity for PCST( $x$ ) ceramics with and without electric field, and (b) diffusion exponent *versus* electric field curves of PCST( $x$ ) ceramics

and the corresponding temperature,  $\gamma$  the diffusion exponent, and  $\sigma$  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( $x \leq 0.10$ ) is second-order transition, while the phase transition order is first order in PCST(0.15)<sup>[12]</sup>. In general,  $\gamma$  increases with electric field when a second order phase transition occurred ( $x \leq 0.10$ ). For  $x=0.15$ , where the first order phase transition happened,  $\gamma$  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<sup>[13-14]</sup>.

### 2.2 Ferroelectric properties

Fig. 2 shows the  $P$ - $E$  loops of PCST( $x$ ) ceramics at 5 °C, 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<sup>[15]</sup>, the adiabatic temperature change ( $\Delta T$ ) of EC effect can be calculated by,

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

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

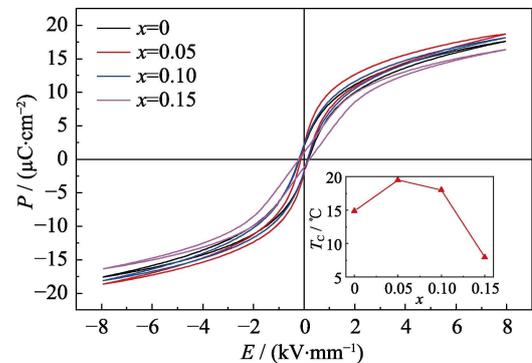


Fig. 2  $P$ - $E$  loops of PCST( $x$ ) ceramics at 5 °C with inset showing the composition dependence of Curie temperature in PCST( $x$ ) ceramics

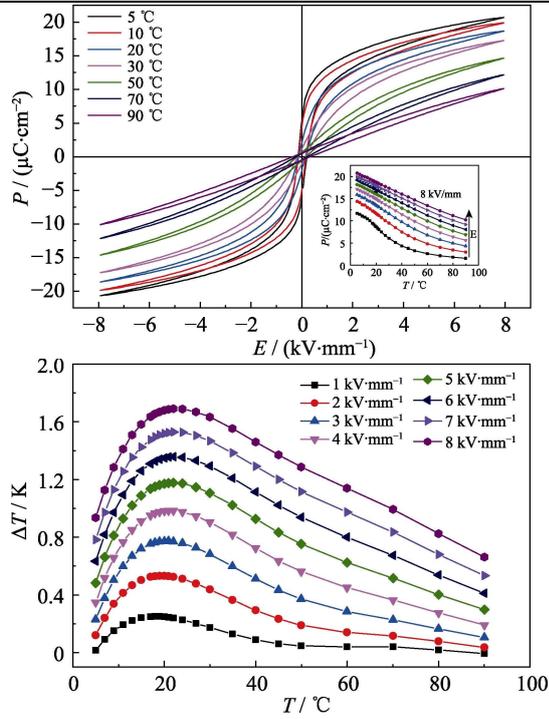


Fig. 3 (a)  $P$ - $E$  loops under different temperatures, and (b) calculated  $\Delta T$ - $T$  curves under different electric fields of PCST(0.05) sample

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

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

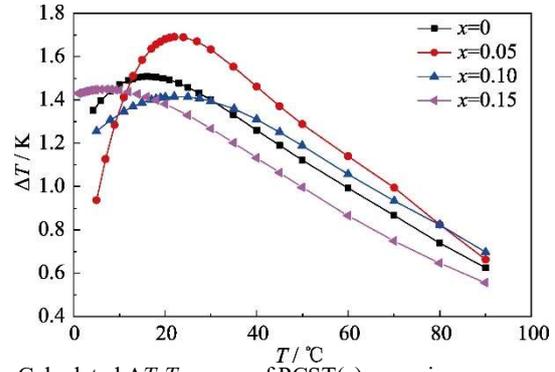


Fig. 4

Calculated  $\Delta T$ - $T$  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  $\Delta T$  of PCST(0.05) ceramic larger than 1 K from 5 °C to 70 °C. 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 °C, and it is larger than 1 K in a wide temperature range from 5 °C to 70 °C. 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	$T_C/^\circ\text{C}$	$\Delta T/\text{K}$	$\Delta E/(\text{kV}\cdot\text{mm}^{-1})$	$(\Delta T/\Delta E)/(\times 10^{-6}, \text{K}\cdot\text{m}\cdot\text{V}^{-1})$	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 <sub>0.95</sub> Ti <sub>0.05</sub> O <sub>3</sub>	Film	226.0	12.00	77.6	0.15	Indirect	[4]
PbMg <sub>1/3</sub> Nb <sub>2/3</sub> O <sub>3</sub>	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 <sub>0.94</sub> Dy <sub>0.04</sub> TiO <sub>3</sub>	Ceramic	138.0	1.04	3.0	0.35	Direct	[18]
BaZr <sub>0.2</sub> Ti <sub>0.8</sub> O <sub>3</sub>	Ceramic	39.0	4.50	14.5	0.31	Direct	[19]
BaTiO <sub>3</sub>	Single crystal	129.0	0.90	1.2	0.75	Direct	[7]

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