

Coexistence of large positive and negative electrocaloric effects near room temperature in $\text{Pb}_{1-x}(\text{Li},\text{La})_x \text{ZrO}_3/\text{Ca}_3\text{Mn}_2\text{O}_7$ heterojunction

Wenyue Zhao, Zhao Wang, Yazhou Peng, Lei Shi, Wenjing Hua, Xiaoxia Yang, Jie Wang, Weidong Fei, Yu Zhao *

The thickness of CMO layer and PLLZ layer is measured by scanning electron microscope. The image of backscattered electron could reveal topography of the bilayer film, and the contrast difference can be used to distinguish each layer and obtain the thickness of the film. The CMO layer is about 60 nm and the PLLZ layer is about 300 nm in PLLZ/CMO bilayer ($x=0.02$, 0.03, and 0.04).

Figure S2 shows the interface between the PLLZ layer and the CMO layer and its energy spectrum when $x=0.03$ and 0.04 under TEM. The energy spectrum results of the interface of $x=0.02$ PLLZ/CMO bilayer film are shown in Figure 2 (c). The interfaces of PLLZ/CMO bilayer films are clear and no element diffusion occurs. The well-defined interface helps to form the PLLZ-CMO heterojunction.

Geometric phase analysis is used to characterize the local stress in PLLZ layer formed by “ $\text{Li}^+-\text{La}^{3+}$ ” doping, the results are shown in Figure 1 (d-e) and Figure S3. The crystal plan in PLLZ high-resolution phase is (100) and (110). It is obvious that there are some dispersive local stress pairs in PLLZ layer ($x=0.02$, 0.03, and 0.04).

The temperature dependence of the dielectric properties at different frequencies is performed to analyze the phase transition in the PLLZ/CMO bilayer films. As can be seen in Fig. S4, there is no phase transition peak in the $x=0.02$, 0.03 and 0.04 PLLZ/CMO bilayer films. The dielectric constant of the PLLZ/CMO bilayer films increases slightly with temperature, especially in $x = 0.03$ PLLZ/CMO bilayer film. The variation of the dielectric loss with temperature is less pronounced in the $x=0.02$ and $x=0.04$ PLLZ/CMO bilayer films. The dielectric loss of the $x=0.03$ PLLZ/CMO bilayer film increases slightly with temperature.

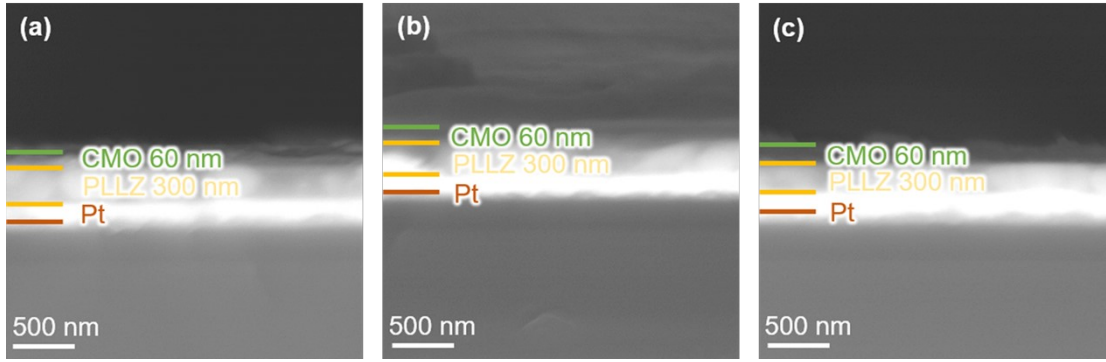


Figure S1 The thickness of CMO layer and PLLZ layer under SEM: (a) $x=0.02$; (b) $x=0.03$; (c) $x=0.04$.

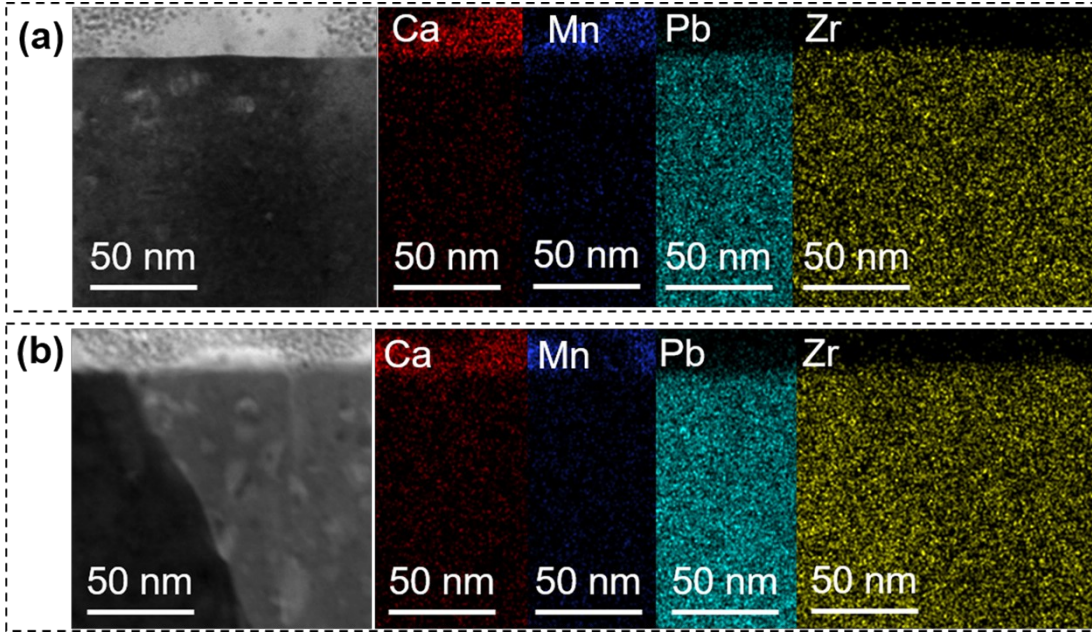


Figure S2 Energy spectrum of PLLZ/CMO bilayer films under the transmission electron microscope: (a) $x=0.03$; (b) $x=0.04$.

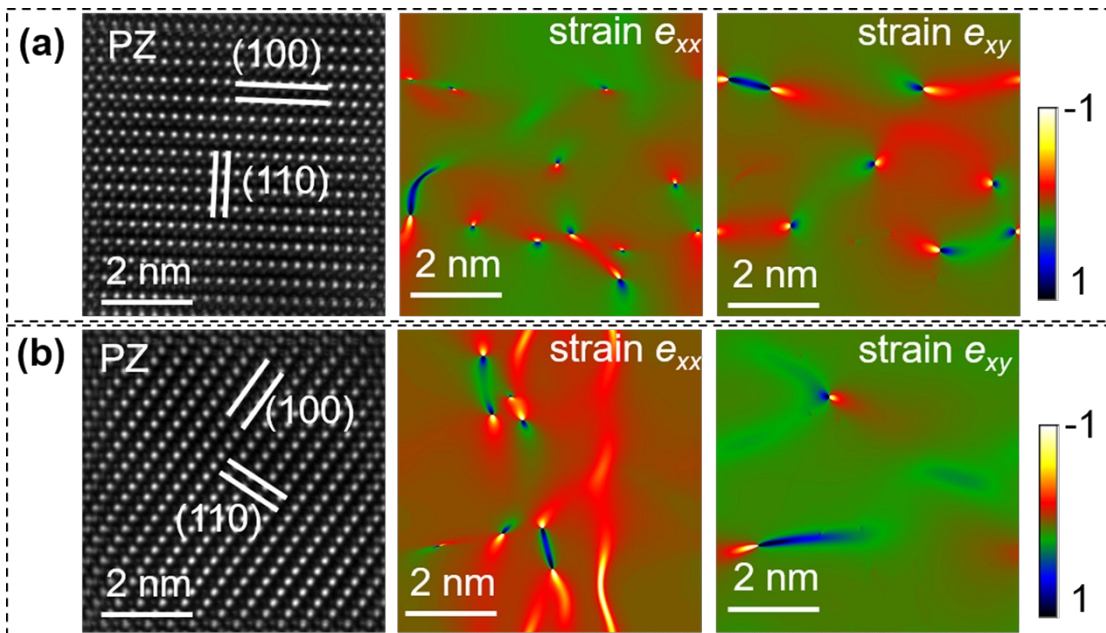


Figure S3 Geometric phase analysis results of PLLZ: (a) $x=0.03$; (b) $x=0.04$.

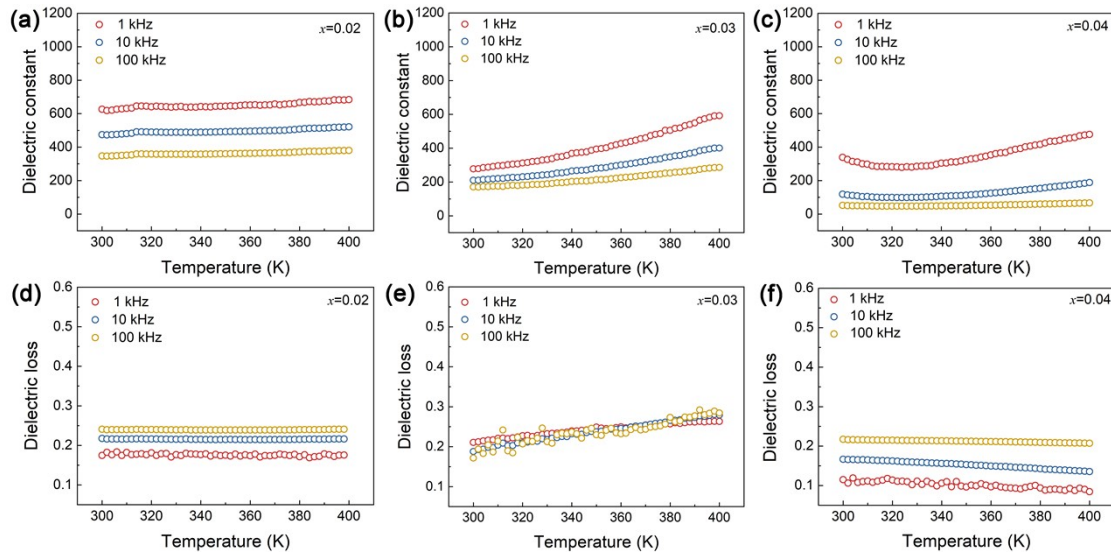


Figure S4 Temperature dependence of dielectric properties under different frequency: (a)-(c) Temperature dependence of dielectric constant of $x=0.02$, 0.03 and 0.04 PLLZ/CMO bilayer films; (d)-(f) Temperature dependence of dielectric loss of $x=0.02$, 0.03 and 0.04 PLLZ/CMO bilayer films.