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Polar elastic dielectric of large electrocaloric effect and deformation

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ABSTRACT

The alternation of temperature and entropy induced by an electric field in a polar dielectric material is known as the electrocaloric effect (ECE). This paper develops a thermodynamic theory of the polar elastic dielectric with large ECE and large deformation compatibility. The theory characterizes the equilibrium condition of the polar elastic dielectric which is subjected to mechanical forces, electric field and thermal field. The mechanical behavior and large deformation of the polar elastic dielectric thermo-electro-mechanical system are analyzed under the coupling influence of hyperelastic, polarization, electrostriction and thermal contribution on the system. The typical thermodynamics cycles of the polar elastic dielectric are described as cooling devices and generators and the electrocaloric and pyroelectric energy conversion are calculated. Ferroelectric polymer, as an important category of electroactive polymers, is a typical polar dielectric with a large ECE and a large deformation. As an example, when subjected to different voltage, the ferroelectric polymers are regarded as cooling devices. We calculated their temperature change, entropy change, heat absorptions and work generation. We also calculated the voltage change, electric quantity change and work of the ferroelectric polymer which is regarded as generators when subjected to different temperatures. Finally, we investigated the thermo-electro-mechanical coupling behavior of the ferroelectric polymers undergoing ferroelectric–paraelectric phase transition.

1. Introduction

Polar dielectrics may possess large pyroelectric effect (PCE) and large electrocaloric effect (ECE) (Neese et al., 2008; Lu and Zhang, 2009). After applying a thermal field to the polar dielectric, we could observe an alternation in the polarization and consequently leading to the change of the electric charge (under a constant voltage) or the voltage (under a constant charge). This phenomenon is known as the PCE. On the other hand, the electric field induced change of the entropy (under isothermal conditions) and the temperature (under adiabatic conditions) is named as the ECE (Scott, 2007; Mischenko et al., 2006a). PCE and ECE are mutually reversible in practical applications. The former can be used to design and manufacture generators while the later is frequently explored in cooling devices.

Although ECE has been studied for decades and described in various materials, such as $BaTiO_3$, $KTaO_3$, KH_2PO_4, triglycine sulfate (TGS), $P_b(ZrTi)O_3$, $Pb(ScTa)O_3$, and $SrTiO_3$, the relatively small ECE made it unsuitable for practical applications (Lu and Zhang, 2009; Liu et al., 2010, 2012). Recent findings of large ECE in several

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ferroelectric materials revived the research interest in their applications of dielectric cooling devices (Mischenko et al., 2006b; Neese et al., 2009; Li et al., 2010; Kar-Narayan and Mathur, 2010;Qiu and Jiang, 2009). The manufacture, performance test and application of materials within large ECE are consequently widely investigated (Lu et al., 2010a,b, 2011; Pirc et al., 2011).

Recent experimental results show that antiferroelectric ceramic ($PbZr_{0.95}Ti_{0.05}O_3$) (Lu and Zhang, 2009), normal ferroelectric polymers (poly(vinylidene fluoride–trifluoroethylene) [P(VDF–TrFE)]) (Neese et al., 2008), relaxor ferroelectric polymers poly(vinylidene fluoride–trifluoroethylene–chlorofluoroethylene) P(VDF–TrFE–CFE) (Neese et al., 2008), organic and inorganic relaxor ferroelectrics (high energy electron irradiated poly(vinylidene fluoride–trifluoroethylene) relaxor copolymer in the La-doped $Pb(ZrTi)O_3$ relaxor ceramic thin films (Lu et al., 2010a) have large ECE when the temperature range is above a ferroelectric (polarization-ordered)–paraelectric (polarization-disordered) (F–P) phase transition (Neese et al., 2008;Lu and Zhang, 2009; Scott, 2007; Mischenko et al., 2006b; Neese et al., 2009; Li et al., 2010; Kar-Narayan and Mathur, 2010; Qiu and Jiang, 2009; Lu et al., 2010a,b, 2011; Pirc et al., 2011). Mischenko et al. demonstrated a large ECE in antiferroelectric ceramic $PbZr_{0.95}Ti_{0.05}O_3$ above the F–P phase transition (ferroelectric Curie temperature 222 °C), where the electric field is 48 MV/m and the temperature is 230 °C. An adiabatic temperature change of more than 12 °C and isothermal entropy change of more than 8 J/(kg K) were observed (Mischenko et al., 2006a). Zhang et al. fabricated the ferroelectric poly(vinylidene fluoride–trifluoroethylene) [P(VDF–TrFE)] 55/45 mol% copolymer at temperatures above the ferroelectric–paraelectric phase transition, when the electric field is 209 MV/m and the temperature is 80 °C. An isothermal entropy change of more than 55 J/(kg K) and adiabatic temperature change of more than 12 K were observed (Neese et al., 2008). Recently, Lu et al. investigated the electrocaloric effect of inorganic thin film and organic relaxor ferroelectrics (Lu et al., 2010a). The results revealed that giant ECEs can be obtained in the high energy electron irradiated poly(vinylidene fluoride–trifluoroethylene) relaxor copolymer and in the La-doped $Pb(ZrTi)O_3$ relaxor ceramic thin films, which are much larger than that from the normal ferroelectric counterparts. Lu et al. reported the directly measured ECE of relaxor ferroelectric poly(vinylidene fluoride–trifluoroethylene–chlorofluoroethylene) terpolymer and its blend with poly(vinylidene fluoride–chlorotrifluoroethylene). An adiabatic temperature change of 12 °C and isothermal entropy change of 55 J/(kg K) have been demonstrated for the terpolymer blend films with 5 wt.% of P(VDF–CTFE) under 170 MV/m and ambient condition (Lu et al., 2010b). Lu et al. also measured the ECE of the ferroelectric poly(vinylidene–fluoride/trifluoroethylene) 55/45 mol% copolymer over a broad temperature range using a specially designed calorimetry method. The data revealed that a large ECE occurring at the ferroelectric–paraelectric (FE–PE) phase transition where the adiabatic temperature change was 12 K, under the electrical field of 120 MV/m, which is much higher than that previously observed at above the FE–PE transition (Lu et al., 2011).

However, the theoretical studies of electrocaloric effect in ferroelectric polymer are relatively rare, most of which are based on the Maxwell relation and calculate the adiabatic temperature change and isothermal entropy change of ferroelectric polymers subjected to diverse electric field (Neese et al., 2008, 2009; Lu and Zhang, 2009). Pirc et al. used thermodynamic and statistical mechanics arguments and derived physical upper bounds on the electrocaloric effect in bulk polar solids (Pirc et al., 2011). Liu et al. modeled polar dielectric based on cooling devices as a system of two degrees of freedom, represented by either the entropy–temperature plane or the electric displacement–electric field plane. Typical thermodynamic energy cyclic path in polar dielectric as cooling devices is proposed. By considering the influence of temperature, the free energy of the thermal–electrical coupling system of polar dielectrics is formulated, and the variation of temperature, entropy, the absorption of heat and the work under different electric field are calculated for several typical polar dielectrics. The simulation results fit well with the recently published experimental data (Liu et al., 2011a).

Electroactive polymers are a category of smart soft materials, which can change their shapes or volumes when subjected to electric fields and can recover the original shapes and volumes when the electric fields are removed (Wissler and Mazza, 2007; Suo et al., 2008; Suo, 2010 Hong, 2011). As a kind of electroactive polymers, ferroelectric polymer could generate large deformation when subjected to electric field, and hence is worthy for our research attentions.

This paper develops a thermodynamic theory of polar dielectrics within large ECE and deformation. The theory characterizes the equilibrium condition of the polar dielectric subjected to mechanical forces, electric field and thermal field. We consider the coupling influence of hyper elastic, polarization, electrostriction and heat contribution to the polar dielectric subject to mechanical forces, electric and thermal fields, and investigate the mechanical behavior and large deformation of the system. The typical thermodynamics cycles of polar dielectric as cooling devices and energy generator are described. The energy transformation between electricity and heat is also calculated. Ferroelectric polymer, as an important category of electroactive polymers, is a typical polar dielectric featuring large ECE and deformation. As an example, we calculated the temperature change, entropy change, absorption of heat and the work of the ferroelectric polymer as cooling devices after different voltage is subjected. We also calculated the voltage change, electric quantity change and work of ferroelectric polymer as energy generator when subjected to different temperatures. Finally, we investigated the mechanical behavior of polar dielectric of large electrocaloric effect and deformation undergoing ferroelectric–paraelectric phase transition.

2. Polar elastic dielectric in equilibrium with an electric field, a thermal field and a set of forces

Fig. 1 illustrates a block of polar-elastic dielectric with large electrocaloric effect and deformation. As shown in