

Why is the electrocaloric effect so small in ferroelectrics?

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Ferroelectrics are attractive candidate materials for environmentally friendly solid state refrigeration free of greenhouse gases. Their thermal response upon variations of external electric fields is largest in the vicinity of their phase transitions, which may occur near room temperature. The magnitude of the effect, however, is too small for useful cooling applications even when they are driven close to dielectric breakdown. Insight from microscopic theory is therefore needed to characterize materials and provide guiding principles to search for new ones with enhanced electrocaloric performance. Here, we derive from well-known microscopic models of ferroelectricity meaningful figures of merit which provide insight into the relation between the strength of the effect and the characteristic interactions of ferroelectrics such as dipole forces. We find that the long range nature of these interactions results in a small effect. A strategy is proposed to make it larger by shortening the correlation lengths of fluctuations of polarization.

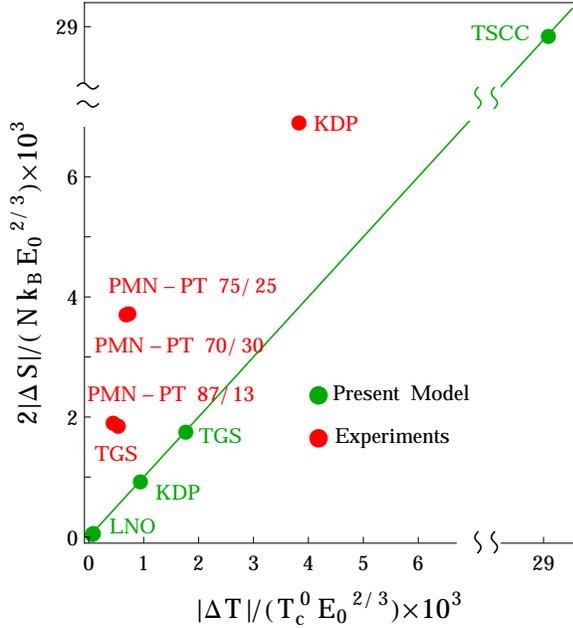


FIG. 1. Figure of merit at the paraelectric-to-ferroelectric transition for several ferroelectrics. Axes are in units of $(\text{statvolt}/\text{cm})^{2/3}$. Here, TSCC = $(\text{CH}_3\text{NHCH}_2\text{COOH})_3\text{CaCl}_2$, KDP = KH_2PO_4 , TGS = $(\text{NH}_2\text{CH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4$, LNO = LiNbO_3 , and PMN-PT $1-x/x = (\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3)_{1-x}(\text{PbTiO}_3)_x$. Data taken from Refs. [2, 5, 6].

The thermal changes that occur in ferroelectric (FE) materials upon the application or removal of electric

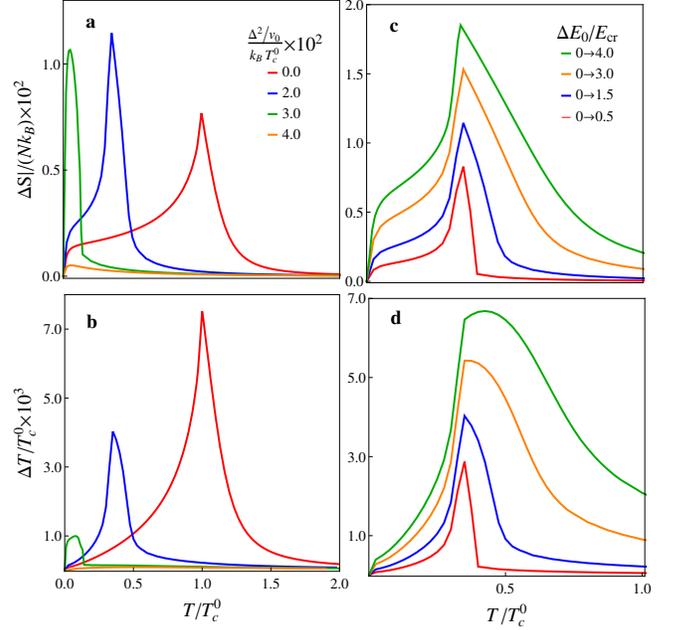


FIG. 2. (a)-(b) Calculated dependence of the ECE with compositional disorder for strong changes in the electric field $\Delta E_0/E_{cr} = 0 \rightarrow 1.5$. (c)-(d) Calculated ECE of a FE with moderate compositional disorder for several electric field strengths.

fields are known as the electrocaloric effect (ECE).²⁻⁴ The effect is the electric analogue of the magnetocaloric effect, which is commonly used to reach temperatures in the milliKelvin range. The ECE is the result of entropy variations with polarization, e.g., isothermal polarization of a ferroelectric reduces its entropy while depolarization increases it. It is parametrized by isothermal changes in entropy ΔS and adiabatic changes in temperature ΔT and it is strongest near the ferroelectric transition.

It has been recently pointed out that insight from microscopic theory into the ECE may contribute to characterize known materials and provide guiding principles to search for new ones with enhanced electrocaloric performance.² Here, we provide such insight by deriving meaningful figures of merit from well-known microscopic models of ferroelectricity. Our figure of merit allow us to set trends across different classes of FE materials (see Fig. 1) and provides insight into the relation between the magnitude of the ECE and the characteristic interactions of FEs (e.g. dipolar and strain). We find that the long-range nature of these interactions produces trade-offs in the ECE: while

they can give rise to high transition temperatures (i.e., comparable to room temperature), they concomitantly give rise to long correlation lengths of polarization at finite electric fields, which, as we show here, result in a small effect. We make contact with well-known results derived from Ginzburg-Landau (GL) theory⁷ and those from heuristic arguments.⁸ Based on these findings, we then study the effects of compositional disorder. The purpose of this is twofold: to propose a strategy to increase the magnitude of the ECE and to model the

ECE of relaxor ferroelectrics (see Fig. 2).⁹⁻¹¹ We find that the commonly observed broad peak in the ECE of relaxors is expected in any ferroelectric that is deep in the supercritical region of their phase diagram. Our results also bring into question the common practice of defining the electrocaloric strength of a material as the ratio of the entropy or temperature changes over the change in applied electric field.

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