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Microarticle

# In the search of new electrocaloric materials: Fast ion conductors

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ABSTRACT

We analyse the effects of applying an electric field on the critical temperature at which superionicity appears in archetypal fast ion conductor $CaF_2$, by means of molecular dynamics simulations. We find that the onset of superionicity can be reduced by about 100 K when relatively small electric fields of $\sim$50 KV cm$^{-1}$ are applied. Under large enough electric fields, however, ionic conductivity is depleted. The normal to superionic phase transition is characterised by a large increase of entropy, thereby sizeable electrocaloric effects can be realised in fast ion conductors that are promising for solid-state cooling applications.


## Introduction

In electrocaloric materials, the adiabatic switch of an electric field causes a change in the temperature of the system that is equal to

$$\Delta T = -\int_0^{\epsilon} \frac{T}{C_p}\cdot\left(\frac{\partial S}{\partial E}\right)_T dE, \quad (1)$$

where $C_p$ represents the heat capacity, $S$ the entropy, and $E$ the external electric field. Ferroelectrics, which exhibit a spontaneous electrical polarisation below a certain critical temperature $T_C$ that can be shifted by an external electric field, are the archetypal electrocaloric compounds [1]. Electrocaloric effects are observed at $T > T_C$, when the crystal is paraelectric but responds to the presence of an external electric field by aligning its dipole moments parallel to it. In those conditions, the adiabatic switch of an electric field causes a positive $\Delta T$ in the crystal because the entropy of the ordered state is smaller than that of the paraelectric phase [$\Delta S < 0$ hence $\Delta T > 0$, see Eq. (1)]. Conversely, when the electric field is adiabatically removed the material gets cooler ($\Delta S > 0$ hence $\Delta T < 0$). Diverse thermal cycles based on the electrocaloric effect can be engineered that are promising for solid-state refrigeration applications [1]. Nevertheless, ferroelectric materials present a series of technical issues like, for instance, the presence of ferroelectric domains and leakage currents, that are hindering the practical development of electrocaloric applications [1]. Therefore, it is very desirable to find new electrocaloric materials with improved cyclability and electrical resistivity features. Promising materials rivalling ferroelectrics, overall, must display a large change of entropy under the application of an external electric field.

Long time ago, Kharkats et al. proposed, based entirely on theoretical arguments, that the application of an external electric field could drastically lower the critical temperature, $T_s$, at which superionicity appears in fast ion conductors (FIC) [2]. Superionicity refers to the unusually large mobility (of the order of 1 $\Omega^{-1}$ cm$^{-1}$) that a particular atomic species in a multicomponent ionic material acquires when the temperature is raised (below its melting point). The normal to superionic phase transition is experimentally characterised by a sudden increase in the heat capacity and entropy of the crystal ($\Delta S \sim$10 J mol$^{-1}$ K$^{-1}$) [3]. The possibility of externally stimulating superionicity by means of an electric field has been, to the best of our knowledge, totally overlooked to date. This idea, however, can motivate original searches on new electrocaloric materials for solid-state cooling applications, as we schematically depict in Fig. 1. In this molecular dynamics work, we show that $T_s$ can be modified appreciably in archetypal fast ion conductor $CaF_2$ by applying an external electric bias. In particular, we find that when $E$ is relatively small ($\sim$10 KV cm$^{-1}$) $T_s$ can be shifted down by about 100 K. However, under the action of larger electric fields ionic conductivity is depleted.

## Methods

Our $(N,P,T)$ simulations were performed with the LAMMPS code [4], keeping the temperature and pressure fluctuating around a set-point value by using Nose–Hoover thermostats and barostats.

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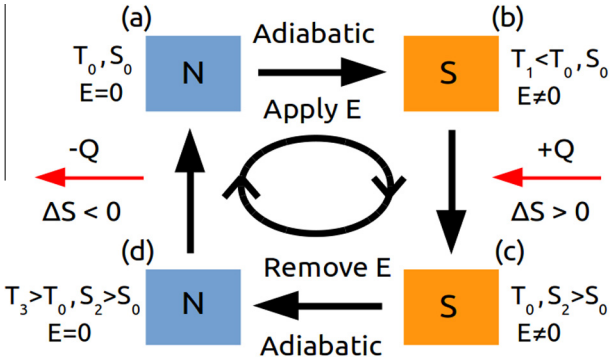


**Fig. 1.** Schematic diagram of an electrocaloric cooling cycle considering FIC at $T < T_s$. "N" and "S" represent the normal and superionic states. (a)→(b) An electric field is adiabatically applied that triggers superionicity, hence the crystal gets cooler. (b)→(c) The system receives heat from the environment, hence $T$ and $S$ increase. (c)→(d) The electric field is adiabatically removed, hence the system becomes normal and $T$ increases. (d)→(a) Heat is ejected from the system.

Large boxes containing 6144 atoms (of typical size $45 \times 45 \times 45$ Å) were simulated over long times of ~100 ps, and periodic boundary conditions were applied along the three Cartesian directions. Newton's equations of motion were integrated using the customary Verlet's algorithm and a time-step length of $10^{-3}$ ps. A particle–particle particle–mesh $k$-space solver was used to compute long-range van der Waals and Coulomb interactions and forces beyond a cut-off distance of 12 Å at each time step. The interactions between ions were modelled with the Born–Mayer–Huggins ion-rigid potential described in work [5]. The suitability of this approach for studying the energy, structural, and superionic properties of $CaF_2$ at low pressure has already been demonstrated [5,6]. We simulated the effect of applying an uniform external electric field by adding a force equal to $-q\mathbf{E}$ on each atom (where $q$ represents the corresponding ionic charge). Following previous works [5,6], we identified the onset of superionicity with the appearance of a non-zero slope in the mean squared displacement function (MSD) of the fluorine ions. The MSD function is defined as $\langle \Delta r^2(t) \rangle = \langle (r_i(t+t_0) - r_i(t_0))^2 \rangle$, where $r_i(t)$ is the position of atom $i$ at time $t$, $t_0$ an arbitrary time origin, and $\langle \cdots \rangle$ denotes average over fluorine ions and time origins.

## Results

Fig. 2 shows the fluorine MSD features calculated at $T < T_s$ and $T > T_s$ [where $T_s = 1350(25)$ K is the transition temperature computed at $E = 0$] [5] considering different values of the electric field. $E$ was applied along the three inequivalent crystalline directions [100], [110], [111], and in all the cases we obtained equivalent results. In our analysis we only consider electric fields smaller than 500 KV cm$^{-1}$ since otherwise we found that the $Ca^{2+}$ cations started to drift. At $T = 1250$ K, that is, 100 K below $T_s$, the onset of superionicity appears at $E = 50$ KV cm$^{-1}$. When the module of the electric field is further increased, however, ionic conductivity disappears. Such a counterintuitive effect can be understood as follows. At small values of $E$, the premature creation of Frenkel defects (i.e., simultaneous formation of an interstitial-vacancy pair) is stimulated by the presence of the external electric field and the accompanying increase in entropy, which minimises the free energy of the system. Importantly, under such conditions the diffusion of the $F^-$ ions is Brownian (that is, $\langle r(t) \rangle = 0$), exactly as it is observed at $T > T_s$ in the absence of an electric bias. Eventually, as $E$ is increased, the diffusion of the anions starts being non-erratic ($\langle r(t) \rangle \neq 0$) and thus the entropy of the system starts to decrease. Consequently, the anions prefer to remain in the

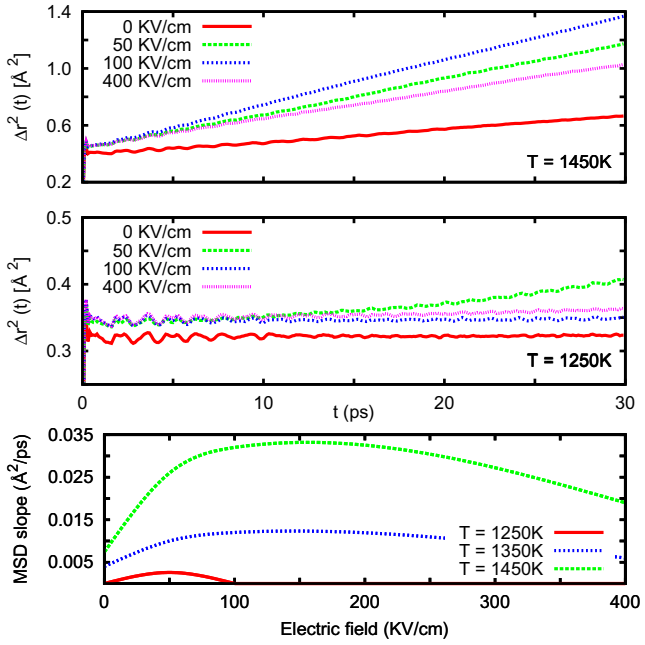


**Fig. 2.** Anionic MSD function and slope calculated in $CaF_2$ considering different temperatures and electric fields.

ordered normal state where the Coulomb interactions are most favourable and the free energy reaches its minimum. At $T = 1450$ K, superionicity is fully developed and the effect of applying an electric field is to further promote the diffusion of anions. The ionic conductivity is maximum at $E = 100$ KV cm$^{-1}$, however under increasing electric bias the slope of the MSD function is reduced (although this is always larger than obtained at $E = 0$). The origins of this effect can be understood in terms of similar entropy and electrostatic energy arguments than just explained. Finally, we calculated the heat capacity and change of entropy associated to the superionic transition in $CaF_2$ under $E \leqslant 100$ KV cm$^{-1}$ and $T \leqslant 1350$ K conditions. We found that the resulting change of temperature assuming adiabaticity generally is $|\Delta T/T| \approx 1\%$.

## Summary

In conclusion, our molecular dynamics work shows that it is possible to vary $T_s$ in FIC by applying relatively small external electrical fields. This effect has the potential to change our paradigm in the search of new electrocaloric materials, which are promising for solid-state cooling applications. Analogous studies performed on similar FIC with lower $T_s$'s (e.g., $\alpha$-$PbF_2$) are highly desirable.

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