In the search of new electrocaloric materials: Fast ion conductors

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We analyse the effects of applying an electric field on the critical temperature, \( T_c \), 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 employed. 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

\[
\Delta T = - \int_{E_0}^{E} \frac{T}{C_p} \left( \frac{\partial S}{\partial E} \right)_T \, dE ,
\]

where \( C_p \) represents the heat capacity, \( S \) the entropy, and \( E \) the external electric field. Ferroelectrics are the archetypal electrocaloric compounds. They exhibit an spontaneous electrical polarization below a certain critical temperature, \( T_c \), that can be shifted by an external electric field. Electrocaloric effects are observed at \( T > T_c \), when the system is paraelectric but responds to the presence of an external electric field by aligning its dipole moments parallel. In those conditions, the adiabatic switch of an electric field causes a positive \( \Delta T \) in the crystal because the entropy in the ordered state is smaller than in 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 \( \Delta T < 0 \). Several thermal cycles based on the electrocaloric effect just described can be engineered, which are promising for solid-state refrigeration applications. Nevertheless, ferroelectric materials present a series of technical issues, like for instance the presence of ferroelectric domains and leakage currents, that are hindering the development of practical electrocaloric applications. Therefore, is very desirable to find new electrocaloric materials with improved cyclability and electrical resistivity features. Promising materials rivaling ferroelectrics, overall, must display a large change of entropy upon 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). 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 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\(^{-1}\). 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, has the potential to motivate original searches on new electrocaloric materials for solid-state cooling applications, as we schematically show 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 show 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, keeping the temperature and pressure fluctuating around a set-point value by using Nose-Hoover thermostats and barostats. Large boxes containing 6,144 atoms were simulated over long times of \( \sim 100 \) 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 modeled 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 normal pressure has already been demonstrated. We simulated the effect of applying an uniform external electric field by adding a force equal to $-qE$ on each ion (where $q$ is the corresponding charge). Following previous works, we identified the onset of superionicity with the appearance of a non-zero slope in the mean squared displacement function (MSD) calculated for 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 F$^-$ ions and time origins.

Results. Figure 2 shows the fluorine MSD function calculated at $T < T_s$ and $T > T_s$ [where $T_s = 1350$ (25) K is the transition temperature computed at $E = 0$] 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, about 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 estimated by the presence of the external electric field and the accompanying increase in the entropy, which minimises the free energy of the sytem. Importantly, at these conditions the diffusion of the F$^-$ ions is Brownian (that is, $\langle r(t) \rangle = 0$), exactly as it is observed in the crystal 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 decreases and the Coulomb interactions between ions are not optimal. Consequently, the anions prefer to remain in the ordered normal state, in which the total electrostatic energy is most favourable, in order to lower the free energy of the crystal. 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 positive and larger than the obtained at $E = 0$). The origins of this effect can be understood in terms of similar entropy and electrostatic energy arguments than explained above. Finally, we calculated the heat capacity and change of entropy associated to the superionic transition in CaF$_2$ at $E \leq 100$ KV cm$^{-1}$ and $T \leq 1350$ K. We found that the resulting change of temperature assuming adiabatic conditions 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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