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Ferroelectricity in perovskitelike NaCaF_3 predicted *ab initio*

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The ability of zero-stress simulations, using Gordon-Kim pair potentials, to describe the structures and transformations of known fluoride-based perovskites is demonstrated for the case of KCaF_3 . When K^+ is replaced by Na^+ a new ferroelectric crystal isomorphous with LiNbO_3 is predicted. The equivalent relationships of the ferroelectric lithium niobate structure with the perovskite and antiperovskite structures are examined. A polarization of $21 \mu\text{C}/\text{cm}^2$ at room temperature and a transition temperature of 550 K are predicted for NaCaF_3 . Surface effects are examined in simulations of a 1080-ion cluster.

Perovskitelike crystal structures are extremely important in many areas of physics: Perovskites are believed to be the most abundant mineral type in the earth; it is the dominating form of scientifically and technologically important ferroelectric materials; and it is a common feature of the recently discovered high-temperature superconducting oxides. We report results of simulations of halide-based perovskitelike solids using *ab initio* potentials which (a) predict a new class of ferroelectric materials of which NaCaF_3 is the prototype; (b) demonstrate that ionic polarizability is not, in general, necessary for ferroelectricity in perovskitelike compounds; and (c) lead to a new interpretation of the relationships between the perovskite, lithium niobate, and antiperovskite structures. Ferroelectric fluoride-based compounds are known to exist;¹ but, since the combination of oxide-ion polarizability and highly charged ions to exploit it is probably essential for ferroelectricity in oxide-based perovskites, it has been commonly believed that ferroelectricity in fluoride-based perovskites might not be possible.

Zero-stress dynamics simulation is used both with² and without³ periodic boundary conditions. Rigid-ion interactions are described by the *ab initio* electron-gas model of Gordon and Kim.⁴ To demonstrate the reliability of this approach, data from simulations of the known ferroelastic perovskite KCaF_3 are presented. When K^+ is replaced by Na^+ , simulation predicts a new ferroelectric crystal that is isomorphous with the well-known ferroelectric solid LiNbO_3 . The ferroelectric lithium niobate structure, as we shall demonstrate, is the structure that occurs midway in a sequence of continuous deformations which transform the perovskite structure into the antiperovskite structure (or *vice versa*).

The perovskite structure accommodates compounds of the form ABX_3 where A and B are positively charged with the charge of B greater than that of A . The undistorted structure has a simple cubic lattice with one ABX_3 unit per unit cell. B lies in the center of the cube, with A at the

corners and the X ions in the face centers. This structure is often described as a cubic array of B -centered octahedra linked by shared X ions at the octahedral corners, with A ions in the interstitial regions (outside the octahedra). Such a description is motivated by the fact that the B ions are more highly charged and generally smaller than the A ions, which produces rather tightly bound BX_6 octahedral units. Specifically, a given B ion is separated from its six neighboring X ions by a distance of only $a/2$, where a is the cubic-cell parameter. By contrast, each A ion has twelve neighboring X ions at $\sqrt{2}a/2$.

Compounds with sufficiently small A ions, relative to the B ions, prefer the antiperovskite structure, obtained from the perovskite structure by interchanging the roles of A and B by placing the more highly charged ion in the interstitial regions rather than at the octahedral centers. Between the two extremes of large and small A ions, a rich assortment of distorted structures can occur which can be described in terms of various patterns of rotations or tilts of the octahedra.

Many halide-based perovskites, both real and simulated, such as CsCaF_3 ,⁵ are stable in the cubic structure.⁶ RbCaF_3 and KCaF_3 are examples of instability of the cubic structure that occurs when smaller cations, but still large compared to the calcium ion, occupy the interstitial regions between the linked octahedra.⁷ If the size of A is decreased further until it is approximately equal to the size of B , the lithium niobate structure⁸ can result. Along each of the cubic axes, alternate planes of linked octahedra rotate in opposite directions, straining the cubic cell into a rhombohedral one. When viewed parallel to the $[111]$ direction, the lithium niobate structure is related to the cubic perovskite structure by octahedral rotations of less than 30° . These rotations, which can be considered the $[111]$ linear combination of triply degenerate R_{25} modes,⁹ start with a displacement of each X along one of the twelve $[110]$ directions. As a result of the rotations, three of the six X ions around each A ion in a (111) plane

move closer to the A ion. This divides the region around the A ion into two new X octahedra which share the A site in a common face.¹⁰ At this stage, the structure is that of paraelectric lithium niobate, with a repeated pattern of two empty octahedra sharing an A ion, followed by a B -centered octahedron, all linked in the trigonal [111] direction by shared faces.

If A is small enough, it moves out of the shared face of the two empty octahedra toward the center of one. This is aided by parallel displacement of the B ion toward which A moves, and by similar displacements of all A and B ions in the crystal.

If A is made even smaller, it will move into the center of its octahedron while B moves into a shared face, producing the paraelectric lithium niobate structure except with the roles of A and B reversed. The final stage in the reduction of the size of A relative to B causes the new octahedra centered about A to rotate into the antiperovskite structure. These final rotations complete the displacement of each X ion along one of the [110] directions and add an additional displacement of $+a/4$ onto the component that was zero. LiBaF_3 is an example of a cubic antiperovskite;¹¹ if LiBaF_3 is simulated starting from the perovskite, it switches to the antiperovskite structure in the way described above. The end result of this perovskite-to-antiperovskite transformation is a displacement of each cation by a quarter of the cubic cell along [111], and of each anion also by a quarter cell along a particular one of the eight [111] directions.

Thus, the ferroelectric lithium niobate structure lies between perovskite and antiperovskite. If A and B are switched in this structure, with a small relaxation of the octahedral network, the result is equivalent to a ferroelectric reversal (which would normally occur by A moving from one octahedron through the shared face into an empty octahedron).

We find the zero-temperature structure of a simulated perovskitelike solid by quenching a 40-ion cell ($2 \times 2 \times 2$ perovskite cells) with periodic boundary conditions from the cubic structure at high temperatures. The 40-ion cell is large enough to accommodate tilts of the backbone of linked octahedra. Quench rates of less than 100 K/psec are required in some compounds to avoid metastable states. Even then, repeated heating and cooling of the sample is required to insure that the minimum-energy structure has been found. This annealing also reveals the possible phase transformations. Thermal effects are simulated using a 320-ion cell obtained by doubling the 40-ion cell in each direction.

We discuss KCaF_3 first because it is a real compound for which experimental data exist. The results of heating a periodic 320-ion cell of KCaF_3 are shown in Fig. 1. These data were collected at temperatures separated by approximately 50 K with a sampling time of 1.55 psec at each temperature. Figure 1 demonstrates that the simulated lattice is cubic at high temperatures, but upon cooling, the angle opposite one lattice vector moves away from 90° while the temperature dependence of the length of that vector becomes different from that of the other vectors. The 1.8% error in the lattice-vector lengths is typical of results obtained with Gordon-Kim potentials. The

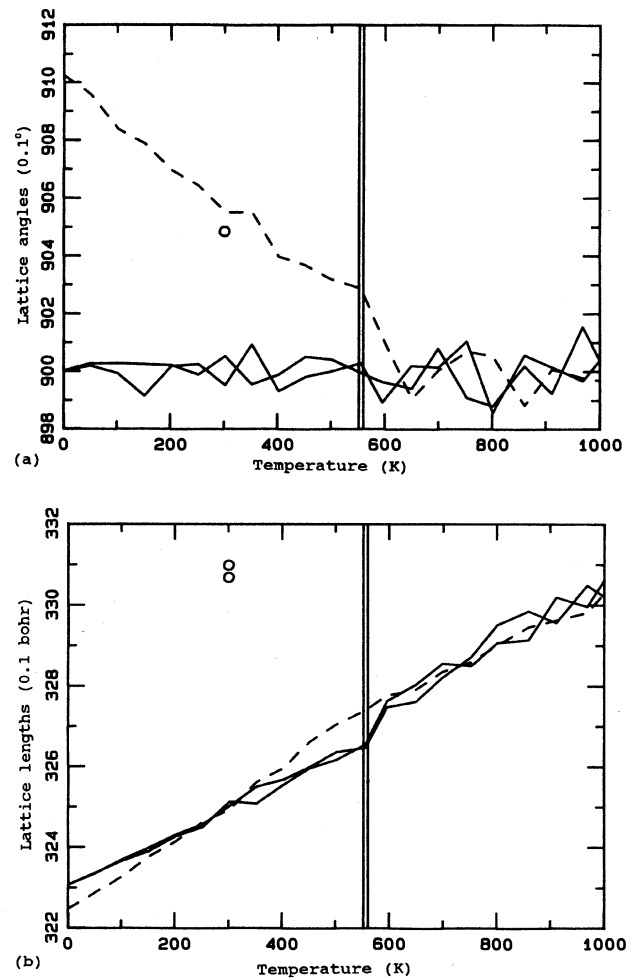


FIG. 1. Angles (a) between, and lengths (b) of the three pseudocubic vectors vs temperature during heating of KCaF_3 with 320 ions/cell. Circles mark experimental points, and the two vertical bars mark experimentally determined transition temperatures. The dashed lines in (a) and (b) are the obtuse angle and the length of the corresponding lattice vector, respectively.

low-temperature space group is orthorhombic with a 20-ion cell rotated 45° about the unique pseudocubic axis.¹² There is an intermediate orthorhombic phase of real KCaF_3 indicated in Fig. 1 that exists over a temperature range too small to be studied easily.

Results of simulation of NaCaF_3 , shown in Fig. 2, predict it to be a lithium niobate isomorph. In the ferroelectric phase, both reduction of the octahedral tilts and expansion of the lattice with heating increase the ability of each sodium ion to move between its two ferroelectric sites by opening the octahedral face in which the average site lies. The transition to the paraelectric phase, which occurs at ~ 550 K when the sodium ions are able to hop between their ferroelectric sites, not only removes the spontaneous polarization, but shows up as a change in the thermal slope of the lattice angles in Fig. 2. The octahedral tilts decrease gradually with heating until at ~ 1400

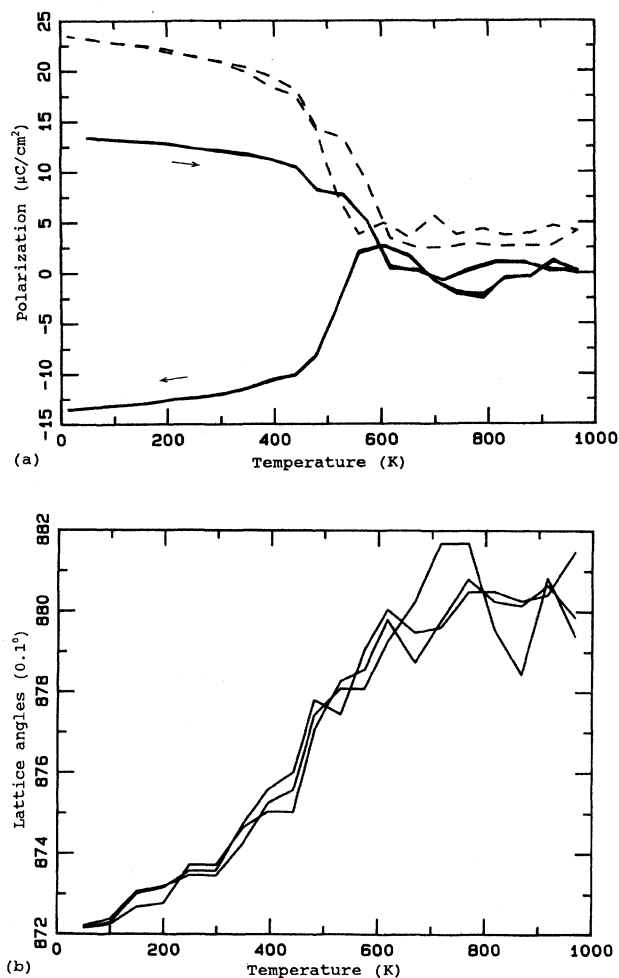


FIG. 2. Components (solid line) and magnitude (dashed line) of (a) spontaneous polarization and (b) angles between pseudocubic vectors of NaCaF_3 with 320 ions/cell. Only data collected while heating are shown in (b).

K the structure melts rather than transform into a cubic phase.

In order to examine surface effects, we have also simulated a 1080-ion cluster ($3 \times 3 \times 3$ of the 40-ion cells described above) of NaCaF_3 . The whole cluster was quenched from the cubic perovskite to ensure that the lithium niobate structure is obtained with or without surfaces. Figure 3 shows the central cell of the cluster above and below the transition temperature, with ion trajectories represented by ellipses. The axes of an ellipse equal the square root of the average deviation from the average position of an ion, with the orientation of the axes chosen to minimize the area. Each elongated sodium-ion ellipse in Fig. 3(b) indicates the approximately equal occupation of the two ferroelectric sites in the paraelectric phase. The ferroelectric displacements of sodium ions (1.33 bohrs at $T=0$ K) can be seen directly by comparing Figs. 3(a) and 3(b), i.e., the sodium ions lie in oxide-ion planes in Fig. 3(b) but lie below those planes in Fig. 3(a). The

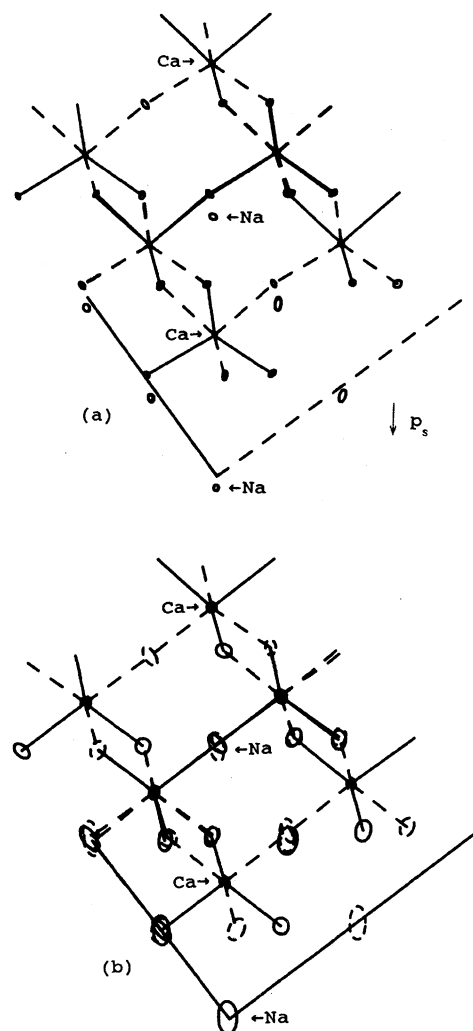


FIG. 3. View perpendicular to the trigonal direction of the central 40 ions of a NaCaF_3 cluster in (a) the ferroelectric phase at 202 K and in (b) the paraelectric phase at 838 K. Solid and dashed ellipses represent the trajectories of ions above and below the page, respectively, in (b). Pseudolattice vectors (as well as they can be determined for a cluster) and vectors from each Ca^{2+} to the six nearest F^- are shown as solid or dashed lines if they have a component out of or into the page, respectively.

calcium-ion displacements (0.33 bohrs at $T=0$ K) appear as slight distortions of the octahedra in Fig. 3(a).

The transition temperature in the cluster is ~ 150 K lower than in the simulation with periodic boundary conditions. This appears to result from surface contraction that occurs in ionic clusters, which will have reduced significance with increasing cluster size. Therefore, the transition temperature from the simulations with periodic boundary conditions are probably better estimates of what should be expected in the real solid. The melting temperature of the cluster is ~ 1400 K also.

In conclusion, a new class of ferroelectric compounds,

with NaCaF_3 as a prototype, has been predicted by simulation using the nonempirical pair potentials of Gordon and Kim which are known to be reliable for other fluoroperovskites. It is remarkable that the mechanism of ferroelectricity in this new lithium niobate isomorph does not require ionic polarizability, but its inclusion would certainly raise the transition temperature and probably increase the spontaneous polarization. The stability of NaCaF_3 to temperatures near 1400 K, simulated either with

periodic boundary conditions or as a free cluster, suggests strongly that this material might be fabricated.

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