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# Molecular-Dynamics Simulations of Some BaXF<sub>4</sub> Compounds

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# Molecular-dynamics simulations of some $BaXF_4$ compounds

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## Abstract

We have carried out molecular-dynamics simulations on  $BaXF_4$  compounds, where  $X$  is Mg, Mn, or Zn. *Ab initio* potentials, with no adjustable parameters, were used to obtain short-range interactions between ion pairs. We found a polar ground-state structure which is in agreement with the  $A2_1am$  space group reported experimentally. We were able to reverse polarization in  $BaMgF_4$  at high temperatures, using large fields, but were unable to reverse polarization in the other compounds. The second-order phase transition in the Mn compound at 250 K was reproduced. We believe this to be the first extension of molecular dynamics to materials consisting of chains of F octahedra.

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We have carried out molecular-dynamics simulations on  $BaXF_4$  compounds, where  $X$  is Mg, Mn, or Zn. *Ab initio* potentials, with no adjustable parameters, were used to obtain short-range interactions between ion pairs. We found a polar ground-state structure which is in agreement with the  $A2_1am$  space group reported experimentally. We were able to reverse polarization in  $BaMgF_4$  at high temperatures, using large fields, but were unable to reverse polarization in the other compounds. The second-order phase transition in the Mn compound at 250 K was reproduced. We believe this to be the first extension of molecular dynamics to materials consisting of chains of F octahedra.

### I. INTRODUCTION

Molecular-dynamics simulations have been performed on a number of fluoride based perovskites in recent years.<sup>1-3</sup> The results of these computations have, in general, been in quite good agreement with experiment, indicating a high degree of reliability of the short-range, rigid-ion pair potentials. This is reasonable to expect in pure perovskitelike fluorides, in which all of the F ions are shared by adjoining octahedra. In such a high-symmetry situation, spherical ionic charge distributions should be appropriate. It is not obvious that the same success would be achieved in compounds containing chains or layers of octahedra, such as in the various  $ABF_4$  structures, where there are F ions which do not couple adjoining octahedra. In these materials, polarization effects may cause a sufficient distortion of the electron charge clouds as to result in a simulated structure completely different from that found in nature.

The sequence of materials  $BaXF_4$ , with  $X = Mn, Fe, Co, Ni, Zn,$  and  $Mg$  has been studied experimentally,<sup>4-6</sup> and the properties of these materials are well known. They all are reported to have the structure shown in Fig. 1, belonging to the space group  $A2_1am$ , which is a polar structure. No ferroelectric phase transitions have been reported for these materials below the melting point, although  $BaMnF_4$  is found to undergo an incommensurate structural phase transition at about 250 K.<sup>6</sup> All of them are ferroelectric, however, reversal of polarization has not been achieved for the Fe and Mn compounds, even with extremely large fields. Keve, Abrahams, and Bernstein<sup>5</sup> suggested a mechanism for reversal of polarity which results in a state in which the coordinates of the ionic positions along the  $a$  axis are reversed in sign. This is equivalent to a mirror plane symmetry element parallel to the  $b$  axis passing through the  $X$  ions (Fig. 2). Hence, whether or not actual reversal is attainable in the labora-

tory, there should be an equilibrium structure identical in energy to the original, if the Ba and F ions are translated to these new positions.

We chose to study  $BaMnF_4$ ,  $BaZnF_4$ , and  $BaMgF_4$ , to determine how closely we could reproduce the experimental results for these materials, including the absence

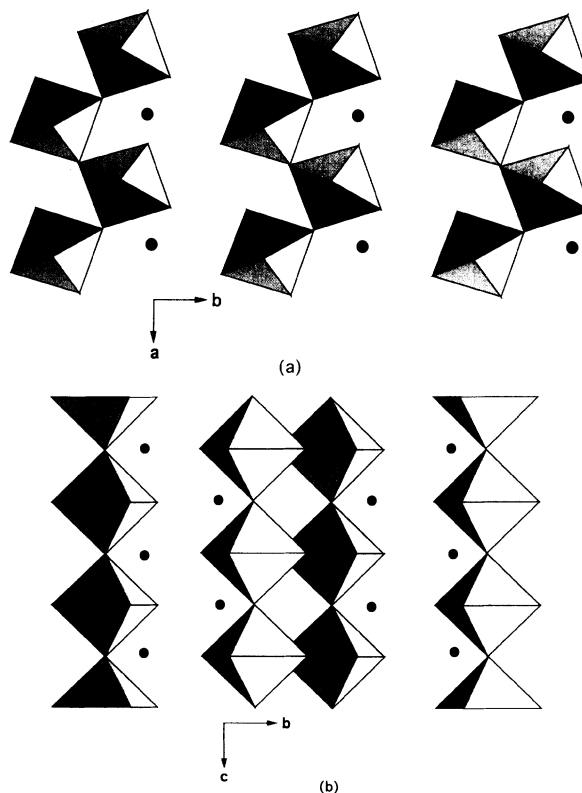


FIG. 1. (a) Structure of  $BaXF_4$  compound viewed along the  $c$  axis; solid circles denote Ba ions,  $X$  ions are at the centers of the octahedra and F ions at the corners. (b) Structure of  $BaXF_4$  viewed along the polar  $a$  axis.

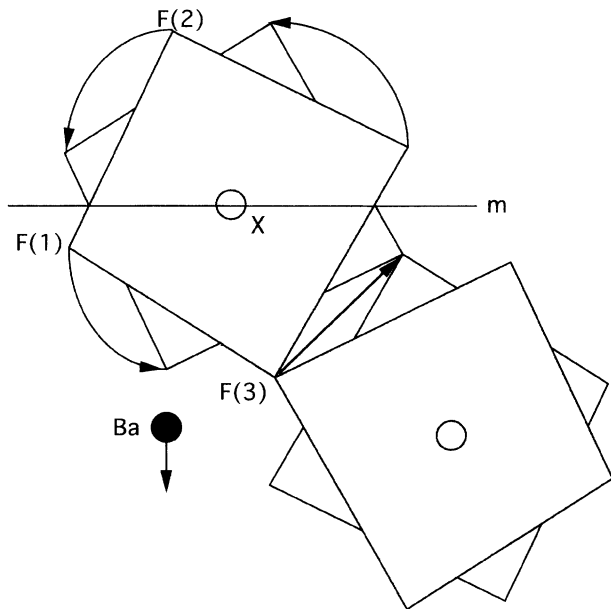


FIG. 2. The mechanism by which polarization reversal may take place in  $\text{BaXF}_4$  compounds, showing the mirror plane perpendicular to  $a$ .

of ferroelectric transitions and the existence of a second-order incommensurate transition in the Mn compound, as well the magnitudes of the polarization and the mechanism of reversal discussed in Keve, Abrahams, and Bernstein.<sup>5</sup>

## II. COMPUTATIONAL TECHNIQUES

The approaches used in obtaining interionic potentials and performing lattice statics and molecular-dynamics computations have been described in detail elsewhere.<sup>1</sup> We will discuss here only the details which pertain directly to the current work.

The minimum sample size which will accommodate the initial structure and the polarization reversal mechanism is four formula units, a total of 24 ions. The initial positions for the Ba, Mn, and F ions within this structure were obtained from Ref. 6. Lattice statics codes were used to relax the lattice constants and ionic positions to obtain a minimum energy configuration, simulating a "0 K" temperature. Lattice-dynamics computations were then used to search for "imaginary" frequencies in the phonon spectrum.

For molecular-dynamics simulations the lattice was doubled in each direction, increasing the sample size to

192 ions. Periodic boundary conditions were used to simulate an infinite crystal. In order to permit variations in lattice constants and internal angles, the lattice vector components were each assigned a mass (350 u) and treated as a dynamical variable. Temperature increases were simulated by adding kinetic energy in amounts equivalent to temperature increments of 30 K, and the sample was held at each temperature for 20 ps. Lattice positions, forces on ions, and instantaneous accelerations and velocities were recomputed every 5 fs. A temperature range from 0 to 1200 K was scanned in this fashion, recording lattice constants, internal angles, lattice energy, and lattice volume at each temperature. Normally, polarization components can also be computed in this fashion if there is an initial nonpolar state available for comparison, however, that was not the case for these materials and polarizations were computed separately using the method suggested by Abrahams *et al.*<sup>7</sup> of averaging the polarization computed for the "forward" and "reverse" poled states, which is straightforward since only the polarization along the  $a$  axis is nonzero.

Lattice statics codes were used to verify the existence of the reversed polarity state, in which the signs of the  $x$  components of position are reversed, and to attempt to determine the ionic positions in the "intermediate state" forming the barrier between the two.

In order to test reversibility, the original 24 ion sample was used, again with periodic boundary conditions. It has been reported that  $\text{BaMgF}_4$  can be reversed at room temperatures with fields larger than 85 kV/cm.<sup>4</sup> Hence, we used this value as the initial electric-field strength, directed entirely along the  $a$  axis. The temperature of each sample was raised in 50-K intervals and the sample was held at each temperature for 200 ps. If no reversal took place within the interval from 300 to 1500 K, the field was increased in strength and the process repeated.

## III. RESULTS

Our results verified that for the three compounds examined, the ground-state structure is indeed that of Fig. 1, and no ferroelectric phase transitions were found from 0 to 1200 K. The computed room-temperature lattice constants for the 24-ion sample are shown in Table I and compared to experiment. The results are quite good for the Mg compound, but less so for the other two. The corresponding volume differences, compared to experiment are 0.5% in the case of Mg, 6.0% for Mn, and 12.4% for Zn. This is not unexpected, since the approach used to derive interatomic potentials involves a simple overlap of electron charge clouds and is known to

TABLE I. Comparison of lattice constants at 298 K (bohr).

	$\text{BaMgF}_4$		$\text{BaZnF}_4$		$\text{BaMnF}_4$	
	Theory	Expt.	Theory	Expt.	Theory	Expt.
$a$	11.039	10.983	11.313	11.042	11.325	11.314
$b$	27.965	27.427	30.730	27.529	30.876	28.541
$c$	7.559	7.789	7.816	7.951	7.840	7.980

have difficulties with *d*-shell electrons, present in both Zn and Mn.

We also found, as reported recently<sup>8</sup> that the mirror reflected state with reversed polarity is stable and has the same static energy as the original state. In order to determine the height of the "saddle-point" barrier between these configurations, we attempted to determine the structure of the hypothetical paraelectric state.

The ground-state structure has space-group symmetry *A*2<sub>1</sub>*am* with the Ba and X ions at 4*a* Wyckoff positions and four sets of fluorine ions F(1), F(2), F(3), and F(4), each set of which occupies a 4*a* position (see Fig. 2). In the model of paraelectric to ferroelectric transition suggested by Keve, Abrahams, and Bernstein,<sup>5</sup> there is no cell size change at the transition; the transition loses the least number of symmetry elements possible, induces spontaneous polarization in the *A*2<sub>1</sub>*am* phase (which is absent in the higher-symmetry phase), and the lost symmetry transformation is a mirror plane perpendicular to the *a* axis and passing through the X ions. As can be seen from Table I of Stokes and Hatch,<sup>9</sup> the space group *Amam* is the only space group satisfying the above conditions. The appropriate space-group relationship requires an origin placement on one of the F(3) fluorine ions. This is a different choice of origin to that of Ref. 5. In the paraelectric phase, the Ba and X ions are each at 4*c* Wyckoff positions, while the F(1), and F(2) sets combine to occupy an 8*f* position. The F(3) and F(4) sets occupy 4*a* and 4*c* positions, respectively. The transition from *Amam* to *A*2<sub>1</sub>*am* is obtained by the onset of a one-dimensional order parameter  $\Gamma_2^-$ . No lattice translations are lost in the transition to *A*2<sub>1</sub>*am* and thus there are no antiphase related domain states. However, the change from *mmm* to *2mmm* causes a reduction of order two in the isogonal point group, resulting in only two orientational domain states in the lower symmetry phase. These two domain states are the two switched ferroelectric domains related by the lost mirror plane.

Using projection operator techniques the displacement patterns induced by the transition can be obtained and are shown in Table II. The Ba, X, and F(4) ions are in 4*c* positions and can only move along the polar axis, the F(3) ions occupying 4*a* positions displace in the *ab* plane with alternating *b* axis components, while the F(1) and F(2) ions move in the *ab* plane in a more complex way. This results in the arrangement shown in Fig. 3. This saddle-point structure requires the F(3) ions joining adjacent octahedra to pass midway between two X ions, and the F(4) ions align with the X ions along the *c* axis. Such a structure was studied using lattice statics codes. The energy was minimized allowing lattice constants to relax but constraining F(3) and F(4) ions to the positions shown. It was found that a configuration of still lower energy could be obtained by allowing the Ba ions to displace in the *ab* plane in the directions shown by the arrows in Fig. 3. This indicates that the transition may not be a simple one from one symmetry group to another, but rather a sequence of at least two transitions. At any rate, since this structure preserves the constraints on the F(3) and F(4) ions, we assume this to be the saddle-point configuration. The static energies of these states and those of the corre-

TABLE II. Coordinates and displacements of ions in the *Amam* to *A*2<sub>1</sub>*am* transition.

Ions	Wyckoff pos.	Coordinates	Displacements
Ba, X, F(4)	4 <i>c</i>	$\frac{1}{4}, y, 0$	$\epsilon, 0, 0$
		$-\frac{1}{4}, -y, 0$	$\epsilon, 0, 0$
		$\frac{1}{4}, y + \frac{1}{2}, \frac{1}{2}$	$\epsilon, 0, 0$
		$-\frac{1}{4}, -y + \frac{1}{2}, \frac{1}{2}$	$\epsilon, 0, 0$
F(3)	4 <i>a</i>	0,0,0	$\alpha, \beta, 0$
		$\frac{1}{2}, 0, 0$	$\alpha, -\beta, 0$
		$0, \frac{1}{2}, \frac{1}{2}$	$\alpha, \beta, 0$
		$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$\alpha, -\beta, 0$
F(1), F(2)	8 <i>f</i>	$x, y, 0$	$\gamma, \delta, 0$
		$-x, -y, 0$	$\gamma, \delta, 0$
		$-x + \frac{1}{2}, y, 0$	$\gamma, -\delta, 0$
		$x + \frac{1}{2}, y, 0$	$\gamma, -\delta, 0$
		$x, y + \frac{1}{2}, 0$	$\gamma, \delta, 0$
		$-x, -y + \frac{1}{2}, \frac{1}{2}$	$\gamma, \delta, 0$
		$-x + \frac{1}{2}, y + \frac{1}{2}, \frac{1}{2}$	$\gamma, -\delta, 0$
		$x + \frac{1}{2}, -y + \frac{1}{2}, \frac{1}{2}$	$\gamma, -\delta, 0$

sponding ground states are given in Table III. The energy difference is smallest for BaMgF<sub>4</sub> (0.0088 hartree/formula unit) and largest for BaZnF<sub>4</sub> (0.026 hartree/f.u.) indicating that the Mg compound should be more susceptible to the rotational transition than the other materials. However, it is found experimentally that the Zn compound can also be readily poled, which would not be expected from these energy considerations.

In Table III we also compare the polarizations reported experimentally with those computed by multiplying the ionic charge of each ion by half of the *a* component of displacement in going from the positively to negatively polarized structure, then dividing by cell volume. As can be seen, the computed polarizations are 10% too high for the Mg compound and 20% too high for the others. Much of this discrepancy can be attributed to representing the ionic charge as being an integral point charge and neglecting the effects of ionic polarization and, again, the pair potentials involving Zn and Mn can be expected to give results which are not as good as those for Mg. Nonetheless, the computed polarizations can be regarded as being in fairly good agreement with experiment.

In attempting to reverse the polarity of the three compounds, it was found that only the Mg material could be

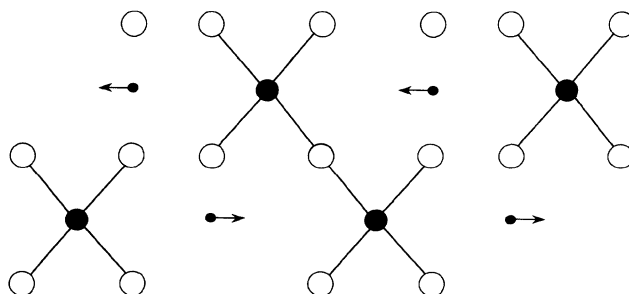


FIG. 3. The apparent midpoint structure for the pole reversal mechanism, with Ba ions aligned with X and F ions.

TABLE III. (a) Static (0 K) energies of the polar and mid-point states (hartree/4 f.u.)

Compound	Polar state	Midpoint
BaMgF <sub>4</sub>	-8.229	-8.194
BaZnF <sub>4</sub>	-7.803	-7.701
BaMnF <sub>4</sub>	-7.792	-7.739

(b) Polarization ( $\mu\text{C}/\text{cm}^{-2}$ )

	Theoretical	Experimental
BaMgF <sub>4</sub>	8.5	7.7
BaZnF <sub>4</sub>	11.7	9.7
BaMnF <sub>4</sub>	13.9	11.5

poled and even then only at temperatures above 900 K using fields of 850 kV/cm; 10 times larger than those used experimentally. A "softness" of BaMgF<sub>4</sub> to a rotation of the F octahedra about the *c* axis is evidenced from an examination of the variations of the interaxis angles vs temperature, obtained from the molecular-dynamics simulation, as shown in Fig. 4; the angle perpendicular to the *c* axis (solid line) shows much more striking fluctuations, even at fairly low temperatures, than do the other two angles. The Zn and Mn compounds also show a change in structure under these very large external electric fields, but not to the reverse polar structure. Instead, the F octahedra tilt about all three axes, (which do not remain perpendicular to each other) so that, viewed along the *c*-axis octahedra in alternate layers of a chain rotate in an antiphase, rather than in-phase sense. Since such huge fields are not physically realistic, it is not expected that these distorted structures would be seen experimentally.

Polarization reversal can only take place if the *X-X* bond length is approximately twice the *X-F* bond length involving the F(3) ions. Experimentally, this is the case for BaMgF<sub>4</sub> and BaZnF<sub>4</sub>, both of which can be poled at room temperature; it is not the case for BaMnF<sub>4</sub>, however.

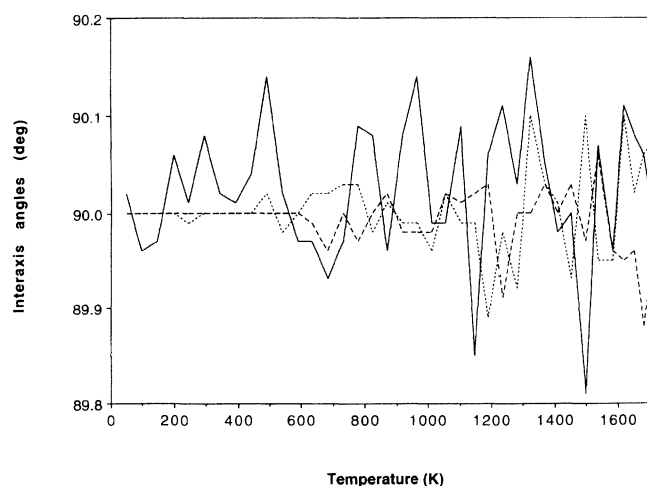


FIG. 4. Internal angles as a function of temperature for BaMgF<sub>4</sub>.

TABLE IV. *X-X* and *X-F*(3). Bond lengths in bohr.

Mg-Mg	7.17-7.2	Mg-F	3.45-3.8
Zn-Zn	7.03-7.04	Zn-F	3.71-3.83
Mn-Mn	7.42-7.49	Mn-F	4.05-4.2

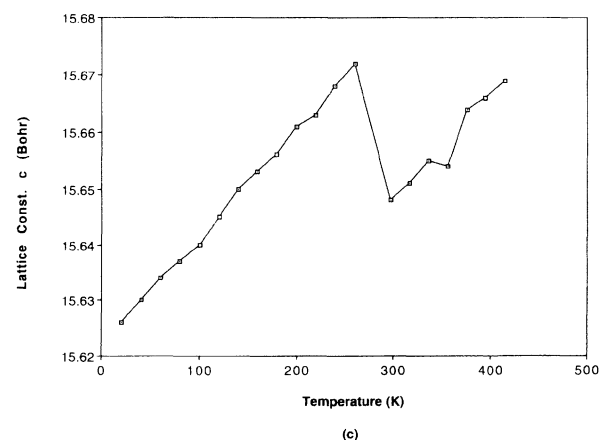
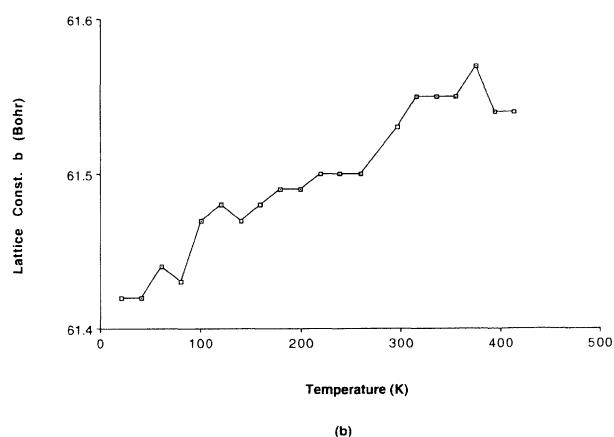
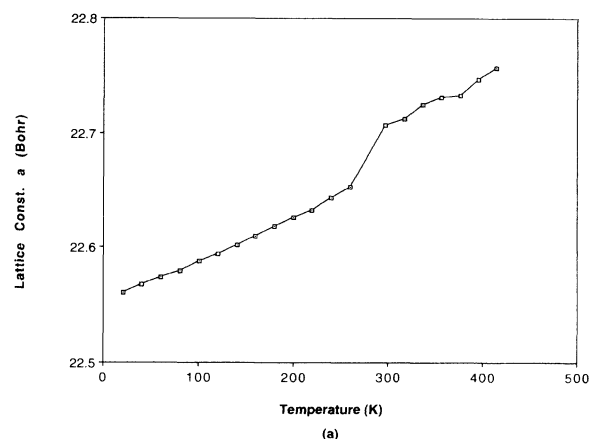


FIG. 5. (a) Lattice constant *a* as a function of temperature for BaMnF<sub>4</sub>. (b) Lattice constant *b* as a function of temperature for BaMnF<sub>4</sub>. (c) Lattice constant *c* as a function of temperature for BaMnF<sub>4</sub>.

We have examined the bond lengths for the appropriate  $X-X$  and  $X-F(3)$  bonds for the materials simulated and these are shown in Table IV. The values are all taken from simulations done near 300 K. It is evident that neither  $BaMnF_4$  or  $BaZnF_4$  satisfy the condition that the  $X-F(3)$  bond be less than half of the  $X-X$  nearest-neighbor bond at room temperature, but  $BaMgF_4$  does. Hence, it would appear that the simulations for  $BaMgF_4$  and  $BaMnF_4$  agree with experimental observation in this regard, but the results for  $BaZnF_4$  do not.

We next turn our attention to the second-order incommensurate phase transition in  $BaMnF_4$ . This transition requires a cell doubling in the  $bc$  plane and results in the  $a$ -axis translation becoming incommensurate. Strictly speaking, since periodic boundary conditions are used a truly incommensurate transition cannot be reproduced. However, it is still possible to observe a similar transition within the context of the arguments presented by Edwardson *et al.*<sup>10</sup> The incommensurate transition arises from an instability involving rotations of the Mn-F octahedra about the  $a$  axis, and cell doubling in the  $bc$  plane appears to be sufficient to allow this type of distortion to appear. Hence, a transition still takes place, but results in rotations with a shorter period than is actually observed. Figure 5 shows the variation in lattice constants as a function of temperature obtained from molecular-dynamics using the large (192 ion) sample. It is apparent that a phase transition takes place which has its onset at approximately 250 K, and which results in a lengthening of the  $a$  and  $b$  axes and a sharp decrease in the length of the  $c$  axis. Figure 6, which shows variations in interaxis angles with temperature, indicates that the transition is accompanied by a rather slight variation of the interaxis angle perpendicular to the  $b$  axis so that the structure above the transition is more closely orthorhombic. An examination of the structure shows antiphase tilting about  $a$  of the F octahedra in each chain, requiring the cell doubling along  $c$ ; but in addition, the Mn-F bonds become bent in opposite directions in alternating chains,

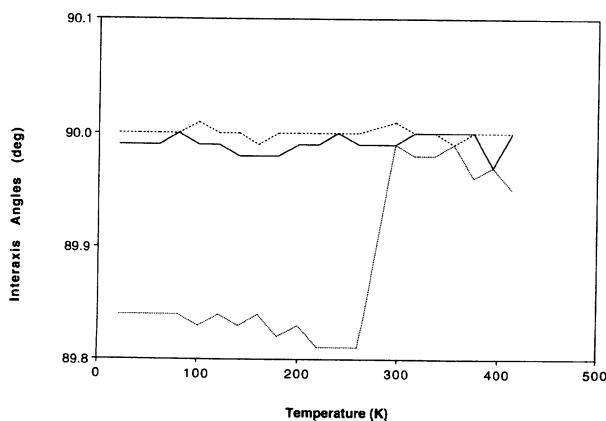


FIG. 6. Internal angles as a function of temperature for  $BaMnF_4$ .

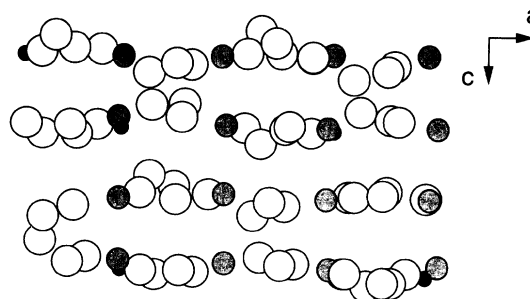


FIG. 7. Simulated structure of  $BaMnF_4$  at 400 K, viewed along the  $b$  axis. Solid circles are Ba, shaded circles Mn, and open circles F ions.

requiring cell doubling along  $b$  as well, and altering the translation vector along  $a$ , as shown in Fig. 7. No similar transition seems to exist for the Zn material.

#### IV. CONCLUSIONS

We have performed molecular-dynamics simulations on  $BaMgF_4$ ,  $BaMnF_4$ , and  $BaZnF_4$ , all of which are predicted to have a polar ground state. We find a ground-state structure completely in agreement with that proposed by Keve, Abrahams, and Bernstein.<sup>5</sup> This is of special interest in that this structure contains F ions at the corners of octahedra which are not shared by other octahedra, such that the crystal field at these sites might be expected to be quite high compared to that at the positions of shared F ions. Moreover, we find that a reversed polar state of identical energy exists for all three compounds. In general, results for  $BaMgF_4$ , the most strongly ionic of the three compounds studied, are quite close to those reported experimentally, although much higher temperatures and field strengths are required to achieve pole reversal.

In the case of  $BaMnF_4$ , we were able to detect a structural phase transition with an onset at 250 K, the same temperature at which a second-order incommensurate phase transition is found experimentally. This close agreement is undoubtedly fortuitous, since previous experience indicates that with this size of sample, we would expect the computed transition temperature to be lower than the actual value. We also found the simulated  $X-F(3)$  bond lengths for this material to be so large as to preclude a pole reversal by the mechanism suggested and indeed were not able to induce such a transition even at high temperatures and electric-field strengths.

$BaZnF_4$  has experimental properties which are between those of the Mg and the Mn compounds; its polarization strength is between the values for the other materials, and the size of the Zn ion should be small enough to allow poling at room temperature. Our results did produce the proper relative polarization, but the computed lattice constants and bond lengths resulted in a structure too

“tight” to allow poling. In this instance we believe that Zn must be regarded as being a “border line” case, where results of the simulation must be viewed with some caution. We conclude that deriving interionic potentials by a direct overlap of spherical charge distributions is not appropriate for Zn, due to the presence of 3d electrons. It appears that, at least for this class of  $ABX_4$  structure,

good qualitative results can be expected so long as the bonding involved is predominantly ionic.

#### ACKNOWLEDGMENTS

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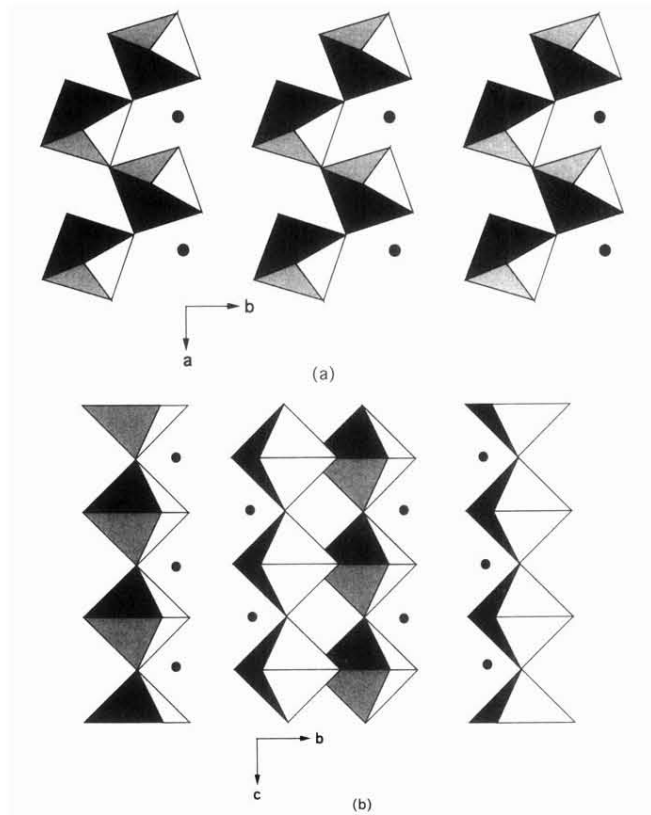


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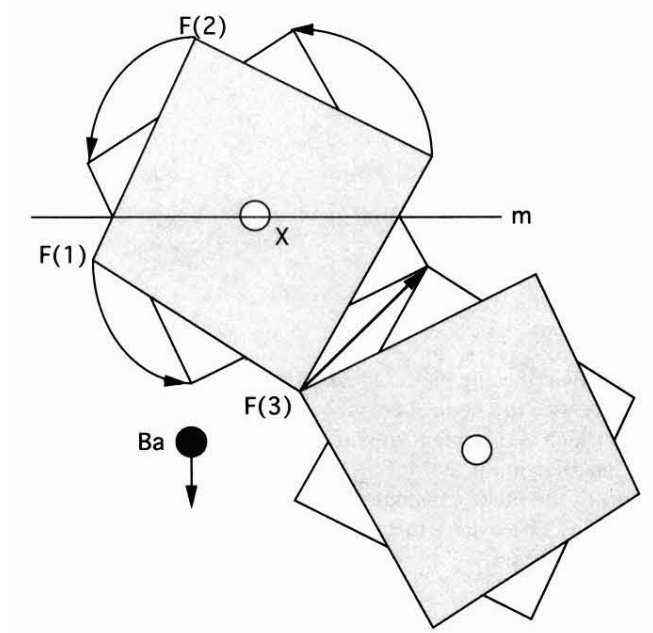


FIG. 2. The mechanism by which polarization reversal may take place in BaXF<sub>4</sub> compounds, showing the mirror plane perpendicular to *a*.

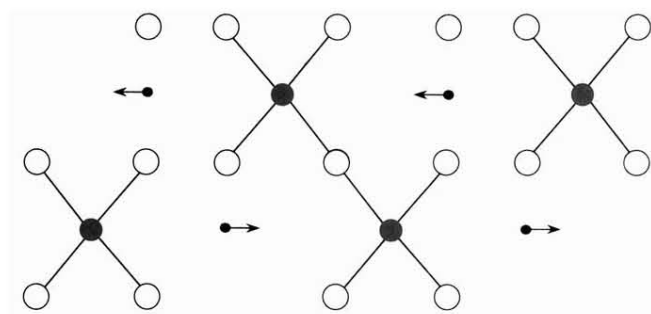
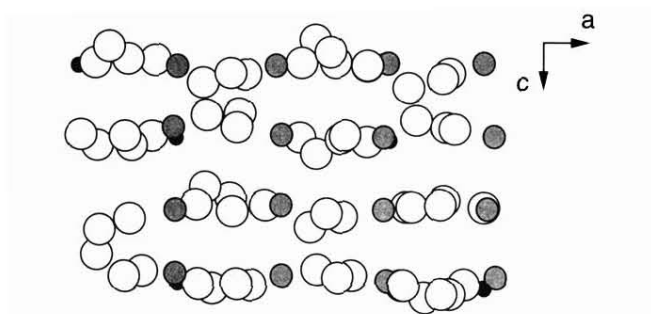


FIG. 3. The apparent midpoint structure for the pole reversal mechanism, with Ba ions aligned with  $X$  and  $F$  ions.



**FIG. 7.** Simulated structure of  $\text{BaMnF}_4$  at 400 K, viewed along the  $b$  axis. Solid circles are Ba, shaded circles Mn, and open circles F ions.