Abstract

Dipropylammonium chloride (DIPAC) and dipropylammonium bromide (DIPAB) crystalize in the P212121 phase and have recently been shown to undergo a ferroelectric transition along the b crystallographic axis. These crystals revert to a centrosymmetric disordered phase P21/m above their Curie temperatures, 440 K and 426 K, respectively. The mechanism for the interconversion of the two polar forms during the ferroelectric transition has not yet been reported. This work explores three possible models for the polar reversal for the DIPAC system, (1) an internal double-hydrogen atom migration requiring minimal rotation of the dipolar unit and a possible switching through the tetragonal phase (DIPAF) and (2) a possible switching through the orthorhombic phase (DIPAI). All four showed a stable minimum monocrystalline structure of approximately P21/m symmetry, and the parameters in Table 1.

Table 1: Parameters for calculated unit cells for DIPAC, DIPAB, DIPAF (calculated) compared to experimental systems

<table>
<thead>
<tr>
<th>System</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIPAC</td>
<td>7.307</td>
<td>7.803</td>
<td>7.684</td>
<td>115.2</td>
</tr>
<tr>
<td>DIPAB</td>
<td>7.616</td>
<td>7.932</td>
<td>7.750</td>
<td>115.21</td>
</tr>
<tr>
<td>DIPAF</td>
<td>7.799</td>
<td>8.066</td>
<td>7.865</td>
<td>116.34</td>
</tr>
<tr>
<td>DIPAI</td>
<td>8.268</td>
<td>8.528</td>
<td>8.310</td>
<td>116.29</td>
</tr>
</tbody>
</table>

Model 3: Halogen-assisted hydrogen transfer

Strong vibrational interactions are seen between chlorine and N-halogen systems highlighted in Figure 1 during molecular dynamics simulation. The corresponding distances between these positions for the DIPAC halide salts are summarized in Table 2. In all cases the X–H–N bonds are within the sum of the van der Waals radii for X-H (positive values in second last column) and X–H–C distances are no more than 0.56 Å away from the sum of the van der Waals radii for X–H (last column). Molecular dynamics results to date have failed to detect group 18, or (3) halogen, but efforts are ongoing.

Table 2. Comparison of distances (Å) between halogen (X) and H's which would undergo migration during halogen-assisted hydrogen transfer

<table>
<thead>
<tr>
<th>System</th>
<th>X–H (Å)</th>
<th>X–N (Å)</th>
<th>X–H–N (°)</th>
<th>X–H–C (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIPAF</td>
<td>1.551</td>
<td>3.119</td>
<td>1.46</td>
<td>2.56</td>
</tr>
<tr>
<td>DIPAB</td>
<td>2.965</td>
<td>2.981</td>
<td>1.76</td>
<td>2.69</td>
</tr>
<tr>
<td>DIPAI</td>
<td>2.200</td>
<td>2.744</td>
<td>1.87</td>
<td>2.97</td>
</tr>
</tbody>
</table>

Computer Methods

All calculations were performed using the Vienna ab initio Software Package 3 (VASP) using projector augmented wave 4 (PAW) potentials supplied by VASP; these were generated using the generalized gradient approximation (GGA) as parameterized by Perdew, Burke, and Ernzerhof5 (PBE) for the exchange-correlation functional. We used the default energy cutoff of 400 eV for all calculations. Geometry optimizations were run at 0 K and 0 ATM. K-point meshes were generated automatically using the Monkhorst-pack method: a 9x9x9 input k-point mesh was used for the single-cell geometry optimization, and a 1x1x11 k-point mesh was used for the supercell calculations. VASP-recommended values for generating grid points were then used for each run. Geometry convergence was assumed when energy differences reached 0.1 eV. Starting geometries for DIPAC and DIPAB were generated using coordinates from the Cambridge Crystallographic Database and all other input geometries (ground state and proposed transition states) were built by hand with the assistance of one or more of the following programs: Avogadro, Mercury, VESTA, as well as data manipulations using Microsoft Excel and text editors.

References


Possible mechanisms for the interconversion of polar forms for the ferroelectric dipropylammonium halides

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