Ferroelastic domain wall orientations in the \((\text{NH}_4)_3\text{H(SeO}_4\text{)}_2\) crystal

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Experimental and theoretical studies of the ferroelastic domain structure of the \((\text{NH}_4)_3\text{H(SeO}_4\text{)}_2\) crystal in phases III and IV are performed. Using the refined structural data the orientations of \(W\) - and \(W'\)-type domain walls, as well as the temperature evolution of the domain structure are investigated. It is shown that in spite of the fact that the room temperature phase III has a triclinic symmetry with small deviations from monoclinic, the domain structure in this phase differs strongly from the structure in the case of a monoclinic symmetry which has been previously accepted in this temperature range. In the monoclinic phase IV all the \(W'\)-type domain walls lie almost in parallel to the \(001\)-plane which explains the invisibility of \(W'\) walls after III-IV phase transition during the observation of the domain structure in the \(001\)-plane.

Key words: domain structure, ferroelasticity

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1. Introduction

The \((\text{NH}_4)_3\text{H(SeO}_4\text{)}_2\) crystal belongs to the family of hydrogen disulphates and diselenates of the chemical formula \(M_3\text{H(}X\text{O}_4\text{)}_2\), where \(M\) denotes \(\text{NH}_4\), K, Rb and Cs. The crystalline structure of the family is characterized by dimers formed by \(X\text{O}_4\) tetrahedra linked with H-bonds. The dynamics of the \(X\text{O}_4\) groups and the proton ordering in crystals result in a sequence of phases exhibiting various long-range orderings. The following phase diagram is now accepted for the \((\text{NH}_4)_3\text{H(SeO}_4\text{)}_2\) crystal:
<table>
<thead>
<tr>
<th>Phase</th>
<th>Phase transition temperature</th>
<th>Point group</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>328 K</td>
<td>R̅3m</td>
<td>[1,2]</td>
</tr>
<tr>
<td>II</td>
<td>302 K</td>
<td>R3</td>
<td>[2]</td>
</tr>
<tr>
<td>III</td>
<td>275 K</td>
<td>C̅1</td>
<td>[3]</td>
</tr>
<tr>
<td>IV</td>
<td>181 K</td>
<td>A2/a</td>
<td>[4,5]</td>
</tr>
<tr>
<td>V</td>
<td>101 K</td>
<td>Aa</td>
<td>[6]</td>
</tr>
<tr>
<td>VI</td>
<td></td>
<td>Aa</td>
<td>[6]</td>
</tr>
</tbody>
</table>

At 302 K the crystal undergoes a transition to the superprotonic phase [1,7] and this transition coincides with the ferroelastic-paraelectric one [1,8]. It should be noted that the ferroelastic domain structure was observed not only in the triclinic phase III but also in the monoclinic phase IV [8–12]. Moreover, dilatometric studies of the crystal [8] revealed drastic changes in the lattice dilatation at 275K. A long range electric ordering was reported in phase V and the ferroelectric-paraelectric phase transition took place at 181 K [13]. Here we would like to present the results of theoretical studies of the ferroelastic domain structure in \((\text{NH}_4)_3\text{H(SeO}_4)_2\) single crystals and the comparison of the results with the experimentally observed variations in the domain pattern.

2. Domain structure of phases III and IV

According to the recent structural investigations [3,4] in \((\text{NH}_4)_3\text{H(SeO}_4)_2\) two ferroelastic phases occur on cooling. In particular, at room temperature (phase III) the symmetry of the crystal is triclinic C̅1 with a small deviation from monoclinic. The elementary unit cell shown in figure 1(a) has the following parameters \(a_t = 15.81\text{Å}, b_t = 6.052\text{Å}, c_t = 10.482\text{Å}, \alpha = 90.79^\circ, \beta = 102.31^\circ\) and \(\gamma = 89.13^\circ\). Only below 279 K the symmetry of \((\text{NH}_4)_3\text{H(SeO}_4)_2\) changes to monoclinic C2/c (phase IV) with the unit cell parameters \(a_m = 10.44\text{Å}, b_m = 6.011\text{Å}, c_m = 15.825\text{Å}\) and \(\beta = 103.99^\circ\) (figure 1(b)). Orientations of the crystallographic axes of phases III and IV in the hexagonal setting perpendicular to the \(x_3\)-axis are shown in figure 2. Observations of the ferroelastic domain structure in phases III and IV have revealed a drastic change of the domain wall orientations at the transition III-IV. The domain walls separating ferroelastic domains with different values of the components of the spontaneous strain tensor can be of two types: three domain walls of the \(W\)-type with crystallographically prominent and independent of temperature directions, and the \(W'\)-type domain walls with orientations varying with the temperature change. In our case both types of boundaries are observed in phase III, whereas in phase IV only the \(W\)-type domain walls were noticed in the plane of observation (figure 3).
Ferroelastic domain wall orientations in the \((\text{NH}_4)_3\text{H(SeO}_4)_2\) crystal

**Figure 1.** The unit cell of the \((\text{NH}_4)_3\text{H(SeO}_4)_2\) crystal in (a) triclinic phase III; \((x_1, x_2, x_3)\) is the Cartesian coordinate system and (b) monoclinic phase IV with the Cartesian coordinate system \((x_4'^I, x_2'^I, x_3)\).

Theoretical analysis of the domain structure is based on the theory of Sapriel [14]. In our case, after transition from the trigonal prototype phase \(R\bar{3}m\) to the ferroelastic phase \(\bar{C}1\), six different orientational states (domains) can exist [15] and, consequently, 12 permissible domain walls are predicted [14].

The components of the spontaneous strain tensor \(e^s_{ij}(S_k)\) can be determined as [15]:

\[
e^s_{ij}(S_k) = e_{ij}(S_k) - \frac{1}{N} \sum_{l=1}^{N} e_{ij}(S_l), \quad (2.1)
\]

where \(N\) denotes the number of orientational states, \(e(S_k)\) is the strain tensor for orientational state \(S_k\).

In the case of the \(3m \rightarrow \bar{1}\) transition and with the additional condition that the 3-folded axis is parallel to the Cartesian coordinate axis \(x_3\) and 2-folded axis - to \(x_2\) in phase \(\bar{3}m\), the components \(e^s(S_k)\) have the following form:

\[
e^s(S_1) = \begin{bmatrix} -a & b & c \\ b & a & d \\ c & d & 0 \end{bmatrix}, \quad e^s(S_2) = \begin{bmatrix} -a & -b & c \\ -b & a & -d \\ c & -d & 0 \end{bmatrix}, \quad (2.2)
\]

here \(a = \frac{1}{3}(e_{22} - e_{11})\), \(b = e_{12}\), \(c = e_{13}\) and \(d = e_{23}\). The components for the four remaining domains can be obtained from equation (2.2) by rotation around the \(x_3\)-axis through \(\pm 2\pi/3\).
Figure 3. Thermal evolution of ferroelastic domains in \((\text{NH}_4)_3\text{H(SeO}_4)_2\). The pictures present the sample surface in phases I, II-(A), III-(B), IV-(C) and again III (D). The arrows show the direction of temperature changes.

In particular, in phase III the components \(a\), \(b\), \(c\) and \(d\) are expressed through the unit cell parameters of the triclinic phase \(\bar{1}\) in the following manner:

\[
\begin{align*}
  a &= \frac{b_t \sqrt{\sin^2 \gamma - z_f^2 - c_t^2 \sin \beta}}{2 b_r}, \\
  b &= -\frac{b_t (c_t \cos \gamma \sin \beta - z_f (3a_t + c_t \cos \beta))}{6 a_t b_r \sin \beta}, \\
  c &= \frac{c_t + 3a_t \cos \beta}{6 a_t \sin \beta}, \\
  d &= \frac{b_t (3a_t \cos \gamma + c_t \cos \alpha)}{6 a_t b_r \sin \beta},
\end{align*}
\]

(2.3)

where \(z_f = \frac{\cos \alpha - \cos \beta \cos \gamma}{\sin \beta}\), \(b_r = 6.064\text{Åin phase I}, \) and are evaluated to be: \(a = -0.69 \cdot 10^{-4}\), \(b = -0.69 \cdot 10^{-2}\), \(c = 0.399 \cdot 10^{-2}\) and \(d = 0.62 \cdot 10^{-2}\).
The orientations of permissible domain walls between two adjacent domains \(S_k\) and \(S_l\) can be determined from the strain compatibility condition [14]:

\[
(e^e(S_k)_{ij} - e^e(S_l)_{ij})x_i x_j = 0. \tag{2.4}
\]

Substituting the spontaneous strain components (2.2) into (2.4), the following equations for domain walls can be obtained:

\[
x_2 = 0 \quad (W_1) \quad \text{and} \quad \begin{cases} b x_1 + d x_3 = 0 & (W_1'), \\ (\sqrt{3}a + b)x_1 + (\sqrt{3}c + d)x_3 = 0 & (W_2'), \\ (\sqrt{3}a - b)x_1 + (\sqrt{3}c - d)x_3 = 0 & (W_3'). \end{cases} \tag{2.5}
\]

The rest of the equations for domain walls (two of the \(W\)-type and three \(W'\)-type for each \(W\)-type wall) can be derived by rotations of the surfaces (2.5) around the \(x_3\)-axis through \(\pm 2\pi/3\). Equations (2.5) yield the following angles between the domain walls \(W_1', W_2', W_3'\) and the \(x_3\)-axis at room temperature:

\[
\begin{align*}
\Theta_1 &= \arctan \left( \frac{d}{b} \right) = -41.8^\circ, \\
\Theta_2 &= \arctan \left( \frac{\sqrt{3}c + d}{\sqrt{3}a + b} \right) = -61.73^\circ, \tag{2.6} \\
\Theta_3 &= \arctan \left( \frac{\sqrt{3}c - d}{\sqrt{3}a - b} \right) = 5.98^\circ.
\end{align*}
\]

Setting formally \(\alpha = \gamma = 90^\circ\) we obtain the monoclinic structure from the triclinic one, in this case \(e_{12} = e_{23} = 0\). Then, from expressions (2.3) one reads: \(b = d = 0\); \(a = \frac{b_m - c_m/\sqrt{3}}{2b_r}\); \(c = \frac{c_m + 3a_m \cos \beta}{6a_m \sin \beta}\).

Considering equations (2.5) for the determination of the domain walls with the constraint \(\alpha = \gamma = 90^\circ\), we can see that the tilt of the \(W_1\)-plane is unchanged, the relation for \(W_1'\) becomes identity (i.e. \(W_1'\)-wall disappears in this case) and another two equations for \(W_2', W_3'\) transform into a single one: \(a x_1 + c x_3 = 0\); that is, we obtain a single domain wall of the \(W'\)-type with the tilt angle \(\Theta = \arctan(c/a)\) to the \(x_3\)-axis, which is to be expected after the transition \(3m \rightarrow 2/m\). Using the structural data of the monoclinic phase IV we have: \(a = -0.138 \cdot 10^{-2}\), \(c = -0.11 \cdot 10^{-1}\) and \(\Theta = \arctan(c/a) = 83.03^\circ\). The value of the angle between the cross-section of the \(W'\)-wall with the \(b_t = 0\) plane (domain wall \(W_1\) in phase III) and the \(x_3\)-axis is \(\Theta' = \arctan(2c/a) = 86.5^\circ\). Thus, the \(W'\)-wall is almost parallel to the \((001)\)-plane and this fact can be the possible explanation of the phenomenon that \(W'\)-type walls were not observed in phase IV (figure 3). The tilt angle of \(W'\)-walls in phase IV differs drastically from the values (2.6) of \(\Theta_2\) and \(\Theta_3\) even with small deviations of the structure from monoclinic (\(\Delta \alpha = \alpha - 90^\circ = 0.79^\circ\), \(\Delta \gamma = \gamma - 90^\circ = -0.87^\circ\)), as well as from the results obtained by Kishimoto et al. in [8] and Schranz et al. in [9].
To explain the influence of pseudomonoclinic symmetry on the orientation of domain walls $W'_2$ and $W'_3$, let us expand expressions (2.6) for $\Theta_2, \Theta_3$ in the powers of small deviations of $b$ and $d$ from zero:

$$\Theta_{2,3} \approx \frac{c}{a} - \frac{1}{1 + (c/a)^2} \frac{1}{\sqrt{3}} \left( \pm \frac{d}{a} \pm \frac{c}{a} \frac{b}{a} \right),$$

(2.7)

for

$$\left| \frac{d}{a}, \frac{b}{a} \right| \ll 1.$$  (2.8)

Even at slight deviations of $\alpha$ and $\gamma$ angles from $90^\circ$, conditions (2.8) do not hold for our structure, since $\left| \frac{d}{a}, \frac{b}{a} \right| \sim 10^2$. Thus, a sharp separation of $W'_2$ and $W'_3$ domain walls is observed after a phase transition to the triclinic phase III.

3. Conclusions

Despite the fact that the determined in [3] symmetry of the room temperature phase of the $(NH_4)_3H(SeO_4)_2$ crystal deviates in a small degree from the accepted in previous investigations monoclinic, the domain structure in this phase differs drastically from the structure in the case of a monoclinic symmetry. This difference manifests itself in the number of permissible domain walls (nine $W'$-type walls instead of three for the monoclinic phase), as well as in its orientations. In particular, the slight deviations $\Delta\alpha, \Delta\gamma$ from $90^\circ$ induce a significant separation of $W'_2$- and $W'_3$-domain walls and the angles between the $W'$-walls and the (001)-plane differ strongly from the previously reported in [8,9] value $47.3^\circ$.

In the case of the monoclinic phase IV, all domain walls of the $W'$-type lie almost parallelly to the (001)-plane. This result confirms disappearance of the domain walls of the $W'$-type in the plane of observation when crystal transforms into phase IV.

References


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Орієнтації фероеластичних доменних стінок у кристалі (NH₄)₃H(SeO₄)₂

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В роботі проведено експериментальне й теоретичне вивчення доменної структури кристалу (NH₄)₃H(SeO₄)₂ у фероеластичних фазах III і IV. Використовуючи найновіші структурні дані, досліджено орієнтації доменних стінок типу W та W'. Показано, що незважаючи на те, що при кімнатній температурі кристал має триклинну симетрію з незначними відхиленнями від моноклінної, домена структура силь но відрізняється від тієї, яка отримується для фази з моноклінною симетрією, що було прийнято раніше для цього температурного інтервалу. У моноклінній фазі IV доменні стінки типу W' майже паралельні.
до площини (001), що пояснює факт їх зникнення при оптичних спостереженнях у цій площині.

Ключові слова: доменна структура, фероеластичність

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