Absolute Sign of Piezoelectric and Pyroelectric Coefficients and Spontaneous Polarization
Temperature Dependence in \( \alpha\)-Cu(IO\(_3\))\(_2\), Nd(IO\(_3\))\(_3\)·H\(_2\)O and LiIO\(_3\)

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The absolute polarity of single crystals of \( \alpha\)-Cu(IO\(_3\))\(_2\) and Nd(IO\(_3\))\(_3\)·H\(_2\)O, determined by anomalous X-ray scattering techniques, has been related to the sense of the piezoelectric \( d_{22}\) and pyroelectric \( P_2\) coefficients in these monoclinic crystals. The absolute sense of \( d_{22}\) in both cases is predictable from a consideration of the behavior of the spontaneous polarization \( P_s\) under stress. \( P_s\) was calculated on the basis of a simple point-charge and dipole model. The positive sense of \( P_2\) in \( \alpha\)-Cu(IO\(_3\))\(_2\) and Nd(IO\(_3\))\(_3\)·H\(_2\)O (each with magnitudes of about 2 \( \times \) \( 10^{-8}\) C m\(^{-2}\) deg\(^{-1}\)) indicates that the secondary pyroelectric coefficients are probably nearly an order of magnitude smaller than the primary piezoelectric coefficients. The absolute sense of \( P_2\) was determined for both crystals in relation to the atomic arrangement. Since \( \alpha\)-Cu(IO\(_3\))\(_2\) with a positive charge on the (010) face, \( d_{22}\) is positive, and that of the unique pyroelectric coefficient \( P_2\) allows the inference that \( P_s\) increases with increasing temperature.

Introduction

Determination of the absolute sense of tensor coefficients provides a unique insight into the relation between the atomic and electronic properties and the macroscopic properties of a material, as recently reviewed by Abrahams (1975). Two newly prepared materials, \( \alpha\)-Cu(IO\(_3\))\(_2\) (Nassau, Cooper, Shiever & Prescott, 1973) and Nd(IO\(_3\))\(_3\)·H\(_2\)O (Nassau, Shiever & Prescott, 1975) were investigated in the present study, both crystallizing in monoclinic point group 2. The absolute sign of one of the eight piezoelectric coefficients \( d_{22}\), and that of the unique pyroelectric coefficient \( P_2\), was determined for both crystals in relation to the atomic arrangement. Since neither \( \alpha\)-Cu(IO\(_3\))\(_2\) nor Nd(IO\(_3\))\(_3\)·H\(_2\)O are ferroelectric, calculation of the spontaneous polarization \( P_s\) allows inference of the \( P_s\) temperature dependence based on the sign of \( P_2\). A similar approach was used for hexagonal LiIO\(_3\), based on the absolute determination of \( P_3\) (Turner, 1976). A model was developed for the origin of the absolute sense of \( d_{22}\) in \( \alpha\)-Cu(IO\(_3\))\(_2\) and Nd(IO\(_3\))\(_3\)·H\(_2\)O, and of \( d_{33}\) in LiIO\(_3\) based on the results of Morosin (1972).

Experimental

The absolute polarity of a single crystal of Nd(IO\(_3\))\(_3\)·H\(_2\)O was determined with the absorption-edge profile method of Barns, Keve & Abrahams (1970), based on the structure determination of Liminga, Abrahams & Bernstein (1975a). In this method the ratio \( \delta = I(hkl)/I(\bar{h}\bar{k}\bar{l})\), where \( I(hkl)\) and \( I(\bar{h}\bar{k}\bar{l})\) correspond to the measured intensities at the low-wavelength side of the absorption edge (normalized at the high-wavelength side) of the Friedel pair of reflections, is compared with a matrix of \( \delta\) values calculated for these reflections based on a range of \( f'\) and \( f''\) real and imaginary dispersion corrections.†

A crystal of Nd(IO\(_3\))\(_3\)·H\(_2\)O grown by Nassau et al. (1975) was ground into a plate approximately parallel to (010) with an area of about 1 cm\(^2\) on each face. The Nd K absorption edge (\( \lambda = 0.2845\) \( \AA\)) for (040) and (004) was measured at three locations on each face. Silver electrodes were applied to these faces and the pyroelectric and piezoelectric coefficients measured as described by Abrahams (1975). The surface that develops a positive charge on heating was found to be (010), with a negative charge on heating (00\( \bar{1}\)). Since \( \delta\) (positive charge/negative charge)\(_{\text{heating}}\) = 1.14 ± 0.03 and the matrix gave 0.04 < \( \delta\) < 0.16, for \( -6 < f' < -3\) and 20 < \( f'' < 70\). Tensile stress applied parallel to the polar b axis generated a positive charge on the (010) face, i.e., \( d_{33} > 0\) (Table 1).

The absolute polarity of \( \alpha\)-Cu(IO\(_3\))\(_2\) could not be determined by the absorption-edge profile method because the available crystals were too small. A single crystal with maximum dimension 0.23 mm, cut from a spherulite [the normal growth form – see Nassau et al. (1973)], was thereupon used to give a full hemisphere set of X-ray intensity measurements including both \( I(hk\ell)\) and \( I(\bar{h}\bar{k}\bar{l})\) (Liminga et al., 1975b). The absolute atomic arrangement of \( \alpha\)-Cu(IO\(_3\))\(_2\) with respect to the

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† The \( \delta\) terms in the dispersion corrections have been omitted, followed the convention adopted in Anomalous Scattering (Ramaseshan & Abrahams, 1975).
assigned Miller indices was thereby determined, making use of the anomalous scattering of Mo Kα radiation by the Cu and I atoms.

Silver electrodes were subsequently applied to this small crystal and the pyroelectric coefficient measured along the polar axis. Measurement of the piezoelectric $d_{22}$ was not possible on this very small crystal, hence a group of crystals in approximately parallel configuration were cut from another spherulite. The absolute crystal shape was readily related to that of the crystal previously studied by the characteristic facets that develop at the spherulite surface. The fragments were encapsulated in Ambroid* and cut to form a plate approximately normal to the polar $b$ axis.

The choice of Miller indices (Liminga et al., 1975b) in $\alpha$-Cu(IO$_3$)$_2$ led to negative values for both the pyroelectric and piezoelectric coefficient, whereas the IEEE Standard 176 (1949) on piezoelectricity requires $d_{22} > 0$. Compliance with this standard is possible by replacing all previous $hkl$ with $hkl$ indices and all $xyz$ with $\bar{x}\bar{y}\bar{z}$ coordinates, thus leaving the diffraction results intact. The resulting coordinates correspond to the apexes of both independent IO$_3^-$ ions pointing toward (010), as in Fig. 1. Experimentally, the (010) face of the crystal (with transformed indices as used hereafter) develops a positive charge on heating, the (010) face a positive charge on cooling. The (010) face generates a positive polarity under tensile stress, a negative polarity under compressive stress (Table 1).

**Pyroelectric coefficients in Nd(IO$_3$)$_3$.H$_2$O and $\alpha$-Cu(IO$_3$)$_2$**

The charge integration technique (Glass, 1969) was used to determine $p_2$ for Nd(IO$_3$)$_3$.H$_2$O and $\alpha$-Cu(IO$_3$)$_2$ by direct measurement of the change in polarization over the temperature range 300–350 K. This measurement includes both primary and secondary pyroelectric effects: higher-order effects were avoided by uniformly heating the crystal. Since a posi-

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**Table 1. Relation of piezoelectric and pyroelectric effects to crystallographic polarity**

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Charge on extension</th>
<th>Charge on heating</th>
<th>Apex of IO$_3^-$ ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-Cu(IO$_3$)$_2$</td>
<td>Positive</td>
<td>Positive 010</td>
<td>(010)*</td>
</tr>
<tr>
<td></td>
<td>Negative</td>
<td>Negative 010</td>
<td>(010)</td>
</tr>
<tr>
<td>Nd(IO$_3$)$_3$.H$_2$O</td>
<td>Positive</td>
<td>Positive 010</td>
<td>(010)</td>
</tr>
<tr>
<td></td>
<td>Negative</td>
<td>Negative 010</td>
<td>(010)</td>
</tr>
<tr>
<td>LiIO$_3$</td>
<td>Positive†</td>
<td>Positive‡ 00.1</td>
<td>(00.1)*</td>
</tr>
<tr>
<td></td>
<td>Negative</td>
<td>Negative 00.1</td>
<td>(00.1)*</td>
</tr>
</tbody>
</table>

* For Miller indices and atomic coordinates transformed as given in text.
† Determined by Morosin (1972): see text.
‡ Determined by Turner (1976).

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Fig. 1. Absolute orientation of IO$_3^-$ and Cu$^{2+}$ ions in $\alpha$-Cu(IO$_3$)$_2$ with respect to the polar axis (after Liminga et al., 1975b but with transformed Miller indices and atomic coordinates, see text). The long I–O bonds (> 2.6 Å) are shown dashed, the shorter Cu–O bonds (≈ 2.0 Å) dotted, and the longer Cu–O bonds (≈ 2.4 Å) dot-dashed. For clarity, not all symmetry-equivalent bonds are shown. The calculated spontaneous polarization sense is given.
positive polarity on (010) is generated for both crystals on heating (Table 1), \( p_2 > 0 \) in both cases. The spontaneous polarization neither vanishes nor can it be reversed in either crystal, hence the absolute sense of \( \mathbf{P} \), cannot be deduced solely from the temperature dependence of \( p_2 \).

The magnitude of \( p_2 = \frac{dP}{dT} \) along the polar axis is approximately \( 2 \times 10^{-5} \text{Cm}^{-2} \text{deg}^{-1} \) for \( \alpha\text{-Cu(IO}_3\text{)}_2 \) and \( 2.2 \times 10^{-5} \text{Cm}^{-2} \text{deg}^{-1} \) for \( \text{Nd(IO}_3\text{)}_3 \cdot \text{H}_2\text{O} \). The error in the latter measurement is estimated to be no more than \( \pm 20\% \), but in the former it may be as much as \( \pm 50\% \) owing to the difficulty in measuring the area of the electroded faces. A continuously recorded charge-integrated variation of \( \frac{dP}{dT} \) with \( T \) was then calibrated for \( \text{Nd(IO}_3\text{)}_3 \cdot \text{H}_2\text{O} \) using \( p_2 = 2.2 \times 10^{-5} \text{Cm}^{-2} \text{deg}^{-1} \) at 300 K, over the range 300-400 K. The

\[ \text{Fig. 2. Variation of } \frac{dP}{dT} \text{ (open circles) with temperature, and of } \Delta P \text{ (crosses) with temperature, in } \text{Nd(IO}_3\text{)}_3 \cdot \text{H}_2\text{O}. \]

\[ \text{Fig. 3. Absolute orientation of } \text{IO}_5^- \text{ and } \text{Nd}^{3+} \text{ ions and } \text{H}_2\text{O in } \text{Nd(IO}_3\text{)}_3 \cdot \text{H}_2\text{O with respect to polar axis (after Liminga et al., 1975a). The calculated sense of the spontaneous polarization is as given. The long } 1- \text{O bonds are shown dashed, the } O \text{ H}\cdots\text{O bonds are dotted [an additional possible hydrogen bond is formed to } \text{IO}_3^- \text{ coinciding nearly with that to } \text{IO}_5^- \text{ in this view, and is hence omitted].} \]
crystal begins to dehydrate at about 405 K. Values of 
\( \Delta P \) as a function of \( T \) were obtained by integration of 
\( dP/dT \), and both coefficients are shown in Fig. 2.

**Model for absolute sense of spontaneous polarization**

The absolute sense of \( P_s \) cannot be experimentally 
determined from the measurement of \( dP/dT \) alone, 
although consideration of a simple point-charge and 
dipole model allows the sense to be calculated. The 
\( IO_3^- \) point-charge location is taken to be at the center 
of the ionic electron distribution, that of the \( Cu^{2+} \) ion 
at the atom position. The resulting polarization is thus 
parallel to the atom position. The resulting polarization is thus 
parallel to the \( b \) axis, as indicated by the arrow in Fig. 1 (note 
that for a purely point-charge model, \( P_s = 0 \) if \( Cu^{2+} \) is 
located exactly in, or alternatively is midway between, 
the sheets of iodate ions normal to \( b \), with a value of 
about \( +12.7 \times 10^{-2} \) Cm\(^{-2} \). The dipolar contribution 
from the \( O^-I \) bonds of the iodate ion is also parallel to 
\( b \), but is reduced by the opposing dipole of the iodine 
lon pairs. Taking the net dipole moment to be about 
11.3 \( \times 10^{-2} \) Cm\(^{-2} \), the spontaneous polarization 
for this crystal is hence about \( +18 \times 10^{-2} \) Cm\(^{-2} \).

The point-charge model for \( Nd(IO_3)_3 \cdot H_2O \) yields a 
polarization parallel to \( b \) of about \( 11.3 \times 10^{-2} \) Cm\(^{-2} \). 
In this case, the \( Nd^{3+} \) is displaced approximately 0.54 Å 
out of the mean plane corresponding to the three 
independent \( IO_3^- \) ions (see Fig. 3). The dipolar contribution 
from the \( IO_3^- \) ions adds to that of the point-charge 
polarization by about \( +18 \times 10^{-2} \) Cm\(^{-2} \), the spontaneous polarization 
for this crystal is hence about \( +18 \times 10^{-2} \) Cm\(^{-2} \).

The primary result of compressive stress is a reduction in 
the \( b \) axis spacing decreases. Further, the network of 
longer I-O bonds with components parallel to the 
\( b \) axis is more readily deformable than the shorter, 
assumed stiffer, \( Cu-O \) bonds. Hence, under compressive 
stress, the charge separation along the \( b \) axis 
decreases and the orientation of the \( IO_3^- \) ion dipole 
changes. The effect of the latter on \( P_s \) is negligible, that 
of the former gives a smaller polarization and therefore 
a negative polarity on \( 010 \). Conversely, a positive 
charge develops on \( 010 \) under tensile stress, in accord 
with experiment (Table 1).

A similar model applies to \( Nd(IO_3)_3 \cdot H_2O \). Each 
independent \( IO_3^- \) ion forms three or four long I-O 
bonds (\( >2.6 \) Å) to other \( IO_3^- \) ions or to the water 
molecule (Fig. 3). The \( Nd^{3+} \) ion occupies a rather 
symmetrical environment of eight iodate oxygen 
atoms (\( Nd-O \) = 2.4-2.5 Å). The long I-O bonds deform 
more readily than the stiffer \( Nd-O \) contacts of equal length. 
Hence, as translationally identical \( IO_3^- \) ions 
(e.g. at \( y \approx 0 \) and 1) become closer under compressive 
stress, the orientation of the three independent \( IO_3^- \) ions 
changes: the resulting displacement of the neutral 
\( H_2O \), assuming no change in H-O-H angle as is the 
primary result of compressive stress is a reduction in 
\( P_s \) and hence development of negative charge on \( 010 \), 
in agreement with experiment (Table 1).

**Model for origin of piezoelectric \( d_{22} \) coefficient sense**

in \( \alpha-Cu(IO_3)_3 \) and \( Nd(IO_3)_3 \cdot H_2O \)

Application of tensile stress parallel to the polar axis of 
either \( \alpha-Cu(IO_3)_3 \) or \( Nd(IO_3)_3 \cdot H_2O \) causes positive 
polarity development on \( 010 \), leading to the absolute 
assignment \( d_{22} > 0 \) for both crystals. The origin of the 
sign of \( d_{22} \) in relation to the atomic arrangement, both 
in \( \alpha-Cu(IO_3)_3 \) and in \( Nd(IO_3)_3 \cdot H_2O \), is most simply 
derived by considering the spontaneous polarization 
behavior under stress. The primary contribution to 
\( P_s \) is shown in the preceding section to be the charge 
separation along the polar axis together with the dipole 
moment of the \( IO_3^- \) ion and additionally, in the case of 
\( Nd(IO_3)_3 \cdot H_2O \), the water molecule.

Fig. 1 shows the arrangement of ions in \( \alpha-Cu(IO_3)_3 \), 
with the pyramidal \( IO_3^- \) ions oriented such that both 
individual iodine apexes point toward \( 010 \). The 
I-O bonds longer than 2.6 Å are represented by dashed 
lines, those within the \( IO_3^- \) ions being about 1.8 Å. The 
\( Cu^{2+} \) ion occupies an octahedral environment, with 
four short \( Cu-O \) bonds (\( \approx 2.0 \) Å) represented by dotted 
lines and two longer bonds (\( \approx 2.4 \) Å) represented by 
dot-dashed lines in Fig. 1. As the translational identity 
between \( IO_3^- \) ions along the \( b \) axis is maintained under 
compressive stress normal to \( 010 \), alternate layers of 
\( IO_3^- \) ions at \( y \approx \frac{1}{2} \) may rotate and simultaneously 
change orientation relative to those at \( y \approx 0 \) (and 1) as 
the \( b \) axis spacing decreases. Further, the network of 
longer I-O bonds with components parallel to the 
\( b \) axis is more readily deformable than the shorter, 
assumed stiffer, \( Cu-O \) bonds. Hence, under compressive 
stress, the charge separation along the \( b \) axis 
decreases and the orientation of the \( IO_3^- \) ion dipole 
changes. The effect of the latter on \( P_s \) is negligible, that 
of the former gives a smaller polarization and therefore 
a negative polarity on \( 010 \). Conversely, a positive 
classical shows that \( \alpha-Cu(IO_3)_3 \) and 
\( Nd(IO_3)_3 \cdot H_2O \) is, by contrast, inferred to 
have a positive charge on \( 010 \) under tensile stress, in accord 
with experiment (Table 1).

**Temperature dependence of pyroelectric spontaneous polarization**

The spontaneous polarization in most ferroelectric 
crystals decreases with increasing temperature, as the 
atomic positions change to accommodate new symmetry 
conditions in which all pyroelectric coefficients 
vanish. The magnitude of \( P_s \) in \( \alpha-Cu(IO_3)_3 \) and 
\( Nd(IO_3)_3 \cdot H_2O \) is, by contrast, inferred to increase 
with rising temperature since both \( P_1 \) and \( P_2 \) are 
positive. Such temperature dependence is not unique, 
even in ferroelectrics. Thus in Rochelle Salt 
(\( NaKC_4H_4O_6 \cdot 4H_2O \)) for example, with phase transitions 
at 255 and 297 K as represented by 
\( PPP(222)FPP(2)PPP(222) \) (Keve & Abrahams, 1970), 
\( P_s = 0 \) at both transitions and reaches a maximum of 
about \( 0.25 \times 10^{-2} \) Cm\(^{-2} \) at 278 K (Hablützel, 1939). 
\( P_s \) is reported to increase sharply in (\( NH_4)_2SO_4 \) from 
room to the transition temperature, before abruptly 
falling to zero (Unruh & Rüdiger, 1972), and \( P_s \) in 
\( LiNbO_3 \) has very recently been shown by Glass &
Lines (1975) to increase at very low temperatures, reaching a maximum at about 10 K.

A consideration of the detailed atomic arrangement giving rise to $P_s$, suggests that, for a simple pyroelectric crystal without phase transition, the spontaneous polarization may in principle either increase or decrease over a given temperature interval. For example, consider a dipole array in space group $Pmn$ with two chemical formulas in the unit cell, each formula being represented by a single non-zero dipole (see Fig. 4). If the angle between the dipole and the mirror plane is $\alpha$, the spontaneous polarization is given by equation (1),

$$P_s = (2\mu \cos \alpha)/V$$

where $V$ is the cell volume. With a molecular or ionic structure in which $\mu$ is not temperature dependent, the only temperature variables are $\alpha$ and $V$. For the ferroelectric case $\alpha$ increases with $T$, reaching 90° at the transition as the symmetry increases to $P2/m$. In the pyroelectric case, however, it is not in general possible to predict the variation of $\alpha$, and hence $P_s$, with $T$.

The total pyroelectric coefficient $p_2$, measured at constant stress, is given by the sum of the coefficient at constant strain (the primary pyroelectric coefficient) and the piezoelectric effect caused by thermal strain (the secondary pyroelectric coefficient). The latter term is the product $\epsilon_{ij} e_{kl} c_{ijkl}$, where $\epsilon_{ij}$ is the elastic stiffness, $e_{kl}$ is the thermal expansion, and $c_{ijkl}$ are coefficients. A literature survey suggests that reasonable maximum values for these coefficients in the case of iodate salts as a class are: $d_{i\mu} < 3 \times 10^{-12} \text{ C N}^{-1}$, $c_{ij\mu} < 20 \times 10^9 \text{ N m}^{-2}$ and $\epsilon_{ij} < 5 \times 10^{-6} \text{ deg}^{-1}$. The secondary pyroelectric coefficients for $\alpha$-Cu(IO$_3$)$_2$ and Nd(IO$_3$)$_3\cdot$H$_2$O are hence probably no larger than about $3 \times 10^{-8} \text{ C m}^{-2} \text{ deg}^{-1}$, i.e., an order of magnitude less than the total pyroelectric coefficients observed at room temperature. For cases in which the secondary pyroelectric coefficient is dominant, with positive $\epsilon_{ij}$, the spontaneous polarization is of course bound to increase with rising temperature.

The change in sign of the slope of $dP/dT$ with $T$ for Nd(IO$_3$)$_3\cdot$H$_2$O together with the overall variation in magnitude of the total pyroelectric coefficient of about $7 \times 10^{-6} \text{ C m}^{-2} \text{ deg}^{-1}$ shown in Fig. 2 is to be noted. If the secondary pyroelectric coefficient is of the expected magnitude, this change in sign must be caused by a corresponding change in the magnitude of the primary coefficient. A similar explanation has been given by Lang (1971) for the pyroelectric coefficient behavior in Li$_2$(SO$_4$)·H$_2$O.

Model for origin of piezoelectric $d_{22}$ coefficient sense in LiIO$_3$

Morosin (1972) has determined the absolute configuration of LiIO$_3$ to be such that the larger end of the hexagonal prismatic crystals develops a positive polarity on compression, with the apex of the pyramidal IO$_3^-$ ions pointing toward the smaller end of the crystal. The absolute configuration of a crystal as determined by X-ray anomalous scattering gives without ambiguity the relation of the atomic coordinates to the assigned Miller indices. For LiIO$_3$, as for $\alpha$-Cu(IO$_3$)$_2$, the choice of indices led to a description of the basal face (normal to the polar axis) on which a positive polarity is produced on extension as (00.1), and hence a piezoelectric coefficient $d_{33} < 0$.

IEEE Standard 176 (1949) on piezoelectricity requires $d_{33} > 0$. For consistency with this standard, the previously assigned $hkl$ indices should be changed to $h'kl$ and correspondingly, the $xyz$ coordinates to $x'y'z'$: the diffraction results are thereby left unchanged. The transformed coordinates thus correspond (Rosenzweig & Morosin, 1966; Boer, Bolhuis, Olthof-Hazekamp & Vos, 1966) to an absolute arrangement (Morosin, 1972) in which the apex of the pyramidal IO$_3^-$ ions points toward (00.1), and $d_{33} > 0$. In addition, each IO$_3^-$ ion is associated with three longer I-O bonds, of about 2.9 Å, completing the distorted octahedron about iodine, as shown in Fig. 5.

The model used for $\alpha$-Cu(IO$_3$)$_2$ and Nd(IO$_3$)$_3\cdot$H$_2$O applies also to LiIO$_3$. The non-crystallographically equivalent Li–O distances are taken as approximately equal with both distances equally deformable: the long I–O distances are assumed to be more readily deformed than the short I–O distances. Since the equality of x/z spacings between sheets of IO$_3^-$ ions remains unchanged under stress, ions in alternate sheets are free to rotate. By contrast, the Li$^+$ ions are free to move along the polar axis, relative to the IO$_3^-$ ions. Thus, compressive stress decreases the separation between Li$^+$ and IO$_3^-$ ions and hence $|P_s|$, resulting in the formation of a negative polarity on (00.1), in accordance with observation (Table 1).

The spontaneous polarization in LiIO$_3$ may be evaluated as about $1.6 \times 10^{-2} \text{ C m}^{-2}$ from point-charge displacements, and an additional dipolar component of $5.5 \times 10^{-2} \text{ C m}^{-2}$, for a total of about $1.7 \times 10^{-1} \text{ C m}^{-2}$, directed toward (00.1) as illustrated in Fig. 5. The absolute determination of the pyroelectric coefficient $p_3$ for LiIO$_3$ by Turner (1976) as positive, together with the calculated spontaneous polarization sense, allows the
inference that $P_s$ in LiIO$_3$, as in $\alpha$-CuIO$_3$ and Nd(IO$_3$)$_3$. H$_2$O, increases with increasing temperature.

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Fig. 5. Absolute orientation of IO$_3^-$ and Li$^+$ ions in LiIO$_3$ with respect to the polar axis [after Morosin (1972) but with transformed coordinates and Miller indices, see text]. The long I-O bonds are shown dashed, the Li-O bonds dotted. The calculated spontaneous polarization sense is as shown.