Piezoelectric, Dielectric, and Pyroelectric Constants of LiH₃(SeO₃)₂

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The complete sets of dielectric, piezoelectric, and pyroelectric constants and a partial set of elastic constants are given for ferroelectric lithium trihydrogen selenite, the first crystal of monoclinic class *m* for which such data have been obtained. The ferroelectric moment is 15 μcoul/cm.^{2} directed 3° from the normal to the (001) plane. It decreases by 6·6% in magnitude and shifts to an angle of 1·1° at 85 °C. The two principal axes of the dielectric tensor in the symmetry plane are nearly 45° from the ferroelectric axis and the principal dielectric constants are $\varepsilon_1'/\varepsilon_0 = 13\cdot0$, $\varepsilon_2'/\varepsilon_0 = 12\cdot9$, and $\varepsilon_3'/\varepsilon_0 = 46$. The strongest piezoelectric effect is given by a constant $d_{33}' = 46 \times 10^{-12}$ coul/newton relating to a direction about 60° from the ferroelectric axis. Prolonged application of a strong d.c. electric field parallel to the ferroelectric axis reverses the sign of all piezoelectric constants but leaves the magnitudes unchanged confirming that the non-ferroelectric reference structure has symmetry $2/m$.

Introduction

Lithium trihydrogen selenite LiH₃(SeO₃)₂ is a ferroelectric crystal of symmetry class *m* (Pepinsky & Vedam, 1959; Vedam, Okaya & Pepinsky, 1960) with the only symmetry element a plane which must contain the ferroelectric direction. The other monoclinic crystal classes, class 2 and class 2/*m*, have respectively a two-fold axis and a center of symmetry. The former is a piezoelectric class, and it may be ferroelectric with the ferroelectric axis along the two-fold axis.

There are ten independent piezoelectric constants in a class *m* crystal and eight in a class 2 crystal. The nonzero constants for one correspond to those which vanish for the other. Piezoelectric measurements have been made for several class 2 crystals (Mason, 1946; Bechmann, 1959), but none have previously been made on a crystal of class *m*.
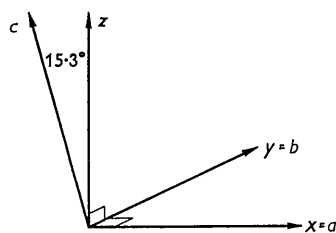

Fig. 1. Choice of orthogonal axes for lithium trihydrogen selenite.

We choose here the normal to the symmetry plane as *Y*-axis, and following Pepinsky & Vedam (1959), the normal to the (001) cleavage plane as *Z*, (Fig. 1), although this latter definition does not conform to a suggestion in the *IRE Standards on Piezoelectric Crystals* (1949).*

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* The dielectric, elastic, and piezoelectric tensors are identical in form, but the values of the constants are different (by a 15° rotation about *Y*).

Measurement procedure

All piezoelectric measurements were made on eight oriented bars using the resonance method (IRE Standards, 1957 and 1958). Each bar was approximately 15 mm. long, 3 mm. wide, and 1 mm. thick, with silver electrodes on the 3 by 15 mm. faces. Orientation of each bar was within ±2°. With thickness *Z'* and length *X'*, the piezoelectric coupling factor k_{31}' is given by:

$$(k_{31}')^2 = (d_{31}')^2/(\varepsilon_{33}'^T s_{11}'^E) , \qquad (1)$$

or

$$(k_{31}')^2/(1-(k_{31}')^2) = \tfrac{1}{2}\pi(f_a/f_r)\tan\left(\tfrac{1}{2}\pi(\Delta f/f_r)\right) , \qquad (2)$$

where

$$s_{11}'^E = 1/(4\varrho f_r^2 l^2) , \qquad (3)$$

and

f_r = fundamental resonance frequency,
f_a = fundamental antiresonance frequency,
$\Delta f = f_a - f_r$,
l = bar length, and
ϱ = density = 3·391 g.cm.$^{-3}$.

Descriptions of the bars are listed below:

1) Length *Y*, thickness *X*.
2) Length *Z*, thickness *X*.
3) Length *X*, thickness *Z*.
4) Length *Y*, thickness *Z*.
5) Length in *XY* plane, 45° between +*X* and +*Y*, width *Z*.
6) Length in *ZY* plane, 45° between +*Z* and −*Y*, width *X*.
7) Length in *ZX* plane, 45° between +*X* and +*Z*, width *Y*.
8) Length in *ZX* plane, 45° between +*Z* and −*X*, width *Y*.

d_{12}, d_{13}, d_{31}, and d_{32} were directly determined from d_{31}' for bars 1), 2), 3), and 4) respectively. For bar 5) $d_{31}' = -\tfrac{1}{4}\sqrt{2}\{(d_{11}-d_{26})+d_{12}\}$, so from bars 5) and 1),

the constant $(d_{11}-d_{26})$ is obtained. For bar 6) $d'_{31}=\frac{1}{4}\sqrt{2}\{(d_{33}-d_{24})+d_{32}\}$, so from bars 6) and 4), the constant $(d_{33}-d_{24})$ is obtained. For bar 7) $d'_{31}=\frac{1}{4}\sqrt{2}\{-(d_{33}-d_{15})+d_{13}-d_{31}+(d_{11}-d_{35})\}$, and for bar 8) $d'_{31}=-\frac{1}{4}\sqrt{2}\{(d_{33}-d_{15})+d_{13}+d_{31}+(d_{11}-d_{35})\}$. From bars 7), 8), 2), and 3), the constants $(d_{33}-d_{15})$ and $(d_{11}-d_{35})$ are obtained. Bars 1) and 4) were subjected to a calibrated hydrostatic stress, and the short-circuit outputs were measured $\{d_h=(\partial D/\partial T_h)_E\}$. For bar 1) $d_h=d_{11}+d_{12}+d_{13}$, and for bar 4) $d_h=d_{31}+d_{32}+d_{33}$. This allows separation of the four combinations $(d_{11}-d_{26})$, $(d_{33}-d_{24})$, $(d_{33}-d_{15})$, and $(d_{11}-d_{35})$. The signs of the piezoelectric constants d'_{31} for bars 1) through 8) and the signs of the hydrostatic d-constants for bar 1) and 4) were determined from pressure tests.

Pyroelectric effects in lithium trihydrogen selenite include a change in the direction as well as the magnitude of the polarization with temperature. There is no unique direction of the polarization vector, symmetry merely requiring that it be in the mirror plane. Pyroelectric effects (constant-stress) were measured on (101) and ($\bar{1}$01) plates, whose normals make angles of 34° 16′ and 47° 24′ respectively with Z. These plates were poled and then successively heated in steps to 40, 55, 70, and 85 °C. while connected in parallel with a 0·1 μf capacitance and an electronic electrometer. Coercive field and remanent polarization values of these plates were measured at 25 °C. by means of charge-field hysteresis loops. The angle θ by which the polarization at 25 °C. deviates from $+Z$ toward $+X$ was then determined using the following relationships:

$$P(101)/P(\bar{1}01)=\cos(\theta+34°\ 16′)/\cos(47°\ 24′-\theta),\quad(4)$$

and

$$E_c(101)/E_c(\bar{1}01)=\cos(47°\ 24′-\theta)/\cos(\theta+34°\ 16′).\quad(5)$$

Reversible piezoelectricity in LiH₃(SeO₃)₂

In this work it was found that the piezoelectric responses of a plate normal to the Z- and the X-axes could be quantitatively reversed by exposure to electric potentials of opposite polarity. This was shown by measurement of the signs of the piezoelectric charges developed on the faces perpendicular to Z by compression along X, Y, and $Z(d_{31}, d_{32}, d_{33})$, and the signs of the piezoelectric charges developed on the faces perpendicular to X by compression along X, Y, and $Z(d_{11}, d_{12}, d_{13})$. In each of the six cases the sign with respect to a given face was reversed by reverse poling along Z. By accurate resonance measurements it was shown that the magnitudes of these piezoelectric constants are *not* changed by reverse poling. From this it was concluded, in agreement with Vedam, Okaya & Pepinsky (1960), that the reference structure midway between the two equivalent ferroelectric configurations is class $2/m$, has a center of symmetry,

and hence is not piezoelectric. This is in contrast to the case with Rochelle salt, which is ferroelectric of symmetry class 2 between its two Curie points (Jaffe, 1937). In the absence of ferroelectricity, as above the upper or below the lower Curie point, its symmetry class is 222. Ferroelectricity in Rochelle salt enhances the piezoelectric effect in the strong face shear mode excited by an electric field along the ferroelectric axis, but is not the basis for it. It is, however, the basis for the weak extensional modes excited by a field parallel to the polar axis, and these disappear at temperatures above the upper and below the lower Curie points.

Results and discussion

The piezoelectric g- and d-tensors and the dielectric tensor are shown in Table 1. Three elastic constants and four combinations of others were also obtained. These are $s_{11}^E=2\cdot94$, $s_{22}^E=3\cdot41$, $s_{33}^E=8\cdot67$, $2s_{12}^E+s_{66}^E=20\cdot7$, $2s_{23}^E+s_{44}^E=23\cdot6$, $s_{35}^E+s_{15}^E=7\cdot5$, and $2s_{13}^E+s_{55}^E=10\cdot8$, all in 10^{-11} m²/newton.

Table 1. *Piezoelectric and dielectric tensors for*
LiH₃(SeO₃)₂

10^{-12} coulombs/newton or 10^{-12} meters/volt
d-tensor

$$\begin{bmatrix} +23\cdot2 & -22\cdot3 & -12\cdot1 & 0 & -46\cdot6 & 0 \\ 0 & 0 & 0 & -12\cdot8 & 0 & -14\cdot6 \\ -18\cdot4 & +5\cdot5 & +19\cdot9 & 0 & +53\cdot2 & 0 \end{bmatrix}$$

$\varepsilon^T/\varepsilon_0$-tensor $\varepsilon_0\beta^T$-tensor

$$\begin{bmatrix} 29\cdot6 & 0 & -16\cdot5 \\ 0 & 12\cdot9 & 0 \\ -16\cdot5 & 0 & 29\cdot4 \end{bmatrix}\quad\begin{bmatrix} 0\cdot0493 & 0 & 0\cdot0277 \\ 0 & 0\cdot0780 & 0 \\ 0\cdot0277 & 0 & 0\cdot0495 \end{bmatrix}$$

Volt meters/newton or meters²/coulomb
g-tensor

$$\begin{bmatrix} +0\cdot0778 & -0\cdot107 & -0\cdot0051 & 0 & -0\cdot0935 & 0 \\ 0 & 0 & 0 & -0\cdot113 & 0 & -0\cdot129 \\ -0\cdot0302 & -0\cdot0391 & +0\cdot0734 & 0 & +0\cdot152 & 0 \end{bmatrix}$$
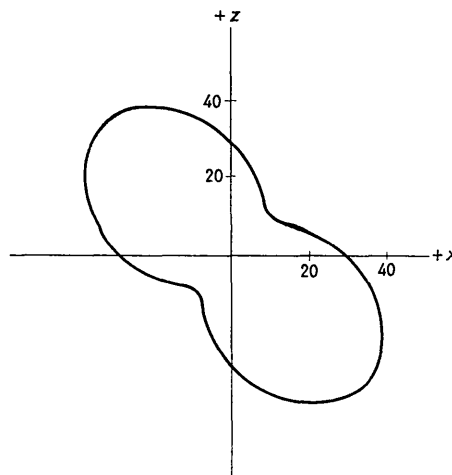

Fig. 2. $\varepsilon'_{33}/\varepsilon_0$ versus orientation in XZ plane of lithium trihydrogen selenite.

Fig. 2 is a polar plot showing $\varepsilon'^{T}_{33}/\varepsilon_0$ as a function of orientation in the XZ plane. The dielectric ellipse in this plane is shown in Fig. 3. The principal axes are also noted in Fig. 3; the maximum permittivity occurs over 45° away from the ferroelectric direction.
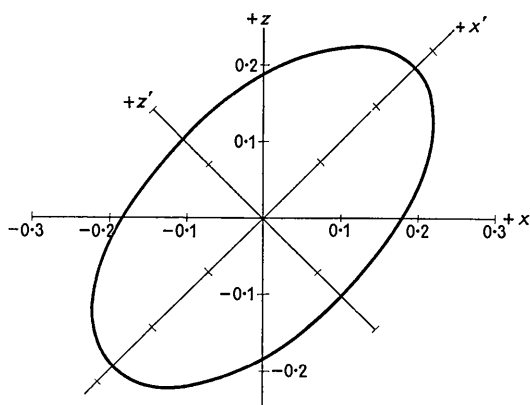
polarization, directed 3° from $+Z$ toward $+X$ in the ZX plane at 25 °C. The temperature variations in magnitude and direction of the polarization, calculated from pyroelectric measurements on these plates are shown in Fig. 5.

Fig. 3. Dielectric ellipse in XZ plane of lithium trihydrogen selenite.

$$\varepsilon_{11}X^2 + \varepsilon_{33}Z^2 + 2\varepsilon_{13}XZ = \varepsilon_0, \quad \text{or}$$

$$\varepsilon'_{11}X'^2 + \varepsilon'_{33}Z'^2 = \varepsilon_0.$$

Fig. 5. Magnitude and direction of remanent polarization versus temperature for lithium trihydrogen selenite. θ measured from $+Z$ toward $+X$ in XZ plane.

Table 2. Lattice constants for $LiH_3(SeO_3)_2$ at 25 and 80 °C.

(Pepinsky & Vedam, 1959)

$a = 6\cdot2534 \pm 0\cdot0005$ Å	$6\cdot25_8$	
$b = 7\cdot8830 \pm 0\cdot0002$	$7\cdot88_6$	at 25 °C.
$c = 5\cdot4335 \pm 0\cdot0011$	$5\cdot43_3$	
$\beta = 105° 18\cdot6' \pm 0\cdot6'$	$105\cdot2°$	

Density: $\varrho = 3\cdot391$ g.cm.$^{-3}$

$a = 6\cdot2711 \pm 0\cdot0008$ Å	
$b = 7\cdot8944 \pm 0\cdot0003$	80 at °C.
$c = 5\cdot437_1 \pm 0\cdot002_1$	
$\beta = 105° 25' \pm 2\frac{1}{2}'$	

Lattice constants for lithium trihydrogen selenite are shown in Table 2 for 25 and 80 °C. For these measurements, the crystal was oriented in a particular plane within a few minutes of its surface. These planes were (100), (010), (001), (101), and ($\bar{1}$01). Orders of reflection were measured using Cu radiation, and the values were extrapolated to $\sin^2 \theta = 1$.
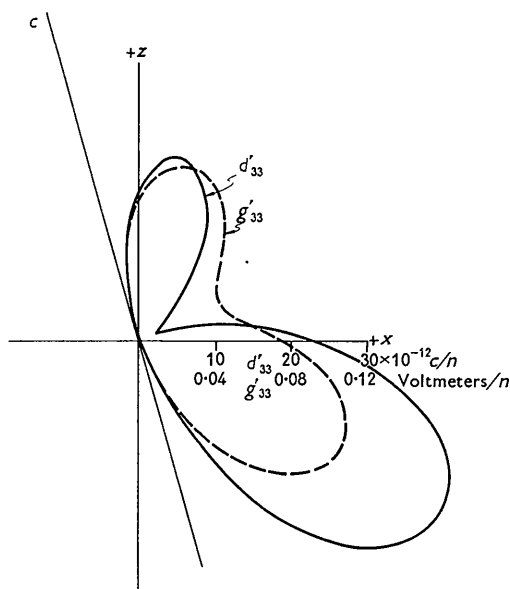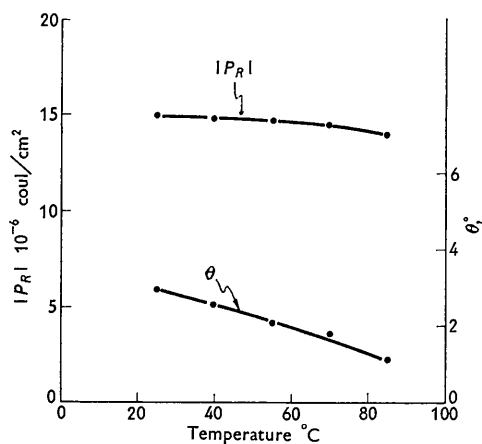

Fig. 4. g'_{33} and d'_{33} versus orientation in XZ plane of lithium trihydrogen selenite.

Fig. 4 is a polar plot showing d'_{33} and g'_{33} as functions of orientation in the XZ plane. This shows that the maximum longitudinal or parallel response ($d'_{33} = 46 \times 10^{-12}$ coul/newton) is not associated with the direction of the polarization. There is considerably more anisotropy in the short-circuit (d'_{33}) than in the open-circuit (g'_{33}) longitudinal response.

Measurements of hysteresis loops on the (101) and ($\bar{1}$01) plates led to a value of 15 μcoul/cm.^{2} for the

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