

THE EVALUATION OF SOME PIEZO-ROTATORY COEFFICIENTS OF α -QUARTZ

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RECENTLY we have investigated the effect of pressure on the optical rotatory power of crystals.¹ The optical activity in crystals may be described by a symmetric second rank axial tensor (g) which may be represented by the tensor surface

$$g_{11} x^2 + g_{22} y^2 + g_{33} z^2 = 1$$

when referred to its principal axes.² There are no *a priori* restrictions laid on the signs of g_{11} , g_{22} and g_{33} .

When the crystal is stressed the surface represented by the tensor (g) deforms. If one assumes that, in the first order theory, the changes in the components of (g) are linear functions of stress X_{kl} or strain x_{kl} then

$$\Delta g_{ij} = -R_{ijkl} X_{kl}$$

$$\Delta g_{ij} = S_{ijkl} x_{kl}$$

where

$$\Delta g_{ij} = g_{ij} - g^{\circ}_{ij}$$

g°_{ij} and g_{ij} are the values of the ij^{th} component of (g) before and after stress. Since (Δg) is an axial tensor of 2nd rank and both X_{kl} and x_{kl} are polar tensors of 2nd rank, the piezo-rotatory tensors R_{ijkl} and S_{ijkl} should be 4th rank axial tensors. This is perhaps the first time such tensors are used to describe a physical property. The number of non-vanishing coefficients of this tensor for different point groups has been worked out by us using group theoretical methods^{3,4} and the forms of the matrices for the point groups have also been determined.¹ Only non-centrosymmetric point groups have non-vanishing coefficients for the piezo-rotatory tensor. These crystals fall under three distinct classes.

Class A.—In the 11 enantiomorphic point groups which show optical activity the piezo-rotation tensor (R) or (S) and the piezo-refractive tensor (q) or (p) have the same form in the matrix representation. These groups with their number of non-vanishing coefficients (shown in parenthesis) are

1(36), 2(20), 222(12), 4(10), 422(7), 3(12), 32(8), 6(8), 622(6), 432(8) and 23(4)

Class B.—The 4 non-enantiomorphic optically active point groups for which piezo-rotatory and piezo-refractive matrices have different forms are

$m(16)$, $mm2(8)$, $\bar{4}(10)$, $\bar{4}2m(5)$.

Class C.—The 6 non-enantiomorphic optically inactive point groups show an interesting result in that the piezo-rotatory coefficients do not vanish, i.e., stress actually induces optical activity in them. These groups with their respective number of non-vanishing coefficients are

$4mm(3)$, $3m(4)$, $6mm(2)$, $\bar{6}(4)$, $\bar{6}m2(2)$, and $\bar{4}3m(1)$.

α -quartz (point group 32) belongs to the class A, and has 8 independent coefficients. Its piezo-rotatory matrix is

$$\begin{array}{cccccc} R_{11} & R_{12} & R_{14} & R_{14} & 0 & 0 \\ R_{12} & R_{11} & R_{13} & -R_{14} & 0 & 0 \\ R_{31} & R_{31} & R_{33} & 0 & 0 & 0 \\ R_{41} & -R_{41} & 0 & R_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & R_{44} & 2R_{41} \\ 0 & 0 & 0 & 0 & R_{14} & (R_{11}-R_{12}) \end{array}$$

One of the major impediments in the way of recovering all the piezo-rotatory coefficients is that it is rather difficult to measure the optical rotatory power in directions other than that of the optic axis. In the case of α -quartz the magnitude of only some of the coefficients, viz., R_{31} and R_{33} may be readily determined. The changes in rotatory power along the optic axis for an uniaxial stress X_0 along the axis and for an hydrostatic stress X_h are given by

$$\Delta \rho_0 = -R_{33} X_0$$

$$\Delta \rho_h = -(2R_{31} + R_{33})X_h$$

and should therefore differ for the same stress, i.e., $X_0 = X_h$.

Recently, Vedam and his collaborators^{5,6} have measured the optical rotation of α -quartz along the optic axis for hydrostatic and uniaxial stress. It was gratifying to note that the changes in rotation per unit stress were significantly different for these two types of stresses, as the theory predicts. The results of their experiment are shown in Table I.

TABLE I

	Pressure in K bar	Percentage strain parallel to optic axis	Percentage strain perpendi- cular to optic axis	$\Delta \rho^{\circ}/$ mm.
1. Hydrostatic pressure	1.366	-0.1	-0.127	-0.232
2. Uniaxial stress along optic axis	1.025	-0.1	+0.013	-0.170

Now $\Delta g_{ij} = S_{ijkl} x_{kl}$ or $\Delta g_i = S_{ij} x_j$
in the one index form.

Hence

$$\begin{aligned} -0.232 &= 2S_{31} (-0.127 \times 10^{-2}) \\ &\quad + S_{33} (-0.1 \times 10^{-2}) \\ -0.170 &= 2S_{31} (+0.013 \times 10^{-2}) \\ &\quad + S_{33} (-0.1 \times 10^{-2}) \end{aligned}$$

giving

$$\begin{aligned} S_{33} &= +1.75 \times 10^2 \text{ degrees/mm./unit strain} \\ S_{31} &= +0.2214 \times 10^2 \text{ degrees/mm./unit strain} \end{aligned}$$

elastic compliances of α -quartz in units of $10^{-12} \text{ cm.}^2/\text{dyne}$ are⁷

$$\begin{aligned} s_{11} &= 1.277, s_{12} = -0.179, s_{31} = -0.122, \\ s_{33} &= 0.96, s_{14} = -0.431, s_{44} = 2.004. \end{aligned}$$

Also since

$$\begin{aligned} R_{ij} &= S_{ik} S_{kj} \\ \therefore R_{33} &= 2S_{31} S_{31} + S_{33} S_{33} \\ R_{31} &= S_{31} (s_{11} + s_{12}) + S_{33} S_{31} \end{aligned}$$

substituting the values one gets

$$R_{33} = +0.16298 \text{ degree/mm./k bar}$$

$$R_{31} = +0.002959 \text{ degree/mm./k bar}$$

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THERMAL EXPANSION OF IRIDIUM DIOXIDE

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IRIDIUM DIOXIDE, which has a tetragonal rutile type structure, has been found to exhibit high electrical conductivity typical of metal-like conductors from the study of the electrical transport properties by Rogers *et al.*¹ and Ryden *et al.*² The lattice parameters of IrO_2 at room temperature have been reported recently.^{1,3} A search of the literature shows that no studies on the thermal expansion of iridium dioxide seem to have been made so far. Hence it interested the authors to include this compound in a general programme of 'Studies on rutile type compounds by the X-ray method'. The present paper gives an account of the precision determination of the lattice parameters at different temperatures and the evaluation of the coefficients of thermal expansion at various temperatures.

The sample used in the present study was kindly supplied by Dr. W. D. Ryden of the University of California. The powder sample for the study was prepared by filling it in a thin-walled quartz capillary. Using a Unicam 19 cm. high temperature powder camera and CuK radiation from a Raymax-60 X-ray unit, powder photographs were taken at different temperatures. The present study was made

for the temperature range 28°C. to 702°C. Reflections from the 213, 402, 510, 332, 501, 303, 422, 521, 323, 440 and 004 planes recorded between 55° to 78° Bragg angles were used in evaluating the lattice parameters at different temperatures. The experimental set-up and the computational procedure have been described in an earlier paper.⁴

The lattice parameters of IrO_2 at room temperature obtained in the present study are listed in Table I along with the other values available in the literature. The values from the present study agree well with the two recent determinations.

TABLE I

Lattice parameters of IrO_2 at room temperature

Source	a (Å)	c (Å)
Goldschmidt ⁵	.. 4.49	3.14
Swanson <i>et al.</i> ³	.. 4.4983	3.1544
Rogers <i>et al.</i> ¹	.. 4.4920 ± 0.0002	3.1516 ± 0.0002
Present study	.. 4.4985 ± 0.0001	3.1548 ± 0.0001

The lattice parameters obtained at different temperatures are given in Table II and shown graphically in Fig. 1. It can be seen that both