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Photo-elastic Behaviour of Barium Nitrate and Lead Nitrate Crystals

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All the constants needed to describe the photo-elastic behaviour of barium and lead nitrate crystals, which belong to the T_h class, have been determined using sodium D light. It is found that these crystals exhibit several exceptional features in regard to this property.

1. Introduction

One of us (Bhagavantam, 1942) has shown that the T and T_h classes of the cubic system of crystals require four photo-elastic constants whereas the maximum number permissible in the T_d, O and O_h classes is only three. Such a conclusion has since been verified by direct measurements in a number of substances. Incidentally, the photo-elastic behaviour of barium nitrate was found to be exceptional in many ways (Bhagavantam & Suryanarayana, 1948), but the values of its individual constants could not be determined as the elastic constants of this substance were not known at that time. In view of the importance of the photo-elastic behaviour of barium nitrate, its complete study is undertaken in the present investigation. The photo-elastic properties of lead nitrate, which is isomorphous with barium nitrate, are also now studied for the first time.

The early crystallographic data (Groth, 1908) indicate that these crystals belong to the class T while the X-ray data (Wyckoff, 1931) fit perfectly with the demands of the space group T_h. The question as to which of the two classes T and T_h, these crystals belong, does not affect the present investigation, since both should have the same scheme of photo-elastic constants.

2. Experimental arrangements

According to the usual notation, the path differences for the various cases studied in the present investigation are given in Table 1.

In the case of barium nitrate, prisms already cut and prepared by Bhagavantam & Suryanarayana (1948) have been used. Crystals of lead nitrate are freshly grown and prisms are now prepared. All the prisms have at least one of their surfaces terminating on a natural face. None of the prisms shows double refraction in the unstrained state.

Table 1. *Expressions for path differences: T and T_h classes*

No.	Direction of pressure	Direction of observation	Path difference
1.	[001]	[100]	$\frac{1}{2}n^3(q_{11}-q_{12})$
2.	[001]	[010]	$\frac{1}{2}n^3(q_{11}-q_{13})$
3.	[001]	[110]	$\frac{1}{4}n^3(2q_{11}-q_{12}-q_{13})$
4.	[001]	$[\bar{1}10]$	
5.	[111]	$[\bar{2}11]$	$\frac{1}{2}n^3(q_{44})$
6.	[111]	$[01\bar{1}]$	

The Babinet fringes are obtained by the usual method using a sodium-vapour lamp as the source. Compression is produced by a lever arrangement described in an earlier paper from this laboratory (Bhagavantam & Suryanarayana, 1947). The mean shift of the Babinet fringe in each case is obtained by taking the average of several readings. The method of localized fringes (Ramachandran, 1947) is adopted for determining the absolute values of the stress-optical constants.

A description of the prisms employed in the investigation is given in Table 2. The orientations are accurate to within 1°.

3. Results

(*a*) *Determination of* $(q_{11}-q_{12})$, $(q_{11}-q_{13})$ *and* q_{44}

The observations with the Babinet compensator are given in Table 3.

The fringe width of the Babinet compensator is 202 divisions of the head scale, which corresponds to a path retardation of one wave-length of sodium light. From the mean shift of the Babinet fringe, the path-difference δ corresponding to unit stress (1 dyne cm.$^{-2}$) and unit length (1 cm.) of light beam in the stressed crystal is calculated. The stress-optical constant in the corresponding direction of observation is $2\delta/n^3$. In the above experiments, the shift is always in the same direction as for common glass. Hence the sign of the constants q_{44}, $(q_{11}-q_{12})$ and $(q_{11}-q_{13})$ is negative.

(*b*) *Determination of the absolute stress-optical constants* q_{11}, q_{12} *and* q_{13}

(i) *Barium nitrate.*—Prism I is used for this purpose. A set of elliptical fringes is obtained, making the observation along [010]. A suitable mark on the crystal itself is used as a reference to determine the shift of the fringes. The spacing of the fringes is about 0·1 mm.

Table 2. *Description of the prisms employed*

	No. of prism	Length cm.	Length parallel to	Breadth cm.	Breadth parallel to	Thickness cm.	Thickness parallel to
Barium nitrate	I	0·51	[001]	0·280	[010]	0·275	[100]
	II	0·36	[001]	0·299	[110]	0·294	$[\bar{1}10]$
	III	0·33	[111]	0·297	$[\bar{2}11]$	0·298	$[01\bar{1}]$
Lead nitrate	I	0·532	[001]	0·404	[010]	0·396	[100]
	II	0·721	[110]	0·510	[001]	0·292	$[\bar{1}10]$
	III	0·555	$[\bar{2}11]$	0·409	$[01\bar{1}]$	0·337	[111]

Table 3. *Photo-elastic constants of barium and lead nitrates: observations with compensator*

Mechanical advantage of lever = 3·992

	Prism	Observation parallel to direction	Observation parallel to cm.	Load (Kg.)	Mean shift of the Babinet fringe in divisions of head scale	Stress optical constant in units of 10^{-13} c.g.s.	Expression for the constant
Barium nitrate	I	[100]	0·275	0·6	132·4	23·84	$(q_{11}-q_{12})$
		[010]	0·280	0·6	96·9	17·13	$(q_{11}-q_{13})$
	II	[110]	0·299	0·5	90·7	20·60	$\frac{1}{2}(2q_{11}-q_{12}-q_{13})$
		$[\bar{1}10]$	0·294	0·5	89·2	20·61	
	III	$[01\bar{1}]$	0·298	1·5	22·1	1·69	q_{44}
		$[\bar{2}11]$	0·297	1·5	21·9	1·68	
Lead nitrate	I	[100]	0·396	1·0	179·3	19·13	$(q_{11}-q_{12})$
		[010]	0·404	1·0	113·3	11·84	$(q_{11}-q_{13})$
	II	$[\bar{1}10]$	0·292	1·5	116·7	14·79	$\frac{1}{2}(2q_{11}-q_{12}-q_{13})$
		[110]	0·721	1·0	194·2	14·95	
	III	$[01\bar{1}]$	0·409	2·0	19·0	1·39	q_{44}
		$[\bar{2}11]$	0·555	2·0	25·6	1·38	

and the dark bands are not very sharp. On this account any shift due to a change of about 20 g. in a load of 500 g. escapes notice. With these limitations, it is found that a load of 500 g. causes a shift of one fringe for the vertically vibrating beam of light and a shift of two fringes for the horizontally vibrating beam of light, the mechanical advantage of load being 3·992. The shift is away from the centre of the fringe system and hence, at the point of observation, the order of interference is increasing.

The values of the individual constants are calculated from the equations

$$n-n_z = \frac{\lambda}{2t_2}\left[\frac{2n}{\lambda}(t_2-t_1)-\delta n\right], \quad q_{11} = -(n-n_z)\frac{2}{n^3P_{zz}},$$

where n is the refractive index of the undeformed crystal, n_z is the refractive index in the stressed crystal for light with vibration direction vertical, (t_2-t_1) is the increase in thickness of the crystal along the direction of observation for the corresponding load, λ is the wave-length of light, δn is the increase in the order of interference at the point of observation and P_{zz} is the stress producing the shift. In this experiment $\delta n = +1$ and $n = 1{\cdot}570$ (Landolt & Bornstein, 1931, p. 719). Similar equations for light vibrating horizontally are used with δn equal to 2.

The elastic constants of barium nitrate, used in these calculations, are (Bhagavantam & Sundara Rao, 1948)

$$c_{11} = 6{\cdot}02\times10^{11},\ c_{12} = 1{\cdot}86\times10^{11},\ c_{44} = 1{\cdot}21\times10^{11}\ \text{dyne cm.}^{-2}.$$

Employing these data, we get

$$q_{11} = 18{\cdot}11\times10^{-13} \quad\text{and}\quad q_{12} = 40{\cdot}0\times10^{-13}\ \text{cm.}^2\,\text{dyne}^{-1},$$

giving a difference of 21·89 compared with 23·84 obtained from compensator observations. From the value of q_{11} given above and the value of $(q_{11}-q_{13})$ obtained by the compensator observations, we get

$$q_{13} = 35{\cdot}2\times10^{-13}\ \text{cm.}^2\,\text{dyne}^{-1}.$$

In view of the facts stated earlier about the fringe displacements, the values of the individual constants should be regarded as somewhat approximate.

(ii) *Lead nitrate.*—Prism II is used to obtain the localized fringes, the direction of observation being $[\bar{1}10]$. The dimensions parallel to $[\bar{1}10]$ and [110] have been reduced to 0·217 cm. and 0·697 cm. respectively. The spacing of the fringes is about 0·05 mm., much less than in the case of barium nitrate, and a change of load of about 25 g. in 400 g. escapes notice. The loads for a shift of two complete fringes for vertically and horizontally vibrating beams are found to be 450 and 400 g. respectively. The refractive index is taken as 1·782 (Landolt & Bornstein, 1931).

The elastic constants used are (Bhimasenachar & Seshagiri Rao, 1950)

$$c_{11} = 4{\cdot}56\times10^{11},\ c_{12} = 3{\cdot}09\times10^{11},\ c_{44} = 1{\cdot}37\times10^{11}\ \text{dyne cm.}^{-2}.$$

Employing these data we get

$$q_{11} = 70\cdot21\times10^{-13} \quad \text{and} \quad \tfrac{1}{2}(q_{12}+q_{13}) = 80\cdot52\times10^{-13}\ \text{cm.}^2\ \text{dyne}^{-1}.$$

(*c*) *Evaluation of the strain-optical constants*

The four strain-optical constants are calculated from the standard equations connecting the p's, q's and the elastic constants. They are cited in Table 4.

4. Discussion of results

The stress-optical and strain-optical constants of barium and lead nitrates are given in Table 4. The values obtained earlier (Bhagavantam & Suryanarayana, 1948) for some of the constants of barium nitrate are

$$(q_{11}-q_{12}) = -23\cdot81\times10^{-13},\ (q_{11}-q_{13}) = -18\cdot06\times10^{-13}$$
$$\text{and} \quad q_{44} = -1\cdot62\times10^{-13}\ \text{cm.}^2\ \text{dyne}^{-1}.$$

There is good agreement between these values and the values obtained in the present investigation.

Table 4(*a*). *Stress-optical constants*

(Units of 10^{-13} c.g.s.)

	$q_{11}-q_{12}$	$q_{11}-q_{13}$	q_{44}	q_{11}	q_{12}	q_{13}
Barium nitrate	−23·84	−17·13	−1·69	18·11	40·0	35·2
Lead nitrate	−19·13	−11·84	−1·39	70·21	89·34	82·05

Table 4(*b*). *Strain-optical constants*

	$p_{11}-p_{12}$	$p_{11}-p_{13}$	p_{44}	p_{11}	p_{12}	p_{13}
Barium nitrate	−0·992	−0·713	−0·0205	2·49	3·40	3·20
Lead nitrate	−0·281	−0·174	−0·0191	8·50	8·78	8·67

The results show that the difference between $(q_{11}-q_{12})$ and $(q_{11}-q_{13})$ is fairly large in both barium and lead nitrates, being about 39% and 60% of the lower value respectively. Both the substances are highly anisotropic, the birefringence produced by a pressure along a cube axis being nearly fourteen times that produced by an equal pressure along a cube diagonal. The values of the photo-elastic constants of both the substances are very large in comparison with many other crystals; in fact the values of the individual constants of lead nitrate are the largest recorded so far in crystals.

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Deterioration of the crystallinity of wet ribonuclease with exposure to X-radiation.

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During the recording of the X-ray diffraction pattern of wet monoclinic ribonuclease (cell dimensions: $a = 30\cdot3$, $b = 38\cdot3$, $c = 53\cdot5$ Å, $\beta = 105\cdot8°$, grown from *n*-PrOH, at pH 6, by Dr M. V. King of this laboratory), it was observed that the intensities of the diffraction spots decreased after many hours of X-ray exposure. Such an effect was observed by Kendrew (1949) while examining the pattern of myoglobin.

To investigate the changes in the pattern with X-ray exposure, a freshly grown crystal was mounted and the precession diagram from one zone (0*kl*) was used as a standard against which to check the variations of the intensities of the X-ray reflections. Two films, taken after 11 hr. and after 143 hr. of irradiation of the crystal, respectively, showed identical diagrams. A film, started after the crystal had been irradiated for 185 hr., showed