Kroon for stimulating discussions. He is indebted to Drs A. J. M. Duisenberg for taking the diffractometer data and to Mr G. J. Dirksen for growing the crystals.

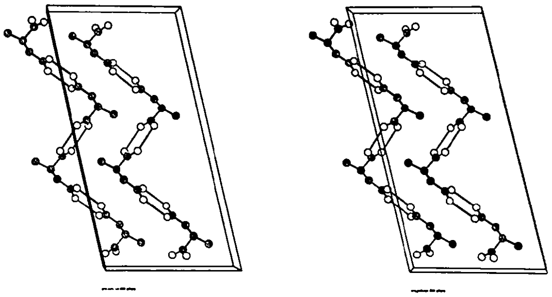

Fig. 2. A stereoscopic view of the crystal structure along [010]. Hydrogen atoms are not included. The carbon atoms are dotted.

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Variation of the Optical Properties of *Laevo-* and *Dextro*-Rotatory $NaBrO_3$ with Crystal-Growth Temperature

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(*Received* 7 *September* 1971; *accepted* 1 *Septemper* 1972)

Single crystals of (+) and (−)-$NaBrO_3$ were grown from slightly supersaturated water solution at various temperatures between 10 and 50°C. It was found that, for both (+) and (−)-$NaBrO_3$, the cube faces become more and more prominent with increase in the crystal-growth temperature (CGT). When crystallized at 10°C the colour of the crystals becomes faint yellow. The observed specific gravity (SG) and the optical properties, *i.e.* (1) the refractive index (RI), (2) the optical rotatory power (ORP) and (3) the Brewster angle (BA), vary with the CGT. The magnitudes of the optical properties mentioned above for (+) and (−)-$NaBrO_3$ crystals agree above 35°C, but differ considerably below 35°C. All the measurements were made at room temperature and with Na light, $\lambda = 5893$ Å.

Introduction

In general, sodium bromate ($NaBrO_3$) is a water-soluble, colourless, stable crystal, which crystallizes in the cubic tetrahedral class and has no water of crystallization. It is an ionic crystal, with four molecules in a unit cell of length $a = 6{\cdot}705$ Å. Solid $NaBrO_3$ is optically active and crystallizes in two isomeric forms, *laevo-* and *dextro*-rotatory, though its aqueous solution is not optically active.

Kremers (1857) and Le Blanc & Rohland (1896) found that crystals of $NaBrO_3$ had a specific gravity 3·339 (with respect to water at 17·5°C), and 3·254. Craw (1896) found that $NaBrO_3$ crystals had a refractive index (RI) 1·5943, for $\lambda = 5893$ Å. The interpolated RI, for $\lambda = 5893$ Å, is 1·6165, obtained from the data given by Rose (1910). Poinsot & Mathieu (1955) gave the value of the RI as 1·6157, for $\lambda = 5893$ Å. Traube (1894) found that $NaBrO_3$ crystals had an ORP of 2·166° mm^{-1}, for $\lambda = 5893$ Å; Rose (1910) found 2·11 and 2·15 °.mm^{-1}, on plates 4·7 and 2·46 mm thick respectively, the weighted mean of which is 2·12 °.mm^{-1}. The calculated ORP, from the formula for the optical rotatory dispersion given by Kizel, Krasilov & Shamraev (1964) is 2·055 °.mm^{-1} for $\lambda = 5893$ Å. A value of 2·102°.mm^{-1} for the ORP is obtained from the formula of Chandrasekhar & Madhava (1967).

It is seen that the values of the SG, RI and ORP given by different workers for $NaBrO_3$ crystals, do not agree well. The variation of the CGT may be one of the causes of the above disagreement. It appears that no attempt has been made to determine systematically the variation of the optical properties of (+) and (−)-$NaBrO_3$ crystals grown at different temperatures. Hence the object of the present investigation was to test whether the optical properties of (+) and (−)-$NaBrO_3$ crystals vary with the CGT or not.

Experimental

Single crystals of (+) and (−)-$NaBrO_3$ were grown from slightly supersaturated water solution (AR grade

NaBrO$_3$ dissolved in distilled water), at temperatures between 10 and 50 °C, using a thermostatic bath. The crystals were grown by the 'sealed jar method' described by Holden & Singer (1968).

The SG for several crystals obtained at each temperature was determined at 25 °C by the hydrostatic method, using carbon tetrachloride and a sensitive balance, with an accuracy of 1×10^{-4} gm. The average weight of the crystals was about 3·5 gm. The maximum deviation in the determination of the SG was about ±0·1 %. The value of the SG has been normalized to that of water at 4 °C.

The RI for the natural crystals, in the shape of tetrahedra, was determined by the method of minimum deviation, using a spectrometer of accuracy $\frac{1}{2}$ min of arc. The area of the faces and the number of crystals employed at each temperature are given in Table 1. The mean prism angle was found to be 70° 32′. The prism faces employed for the measurements were fairly large and there was no serious loss of definition of the image of the slit. The maximum deviation in the determination of the RI was ±0·05 %. The measurements were made for several crystals obtained at each temperature and for all six different pairs of the prismatic faces of the tetrahedron, to ensure reproducibility of results.

Plates of natural crystals are usually formed between the faces of a major tetrahedron and a minor tetrahedron, which are parallel to each other. Cube faces, developed on the skew edges of the major tetrahedron, also form natural plates of the crystal. The ORP of such plates were determined by Lippich's half-shade polarimeter (Bellingham & Stanley Ltd. London, No. 402415), which had an accuracy of 0·05 deg of arc. The measurements of the ORP were made for several crystals obtained at each temperature and along more than one direction in a crystal. The maximum deviation in the determination of the ORP was ±0·8 %. The thickness of the plates was measured with external micrometer calipers to an accuracy of 0·01 mm. The numbers and thicknesses of the plates are given in Table 1. The different directions in a crystal, along which the ORP was measured, are considered as different plates.

The BA for several crystals obtained at each temperature was measured visually with a spectrometer with a polaroid attachment by the dark-adapted eye. The BA was determined for each natural face of the tetrahedron of the crystal. The maximum deviation in the determination of the BA was ±0·23 %. All the optical properties were determined for Na light, $\lambda = 5893$ Å and at room temperature, which was nearly 30 °C.

Results and discussion

All the experimental results are recorded in Table 1. They have also been illustrated graphically in Fig. 1. The following features are of special interest.

(1) For both (+) and (−)-NaBrO$_3$, the cube faces become more and more prominent with increase of

Table 1. *Variation of the optical properties of natural* (+) *and* (−)-NaBrO$_3$ *crystals with crystal-growth temperature, for* $\lambda = 5893$ Å

	CGT (°C)	Number of crystals in each batch	Mean SG	Mean area of the faces of the tetrahedral crystal (cm²)	Mean RI	Molecular refraction From Lorentz–Lorenz formula	Molecular refraction From Gladstone & Dale formula	Number of plates of the crystal in each batch	Mean thickness of the plates (mm)	Weighted mean ORP (°.mm⁻¹)	Mean BA	Calc. RI from Brewster's law
(−)-NaBrO$_3$	10	3	3·316	0·6	1·6158	15·90	28·03	—	—	—	57°40′	1·5797
	21	6	3·316	1·2	1·6159	15·90	28·03	8	12·18	−1·986	57 55	1·5951
	28	4	3·316	1·1	1·6160	15·91	28·03	10	12·33	−2·008	58 3	1·6035
	35	4	3·309	0·8	1·6157	15·93	28·08	10	10·60	−2·005	58 12	1·6128
	42	3	3·303	0·8	1·6154	15·95	28·12	13	11·83	−2·015	58 12	1·6128
	50	5	3·298	1·0	1·6153	15·97	28·15	13	11·01	−2·021	58 12	1·6128
(+)-NaBrO$_3$	10	3	3·318	1·4	1·6167	15·91	28·05	—	—	—	57 56	1·5961
	21	4	3·314	1·1	1·6161	15·91	28·06	10	12·16	+2·036	58 3	1·6035
	28	8	3·307	1·0	1·6158	15·94	28·10	15	11·42	+2·026	58 8	1·6087
	35	6	3·305	1·1	1·6156	15·95	28·11	16	11·23	+2·028	58 12	1·6128
	42	3	3·301	0·8	1·6155	15·96	28·15	10	10·44	+2·024	58 12	1·6128
	50	3	3·302	0·6	1·6156	15·96	28·13	8	11·17	+2·033	58 12	1·6128

CGT. It was also noted that the colour of the crystals becomes faint yellow when they are grown at 10 °C.

(2) (i) In Fig. 1(*a*) the SG of (+)-NaBrO$_3$ crystals decreases between CGT 21 to 35 °C. The SG is steady with CGT below 21 °C and above 35 °C. The SG of (−)-NaBrO$_3$ crystal is steady up to CGT 28 °C. Above this temperature it decreases up to 42 °C and becomes steady at higher temperatures. The SG of (+) and (−)-NaBrO$_3$ almost agree below CGT 21 °C and above 35 °C.

(ii) In Fig. 1(*b*) the RI of (+)-NaBrO$_3$ decreases upto CGT 35 °C. Above this temperature it becomes steady. The RI of (−)-NaBrO$_3$ decreases between CGT 30 and 42 °C. Below CGT 30 and above 42 °C the RI is constant. The RI's of (+) and (−)-NaBrO$_3$ almost agree above CGT 35 °C.

(iii) In Fig. 1(*c*): the ORP of (+)-NaBrO$_3$ is steady throughout. The magnitude of the ORP of (−)-NaBrO$_3$ increases with CGT. The difference between the magnitudes of the ORP of (+) and (−)-NaBrO$_3$ is considerable at temperatures below 35 °C. Above 35 °C, the magnitudes of the ORP of (+) and (−)-NaBrO$_3$ almost agree.

(iv) In Fig. 1(*d*): the BA of (+) and (−)-NaBrO$_3$ increases linearly up to CGT 35 °C. Above 35 °C the BA for both the crystals is the same and constant. Below 35 °C the difference between the BA's of (+) and (−)-NaBrO$_3$ increases with fall in temperature.

(3) Brewster's law does not hold for (+) and (−)-NaBrO$_3$ below CGT 35 °C. Above 35 °C, the law holds.

(4) From Fig. 1(*a*) and (*b*) it is seen that the variations of the SG and RI of (+) and (−)-NaBrO$_3$ with CGT are of a similar nature.

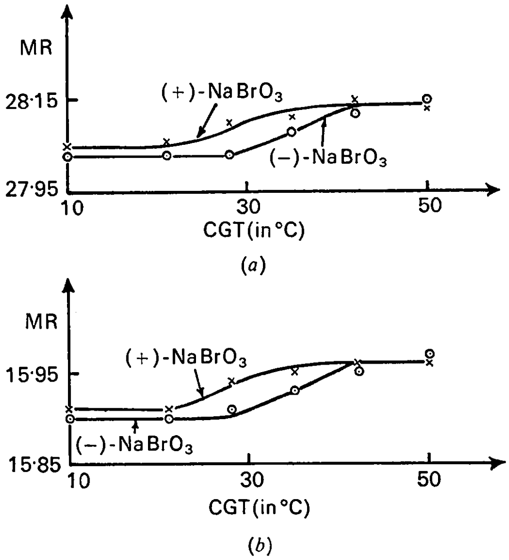

Fig. 2. The variation with crystal-growth temperature of the molecular refraction of (−) and (+)-NaBrO$_3$, for $\lambda = 5893$ Å. The molecular refractions in (*a*) and (*b*) are calculated from the Gladstone & Dale and the Lorentz–Lorenz formulae respectively.

(5) In Fig. 2(*a*) and (*b*): the molecular refraction (MR) of (+) and (−)-NaBrO$_3$ is steady below a CGT of 28 °C and above a CGT of 35 °C. The MR increases from 28 to 35 °C CGT, indicating a transition

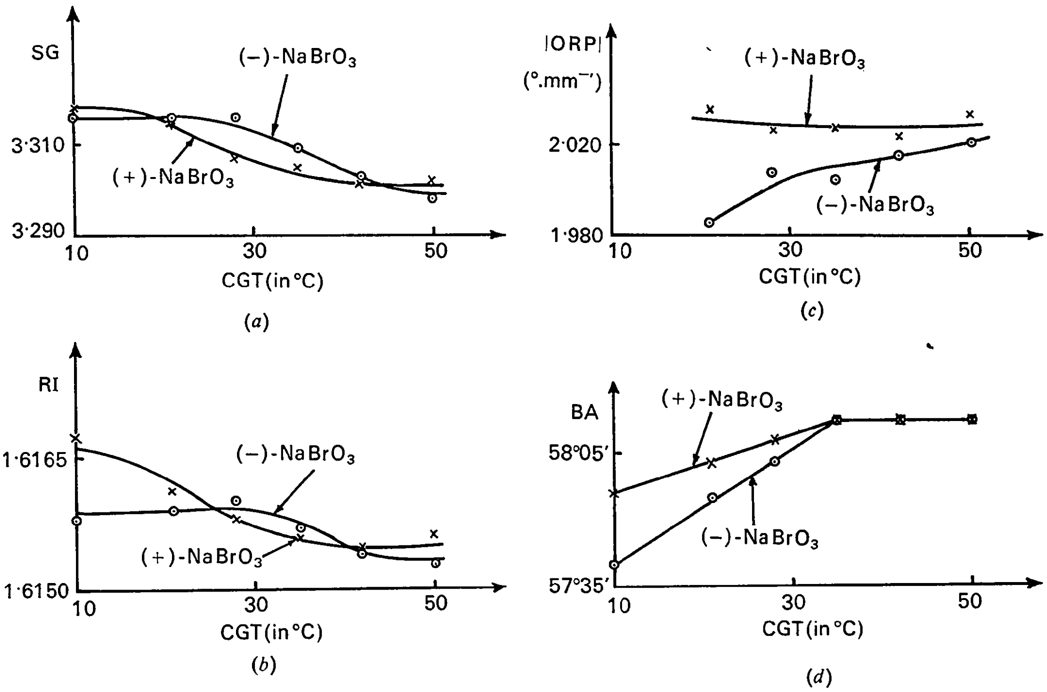

Fig. 1. The variation with crystal-growth temperature of (*a*) the specific gravity, (*b*) the refractive index, (*c*) the optical rotatory power and (*d*) the Brewster angle of (+) and (−)-NaBrO$_3$, for $\lambda = 5893$ Å.

region between 28 and 35 °C. The MR of (+) and (−)-$NaBrO_3$ almost agree throughout.

(6) The changes in the properties indicate that some type of a transition in the crystal structure of (+) and (−)-$NaBrO_3$ takes place between 30 and 35 °C CGT.

An exact comparison of the present data with the previous measurements is not possible, as the CGT of samples used by the previous workers is not known. However, the following comparisons can be shown. The measured value of the SG (with respect to water at 4 °C) for (+) and (−)-$NaBrO_3$ agrees (within 0·5 to 1·2%) with the value of the SG 3·334 (with respect to water at 4 °C) reported by Kremcrs (1857). The SG found here also agrees (within 0·2 to 0·9%) with the value of the SG 3·324, calculated from the unit cell dimension of the $NaBrO_3$ crystal. The RI found in the present investigation for (+) and (−)-$NaBrO_3$, for $\lambda = 5893$ Å, agrees (within 0·013 to 0·075%) with the RI value 1·6165, for $\lambda = 5893$ Å, given by Rose (1910); and agrees (within 0·063%) with 1·6157, for $\lambda = 5893$ Å, found by Poinsot & Mathieu (1955). The magnitudes of the ORP found here for (+) and (−)-$NaBrO_3$, for $\lambda = 5893$ Å, agree (within 0·95 to 3·45%) with the value 2·055 °.mm^{-1}, for $\lambda = 5893$ Å, calculated from the formula for the optical rotatory dispersion given by Kizel, Krasilov & Shamraev (1964).

To make certain that the observed variation of the properties of the crystals is not due to the presence of inclusions, disorder or enantiomorphs in the crystals, the properties were determined for several crystals obtained at the same temperature. The observed properties were found to be reproducible and they vary systematically with the CGT. The optical properties were also found to be reproducible along different directions in the same crystal. Hence, it is concluded that the observed variation of the SG and the optical properties are due to the variation of the CGT. The deviation from Brewster's law was checked for the crystals obtained below 21 °C, by performing a converse experiment.

The authors thank the Principal of the Govt. College of Science, Raipur (M.P.), for providing laboratory facilities. One of the authors (Neelkanth Verma) thanks the Vice-Chancellor of Ravishankar University, Raipur (M.P.), for awarding a research fellowship.

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Acta Cryst. (1973). B**29**, 7

The Structures of Fluorides. I. Deviations from Ideal Symmetry in the Structure of Crystalline UF_6: A Neutron Diffraction Analysis

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(*Received* 25 *April* 1972; *accepted* 18 *September* 1972)

A neutron-diffraction powder pattern of crystalline UF_6 at 21 °C has confirmed the X-ray structure of Hoard & Stroupe [USAEC Report TID-5290 (1958) Paper 45]. From the X-ray data it was not certain whether the fluorine atoms deviated significantly from ideal hexagonal close-packing and the UF_6 octahedra from regularity. The neutron powder pattern of UF_6 was analysed by the profile-fitting method of Rietveld [*Acta Cryst.* (1967), **22**, 151]. Significant deviations from the ideal parameters of Hoard & Stroupe were found. These effects are apparently caused by strong U–U repulsions in the unsymmetrical U^{VI} arrangement and the U–F bonding in the octahedra.

Introduction

An X-ray crystal structure analysis of a single crystal of UF_6 mounted in a capillary was carried out by Hoard & Stroupe (1958) (hereafter H & S) using 60 *hk*0 and 66 *h*0*l* reflexions collected with a Weissenberg camera. The uranium locations were refined by Fourier synthesis, and the fluorine atoms were located