

The x-ray anomalous dispersion and optical rotation in the crystalline solid solution $\text{NaClO}_3 : \text{NaBrO}_3$ *

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Abstract. Sodium chlorate and sodium bromate crystals of the same structural configuration have opposite senses of optical rotation. It is also known that these halates exhibit continuous miscibility in solid solution. In the present work, the conjecture of Bijvoet that in the solid solution of these halates, the crystalline configuration would continue itself, has been directly verified by two approaches: (i) by optical rotation measurements on single crystals which show an annulling trend in proportion with composition and (ii) by measurements of Bijvoet inequality for several reflections from a single crystal (rich in chlorate) which shows an agreeable trend with the calculated values for chlorate.

Keywords. $\text{NaClO}_3 : \text{NaBrO}_3$ solid solution; x-ray anomalous dispersion in solid solution; optical activity in solid solution; structural continuity.

1. Introduction to the end member halates

Sodium chlorate and sodium bromate crystals are isomorphous and belong to the cubic tetartohedral class (space group $P2_13$), lacking a centre of symmetry. By virtue of their symmetry, these halates display optical activity, both dextro† and laevo forms crystallising from aqueous solutions with equal facility. The optical activity in these crystals were first worked out by Ramchandran (1951), assuming that the optical behaviour is completely explained by the polarisability of the oxygen atoms. An interesting development took place when the absolute configuration of these halate crystals were established. Using the x-ray anomalous dispersion method, optically dextro rotatory NaClO_3 was determined (Ramchandran and Chandrasekaran 1957) to have a particular absolute structural configuration, say A , while dextro rotatory NaBrO_3 was found (Gezina *et al* 1963) to have an absolute configuration which is the inverse of A . Thus, although the two halate crystals are closely isomorphous, the same structural configuration led to opposite senses of optical rotation for the two halate crystals. The optical rotation in these crystals were then reexamined (Gezina *et al* 1963). Instead of replacing the three oxygen of a ClO_3 or BrO_3 ion by one anisotropically polarisable particle on the trigonal axis, as was done by Ramchandran (1951), induced dipoles were located at the individual oxygen positions (Gezina *et al* 1963) and with additional parameters, opposite rotation sign for highly similar configurations of NaClO_3 and NaBrO_3

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† We emphasize optical rotation is dextro, if the plane of polarisation is rotated clockwise, for an observer looking towards the source of light.

was found possible. However, Chandrasekhar and Madhava (1967) pointed out that such a theory (in which the influence of all the ultraviolet bands are lumped into the polarisability of the atom) was suspected in that strongly absorbing bands might be weakly optically active and *vice versa*. Furthermore, these authors measured the rotatory dispersion in these halates in a wide range from 0.237 to 0.623 microns over which their hypotheses could be fitted to a very good accuracy and moreover could also account for the refractive dispersion data. The opposite optical rotation of the two halates with the same structural configuration was shown to be due to the relative strengths of the positive and negative terms of the rotatory dispersion expressions for the two halates. In fact, NaClO_3 showed an experimental decrease of the rotatory power in the ultraviolet, thus proving a negative contribution to the dispersion.

The relation between the phonon structure and the ferroelectric type behaviour of the dielectric constant of NaClO_3 (Prasad Rao *et al* 1972) could be cited as a typical example of the recent interest in these halate crystals. To the "lore" on the growth of a particular enantiomorphic form, the interesting finding (Niedermaier and Schlenk 1972) on these halates was that the addition of D-Mannitol as a cosolute in the aqueous solution, induced the growth of (+) chlorate and (−) bromate crystals, while D-Sorbitol, as a cosolute, had the opposite effect.

2. Motivation for the present work on the solid solution NaClO_3 : NaBrO_3

It was known (Structure reports 1947) that these halates exhibit continuous miscibility in solid solution and extensive investigations (Kleber and Koltermann 1958 and Schlenk 1965) were carried out and their findings are cited at appropriate sections below.

In the present work we have been interested in checking directly a conjecture by Gezina *et al* (1963), who cited an old observation of Marbach (1856), namely that in the solid solution of these halates, the crystalline configuration would continue itself. Schlenk (1965) had found that NaBrO_3 crystals, in numerous seeding experiments without exception, always stimulated the growth of NaClO_3 crystals with a sign of optical rotation opposite to that of the seed crystal.

Therefore, in the single crystal of the solid solution, with a given structural configuration, say *A* for NaClO_3 (and therefore with dextro rotatory contribution to the optical rotation), if there is a continuity of the same configuration, also *A* of NaBrO_3 (laevo rotary contribution), one would expect the net optical rotation to show an annulling trend, depending on the mole percentage of each component. Optical rotatory dispersion of a mixed crystal of sodium chlorate-sodium bromate rich in chlorate content (91.7 NaClO_3 Wt.%) had been reported by Chandrasekhar and Madhava (1969). Their measurements of the rotatory power was found to be appreciably less than that of the chlorate indicating that the configurations of the two constituents are similar in the mixed crystal so that there is partial compensation of optical rotation. Furthermore, due to the anomalous dispersion of the Cl and the Br atoms, the Bijvoet inequalities in single crystals of the solid solution could be expected to reveal a trend which can be calculated from the structure of the end member halates. Both these features have been checked and agreed with the cited conjecture (Gezina *et al* 1963).

3. Single crystals of the solid solution $\text{NaClO}_3 \cdot \text{NaBrO}_3$

Such crystals were grown from aqueous solutions of the two halates in various proportions without any seeding and at very slow rates usually from several days to some weeks at room temperature. Generally the crystals were square and rectangular tablets with faces of the form $\{1\ 0\ 0\}$. With higher NaBrO_3 content (above 70 mole per cent of NaBrO_3), some crystals of triangular shape, with broad faces of $\{1\ 1\ 1\}$, were also obtained.

The composition of the crystals need not be the same as that arranged in the aqueous solution. Kleber and Koltermann (1958) had found the variation depicted in the curve (broken line) of figure 1 for the bromate percentage in solution to that in the crystal. This trend was also found in the present work, where a polarographic procedure for analysing the composition of the crystals had been employed. Such an analysis of the crystals yielded the curve (full line) of figure 1. Variations in the compositions of individual single crystals of the solid solution, all taken out of the same initial aqueous solution, are also bound to occur. Therefore in this work, whenever critical statements are made on optical rotation measurements on crystal samples, the percentage composition analysis of the actual crystal specimen employed for such a study was measured polarographically. Indeed, composition changes within a given crystal specimen from one region to the other as well

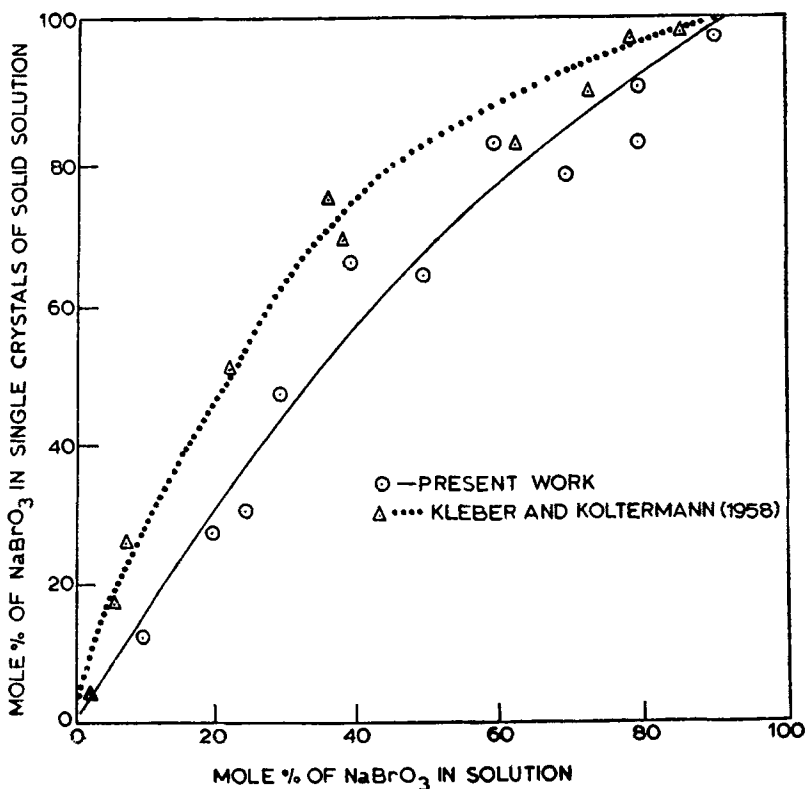


Figure 1. Variation of composition from solution phase to solid phase.

as heterogeneities in the solid solution are possible in principle (Guinier 1959). In the present work, we had checked the uniformity of the composition within the specimen through x-ray absorption measurements, using a finely collimated and crystal monochromatised beam of Cu K_α x-rays (Mohanlal 1971), scanning the crystal specimen in the different regions and the compositional changes within the specimen were found to be negligible.

A common feature in all single crystals at different compositions of the solid solution of the present system is the marked anisotropic behaviour. While the x-ray patterns of the system at all compositions answered a cubic unit cell to a very good accuracy, the crystals do not extinguish under crossed polaroids. This had also been observed and discussed in earlier work (Kleber and Koltermann 1958) and in fact, the birefringent patterns were identical. However, this anisotropy could be removed by annealing heat treatments (Schlenk 1967) for several hours at temperatures around 200°C . Thus, the crystal samples could be rendered reliably isotropic and their optical rotations measured as discussed in the following section.

4. Annulling trends of optical rotation in the solid solution

For the measurements of optical rotation, a parallel monochromatic beam ($\lambda = 5461 \text{ \AA}$) was utilised, taking the first order diffracted beam from a plane optical grating illuminated by a mercury lamp source. The crystal sample was located as usual, between two crossed polaroids with the analyser having a graduated circle of least count 0.1° . The crystals, fairly parallel plates, were measured in several regions for their thickness using a travelling microscope and their average values were taken. The extinction was similarly judged several times for each specimen. The optical rotation could be determined accurately, the maximum deviation in a set of measurements was about $\pm 0.15^\circ/\text{mm}$. As an additional check of the procedure, the rotation of the end member halates were measured and compared with the standard data as in table 1(a). Single crystals of the solid solution, rendered isotropic by annealing, were also similarly examined, choosing several samples, some with high and others with low bromate content. These data are furnished in table 1(b).

The following conclusions could be drawn from tables 1(a) and 1(b):

(i) The measurements of specific optical rotations for the end member halate crystals, as in table 1(a), are in good agreement with the standard values.

(ii) The values for the crystals with low bromate content are all appreciably smaller than the values for NaClO_3 and they are in fair quantitative agreement with a simple calculation based on annulling in proportion to their composition.

(iii) Similarly the crystals with high bromate content exhibit optical rotation significantly smaller than that for NaBrO_3 . The annulling tendency is also qualitatively indicated but this is not quite quantitative for a few samples (*T* and *W*) at this end.

(iv) As in the parent halate crystals, both dextro and laevo rotatory specimens are encountered in the crystals of the solid solution.

It would be of interest to have extended optical rotation measurements on the crystals of the solid solution to the wavelength region about 0.3 micron, where the optical rotations of the two halates exhibit a large difference (Chandrasekhar

Table 1(a). Optical rotation of the end member halates at 5461 Å (present work for check)

Crystal sample	Mean thickness (<i>l</i> mm)	Maximum deviation (Δl)	Measured rotation (θ)	Maximum deviation ($\Delta \theta$)	Optical rotation/mm (θ/l)	Sense of activity
NaClO₃:						
Sample 1	1.465	± 0.035	5.1°	$\pm 0.1^\circ$	3.5° $\pm 0.1^\circ$	Dextro
Sample 2	0.936	± 0.036	3.3°	$\pm 0.1^\circ$	3.5° $\pm 0.2^\circ$	Dextro
Sample 3	1.330	± 0.020	4.9°	$\pm 0.15^\circ$	3.66° $\pm 0.16^\circ$	Laevo
NaBrO₃:						
Sample 1	1.189	± 0.020	3.1°	$\pm 0.1^\circ$	2.61° $\pm 0.1^\circ$	Laevo
Sample 2	0.588	± 0.027	1.54°	$\pm 0.06^\circ$	2.61° $\pm 0.06^\circ$	Dextro

Literature values (*International Critical Tables*, 1933):

$$\left. \begin{array}{l} \text{NaClO}_3 \\ \text{NaBrO}_3 \end{array} \right\} \begin{array}{l} 3.69^\circ \pm 0.02^\circ \\ 2.62^\circ \pm 0.02^\circ \end{array} \text{ at } 20^\circ \text{ C for } 5461\text{Å}$$

Table 1(b). Optical rotations of the single crystals of the solid solution NaClO₃: NaBrO₃ at 5461 Å

Crystal sample	Mean thickness (<i>l</i> mm)	Maximum deviation (Δl)	Measured rotation (θ)	Maximum deviation ($\Delta \theta$)	Optical rotation		Sense of activity	Mole% NaBrO ₃
					Measured rotation/mm (θ/l)	Calculated for annulment by composition		
Crystal with low bromate content:								
P	0.906	± 0.100	2.75°	$\pm 0.15^\circ$	3.07° $\pm 0.37^\circ$	3.06	Laevo	10%
Q	0.737	± 0.005	2.07°	$\pm 0.06^\circ$	2.81° $\pm 0.08^\circ$	3.06°	Laevo	10%
R	0.392	± 0.010	1.24°	$\pm 0.06^\circ$	3.18° $\pm 0.17^\circ$	3.06°	Dextro	10%
S	1.060	± 0.126	2.64°	$\pm 0.16^\circ$	2.56° $\pm 0.34^\circ$	2.43°	Dextro	20%
Crystals with high bromate content:								
T	1.070	± 0.137	1.3°	$\pm 0.1^\circ$	1.24° $\pm 0.2^\circ$	1.99°	Laevo	90%
U	0.944	± 0.026	1.58°	$\pm 0.18^\circ$	1.67° $\pm 0.2^\circ$	1.99°	Dextro	90%
V	0.291	± 0.015	0.59°	$\pm 0.11^\circ$	2.03° $\pm 0.4^\circ$	1.99°	Dextro	90%
W	0.524	± 0.019	0.75°	$\pm 0.05^\circ$	1.43° $\pm 0.1^\circ$	2.32°	Dextro	95%
X	2.224	± 0.233	4.84°	$\pm 0.14^\circ$	2.20° $\pm 0.24^\circ$	2.43°	Dextro	97%

and Madhava 1967, 1969). However the data presented in table 1 (b) clearly indicate that in the crystals of the solid solution of these halates, the optical rotation tends to annul.

5. Trends in the x-ray anomalous dispersion effect in the solid solution

The principle of the anomalous dispersion of x-ray and its utility for the absolute configuration, together with the indexing procedures, are well known and reviewed (Ramaseshan 1964).

Due to the anomalous scattering by the halogen atoms, Bijvoet inequalities, $F(hkl) \neq F(\bar{h}\bar{k}\bar{l})$, can arise in these crystals, only for reflections with no index zero. The same experimental procedures (Ramachandran and Chandrasekaran 1957) were adopted for a single crystal of the solid solution, with a chlorate content of about 85%, in the form of a thin rectangular plate, [0 1 $\bar{1}$] axis set vertical on the Geiger counter spectrometer (Chandrasekaran *et al* 1972). A few selected reflections were measured, each of them in all the equivalent settings, from which the summarised data as in table 2 were obtained.

Each reflection could be measured with interchangeable angle of incidence and emergence from the crystal plate, giving rise to an asymmetry effect in the measured integrated intensities of $\sin(\theta + \epsilon)/\sin(\theta - \epsilon)$ where ϵ is the angle between the plane and the crystal surface (James 1958). It is seen from table 2 that they have checked. Also, the reflections with any index zero would not, by symmetry display Bijvoet inequality and these served as a further check to the measurements.

Table 2. Anomalous dispersion effect in the solid solution NaClO₃:NaBrO₃

Reflection	Calculated % Bijvoet inequality*		Values derived from integrated intensity measurements at several settings of single crystal of the solid solution with 15 mole % BrO ₃			Agreement with Bijvoet inequality of parent halates
	For NaClO ₃ (Aravindakshan's parameters)	For NaBrO ₃ (Bijvoet's parameters)	Asymmetry** effect measured	Asymmetry** effect calculated	Measured % Bijvoet inequality	
4 1 1	+13.0%	+7.0%	4.42	4.26	+21.6%	Yes
5 1 1	-39.4%	+7.9%	2.38	2.18	-21.4%	Yes
6 1 1	+38.0%	+0.4%	1.89	1.59	+38.0%	Yes
7 1 1	-16.8%	-34.8%	1.29	1.31	+8.1%	No
8 1 1	-28.1%	+7.0%	1.02	1.12	-49.5%	Yes
2 0 0	Cannot arise for reasons discussed in section 5		Cannot arise since the planes are parallel to the surface of the crystal.		0.01%	
4 0 0					0.01%	

* Bijvoet inequality % = $\frac{2\{|F(hkl)|^2 - |F(\bar{h}\bar{k}\bar{l})|^2\}}{\{|F(hkl)|^2 + |F(\bar{h}\bar{k}\bar{l})|^2\}}$ % Which is taken as positive quantity if $|F(hkl)|^2 > |F(\bar{h}\bar{k}\bar{l})|^2$

** James, 1958.

Table 2 also gives the calculated Bijvoet inequalities. The structural parameters for chlorate (Aravindakshan 1969) and for bromate (Gezina *et al* 1963) had been employed using the dispersion corrections (International tables 1962) for Cl and Br atoms in the Bijvoet inequality calculation.

The Bijvoet inequalities for the specimen crystal of the solid solution with 85% chlorate seem to agree in their trend with those of the chlorate and this is indicated by the last column in table 2. The imaginary component of the anomalous scattering for the Br atom is large ($\Delta f''(\text{Br}) = 1.4$ for CuK_α radiation) and is almost twice the value when compared with the Cl atom. However, the Bijvoet inequalities, (considering as the ratio $I_{hkl}/I_{\bar{h}\bar{k}\bar{l}}$) have been found to be large for several reflections, only in the case of NaClO_3 and not for NaBrO_3 . Such intensity ratio in the case of NaBrO_3 is small for several reflections (most of them showing only 10% difference) except for a lone reflection [2 3 1] and even this reflection is only weak (Gezina *et al* 1963). In view of the above, the present approach namely taking a chlorate rich mixed crystal seems to be proper and satisfactory so that Bijvoet inequalities would be large.

A quantitative comparison of the measured Bijvoet inequalities and their calculated dependence on the composition in the solid solution is not feasible. This is because such calculations would be very sensitive to the anisotropic individual thermal parameters which have not been determined so far even for the end member halates. Such a refinement is clearly necessary if the intensities of $(h k 0)$, free of Bijvoet inequality, are considered as in Aravindakshan's (1959) work where, for example, for the reflections, $(6 1 0)$ and $(3 2 0)$, the calculated ratio $\left| \frac{F(h k 0)}{F(k h 0)} \right|^2$ were 0.36 and 29.3 and the corresponding measured values were 0.16 and 15.9 respectively. Therefore, with an overall isotropic temperature correction for the structure factors, one could only check the trend in the Bijvoet inequality for several reflections, as shown in table 2.

6 Conclusions

The conjecture of Gezina *et al* (1963), that in the solid solution $\text{NaClO}_3 : \text{NaBrO}_3$, the crystalline configuration would continue itself is checked as discussed in section 4, through the consequent annulment of optical rotation in proportion to the composition. Further, the x-ray anomalous dispersion effect, leading to Bijvoet inequalities, reveal a supporting trend as seen in section 5.

It seems to us that these are probably the first concurrent measurements of optical rotation and anomalous dispersion effects for any solid solution and could be of interest for several other systems.

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