

X-RAY STUDIES OF ALKALI CHLORIDES DISSOLVED IN B_2O_3 -GLASS

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(Plates VIIA, VIIB and VIIC)

ABSTRACT. X-ray investigation is made of $NaCl-B_2O_3$, $KCl-B_2O_3$ and $RbCl-B_2O_3$ glass systems and the effect of different concentrations of alkali chloride in B_2O_3 glass has also been studied.

It is found that alkali chloride retains its characteristic structure and in some cases it induces crystallinity in the glass itself.

INTRODUCTION

In previous communications, Majumdar and co-workers (1942, 45, 46) have published the results of X-ray diffraction of alkali halides dissolved in boric oxide and borax-glasses. The salts investigated have all polar linkages and the equilibrium in such cases, according to the simpler electro-static theory of Born and others (1938), is the result of mainly two forces, *viz.*, the Coulomb forces between the ions obeying the inverse square law and the short distance repulsive forces. It is well-known that in aqueous solutions the lattice is destroyed primarily on account of the weakening of the electro-static forces in a medium of high dielectric constant, such as water, and the so-called ionisation occurs. It is conceivable therefore that if these polar salts could be dissolved in a medium possessing not such a high dielectric constant as water (lying between 6.5-7.5), the weakening of the electro-static forces may not be so great as to cause ionisation but large enough to produce an enlargement of the lattice. It was with this object that alkali chlorides were dissolved in boric oxide and borax glasses and the properties, of the melt after solidification were studied in various ways, *viz.*, refractometrically, by X-ray diffraction and by studying their diamagnetic susceptibilities.

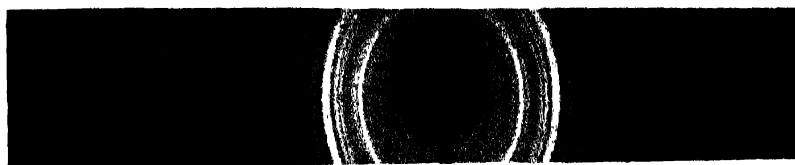
The earlier investigations led one of us (Majumdar, *loc. cit.*) to believe that there was an actual enlargement of the lattice of these crystals when dissolved in the above-mentioned glasses. The subject has since been studied using more refined methods and using more powerful X-ray generator and the results are recorded in the present paper.

NaCl-B.O

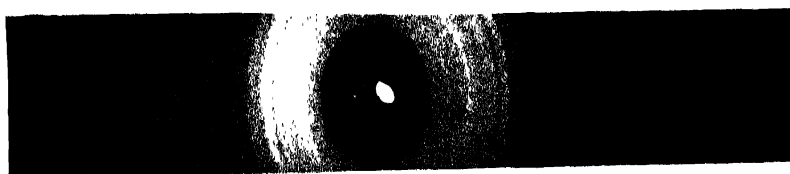
500 μ



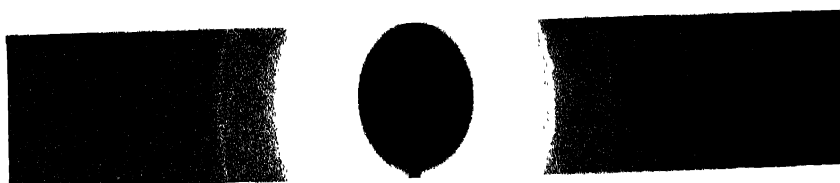
A₁



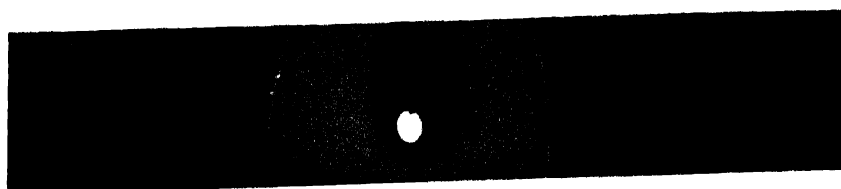
A₂



A₃



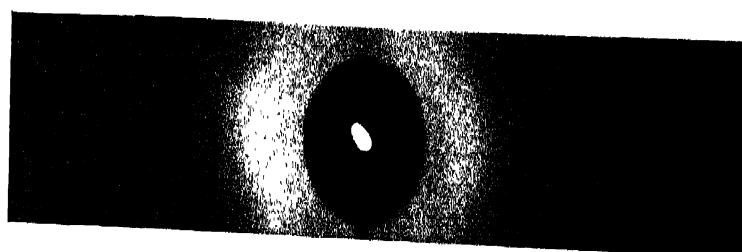
A₄



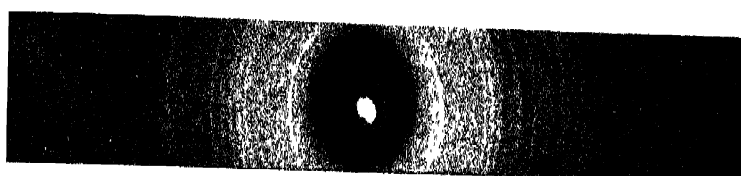
A₅

KCl-B.O

Sample



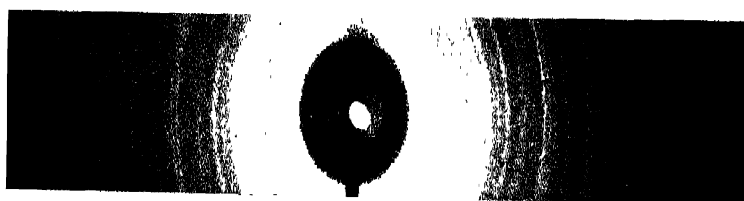
B1



B2



B3



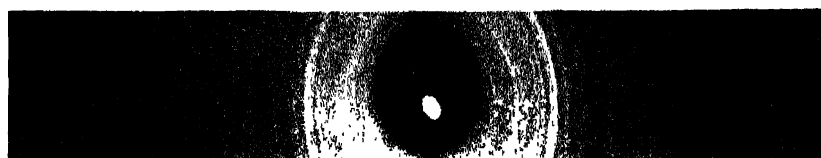
B4

RbCl B.O

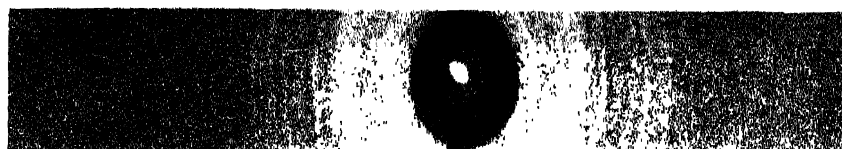
Sample



C₀



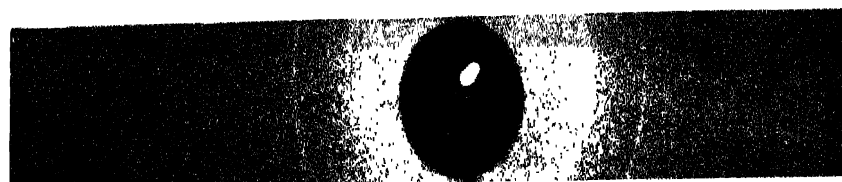
C₁



C₂



C₃



C₄

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According to modern conception regarding structure of glass due to Zachariasen (1932), Warren and others (1938), a sort of *non-repeating* network exists in the glass as opposed to the regular space-lattice obtaining in a true crystal. And hence haloes or diffuse lines are obtained with a glass in X-ray diffraction experiments instead of sharp lines obtained with true crystals. It is of interest, therefore, to examine if the X-ray diffraction patterns of crystals dissolved in a glass reveal sharp lines due to the dissolved crystal and the faint haloes due to the glass. As a result of a large number of experiments this expectation has been realised in every case.

Warren and his co-workers (1937) have studied the diffraction photographs given by B₂O₃-glass, using Fourier analysis method and have come to the conclusion that in the glass, each boron atom is linked with three other oxygen atoms, in a triangular arrangement. Warren and Loring studied the SiO₂-Na₂O-glass system with Na₂O content varying from 0 to 46% Na₂O. With small Na₂O-contents, the pattern shows a single strong peak at $\frac{\sin \theta}{\lambda} = 0.12$, but with increasing Na₂O-content, the peak diminishes in intensity, while a new peak at $\frac{\sin \theta}{\lambda} = 0.18$ appears in the picture and this peak becomes more pronounced with increasing soda-content. It was also found by these authors that with increasing alkali oxide content, B-O-B distance changes and there is a shift from the planar threefold configuration to fourfold tetrahedral configuration. The present communication records the results of the following systems :—NaCl-B₂O₃ ; KCl-B₂O₃ ; RbCl-B₂O₃.

EXPERIMENTAL

The salts as well as boric acid of Merck Pro-Analyse quality were recrystallised from conductivity water and carefully dehydrated first in an air oven and then in a vacuum desiccator for several days. The presence of traces of moisture was tested by taking a sample in absolute alcohol and treating with anhydrous copper sulphate.

The anhydrous B₂O₃ and the salt were then quickly powdered and heated in a platinum crucible over a Mecker burner for several hours until a homogeneous melt was obtained. The crucible was then chilled and the solid extracted. Each piece was tested in a polarisation microscope for optical isotropy. The samples were then powdered, enclosed in a thin-walled capillary tube and the Debye-Scherrer photograph taken. The alkali-content was determined by estimating chlorine volumetrically by back titration method, and in some cases checked by gravimetric method.

X-ray from a Hadding tube with copper anti-cathode run at a voltage of about 40 KV and a tube current of 4.5–5.5 milliamp, after collimation through narrow circular slits was made incident on the sample in the form of a stick of 1 mm diam. placed along the axis of a cylindrical camera of 3.90 cm. radius. The glancing angle θ in degrees is obtained from the

equation, $\theta = \frac{x}{4r} \times 57.3$ degrees, where x is the distance in cm. between two similar lines in the negative and r , the radius of the camera.

An exposure of 10–12 hours was necessary. The analysis of the results are shown in the following tables, in which s stands for strong, m for medium, w for weak and v for very. θ_a and θ_B stand for angles due K_α (1.539 Å) and K_β (1.389 Å) due to copper radiation.

TABLE I
NaCl-B₂O₃ (Sample A₁-3.53% NaCl)

Int.	Observed θ	Calc. NaCl		B ₂ O ₃		Na ₂ B ₄ O ₇	
		θ	Plane	θ	Int.	θ	Int.
mw	6°58'	6°45'	(2)
w	8°27'
s	9°26'
ms	10°6'	9°56'	(2)
w	10°27'	10°47'	(2)
ms	11°33'	11°52'	(1)
s	12°28'	12°25'	($\frac{1}{2}$)
s	13°13'	13°16'	(10)
s	13°46'	14°7'	(10)
vw	14°19'	14°19'	(200) _B
m	14°57'	14°42'	(4)
w	15°25'	15°24'	(1)
mw	16°9'	15°52'	(200)
m	17°4'	17°17'	($\frac{1}{2}$)
w	18°27'	18°35'	(1)
mw	19°39'	19°46'	($\frac{1}{2}$)
w	20°12'	20°7'	(2)
mw	20°39'	20°27'	(220) _B
w	21°7'	21°6'	($\frac{1}{2}$)
w	21°51'	22°9'	($\frac{1}{2}$)
w	22°34'	22°54'	(1)
ms	22°57'	22°45'	(220)
ms	24°25'	24°35'	(1)
mw	24°58'	24°38'	($\frac{1}{2}$)
w	26°1'	25°44'	(1)
ms	27°26'	27°28'	($\frac{1}{2}$)	27°19'	($\frac{1}{2}$)
w	28°38'	28°17'	(222)
w	30°29'	30°36'	($\frac{1}{2}$)
w	37°38'	37°42'	(420)
w	42°13'	42°5'	(422)

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TABLE II
NaCl—B₂O₃ (Sample A₂—5.23% NaCl)

Int.	Observed θ	Calc. NaCl		B ₂ O ₃		Na ₂ B ₄ O ₇	
		θ	Plane	θ	I	θ	I
m	6°28'	6°45'	(5)
m	7°19'	7°30'	(5)
mw	8°26'
s	9°37'
m	10°28'	9°57'	(2)
s	11°33'	10°46'	(2)
s	12°28'	11°52'	(2)
vs	13°7'	12°25'	(1)
vs	13°57'	13°16'	(10)
w	14°19'	13°42'	(111)	14°7'	(10)
ms	15°3'	14°19'	(200) β
s	16°20'	15°24'	(1)
mw	17°15'	15°52'	(200)
m	18°21'
ms	19°27'	18°34'	(1)
mw	20°34'	19°46'	($\frac{1}{2}$)
w	21°51'	20°27'	(220) β	20°7'	(2)
ms	22°57'	22°9'	($\frac{1}{2}$)
m	24°25'	22°45'	(220)
w	25°19'	24°38'	($\frac{1}{2}$)	24°35'	(1)
m	27°21'	25°44'	(1)
w	28°5'	26°59'	(311)	27°28'	($\frac{1}{2}$)	27°19'	($\frac{1}{2}$)
w	29°39'	28°17'	(222)
w	37°49'	29°48'	($\frac{1}{2}$)
w	42°36'	37°42'	(420)
		42°51'	(422)

TABLE III
NaCl—B₂O₃ (Sample A₃—7.83% NaCl)

Int.	Observed θ	Calc. NaCl		Calc. B ₂ O ₃		Na ₂ B ₄ O ₇	
		θ	Plane	θ	I	θ	I
w	8°22'
s	9°42'	9°56'	(2)
w	10°22'	10°47'	(2)
mw	12°7'	12°25'	(1)
m	12°51'	13°10'	(2)
m	13°31'	13°16'	(10)
s	14°19'	14°7'	(10)
w	14°41'	14°19'	(200)
mw	15°25'	15°42'	(1)
m	16°9'	15°52'	(200)
w	16°58'	16°42'	($\frac{1}{2}$)	16°33'	(1)
m	17°37'	17°47'	($\frac{1}{2}$)
mw	18°55'	18°35'	(1)
m	20°12'	20°27'	(220) β
s	23°2'	22°45'	(220)
w	23°58'	23°53'	($\frac{1}{2}$)
ms	25°30'	25°44'	(1)
s	28°22'	28°17'	(222)
mw	33°36'	33°10'	(400)
mw	38°1'	37°42'	(420)
mw	42°17'	42°5'	(422)

TABLE IV
NaCl—B₂O₃ (Sample A₄—14.00% NaCl)

Intensity	Observed θ	Calculated	
		θ	Plane
s	15° 58'	15° 52'	(200)
w	20° 23'	20° 27'	(220) _B
s	22° 46'	22° 45'	(220)
m	28° 16'	28° 17'	(222)
mw	33° 25'	33° 10'	(400)
m	37° 56'	37° 42'	(420)
mw	42° 13'	42° 5'	(422)

TABLE V
NaCl—B₂O₃ (Sample A₅—23.52% NaCl)

Intensity	Observed θ	Calc. NaCl	
		θ	Plane
m	14° 23'	14° 19'	(200) _B
vs	16° 0'	15° 52'	(200)
w	20° 36'	20° 27'	(220) _B
vs	22° 51'	22° 45'	(220)
m	28° 14'	28° 17'	(222)
w	33° 10'	33° 10'	(400)
s	37° 46'	37° 42'	(420)
s	42° 5'	42° 5'	(422)

TABLE VI
KCl—B₂O₃ (Sample—B₁—1.01% KCl)

Intensity	Observed θ	Calculated KCl		B ₂ O ₃	
		θ	Plane	θ	Plane
m	13° 57'	14° 12'	(200)	14° 7'	10
w	15° 10'	15° 24'	1
vw	17° 52'	18° 5'	½
w	20° 12'	20° 17'	(220)
w	25° 5'	25° 8'	(222)

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TABLE VII

KCl—B₂O₃ (Sample B₂—5.99% KCl)

Intensity	Observed θ	Calc. KCl		B ₂ O ₃	
		θ	Plane	θ	I
mw	7° 12'	7° 30'	(5)
s	8° 11'
w	11° 31'	11° 52'	(1)
s	12° 43'	12° 47'	(200) _n	12° 25'	(1)
s	13° 21'	13° 16'	(10)
ms	14° 9'	14° 12'	(200)	14° 7'	(10)
mw	15° 14'	15° 24'	(1)
s	16° 23'	16° 42'	($\frac{1}{2}$)
mw	17° 57'	18° 3'	(220) _n
w	18° 55'	18° 54'	($\frac{1}{2}$)
w	20° 17'	20° 17'	(2)
ms	20° 40'	20° 17'	(220)
w	21° 27'	21° 6'	($\frac{1}{2}$)
mw	22° 48'	22° 32'	(222) _n
w	24° 19'	24° 38'	($\frac{1}{2}$)
m	25° 9'	25° 8'	(222)
mw	28° 40'	28° 58'	($\frac{1}{2}$)
m	29° 45'	29° 22'	(400)
m	33° 10'	33° 14'	(420)
m	36° 58'	36° 56'	(422)

TABLE VIII

KCl—B₂O₃ (Sample B₃—8.77% KCl)

Intensity	Observed θ	Calc. KCl		B ₂ O ₃	
		θ	Plane	θ	I
m	7° 15'	7° 30'	(5)
s	8° 14'
w	11° 27'	11° 52'	(1)
s	12° 13'	12° 25'	(1)
s	12° 56'	12° 47'	(200) _p	13° 16'	(10)
ms	13° 46'	14° 12'	(200)	14° 7'	(10)
mw	15° 3'	15° 24'	(1)
ms	16° 13'	16° 42'	($\frac{1}{2}$)
mw	17° 48'	18° 3'	(220) _p
w	18° 43'	18° 54'	($\frac{1}{2}$)
w	20° 0'	20° 7'	(2)
ms	20° 22'	20° 17'	(220)
w	21° 0'	21° 6'	($\frac{1}{2}$)
mw	22° 46'	22° 32'	(222) _n
w	24° 13'	24° 38'	($\frac{1}{2}$)
m	24° 58'	25° 8'	(222)
mw	28° 33'	28° 58'	($\frac{1}{2}$)
m	29° 45'	29° 22'	(400)
m	33° 14'	33° 14'	(420)
ms	36° 38'	36° 56'	(422)

TABLE IX

KCl—B₂O₃ (Sample B₄—13.53 KCl)

Intensity	Observed θ	Calc. KCl		B ₂ O ₃	
		θ	Plane	θ	I
w	7° 28'	7° 30'	(5)
s	8° 12'
m	11° 30'	11° 52'	(1)
s	12° 42'	12° 25'	(1)
s	13° 22'	12° 47'	(200) _R	13° 16'	(10)
s	14° 12'	14° 12'	(200)	14° 7'	(10)
w	15° 19'	15° 24'	(1)
b	16° 16'	16° 42'	(1)
m	17° 56'	18° 3'	(220) _R
w	18° 52'	18° 54'	(1)
s	20° 16'	20° 17'	(220)
w	21° 20'	21° 6'	(1)
mw	22° 48'	22° 32'	(222) _R
w	24° 28'	24° 38'	(1)
s	25° 13'	25° 8'	(222)
ni	28° 58'	29° 22'	(400)
w	29° 54'	29° 38'	(420) _R
s	33° 17'	33° 14'	(420)
s	37°	36° 56'	(422)

TABLE X

RbCl—B₂O₃ (Sample C₁—1.44% RbCl)

Intensity	Observed θ	Calc. RbCl		B ₂ O ₃	
		θ	Plane	θ	I
ms	6° 57'	6° 45'	(5)
ms	7° 50'	7° 30'	(5)
m	11° 27'	11° 42'	(111)
s	12° 51'	13° 16'	(10)
s	13° 40'	13° 33'	(200)	14° 7'	(10)
m	15° 48'	15° 24'	(1)
mw	17° 44'	17° 23'	(220) _R
ms	19° 27'	19° 21'	(220)
mw	20° 55'	20° 31'	(311) _R	20° 7'	(2)
vw	21° 50'	21° 29'	(222) _R
m	22° 57'	22° 52'	(311)
mw	24° 14'	23° 57'	(222)
w	28° 10'	27° 57'	(400)
w	31° 56'	31° 36'	(420)

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TABLE XI

RbCl—B₂O₃ (Sample C₂—2.07% RbCl)

Int.	Observed θ	Calc. RbCl		B ₂ O ₃	
		θ	Plane	θ	I
m	7° 9'			7° 30'	(5)
w	8° 31'				
s	9° 25'				
w	10° 11'				
w	11° 45'	11° 42'	(111)	11° 52'	(1)
m	12° 20'	12° 12'	(200) β	12° 25'	(1)
m	13° 13'			13° 16'	(10)
s	13° 51'	13° 33'	(200)		
w	14° 24'			14° 7'	(10)
m	15° 9'			15° 24'	(1)
w	16° 31'			16° 42'	(1/2)
mw	17° 15'	17° 23'	(220) β		
m	19° 39'	19° 21'	(220)		
w	20° 39'	20° 31'	(311) β	20° 7'	(2)
w	21° 40'	21° 29'	(222) β		
mw	23° 7'	23° 1'	(311)		
m	24° 15'	23° 57'	(222)		
mw	27° 36'	27° 57'	(400)		
m	31° 57'	31° 36'	(420)		
w	34° 53'	35° 1'	(422)		

TABLE XII

RbCl—B₂O₃ (Sample C₃—3.154% RbCl)

Int.	Observed θ	Calc. RbCl		B ₂ O ₃	
		θ	Plane	θ	I
m	7° 20'			7° 30'	(5)
s	8° 4'				
mw	9° 32'				
ms	11° 22'	11° 42'	(111)	11° 52'	(1)
w	12° 7'	12° 12'	(200) β		
s	12° 40'			12° 25'	(1)
m	13° 24'	13° 33'	(200)	13° 16'	(10)
w	14° 30'			14° 7'	(10)
s	15° 47'			15° 24'	(1)
mw	17° 48'	17° 23'	(220) β		
s	19° 33'	19° 21'	(220)		
s	20° 23'			20° 7'	(2)
s	21° 7'			21° 6'	(1/2)
w	21° 51'	21° 29'	(222) β		
mw	22° 40'	22° 52'	(311)		
mw	24° 14'	23° 57'	(222)		
mw	25° 7'	25° 1'	(400) β	24° 38'	(1/2)
w	28° 16'	27° 57'	(400)		
w	31° 37'	31° 39'	(420)		

TABLE XIII

RbCl-B₂O₃ (Sample C₄-6.95% RbCl)

Int.	Observed θ	Calc. RbCl		B ₂ O ₃	
		θ	Plane	θ	I
w	12° 25'	12° 12'	(200) β	15° 24'	(1)
s	13° 44'	13° 33'	(200)		
w	15° 42'				
w	17° 34'	17° 23'	(220) β		
s	19° 21'	19° 21'	(220)		
w	21° 7'	21° 29'	(222) β		
w	22° 48'	22° 52'	(311)		
m	24° 7'	23° 57'	(222)		
w	27° 40'	27° 57'	(400)		
m	31° 58'	31° 36'	(420)		
mw	35° 3'	35° 1'	(422)		

TABLE XIV

RbCl-B₂O₃ (Sample C₅-7.98% RbCl)

Int.	Observed θ	Calc. RbCl	
		θ	Plane
w	11° 22'	11° 42'	(111)
w	12° 18'	12° 12'	(200) β
s	13° 30'	13° 33'	(200)
mw	17° 15'	17° 23'	(220) β
s	19° 16'	19° 21'	(220)
vw	21° 8'	21° 29'	(222) β
w	22° 40'	22° 52'	(311)
mw	23° 41'	23° 57'	(222)
w	27° 32'	27° 57'	(400)
mw	31° 18'	31° 36'	(420)
mw	34° 42'	35° 1'	(422)

DISCUSSION

- It is clear from the tables that the lines due to the pure salts appear in every case in the dispersed glass system and certain foreign lines are present in many cases. It should be stated here that no lines other than the characteristic haloes were obtained with pure B₂O₃ & Na₂B₄O₇-glasses respectively prepared under exactly similar conditions.

The analysis was carried out in the following indirect way. Granting that the main lines were due to the dissolved alkali salts, the values of θ for different planes were calculated from the known radius of the camera and also checked in many cases with the negatives of the pure salts themselves and these values were compared with the experimental values. It was found that barring a number of lines, the values remarkably agreed with the experimental values, as will be seen from the tables given before. The discrepancy in the case of some of the extra lines was sought to be explained in a number of ways. The lines correspond to any of the well-known crystalline borates for which experimental data are available. It was found however that Cole, and Taylor (1934) and Cole, Taylor and Scholes (1935) had measured the diffraction lines of crystalline anhydrous B₂O₃ and crystalline anhydrous Na₂B₄O₇. Tables in their paper give the values of θ for these substances and the intensities according to their own scale the strongest corresponding to 10 and the weakest 1/2. It is thus seen that with NaCl, the main lines are due to the salt and the extra lines are due to anhydrous B₂O₃ and anhydrous Na₂B₄O₇. Further, the foreign lines persist at higher concentrations of the salts. This is also true of KCl more or less. With RbCl however at higher concentrations of the salt the foreign lines are remarkably absent.

The question now arises whether the systems studied represent true solutions or merely non-homogeneous suspensions of the salt in the glass medium. Ultramicroscopic observations with such systems and with gold and platinum dispersed in similar medium (Nature) failed to detect any diffraction cones. The sharpness of the lines however indicates that the size of the particles are bigger than the colloidal suspension for example of gold and platinum studied by Zsigmondy. The existence of the lattice in the glass systems further raises the question whether the ions of the alkali halides take up their respective positions within the non-repeating hollows of B₂O₃-glass (Warren) or they exist as definite clusters, more or less of the nature of a true colloidal suspension. In the former case, the lattice dimensions are liable to be altered on account of the dielectric effect of the glass medium on the Coulomb and short distance forces (Majumdar and Palit) and this would lead us to expect an enlargement of the lattice. The results recorded in this paper shows however that there is no appreciable alteration of the lattice dimensions of the dissolved salts in the glass.

The question why there is a partial devitrification of the glass (B₂O₃) when fused with the salts requires explanation. It should be stated that in blank

experiments with the B_2O_3 -glass alone, no evidence of devitrification was obtained and further with strong concentrations of $RbCl$ also, no such devitrification was noticeable. Similar results have been obtained with gold and platinum dispersed in B_2O_3 and $Na_2B_4O_7$ -glasses. The ability of the dissolved substance to release the instability of the glass therefore is in some way connected with its structure and physical properties like dipole moment in the salts and atomic number in the case of the dispersed metals. This point is being further pursued.

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