PART - I

GENERAL INFORMATION ON SODIUM CHLORIDE, POTASSIUM CHLORIDE AND POTASSIUM BROMIDE

AND

TECHNIQUES AND GRAPHICAL ANALYSIS

CHAPTER - 1

GENERAL INFORMATION ON SODIUM CHLORIDE, POTASSIUM CHLORIDE AND POTASSIUM BROMIDE

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REFERENCES

1.1 INTRODUCTION:

The applications of single crystals in industries are wide and manifold. e.g. Single crystals of semiconducting materials are employed on a very large scale in diverse fields of technology and engineering. It is therefore obvious to study properties by employing single crystals. The present work is centered on studying microhardness and chemical dissolution of single crystals of Sodium Chloride (NaCl), Potassium Chloride (KCl) and Potassium Bromide (KBr), all grouped under the name of alkali halides. These halides form a very important class of materials exhibiting thermal stability at elevated temperatures. It is therefore decided to grow single crystals of these materials from melt by using Kyropoulos method.

1.2 CRYSTALLOGRAPHY OF SODIUM CHLORIDE, POTASSIUM CHLORIDE AND POTASSIUM BROMIDE:

1.2.a Group and Structure :-

Alkali halides belong to cubic system. The X-ray studies indicate the arrangement of atoms to be that of a simple cubic lattice. For NaCl the symmetry is cubic holohedral whereas it is plagihedral for KCl and KBr. The crystal class and space group are m3m and Fm3m respectively /1,2/. The crystal structure of these crystals studied by X-rays indicates thate, Sodium (or Potassium) and Chlorine (or Bromine)atoms considered form a face-centered cubic lattice, the two cubic lattices interpenetrating each other. The octahedral plane (111) alternately contain all Sodium (or

Potassium) or all Chlorine (or Bromine) atoms. Whereas cubic planes contain alternately Na and Cl atoms along directions $\langle 100 \rangle$. There are four molecules in a unit cell.

The isometric system embraces all the forms which are referred to three axes of equal lengths at right angles to each other. Since these axes are mutually interchangeable it is customary to designate them all by the letter 'a' or a_1, a_2 and a_3. 'a_1' and 'a_2' lie in the horizontal plane and 'a_3' is the vertical axis normal to these plane.

The symmetry elements for all these crystals are as follows :

1. **Axes of Symmetry :**

I **Cubic axes of symmetry :-** There are three principal tetrad axes of symmetry which are coincident with the crystallographic axes and are sometimes known as the cubic axes, since they are perpendicular to the faces of the cube.

II **Diagonal axes of symmetry :-** There are four triad axes of diagonal symmetry which emerge in the middle of the octants formed by the cubic axes. These are called octahedral axes, since they are perpendicular to the faces of the octahedron.

III **Binary axes of symmetry :-** There are six axes of binary symmetry which bisects the plane angles made by the cubic axes. These are the dodecahedral axes.

2. **Planes of Symmetry :**

I **Principal Planes of symmetry :-** There are three principal planes of symmetry which are at right angles to each other and whose intersections fix the position of the crystallographic axes.

II Diagonal planes of symmetry :- There are six diagonal planes of symmetry.

3. Centre of Symmetry :

These crystals possess a centre of symmetry.

Each of the above crystal has three tetrad axes, four triad axes, six binary axes, three cubic planes of symmetry, six dodecahedral planes of symmetry and a centre. i.e., in all there are 23 elements of symmetry.

1.2.b Form and Habit :-

The faces occuring in a crystal group themselves into sets in each of which the members are similarly oriented to the crystal axes. Each of these sets of crystallographically similar faces, having the same Millerian indices (except as regards sign), constitutes a form.

The various possible forms belonging to this class, and possessing the symmetry defined may be grouped under seven types of solids. These are enumerated in the following table

	Types	General form	Miller Indices
(1)	Cube	$\{100\}$	$(100),(010),(001),$ $(\bar{1}00),(0\bar{1}0)$ & $(00\bar{1})$
(2)	Octahedron	$\{111\}$	$(111),(\bar{1}11),(1\bar{1}1),$ $(11\bar{1}),(\bar{1}\bar{1}1),(1\bar{1}\bar{1}),$ $(\bar{1}1\bar{1}),(\bar{1}\bar{1}\bar{1})$

(3)	Dodecahedron	{110}	(110),(101),(011), $(\bar{1}10)$,$(1\bar{1}0)$,$(\bar{1}\bar{1}0)$, $(\bar{1}01)$,$(10\bar{1})$,$(\bar{1}0\bar{1})$, $(0\bar{1}1)$,$(01\bar{1})$,$(0\bar{1}\bar{1})$
(4)	Tetrahexahedron	{hko}	as (310), (210), (320), etc.
(5)	Trisoctahedron	{hhl}	as (331), (221), (332), etc.
(6)	Trapezohedron	{hll}	as (311), (211), (322), etc.
(7)	Hexoctahedron	{hkl}	as (421), (321), etc.

It should be noted that in the present work single crystals are grown from melt. Hence all of them are having cylindrical forms from which cubes {100} were obtained. If the crystals are grown from their solutions it is possible to observe some forms during growth and some after growth.

1.3 CLEAVAGE, GLIDING AND TWINNING :

All these three crystals have perfect cleavage planes {100}. The fracture is conchoidal in NaCl and uneven in both KCl and KBr. NaCl is rather brittle and KCl not as brittle as NaCl, whereas KBr is soft enough to be readily scratched with a knife.

The phenomenon of twinning occurs in almost identical fashion in all these crystals on {111} only. Translation gliding is observed with T{100},T{110} and possibly with T{111}.

1.4 PERCUSSION FIGURE :

A blow with a somewhat dull-pointed nail on a crystal surface develops a figure usually referred to as percussion figure for mark or star) which reflects some characterestics of the surface. In the absence of natural faces of crystal, the study of this figure brings out certain characterestics such as plane of symmetry, line of symmetry and important crystallographic directions provided surface under consideration is a crystallographic plane of low indices. Pressure, instead of a blow on a surface can also produce figure known as pressure figure which also provides useful information about the crystal.

Percussion stars also produce rosette pattern on crystallographic planes of some crystals /73-77/. The principal physical, chemical and mineralogical informations along with references are given in table I.

TABLE - I

Principal Physical, Chemical and Crystallographic Properties of Sodium Chloride, Potassium Chloride and Potassium Bromide.

Sr. No.		Sodium Chloride	Potassium Chloride	Potassium Bromide
1.	Chemical Formula /8/	NaCl	KCl	KBr
2.	Molecular Weight (gm) /8/	58.44	74.55	119.01
3.	Molar Volume under At. Pressure (cm^3) /1/	27.0	27.4	42.9
4.	Solubility in water at 20°C g/100 g /8/	36.0	34.0	65.2
5.	Colour /3,7,8/	Usually colourless and trans-parent when pure	Colourless and trans-parent when pure	Colourless and trans-parent when pure
6.	Sp.gravity /8/	2.165	1.984	2.750
7.	Melting point under At.pressure °C /8/	801	776	730

Sr. No.		Sodium Chloride	Potassium Chloride	Potassium Bromide
8.	Boiling point Under At.Pressure °C /8/	1413	Sub: 1500	1435
9.	Hardness on mho's Scale /10/	2.5	2.0	Less than 2.0
10.	Elastic constants (Elastic coefficients, bars) at 27°C /6/	C_{11}:4.85 C_{12}:1.23 C_{13}: C_{33}: 1.26 C_{44}:	C_{11}:3.98 C_{12}:0.62	C_{11}:3.45 C_{12}:0.54 C_{44}:0.508
11.	Elastic Moduli/6/ a.Young's Modulus b.Bulk Modulus (dynes/cm^3)	 3.9989×10^{11} 2.4338×10^{11}	 2.9640×10^{11} 2.7375×10^{11}	 2.6889×10^{11} 1.5030×10^{11}
12.	Sp.heat g-cal/g(15°) /6/ :at 0°C :at 100°C	 0.204 0.217	 0.162 0.168	 0.104 0.108
13.	Thermal conductivity cals/cm-S-°C /6/	0.0155 at 16°C	0.0156 at 42°C	0.0115 at 46°C

Sr. No.		Sodium Chloride	Potassium Chloride	Potassium Bromide
14.	ΔH - Heat of formation at 25°C Kg.-Cal/mol., -ve values indicate heat is evolved in the process of formation /7/	-43.50	-51.6	-93.73
15.	ΔF - Free energy of formation at 25°C, Kg-cal/mol. /7/	-	-56.2	-90.63
16.	Dielectric constant /1/ (frequency 10^4 Hz)	6.16	5.03	4.90
17.	Velocity of sound at room temperature (longitudinal velocity) Km/sec. /8/	4.53	3.88	3.08
18.	Electrical conductivity.: at390°C mho/cm : at600°C /11-16/	1.62×10^{-12} 3.17×10^{-11}	7.12×10^{-9} 9.52×10^{-9}	1.00×10^{-7} 3.33×10^{-6}

Sr. No.		Sodium Chloride	Potassium Chloride	Potassium Bromide
19.	Refractive Index /10/	1.5442	1.4900	1.5590
20.	Crystallographic data :/3,4,7,8,9, 25-35/			
	(I) System (Point group)	Cubic (4/m $\bar{3}$ 2/m)	Cubic (4/m $\bar{3}$ 2/m	Cubic (4/m $\bar{3}$ 2/m)
	(II) Class	m3m	m3m	m3m
	(III) Space group	Fm3m	Fm3m	Fm3m
	(IV) Lattice parameters A.U.	a. b. 6.5780 c.	a. b. 6.2800 c.	a. b. 5.6273 c.
	(V) Unit cell	f.c.c.	f.c.c.	f.c.c.
	(VI) Symmetry	Cubic (Holohedral)	Cubic (Plagi-hedral)	Cubic (Plagi-hedral)
	(VII) Cleavage (Perfect)	{001}	{001}	{001}
	(VIII) Fracture	Conchoidal	Uneven	Uneven
	(IX) Slip system	{110} $\langle 1\bar{1}0 \rangle$	{110} $\langle 1\bar{1}0 \rangle$	{110} $\langle 1\bar{1}0 \rangle$
	(X) Elasticity	Brittle	Not as brittle as NaCl	Soft

Sr. No.		Sodium Chloride	Potassium Chloride	Potassium Bromide
20.	(XI) TWINNING	{111}	{111}	{111}
	(XII) Lustre	Vitreous	Vitreous	Vitreous
	(XIII) Fusibility	Fusible often with decrepitation	Easily fusible	Decomposes rather more easily than the chlorides when fused with clay or silica.
	(XIV) Habit	Usually Cubic, rarely octahedral	Cubic, less commonly Cubo-octahedral or octahedral	Cubic
	(XV) Structure cell, 4 molecules (cell content)	Na_4Cl_4	K_4Cl_4	K_4Br_4
	(XVI) Streak	Colourless to white	Colourless	Colourless

Sr. No.		Sodium Chloride	Potassium Chloride	Potassium Bromide
20.	(XVII) Diaphaneity	Transparent to translucent	Transparent	Transparent
	(XVIII) Occurrence and mineral associations	Occurs in extensive bends formed by the evaporation of enclosed bodies of salt water subsequently buried by other sedimentry deposits.	Occurs basically in basin-like bedded salt deposits of sedimentary orgin but in much less common than NaCl.	Does not occur in compact masses in nature, and is made in practice from the reaction of free Bromine with potassium Hydroxide.
	(XIX) Uses	Main uses are culinary and preservative. For soda ash preparation	As a source of potash compound used in fertilizer.	In chemical laboratories, medically in some nervous diseases and in photography.
	(XX) Artificial growth /17-24/	From soln. and also from melt	From soln. and also from melt	From soln. and also from melt

Sr. No.		Sodium Chloride	Potassium Chloride	Potassium Bromide
21.	Dissolution :			
	(a) Chemical /36-53/	Organic acids and alcohols which may or may not contain active ions.	Same as NaCl	Same as NaCl
	(b) Thermal /11,54-63/	Thermal dissolution at elevated temperatures	Same as NaCl	Same as NaCl
22.	Hardness /64-72/	Maximum for octahedral face, minimum for cubic face and a value in between for dodecahedral face.	Same as NaCl	Same as NaCl

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