

Crystallography and Preparation of Some $ABCl_3$ Compounds

H. F. McMurdie, J. de Groot, M. Morris, and H. E. Swanson

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

(August 20, 1969)

Compounds of the composition $ABCl_3$, in which A is K, Rb, NH_4 , or Cs and where B is a divalent element, have been reviewed. Ten new compounds were prepared on which there was little or no previous crystallographic information. Refined unit cell parameters were obtained on these and on fifteen other compounds in this group. A general review of the structural information on this group is presented in tables, and a comprehensive list of references is included.

Key words: Chlorides; crystal structures; double chlorides; lattice constants; melting point; perovskites; polymorphism; x-ray diffraction.

1. Introduction

The ABO_3 group of compounds has been intensively investigated and the relationship between factors such as ionic size, type of bonding and atomic arrangement have been outlined. There has been particular interest in the perovskite type structures, their distortions with temperature or compositional change, and their electrical properties. Similar structures occur in $ABCl_3$ compounds. There are not nearly as many compounds in this group since with Cl having a valence of one, the valence of A and B must always be one and two respectively.

Recently work has been done at the National Bureau of Standards on the $ABCl_3$ compounds where A is K, Rb, NH_4 , or Cs and B is one of the divalent elements: Mg, Ni, Fe, Co, Ca, Cd, Hg, Sr, or Pb. The study was a part of the project at the National Bureau of Standards, sponsored in part by the Joint Committee for Powder Diffraction Standards, in which X-ray powder patterns of pure phases are prepared to extend and improve the Powder Diffraction File.¹ In this work patterns of all compounds which could be made of sufficient purity, which could be handled satisfactorily, and which were not already represented in the File by good data, were prepared. Ten compounds were studied on which there was previously little or no crystallographic data. X-ray patterns and refined cell sizes on these and on 15 others in this group were obtained. A literature search covering this group of compounds was made. It was felt that it would be useful to present these data together so that the crystal chemical relation-

ships might be seen, as had been done for ABO_3 compounds [23, 27].

The complete indexed powder patterns of these compounds and their optical properties, as well as a description of our methods of producing and refining powder data are recorded in the series NBS Monographs 25.² [38, 39, 40].³ Briefly, the x-ray work was done on powders using a diffractometer, with an internal standard (Ag or W) for calibration of the d spacing measurements.

This paper will first discuss those phases prepared in this laboratory which represent new information. Secondly, we will briefly describe the preparation of those phases for which we determined a refined cell. The third section is a tabular record of the crystallographic data of all the compounds with a brief discussion of the structure.

2. New Compounds Prepared in This Study

(1) $CsSrCl_3$

The sample was prepared by melting a stoichiometric mixture of CsCl and $SrCl_2$ at above 900 °C. The material was found to show very low birefringence and to show polysynthetic twinning under crossed nicols. The material was hygroscopic and the x-ray powder patterns were made with the sample in a dry mount to prevent hydration. The x-ray powder pattern was of the perovskite type with a tetragonal distortion. It was indexed on a cell with $a = 5.593$ Å and $c = 5.628$ Å. This would be in the space group $P4mm$ with $Z = 1$. A differential thermal analysis of $CsSrCl_3$ indicated that a reversible heat effect occurs at 125 to 130 °C. It is presumed from analogy to other perovskite studies that it is cubic above this temperature.

¹The Powder Diffraction File. Compiled under the auspices of the Joint Committee for Powder Diffraction Standards. For information refer to Joint Committee on Powder Diffraction Standards, Diffraction Data Department, ASTM Building, 1916 Race Street, Philadelphia, Pa. 19103.

²National Bureau of Standards Monograph 25. Standard X-Ray Diffraction Powder Patterns. Sections 1 to 7 have been published. They are available from the U.S. Government Printing Office, Washington, D.C. 20402.

³Figures in brackets indicate the literature references at the end of this paper.

(2) CsCaCl₃

This material was prepared by melting together CsCl and anhydrous CaCl₂ above 910 °C. The x-ray powder patterns were improved by annealing at about 800 °C overnight. The material was found to be isotropic by petrographic microscope examination and the patterns could be indexed as a cubic perovskite with $a = 5.396 \text{ \AA}$ and $Z = 1$.

(3) CsHgCl₃

This compound was prepared by slow evaporation, or on cooling a saturated aqueous solution of CsCl and HgCl₂. This phase is reported to be cubic [29, 28], but the sample made in this laboratory was definitely double refractive when viewed under crossed nicols and its powder diffraction pattern showed definite splits in the higher angle lines. It was indexed as an orthorhombic distorted perovskite with $a = 7.688 \text{ \AA}$, $b = 10.878 \text{ \AA}$, and $c = 7.669 \text{ \AA}$ and $Z = 4$. There are several lines with very weak (< 1) intensities which can not be indexed with this cell. This suggests that it may have a more complex super lattice.

(4) RbCaCl₃

This sample was prepared by melting a mixture of RbCl and anhydrous CaCl₂ above 855 °C. It was found to be very weakly double refracting and to exhibit polysynthetic twinning by microscopical examination. The sample was very hygroscopic and x-ray powder patterns were made with the sample protected in a dry mount. The pattern could be indexed as an orthorhombic distorted perovskite, similar to NaZnF₃, with $a = 7.541 \text{ \AA}$, $b = 10.667 \text{ \AA}$ and $c = 7.469 \text{ \AA}$ and $Z = 4$.

(5) RbCdCl₃

When equimolar amounts of RbCl and CdCl₂ are fused together (above 500 °C) a form of RbCdCl₃ is produced which differs from that obtained by precipitation from solution at or near room temperatures. This material shows very low double refraction under crossed nicols. The x-ray powder pattern could be indexed as a tetragonal distorted perovskite with $a = 10.304 \text{ \AA}$, $c = 10.399 \text{ \AA}$ and with $Z = 8$. This form was found to be unstable at room temperature, inverting in a few days to the orthorhombic form described by MacGillavry [20]. Observations on the hot stage of a petrographic microscope show that the low (orthorhombic) form changes to this high form when heated to between 135 to 140 °C. At about 190 °C the high form loses its double refraction and it is presumed that it changes to an undistorted cubic perovskite form.

(6) KCaCl₃

This was produced by melting a 1:1 molar mixture of KCl and anhydrous CaCl₂ at about 900 °C. The compound was found to have a very low double refraction and showed polysynthetic twinning under crossed nicols. It was very hydroscopic and x-ray powder patterns were prepared with the sample in a protective dry mount. The pattern was indexed as an orthorhombic distorted perovskite with

$a = 7.551 \text{ \AA}$, $b = 10.44 \text{ \AA}$, $c = 7.251 \text{ \AA}$ and with $Z = 4$. This was assumed to be in the space group Pnma analogous to NaZnF₃ and BaTiO₃. This material appears to be identical with the natural occurring mineral, chlorocalcite [44].

(7) RbSrCl₃

This material was made by fusing RbCl and SrCl₂ together at about 700 °C. The material shows low double refraction under crossed nicols. The x-ray powder pattern was indexed as an orthorhombic distortion of the perovskite structure, with $a = 7.924 \text{ \AA}$, $b = 10.973 \text{ \AA}$ and $c = 7.631 \text{ \AA}$ and with $Z = 4$. This is assumed to be isostructural with NaZnF₃ and other similar compounds in space group Pnma. A dry mount was used in making the patterns of RbSrCl₃ because the material was hygroscopic.

(8) NH₄NiCl₃

For the preparation of this material NiCO₃ was first precipitated from a solution of NiCl₂ and (NH₄)₂CO₃. After this was washed, dried and analyzed it was mixed with NH₄Cl and moistened with HCl solution. This mixture was dried on a hot plate and then the anhydrous material was heated to 300 °C in a sealed glass tube. A microscopic examination showed this material to be uniaxial positive, which is consistent with similar data for hexagonal CsNiCl₃. It was indexed analogous to CsNiCl₃ in the space group P6₃mmc with $a = 6.9216 \text{ \AA}$, $c = 5.915 \text{ \AA}$ and $Z = 2$. The sample was hygroscopic and x-ray powder patterns were made with the sample protected in a dry mount.

(9) NH₄CoCl₃

This material was made by evaporating a 1 to 1 solution of NH₄Cl and CoCl₂ to dryness on a hot plate followed by a heating at 300 °C in a sealed tube for 2 hr. The sample was found by microscopical examination to be uniaxial positive, also similar to CsNiCl₃ and the x-ray powder pattern was so indexed, with $a = 6.967 \text{ \AA}$, $c = 6.010 \text{ \AA}$ and $Z = 2$. A dry mount was used when the x-ray powder patterns were made because this compound was hygroscopic.

(10) RbNiCl₃

This material was prepared by the same method as NH₄NiCl₃ using RbCl and NiCO₃. It was found to be isostructural with CsNiCl₃ and unlike the study by Allamagny [1] we indexed all lines of the powder diffraction pattern using half the c length similar to CsNiCl₃, with $a = 6.9534 \text{ \AA}$, $c = 5.906 \text{ \AA}$ and $Z = 2$.

3. Other ABCl₃ Compounds Prepared

The preparation, crystal system and reference used for indexing other ABCl₃ compounds made in this laboratory are given in table 1. For each of these a refined cell was determined from the indexed x-ray powder pattern. Information on the refined cell size and other information on the phases are given in tables 2 to 7. Details of the powder diffraction patterns are reported in the NBS Monograph 25 series.

TABLE 1. Preparation of other $ABCl_3$ compounds

Compound	Sys.	Method of Preparation	Structure Reference	Remarks
KCdCl ₃	Ortho.	Fused above 430 °C.	[4]	
RbCdCl ₃	Ortho.	Precipitated during cooling of sat. aqueous solution.	[20]	To perovskite > 140 °C [37].
NH ₄ CdCl ₃	Ortho.	Precipitated during cooling of sat. aqueous solution.	[5]	
NH ₄ CuCl ₃	Mono.	Slow evaporation of sat. solution in conc. HCl solution.	[44]	Very hygroscopic.
KCuCl ₃	Mono.	Evaporation of a sat. ethyl alcohol solution.	[44]	Very hygroscopic.
CsNiCl ₃	Hex.	CsCl and NiCO ₃ mixture, treated with HCl, dried, and heated to 300 °C in sealed glass tube.	[41]	Slightly hygroscopic.
CsCoCl ₃	Hex.	CsCl and CoCl ₂ , coprecipitated, dried, and heated at 300 °C in sealed glass tube.	[33]	Slightly hygroscopic.
CsCdCl ₃	Hex.	Fused above 550 °C.	[32]	
NH ₄ HgCl ₃	Tet.	(a) Fused at about 350 °C in sealed glass tube. (b) Precipitated on cooling of sat. aqueous solution.	[45]	
CsCuCl ₃	Hex.	Precipitated during cooling of a sat. aqueous solution.	[43]	
CsPbCl ₃	Tet.	Fused above 500 °C.	[25]	

4. Summary and Discussion

Tables 2 to 6 summarize the known crystallographic data of the compounds of this group. Also included is the card number of the x-ray powder pattern in the Powder Diffraction File (PDF), the melting point and relevant references. The tolerance factor given here is the figure formulated by Goldschmidt [14]. The factor, t , was defined as

$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_A)}$$

where R_A , R_B , and R_X are the ionic radii of A, B, and X respectively.

This factor was developed as an aid in forecasting the structure types to be expected in ABO_3 compounds, particularly those which will form perovskite type crystals. This factor is concerned only with relative atomic radii and does not take into consideration the type of bonding or polarization. It was found with oxides that perovskite type structures (with or without distortion) occurred when the tolerance factor is between 0.80 and 1.00.

A large number of the $ABCl_3$ compounds considered here occur in the perovskite form as shown in table 2. These had tolerance factors between 0.79 and 0.90. The simple cubic form of perovskite is a monomolecular cell with the B ions in 6 fold coordination and with these octahedral groups sharing corners. The larger A ions are in 12 fold coordination between these groups. As with the oxide perovskite, a number of distortions occur, only one of this group being cubic at room temperature ($CsCaCl_3$). The orthorhombic form is

derived from the cubic by a shear action leaving the two original edges equal. A new orthorhombic cell is achieved by drawing new a and c edges as diagonals in that face. In some cases doubling of cell edges is required to index all lines. These distortions in oxide perovskites are discussed by Megaw [23] and Naray-Szabo [27]. At higher temperatures many of these distorted forms go through a transition to the cubic form. Where the temperatures of transition are known, they are indicated in the table.

Table 3 gives data on $ABCl_3$ compounds which form in the $CsNiCl_3$ (hexagonal) type. This arrangement is isostructural with hexagonal $BaTiO_3$ and has, like perovskites, octahedral coordination around B but with an irregular 9 fold coordination around A. In the $ABCl_3$ compounds these have tolerance factors between 0.9 and 1.0, but it should be noted that the B elements involved are not those which have highly ionic bonding, but those which tend to show greater polarization. It can be seen that there is a variation of the relative length of c and therefore of Z . It is possible that the c length in a particular sample may be affected by the thermal history and the resultant degree of lack of stoichiometry which may result from heating compounds which have elements with variable valence.

Three compounds (see table 4), all with Cd, form orthorhombic crystals. This structure with irregular 6 and 9 fold coordination is described by MacGillavry and coworkers [20]. The K and NH_4Cu chlorides (see table 5) form a unique structure described by Willett and co-workers [44]. This arrangement has discrete planar Cu_2Cl_6 groups with irregular 9 fold coordination around the large cation.

The structure of CsCuCl_3 (table 6) was studied by Wells [43]. He found the Cu atoms surrounded by four Cl atoms in a square with two more Cl's at a greater distance. The structure of NH_4HgCl_3 as described by Harmsen [15] consists of HgCl_2 groups linked together. The NH_4^+ ions are surrounded with eight Cl^- 's.

It can be seen that almost all of these compounds had tolerance ratios between 0.8 and 1.0. While a number formed in perovskite structure, those with Cu, Cd, and other elements of high polarizability in the B position tended, regardless of the ratio, to form other structure types. In our study only one compound (RbCdCl_3) was found to crystallize in two distinct forms.

TABLE 2. Summary of ABCl_3 compounds of the perovskite type

Compound	Distortion type	Cell size (Å)	Space group	Z	Tolerance factor	Melting point °C	Polymorphism	PDF No.	Other references
RbSrCl_3	Orthorhombic	$a = 7.924$ $b = 10.973$ [40] $c = 7.631$	Pnma [40]	4	0.79	705° [10]			
KCaCl_3 (Chlorocalcite)	Orthorhombic	$a = 7.551$ $b = 10.442$ [40] $c = 7.251$	Pnma [40]	4	.79	752° [30]		20-18	[3] [24] [45]
CsPbCl_3	Tetragonal	$a = 5.584$ [38] $c = 5.623$	P4mm[25]	1	.82		Cubic > 46.9 °C [25]	18-366	[26]
RbCaCl_3	Orthorhombic	$a = 7.541$ $b = 10.667$ [40] $c = 7.469$	Pnma [40]	4	.83	855° [30]		20-16	
RbCdCl_3 (High form)	Tetragonal	$a = 10.304$ $c = 10.399$ [38]	P4mm [38]	8	.84	500° [9]	Cubic > 190 °C. Ortho at room temp. [38]	18-1104	[36]
CsSrCl_3	Tetragonal	$a = 5.593$ $c = 5.628$ [39]	P4mm[39]	1	.84	907° [10]		20-289	
CsHgCl_3	Orthorhombic	$a = 7.688$ $b = 10.878$ [40] $c = 7.669$	Pnma [40]	4	.85				[13] [27] [28] [29]
KMnCl_3	Tetragonal	$a = 10.02$ [8] $c = 9.97$	P4mm	8	.85	507° [8]	Cubic > 458°C [8]	19-975	[11] [35]
CsCaCl_3	Cubic	$a = 5.396$ [38]	Pm3m[38]	1	.88	910° [30]		18-338	
KMgCl_3	Orthorhombic	$a = 6.954$ $b = 6.971$ [6] $c = 9.922$	Pbnm or [6] Pbn2 ₁	4	.90			20-905	

TABLE 3. Summary of the $ABCl_3$ compounds of the $CsNiCl_3$ type

Hexagonal—Space Group $P6_3/mmc$ [41]							
Compound	Cell size		Z	Tolerance factor	Melting point ($^{\circ}C$)	PDF No.	Other references
	a (\AA)	c (\AA)					
RbMnCl ₃	7.165	17.82 [35]	6	0.89	571° [17]	20-999	[11] [21] [33]
KNiCl ₃	6.80	11.29 [1]	4	.89		16-111	
CsCdCl ₃	7.416	18.440 [38]	6	.89	545° [9]	18-337	[13] [21] [32] [36]
NH ₄ CoCl ₃	6.967	6.010 [39]	2	.90		18-89	
RbFeCl ₃	7.060	6.020 [34]	2	.91	501° [34]	19-1099	
RbCoCl ₃	7.0013	6.002 [39]	2	.92	485° [33]	17-638	[12]
NH ₄ NiCl ₃	6.9216	5.915 [39]	2	.92		20-98	
RbNiCl ₃	6.9534	5.906 [39]	2	.93		18-1122	[2]
CsMnCl ₃ *	7.288	27.44 [17]	9	.95	617° [17]	20-280	[11] [21]
CsFeCl ₃	7.237	6.045 [34]	2	.97	565° [34]	18-331	
CsCoCl ₃	7.203	6.032 [39]	2	.98	547° [33]	18-347	[37]
CsNiCl ₃	7.1700	5.941 [39]	2	.99		18-367	[1] [2]

*May be different space group.

TABLE 4. Summary of the $ABCl_3$ compounds of the $KCdCl_3$ type

Orthorhombic—Space Group $Pnma$ [4] [20]								
Compound	Cell size			Z	Tolerance ratio	Melting point $^{\circ}C$	PDF No.	Other references
	a (\AA)	b (\AA)	c (\AA)					
KCdCl ₃	8.785	14.584	3.9969 [38]	4	0.80	430°[9]	18-995	[4]
NH ₄ CdCl ₃	9.017	14.911	3.9896 [38]	4	.84		18-81	[4] [5] [20]
RbCdCl ₃	8.959	14.967	4.0346 [38]	4	.82	Tetragonal Perovskite type $> 140^{\circ}$ [38]	18-1103	[20] [36]

TABLE 5. Summary of $ABCl_3$ compounds of the $KCuCl_3$ type

Monoclinic—Space Group $P2_1/c$ [44]								
Compound	Cell size				Z	Tolerance factor	PDF No.	Other references
	a (\AA)	b (\AA)	c (\AA)	β				
KCuCl ₃	4.031	13.788	8.732	97°10' [40]	4	0.88	20-874	[44]
NH ₄ CuCl ₃	4.030	14.187	8.978	96°28' [40]	4	.82	20-17	[44]

TABLE 6. Summary of $ABCl_3$ compounds of miscellaneous types

Compound	System	Space group	Cell size		Z	Tolerance factor	Melting point °C	PDF No.	Other references
			a(Å)	c(Å)					
NH_4HgCl_3	Tet.	P4/mmm [15]	4.1977	7.9353 [38]	1	0.79	350° [16]	18-116	
$CsCuCl_3$	Hex.	P6 ₃ 22 [43]	7.2165	18.180 [38]	6	.90		18-347	[19]

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(Paper 73A6-576)