

A Ferroelectric Chloride of Perovskite Type

Crystal Structures of CsGeCl₃

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Cesium germanium(II) chloride is a possible model compound for BaTiO₃. Two crystal forms exist with a transition temperature of 155°C. The structures of the two forms have been determined by X-ray analysis. The low temperature form is rhombohedral, the space-group is *R* 3, (No. 146), with $a = 5.44_4$ Å, $\alpha = 89.63^\circ$, and one formula unit per unit cell. The structure is of deformed perovskite type. The high temperature modification is cubic; the space-group is *Pm*3*m* (No. 221) with $a = 5.47_4$ Å. The structure is of ideal perovskite type.

Refinement was carried out by systematic variation of geometric and thermal parameters. Atomic coordinates, temperature factors and other crystallographic data are reported.

Measurements of differential thermal analysis, of electrical conductance, of dielectric constant and the crystallographic results show that CsGeCl₃ exhibits the characteristic behaviour of a ferroelectric.

In Goldschmidt's¹ sense, CsGeCl₃ is a possible model compound for BaTiO₃. It crystallizes with a perovskite-like structure. The ratio between the lattice constants of CsGeCl₃ and BaTiO₃ is about 1.35. Using Pauling's radii, the following ratios are obtained:

$$r_{\text{Cs}^+}/r_{\text{Ba}^{2+}} = 1.25 \quad r_{\text{Cl}^-}/r_{\text{O}^{2-}} = 1.37 \quad r_{\text{Ge}^{2+}}/r_{\text{Ti}^{4+}} = 1.30, \text{ assuming a } r_{\text{Ge}^{2+}} \text{ of } 0.90 \text{ \AA.}$$

Few chlorides could be model compounds for BaTiO₃. The cesium ion is the only monovalent ion which is large enough to fit into an MCl₃ close-packing of metal and chloride ions, and few divalent ions fit into the octahedral holes of the chloride packing. Only Ca²⁺, Cd²⁺, Cu²⁺, and Ge²⁺ have approximately suitable sizes. The crystal structure of CsCdCl₃ is described by Siegel and Gebert.² Møller³ has determined the structures of CsPbCl₃ and other cesium-lead double halides.

CsGeCl₃ was prepared originally by Karantaesis and Capatos.⁴ The compound used in this investigation was prepared by a modified procedure. The crystals occur generally as flakes or needles and are often twinned. They are birefringent; the birefringence disappears around 155°C and is reestablished on cooling. The crystals are strongly piezoelectric, a qualitative test for pyroelectricity was positive.

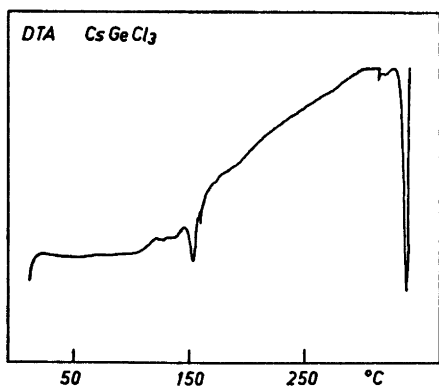


Fig. 1. DTA diagram of CsGeCl₃.

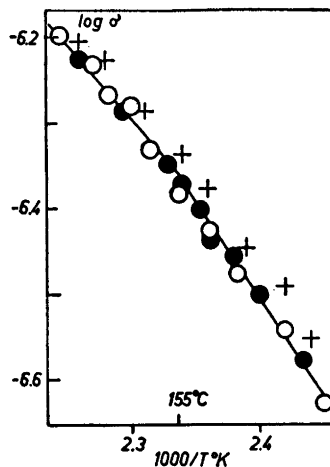


Fig. 2. Logarithm of specific electrical conductance of CsGeCl₃ as function of temperature.

A differential thermal analysis showed a phase transformation at 155°C (Fig. 1). Measurements of electrical conductance were carried out on a pressed and sintered powder tablet. The plot of \log (specific conductance) versus $1000/T$ shows a discontinuity at 155°C (Fig. 2).

The activation energy which can be calculated from this plot is higher for the low temperature form.

The dielectric constant was measured on the same powder tablet as a function of temperature and was found to be about 1500 at 25°C, rising to 5800 at 155°C and again decreasing above the Curie point. The measurements are shown in Fig. 3.

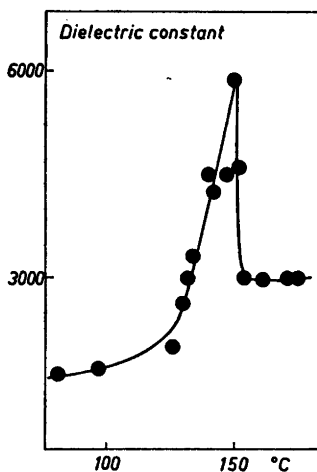


Fig. 3. Dielectric constant of CsGeCl₃ as function of temperature.

Table 1. Lattice constants and densities.

	a (Å)	α	density, calc.	density, obs.
25°C	5.444	89.63	3.22 g/cm ³	3.15 g/cm ³
75°C	5.448	89.77		
110°C	5.453	89.85		
175°C	5.475	90.00		

Table 2. Coefficients employed in structure factor calculations.

$f(s) = Z - s^2/(a + b s + c s^2 + d s^3 + e s^4)$ $s = \sin \Theta/\lambda$			
	Cs	Ge	Cl
Z	55	32	17
a	0.00242239	0.00335550	0.00530062
b	-0.00321281	-0.00365058	0.00310457
c	0.06585695	0.1217671	0.02022903
d	-0.08366765	-0.1875032	0.1906431
e	0.04958198	0.1164589	-0.1599024

From Guinier powder photographs the lattice of the low temperature form was found to be rhombohedral and the lattice of the high temperature form was found to be cubic.

Single crystal photographs of the low and of the high temperature forms showed no splitting of spots and were in agreement with findings from the powder photographs. The crystals were optically of good quality.

EXPERIMENTAL

Chemistry. CsGeCl₃ was prepared by reacting a solution of Ge(OH)₂ in conc. HCl with a solution of CsCl, Merck analytical grade, in conc. HCl. Ge(OH)₂ was prepared from purified GeO₂, 99.999 %, Light. GeO₂ was melted with NaOH in a silver crucible. The product was dissolved in water and reduced with H₃PO₂ as described by Everest and Terry.⁵ H₃PO₂ was prepared from pure Merck NaH₂PO₂, H₂O. Operations on reduced materials were performed in a glove-box under oxygen free nitrogen. CsGeCl₃ precipitated immediately and was recrystallized from a solution of one part conc. HCl and one part absolute alcohol, giving colourless crystals of the compound. The crystals were dried in vacuum over P₂O₅. Chloride was determined as AgCl; CsGeCl₃ was decomposed by melting with NaOH containing KNO₃. (Found: Cl 34.35. Calc. for CsGeCl₃: Cl 34.10).

X-Ray technique. Single crystal fragments of about 0.4 mm length and with rectangular dimensions of about 0.03 × 0.05 mm² were selected under the polarizing microscope and were investigated by Weissenberg, Precession and Rimsky retigraph methods using Zr-filtered Mo-radiation. Integrated precession and Weissenberg photographs were taken at room temperature of 4 crystals. Integrated Weissenberg photographs were taken of a fifth crystal of the ($h, k, 0$) zone at 180° ± 4°C. Intensities were measured photometrically.

Table 3. Atomic coordinates and temperature factors.

Weissenberg data, 57 reflections, $R = 6.1\%$, Crystal 1, 25°C.						
Atom	x/a	y/a	z/a	$\sigma x/a$	$B (\text{Å}^2)$	σB
Cs	0	0	0		3.15	0.13
Ge	0.481	0.481	0.481	0.0028	0.82	0.14
Cl	0.4974	0.4931	0.0639	0.0029	2.69	0.27
Weissenberg data, 113 reflections, $R = 8.1\%$, Crystal 2, 25°C.						
Atom	x/a	y/a	z/a	$\sigma x/a$	$B (\text{Å}^2)$	σB
Cs	0	0	0		2.41	0.08
Ge	0.482	0.482	0.482	0.0016	0.90	0.09
Cl	0.4901	0.4952	0.0581	0.0023	3.52	0.21
Precession data, 127 reflections, $R = 7.6\%$, Crystal 3, 25°C.						
Atom	x/a	y/a	z/a	$\sigma x/a$	$B (\text{Å}^2)$	σB
Cs	0	0	0		3.70	0.06
Ge	0.483	0.483	0.483	0.0011	1.34	0.06
Cl	0.5024	0.5008	0.0553	0.0014	3.41	0.11
Precession data, 132 reflections, $R = 8.7\%$, Crystal 4, 25°C						
Atom	x/a	y/a	z/a	$\sigma x/a$	$B (\text{Å}^2)$	σB
Cs	0	0	0		1.94	0.08
Ge	0.4874	0.4874	0.4874	0.0035	3.25	0.20
Cl	0.4915	0.4861	0.0567	0.0037	5.70	0.41
Weissenberg data, 16 reflections, $R = 7.4\%$, Crystal 5, 180°C						
Atom	x	y	z		$B (\text{Å}^2)$	σB
Cs	0	0	0		7.46	0.51
Ge	0.5	0.5	0.5		0.85	0.27
Cl	0.5	0.0686	0.5		3.56	1.43

Lorentz-polarisation corrections were performed by digital computation. No absorption correction was applied.

Two powder cameras of Guinier type were employed. One was a quadruple camera of de Wolff's design, employing a monochromator crystal bent in the form of a logarithmic spiral. A sample holder, which could be heated electrically to 200°C, was employed. Exposures were made with this camera at various temperatures (Table 1).

The other camera was built in the workshop of the institute. The monochromator crystal is a cylindrically ground and bent quartz crystal with a radius of curvature of 500 mm. Attention is drawn to the advantage of using a microfocuss tube as X-ray source in the Guinier technique. Using a focal line of dimensions $0.1 \times 6 \text{ mm}^2$ the α_1 or the α_2 components of Cu-radiation could be selected at will with a small change in distance between monochromator and X-rays focus.

With the de Wolff camera it was not possible to isolate one component only of the α -doublet because of the aberration of the logarithmic spiral.

In the powder patterns Ge (99.999 %, Light) was used for reference.

Other physical measurements. Cylindrical tablets of 10 mm diameter and 0.8 mm thickness were pressed. They were sintered at 200°C for 24 h in a purified nitrogen atmos-

Table 4. Interatomic distances in Å.

Low temperature form		High temperature form	
Cs — Cl	3.851 ± 0.010	Cs — Cl	3.87
Cs — Cl	3.854 ± 0.010	Ge — Cl	2.74
Cs — Cl	3.844 ± 0.010		
Cs — Cl	3.888 ± 0.010		
Ge — Cl	3.127 ± 0.012		
Ge — Cl	2.318 ± 0.012		

phere. The tablets were painted with silver paste Auromal 40 and dried. All measurements on the tablets were carried out in a nitrogen atmosphere.

Electrical conductance was measured, using a constant potential d.c. source (5 V), by measuring the voltage drop over the specimen.

The dielectric constant was measured at frequencies of 1 kHz and 5 kHz using a bridge circuit allowing for compensation of the conductivity of the sample. Readings were taken at temperatures kept constant within one degree. The equipment was tested with a BaTiO₃ tablet of the same size as the CsGeCl₃ tablet.

Differential thermal analysis was carried out with a Du Pont 900 Differential Thermal Analyzer.

CRYSTAL DATA

The low temperature form is rhombohedral with space group *R* 3, (No. 146). Above the Curie point the lattice is cubic within accuracy of measurements and the probable space group is *Pm*3*m*, (No. 221).

Lattice constants at various temperatures are given in Table 1.

The refinement was carried out using the method of Bhuiya and Stanley.⁶ An ALGOL programme written by Danielsen⁷ was used. The programme allows variation of three geometric parameters and one isotropic thermal parameter for each atom. Atomic scattering factors were calculated by Bassi's method⁸ using values from *International Tables of Crystallography*, Vol. III. The coefficients used are given in Table 2.

The intensity data from each crystal were treated separately. The agreement between calculated and observed structure factors is good. A total of about five hundred structure amplitudes was measured. A table of observed and calculated structure factors has been deposited with the editor. The table is not printed to save space. The authors will gladly send tables to interested crystallographers on request.

In Table 3 the results of the different computations are given.

A Fourier projection on 001 (Fig. 4) of the high temperature form was calculated using phases determined by Cs and Ge alone. The projection indicates a marked anisotropic vibration of the Cl-atoms.

Allowance was made for this by placing two half Cl-atoms a small distance apart across the mirror plane and using this distance and one common temperature factor as parameters in the refinement beside the thermal parameters of the cesium atom and the Ge atom.

Table 4 gives interatomic distances.

Table 5. Indexing of the powder pattern of CsGeCl₃.

25°C $a = 5.44_4 \text{ \AA}$, $\alpha = 89.63^\circ$					175°C $a = 5.47_6 \text{ \AA}$						
<i>d</i> obs	<i>d</i> calc	<i>h</i>	<i>k</i>	<i>l</i>	<i>I</i>	<i>d</i> obs	<i>d</i> calc	<i>h</i>	<i>k</i>	<i>l</i>	<i>I</i>
5.484	5.444	1	0	0	vw	3.895	3.871	1	1	0	s
3.862	3.862	1	1	0	s	3.167	3.161	1	1	1	m
3.840	3.837	-1	1	0	s	2.740	2.737	2	0	0	s
3.161	3.163	1	1	1	w	2.235	2.235	2	1	1	m
3.134	3.136	-1	-1	1	m	1.935	1.936	2	2	0	w
2.721	2.722	2	0	0	s	1.732	1.731	3	1	0	w
2.429	2.428	2	-1	0	vw	1.651	1.651	3	1	1	w
2.230	2.234	2	1	1	w	1.579	1.581	2	2	2	w
2.218	2.220	2	-1	1	s	1.463	1.463	3	2	1	w
1.930	1.931	2	2	0	m						
1.919	1.918	2	-2	0	m						
1.815	1.815	3	0	0	vw						
1.725	1.725	3	1	0	m						
1.717	1.718	3	-1	0	m						
1.647	1.648	3	1	1	vw						
1.640	1.640	3	-1	1	w						
1.568	1.568	2	-2	2	w						
1.464	1.462	3	1	2	w						
1.455	1.456	3	-1	2	w						
1.451	1.452	3	-2	1	w						
1.362	1.361	4	0	0	w						

DISCUSSION

The coordinates arrived at from intensity measurements on crystals 1–3 do not differ significantly.

Considering the good agreement between observed and calculated structure factors we conclude that the structure of the low temperature form is essentially correct. The thermal parameters exhibit less mutual consistency. These parameters also include absorption effects and are somewhat dependent upon the shape of the crystals.

Refinement of data from the crystal labelled No. 4 in Table 3 gave coordinates which differ somewhat from the coordinates obtained from the three other crystals. Crystal No. 4. deviates less from ideal perovskite structure than the other crystals and its atoms has apparently large vibration amplitudes. The standard deviations of coordinates and temperature factors are large compared with those of crystals 1–3. We suppose that this crystal exhibits a multi-domain structure.

We have collected much less data at high temperature than at low temperature. Our conclusions about this cubic structure are therefore less certain. If the space group is correctly determined no variation of the geometric parameters is possible. The agreement between observed and calculated structure factors is as good as can be expected with photographic data. The influence of the thermal parameters is so big, however, that a static description of the crystal structure appears to be inadequate and a satisfactory dynamical

Fig. 4. Fourier projection of CsGeCl_3 at 180°C .

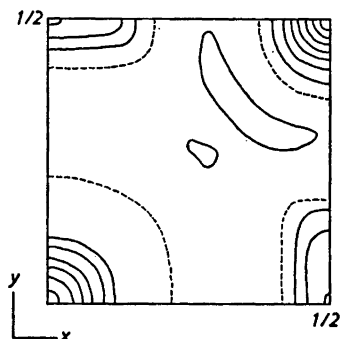
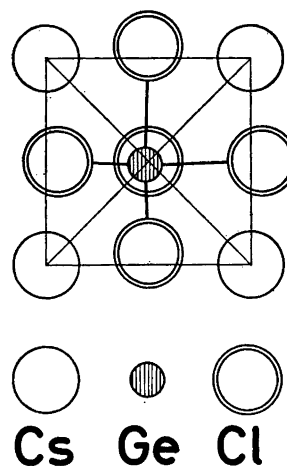


Fig. 5. Projection of unit cell of CsGeCl_3 at room temperature.



description cannot be given on basis of X-ray data alone. The apparent anisotropic movement of the Cl-atoms and the size of the temperature factors indicate a somewhat disordered structure.

The deformation of the low temperature form can be interpreted most simply as a movement of the germanium atoms along the threefold axis. The chlorine atoms are also displaced from ideal perovskite positions (Fig. 5). However, the cesium-chlorine distances vary hardly significantly: from 3.85 to 3.88 Å. The Cl-lattice differs little from face-centered cubic packing. The Ge—Cl distances are significantly different: Three Ge—Cl distances of 3.13 Å and three others of 2.31 Å. In the high temperature form the Ge—Cl distance is 2.74 Å, close to the mean of the distances of the two low temperature distances. The Cs—Cl distance of the high temperature form is not significantly different (3.87 Å) from any of the Cs—Cl distances of the low temperature form.

The crystal structure offers a qualitative explanation of the piezoelectricity and pyroelectricity of rhombohedral CsGeCl_3 , and of the existence of a large

spontaneous electric dipole moment. It remains to be explained why the crystal exhibits the polar structure below the transition point. A pure electrostatic description is inadequate.

With the simple equipment used for dielectric measurements our results are necessarily of limited value.

The dielectric constant is unusually large for a chloride. It was found to be of the same order of magnitude as for a pressed powder tablet of BaTiO_3 . Fig. 3 shows that a peak in dielectric constant was found at the transition temperature. CsGeCl_3 has many properties characteristic of a ferroelectric.

We have not observed a tetragonal phase for CsGeCl_3 but have not searched systematically for phases other than the two which we have found.

It may prove to be an important advantage for investigations of single crystals that CsGeCl_3 crystals can be grown from solutions at temperature below the Curie point. Oxide perovskite crystals generally have to be grown from melts at temperatures above the Curie points. Although we have prepared microcrystals of BaTiO_3 by hydrothermal methods⁹ and hope to get larger crystals by use of improved equipment, crystals of BaTiO_3 are most likely to be grown at temperatures above the Curie point.

Acknowledgements. We wish to thank Professor V. Frank, Physics Department, Technical University of Denmark, for measuring the piezoelectricity of CsGeCl_3 , and Mr. J. C. Madsen, Physics Department, Aarhus University, for helping us with the measurements of the dielectric constant.

Professor L. T. Muus, Department of Physical Chemistry, Aarhus University, is thanked for placing the differential thermal analyser at our disposal. Mr. J. Danielsen and Miss R. Grønnebæk are thanked for the use of their Algol programmes.

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Received December 12, 1964.