AN INVESTIGATION OF GADOLINIUM MIXED HALIDES

MICHIGAN STATE UNIVERSITY

Thesis for the Degree of M. S.

LAURA R. SEIDEMANN

1976

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ABSTRACT

AN INVESTIGATION OF GADOLINIUM MIXED HALIDES

By

Laura R. Seidemann

A series of gadolinium mixed halides has been prepared. The mixed halides were prepared by: (1) sealing in an ampoule a 1:0.5:$\underline{n}$ (where $\underline{n}$ = 3.5 and 4) molar ratio of Gd:$HgCl_2$:HgI_2 and heating in a furnace overnight at 300°C, with subsequent sublimation of the mercury contaminants and, (2) heating a $GdCl_3$ + GdI_3 melt. The far-infrared and X-ray powder diffraction data indicated that as the temperature is raised the composition of the sample changes. The product formed from the molar ratio 1:0.5:4 produces a sublimate which appears to have a constant composition regardless of the temperature of sublimation.

The far-infrared spectra of both $GdCl_3$ and GdI_3 are reported together with those of the mixed halides.

AN INVESTIGATION OF GADOLINIUM MIXED HALIDES

By

Laura R. Seidemann

A THESIS

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1976

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3 T
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4 A
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5 P
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6 F

7 F

8 F
f

9 F
f

10 F
f

11 F

12 F

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CHAPTER I

INTRODUCTION

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INTRODUCTION

The literature abounds with reports of divalent and trivalent mixed halides. Early work on alkaline earth fluoride-chlorides and fluoride-bromides dates back to the 1890s.[1] Lead mixed halides, along with those of other Group 4 metals, have been known for some time. Several mixed halides of trivalent and tetravalent uranium were reported in the late 1950s.[2,3] In 1973, EuFCl[4-6] was synthesized, and shortly thereafter, EuFBr was prepared,[8] followed by EuFI[9] and EuClBr.[10] Until recently, no trivalent lanthanide mixed halide has been reported, but Haschke[7] predicted on the basis of structural relationships that such phases should exist.

The reported mixed halides of uranium, Table 1, are thought to result from the formation of solid solutions. The crystal structures of the trivalent and tetravalent uranium halides are such that it is possible to substitute certain halogen atoms for others, thus yielding a wide range of stable compositions.

According to the reports, halogen displacement reactions will not work for the preparation of any uranium(III) mixed halide. The methods used for the preparation of uranium(IV) mixed halides either treat the trivalent uranium halide with a halogen of higher atomic number or allow two different tetravalent halides to react at high temperatures. The uranium(III) halides can be prepared by thermal decomposition or hydrogen reduction of a mixed uranium(IV) halide or by fusion of two trivalent halides. No work other than the initial characterization of these compounds has been reported. In addition, very little is known about their physical and chemical properties.

Table 1.

Uranium

Uranium

Table 1. Uranium Mixed Halides[3]

	Compound	Preparation
Uranium(III)	UCl_2Br	$2UCl_3 + UBr_3$ (fusion)
	$UClBr_2$	$UClBr_3 + H_2$
	UCl_2I	$UCl_2I_2 \rightarrow UCl_2I + 1/2I_2$
	$UClI_2$	$UCl_3 + 2UI_3$ (fusion)
	UBr_2I	$UBr_2I_2 \rightarrow UBr_2I + 1/2I_2$
	$UBrI_2$	$UBrI_3 \rightarrow UBrI_2 + 1/2I_2$
Uranium(IV)	UF_3Cl	$UF_3 + 1/2Cl_2$ (310°)
	UF_2Cl_2	$UO_2F_2 + 2CCl_4$ (450°)
	UF_3Br	$UF_3 + 1/2Br_2$ (250°)
	UF_3I	$UF_3 + 1/2I_2$ (250°)
	UCl_3Br	$UCl_3 + 1/2Br_2$ (500°)
	UCl_2Br_2	$UCl_4 + UBr_4$ (fusion)
	$UClBr_3$	$UCl_4 + 3UBr_4$ (fusion)
	UCl_3I	$UCl_3 + 1/2I_2$ (500°)
	UCl_2I_2	$UCl_4 + UI_4$ (fusion)
	$UClI_3$	$UCl_4 + 3UI_4$ (fusion)
	UBr_3I	$UBr_3 + 1/2I_2$ (500°)
	UBr_2I_2	$UBr_4 + UI_4$ (fusion)
	$UBrI_3$	$UBr_4 + 3UI_4$ (fusion)

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Two different methods for preparing EuFX (X = Cl, Br, I) have been reported. The preparatory schemes involved (1) reaction of the dehydrated Eu(II) halide with the corresponding fluoride, and (2) fluorination of the appropriate dihalide with MnF_2. These Eu(II) mixed halides, like the corresponding alkaline earth mixed halides, have been shown to crystallize in the PbFCl structure type (Table 2). The compound PbFCl forms a layered, tetragonal structure in which the Pb(II) cation is surrounded by five chlorine and four fluorine anions. For the M(II) (M = Ba, Sr, Eu, Ca) mixed halides, which also belong to the PbFCl structure type, the metal coordination sphere may be defined in two ways. The structure of the fluoride-chlorides can be described as a three-dimensional cation coordination lattice, whereas that of the fluoride-iodides may be visualized as a layered structure. These structural differences have been discussed in detail.[11]

Two mixed halide phases of EuClBr have been prepared. These are: $EuCl_{0.46}Br_{1.56}$ and $EuCl_{0.16}Br_{1.85}$. The methods used to prepare these mixed halides involved (1) heating, <u>in vacuo</u>, a 1:1.25 molar ratio of $EuCl_3$:NH_4Br with subsequent removal of the excess ammonium halide, and (2) dehydration of a mixture which consists of the hydrated lanthanide halide and ammonium bromide. The unit cell of crystals grown from the first phase was determined to be orthorhombic with lattice parameters: $\underline{a} = 7.879_7 \pm 0.0003_5$, $\underline{b} = 9.197_7 \pm 0.004_3$, and $\underline{c} = 4.611_1 \pm 0.002_0$ Å. The structure was solved based on the atomic coordinates of $EuCl_2$ ($PbCl_2$ structure

Table

CaFCl	
CaFBr	
CaFI	
SrFCl	
SrFBr	
SrFI	
EuFCl	
EuFBr	
EuFI	
BaFCl	
BaFBr	
BaFI	
EuFCl	

Table 2. Lattice Parameters of MFX Compounds With the PbFCl Structure Type.[9]

	a	c
CaFCl	3.894(3) Å	6.809(6) Å
CaFBr	3.883(1)	8.051(3)
CaFI	4.29	8.70
SrFCl	4.129(2)	6.966(4)
SrFBr	4.218(2)	7.337(5)
SrFI	4.253(2)	8.833(7)
EuFCl	4.118(2)	6.971(3)
EuFBr	4.219(2)	7.312(5)
EuFI	4.249(2)	8.732(4)
BaFCl	4.391(3)	7.226(4)
BaFBr	4.503(2)	7.435(4)
BaFI	4.654(3)	7.977(5)
EuFCl	4.127	6.984[4]
	4.075(6)	7.080(8)[5]

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type) with various concentrations of bromide ion substituted for chloride ion. The substitution of the bromide ion for a chloride was found to be selective rather than random.

The intent of this work was the preparation of mixed halide phases of gadolinium and possibly a study of their structural properties.

Gadolinium was chosen, primarily because it usually exhibits only one oxidation state, +3, and thus appears to be a more typical lanthanide than does europium. The halogens, I-Cl, were chosen primarily to simplify analytical problems.

CHAPTER II

BACKGROUND AND THEORETICAL CONSIDERATIONS

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PREPARATION OF ANHYDROUS LANTHANIDE HALIDES

Numerous methods have been reported in the literature for preparing anhydrous lanthanide halides. Of the anhydrous halides, the chlorides have been studied the most.

Although lanthanide halides can be made directly from the elements, such schemes were limited by the lack of availability of pure metals. When all metal salts were considered, oxides appeared to be the most likely starting candidates because they were available in the highest purity. In addition, many elements occur naturally in the form of their oxides.

Taylor[12] reviewed several methods for preparing lanthanide halides. He concluded that many methods which yield pure chlorides use the oxides with volatile reagents that act simultaneously as reducing and chlorinating agents. Among the first compounds used were volatile halides of carbon such as: CCl_4, $HCCl_3$, $COCl_2$. Later reactions used SCl_2, S_2Cl_2, and $SOCl_2$ as reactants. Many of these methods yield impure products.

Hydrated salts of the rare earth metals are readily obtained by reaction of the sesquioxides with hydrohalic acid solutions. Attempts to dehydrate these salts often lead to their hydrolysis:

$$LnX_3 \cdot H_2O \rightarrow LnOX + 2HX$$

where X = Cl, Br, or I. The anhydrous triiodide also undergoes decomposition in the presence of oxygen:

$$LnI_3 + 1/2O_2 \rightarrow LnOI + I_2 \ .$$

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Hydrolysis can be prevented by performing the dehydration in a completely moisture and oxygen free atmosphere of the hydrogen halide.

Taylor and Carter[13] have described a general method for the preparation of lanthanide(III) halides. It consists of heating, in vacuo, a mixture of the hydrated lanthanide halide with the appropriate ammonium halide to first expel the water and then the ammonium halide. The ammonium halide is thought to prevent hydrolysis of the lanthanide halide, thus permitting a pure product to be obtained.

Recently, a new method for preparing anhydrous lanthanide trihalides was described by Carter and Murray.[14] This method involves the reaction of the rare earth metal with excess mercuric halide. This technique can be utilized at the present time because of the availability of pure metal samples.

While all of these methods yield suitable products if pure reactants are used, most are limited to small sample sizes. The Carter-Murray procedure has the added feature of allowing preparation of gram size samples.

STRUCTURAL INFORMATION

Structural data for the lanthanide(III) chlorides and iodides are illustrated in Table 3.

Gadolinium trichloride has a UCl_3 structure type. The metal ion is nine-coordinated and is surrounded by chloride ions which define a tricapped trigonal prism. The three chlorides in the

Table

METAL
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

Table 3. Structural Types Reported For Lanthanide Halides

METAL	HALIDE			
	Chloride	Ref.	Iodide	Ref.
La	UCl_3	16	$PuBr_3$	17
Ce	UCl_3	18	$PuBr_3$	17
Pr	UCl_3	18	$PuBr_3$	17
Nd	UCl_3	16	$PuBr_3$	17
Pm	UCl_3	2	---	18
Sm	UCl_3	18	BiI_3	17
Eu	UCl_3	16	---	18
Gd	UCl_3	16	BiI_3	17
Tb	$PuBr_3$	2	BiI_3	17
Dy	YCl_3	18	BiI_3	17
Ho	YCl_3	18	BiI_3	17
Er	YCl_3	18	BiI_3	17
Tm	YCl_3	18	BiI_3	17
Yb	YCl_3	18	BiI_3	17
Lu	YCl_3	18	BiI_3	17

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tricapped positions lie in the same plane as the metal, approximately perpendicular to the faces of the prism. The structural details were determined by Au and Au[15] and refined by Morison.[16]

Gadolinium triiodide crystallizes in the hexagonal BiI_3 structure type. The metal resides at the center of an almost perfect octahedron of iodide ions. The structure of GdI_3 was determined by Asprey, Keenan and Kruse[17] through powder diffraction techniques.

THE APPLICATION OF FAR INFRARED SPECTROSCOPY

The region beyond 650 cm^{-1} is considered to be the "far infrared." This region is important in the study of organometallic and inorganic compounds with heavy atoms and non-ionic bonds.

The vibrations of molecules are not random but occur at specific frequencies determined by the atomic masses and the strengths of the chemical bonds. The vibrational frequencies can be expressed as:

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

where $\bar{\nu}$ is the frequency of vibration, c is the speed of light, k is the force constant, and μ is the reduced mass of the atoms involved.

The spectrum obtained depends on the physical state of the sample. Gaseous samples usually exhibit rotational fine structure. A solution does not because molecular collisions in the condensed phase occur before a rotation is completed. In addition, frequency shifts, band splitting and additional bands appear in the liquid and solid states. Frequently, the additional bands in the solid state spectrum appear below 300 cm^{-1}.[19]

The bands below 300 cm^{-1} are often caused by lattice vibrations, i.e., translational and torsional motions of the molecules in the lattice. These vibrations can interact with the intramolecular vibrations to form combination bands and can cause pronounced frequency shifts. An additional complication arises if the unit cell of the crystal contains more than one chemically equivalent molecule. The vibrations of the individual molecules can then couple with each other and give rise to frequency shifts and band splittings.

The low-frequency molecular vibrations found in the far-infrared are particularly sensitive to the overall structure of the molecule. The symmetry of the surroundings of a molecule in the unit cell, termed the "site symmetry," determines the selection rules. The general problem of the effect of site symmetry on the selection rules has been treated theoretically.[20,21] Bands that are forbidden in the gaseous state often appear in the solid, and degenerate vibrations in the gaseous state are split in the solid.

As a result of all these possible complications, the interpretation of spectra obtained on solids is difficult.

POTENTIOMETRIC DETERMINATION OF CHLORIDE AND IODIDE

The wet chemical technique involved potentiometric titrations and has been thoroughly described in the literature.[22]

SOLID SOLUTIONS

Solids are capable of dissolving other materials to form what is termed a solid solution.[23,24] Thus, a solid solution is simply a solid phase which contains more than one component. The phase rule

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makes no distinction as to the state of the phase (gas, liquid or solid) that dissolves; it only deals with the number of phases that are present. Therefore, most of the phase diagrams typical of liquid-vapor and liquid-liquid systems have counterparts among the solid-liquid or solid-solid systems.

Solid solutions can form between two or more components provided that their atomic radii and valence electronic and crystal structures are similar. Although these conditions constitute good guidelines, they are not necessarily adhered to.

Based on structural grounds, two general classes of solid solutions can be distinguished. A substitutional solid solution is one in which solute atoms or groups of atoms are substituted for solvent atoms or groups. This type of substitution is limited by the size of the atoms or groups. An intersitial solid solution is one in which solute atoms or groups of atoms occupy the interstices of the solvents crystal structure. However, the solute atoms must be small compared to the solvent atoms in order to fit in the interstices.

Just as two liquids can be partially miscible, so also may two solids. Thus if the components are completely miscible in the solid state, the solid solution constitutes one phase, and a continuous solid solution can be formed. If there is only partial miscibility, a broken series of phases may be formed. The crystalline solid solutions can be formed either by sublimation or from the liquid phase.

Binary systems which form solid solutions may exhibit either a maximum or minimum in melting point. These liquidus-solidus curves have an appearance similar to that of the liquid-vapor curves in

systems which form azeotropes. The mixture having the composition of the maximum or minimum of the curve melts sharply and simulates a pure substance in this respect, as does an azeotrope.

CHAPTER III

EXPERIMENTAL MATERIALS, EQUIPMENT AND PROCEDURES

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CHEMICALS

(a) gadolinium oxide, 99.9%, Michigan Chemical Corp., St. Louis, MI; (b) gadolinium metal sponge, 99.9%, Lunex Co., Davenport, IA; (c) potassium nitrate, mercuric chloride, sodium sulfite, cupric sulfate and potassium iodide, reagent grade, Matheson Coleman and Bell, Norwood, OH; (d) sodium chloride, reagent grade, Allied Chemical, New York, NY; (e) mercuric iodide, reagent grade, Mallinkrodt Chemical Works, St. Louis, MO; (f) ammonium chloride, certified ACS, Fisher Scientific Co., Fair Lawn, NJ; (g) argon, Air Reduction Co. Inc., New York, NY; (h) nitrogen, technical prepurified, Air Reduction Co. Inc., New York, NY; (i) silver nitrate, 99.9%, J. T. Baker Chemical Co., Phillipsburg, NJ; (j) mercury, hydrochloric and nitric acid, analytical reagent, Mallinckrodt, St. Louis, MO; (k) agar, laboratory grade, Fisher Scientific Co., Fair Lawn, NJ. Chemicals were used as received without further purification.

MATERIALS

(a) vitreous carbon boats, Beckwith Carbon Corp., Van Nuys, CA; (b) quartz tubing, Englehard Industries, Inc., Hillsdale, NJ; (c) platinum, J. Bishop and Co., Malvern, PA; (d) fluorolube, Hooker Chemical Corp., Niagara Falls, NY; (e) parafilm "M," American Can Co., Neenah, WI; (f) mineral oil, Fisher Scientific Co., Fair Lawn, NJ.

PREPARATIVE PROCEDURES AND EQUIPMENT

Anhydrous Lanthanide(III) Chlorides

Gadolinium trichloride was prepared according to the methods of both Taylor and Carter[13] and Carter and Murray.[14]

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A. Taylor-Carter Procedure

Reagent grade ammonium chloride was mixed with gadolinium sesquioxide in a 6:1 molar ratio. This mixture was then added to 100 ml of 6 N HCl and the mixture dissolved with heating. This oxide, like those of the other heavier lanthanides, did not dissolve until the mixture was boiled. The solution was then gently evaporated to dryness and towards the end of the evaporation, was stirred vigorously to prevent the white solid from sticking to the beaker.

The white powder was then transferred to the drying vessel shown in Fig. 1. The vessel was evacuated and the sample heated at 225°C for approximately 8 hours to remove the water. The temperature was then increased to 300°C and maintained for ∿11 hours to sublime the NH_4Cl. The apparatus was permitted to cool, the furnace was removed, and the drying vessel was sealed off under vacuum. The ampoule thus formed was then transferred into the argon-filled glove box for storage and future handling.

This crude $GdCl_3$ was subsequently sublimed in an outgassed quartz vessel,[3] as shown in Fig. 2. Sublimation was effected by heating the sample at 950°C for 15 minutes in high vacuum ($\sim 10^{-5}$ torr). The apparatus was allowed to cool and the sublimation vessel was transferred from the quartz heating tube to a transfer tube under a high argon flow. The transfer tube was then capped, evacuated and placed in the glove box.

B. Carter-Murray Procedure

An appropriate amount of 99.9% pure gadolinium metal sponge was weighed in air and placed in an outgassed quartz test tube. To this

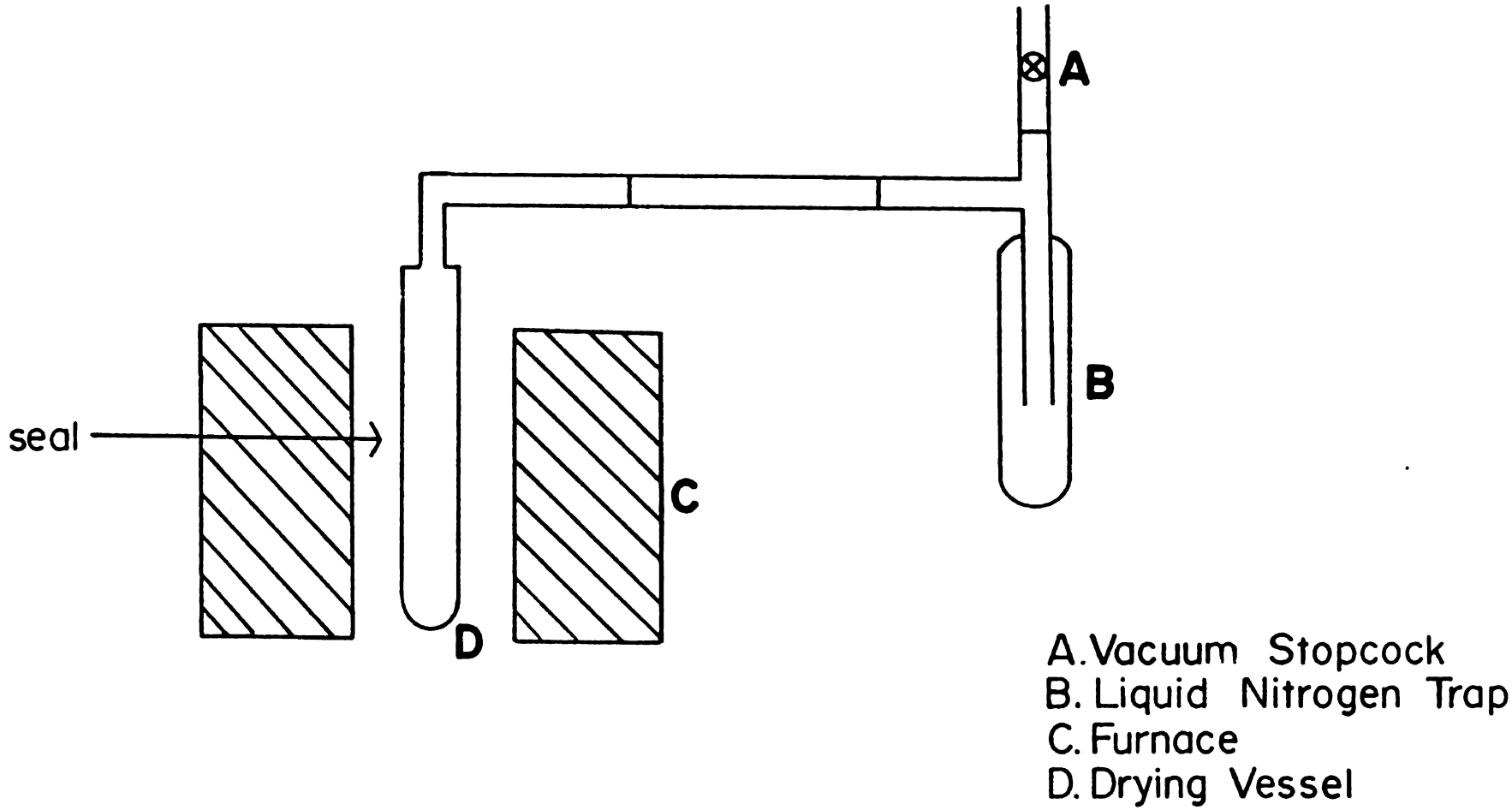
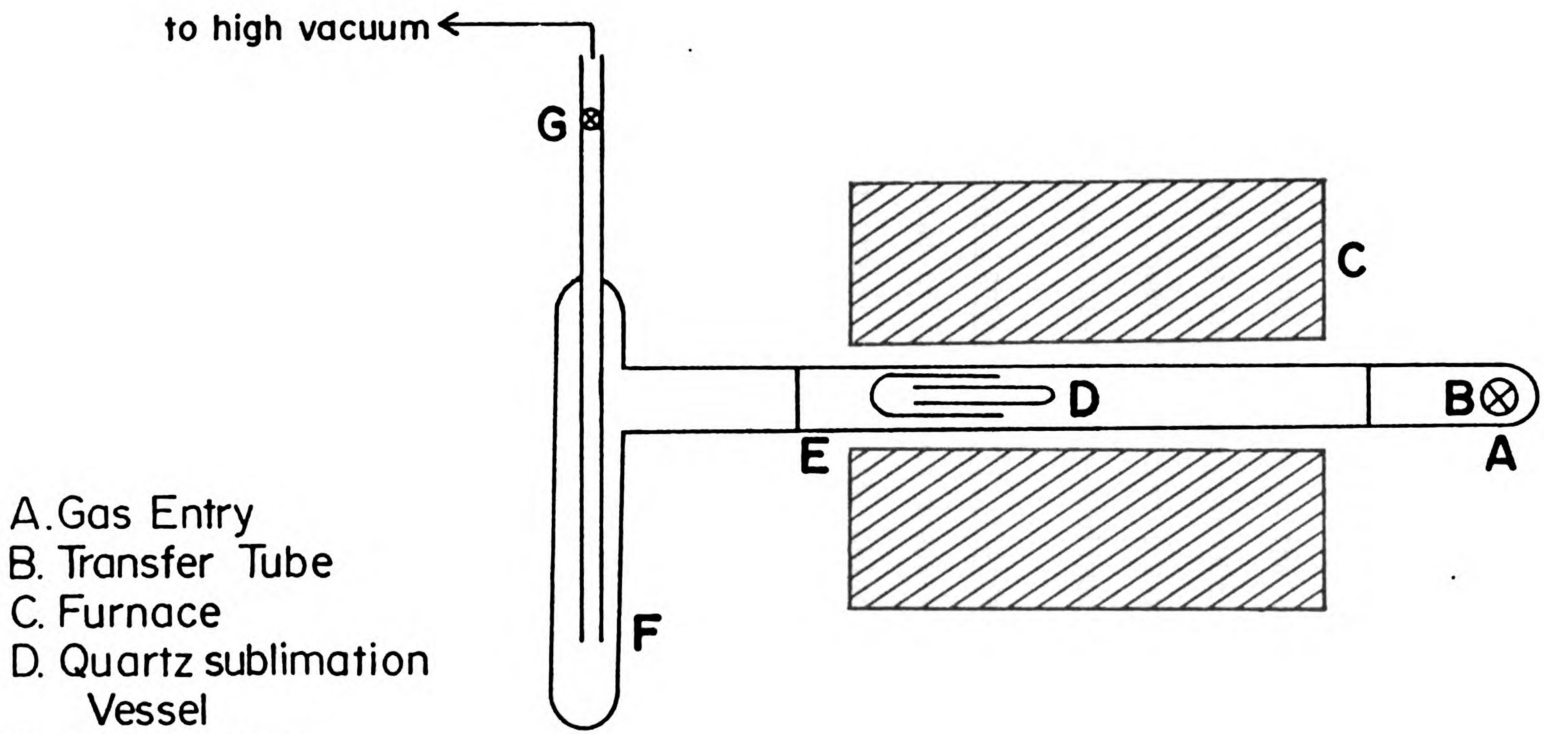


Figure 1. Drying apparatus used for the preparation of $GdCl_3$.


to high vacuum



HIGH VACUUM APPARATUS

Figure 2. High vacuum apparatus used for sublimation of the anhydrous trihalides.

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was added a fourfold molar excess of mercuric chloride. The tube was evacuated and sealed; the ampoule so formed was then placed in the furnace overnight, shown in Fig. 3, and heated at 300°C. It was placed in the furnace such that a slight temperature gradient existed between the two ends of the ampoule. This gradient aided in the separation of the mercury products from the crude $GdCl_3$. The ampoule was allowed to cool and transferred to the glove box. The crude $GdCl_3$ was subsequently sublimed in the manner described above.

Anhydrous Lanthanide(III) Iodides

Gadolinium triiodide was prepared by the Carter-Murray method utilized for preparation of the chloride. A fourfold excess of mercuric iodide was used.

Lanthanide(III) Mixed Halide

The mixed halide was prepared both by a method similar to that described by Carter and Murray and by direct melting of the trichloride and triiodide.

A. Pseudo Carter-Murray Procedure

A 1:0.5:n molar ratio of 99.9% pure gadolinium metal sponge: mercuric chloride:mercuric iodide was sealed in an outgassed quartz tube under vacuum and heated in a furnace overnight at 300°C. The ampoule was allowed to cool and subsequently transferred into the glove box. In these preparations initially $0.5 \leq n \leq 6.0$; as a result of later investigations n was fixed at 4.

Figur

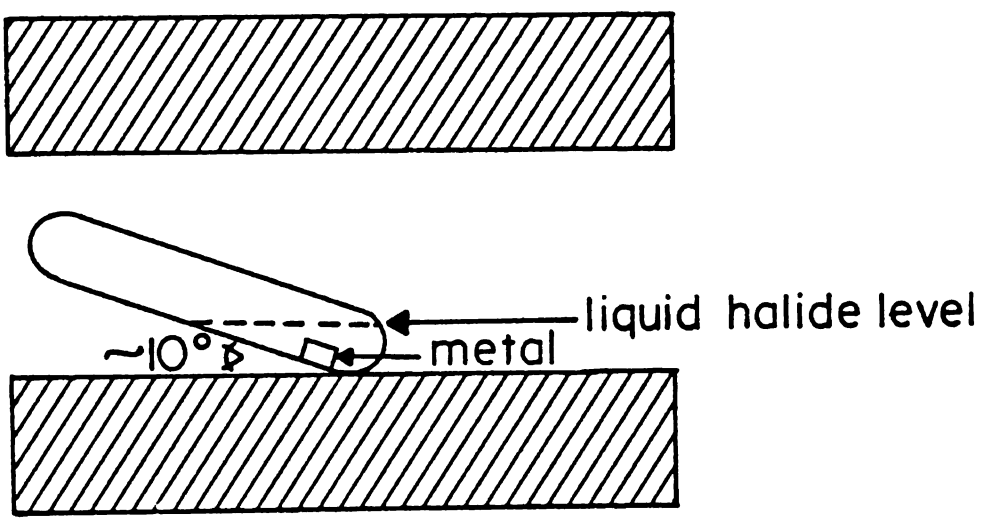

Figure 3. The reaction is carried in a quartz ampoule which is placed in a furnace overnight at 300°C.

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The sample was pulverized and placed into an outgassed carbon boat in the glove box and then removed in the transfer tube. It was then slowly heated (∿50°C per hour) to 500°C under high vacuum, at which temperature it was maintained for ∿10 hours. The slow heating rate was necessary to prevent loss of the powdered product and to aid in the separation of the mercury contaminants. When the unwanted mercury products appeared to have been removed, as evidenced by the absence of the red or yellow coloration of Hg^{2+} compounds, the light grey sample was allowed to cool and transferred to the glove box for further handling.

In one preparation the sample was again placed in an outgassed carbon boat which was inserted in an outgassed quartz tube. This assembly was heated (∿150°C per hour) under high vacuum to 550°C and allowed to remain for several hours. A white sublimate appeared on the surface of the quartz tube. The apparatus was cooled and the powder and sublimate again removed to the glove box for further handling and storage.

The process was repeated two more times, first heated to 600°C and then 700°C at which temperature both the sublimate and residue appeared white.

B. $GdCl_3$ + GdI_3 Melt

A 1:1 molar ratio of $GdCl_3$:GdI_3 was sealed in a degassed quartz ampoule and heated in a furnace until melted (∿700°C). The mixture was allowed to cool slowly (∿50°C per hour) until the melt

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recrystallized at about 550°C. The ampoule was removed from the furnace, allowed to cool to room temperature and transferred to the glove box for storage.

Storage of Samples

All of the lanthanide halides were stored in snap cap vials which were sealed in PVC bags in the recirculating argon atmosphere glove box, which has been described previously.[25] The purification manifold of the glove box contained Linde Molecular Sieve pellets to remove moisture from the argon and a BASF catalytic oxygen remover, R 3-11. A petri dish of phosphorus pentoxide was maintained in the glove box to aid in the removal of water.

ELEMENTAL ANALYSIS

Qualitative Analysis Procedures

A. Detection of Iodine

Approximately 2 mg of sample was placed in a test tube and dissolved in 5 ml of distilled water. To this was added 6 F HNO_3 until the solution acquired a pH $\leq$ 1. One ml of CCl_4 and one drop of 1 F KNO_2 were added and the mixture shaken vigorously until the two solutions were mixed well. The two phases were allowed to separate and the violet color in the CCl_4 layer was removed. The process was repeated until all iodine had been removed.[26]

B. Detection of Chlorine

After all of the iodine had been removed, the solution was heated over a flame and 1 drop of $AgNO_3$ was added. A white precipitate indicated the presence of chloride.[26]

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C. Test for Mercury

One drop (.05 ml) of potassium iodide-sodium sulfite solution was placed on a piece of filter paper, followed by a drop of copper sulfate solution. Finally a drop of approximately 1 N sample solution was added. If mercury were present a red or orange color, depending on the quantity, would be expected.[27]

Quantitative Analysis Procedures

A. Potentiometric Determination of Chloride and Iodide

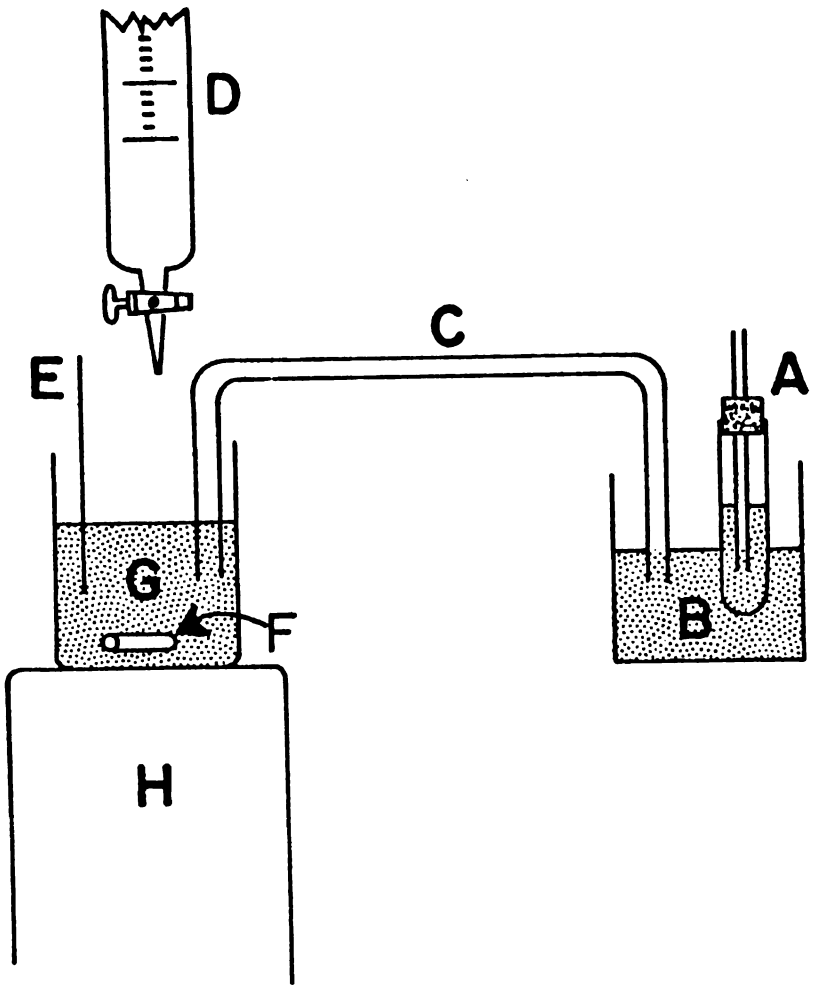
The determination of chloride and iodide was effected with the titration assembly shown in Fig. 4. Measurements were made with a Fisher Accumet pH Meter (model 320). A silver wire and a calomel electrode (Fisher Scientific Co., Pittsburg, PA.) served as the indicator and reference electrodes, respectively.

The Ag wire was sensitized by dipping it into 8 F HNO_3 until gassing began. The wire was washed with distilled water prior to use.

Between titrations, the calomel electrode was stored in 1 F KNO_3 and washed with distilled water prior to use.

The salt bridge[28] was prepared by adding 15 g of KNO_3 and 1.5 g of agar to 50 ml of distilled water. This mixture was dissolved by heating on a steam bath and then placed on a hot plate until bubbling ceased and the solution began to gel. This mixture was then poured into a U-shaped tube and allowed to cool until gelled. This salt bridge was stored in saturated KNO_3 solution between titrations.

Figure 4. Apparatus used for the potentiometric determination of chloride and iodide.



A. reference electrode
B. 1 F KNO_3
C. KNO_3 salt bridge
D. Buret
E. Pt. indicator
F. magnetic stirring bar
G. sample solution
H. magnetic stirrer

APPARATUS for POTENTIOMETRIC TITRATION of CHLORIDE and IODIDE

Figure 4.

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Stock solutions of $AgNO_3$ (0.1 N) were diluted to working solutions of 0.01 N. These working solutions were standardized against reagent grade sodium chloride.

The mixed halide sample was weighed in the glove box and placed in a 250 ml beaker, which was then removed from the box. Approximately 50 ml of distilled water saturated with N_2 was added.

The titration was effected by standard procedures.

B. Gravimetric Analysis of Gadolinium

The samples were weighed in the glove box directly into constant-weight unglazed porcelain crucibles and ignited to the sesquioxide at 950°C in a muffle furnace.[29]

C. Data Reduction

1. Potentiometric Titration

The potential readings were plotted versus the volume of titrant added. A typical titration curve is shown in Fig. 5. The titration endpoint was determined by visual inspection. A line was drawn vertically through the steepest portion of the curve to intersect the horizontal axis. The point of intersection was taken as the volume of titrant added at the endpoint.

From the volume of $AgNO_3$ at each endpoint and its normality, the millimoles of halide per milligram of sample were calculated. At least three independent samples were titrated. The average millimoles of halide per milligram of sample is reported along with the standard deviation.

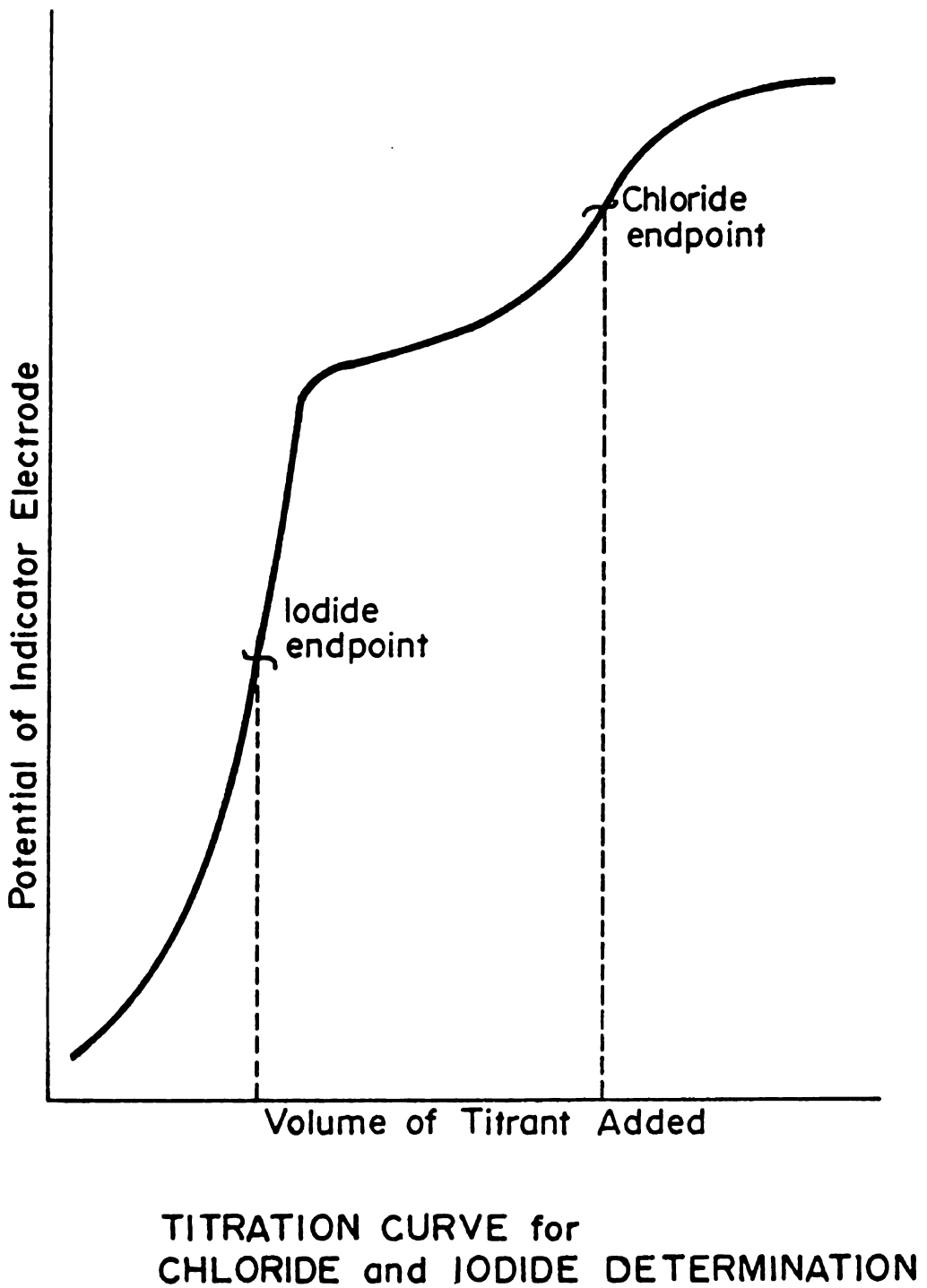

Figure 5. Plot of potential vs volume of titrant added for the titration of chloride and iodide.

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2. Gravimetric Analysis

The metal-analysis results are also reported in terms of millimoles of metal per milligram of sample. Three samples were analyzed and the average value and the standard deviation are reported.

X-RAY POWDER DIFFRACTION ANALYSIS

X-Ray powder diffraction patterns were obtained for all samples with a Haegg Type Guinier forward-focussing camera (radius 80 mm) and Cu $K\alpha_1$ radiation, $\lambda\alpha_1$ = 0.154051 nm, t = 24 $\pm$ 1°C. The fine focus X-ray tube was powered by a Picker 809B generator.

Sample preparation, film measurement and Guinier techniques have been described elsewhere.[30] Hygroscopic materials such as $GdCl_3$ were protected by a thin layer of sodium-dried mineral oil. Samples such as GdI_3 which are extremely air and moisture sensitive were protected by mineral oil over which was placed a thin piece of Pyrex. Platinum powder served as an internal standard ($\underline{a}$ = 0.39238 $\pm$ 0.00003 nm) to compensate for film shrinkage and to calibrate the film cassette. The X-ray diffraction photographs were used to identify the number of phases present in the sample and their purity.

INFRARED SPECTRA

Infrared spectra in the 500-50 cm^{-1} spectral region were obtained on the Digilab FTS-16 Interferometer. Mull samples were prepared in the glove box by adding one drop of a heavy oil (Mineral oil or Fluorolube) to an appropriate amount (2-5 mg) of finely ground sample. The mull samples were held between polyethylene plates.

CHAPTER IV

RESULTS

ANHYDROUS GADOLINIUM TRICHLORIDE

The preparation of $GdCl_3$ yielded white, needle-like hygroscopic crystals. The observed interplanar d-spacings and intensities, together with the values calculated from single crystal data, are listed in Appendices A and B.[31]

The far-infrared spectrum is shown in Fig. 6. The spectrum shows three absorption bands: 168, 199, and 223 cm^{-1}, in the region 230-160 cm^{-1}.

ANHYDROUS GADOLINIUM TRIIODIDE

Preparations of GdI_3 yielded pale green, hygroscopic crystals. The observed X-ray powder diffraction pattern and that calculated from the BiI_3 structural parameters are listed in Appendices C and D.

The far-infrared spectrum is shown in Fig. 7. The spectrum indicates four absorption bands: 75, 93, 120, and 158 cm^{-1}, in the region 170-75 cm^{-1} and one sharp absorption band at 383 cm^{-1}.

GADOLINIUM MIXED HALIDES

Pseudo Carter-Murray Procedure

A. Initial Investigations

During the early attempts to produce a mixed halide, the pseudo Carter-Murray procedure was used. A 1:0.5 molar ratio of gadolinium: mercuric iodide was mixed with a varying number of moles of mercuric chloride. When the reactants consisted of Gd; HgI_2; $HgCl_2$ in the molar ratio 1:0.5:2, the product was pure $GdCl_3$ with liberation of Hg and I_2. Other samples in which the molar ratio of $HgCl_2$:Gd was greater than 2 also yielded principally $GdCl_3$. By qualitative analysis iodide ion was not detected.

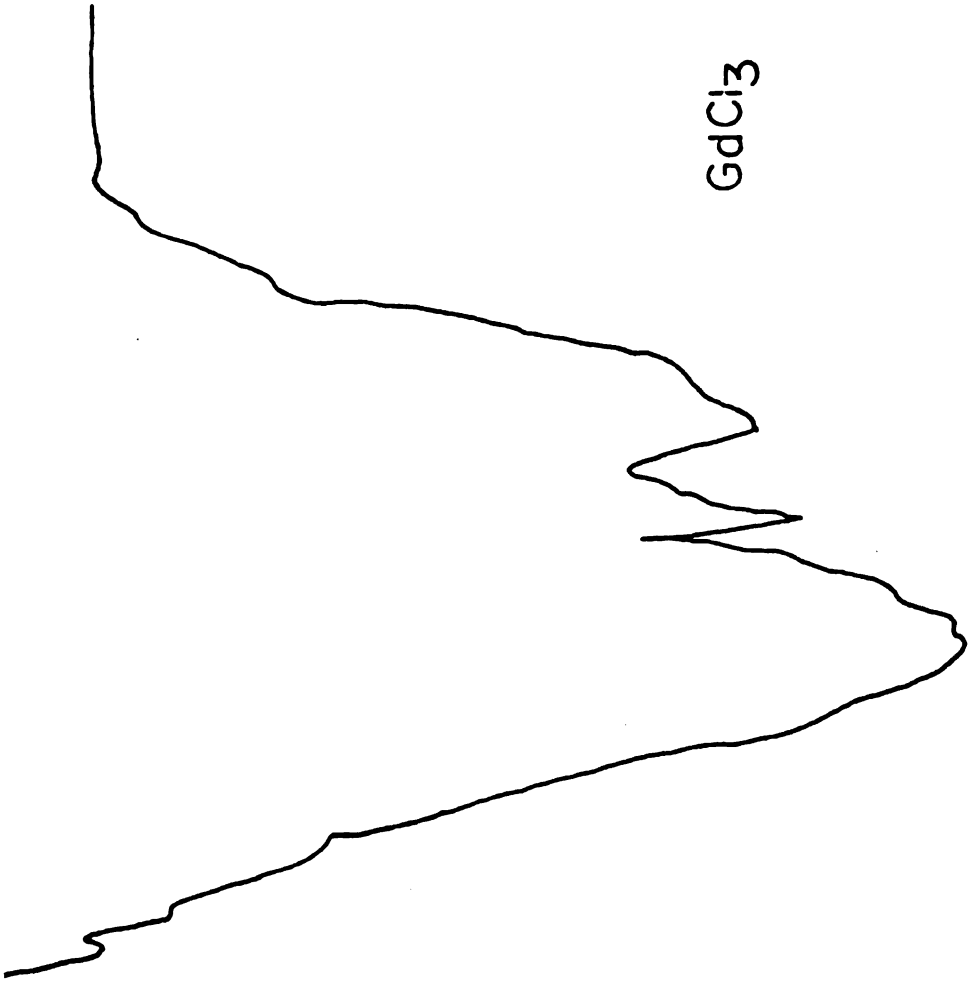


Figure 6. Far infrared spectrum of $GdCl_3$.

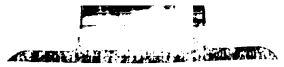
Figure 7. Far infrared spectrum of GdI_3.

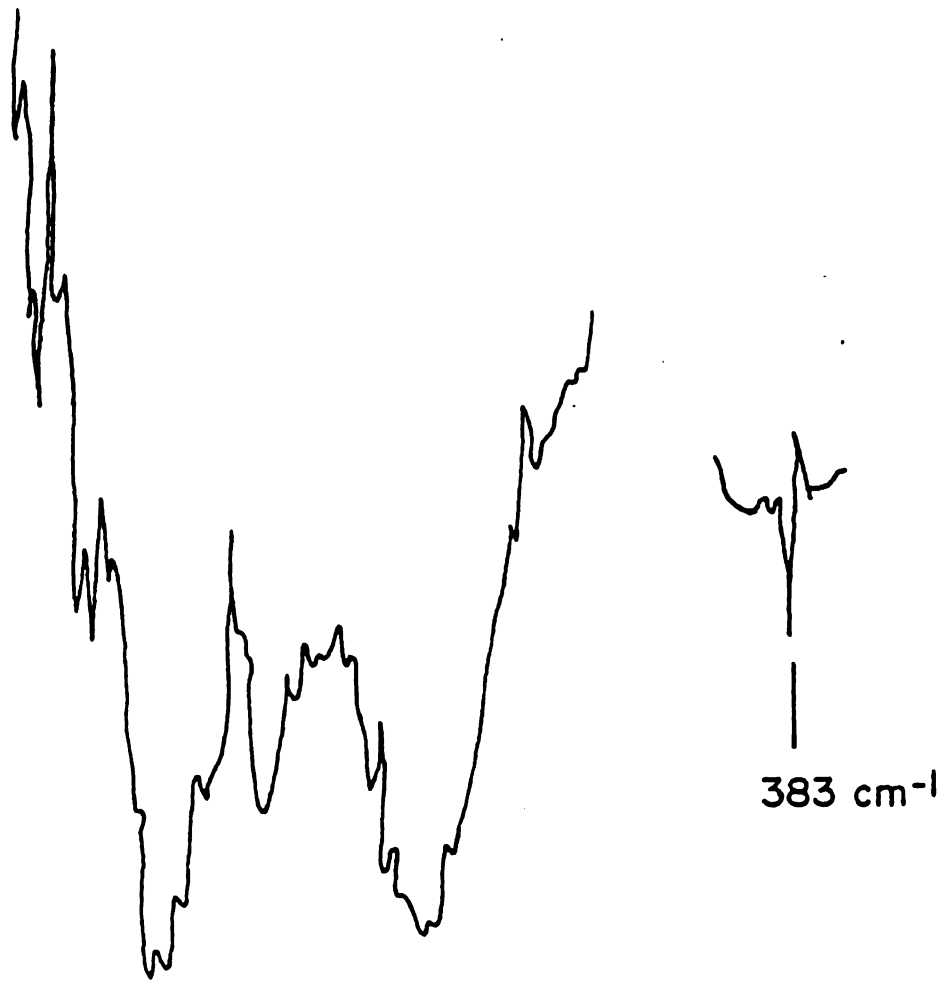
Preparations with a 1:0.5 molar ratio of Gd:$HgCl_2$ and various molar ratios, $\underline{n}$, of HgI_2, where $\underline{n}$ = 0.5-6.0, yielded light grey hygroscopic powders upon heating to 450°C. The initial X-ray powder patterns of the reactions in which $0.5 \leq \underline{n} \leq 3.0$ indicated all the products were $GdCl_3 \cdot xH_2O$. The powder patterns where $4.0 \leq \underline{n} \leq 6.0$ indicated the products to be $GdI_3 \cdot xH_2O$. Wet chemical qualitative analysis results indicated that both chloride and iodide were present in all sample preparations which involved excess HgI_2. (See Appendices O and P for X-ray powder patterns of the hydrated $GdCl_3$ and GdI_3.)

The far-infrared spectrum of the product of the reaction which involved $\underline{n}$ = 5.6 moles of HgI_2 shows five absorption bands in the 250-75 cm^{-1} range (Fig. 8). The four absorption bands in the 170-75 cm^{-1} range and the sharp peak at 383 cm^{-1} indicate the presence of GdI_3. The strong band at approximately 213 cm^{-1} represents the presence of at least one mixed halide phase. The apparent discrepancy between the X-ray results discussed in the preceding paragraph and these i.r. results is discussed later.

B. The Molar Ratio, HgI_2:Gd:$HgCl_2$ = 3.5:1:0.5

Preparations with a molar ratio of $\underline{n}$ = 3.5 also yielded a light grey, hygroscopic powder after being heated to 500°C. The observed d-spacings and intensities are listed in Appendix E. The far-infrared spectrum is shown in Fig. 9. Qualitative elemental analysis indicated the presence of chloride and iodide and the absence of mercury.





$$Gd^{\circ} + \tfrac{1}{2}HgCl_2 + 5.6HgI_2 \xrightarrow{450^{\circ}C} GdI_3 + \text{mixed halide}$$

90-250 cm^{-1}

Figure 8. Far infrared spectrum of the product prepared at 450°C from the molar ratio, HgI_2:Gd:$HgCl_2$ = 5.6:1:0.5.

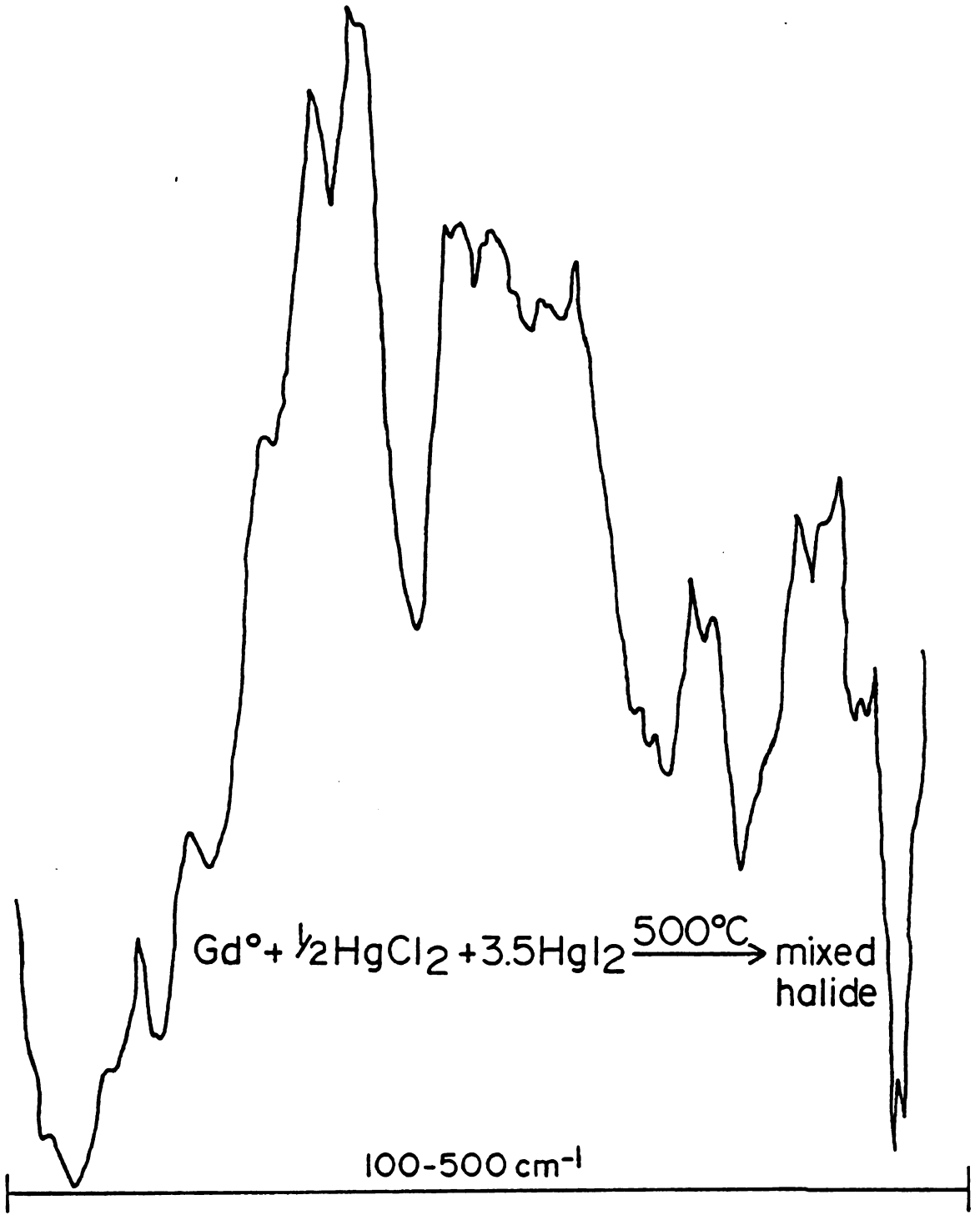


Figure 9. Far infrared spectrum of product prepared at 500°C from the molar ratio, HgI_2:Gd:$HgCl_2$ = 4.0:1:0.5.

C. The Molar Ratio, HgI_2:Gd:$HgCl_2$ = 4.0:1:0.5

1. Heating 1

Preparations with a $\underline{n}$ = 4.0 molar ratio were initially heated to 450°C in order to remove the unwanted mercury contaminants.

The X-ray powder pattern is presented in Appendix F. A large quantity of GdI_3 appears to be present along with a mixed halide phase and a trace amount of $GdCl_3$.

The far-infrared spectrum shown in Fig. 10 substantiates these results.

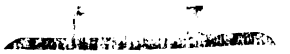
The results of the chemical analysis are listed in Table 4.

Table 4. Analysis of Heating 1 ($GdI_{3-x}Cl_x$)

Species	$\frac{\text{millimoles}}{\text{milligram}}$ of Sample	Empirical Formula
Iodide	$4.7_0 \pm 0.3_6$	$GdCl_{1.0}I_{2.0}$
Chloride	$2.3_4 \pm 0.1_6$	
Gadolinium	$2.3_5 \pm 0.1_6$	
Mercury	none	

2. Heating 2

The product obtained from heating 1 was subsequently heated to 550°C. The residue remained light grey and a small quantity of a white hygroscopic sublimate was collected.



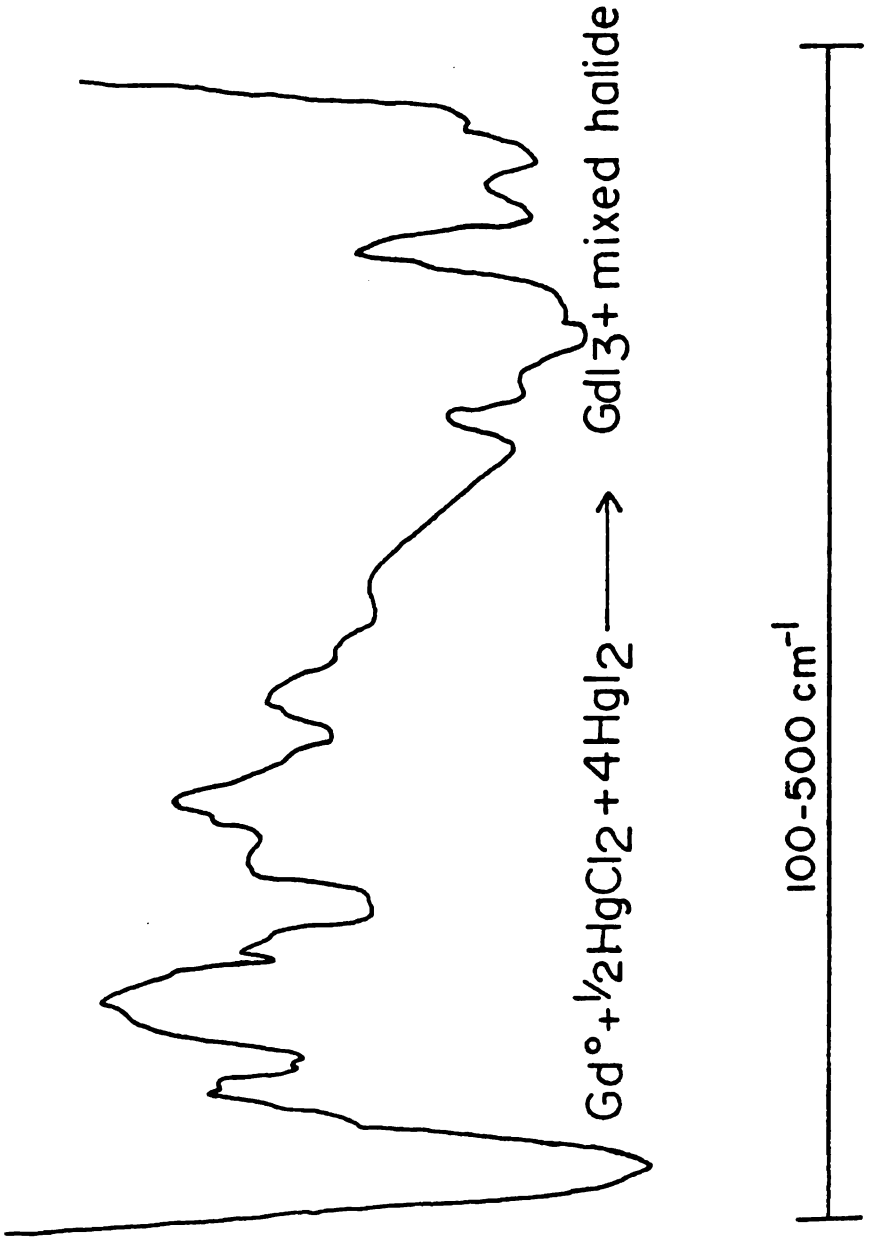


Figure 10: Far infrared spectrum of the product prepared at 450°C from the molar ratio, HgI_2:Gd:$HgCl_2$ = 4.0:1:0.5.

The X-ray powder patterns for both the residue and the sublimate are in Appendices G and H. From comparison of their powder patterns it can be seen that while certain lines are common to both, other distinct sharp lines are also observed. These observations are interpreted as an indication of a series of mixed halide phases.

The far-infrared spectrum of the residue is shown in Fig. 11. Several strong absorption bands: 130, 210, 270, 325, 370, 413, 438, and 475 cm^{-1}, are in the 500-100 cm^{-1} range.

Results of the elemental analysis are listed in Table 5.

Table 5. Analysis of Residue of Heating 2

Species	$\frac{\text{millimoles}}{\text{milligram}}$ of Sample	Empirical Formula
Iodide	$4.4_3 \pm 0.1_4$	$GdCl_{1.0_4}I_{1.9_6}$
Chloride	$2.3_4 \pm 0.3_0$	
Gadolinium	$2.2_6 \pm 0.0_6$	
Mercury	none	

3. Heating 3

The residue obtained from heating 2 was heated to 600°C. It remained light grey and a white hygroscopic sublimate was again produced.

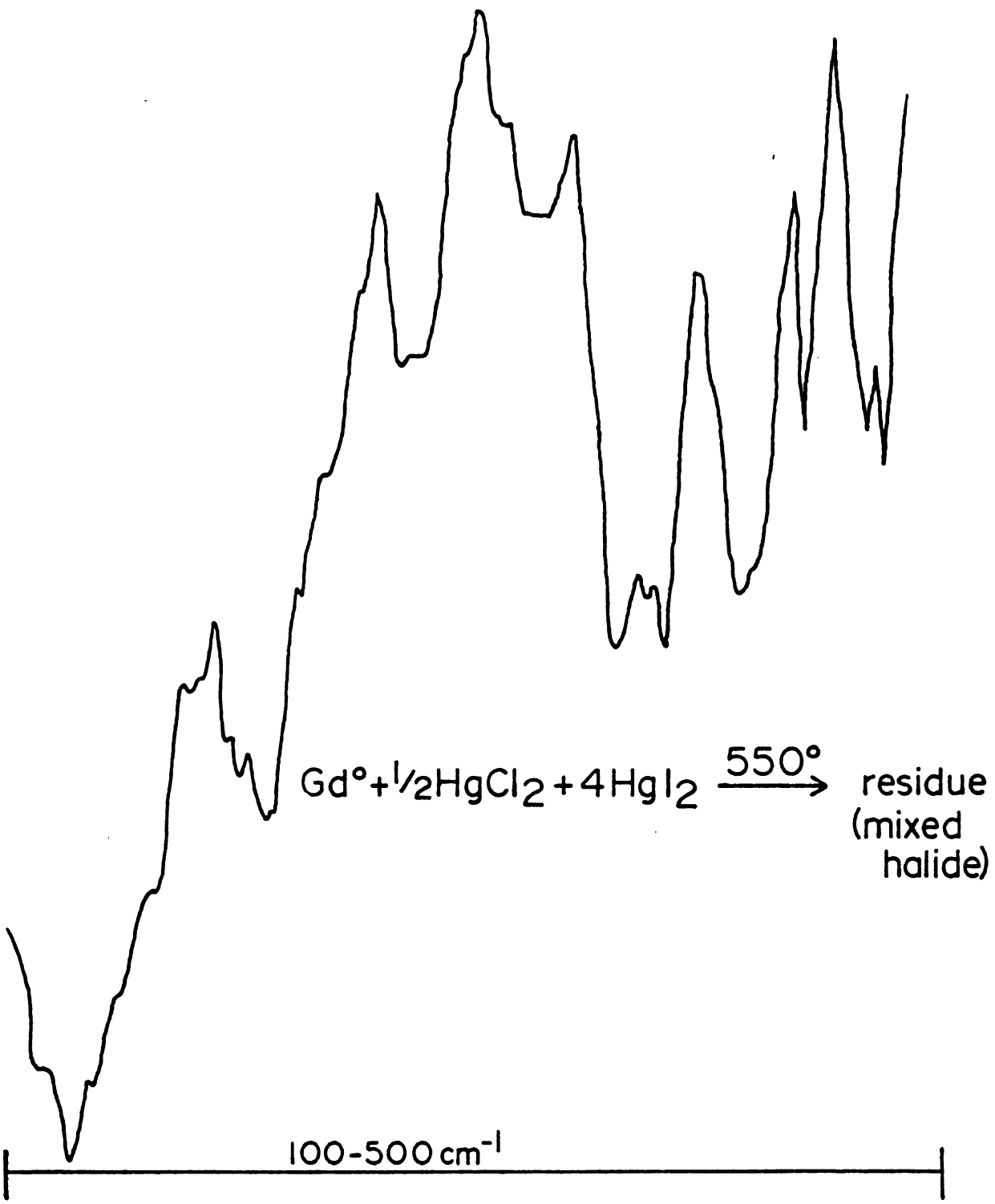


Figure 11. Far infrared spectrum of the residue prepared at 550°C.

The X-ray powder patterns for the residue and sublimate are presented in Appendices I and J, respectively; the infrared spectra are presented in Figures 12 and 13. A number of mixed halide phases appear to be present.

Analytical results for both the residue and sublimate are compiled in Table 6.

Table 6. Analysis of Residue and Sublimate of Heating 3

	millimoles / milligram	
Species	Residue	Sublimate
Iodide	$4.2_3 \pm 0.0_6$	$4.3_7 \pm 0.2_4$
Chloride	$2.7_4 \pm 0.0_2$	$2.4_7 \pm 0.0_6$
Gadolinium	$2.3_2 \pm 0.2_1$	$2.3_8 \pm 0.01$
Mercury	none	none
Empirical Formula	$GdCl_{1.1_8}I_{1.8_3}$	$GdCl_{1.0_8}I_{1.9_2}$

4. Heating 4

The residue from heating 3 was heated to 700°C after which the residue and sublimate were both white. Only a small quantity of residue remained in the boat.

X-Ray powder patterns for both the residue and sublimate are in Appendices K and L. The far-infrared spectrum for the sublimate

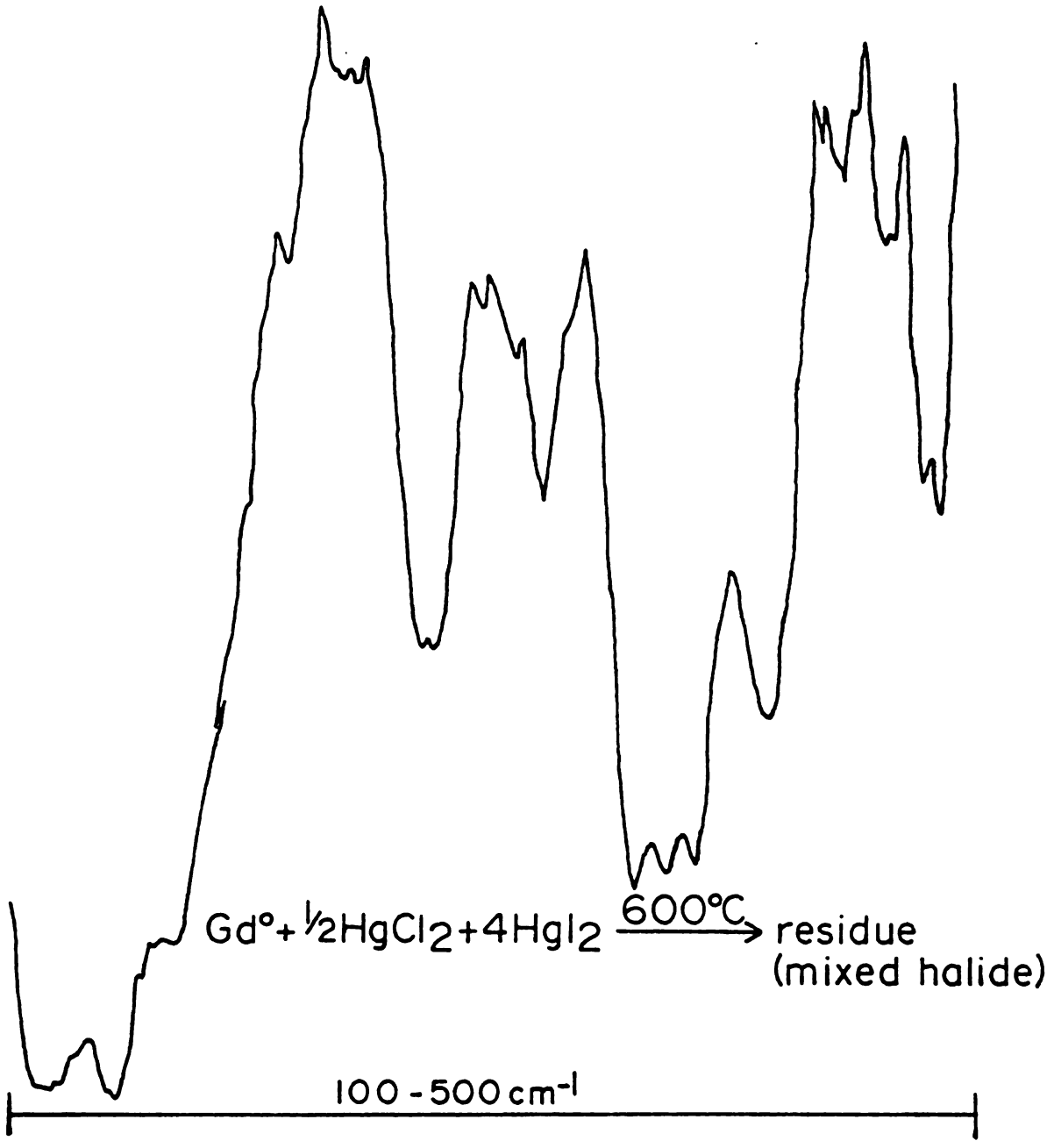


Figure 12. Far infrared spectrum of the residue prepared at 600°C.

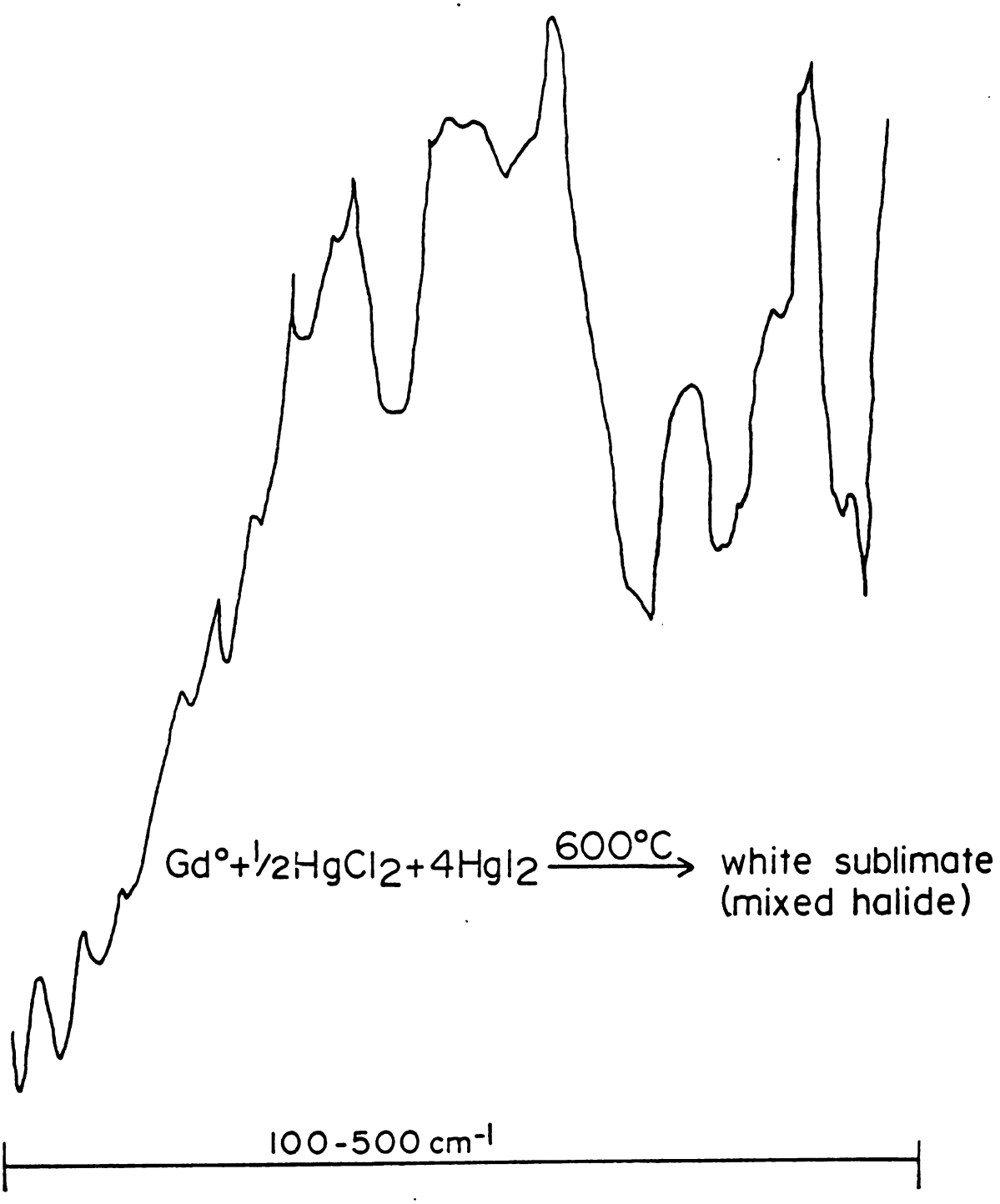


Figure 13. Far infrared spectrum of the sublimate prepared at 600°C.

exhibits bands at: 125, 157, 180, 207, 240, 268, 316, 370, 408, and 475 cm^{-1}; and that of the residue at: 125, 223, 268, 316, 370, 408, and 475. The far-infrared spectra are shown in Fig. 14 and 15, respectively.

The elemental analysis for the sublimate is listed in Table 7.

Table 7. Analysis of Sublimate of Heating 4

Species	$\frac{\text{millimoles}}{\text{milligram}}$ of Sample	Empirical Formula
Iodide	4.39 ± 0.00	$GdCl_{1.0_9}I_{1.91}$
Chloride	$2.4_6 \pm 0.0_4$	
Gadolinium	$2.2_7 \pm 0.0_1$	
Mercury	none	

$GdCl_3 + GdI_3$ Melt

The product appeared as light grey mica-like crystals. The interplanar d-spacings and intensities are listed in Appendix M. A small amount of $GdCl_3$ appears to have been retained along with a number of mixed halide phases.

EVIDENCE OF GLOVE BOX CONTAMINATION

Attempts to store the hygroscopic materials were generally unsuccessful, especially when the room atmosphere was excessively humid. Immediately upon exposure of the products to the glove box

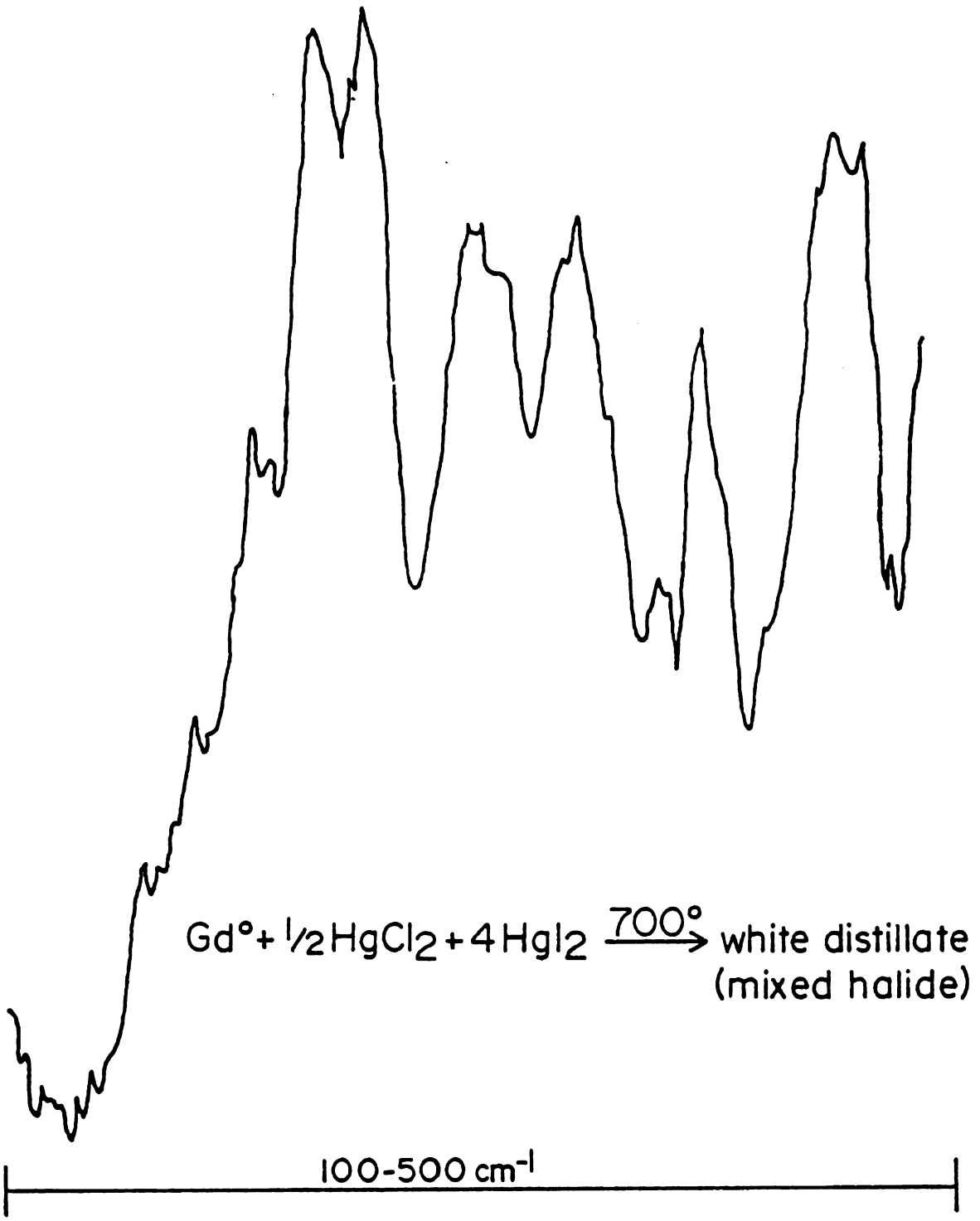
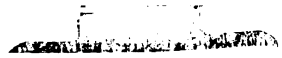


Figure 14. Far infrared spectrum of the sublimate prepared at 700°C.



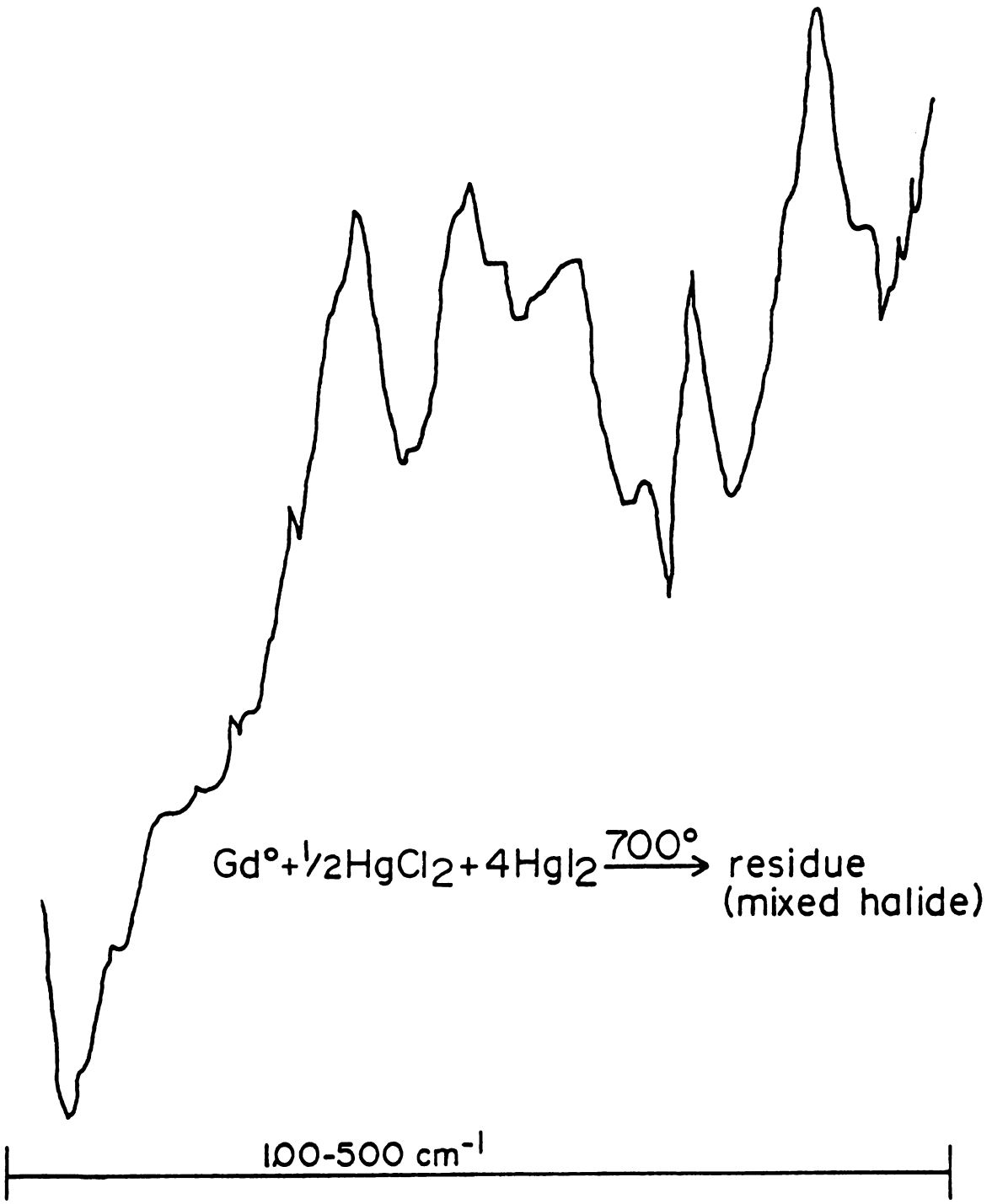


Figure 15. Far infrared spectrum of the residue prepared at 700°C.

atmosphere, conversion to the hydrates occurred. When the humidity lowered, it was possible to store the materials in the glove box for a few weeks without their becoming contaminated. After this period of time, primarily the oxyhalides were produced.

CHAPTER V

DISCUSSION

FAR-INFRARED ANALYSIS OF $GdCl_3$ AND GdI_3

Very little use has been made of i.r. techniques for structural analysis of pure solids. This is probably due to the extreme difficulty encountered in interpreting the data theoretically. Taylor[32] investigated the dependency of infrared spectra on structure for several rare earth halides. He measured the i.r. absorption spectra for the fluorides, chlorides, bromides, and iodides of several rare earth metals over a frequency range of 4000-200 cm^{-1}. From these spectra he was unable to distinguish between crystal structure types. Taylor may have been able to obtain more information had he studied the region below 200 cm^{-1}.

The vibrational and structural properties of a number of rare earth dihalides and trihalides have been studied recently.[33-35] These investigations employed the general technique of high-temperature matrix isolation spectroscopy, which has been described by several investigators.[33]

Of the five characteristic absorption bands observed in the infrared spectrum of GdI_3, only the band at 383 cm^{-1} was also reported by Taylor.[32] The $GdCl_3$ spectrum was not reported by Taylor.[32]

INITIAL INVESTIGATIONS

Carter and Murray[14] noted that excess mercuric halide was essential in their preparation of LnX_3 because the reaction proceeds smoothly only when the metal is completely immersed in the liquid melt.

After preparations with a 1:$\underline{n} \geq$ 2:0.5 molar ratio of Gd:$HgCl_2$:HgI_2 had been effected, it was concluded that formation of $GdCl_3$ was more favorable than either formation of GdI_3 or a mixed halide phase. Any GdI_3 or $Gd(Cl, I)_3$ formed probably reacted with the less volatile $HgCl_2$ and iodide ion was displaced as HgI_2, which subsequently decomposed to Hg and I_2.

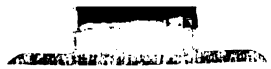
In subsequent preparations, a variable excess of HgI_2 was used in the molar ratio, Gd:$HgCl_2$:HgI_2 = 1:0.5:$\underline{n}$. The far-infrared spectrum taken immediately after sample preparation for the $\underline{n}$ = 5.6 sample, gave evidence for the formation of GdI_3 and a mixed halide phase. The five characteristic GdI_3 absorption bands are present along wtih one strong absorption at approximately 223 cm^{-1}. This latter band was attributed to the presence of a mixed $Gd(Cl, I)_3$ phase.

Exposure of the reaction products to the glove box atmosphere yielded hydrates, apparently the glove box was not sufficiently devoid of water. During the investigation of preparations in which $\underline{n}$ = 3.5, the reaction product was converted to pure GdOCl, Appendix N, apparently from contamination of only trace amounts of water present in the glove box atmosphere.

Due to the relatively small sample size involved in the powder diffraction analysis, the possibility of hydration to occur while the camera is being evacuated cannot be excluded.

THE MOLAR RATIO HgI_2:Gd = 4.0

The only difference in the experimental conditions for the preparations of heatings 1 through 4 was the temperature. X-Ray powder diffraction patterns obtained for the residue and sublimate



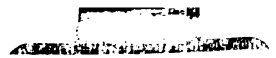
of every phase were analyzed and compared. It was found that certain distinct, sharp lines that were correlated with the formation or absence of new bands in the i.r. appeared or disappeared in the X-ray powder photographs.

From comparison of the infrared spectra and the X-ray powder diffraction patterns, it can be seen that the composition of the sample varies at different temperatures. The composition of the residues are also different from those of the sublimate at each temperature where samples were analyzed. At 450°C the infrared spectrum shows two bands, at 120 and 158 cm^{-1}, which indicate the presence of GdI_3. Two more bands are expected, but instrumental alterations prevented measurements below 100 cm^{-1}. The other bands at 210, 265, 363, 403, and 468 cm^{-1} indicate the presence of one or more mixed halide phases. The X-ray powder diffraction pattern taken of the sample prepared at 450°C indicates the presence of GdI_3, a trace amount of $GdCl_3$ and a mixed halide phase. The infrared spectrum and X-ray powder photograph of the residue remaining at 550°C indicate the absence of GdI_3 and a change in the composition of the residue. The only band found in the spectra of the 450 and 550°C products is the absorption band at 210 cm^{-1}. The X-ray powder photograph of the 550°C sample has only a few lines in common with the one taken at 450°C. The infrared spectrum of the residue remaining at 600°C has only four bands in common with that of the 550°C residue: 270, 370, 440 and 475 cm^{-1}. New absorption bands at 125 cm^{-1} (split into two peaks), 215, 316, 408 and 460 cm^{-1} indicate the presence of a new mixed halide phase at 600°C. The

X-ray photograph of the 600°C residue has some lines in common with that of the 550°C residue and, in addition, several new lines appear. The infrared spectrum of the residue remaining at 700°C has some absorption bands that were present in the 600°C residue: 268, 316, 370, 408 and 475 cm^{-1}. The band at 125 cm^{-1} is no longer split. The changes in the i.r. absorption bands with specimen preparation temperatures seem to indicate that the composition of the residue varies with respect to temperature.

The compositions of the residues and sublimates at a particular temperature also vary. The far-infrared spectra of the sublimate and residue produced at 600°C both have peaks at 125, 215, 240, 268, 316, 370, 408 and 475 cm^{-1}. In addition weak bands appear at: 107, 143, 155, 180, 207 and 435 cm^{-1} in the spectrum of the sublimate. Likewise, the spectrum of the 700°C sublimate has some bands in common with the 700°C residue in addition to other bands. The relative band intensities for certain absorptions also changes in the i.r. spectral series. These intensity changes are taken as evidence for the formation of a number of mixed halide phases, with particular phases apparently stable over select temperature ranges.

The mixed halide $UClI_2$ was synthesized but no structural work was done on it.[3] The ionic radius of U^{+3} is 1.04 Å as reported by Shannon and that of Gd^{+3} is 0.98 Å.[34] Since the ionic radii of U^{+3} and Gd^{+3} are relatively close, the two mixed halides may have comparable structure types.



The results of the quantitative analysis are of considerable interest. The empirical formulas for the residues and sublimates are summarized in Table 8.

Table 8. Summary of Empirical Formulas

Temperature °C	Residue	Sublimate
450	$GdCl_{1.0}I_{2.0}$	
550	$GdCl_{1.04}I_{1.96}$	
600	$GdCl_{1.08}I_{1.92}$	$GdCl_{1.08}I_{1.92}$
700		$GdCl_{1.09}I_{1.92}$

The components of the 450°C preparation, according to the X-ray results are GdI_3, a mixed halide phase and a trace amount of $GdCl_3$. The principal components, GdI_3 and the mixed halide phase, mask the presence of $GdCl_3$. Thus, its bands are not observed in the i.r., and only after excessive exposure is $GdCl_3$ observed in the X-ray photograph. When the excess of mercuric iodide that was used in the preparation is considered, it is not surprising that a fair amount of GdI_3 was produced. At 550°C neither $GdCl_3$ nor GdI_3 can be seen in the X-ray diffraction or far-infrared results. From comparison of the empirical formulas, it is apparent that as the temperature increases the Cl^-/I^- ratio increases in the residue. The similarity between the empirical formulas of the sublimates at 600°C and 700°C, is indicative that the sublimate has a constant composition regardless of the temperature of formation.

This observed constant composition of the sublimate appears at first glance to be inconsistent with the far i.r. and X-ray powder diffraction results. A careful inspection of the character of the lines on the X-ray films indicates that the product prepared at the higher temperature is considerably more ordered than that prepared at the lower temperature. The extra weak reflections which appear in the pattern of the higher temperature product probably stems from increased order in the solid. Likewise, this increased order produces increased resolution in the i.r. and leads to narrowing of the band widths and peak sharpness.

The components of the product formed at 450°C are GdI_3, $Gd(Cl, I)_3$, and $GdCl_3$. As the temperature is increased to 550°C these constituents react and produce a sublimate. The composition of the residue at 550°C consists of a new series of mixed $Gd(Cl, I)_3$ phases. Since the vapor pressure of GdI_3 is greater than that of $GdCl_3$, the vapor is assumed to be $GdCl_3$ and GdI_3 which again react on the hot surface of the sublimation tube to form a series of mixed halide phases different from those in the residue. That the composition of the vapor is apparently rich in iodide can be seen in the increasing molar ratio of Cl^-/I^- as the temperature increases, in the empirical formulas of the residues. The observation is consistent with the volatilities of the trichloride and triiodide. As the temperature is raised to 700°C the composition of the residue becomes more chloride rich and a vapor phase of $GdCl_3$ and GdI_3 which again react to form a series of mixed halide phases is observed. Due to

the initial small sample size, at 700°C a very small amount of residue remained. The composition of the vapor might be determined by quenching.

THE MOLAR RATIO HgI_2:Gd = 3.5

The X-ray powder diffraction data along with the infrared spectra indicate that at 500°C no GdI_3 or $GdCl_3$ was present. The absence of the pure halides is consistent with the increased preparatory temperature. It appears that a number of mixed halide phases is present, probably as a result of a lack of equilibrium in the system. When the temperature was raised to 550°C the only product found was GdOCl. The formation of GdOCl with liberation of I_2 was a result of water contamination which attacks the sample in the glove box atmosphere.

SOLID SOLUTION

At the present time it is difficult to conclude positively whether these mixed halide phases are a continuous series of solid solutions or a series of discrete phases. However, the formation of a solid solution is unlikely. The difference in structure type of GdI_3 and $GdCl_3$ would probably prevent formation of a continuous solid solution. The large difference in ionic radii[36] between the chloride, 1.8. Å, and iodide, 2.16 Å, also makes the formation of a solid solution unlikely. However, particular sets of distinct sharp lines were observed, not a continuous shifting. A solid solution was postulated for the uranium mixed halides. However, the structure types of the uranium halides are different from those of gadolinium.

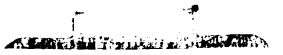
CHAPTER VI

CONCLUSIONS AND SUGGESTIONS FOR FURTHER RESEARCH

CONCLUSIONS AND SUGGESTIONS FOR FURTHER RESEARCH

One may conclude from this work that an undetermined number of mixed halide phases has been prepared. It is impossible to definitely conclude whether a series of compounds or a solid solution has been formed. Evidence seems to indicate that the formation of a solid solution is unlikely. The use of far-infrared spectroscopy has proven to be an important tool in determining the presence of the mixed halide phase.

This investigation, as with many, appears to have raised more questions than it has answered. Further investigations with different preparatory methods may lead to isolation of the different mixed halide phases. Investigation of $GdCl_3$ + GdI_3 melt preparation, by varying the stoichiometry of the reactions and examining closely the X-ray and far-infrared data, may answer the question of whether a solid solution has been formed. The composition of the vapor might be determined by quenching.

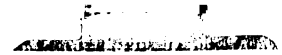


APPENDICES

APPENDIX A

Observed $\sin^2\theta$ (λ = 1.54051 Å)
and Interplanar d-Values for $GdCl_3$

Relative Intensity	d-Value Å	$\sin^2\theta$
5	6.617	0.0136
10	4.194	0.0337
3	3.754	0.0422
6	3.508	0.0482
2	2.780	0.0768
6	2.547	0.0945
1	2.142	0.1293
4	2.097	0.1349
1	2.070	0.1384
1	1.807	0.1817
1	1.736	0.1970
1	1.633	0.2226
1	1.569	0.2407
1	1.485	0.2691
1	1.343	0.3287
1	1.262	0.3726
1	1.193	0.4166



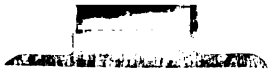
APPENDIX B

Calculated $\sin^2\theta$ (λ = 1.54051 Å)
and Interplanar d-Values for $GdCl_3$

Relative Intensity	d-Value Å	$\sin^2\theta$
9	6.3794	0.0146
7	3.6832	0.0437
10	3.4526	0.0498
2	3.1897	0.0583
1	2.7417	0.0789
6	2.5189	0.9350
2	2.4112	0.1020
3	2.1265	0.1312
7	2.0792	0.1372
1	2.0530	0.1408
1	1.9543	0.1553
2	1.8416	0.1749
2	1.7932	0.1845
1	1.7693	0.1895
1	1.7263	0.1991
3	1.6249	0.2247
1	1.5949	0.2333
1	1.5631	0.2428
1	1.4660	0.2684
2	1.4770	0.2720
1	1.4635	0.2770
2	1.3921	0.3063
2	1.3786	0.3122
1	1.3708	0.3157
1	1.3403	0.3303
1	1.3382	0.3313
1	1.2759	0.3645
1	1.2595	0.3740
1	0.2577	0.3750
1	0.2277	0.3936
1	1.2184	0.3996
1	1.2056	0.4084
1	1.1917	0.4178
1	1.1903	0.4188
1	1.1568	0.4434
2	1.1522	0.4469
1	1.1458	0.4519
1	1.1036	0.4871
1	1.0837	0.5052

APPENDIX B. (Cont'd.)

Relative Intensity	d-Value Å	$\sin^2\theta$
1	1.0826	0.5062
1	1.0632	0.5248
1	1.0573	0.5344
1	1.0488	0.5394



APPENDIX C

Observed $\sin^2\theta$ (λ = 1.54051 Å) and Interplanar d-Values for GdI_3

Relative Intensity	d-Value Å	$\sin^2\theta$
2	6.4132	0.0144
5	4.2088	0.0335
2	3.8579	0.0399
10	3.3842	0.0581
3	2.6052	0.0874
1	2.5041	0.0946
2	2.3071	0.1115
10	2.2214	0.1202
1	2.1171	0.1324
1	2.0084	0.1477
1	1.8756	0.1687
7	1.8547	0.1725
2	1.6885	0.2081
1	1.4910	0.2669
4	1.4244	0.2924
2	1.3442	0.3284
1	1.2823	0.3608
1	1.2050	0.4086

APPENDIX D

Calculated $\sin^2\theta$ (λ = 1.54051 Å)
and Interplanar d-Values for GdI_3

Relative Intensity	d-Values Å	$\sin^2\theta$
2	6.4935	0.0141
1	6.1952	0.0155
1	3.7490	0.0422
10	3.6889	0.0436
8	3.5245	0.0478
1	3.2467	0.0563
2	3.2074	0.0577
5	2.4543	0.0985
5	2.4372	0.0999
1	2.3880	0.1040
3	2.1645	0.1266
1	2.1527	0.1280
1	2.1186	0.1322
2	2.0651	0.1391
1	1.8745	0.1688
1	1.8668	0.1702
2	1.8444	0.1744
1	1.8088	0.1813
1	1.8010	0.1829
1	1.7942	0.1843
2	1.7743	0.1885
1	1.7622	0.1910
1	1.7425	0.1954
2	1.6184	0.2265
1	1.6037	0.2307
1	1.5801	0.2376
1	1.4897	0.2673
1	1.4859	0.2687
1	1.4745	0.2729
1	1.4561	0.2798
1	1.4315	0.2895
2	1.4137	0.2969
1	1.4039	0.3010
1	1.3880	0.3080
1	1.3666	0.3177
1	1.3405	0.3302
1	1.2961	0.3532
1	1.2762	0.3642

APPENDIX D. (Cont'd.)

Relative Intensity	d-Values Å	$\sin^2\theta$
1	1.2596	0.3740
1	1.2497	0.3799
1	1.2296	0.3924
1	1.2271	0.3940
1	1.2250	0.3954
1	1.2186	0.3995
1	1.2082	0.4065
1	1.1940	0.4162
1	1.1765	0.4287
1	1.1748	0.4298
1	1.1663	0.4362
1	1.1644	0.4376
1	1.1589	0.4417
1	1.1499	0.4487
1	1.1225	0.4709

APPENDIX E

Observed $\sin^2\theta$ (λ = 1.54051 Å)
and Interplanar d-Values for the Product Produced
at 500°C for the Molar Ratio HgI_2:Gd = 3.5

Relative Intensity	d-Values Å	$\sin^2\theta$
2	6.9725	0.0122
2	3.4807	0.0490
10	3.3156	0.0540
1	3.01775	0.0652
1	2.7426	0.0789
5	2.5559	0.0908
5	2.1662	0.1264
1	1.9757	0.1520

APPENDIX F

Observed $\sin^2\theta$ (λ = 1.54051 Å)
and Interplanar d-Values
for the Product Prepared at 450°C

Relative Intensity	d-Values Å	$\sin^2\theta$
3	7.0210	0.0120
2	6.4165	0.0144
1	6.1082	0.0159
1	5.5932	0.0190
1	5.2877	0.0212
2	5.1632	0.0223
1	4.9664	0.0241
2	4.7970	0.0258
1	4.5366	0.0288
4	4.2770	0.0324
1	4.1872	0.0338
8	4.1228	0.0349
1	4.0446	0.0363
6	3.8707	0.0396
5	3.7389	0.0424
2	3.4913	0.0487
2	3.3743	0.0521
10	3.3353	0.0533
1	3.2034	0.0578
1	3.1621	0.0593
4	3.0871	0.0623
3	2.9778	0.0669
1	2.8431	0.0734
2	2.8187	0.0747
2	2.7548	0.0782
1	2.7199	0.0802
1	2.6632	0.0837
1	2.5829	0.0889
8	2.5660	0.0901
3	2.5235	0.0932
1	2.4973	0.0951
1	2.4466	0.0991
2	2.4016	0.1029
2	2.3464	0.1078
1	2.3128	0.1109
1	2.2143	0.1210
6	2.1907	0.1236

APPENDIX F. (Cont'd.)

Relative Intensity	d-Values Å	$\sin^2\theta$
2	2.1342	0.1303
2	2.1091	0.1334
1	2.0849	0.1365
4	1.9805	0.1513
1	1.8518	0.1730
2	1.8286	0.1774
1	1.8128	0.1805
2	1.6683	0.2123
1	1.6518	0.2175
1	1.5951	0.2332
1	1.4679	0.2754
1	1.4019	0.3019
1	1.3631	0.3193

APPENDIX G

Observed $\sin^2\theta$ (λ = 1.54051 Å)
and Interplanar d-Values
for the Residue Produced at 550°C

Relative Intensity	d-Values Å	$\sin^2\theta$
2	6.9201	0.0124
1	4.2578	0.0327
3	3.8407	0.0402
3	3.7648	0.0419
3	3.4050	0.0512
10	3.2754	0.0553
10	3.0043	0.0657
3	2.8044	0.0754
1	2.7515	0.0784
2	2.5408	0.0919
2	2.0113	0.1467
1	1.9832	0.1508
1	1.9025	0.1639
1	1.9729	0.1524
1	1.7418	0.1955
1	1.6502	0.2179

APPENDIX H

Observed $\sin^2\theta$ (λ = 1.54051 Å)
and Interplanar d-Values
for the Sublimate Produced at 550°C

Relative Intensity	d-Values Å	$\sin^2\theta$
3	6.8842	0.0125
1	6.7529	0.0130
1	3.6529	0.0445
1	3.4911	0.0487
1	3.4351	0.0503
1	3.2632	0.0557
3	3.0061	0.0657
10	2.1389	0.1297

APPENDIX I

Observed $\sin^2\theta$ (λ = 1.54051 Å)
and Interplanar d-Values
for the Residue Produced at 600°C

Relative Intensity	d-Values Å	$\sin^2\theta$
3	6.7937	0.0129
1	6.2909	0.0150
5	3.6309	0.0450
5	3.4583	0.0496
5	3.2797	0.0552
10	2.9989	0.0660
2	2.7921	0.0761
1	2.7266	0.0798
1	2.5370	0.0922
2	2.1388	0.1297
1	2.1026	0.1342
1	1.9778	0.1517

APPENDIX J

Observed $\sin^2\theta$ (λ = 1.54051 Å)
and Interplanar d-Values
for the Sublimate Produced at 600°C

Relative Intensity	d-Values Å	$\sin^2\theta$
5	6.8967	0.0125
1	6.4950	0.0141
1	4.2875	0.0323
1	3.8488	0.0401
2	3.6668	0.0441
2	3.4949	0.0486
10	3.2814	0.0551
7	3.0112	0.0654
5	2.5271	0.0929
10	2.1443	0.1290
1	2.1074	0.1336
2	2.0424	0.1422
1	1.7895	0.1853

APPENDIX K

Observed $\sin^2\theta$ (λ = 1.54051 Å)
and Interplanar d-Values
for the Residue Produced at 700°C

Relative Intensity	d-Values Å	$\sin^2\theta$
2	9.5021	0.0066
2	6.9808	0.0122
3	3.6617	0.0443
2	3.5003	0.0484
2	3.2942	0.0547
10	3.0116	0.0654
8	2.8025	0.0755
2	2.4240	0.1010
1	2.3957	0.1034
3	2.1414	0.1293
1	2.1116	0.1331
1	2.0389	0.1427
4	1.9778	0.1517
1	1.7754	0.1882
1	1.8288	0.1774
5	1.64858	0.2183
1	1.5322	0.2527

APPENDIX L

Observed $\sin^2\theta$ (λ = 1.54051 Å)
and Interplanar d-Values
for the Sublimate Produced at 700°C

Relative Intensity	d-Values Å	$\sin^2\theta$
3	6.8844	0.0125
2	6.4338	0.0143
2	4.5028	0.0293
2	4.2415	0.0330
2	3.8260	0.0405
3	3.6536	0.0445
3	3.4858	0.0488
2	3.4308	0.0504
2	3.2618	0.0558
8	3.0047	0.0657
5	2.7979	0.0758
10	2.1422	0.1293
2	1.8737	0.1690

APPENDIX M

Observed $\sin^2\theta$ (λ = 1.54051 Å)
and Interplanar d-Values
for the Product Produced From the GdI_3 + $GdCl_3$ Melt

Relative Intensity	d-Values Å	$\sin^2\theta$
1	1.1042	0.4866
1	1.1137	0.4784
1	1.1232	0.4703
1	1.1435	0.4537
10	1.1499	0.4487
2	1.1708	0.4328
1	1.1772	0.4281
1	1.1838	0.4233
2	1.2235	0.3963
4	1.2556	0.3763
2	1.2663	0.3700
1	1.2741	0.3655
4	1.3053	0.3482
1	1.3455	0.3277
3	1.3659	0.3180
1	1.4517	0.2815
1	1.4527	0.2811
1	1.5169	0.2578
1	1.6316	0.2229

APPENDIX N

Observed $\sin^2\theta$ (λ = 1.54051 Å)
and Interplanar d-Values for GdOCl

Relative Intensity	d-Values Å	$\sin^2\theta$
1	7.8389	0.0097
1	6.7181	0.0132
1	3.5812	0.0463
8	3.3986	0.0514
8	2.7906	0.0762
1	2.7433	0.0788
1	2.6427	0.0850
9	2.4986	0.0950
1	2.1370	0.1300
2	1.9683	0.1531
1	1.7337	0.1974
2	1.7025	0.2047
2	1.5567	0.2443

APPENDIX O

Observed $\sin^2\theta$ (λ = 1.54051 Å)
and Interplanar d-Values for $GdCl_3 \cdot \underline{n}H_2O$

Relative Intensity	d-Values Å	$\sin^2\theta$
2	6.6044	0.0136
3	6.3809	0.0146
3	5.4394	0.0201
3	5.0727	0.0231
3	4.8447	0.0253
3	4.5639	0.0284
3	4.4145	0.0304
1	4.1382	0.0347
5	3.9773	0.0375
5	3.5660	0.0467
4	3.4224	0.0507
2	3.1003	0.0673
1	2.5921	0.0883
1	2.5269	0.0929
1	2.4646	0.0977
3	2.4147	0.1018
1	2.3365	0.1087
1	1.1309	0.4638

APPENDIX P

Observed $\sin^2\theta$ (λ = 1.54051 Å)
and Interplanar d-Values for $GdI_3 \cdot \underline{n}H_2O$

Relative Intensity	d-Values Å	$\sin^2\theta$
1	6.8263	0.0127
1	6.1709	0.0159
1	7.4033	0.0108
1	5.8010	0.0176
1	5.5624	0.0192
1	5.1550	0.0223
10	4.2004	0.0336
9	4.0469	0.0362
6	4.9343	0.0244
6	4.5693	0.0284
9	3.9630	0.0378
2	3.3419	0.0531
7	3.0948	0.0619
7	2.9955	0.0661
7	2.8827	0.0714
8	2.6614	0.0838
4	2.4189	0.1014
9	2.1380	0.1298
6	2.1251	0.1314
3	2.1008	0.1344
8	2.2060	0.1219
3	2.1926	0.1234
2	2.0639	0.1393
1	2.1151	0.1326
1	2.0230	0.1450
2	1.9885	0.1500
4	1.8168	0.1798
3	1.7185	0.1869
2	1.7189	0.2009
2	1.7049	0.2041
1	1.6659	0.2138
1	1.6268	0.2242
1	1.6042	0.2305
1	1.5841	0.2364
1	1.5627	0.2430
1	1.5291	0.2538
1	1.5197	0.2570

APPENDIX P. (Cont'd.)

Relative Intensity	d-Values Å	$\sin^2\theta$
1	1.5055	0.2618
1	1.4844	0.2693
1	1.4603	0.2782
1	1.4269	0.2914
1	1.4039	0.3010

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