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Synthesis and Nonstoichiometry of the Zirconium Trihalides

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The synthesis of ZrX_3 (X = Cl, Br, I) by reaction of the corresponding tetrahalides with ZrCl, ZrBr, or $ZrI_{1.8}$ in sealed tantalum tubing gives high-purity, single-phase products, thereby avoiding problems of the relatively low reactivity of and contamination by zirconium powder reductant used previously. Phase limits for the three trihalides established by isopiestic equilibration with the adjoining phases are $2.94\ (2) \leq \mathrm{Cl{:}Zr} \leq 3.03\ (2)$ (440 °C), $2.87\ (2) \leq \mathrm{Br{:}Zr} \leq 3.23\ (2)$ (435 °C), and $2.83\ (5)$ (775 °C) $\leq \mathrm{I{:}Zr} \leq 3.43\ (5)$ (475 °C). The hexagonal lattice constants for the bromide phase (Guinier techniques) decrease linearly with increasing bromide content across the entire range without the development of any additional lines. The variation of the *c* dimension for ZrI_3 (and HfI_3) on oxidation is in the opposite direction, and in this case extra lines from a presumed superlattice structure develop toward the upper limit. The structural implications of these results are considered. The reported structure for α-$ZrCl_3$, an unusual BiI_3-type variant, was based on a misassigned ZrCl powder pattern and therefore appears to be in error.

Introduction

Although the zirconium (and hafnium) trichloride, tribromide, and triiodide have been known for a relatively long time, only recently have good routes to still more reduced phases been found. The monohalides ZrCl and ZrBr have been especially well studied among the latter,[1-3] and the dihalides have also recently been identified and characterized structurally.[4] The ready availability of these lower halides provides a ready route to the pure trihalides which avoids substantial problems of slow and incomplete reactions found with Zr–ZrX_4 reactions. This improvement has also now allowed definitive biphasic equilibrium experiments on the sometimes substantial composition ranges of the trihalides.

The trihalide structure proposed first by Dahl et al.[5] from powder work consisted of hexagonal-close-packed halide layers between which equally spaced zirconium (or hafnium) atoms occupied one-third of the octahedral interstices so as to form infinite linear chains of metal atoms or, in terms of the coordination polyhedra, infinite chains of MX_6 octahedra sharing opposite faces. Shortly thereafter, Watts[6] concurred on the structure of $ZrCl_3$ based also on powder data, while more recently Kleppinger et al.[7] obtained the same results from a diffraction study of $ZrBr_3$. Single crystals for the latter were grown from a $ZrBr_4$–Al_2Br_6 melt in contact (in another part of the container) with aluminum or zirconium at 270–290 °C.[8]

Interphase reactions in the binary systems are characteristically slow, especially where zirconium is one of the reductants, and so much of the early work involving direct ZrX_4–Zr reaction has been complicated by the lack of equilibrium and poorly crystalline products. Thus, unreacted metal was always found in the products utilized by Dahl et al.[5] (bomb reduction, glass container, 500–700 °C[9]). Troyanov[10] avoided this problem in the preparation of $ZrCl_3$ by using steel balls in a rotating autoclave (550 °C, 60 atm) to continually expose fresh metal surface while Schläfer and co-workers[11,12] employed a modified bomb technique (483–500 °C, 40–60 atm in glass) to prepare $ZrCl_3$ and $ZrBr_3$ from excess tetrahalide and very finely powdered metal. However, the latter required a three- to fourfold excess of ZrX_4 and total times of 7–8 weeks to obtain trihalides which still contained up to 1.1% unreacted metal. A key to the improvement of these synthesis routes was found in early work on ZrCl, where the stronger reducing conditions for the Zr–$ZrCl_4$ reaction (600/500 °C, 12 days, sealed tantalum tube) yielded, in addition to ZrCl, sublimed (or transported) $ZrCl_3$.[1] The more reactive monohalides prove to be much more effective reducing agents for the tetrahalides.

Throughout earlier investigations of ZrX_3 phases there have been some hints that these were nonstoichiometric, though this possibility has been generally ignored in the measurement of other properties. However, many of the earlier syntheses involved nonequilibrium conditions so that a well-crystallized, single-phase product was not ensured, and the stoichiometric deviations, particularly in low X:Zr ratios, could be attributed to the presence of a poorly crystalline second phase. Thus, $ZrX_{2.8}$ compositions, X = Cl, Br, obtained[13-16] by ZrX_3 disproportionation under vacuum at temperatures up to 450 °C without an evident phase change could have contained some of the poorly crystalline second-stage product (ca. ZrX_2) which is obtained on further decomposition. A composition $ZrI_{2.86}$ has been obtained likewise.[17] In the other extreme, Struss and Corbett[18] used isothermal equilibration experiments to establish that a significant range of composition existed for the supposedly isostructural HfI_3, the phase being only superstoichiometric ($3.0 \leq \mathrm{I{:}Hf} \leq 3.5$ at 475 °C) with clear development of a superlattice toward the upper composition limit. The nonstoichiometry turns out to be a general property of the zirconium trihalides as well.

Experimental Section

Syntheses. High-purity (>99.5%) anhydrous trihalides of desired compositions were prepared by quantitative reaction of weighed amounts of the respective tetrahalide and the most reduced phase, viz., ZrCl, ZrBr, or $ZrI_{1.8}$. These reductants prove to be much more reactive than the metal, and their use not only allows considerably shorter reaction times to gain homogeneous products but also eliminates the problems reported earlier (cf. Introduction) of separating the trihalide from unreacted metal and intermediate products of uncertain composition.

Synthetic methods utilized for the preparation of the tetrahalides from the elements and of stoichiometric ZrCl and ZrBr from metal and tetrahalide have been described elsewhere.[3] Reactor-grade crystal bar zirconium (<500 ppm Hf) was used in all preparations. Tetrahalides were purified by vacuum sublimation ($<10^{-5}$ Torr) through a coarse-grade Pyrex frit. Transfer and manipulation of these and all reduced halides were carried out in a drybox filled with a prepurified nitrogen atmosphere which constantly recirculated through a column of molecular sieve. All subsequent reactions were performed in tantalum containers which had been sealed by arc welding under helium.

The stoichiometric trihalides were prepared in 5–15-g quantities by grinding weighed amounts of the very soft ZrCl or ZrBr or moderately soft $ZrI_{1.8}$ with the relatively hard ZrX_4 to produce homogeneous reaction mixtures which were then heated in sealed tantalum containers of minimal free volume (1–3 cm^3). For the Zr–Cl and Zr–Br systems the reaction temperature was raised slowly from 350 to 450 °C over a period of 3 days and maintained there for 7–10 days. (The autogenous $P(ZrX_4)$ over ZrX_3(s) at 450 °C is $\simeq 1$ atm and 5×10^{-2} atm, respectively.) For the Zr–I system the temperature was raised from 450 to 600 °C over 3 days and maintained there for 10 days ($P(ZrI_4) \leq 10^{-2}$ atm). Guinier powder patterns of the trihalide products gave no evidence of unconsumed reactants. With these and more reduced samples an insignificant percentage of the products

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consists of $ZrX_4(g)$ at the equilibration temperature. The diiodide composition used to prepare stoichiometric ZrI_3 was made by reduction of ZrI_4 with a 50-fold excess of metal foil at 800 °C for 3 weeks, the product being analyzed[3] for both elements to be $ZrI_{1.95}$ (99.94% recovery).

Phase Limits. Composition limits of the three trihalide phases were determined from isothermal, isopiestic equilibrations of the sort described earlier[18] between approximately stoichiometric trihalides and the corresponding tetrahalide or "dihalide". The two-compartment apparatus is 5–8 cm long and employs concentric 9.5 and 6.4 mm o.d. tubes crimp-welded together at one end with the outer tube capped at the other. One reactant is placed inside the 6-mm tube and the other between the tubes. This design serves to keep the reacting solids physically separate and to minimize free volume while permitting free passage of gaseous ZrX_4 between compartments. Pressures up to 30–40 atm can be contained.

One-week equilibrations of ZrX_3 with excess ZrX_4 were sufficient to yield upper-limit compositions for the trihalides. System pressures, fixed by the vapor pressure of the condensed tetrahalide, were approximately 20 atm above $ZrCl_4$ at 440 °C, 10 atm above $ZrBr_4$ at 435 °C, and 5 atm above ZrI_4 at 475 °C.

Preparation of trihalides at their reduced limit via biphasic equilibrations were complicated by the tendency of ZrCl and ZrBr starting materials to become coated and blocked with intermediate phases, leading to only a pseudoequilibrium between the trihalide and the next lower phase. In fact, attempts to prepare appreciable amounts of stoichiometric $ZrCl_2$ and $ZrBr_2$ for equilibration with ZrX_3 always produced mixtures of the corresponding ZrX, ZrX_2, and ZrX_3 even after weeks of heating at temperatures where system pressures were several atmospheres. However, a careful study of powder patterns resulting from numerous equilibrations in the Zr–Cl and Zr–Br systems suggests that the monohalides were effectively removed from the system for subsequent equilibrations below 550 °C insofar as the ZrX_3/ZrX_2 (X = Cl, Br) equilibria are concerned. For biphasic equilibrations with ZrX_3 at 600 °C compositions of approximately $ZrX_{2.5}$ which contained no ZrX were used. In two cases equilibration of $ZrCl_{3.00}$ with a $ZrCl_3/ZrCl_2$ mixture at 600 °C unexpectedly produced a trichloride at the lower phase limit mixed with 1–3% of the dichloride, apparently resulting from $ZrCl_3$ disproportionation. In these cases it was necessary to extrapolate the analytical data to an estimated lower limit.

Analyses. All elemental analyses were performed by gravimetric techniques described before[3] on 0.2–0.4-g samples with weights known to 0.1%. Analyses were not performed for trihalide samples which were single phase to x rays and had their composition predetermined by stoichiometric reaction of analytically well-characterized materials. Analysis of other samples (e.g., phase limits) for both elements routinely gave recoveries of 99.8%. In a few cases small sample size permitted analysis for halide only.

X-Ray Data. Powder diffraction data of excellent quality for high-precision line-position measurements (±0.005° in θ) were obtained with the evacuable Model XDC-700 Guinier camera (IRDAB, Stockholm) equipped with a quartz monochromator to provide a clean Cu $K\alpha_1$ incident beam. NBS Si powder was used as an internal standard. A standard least-squares program was used to extract lattice parameters from collected data.

Ground trihalide samples mixed with 10% Si were mounted between two pieces of cellophane tape on a supporting washer in the drybox and this was transferred in a closed container to the camera which was immediately evacuated after the washer was mounted. Even $ZrCl_3$ and $ZrBr_3$ give no visual (discoloration) or x-ray (line broadening) evidence of deterioration over several days as long as the exposure of the mounted sample to air during transfer to the camera was minimized (3–5 s) and the sample was stored in the drybox or in an evacuated container at other times. Discoloration indicated that the triiodide does react slowly with the tape adhesive so that patterns of this phase were always taken immediately after mounting the sample.

Results

It was the purpose of the present work to define precise compositions and lattice constants for the phase limits of the zirconium trichloride, tribromide, and triiodide. Intermediate compositions were also studied to provide information concerning the properties of these nonstoichiometric phases between the phase limits.

Table I. Phase Limits and Crystal Data for Nonstoichiometric Zirconium Trihalides

Phase compn[a]	Reacn temp, °C	In equil with	Lattice constants		
			N[b]	a, Å	c, Å
$ZrCl_{2.94(2)}$	500	$ZrCl_2$			
$ZrCl_{2.94(2)}$[c]	600	$ZrCl_2$	10	6.3863 (5)	6.1374 (7)
$ZrCl_{3.02(2)}$	450	d	21	6.3842 (4)	6.1341 (5)
$ZrCl_{3.03(2)}$	440	$ZrCl_4$			
$ZrBr_{2.87(2)}$	435	$ZrBr_2$	21	6.7565 (5)	6.3245 (5)
$ZrBr_{3.00(2)}$	450		21	6.7472 (6)	6.3135 (6)
$ZrBr_{3.10(2)}$	400		21	6.7399 (5)	6.3050 (5)
$ZrBr_{3.23(2)}$	435	$ZrBr_4$	21	6.7309 (5)	6.2995 (6)
$ZrI_{2.83(5)}$[e]	775	ZrI_2	14	7.2949 (5)	6.6672 (7)
$ZrI_{2.90(3)}$	700		22	7.2907 (5)	6.6663 (5)
$ZrI_{3.00(3)}$	600		26	7.2850 (6)	6.6587 (9)
$ZrI_{3.43(5)}$	475	ZrI_4	15	7.2346 (5)	6.698 (1)

[a] Phase limits are given in bold type. Uncertainty in the last figure is given in parentheses. [b] The number of indexed lines used in the lattice parameter refinement. [c] Extrapolated from analytical data for $ZrCl_{2.87}$ and $ZrCl_{2.91}$ compositions containing small and trace amounts of the dichloride, respectively. [d] Intermediate composition. [e] Estimated from sample of composition $ZrI_{2.2}$ using the observed a cell parameters of $ZrI_{3.0}$ and $ZrI_{2.9}$.

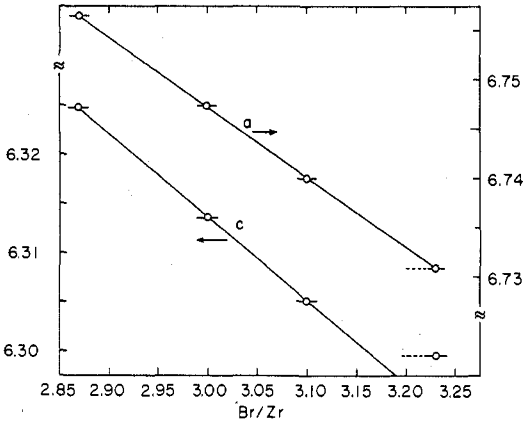

Figure 1. Variation of the lattice constants of the $ZrBr_3$ phase with composition.

Phase limits for the three trihalides together with hexagonal lattice constant data are given in Table I. The phase breadths are found to increase in a reasonable manner from chloride, 2.94 (2) ≤ Cl:Zr ≤ 3.03 (2) (440 °C), through the bromide, 2.87 (2) ≤ Br:Zr ≤ 3.23 (2) (435 °C), to the iodide, 2.83 (5) (775 °C) ≤ I:Zr ≤ 3.43 (5) (475 °C), with significant lattice parameter shifts for the tribromide and triodide but a change that is on the border of significance for the trichloride. Figure 1 illustrates the lattice parameter variation with tribromide composition while Figure 2 compares the ZrI_3 data with those calculated from patterns for superstoichiometric $HfI_{3.0-3.5}$ obtained earlier.[18] (Note the lattice dimension scale is compressed in Figure 2.) There is no evidence that lattice constants at constant composition are dependent on the temperature of equilibration over the range studied. The phase limits are in equilibrium with the tetrahalides and dihalides ($ZrI_{1.8}$) at the extremes; although intermediate cluster compounds Zr_6Cl_{15} and Zr_6I_{12} are known,[19] their rates of formation are so low they are not believed to be effective components of the equilibria.

As observed by other workers, the color of the zirconium trihalides depends on their physical form. Light green needles of $ZrCl_3$ and golden-green needles of $ZrBr_3$ both give rise to dark green powders on grinding and leave a bluish green tinge on the mortar from the grinding. Blue-black needles of ZrI_3 yield a greenish black powder. However, in addition to a color dependency on physical form, powdered tribromide samples

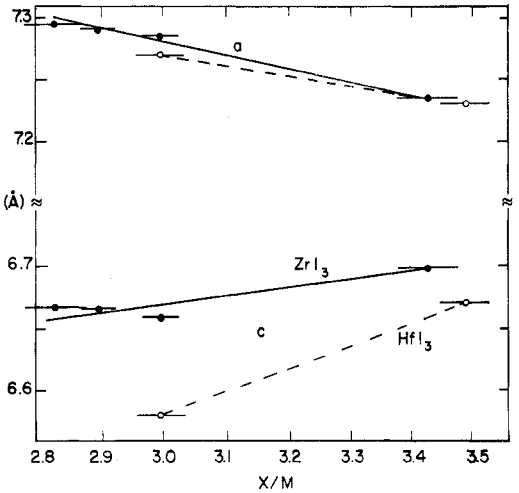

Figure 2. Variation of lattice constants for triiodide phases: solid lines and filled circles, ZrI_3; dashed lines and open circles, HfI_3.[18] The ordinate is compressed relative to Figure 1.

especially show a striking dependence of color on composition. Powdered samples of $ZrBr_{2.9}$ are olive green, those of $ZrBr_{3.0}$ are greenish brown, those of $ZrBr_{3.1}$ are dark brown, and those of $ZrBr_{3.2}$ are bluish black.

Relatively large single-crystal needles of the trihalides (up to 15 mm long and 1 mm in diameter for ZrI_3) are produced by transport under autogenous pressures to the colder zone of a temperature gradient. These have appeared at the higher temperatures investigated and only in systems which are quite reducing. For example, about 100 mg of beautiful (1–3 mm long) needles of the tribromide are transported in 2–3 weeks using a 700/600 °C gradient with a net composition $ZrBr_{1.4}$ (ZrBr and $ZrBr_2$) at the hot end. Both yield and crystal size (up to 1 cm long) are increased by employing $ZrBr_{1.1}$ at the hot end and a 750/600 °C gradient. Guinier patterns of powdered single crystals of both $ZrBr_3$ and ZrI_3 show very clearly that they are substoichiometric with compositions near the lower phase limit. All of these crystals have a metallic sheen and all tend to fray badly into very thin fibers when cut or crushed, consistent with the highly anisotropic character of the structure with its presumed one-dimensional metal–metal bonding.

Discussion

In order to achieve the expressed purpose of this work, good analytical data and precise lattice parameters had to be obtained for samples of high purity and crystallinity. The preparative methods described above produced virtually 100% yields of the pure, highly crystalline trihalides over their defined stoichiometric ranges. The variety of difficulties reported in the literature were overcome through extended isothermal equilibrations at relatively high temperatures in sealed tantalum containers. The use of tantalum as a container material offers the dual advantages over glass of strength and inertness at temperatures where equilibrium is attained in a reasonable time (3 weeks or less) and where reaction pressures may reach 20–30 atm. The use of a high-precision Guinier camera and of silicon as an internal standard has permitted determination of lattice parameters about 1 order of magnitude more precise than most previous literature values for these compounds.

Most "trihalide" products described heretofore in the literature have evidently been neither pure nor equilibrium products but were mixtures containing unconsumed metal and/or other lower halides, for example, the poorly crystalline products of steady-state (nonequilibrium) disproportionation reactions carried out at relatively low temperatures in glass containers.[13-17] The powder pattern of one such disproportionation product which was attributed to ZrI_2[20] is virtually identical with that of lower limit triiodide made in the present study and very different from those of $ZrI_{1.8}$ and Zr_6I_{12} also prepared.[4,19] It therefore seems likely that the product examined was really undisproportionated triiodide mixed with very poorly crystalline and hence undetected "diiodide" etc. Isobaric annealing of these "first-stage" disproportionation products $ZrCl_{2.82}$ and $ZrBr_{2.80}$[15,16] at 320–370 °C was found to improve the crystallinity to some degree. However, x-ray evidence accumulated in this laboratory suggests that very poorly crystalline ZrX_2 is also produced by such a nonequilibrium disproportionation of the trihalides in vacuum, and this cannot be annealed to higher crystallinity at the temperatures selected by these workers; consequently, their trihalide lower limit compositions would probably be too low. There is, however, general agreement that the hexagonal *a* lattice parameter of substoichiometric tribromide decreases with an increase in the BrZr ratio, but the present work shows that the variation of *c* is equally large and both trends extend well to the superstoichiometric region as well (Figure 1).

The reported structure of the (β) zirconium trihalides is that of infinite chains of metal atoms in the [001] direction and normal to the hcp halogen layers. These chains can be viewed as ZrX_6 octahedra sharing opposite faces, with octahedral sites in the other two-thirds of the potential chains being ideally vacant.[5,6] Systematic absences require regular spacing of metal and halogen atom layers along *c*, and the centrosymmetric space group *P6₃/mcm* was selected as most probable by both groups. The recent restudy of the tribromide structure utilizing single-crystal data yielded small anisotropic thermal parameters for all atoms and these were plausibly interpreted in terms of the absence of local metal displacements (pairing etc.) and in support of the choice of the space group.[7] Comparison of both the lattice parameters reported in the last study, $a = 6.7275$ (20) Å and $c = 6.2992$ (14) Å, with those in Table I and the dark brown color for the $ZrBr_3$ product reported earlier[8] with that cited above at first thought suggests that the actual $ZrBr_3$ crystal utilized may have been significantly superstoichiometric through oxidation by the excess of solvated zirconium(IV) in the eutectic melt from which it was grown. However, analytical data have consistently supported a stoichiometry quite near Br:Zr = 3.0:1,[21] in which case another less obvious explanation will be necessary. On the other hand, the color change observed on oxidation from $ZrBr_3$ to $ZrBr_{3.2}$ probably is the source of an erroneous conclusion by Schläfer[11] that $ZrBr_3$ is dimorphic.

A second form of the trichloride, basically a disordered BiI_3 structure sometimes referred to as α-$ZrCl_3$, has been reported by Swaroop and Flengas.[22] The powdered material was obtained in only moderate purity (95–99% based on chloride) from sealed-tube reactions of heated metal with $ZrCl_4$(g) at about 1 atm, a constant 45% conversion being obtained when the metal was heated in the range of 700–850 °C. Other investigators, generally working at lower temperatures, have not reported this $ZrCl_3$ structure, leading Watts[6] to postulate that α-$ZrCl_3$ probably formed only at higher temperatures. However, no other $ZrCl_3$ structure has been seen in the present study either, even after extended equilibrations as high as 600 °C. Furthermore, certain aspects of the α structure deduced seem unusual, particularly the low x-ray density, 2.20 g cm^{-3} vs. 3.05 g cm^{-3} for the usual (β) $ZrCl_3$,[6] 2.33 Å for the shortest Zr–Cl distances, the same as in $ZrCl_4$[23] rather than closer to those in β-$ZrCl_3$ (2.55 Å), and Cl–Cl distances of 3.13 Å between adjacent chlorine layers *with or without* intervening metal atoms rather than more usual values, ca. 3.6 Å for at least the latter. These observations led to a reconsideration of the powder data used and the discovery that all but 2 (of

19) lines reported correspond to those of ZrCl[2] when given a constant 1.8% displacement of reported distances. The presence of some ZrCl is not an illogical result of the preparative method since $P(ZrCl_4)$ was well short of that estimated above $ZrCl_3$(s) (Experimental Section—Syntheses). The $ZrCl_2$ pattern reported by the same authors[24] is clearly that of monoclinic ZrO_2.[4]

The nonstoichiometry found for the trihalides as well as the weak binding between strands or crystallites in the fibrous macrocrystals suggests a variety of defects must occur in the real crystals. Diffraction lines forbidden by the space group (a point of some dispute for $ZrCl_3$[5]) have never been observed in powder patterns of any tribromide composition across the entire homogeneity range $2.87 \leq Br{:}Zr \leq 3.23$, even after considerable annealing. But in substoichiometric trichloride a weak and very broad 001 band (6–10 times normal line width) is generally present, especially at the lower limit, although no extra lines have ever been found in Guinier patterns of the slightly superstoichiometric chloride. On the other hand, triiodide samples at the upper limit exhibit three symmetry-forbidden reflections as weak but sharp lines (001, 101, 103) along with four other sharp, faint lines at 9.65, 7.43, 3.78, and 2.50 Å. These presumably originate from some superstructure analogous but not identical with that deduced for the superstoichiometric hafnium triiodide.[18]

There is not much which can be added to the earlier[18] speculation regarding the likely mechanism for superstoichiometry involving normal cation sites, viz., $4Zr^{3+} = 3Zr^{4+} + V_{Zr}$. Extended Zr–Zr interactions and delocalization which presumably (but not assuredly) occur along the metal chains would thus be interrupted. Of course, displacement of zirconium(III) or zirconium(IV) atoms to isolated positions in otherwise empty octahedral chains is possible, even at stoichiometry, thereby severely limiting the possibility of significant one-dimensional conductivity. No substantial electron conduction in these materials along the chains has ever been found. With two metal atoms per cell a splitting of the presumed band to give an insulating material has been proposed.[25] The simplest substoichiometry mechanism would appear to be the interchain substitution of additional metal atoms (i.e., $Zr_{1+x}X_3$), with possible electron transfer to the chains already present, but long-range organization of these additional defects into proposed[13] 001 shear planes is not evident to x rays.

In all compounds studied oxidation (metal elimination) is accompanied by a logical contraction of the *ab* plane over the entire composition range (Figures 1, 2). In $ZrBr_3$ and $ZrCl_3$ oxidation also yields contraction in *c*, suggesting that elimination of metal atoms is more than compensated by increased binding by the high oxidation states left behind or, perhaps better, that the metal–metal bonding holds the halogen layers apart somewhat. But with the largest iodide, the *c*/*a* ratio is the smallest, the observed *c* dimension elongation with oxidation for both ZrI_3 and HfI_3 is exactly opposite, and only here do superlattice effects appear on oxidation. Additional investigations are certainly needed to clarify the nonstoichiometry as well as conduction processes.

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Lower Oxidation States of Sulfur. 1. Spectrophotometric Study of the Sulfur–Chlorine System in Molten NaCl–AlCl$_3$ (37:63 mol %) at 150 °C

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Four different cationic sulfur species were produced by anodic oxidation of sulfur in a NaCl–AlCl$_3$ (37:63 mol %) melt at 150 °C. Good evidence was found for the existence of S(IV) and for the existence of S(II). The most likely oxidation states for the two other species were found to be +1 and $+^1/_2$. The spectra of S(IV) and S(II) as well as the spectra of the possible S_2^{2+} and S_4^{2+} species were calculated from the measured spectra.

Introduction

It is well-known that sulfur in analogy with selenium and tellurium is able to form low positive oxidation states in acidic media such as $H_2S_2O_7$, HSO_3F, HF + SbF_5, and SO_2 + SbF_5.[1,2] It is also possible to stabilize some of these oxidation states in crystals with SO_3F^-, AsF_6^-, SbF_6^-, and $Sb_2F_{11}^-$ as anions. The species S_4^{2+}, S_8^{2+}, and S_{16}^{2+} have been isolated in this way.[1,2]

Low oxidation states of the chalcogens can also be formed in acidic chloroaluminate melts.[3] In the case of selenium and

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