For Symposium Volume

"High Temperature Metal Halide Chemistry"

Electrochemical Society Meeting   MASTER
Atlanta, GA, Oct. 10 - 14, 1977

for title, see inside

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NEW REDUCED ZIRCONIUM HALIDE PHASES
FROM HIGH TEMPERATURE REACTIONS

John D. Corbett, Richard L. Daake, Alan Cisar
and Dennis H. Guthrie

Ames Laboratory-ERDA and Department of Chemistry
Iowa State University, Ames, Iowa 50011

The number of reduced phases known in the $Zr-ZrX_4$ systems (X = F, Cl, Br, I) has recently been increased considerably by the results of high temperature equilibrations and transport reactions in sealed tantalum containers. Syntheses and properties are considered for the six new phases characterized structurally, namely, the double metal sheet structures of the metallic ZrCl and ZrBr, the single metal layers of $ZrCl_2$ ($3R-NbS_2$ type), and the first isolated zirconium clusters which occur in $(Zr_6Cl_{12})Cl_3$, Zr_6I_{12} and Zr_6Cl_{12}. The appreciable phase breadths which have been established for the $ZrCl_3$, $ZrBr_3$ and ZrI_3 phases are also presented together with x-ray powder diffraction evidence on the process.

Reactions of oxidizing halide media with zirconium metal at elevated temperatures, conditions appropriate for corrosion of this important structural metal, have been found to yield a variety of new reduced halides. These products are particularly remarkable in the diversity of metal-metal bonded structures exhibited. Prior to the present studies only the trichlorides, bromides, and iodides had been prepared in the pure form and characterized structurally.[1] It is now evident that earlier difficulties in obtaining lower phases are of kinetic rather than thermodynamic origin, and that very slow formation reactions for the reduced phases result from the combination of structural complexities in the products, slow diffusion in the solid state, and only minor amounts of any reduced species in the gas phase which might contribute to transport reactions. Thus successful syntheses in $Zr-ZrX_n$ or $ZrX-ZrX_n$ (n = 3, 4) systems customarily require periods of weeks at 700 - 1000° C in sealed 15 mil tantalum tubing, the latter proving to be an excellent inert container capable of withstanding 30 - 40 atm. Slow but effective transport reactions, presumably involving $ZrX_3(g)$, have allowed the

production of single crystals and thence the crystallographic characterization of most of the new phases produced. The structural results for the compounds discussed below are summarized in Table I.

ZrCl, ZrBr: These "line compounds" occur in equilibrium with the metal. Their direct synthesis is achieved as, for example,

$$3Zr \text{ (turnings, 3-4 mil) } + ZrX_4(g) \xrightarrow[\text{3 weeks}]{450\text{-}825°\text{ C}} 4ZrX(s),$$
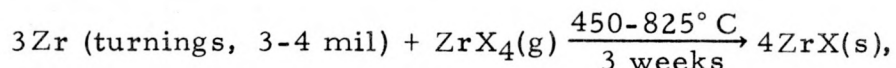
the temperature being gradually increased over the indicated range to accomplish a presumed step-wise reduction. The monohalides consist of close packed homoatomic layers sequenced X-Zr-Zr-X, alternate packing of these four layer slabs differentiating ZrCl (ABC) and ZrBr (ACB) (Figure 1). The difference in packing between ZrCl and ZrBr, particularly in second nearest neighbors, results in substantial differences in the stability of these phases to mechanical damage, ZrCl being graphitic and ZrBr quite brittle. Both are metallic conductors.[2,3]

ZrCl$_2$: Reaction of $ZrCl+ZrCl_3$ at 650/750° C for $\sim$1 month yields transported crystals of $ZrCl_2$. The phase exhibits the 3R-NbS$_2$ structure with close packed Cl-Zr-Cl slabs providing an unusual trigonal prismatic coordination of the metal by halogen. (The sequencing of the layers normal to the c axis is (AcA BaB CbC $\cdots$) where the capital letters refer to halogen layers, the lower case to the metal.) A substantial substoichiometric region, possibly as low as $ZrCl_{1.6}$, is thought to result from addition of zirconium atoms in normally vacant interstice positions between the three-layer sheets. The stoichiometric dichloride is a conductor with a good density of states at the Fermi level according to its XPS spectrum.

ZrCl$_{2.5}$: A reaction similar to that just described also yields very small amounts of transported crystals resembling gem-cut smoky quartz. These turn out to represent the first example of a cluster ion for group IV elements, namely $Zr_6Cl_{12}^{3+}(Cl^-)_3$, with 9 delocalized bonding electrons in the metal cage rather than the 15 in the better known, isostructural[5] Ta_6Cl_{15}. In the view of the Zr_6Cl_{15} structure shown in Figure 2 chloride atoms bridge each edge of the octahedron of metal atoms (solid circles) to give $Zr_6Cl_{12}^{3+}$, and the other chloride ions are outward bonded (exo) from each metal atom of the octahedron so as to bridge between $Zr_6Cl_{12}^{3+}$ clusters.

ZrI_2: This phase, produced by transport of a $ZrI_{1.8}$ composition from 800° to 900° C for four weeks, is remarkable in its relative stability to air and to dilute HCl. It contains still another cluster example, the 12 electron cage Zr_6I_{12}. The view of the independent structural unit shown in Figure 3 emphasizes the simplicity of the arrangement. Nearly cubic close packed layers of iodine atoms run horizontally in the figure, and between these pairs of triangles of zirconium atoms about the three-fold axis (with the intervening iodine missing) are drawn together through metal-metal bonding to form the cluster. The cluster is required to have only $\overline{3}$ symmetry although within experimental error it is a perfect octahedron. Again, iodine atoms (open ellipsoids) bridge each of the twelve edges of the octahedron. Because of the reduced ratio of halogen to metal relative to Zr_6Cl_{15} and the evident need to occupy an outward directed orbital from each zirconium atom, some inner iodine atoms are shared between clusters. Thus those in the top and bottom layers belong only to this unit, while the six edge-bridging iodines in the middle layer simultaneously occupy exo positions in other clusters. Likewise the singly-bonded iodines shown (shaded) about each zirconium are regular edge-bridging atoms in other clusters. The strong tendency to occupy these outward directed orbitals is a common property of all of the better known niobium and tantalum clusters.

Very recently it has proved possible to also synthesize the isostructural Zr_6Cl_{12} compound by long term reactions in the corresponding chloride system at 700° C. It has not yet been established which of the dichlorides - this cluster compound, or the layered compound above - is the equilibrium phase although the cluster is formed at the higher temperature. Metal-metal distances in the zirconium clusters (Table I) are about 0.3 Å longer than in the tantalum and related niobium compounds as the number of bonding electrons has dropped from 15 to either 12 or 9. Condensation of these clusters with elimination of halide can be viewed as a route to the double metal layer structures of the monohalides, Figure 1. It is to be presumed that intermediate structures where clusters have been partially condensed to form one-dimensional strings will also occur, as has been demonstrated for analogous scandium compounds.[6]

ZrX_3: A ready route to these compounds which avoids problems introduced by the low reactivity of the metal with ZrX_4 has been achieved through use of $ZrCl$, $ZrBr$, or $ZrI_{1.8}$ as a more active reductant. Reactions under these circumstances require 450° C

for 7 to 10 days. The phases appear to have appreciable breadth as determined by isopiestic (two-compartment) experiments within sealed tantalum tubing where the phase is equilibrated via $ZrX_4(g)$ with the adjoining higher (ZrX_4) or lower (ZrX_2) condensed phase. The phase limits so determined are listed in Table II. Sizable single crystals of the trihalides 1 to 15 mm long are transported from fairly reducing systems, that is, a $ZrBr_3$_ crystal from a $ZrBr_{1.4}$ composition in a 700°/600° C gradient for two to three weeks, and $ZrI_{2.9}$ crystals from a $ZrI_{2.5}$ composition in 7 days at 900°/800° C.

High resolution powder x-ray data (Guinier technique) confirm the stoichiometry variations. The sizable variation in lattice constants over the range $ZrBr_{2.87}$-$ZrBr_{3.23}$ is shown in Figure 4. The diffraction lines remain sharp over the entire composition with no evidence for any superstructures. In contrast, a broad 0 0 1 reflection or band appears for substoichiometric trichloride, while the upper limit $ZrI_{3.4}$ composition exhibits several sharp lines indicative of a superstructure. The last behavior is analogous to that of $HfI_{3.4}$.[7] The structure known for the ZrX_3 phases[4,8] consists of hexagonal close packed halogen layers between which zirconium atoms occupy rows of octahedral sites so as to form infinite chains parallel to the c-dimension and normal to the halogen layers. Although an infinite chain of metal atoms implies a more or less one-dimensional conductor, we have been unable to find any evidence of substantial conductivity in either the above single crystals or pressed pellets. An appreciable number of vacancies or defects may occur along the chains in the real crystals, or the presumed band may be split,[9] or both. The contraction observed in both the a and c dimensions on oxidation, Figure 4, is interesting. This may be viewed either as an increased binding caused by substitution of zirconium(IV) by the oxidation mechanism $4Zr^{3+} \rightarrow 3Zr^{4+} + V_{Zr}$ or as evidence that the metal-metal bonding actually holds the halogen layers apart. Oxidation of ZrI_3 and HfI_3 produces the opposite trend in the c axis dimension only. The latter effect is not understood but may be associated with the superlattice developed.

Other phases which have been identified but not yet characterized structurally include the non-isostructural $ZrI_{1.8}$ and $ZrBr_{1.8\pm}$, and a still lower iodide. Similar reactions of ZrF_4 with Zr in sealed Ta for several days at 1000° C give no indication of the formation of a new phase, thereby indicating that the reported ZrF_3 is probably metastable.[10]

Acknowledgement

References

1. E. M. Larsen, Adv. in Inorg. Chem. and Radiochem., 13, 1 (1970).

2. D. G. Adolphson and J. D. Corbett, Inorg. Chem., 15, 1820 (1976).

3. R. L. Daake and J. D. Corbett, Inorg. Chem., 16, 2029 (1977).

4. L. F. Dahl, T. Chiang, P. W. Seabaugh and E. M. Larsen, Inorg. Chem., 3, 1236 (1964).

5. D. Bauer and H. G. von Schnering, Z. Anorg. Allg. Chem., 361, 259 (1968).

6. K. R. Poeppelmeier and J. D. Corbett, Inorg. Chem., 16, 1107 (1977).

7. A. W. Struss and J. D. Corbett, Inorg. Chem., 8, 227 (1969).

8. J. Kleppinger, J. C. Calabrese and E. M. Larsen, Inorg. Chem., 14, 3128 (1975).

9. G. D. Stucky, A. J. Schultz and J. M. Williams, Ann. Rev. Mater. Sci., 7, 321 (1977).

10. M. Fukutomi and J. D. Corbett, J. Less-Common Metals, 55, 125 (1977).

Table I. Crystallographic Data and Metal-Metal Distances for the Reduced Zirconium Halides.

	Space Gp.	Lattice Const., Å	Refinement Residual (R)	d_{Zr-Zr}, Å
$ZrCl$[a]	$R\bar{3}m$	$a = 3.421$ $c = 26.693$	0.07	3.09 (x3), 3.42 (x6)
$ZrBr$[b]	$R\bar{3}m$	$a = 3.503$ $c = 28.091$	0.16	3.13 (x3), 3.50 (x6)
$ZrCl_2$	$R3m$	$a = 3.382$ $c = 19.378$	0.09	3.38 (x6)
Zr_6I_{12}	$R\bar{3}$	$a = 14.502$ $c = 9.995$	0.11	3.20 (x4)
Zr_6Cl_{15}	$Ia3d$	$a = 21.141$	0.11	3.20 (x2), 3.22 (x2)
$ZrCl_3$	$P6_3/mcm$[c]	$a = 6.384$ $c = 6.134$	—	3.07 (x2)
$ZrBr_3$	$P6_3/mcm$[c]	$a = 6.747$ $c = 6.314$	—	3.16 (x2)
ZrI_3	$P6_3/mcm$[c]	$a = 7.285$ $c = 6.659$	—	3.33 (x2)

[a] Ref. 2.
[b] Ref. 3 (powder data).
[c] Ref. 4.

Table II. Phase Limits for the Zirconium Trihalides.[a]

	Lower Limit		Upper Limit	
	X/Zr	t, °C	X/Zr	t, °C
Cl	2.94(2)	500, 600	3.03(2)	440
Br	2.87(2)	435	3.23(2)	435
I	2.83(5)	775	3.43(5)	475

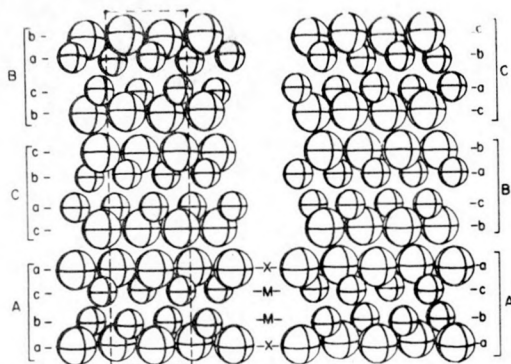[a] Standard deviations in the last figure are given in parentheses.

Figure 1

A depiction of the structures of
ZrBr (left) and ZrCl (right).
The close packed layers are
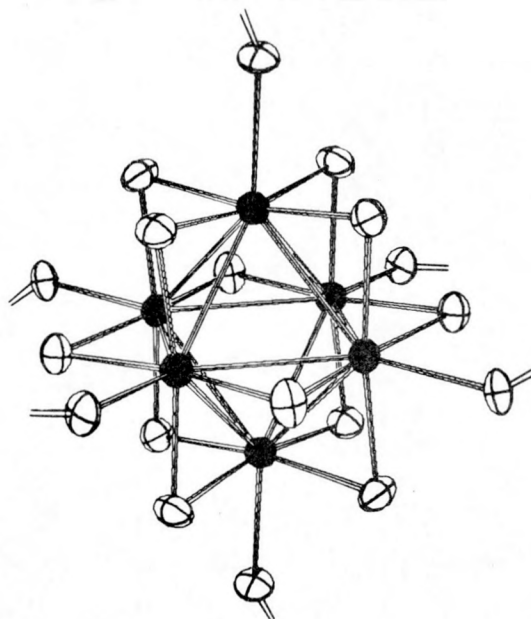horizontal, the $\underline{c}$ axis vertical.

Figure 2

The cluster unit in $Zr_6Cl_{12}Cl_{6/2}$.
The metal atoms are the solid
ellipsoids. The six chlorine
atoms exo to the metals are
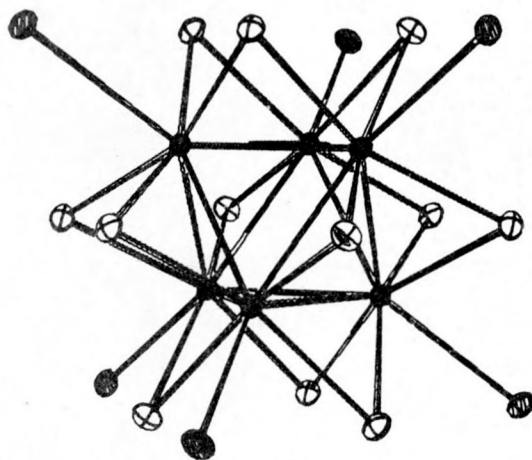bridging between clusters.

Figure 3

The cluster unit in Zr_6I_{12} with
the $\underline{c}$ axis vertical and close
packed layers horizontal. The
singly-bonded, shaded iodine
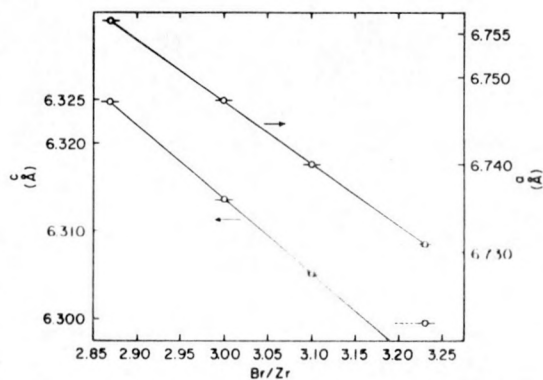atoms are edge-bridging types
in other clusters.

Figure 4

The dependence of the hexagonal
lattice constants of the $ZrBr_{3\pm}$
phase on composition.