The Preparation of ZrX_3 Single Crystals and the Differential Reduction of Zirconium from Hafnium in Molten Al_2X_6

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Summary Zirconium tetrahalides containing hafnium in natural abundance are reduced by metallic zirconium or aluminium in molten aluminium halides at 260—310° to yield soluble intermediates from which are deposited single crystals of ZrX_3 which have a reduced hafnium concentration.

THE difference in the ease of reduction of zirconium(IV) as compared with hafnium(IV) has been previously observed by several investigators,[1] although the effectiveness of this technique for separation purposes is hindered by the deposition of the ZrX_3 product on the surface of the metallic reducing agent with subsequent encapsulation of the metal and cessation of the reaction. In the present investigation the reaction of zirconium tetrachloride dissolved in molten Al_2X_6 (about 76 mole per cent[2]) with a metallic reducing agent has been observed to yield a *soluble* blue intermediate species (in the iodide case this cannot be observed visually) with the subsequent deposition of single crystals of ZrX_3 on the glass walls of the sealed ampoule starting at the edge of the menicus and continuing up the side walls. The growth continues over a period of several days until the concentration of ZrX_4 in the liquid phase is substantially depleted at which time the blue colour is also absent. The single crystals grow to 4—5 mm in length perpendicular to the side walls. The crystals of the trichloride are yellow-green, the bromide brown-black, and the iodide black. The analysis and powder patterns[3] correspond to stoicheiometric ZrX_3. The iodide system requires a higher temperature than the bromide or chloride, 310° as against 260°. The chloride and bromide are unstable in liquid aluminim halides, presumably by disproportionation, to yield brown products with halide to zirconium ratios of less than three. In the case of the iodide only the stoicheiometric product is obtained. Typical reaction systems are given in the Table 1.

TABLE 1

Typical experimental data

	Moles × 10^3				
X^-	ZrX_4	M	AlX_3	T°	Compn.
I^-	8·8	1·67	29	310	$ZrI_{3\cdot02}$
I^-	8·8	1·67	29	310	$ZrI_{2\cdot96}$
Br^-	5	1·6	47	265	$ZrBr_{3\cdot02}$
Br^-	8	1·2	37·5	240	$ZrBr_{2\cdot80}$
Cl^-	10	3·3	90	260	$ZrCl_{2\cdot87}$ + green crystals
Cl^-	17·3	3·5	112	260	$ZrCl_{2\cdot78}$ + green crystals

Hafnium tetrahalides under the same temperature and time conditions remain substantially unreduced and can be separated from the nonvolatile ZrX_3 by sublimation along with the aluminium halide solvent. The most effective separation of zirconium and hafnium occurs in the chloride system. Typical separation data are presented in Table 2.

TABLE 2

Separation as a function of halide

	Hf/Zr[a], *mole ratio* × 10^2		
X^-	Initial	Final	Sepn. factor R_i/R_f
Cl^-	1·19	0·051	23
	1·05	0·036	29
Br^-	0·910	0·173	5·3
	0·910	0·152	6·0
I^-	0·910	0·319	2·9
	0·910	0·410	2·2

[a] Spectrographic analyses by National Spectrographic Laboratories, Cleveland, Ohio.

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