

Chapter Four

SOME SIGNIFICANT SOLIDS

In recent years the area of solid-state chemistry has become increasingly important to chemists. The development of memory cores for computers, phosphors, transistors, lasers, etc., has resulted in the synthesis of many new materials. Methods have had to be developed for both the preparation and characterization of these compounds.

In the past, most solids were prepared on a large scale by standard ceramic techniques, in which accurate control of the composition, as well as uniform homogeneity of the product, were not readily achieved. Unfortunately, this has sometimes led to uncertainty in the interpretation of the physical measurements. In recent years more novel methods have been developed to facilitate the reaction between solids. This is particularly true for the preparation of polycrystalline samples, on which the most measurements have been made. It is of utmost importance to prepare pure single-phase compounds, and this may be very difficult to attain. Even for a well-established reaction, careful control of the exact conditions is essential to ensure reproducible results. For any particular experiment, it is essential to devise a set of analytical criteria to which each specimen must be subjected. It will be seen from the solid-state syntheses included in this volume that one or more of the following common tests of "purity" are used to characterize a product.

1. Chemical analysis for cation composition, cation/anion ratio, and chemical impurities.
2. Crystallographic investigation, including the determination of lattice parameters, absence of foreign phases by x-rays, density determination, and optical examination.
3. Electrical conductivity (a.c. and d.c.), Hall measurements, and determination of Seebeck voltage.
4. Check of known magnetic properties, e.g., magnetic moment, Curie temperature determination, etc.
5. Optical properties, e.g., transmission, fluorescence, phosphorescence, and photoconductivity.

Obviously, it would be impractical to perform all the above tests on each new compound synthesized. The selection of appropriate characterization techniques is dependent upon the nature and properties of the compound being studied.

Most methods for synthesizing polycrystalline samples are basically similar and depend upon well-known ceramic techniques. The reactants are weighed out carefully, mixed, and placed in a suitable container. They are heated at a temperature high enough to initiate solid-solid reactions. This process is repeated several times until there is evidence of complete reaction. Among the many factors which must be controlled carefully are an accurate control of purity and composition of starting materials, an avoidance of impurities during the mixing process, a careful control of the atmosphere in the furnace to prevent oxidation or reduction, the firing temperatures and times, and the cooling rates. At present, the exact procedure for any particular compound must be carefully worked out and followed by analysis of the product.

For some investigations single crystals are essential, and for many they are desirable, both to determine the effects of anisotropy and to obtain higher purity. If the compound to be prepared melts congruently, large single crystals can generally be obtained by slow cooling of, or pulling from, the melt. Another common and simple method of growing crystals is from solution, either by evaporation or slow cooling of a molten flux. So far,

most work with fluxes has been based on the slow-cooling method of crystallization, but there seems to be no reason against using controlled evaporation of the solvent at constant temperature, as is done for aqueous solutions.

In recent years, more novel methods have been developed by chemists in order to hasten the reaction between solids or to grow single crystals of new and exotic solids. Among those included in the following syntheses are electrolysis of fused salts, chemical transport, and hydrothermal crystal growth.

I. HALIDES AND OXYHALIDES

20. IRON(II) HALIDES

Submitted by G. WINTER*

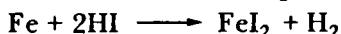
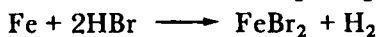
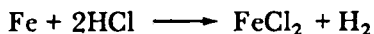
Checked by D. W. THOMPSON† and J. R. LOEHE†

Iron(II) chloride and bromide may be obtained from the reaction of the metal with the appropriate hydrogen halide at elevated temperatures.¹ The chloride has also been made by the reduction of iron(III) chloride with hydrogen,¹ from iron(III) chloride and the metal in tetrahydrofuran,² and by the reaction of iron(III) chloride with chlorobenzene.³ The iodide has been prepared from the metal and iodine in a sealed tube at elevated temperatures.¹

The simplest procedure, dissolution of metallic iron in the aqueous mineral acid, suffers from the risk of accidental oxidation. The following relatively simple procedure overcomes this difficulty. This method, with minor modifications, has also been used successfully by the author for the preparation of chromium-(II) halides.

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Procedure**A. IRON(II) HALIDES**

The apparatus shown in Fig. 10 is flushed with nitrogen, and vessel *B* is stoppered. With the plug removed, a stream of nitrogen is passed through the sidearm and so provides an efficient gas curtain to prevent diffusion of atmospheric oxygen. Then 10 g. (0.18 g. atom) of iron powder (hydrogen reduced) is placed in vessel *A*, followed by 100 ml. of methanol* and the mineral acid, see Table I. The ensuing reaction is maintained under a nitrogen atmosphere at a vigorous rate by immersion of vessel *A* in hot water. It is completed within 2-3 hours. Cessation of hydrogen evolution must be ensured to prevent pressure from developing during later stages when the apparatus is closed.

*Methanol is used in preference to water to facilitate evaporation. Deaeration is not necessary.

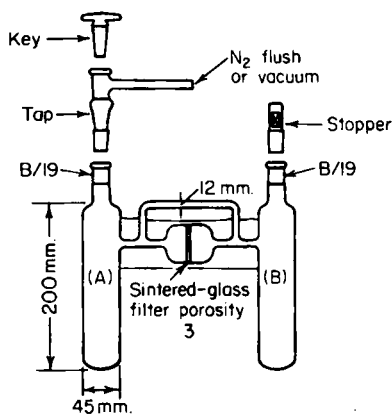


Fig. 10

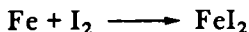
TABLE I

Acid	Approx. strength, %	Amount, cc.	Approx. yield of FeX_2 , g.	X, %	
				Calcd.	Found
HCl	32	40	21	56.5	56.2
HBr	50	45	40	74.1	73.7
HI	55	60	45	81.9	81.0*

*The checkers report a value of 78.2% I present in their samples of FeI_2 .

The stream of nitrogen is discontinued and the apparatus closed by replacing the key in the tap. The greenish-gray solution is filtered through the sintered-glass disk into vessel *B*, and the filtrate cooled by immersion in a Dry Ice-alcohol slush bath. With the tap in the open position, the apparatus is evacuated through the sidearm by an efficient mechanical pump. The apparatus is sealed by closing the tap, and the solvent is evaporated from vessel *B* and condensed in vessel *A* by immersing *A* in the Dry Ice slush bath and slowly warming *B* to 100°C . When all the green crystalline hexamethanol solvate is converted into the white dimethanol solvate (about 3 hours), nitrogen is admitted. With the key of the tap removed and a stream of nitrogen flowing through the sidearm, the solvent collected in vessel *A* is poured out and discarded. The final desolvation is accomplished by heating the product in vessel *B* for 4 hours at 160°C . under vacuum. (For the iodide, heating for 2 hours at 100°C . is sufficient; excessive heating may result in loss of iodine.) This is conveniently achieved by connecting the apparatus to a mechanical pump protected by a suitable vapor trap, and immersing vessel *B* in an oil bath or small furnace. After cooling, nitrogen is again admitted, and the product is transferred to storage containers.

The amounts of mineral acid recommended for 10 g. of iron powder, the approximate yield of product, and halogen analyses are shown in Table I.

B. IRON(II) IODIDE

For the preparation of FeI_2 an alternative procedure involving reaction of the elements may be used.

The apparatus (Fig. 10) is flushed with nitrogen and protected from ingress of oxygen as described in Procedure A. Five grams (0.09 g. atom) of iron powder (hydrogen reduced) is placed in vessel *A*, and then 100 ml. of methanol and 2 ml. of 55% hydroiodic acid to activate the iron. Finely powdered, sublimed iodine, 23 g. (0.09 mole), is added over a period of $\frac{1}{2}$ hour, the methanol being maintained at its boiling point by occasional immersion of vessel *A* in hot water. The dark green solution is filtered through the sintered-glass disk into vessel *B*. The evaporation of the solvent and desolvation of the product are performed as described in Procedure A. Approximate yield is 23 g. *Anal.* Calcd. for FeI_2 : I, 81.9. Found: I, 81.5.

Properties

Iron(II) chloride is a pale buff-colored solid, iron(II) bromide is pale yellow, and iron(II) iodide is deep red. They can be stored in air, provided moisture is rigorously excluded.

References

1. G. Brauer, "Handbook of Preparative Inorganic Chemistry," Academic Press, Inc., New York, 1965.
2. M. F. Hawthorne, T. D. Andrews, P. M. Garrett, F. P. Olsen, M. Reintjes, F. N. Tebbe, L. F. Warren, P. A. Wegner, and D. C. Young, *Inorganic Syntheses*, 10, 112 (1967).
3. P. Kovacic and N. O. Brace, *Inorganic Syntheses*, 6, 172 (1960).