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Synthesis of Oxides Containing Transition Metals

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Various techniques are described for the preparation of polycrystalline and single crystal samples of transition metal oxides. The importance of "precursors" in facilitating the formation of the desired product is discussed. The various problems encountered in the preparation of pure, homogeneous, uniform materials are related to the characterization of these compounds in order to properly describe their properties.

Solid state chemistry research today is concerned with the effort to understand properties in terms of a particular composition and structure. However, there remains a need to distinguish between property studies carried out on ill-defined or well-defined materials. The procedure chosen for the preparation of a material should be given far more attention than it has received in the past. The quality of the starting materials, as well as the subtleties of the techniques used, will determine in large measure the quality of the final product. The complete control of preparative conditions is essential for an understanding of properties and their ability to be varied. In this discussion concerning the preparation of transition metal oxides, the writers will illustrate different aspects of problems encountered from their own research experience. It is hoped that these examples will demonstrate a number of different synthetic approaches as well as justify why a particular method was chosen. Unfortunately, much of what follows does not appear in textbooks, but the information is generally accepted among solid state chemists.

I. Preparation of Polycrystalline Solids

Direct reaction of the elements or single binary compounds is undoubtedly the most widely used method for the preparation of polycrystalline solids. In order for the reaction to proceed within a reasonable period of time, high mobility of the reactants is desirable as well as maximum surface contact between the reacting particles. The rate of diffusion and reactivity can be increased by raising the temperature or forming a more reactive structure. In general, complete reaction can be achieved if the reaction temperature reaches $\frac{2}{3}$ of the melting point of one of the solid reactants. In order to ensure maximum common surfaces of the different reactants,. high surface area powders are usually used. These powders are completely mixed and can be compressed into tablets, thus increasing the contact surfaces of the reactants. For the preparation of oxides,

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which can be carried out in air, ceramic or platinum crucibles are used. It is necessary to start with the purest, assayed simple oxides, accurately weighed, intimately mixed, and reacted without the preferential loss of one reactant or the introduction of nonvolatile impurities. In order to obtain a pure product, it is necessary to pulverize the reactants thoroughly and heat them a second or even a third time. This is particularly true of compounds prepared from refractory materials such as MgO.

"Precursor" methods have been developed for the preparation of stoichiometric ferrites and chromites (*1, 2*). These methods achieve excellent stoichiometry, low trace impurity content, and homogeneity approaching the maximum theoretically possible. The principal advantage of the "precursor" method is that the two metals are mixed on an atomic scale so that greater reactivity and more homogeneous products result than by direct combination of ground oxides. The procedures involve the crystallization from solution of precursor compounds which contain the metals in the desired atomic ratio. Any other element which may be present is volatilized at elevated temperatures. Decomposition of these crystalline precursors in air yields a mixture of metallic oxides which are finely divided and intimately mixed. The ignition of these compounds at relatively low temperatures (<1200°C) results in the formation of the desired product.

The precursor technique used by Wickham and co-workers (*1, 3*) to prepare ferrites with the composition $M\mathrm{Fe_2O_4}$ involved the thermal decomposition of oxalate (*3*) or pyridinate salts (*1*). The synthesis of ferrites from mixed oxalates yields homogeneous products in a short time. It was shown that iron(II) oxalate dihydrate $\mathrm{FeC_2O_4 \cdot 2H_2O}$ can be coprecipitated from boiling solutions of salts with the corresponding oxalates of manganese(II), cobalt(II), nickel(II), or zinc(II) in the form of mixed crystals.

The products are finely crystallized, free-flowing powders which are handled easily and contain the iron and other metals mixed on an atomic scale. The mixed oxalates are decomposd to ferrites upon heating in the presence of air:

$$M\mathrm{Fe_2(C_2O_4)_3 \cdot 6H_2O + 2O_2 \rightarrow} M\mathrm{Fe_2O_4 + 6H_2O + 6CO_2}.$$

Only relatively low temperatures are required except in the case of manganese ferrite. However, values for the atomic ratio Fe/M deviating by less than 1% from the theoretical value of two are seldom obtained. This fact is a consequence of small differences in the solubility and the tendency of the oxalate to form supersaturated solutions. Atomic ratios Fe/M very close to the theoretical values of two were obtained by Wickham *et al.* (*1*) by the thermal decomposition of crystallized salts $M_3\mathrm{Fe_6(CH_3CO_2)_{17}O_3OH \cdot 12C_5H_5N}$. The products were ignited in air at temperatures chosen to give the correct oxygen content. The preparations of the compounds $M_3\mathrm{Fe_6(CH_3CO_2)_{17}O_3OH \cdot 12C_5H_5N}$ reported by Wickham are given in Table I.

The results of the chemical analyses are given in Table II and indicate that the preparative methods described were reasonably successful for manganese, cobalt, and nickel ferrites. The lattice constants listed in Table II are in good agreement with the best values given in the literature. The saturation magnetic moments (n_B), with the exception of that for manganese ferrite (*1*), are also in good agreement with accepted values. The value of n_B is less sensitive to small departures from stoichiometry than it is to variations in the thermal history of the sample, which influences the distribution of cations between the tetrahedral and octahedral sites of the spinel structure.

The "precursor" method has also been applied (*2*) to the preparation of the chromites which have the formula $M\mathrm{Cr_2O_4}$ and possess the spinel structure. Previous meth-

TABLE I

PREPARATION OF THE COMPOUNDS $M_3^{2+}Fe_6(CH_3CO_2)_{17}O_3(OH) \cdot 12C_5H_5N$

Starting materials compound	Quantity	Volume of pyridine solvent	Number of recrystallizations	Yield (g)	%
$MgFe_3(AcO)_8(OH)_3 \cdot 10H_2O$	69	500	1	54.1	58
$Mg(AcO)_2 \cdot 4H_2O$	8.1				
$MnFe_3(AcO)_8(OH)_3 \cdot 5H_2O$	71	500	0	78	70
$Mn(AcO)_2 \cdot 4H_2O$	10.5		1	55	49
$CoFe_3(AcO)_8(OH)_3 \cdot 8H_2O$	44.7	500	1	28.5	45
$Co(AcO)_2 \cdot 4H_2O$	6.2				
$Co_4Fe_9(AcO)_{26}(OH)_9 \cdot 23H_2O$	80	500	2	24	25
$Ni_4Fe_9(AcO)_{26}(OH)_9 \cdot 23H_2O$	75	500	2	29	33

ods employed for the synthesis of chromites consisted simply of preparing an intimate physical mixture of two appropriate oxides and heating this mixture to a sufficiently high temperature (1400–1700°C) to cause the two oxides to react to form the desired product. The method does not yield pure products easily because of the refractory nature of chromium(III) oxide and of many of the divalent metal oxides involved. Tedious grinding procedures and firings must be done, and extraneous impurities are usually introduced as a result of the grinding. Ignition at elevated temperatures occasionally results in the preferential loss of some of the divalent oxides, e.g., ZnO, CuO.

The precursor methods used by Whipple and Wold (*2*) to prepare a number of chromites are given in Table III. These precursors achieve excellent stoichiometry, low trace impurity content, and homogeneity approaching the maximum theoretically possible. The principal advantage of the "precursor" method is that the two metals are mixed on an atomic scale so that greater reactivity and more homogeneous products result than by heating a mixture of ball-milled (or mortar ground) oxides. The procedures involve the crystallization from solution of compounds containing chromium and another metal in the atomic ratio 2 : 1. Any other element which may be present is volatized at elevated temperatures. Decomposition of these crystalline precursors yields a mixture of the oxides MO and Cr_2O_3 which are finely divided and intimately

TABLE II

CHEMICAL ANALYSES AND PROPERTIES OF FERRITES PREPARED BY IGNITION OF "PYRIDINATES"

Compound sought	Weight iron (%)		Weight M^{2+} (%)		Mole ratio Fe/M^{2+}	Ignition temperature (°C)	Active O (eq/mole)	Cubic lattice constant a_0 (Å)	Saturation magnetic moment[a] (ne/molecule)
	Found	Theory	Found	Theory					
$MgFe_2O_4$	55.69 ± 0.03	55.84	12.41 ± 0.06	12.16	1.954 ± 0.012	1000	0	8.384 ± 0.001	1.37 ± 0.02
$MnFe_2O_4$	48.32 ± 0.02	48.43	23.68 ± 0.03	23.82	2.008 ± 0.005	1300[b]	0.034	8.512 ± 0.001	4.50 ± 0.01
$CoFe_2O_4$	47.55 ± 0.01	47.60	25.24 ± 0.08	25.12	1.990 ± 0.01	1000	0.004	8.388 ± 0.001	3.57 ± 0.01[c]
$NiFe_2O_4$	47.54 ± 0.03	47.65	25.03 ± 0.01	25.05	1.997 ± 0.004	1000	0	8.338 ± 0.002	2.12 ± 0.01

[a] Measured at 4.2°K in a field of 10,000 Oe.

[b] Quenched in nitrogen and contains 0.12% by weight excessive active oxygen.

[c] Cobalt ferrite is not saturated at 10,000 Oe.

TABLE III

PREPARATION OF THE STOICHIOMETRIC CHROMITES

Chromite	Precursor	Cr/M^2	Yield of precursor (%)
$MgCr_2O_4$	$(NH_4)_2Mg(CrO_4)_2 \cdot 6H_2O$	2.010[a] ± 0.002	70
$NiCr_2O_4$	$(NH_4)_2Ni(CrO_4)_2 \cdot 6H_2O$	1.999 ± 0.002	75
$MnCr_2O_4$	$MnCr_2O_7 \cdot 4C_5H_5N$	2.015[b] ± 0.002	90
$CoCr_2O_4$	$CoCr_2O_7 \cdot 4C_5H_5N$	2.012[a] ± 0.002	90
$CuCr_2O_4$	$(NH_4)_2Cu(CrO_4)_2 \cdot 2NH_3$	2.000 ± 0.003	43
$ZnCr_2O_4$	$(NH_4)_2Zn(CrO_4)_2 \cdot 2NH_3$	1.995 ± 0.0006	77
$FeCr_2O_4$	$NH_4Fe(CrO_4)_2$	1.995 ± 0.003	80

[a] Based on total Cr only.

[b] Based on total Mn only.

mixed. The ignition of these compounds, at a relatively low temperature (<1200°C), results in the formation of the crystalline chromite.

The lattice constants for the various chromites prepared from precursors are given in Table IV. They are in good agreement with those reported in the literature. The cubic to tetragonal transformation point of iron chromite was found to be −138 ± 3°C. This point is considerably lower than −90°C reported by Francombe (*4*). The lower value would indicate some improvement in the homogeneity and purity of the iron chromite prepared by the precursor method.

The saturation magnetic moments (n_B) for nickel, manganese, and iron chromites are in good agreement with those reported by Lotgering (*5*). The values given in Table IV for magnesium, cobalt, copper, and zinc chromites were not reported previously. Lotgering has indicated that the chromite spinels have a *B–B* interaction which is of the same order of magnitude as the *A–B* interaction. This interaction usually results in lower saturation moments than are pre-

TABLE IV

CRYSTALLOGRAPHIC AND MAGNETIC PROPERTIES OF THE CHROMITES

Compound	Cubic (a_0) Å	Tetragonal	Transformations	μ_B/mole, 10,000 Oe, 4.2°K
$MgCr_2O_4$	8.333 ± 0.002			0.15
$NiCr_2O_4$		$a = 8.248 \pm 0.002$ $c = 8.454 \pm 0.002$	Tetragonal to cubic at 37 ± 2°C	
$MnCr_2O_4$	8.437 ± 0.002			1.20
$CoCr_2O_4$	8.332 ± 0.002			0.18
$CuCr_2O_4$		$a = 8.532 \pm 0.003$ $c = 7.788 \pm 0.003$		0.72
$ZnCr_2O_4$	8.327 ± 0.002			0.12
$FeCr_2O_4$	8.377 ± 0.002		Tetragonal to cubic at −138 ± 3°C	0.84

dicted by the Néel theory of ferrimagnetism.

For the preparation of a number of complex transition metal oxides, stabilization of high valence states requires the development of synthetic techniques which can be carried out at low temperatures. The complete solid state reaction of refractory oxides at a low temperature is a difficult problem. Direct combination of reactants to produce a mixed metal oxide requires high temperature heating with frequent regrinding. Reaction proceeds rapidly at first, but, as the layer of product forms, diffusion paths become longer and the reaction slows down. Extremely small reactant particles of about several hundred angstroms in diameter can be prepared by freeze drying (*6, 7*) or by coprecipitation (*8, 9*). As a result of smaller particle size of the reactants, the reactivity improves markedly. However, the diffusion paths still are rather large and hence "precursors" are the best method for achieving rapid reaction at low temperatures. The use of compound precursors, such as those used to synthesize ferrites and chromites (*1–3*), require that the stoichiometry of the precursor corresponds with that of the desired product. Where this is not possible, the use of solid–solution precursors (*10, 11*) can, in some cases, be as effective as compound precursors, and yet avoids the limitations of stoichiometry. This method was used, for example, by Horowitz and Longo (*11*) to study the phase relations in the manganese-rich portions of the Ca–MnO system below 1000°C. Both $CaCO_3$ and $MnCO_3$ crystallize with the calcite structure, and hence a complete series of Ca–Mn carbonate solid–solutions could be prepared. These precursors allowed the calcium to manganese ratio to be continuously varied so that the entire Ca–MnO phase diagram could be studied. Vidyasagar *et al.* (*12*) prepared several members of the system $Ca_{1-x}Fe_xCO_3$, where $x = \frac{1}{3}, \frac{2}{5}, \frac{1}{2}, \frac{2}{3}, \frac{4}{5}$, and $\frac{12}{13}$ by low temperature decomposition of carbonate solid–solutions. In addition, they prepared two members of the system $Ca_{1-x}Co_xCO_3$ with $x = \frac{1}{2}$ and $\frac{1}{3}$.

Many solid state chemists have prepared complex oxides by codecomposition of the corresponding nitrates. Decomposition of nitrates results in the formation of reactive oxides which can readily combine to form the desired product. In most cases, the nitrates are readily formed from the dissolution of the metals or carbonates in nitric acid.

Another interesting synthetic technique, first described by Hilpert and Wille (*13*), appears to have been neglected in recent years. The authors prepared several ferrites by a solid state, double decomposition reaction which can be represented by the following equation:

$$M^2 + Cl_2 + Na_2M\,{}^{3+}_{2}O_4 \xrightarrow{400\text{–}500°C} M^{2+}M^{3+}_{2}O_4 + 2NaCl.$$

This procedure can be used advantageously when the more common methods become difficult, as in the preparation of mixed oxides containing very refractory components. Wickham *et al.* (*1*) successfully prepared Fe_3O_4, $FeCr_2O_4$, $FeTiO_3$, and $FeAl_2O_4$ by this procedure.

Brixner (*14, 15*) has used a flux reaction for the preparation of a variety of ternary oxides. The products are usually obtained in the form of small, well-defined, single crystals. In this technique a salt melt ($CaCl_2$ or $BaCl_2$) serves both as a flux and a reactant. Brixner reported (*16*) the preparation of $BeFe_{12}O_{19}$ by this method. The phase separated as transparent red crystals and the reaction can be represented by the following equation:

$$BaCl_2 + 6Fe_2O_3 + H_2O \rightarrow BaFe_{12}O_{19} + 2HCl.$$

This reaction occurs at 1300°K and it is essential that $BaCl_2$ hydrolyzes to BaO. Bi-

TABLE V

REACTION PRODUCTS FROM $CaCl_2$ WITH VARIOUS OXIDES

Oxide reacted	Product and comment
Fe_2O_3	$CaFeO_4$ in red transparent fibrous form
Al_2O_3	$Ca_3Al_{10}O_{18}$ as transparent hexagonal plates
Cr_2O_3	$CaCrO_4$ in dendritic form
SiO_2	Ca_2SiO_4 fine acicular particles, surface area 120 m^2/g
P_2O_5	Ca_2PO_4Cl (chlorspodiosite) as flat transparent platelets

chowsky and Rossini (*17*) indicated that the ΔH for the hydrolysis of $BaCl_2$, i.e.,

$$BaCl_2 + H_2O \rightarrow BaO + 2HCl,$$

is +78 kcal/mole. This heat of reaction must be supplied by the formation of $BaFe_{12}O_{19}$. The conversion of $BaCl_2$ to BaO is a slow reaction and, hence, the product $BaFe_{12}O_{19}$ will form as transparent red crystals up to a few millimeters in length. It has been observed (*14*) that the most stable composition between the two constituent oxides will be the only composition if there is a significant difference between the heats of formation of competing phases. By the flux reaction technique, Brixner was able to incorporate a considerable quantity of chlorine with the formation of the halide phosphates and vanadates of strontium $Sr_5(PO_4)_3Cl$ and $Sr_2(VO_4)Cl$ (*15*). Examples of reaction products from $CaCl_2$ and $BaCl_2$ with various oxides are given in Tables V and VI.

Various synthetic techniques have been developed for the known oxide systems. It is not possible to outline all of the approaches; however, the choice of the atmosphere under which the preparation is being carried out will determine the oxidation state of the constituent metallic species in the final product. High surface area products >100 m^2/g usually are made by low temperature decomposition of an appropriate precursor. In general, oxides require successive heat treatments with intimate grinding of the products after each heating.

II. The Growth of Oxide Single Crystals

A. *Growth from the Melt*

There are five general methods for the growth of crystals from the melt which will be discusssed in this section and have been in use for many years. The flame fusion method was invented by Verneuil (*18*) for the production of synthetic ruby crystals. The apparatus is shown in Fig. 1. The starting material is a mixture of $NH_4Al(SO_4)_2 \cdot 12H_2O$ and Cr_2O_3 which is kept in a hopper

TABLE VI

REACTION PRODUCTS FROM $BaCl_2$ AND VARIOUS OXIDES

Oxide reacted	Product and comment
Fe_2O_3	$BaFe_{12}O_{19}$ red transparent ferromagnetic flakes
WO_3	BaWO4 transparent slightly acicular rectangular prisms
SiO_2	$BaSi_2O_5$ fine acicular particles
PbO	$BaPbO_3$ brown crystals
TiO_2	$BaTi_3O_7$ transparent flat crystals

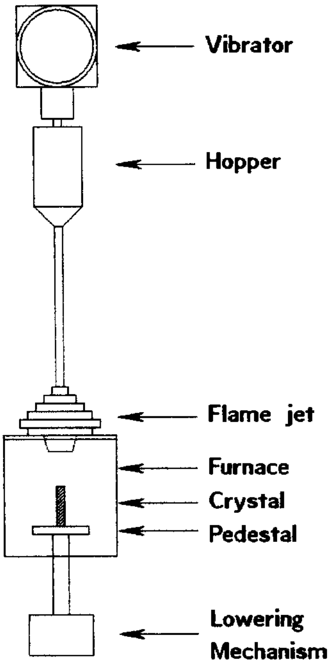

FIG. 1. Verneuil apparatus.

with a fine mesh screen at its base. Vibration of the sieve causes the powder to be fed into an oxygen stream which flows through the central tube of an oxyhydrogen burner. Hydrogen is also supplied to the flame which is contained in a cylindrical ceramic muffle. At the base of the muffle is a pedestal whose height can be adjusted. The powder which falls through the flame builds up a sintered cone on top of the pedestal. The tip of this cone is melted by increasing the flow of hydrogen to the flame. As more powder falls on the cone, the alumina pedestal is lowered at a uniform slow rate. The lowering rate is adjusted so that the surface of the molten cap remains at a fixed position in the flame. If the original cone is sufficiently narrow so that only one nucleus forms, the resulting solid is a single crystal. One problem with this method is the cracking of many crystals because of steep temperature gradients from the top to the bottom of the boule during crystal growth. A further problem is the reoxidation which occurs subsequent to crystallization as the surface of the boule cools. The boules are usually carefully annealed to remove the internal stresses induced during the growth process.

The Stöber method of crystal growth from the melt (*19*) places a crucible loaded with material in a furnace with a temperature gradient so that the top of the crucible is hotter than the bottom. Usually a crucible with a conical tip is used. Initially the temperature of the entire crucible is above that of the melting point of the crystal to be grown. The power to the furnace is reduced and if there is a single nucleus formed and no complications, a single crystal will be grown. Reduction of the power to the furnace slowly allows the crystal to be annealed *in situ*.

The Bridgman–Stockbarger method (*20*) utilizes a furnace with a steep temperature gradient situated approximately at its center. The top half of the furnace is the higher temperature zone. The crucible is supported from below and has a controlled heat leak to the bottom. The crucibles, in general, have conical tips and are moved with respect to the furnace. The crucible is first placed in the upper part of the furnace and remains there until all of the material is molten. It is then drawn through the temperature gradient into the lower portion of the furnace which is at a temperature below the melting point of the crystal being grown. After the boule has completely solidified, it can be annealed in the lower portion of the furnace by slowly reducing the power.

The Kyropoulis method (*21*) makes use of a furnace without a temperature gradient. The contents of the crucible are melted and a rod with a seed crystal attached to one end is lowered into the melt. The rod is cooled, creating the necessary temperature gradient. The rod is rotated and slowly withdrawn from the melt and the crystal is pulled out as the rod moves. This method is undoubtedly one of the most versatile methods for crystal growth from melts despite the difficulties involved.

Skull melting is another high temperature method for the growth of oxide crystals. A power supply of 50 kW at 3 MHz has been used (*22*) to produce radio frequency power which is transferred to a power coil. The coil is wrapped about a skull crucible which can be water cooled. Provision is also made for adjusting the ambient atmosphere in order to obtain a single phase of the proper stoichiometry. A graphite susceptor ring is inserted with the charge into the skull container. The graphite ring couples the charge to the power source so that heating can be achieved even if the conductivity of the charge is low. The process is crucibleless since the molten charge is isolated from the copper container by a thin layer of sintered material which is next to the water-cooled skull. The graphite susceptor is burnt off as CO or CO_2 during the growth process. To achieve stabilization of mixed oxidation states (e.g., Fe_3O_4) the chamber above the container is closed, evacuated, and then can be filled with CO_2 (or CO/CO_2 mixtures). The boule is kept under a controlled atmosphere and the crucible can be lowered out of the stationary power coil. Relatively large crystals (few centimeters) of numerous oxides have been grown by this method.

B. High Temperature Solution Growth

In this technique the constituents of the crystals to be grown are dissolved in a suitable solvent and crystallization occurs as the solution becomes critically supersaturated. Supersaturation can be achieved by evaporation of the solvent, cooling the solution, or transporting the solute from a hot to a cooler zone. The growth of crystals from a solvent is of particular value for compounds which melt incongruently since crystal growth occurs at a lower temperature than that required for growth from the melt. Unfortunately, crystal growth from solution usually results in the incorporation of solvent ions into the crystal.

Liquid phase epitaxy (LPE) is an important process in which a thin layer of crystalline material is deposited onto a substrate of similar composition or surface structure. This technique is used specifically for the deposition of thin films and requires that there is a match between the lattice parameters of the film and the substrate.

C. Flux Growth

One of the most widely used techniques which is classified as a high temperature solution method is flux growth. Crystals of ceramics, ferrites, and other oxides have been grown by the slow cooling of a solution in a molten flux. For examples of this technique the reader is referred to the work of Remeika (*23, 24*) who has grown barium titanate crystals from molten KCl and some ferrite crystals from molten PbO. One serious disadvantage of growing from such solutions is that the crystals usually contain traces of solvent.

D. Chemical Vapor Transport

Chemical-transport reactions have been used (*25*) to prepare single crystals of triiron tetraoxide (magnetite) and other ferrites, which constitute the majority of all known ferrimagnetic materials. The work of Darken and Gurry (*26*) suggested that stoichiometric magnetite powder could be prepared by heating iron(III) oxide in an atmosphere of CO and CO_2, and pure Fe_3O_4 starting material for transport was prepared by this method (*27*).

The procedure which Hauptman (*25*) used for the growth of ferrite crystals can be summarized as follows: the powdered charge material is introduced into a silica tube which is then evacuated. The transport agent is introduced and the tube sealed off. The tube is then placed in a two-zone transport furnace which has a temperature difference between the zones. The powdered charge material reacts with the transport agent to form a more volatile compound. The vapor diffuses along the tube to a region of lower temperature, where some of the vapor undergoes the reverse reaction. The starting compound is reformed and the transport agent is liberated. The latter then is free to react once again with the charge. Under the proper conditions the compound is deposited as crystals. The transport of Fe_3O_4 using HCl as the transport agent occurs by the reversible reaction: $Fe_3O_4 + 8HCl \rightleftharpoons FeCl_2 + 2FeCl_3 + 4H_2O$. The same transport procedure has been used to prepare crystals of other metal oxides.

Gray *et al.* (*28*) have used chemical vapor transport to prepare single crystals of V_2O_3. Single crystals of V_2O_3 grown with HCl as the transport agent exhibited a first-order electrical transition from a metal to a semiconductor at 158 K on cooling, in agreement with the results first reported by Morin (*29*). However, single crystals which were prepared by chemical vapor transport using $TeCl_4$ as a transport agent remained metallic to 96 K on cooling. The suppression of the semiconducting phase was reported by Pouchard and Launay (*30*) and was attributed to the oxidation of V(III) to V(IV) by Cl_2. It was demonstrated (*28*) that such crystals contained V_3O_5. The procedure of chemical vapor transport can produce products which contain controlled amounts of several oxidation states of the transition metal.

E. Electrolytic Reduction of Fused Salts

Andreiux (*31, 32*) showed that it was possible to obtain a number of transition metal oxide single crystals by the electrolysis of molten salts containing mixtures of the appropriate oxides. Andreiux and Bozon (*33, 34*) were able to prepare a number of vanadium spinels by electrolyzing melts of sodium tetraborate and sodium fluoride in which were dissolved the appropriate mixtures of transition metal oxides. The products were shown to have the composition MV_2O_4 (M = Fe, Mn, Co, Zn, and Mg).

The reduction of TiO_2 or $CaTiO_3$ dissolved in a calcium chloride melt has been reported by Bertaut and Blum (*35, 36*) and Bright *et al.*(*37*). The electrolysis was carried out by Bright at 850°C for 10 min using a current of 14 A. Black, lustrous crystals formed at the cathode which had the composition $CaTi_2O_4$. It has not been possible to synthesize this compound except by electrolysis.

Dodero and Déportes (*38*) have prepared a number of compositions of $NaMO_2$ (M = Fe, Co, and Ni) by the electrolysis of sodium hydroxide melts contained in alumina crucibles. Electrodes of iron, cobalt, or nickel were used, depending on the desired composition of the final product.

Crystals of tungsten and molybdenum oxide "bronzes" have been grown by electrolytic reduction of tungstate or molybdate melts. Extensive reviews of the preparation and properties of the bronzes studied through 1980 are given in three review papers (*39–41*).

These are only representative examples of unusual transition metal oxides which can be prepared (usually as single crystals) by electrolysis of fused salts.

Summary

The methods of preparation of transition metal oxides discussed in this paper are representative techniques based upon the authors' experiences. In all cases, purity of starting materials and care to avoid contamination during the synthesis are essential if meaningful characterization of the product is to be obtained. Often, X-rays of the products are not sufficient to ensure completeness of reaction. They must usually be supplemented with other characterization techniques. Finally, the synthesis of materials is often undervalued as an important component in valid scientific research.

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