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New Compounds from High Pressure

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The purpose of this paper is to give insight into materials synthesis in which high-pressure conditions can be used with success. Typical examples of synthesis have been chosen from the literature and include the results of our investigations on high-pressure synthesis of mixed oxide compounds.

I. Introduction

Since 1955, the date of the announcement of the synthesis of diamonds by the General Electric Company, the advantages of using high-pressure conditions for the synthesis of new materials have become evident to chemists. At that time many laboratories developed high-pressure facilities, and chemists started to investigate pressure–temperature phase diagrams of the elements. Over several years a large number of new, denser phases of the elements were discovered, some of them having physical properties quite different from those of the ambient-pressure phases.

The investigation of two-component systems under pressure began about 1960, with the discovery of dense metallic phases of the III-V and II-VI semiconducting compounds. Between 1965 and 1975, because of rapid developments in high-pressure technology, high-pressure, high-temperature conditions were extensively used by chemists for the synthesis of new, denser phases of well-known binary or ternary compounds or for the synthesis of new compounds with different stoichiometries.

High-pressure solid-state chemistry is presently somewhat neglected despite the availability of excellent equipment. Undoubtedly the tendency will change again, and the high-pressure technique will eventually be considered as a major tool for the synthesis and also the characterization of materials, in those solid-state laboratories which can afford the equipment.

The reason for using high pressure in addition to high temperature is clear: If one considers, for instance, a two-component system, one can generally find two or three stable binary compounds with definite stoichiometry in the phase diagram at ambient pressure. Very few of these compounds are stable when subjected to high-pressure conditions, i.e., between 5 and 100 kbar. Many undergo a phase transition to a denser phase with the same stoichiometry; others disproportionate into their components and often into new binary phases. Frequently new compounds form from two-phase regions. Many of these new dense phases can be quenched while under pressure and can thus be preserved as metastable phases at normal pressure and temperature; so it becomes evident that high-pressure equipment is a powerful tool for the synthesis of new materials. Sometimes single crystals can be prepared, as is the case for synthetic diamonds and cubic boron nitride, leading to an easier characterization of the reaction products.

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II. High-Pressure Facilities Suitable for the Synthesis of New Materials

We first give a short description of a few devices which have proved to be convenient to use for the synthesis of new inorganic materials.

A. The 1- to 10-kbar Pressure Range

Among the high-pressure apparatuses suitable for use in the 1- to 10-kbar pressure range the simplest device is the conventional hydrothermal synthesis facility represented in Fig. 1. Two different types of runs can be performed with this apparatus. First, it can be used as an open system, which means that the sample is in direct contact with the gas from the intensifier tank. Direct reactions with the oxygen, fluorine, nitrogen, etc., vapor phases can be conducted in an open capsule which does not allow reaction of the sample with the autoclave wall.

Several new phases have been synthesized by this method, including $LaCu^{3+}O_3$ (*1, 2*), $SrGdNi^{3+}O_4$ (*3*), $Na_2Ni^{4+}F_6$ (*4*), etc. Undoubtedly a large number of new compounds in which the transition metals are in an unusually high valence state will be obtained even in this rather limited range of pressures.

Second, to avoid the hazard associated with the accumulation of a rather large volume of oxidizing gas at high pressure and high temperature, one can use a closed system if some high-oxidation-state oxide or an internal oxidant can be encapsulated. The decomposition of the higher-valence oxide provides the oxygen, which, because of the collapsible gold capsule, is in pressure equilibrium with the surrounding medium, namely, supercritical water or argon. However, it is necessary to have enough oxygen released to fill all pore space in the capsule at the pressure of the system. This technique seems to have wide application in the preparation of high-valence oxide material. It has been used with success in the synthesis of near-stoichiometric cubic TbO_2 (*5*) and for the synthesis of several rare earth pyrochlores containing tetravalent platinum and palladium (*6*) according to the reactions:

$$Tb_2O_3 \xrightarrow[700°C,\ 3\ kbar]{HClO_4H_2O} Tb^{4+}O_2 \text{ cubic, fluorite type,}$$

$$Ln_2O_3 + PtO_2 \xrightarrow[700°C,\ 3\ kbar]{KClO_3H_2O} Ln_2Pt_2^{4+}O_7,$$

$$Ln_2O_3 + Pd^{2+}O \xrightarrow[700°C,\ 3\ kbar]{KClO_3H_2O} Ln_2Pd_2^{4+}O_7.$$

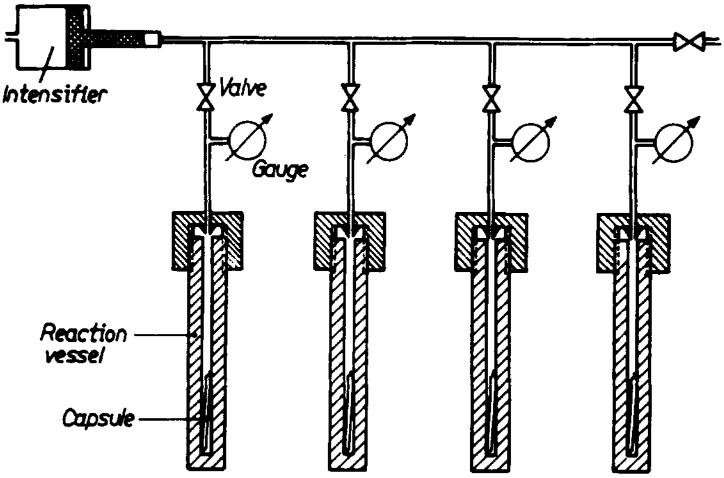

FIG. 1. The conventional hydrothermal synthesis apparatus. Pressures up to 5 kbar and temperatures to 850°C can be achieved in autoclaves having a volume of 10 to 50 cm^3.

At 700°C, $KClO_3$, and $HClO_4$ decompose and provide extra oxygen pressure within the limited volume of the gold capsule. The presence of the water greatly increases the kinetics of many reactions. Preparation of single crystals is possible in several cases. The method not only offers the advantage of simplicity, but it can be used for the synthesis of rather large quantities of material, a few grams or more if necessary. This will not be the case for methods with a higher-pressure working range.

B. The High-Pressure Range

Experimentation at pressures higher than 10 kbar requires the use of more sophisticated techniques. Many routine runs have been successfully performed in two main types of apparatus.

The belt-type apparatus. The tungsten carbide chamber and piston assembly is represented in Fig. 2. The sample is contained in a platinum or gold capsule surrounded by pyrophyllite, a soft material which has been proved to be a good pressure transmitter. An internal microfurnace, made of molybdenum or graphite sleeves, is connected to a low-voltage, high-current power generator through the tungsten carbide pistons. Temperatures of 1500 to 2000°C can be obtained, and pressures up to 100 kbar are possible in a 0.1-cm^3-volume capsule using a 400-ton press (*7, 8*).

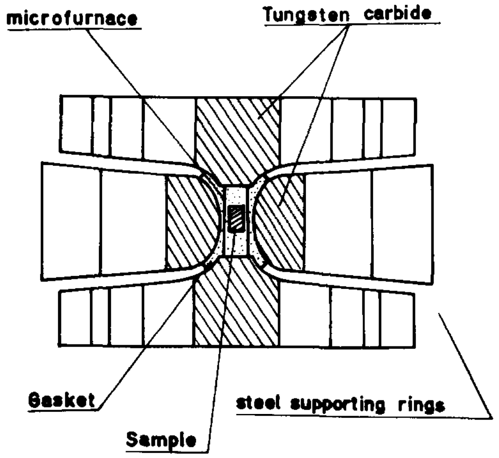

FIG. 2. The belt apparatus. With graphite heaters pressures up to 150 kbar and temperatures to 2000°C can be achieved.

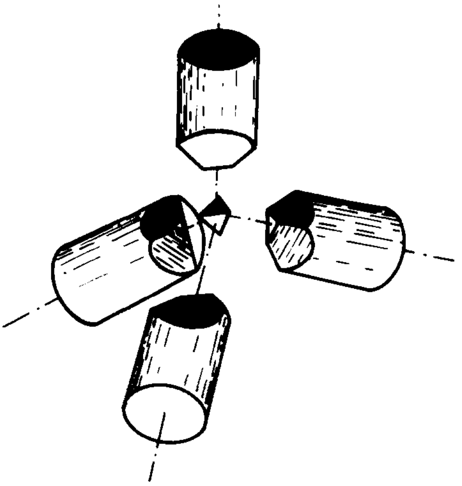

FIG. 3. Schematic drawing of the tetrahedral anvil press. Four independent pistons are pushed against each other by a hydraulic system.

The tetrahedral apparatus. A competitive, although more sophisticated, device is the tetrahedral anvil apparatus (*9, 10*) represented in Fig. 3, which can be operated in the same range of pressure and temperature as the belt systems with comparable volume.

Two closely related facilities are the hexahedral press and the cubic press (*9, 11*), both of which have six anvils instead of four. Rather few routine runs have been performed up to now with these types of apparatus, although the results obtained with the cubic press seem most encouraging.

III. Empirical Rules Which Govern the Structure of Crystals under Pressure

If we consider a model of spheres with a constant radius R, the fraction of total space occupied by such spheres is equal to 74% in the fcc and the hcp structures but is only 68% in the bcc arrangement. The arrangement with tetrahedral coordination, found, e.g., in the structures of diamonds, silicon, germanium, etc., is even less favorable with regard to space filling. Such considerations lead to the expectation that pressure will cause an increase in the coordination number. This has been observed in many elements, e.g., graphite, which goes from three to four coordination (diamond), in silicon and germanium, which go from four to six coordination (white tin type).

In alloys and compounds, where two or more different elements are packed together in an ordered way, the situation is more complex, and one has to take into account the fact that the compressibilities of the various elements are different and will also depend on the type of chemical bonding. In general, compressibilities of large anions are greater than those of smaller cations. Such a situation leads, under pressure, to an increase of the radii ratio r_c/r_a and the stabilization of structures having increased coordination numbers (Table I). For instance, CdTe undergoes a pressure-induced phase transition from a four-coordinated zinc blende structure type to a hexacoordinated rock salt type (*12*); HgTe and HgSe undergo a phase transition from the zinc blende structure type to the hexacoordinated cinnabar structure type (*13*). InSb goes from a four-coordinated zinc blende structure to the hexacoordinated white tine structure type (*14*). Coesite (SiO_2) with tetrahedral Si^{4+} undergoes a phase transition to a high-pressure rutile-type polymorph stishovite (*15*), whereas MnF_2 with hexacoordinated rutile structure type goes to a seven- to eight-coordinated distorted fluorite type (*16*). CaF_2 itself transforms into a nine-coordinated $PbCl_2$ structure type (*17*). Shannon and Prewitt (*18*) listed a large number of high-pressure transitions accompanied by an increase in both cation and anion coordinations and emphasized that the volume change at these transitions is generally considerably greater (10–40%) than those in which no coordination change exists (0–10%) (Table II).

TABLE I
EXAMPLES OF PHASE TRANSFORMATIONS WITH AN INCREASE OF ATOM COORDINATION

Compound	Structure and coordination		High-pressure structure and coordination	
C	Graphite	3	Diamond	4
Bn	Graphite (ordered)	3	Wurtzite	4
Si(Ge)	Diamond	4	β-Sn	6
InSb	Blende	4	β-Sn	6
ZnS	Blende	4	NaCl	6
CdTe	Blende	4	NaCl	6
HgTe	Blende	4	Cinnabar	6

Although pressure-induced phase transformations of ionic compounds are often accompanied by an increase of the cation and anion coordinations, many transformations are known in which the cation and anion coordinations remain constant. For instance, this is the case for the quartz to coesite transition, for the PbO_2 rutile to α-PbO_2 transition (*19*), for the olivine to spinel transition (Fe_2SiO_4 (*20, 21*), Co_2SiO_4 (*22*), Ni_2SiO_4), etc. The only common trend among the transformations of ionic compounds is that the anion packing is more efficient in the high pressure than in the low-pressure phase (*24*).

From these few examples one can conclude that a general rule will govern the pressure-induced phase transitions, namely, the packing efficiency, and therefore *the density of the high-pressure phase must be greater than that of the starting phase* (*25*).

IV. New Compounds from High Pressure

A. Quenchable and Unquenchable High-Pressure Phases

To increase the kinetics of a phase transformation of a compound, $(A_xB_y)_{LP} \rightarrow (A_xB_y)_{HP}$, one generally uses rather high temperatures, from about 700 to 2000°C. If the sample can be cooled rapidly

TABLE II

CONDITIONS FOR THE SYNTHESIS OF THE HIGH-PRESSURE POLYMORPHS OF IONIC COMPOUNDS[a]

Compound	Structure type	Pressure (kbar)	Temperature (°C)	Coordination, high-temperature phase	Structure type	$-\Delta V/V$ (%)	Ref.
$^{IV}SiO_2$	Quartz	100	900	$^{VI}SiO_2$	Rutile (SnO_2)	60	*15*
$^{IV}K(AlSi_3)O_8$	Feldspar	120	900	$^{IV}K(AlSi_3)O_8$	Hollandite	45	*51*
$^{III}B_2O_3$	Hexagonal	20	500	$^{IV}B_2O_3$	Orthorhombic	27	*52*
$^{VIII}Ca^{III}B_2O_4$	Orthorhombic	40	1000	$^{XII}Ca^{IV}B_2O_4$	Cubic	23	*53*
$^{VI}Mn_2{}^{IV}GeO_4$	Olivine	120	900	$^{VI}Mn_2{}^{VI}GeO_4$	Sr_2PbO_4	17	*54*
$^{VI}Ca_2{}^{IV}GeO_4$	Olivine	110	900	$^{IX}Ca_2{}^{VI}GeO_4$	K_2NiF_4	25	*55*
$^{VI}Gd_2{}^{iV}Ge_2O_7$	Thortveitite	65	1100	$^{VIII}Gd_2{}^{VI}Ge_2O_7$	Pyrochlore	~20	*56*
$^{VI}Sc_2{}^{IV}Si_2O_7$	Thortveitite	120	1000	$^{VIII}Sc_2{}^{VI}Si_2O_7$	Pyrochlore	~25	*57*
$^{VI}Mn^{IV}GeO_3$	Pyroxene	60	700	$^{VI}Mn^{VI}GeO_3$	Ilmenite	~15	*58*
$^{VI}Mn^{IV}SiO_3$	Pyroxene	120	900	$^{VIII}Mn_3{}^{VI}(MnSi)^{IV}Si_3O_{12}$	Garnet	~15	*59*
$^{VI}Cd^{VI}TiO_3$	Ilmenite	~2–3	300	$^{VIII}Cd^{VI}TiO_3$	Distorted perovskite	10	*60*
$^{VII}Y^{V}AlO_3$	Hexagonal	40	900	$^{VIII}Y^{VI}AlO_3$	Distorted perovskite	10	*61*
$^{VIII}SrF_2$	Fluorite	70	900	$^{IX}SrF_2$	$PbCl_2$	12	
$^{VI}Fe_2{}^{IV}SiO_4$	Olivine	60	900	$^{VI}Fe_2{}^{IV}SiO_4$	Spinel	9	*62*
$^{VIII}Zr^{IV}SiO_4$	Zircon	60	900	$^{VIII}Zr^{IV}SiO_4$	Scheelite	8	*63*
$^{VI}PbO_2$	Rutile	3–4	500	$^{VI}PbO_2$	α-PbO_2	6	*19*

[a] The coordination number is given on the left side of the cation concerned.

while it is maintained under pressure, the dense phase can be "quenched" and recovered under normal conditions after the release of the pressure. Not all high-pressure phases can be "quenched" and recovered. In general, before the experiment is performed it is not possible to know if an expected dense phase will be preserved as a metastable phase under normal pressure and temperature conditions.

From empirical considerations based on the already extensive literature one can deduce some principles which help one to predict and to understand the stability of the high-pressure phases.

First, it seems that the more complex the chemical formula and the structure of the compound, the greater the chances of recovering the dense form as a metastable phase. In such compounds one generally observes at the transition a reconstruction of the entire structure; old bonds are broken and new bonds are established, while the relative positions of all the atoms are strongly modified. To return to their initial positions, the atoms have to jump over rather high potential barriers, and this generally requires considerable energy; no wonder, then, that some high-pressure phases have to be heated up to 1000°C before undergoing a phase transition to a less dense phase.

On the other hand, transitions in which atoms travel relatively small distances without crossing will generally be difficult to quench, even in the cases in which old bonds are broken and new bonds are formed with higher coordinations of the atoms. For instance, this is the case for the six-coordinated metallic phases of germanium and silicon (white tin type) (*26*) which cannot be preserved when one releases the pressure.

Even in the case of reconstructive transformations, the high-pressure phases may not be retained at normal pressure: This happens when the high-pressure phase can give a third phase without major rearrangements of the atoms, which only slide against each other parallel to favorable crystallographic planes. For instance, at 100 kbar rutile-type MnF_2 undergoes a transformation to an eight-coordinated cubic fluorite type; this structure transforms on the release of the pressure into the closely related α-PbO_2 type of structure, with octahedral coordination of the Mn atoms and an intermediate density between the starting phase and the high-pressure phase (*27–29*).

A similar relaxation of the high-pressure phase into a phase of lower density involving a gliding process of the atoms along preferential crystallographic planes can explain the extreme instability of the hexagonal diamond phase in comparison to the cubic phase.

B. Phase Diagrams under High Pressure

Phase equilibria of pure elements at high pressures have been studied rather well. The P–T diagrams have been constructed for the majority of elements (see, for instance, Klement and Jayaraman (*25, 30*)), and the crystal structures of polymorphic modifications formed at high pressure have been established in certain cases. Investigation of the effects of high pressures on phase equilibria in multicomponent systems (metallic, semiconductor, ionic compound) has only begun, even for binary systems. Most of the systems have been investigated in a rather limited range of compositions, generally the same as those giving definite compounds under normal conditions, in the search for high-pressure phases of these compounds.

It would appear that it is now time to investigate binary (and even ternary) phase diagrams, not only with the goal of discovering high-pressure phases of compounds stable at normal pressures but also with the goal of finding phases with different compositions which require high-pressure conditions for their synthesis. In several cases which have already been carefully investigated both thermodynamic calculations and experimental data have shown that even comparatively low pressures can lead to drastic changes of the phase diagram.

Thus, for example, in the iron–carbon system (*31*) at a temperature of 1000°C a pressure of only 3 to 4 kbar shifts the equilibrium of the reaction

$$Fe_3C \leftarrow 3Fe+C$$

from the right to the left, leading to a considerable change in phase formation processes during annealing of both white and gray iron.

C. Examples of High-Pressure Synthesis of New Compounds

Solid-state chemists are mainly interested in the synthesis of new quenchable phases, with the object of using these phases as a source of new materials. From the large number of new high-pressure phases which have been discovered even in the one-component systems, it becomes evident that many new phases will be discovered in most of the binary and ternary systems, *probably several times more than the number which are known to exist under normal conditions.*

To illustrate the general principles developed above, we now present a few typical examples in which high-pressure conditions have been successfully used for the synthesis of new materials.

Synthesis of high-pressure polymorphs of compounds having a stable phase at normal pressures. The search for high-pressure polymorphs has always been the most thoroughly investigated and the most fruitful field in high-pressure research on solids. We mentioned above that quite often the coordination of at least some of the atoms increases under pressure. We can thus expect that in many cases the coordination of one kind of atom in the high-pressure phase will be the same as the coordination adopted at normal pressure by the heavier atoms from the same group of the periodic system, the corresponding compounds being isostructural.

Of special interest are the syntheses of the high-pressure polymorphs of carbon and boron nitride, respectively, with diamond- and wurtzite-type structures. The atom coordination increases from 3 to 4, leading to drastic changes of the optical, electrical, and mechanical properties.

However, ionic compounds are among the most extensively investigated compounds under high-pressure, high-temperature conditions, essential because the dense phases are easy to quench and generally have a rather high thermal stability. Table II contains typical examples of such phase transformations, which obey quite well the general principles described earlier. Hundreds of such phase transformations have been described in the literature (*32*).

Synthesis of new compounds having no stable phase under normal pressure conditions. The first idea which comes to mind is that the normal pressure phases are not stable because of unsatisfactory size conditions; this may be due to the relative sizes of two metallic elements, or the relative sizes of a metallic and a nonmetallic element, or even to the sizes of the different cations relative to the sizes of the anions. Usually, one of the two species is more compressible than the other, and the use of high-pressure conditions may help to reestablish the suitable radii ratio—provided that the pressure effect acts in the proper manner. To anticipate the effect of the pressure and to avoid useless experiments one should first consult a table of compressibilities of the elements.

Thus many superconducting alloys of the A_3B formula crystallize in the cubic $A15$ structure (for example Nb_3Sn, V_3Si). In all of these, the radii ratio R_A/R_B verifies the relation $0.95 < R_A/R_B < 1.15$. In fact Nb_3In and Nb_3Si are known to be unstable at normal pressure, because of unsatisfactory size conditions; indium is too large and silicon is too small for niobium. Superconductor Nb_3In was successfully synthesized under high-pressure conditions (*33*), while no $A15$ phase was obtained for Nb_3Si under comparable conditions (*34*) because both indium and silicon are more compressible than niobium. Many metastable Laves phases ($MgCu_2$ type) have been produced under pressure, for instance, $LaCo_2$, $PrFe_2$, $NdFe_2$, etc.

However, the use of high-pressure conditions should not be limited to the synthesis of denser allotropic phases or to extending the stability field of a typical structure. These techniques open a new dimension in the fields of solid-state chemistry and metallurgy.

Most of the phase diagrams have been investigated under normal pressure conditions. Many well-known compounds in these diagrams seem to have no dense phase at high pressure and decompose into the components or into new phases. Conversely, many new metastable high-pressure phases have been found to have no phase of equivalent composition at normal pressure. This is the case, for instance, in the system Al_2O_3–B_2O_3. Two ternary compounds are known to be stable at room pressure, corresponding to the compositions 9 Al_2O_3–$2B_2O_3$ and $2Al_2O_3$, B_2O_3. None of these two compounds is found in the phase diagram at 40 kbar, while two new compounds have been identified, namely Al_3BO_6 and $AlBO_3$ (*35*). Another example is given by the system Cd–As. Two compounds are known in this system under normal conditions, namely, Cd_3As_2 and $CdAs_2$. Both compounds are unstable at high pressure, while a new composition CdAs appears to be stable with the metastable Si III structure type (*36*). This is rather surprising because (CdAs) is not isoelectronic with Si.

New types of binary systems can be investigated, between an oxide and a fluoride, an oxide and a nitride, a nitride and a fluoride, etc. Usually these systems do not react together because of very different chemical properties or stabilities (melting temperatures, vapor pressure, etc.). Under pressure they can give intermediate compounds whose densities are bigger than the density of the mixture of equivalent composition. For instance, in the system TiO_2–KF, a ternary compound $KTiO_2F$ with perovskite structure has been synthesized at 50 kbar and 1000°C (*37*).

Going further, one can use the high-pressure technique to confine a solid and a liquid in order to investigate solid–liquid phase diagrams. When the liquid is water, one is dealing with the well-known hydrothermal synthesis technique, and intermediate compounds such as Al_5HO_8, AlOOH, $Al(OH)_3$, and $Cd(OH)_2$ can be prepared, some of which assume several phases with increasing pressure. Compounds such as FeOOH have been shown to be stable up to 1100°C under a pressure of 80 kbar. This means that under such conditions, the density of the high-pressure phase γFeOOH is higher than the density of the mixture $Fe_2O_3 + H_2O$.

Binary solid–gas systems can also be investigated, such as metal–hydrogen and metal–nitrogen, leading to hydrides or interstitial-type alloys. Of special interest are the transition metal oxide-oxygen systems, as they allow one to prepare compounds containing cations in unusual valency states. Thus the corundum phase Co_2O_3 has been obtained at 80 kbar and 900°C (*38*) from Co_3O_4 + oxygen, while the perovskite $Ln\text{Ni}^{3+}O_3$ series was obtained from a mixture of lanthanide oxide Ln_2O_3, NiO + oxygen at 60 kbar, 1000°C (*39*). In each case the extra oxygen was produced in the high-pressure cell from thermic decomposition of an oxygen generator such as Na_2O_2, $KClO_3$, CrO_3 etc. Figure 4 shows the sealed cell assembly containing the starting materials and the oxygen generator.

Many oxides and fluorides with high-valency-state cations have been obtained by this technique. The oxygen generator is sometimes used in order to prevent the rapid decomposition at high temperature of one of the starting oxides. This was the case in the synthesis of pyrochlores $Hg_2Nb_2O_7$ and $Hg_2Ta_2O_7$ (*40*) starting from unstable HgO oxide, for the synthesis of UCr_2O_6 (*41*) starting from unstable UO_3, and for the synthesis of pyrochlores $Y_2Mn_2^{4+}O_7$ (*42*) starting from the unstable manganese dioxide MnO_2.

Conversely, extralow oxygen pressure can be ensured by the confinement of an oxide plus a metallic element in the sealed cell under high pressure. Suboxides can be obtained by this method— for instance, YbO, which was prepared by reaction at 40 kbar and 600°C from a mixture of composition $Yb_2O_3 + Yb$ (*43*). The nonsymmetrical analog of graphite B_2O was

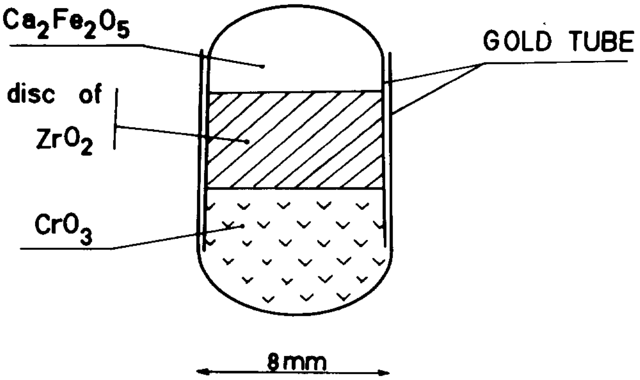

FIG. 4. Sample assembly for preparation of $CaFe^{4+}O_3$.

obtained under high-pressure high-temperature conditions from a mixture of composition B_2O_3+4B (*44*). The synthesis of the hypothetical B_3F with ordered graphite structure which has been anticipated by Hulliger (*45*) would probably also require high-pressure high-temperature conditions.

D. Crystal Growth under High Pressure

Crystal growth in a flux. The possibility of synthesizing single crystals of dense metastable phases was clearly demonstrated by the growth of centimeter-sized diamonds from graphite in a belt-type apparatus (*46*). Many "catalysts" have been tested, but the best results have been obtained in the ternary Ni–Fe–C system. Actually these "catalysts" were acting as a high-temperature solvent (flux) for carbon.

The cubic high-pressure phase of boron nitride has also been extensively investigated. Roughly the same pressure and temperature as those required for diamonds are necessary for cubic BN called "Bozaron". However, the "catalyst" materials (actually the flux) are quite different, consisting of the alkali and alkaline earth metals and their nitrides. Cubic boron nitride can be grown as rather nice, clear crystals with the shape of tetrahedra 1 to 2 mm in cross section (*47, 48*).

One of the difficulties in growing crystals under high pressure by the fiux method is finding the right solvent. Most conventional solvents are inadequate, either because they react with the material at high pressure or because their melting points increase sharply with pressure, thus requiring high-temperature conditions, For instance, the melting point of NaCl is about 1550°C at 65 kbar as against 800°C at room pressure. If the pressure is not too high, one can still use a conventional flux: When the pressure required to stabilize the denser phase is high, it is necessary to find new types of fluxes with relatively low melting points at high pressure. Dry NaOH has been proved to be an adequate flux for the growth of several high-pressure phases of oxides.

Crystal growth by hydrothermal synthesis under very high pressure. The properties of water under high-pressure, high-temperature conditions are rather well known. For instance, measurements have shown that at supercritical temperatures, for example, 500°C, the viscosity of the fluid is lower than that of liquid water at room temperature by a factor of 10 or 20 (*49*). Dense supercritical water is thus a medium of very high fluidity, and consequently dissolved neutral or ionic particles have high diffusion coefficients and ion mobilities in this medium (*50*). Under such conditions supercritical water becomes vigorously active, and even when present as trace in the high-pressure cell its acts as a powerful "catalyst" for the synthesis of single crystals. During the last few years we have developed a technique which allows us to perform hydrothermal synthesis of inorganic materials in a belt apparatus up to 100 kbar and more than 1500°C. Depending on the temperature and chemical conditions required, sealed capsules made of gold, platinum, or other metals are used.

To increase the kinetics of the crystal growth process, one can add several "catalysts", such as sodium hydroxide, lithium hydroxide, ammonium hydroxide, various acids, etc., to the water solvent.

Table III lists several high-pressure phases we have been able to identify and to obtain as single crystals. All the experiments have been performed in cylindrical platinum cells 6 mm in length and 4 mm in diameter. If a bigger cell could be used, crystals of much larger dimensions could probably be obtained under the same conditions.

Conclusion

While an exhaustive survey of the thousands of compounds which have been synthesized via high-pressure, high-

TABLE III

CRYSTALS OF NEW DENSE PHASES OBTAINED BY HYDROTHERMAL SYNTHESIS UNDER EXTREME CONDITIONS

Formula	Structure of high-temperature phase	Starting materials	Temperature (°C)	Pressure (kbar)	Size of crystals (mn)
$AlBO_3$	Calcite	Al_2O_3, $B(OH)_3$	1000	40	0.5
$GaBO_3$	Calcite	$Ga_2O_3+B(OH)_3$	1000	40	0.2
Al_3BO_6	Norbergite	Al_2O_3, $B(OH)_3$	1000	40	0.1–0.2
YBO_3	Pseudovaterite	Y_2O_3, $B(OH)_3$	1200	40	0.1
$LuBO_3$	Pseudovaterite	Lu_2O_3,$B(OH)_3$	1200	40	0.1
$FeNiBO_4$	Olivine	Fe_2O_3, NiO, $B(OH)_3$	1000	40	0.2–0.3
$AlMgBO_4$	Olivine	Al_2O_3, MgO, $B(OH)_3$	1000	40	0.2–0.3
$TeMn_2O_6$	Distorted trirutile	$Te(OH)_6$, Mn_2O_3	1000	80	0.1
Cr_2CdO_4	Fe_2CaO_4	$CrCdO_4$	1000	80	0.2
Mn_3O_4	Mn_2CaO_4	Mn_3O_4 (hausmannite)	1000	80	0.1
$U^{6+}Cr_2^{3+}O_6$	$PbSb_2O_6$	$UO_3+Cr_2O_3$	1000	40	2.0
$Y_2Mn_2^{4+}O_7$	Pyrochlore	$Y_2O_3+MnO_2$	900	60	0.1
$CaCu_3Ge_4O_{12}$	Distorted perovskite	$Ca(OH)_2$, CuO, GeO_2	1000	60	0.5
$LaMn_7O_{12}$	Distorted perovskite	$La_2O_3+Mn_2O_3$	1000	60	0.1

temperature conditions would be difficult to imagine, these very few examples are probably enough to demonstrate that the possibilities of these techniques are endless and quite rewarding for a solid-state chemist attracted by unusual compounds possibly containing new types of bonding.

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