DOI: 10.1002/anie.200462170

Synthesis in Metal Flux

The Metal Flux: A Preparative Tool for the Exploration of Intermetallic Compounds

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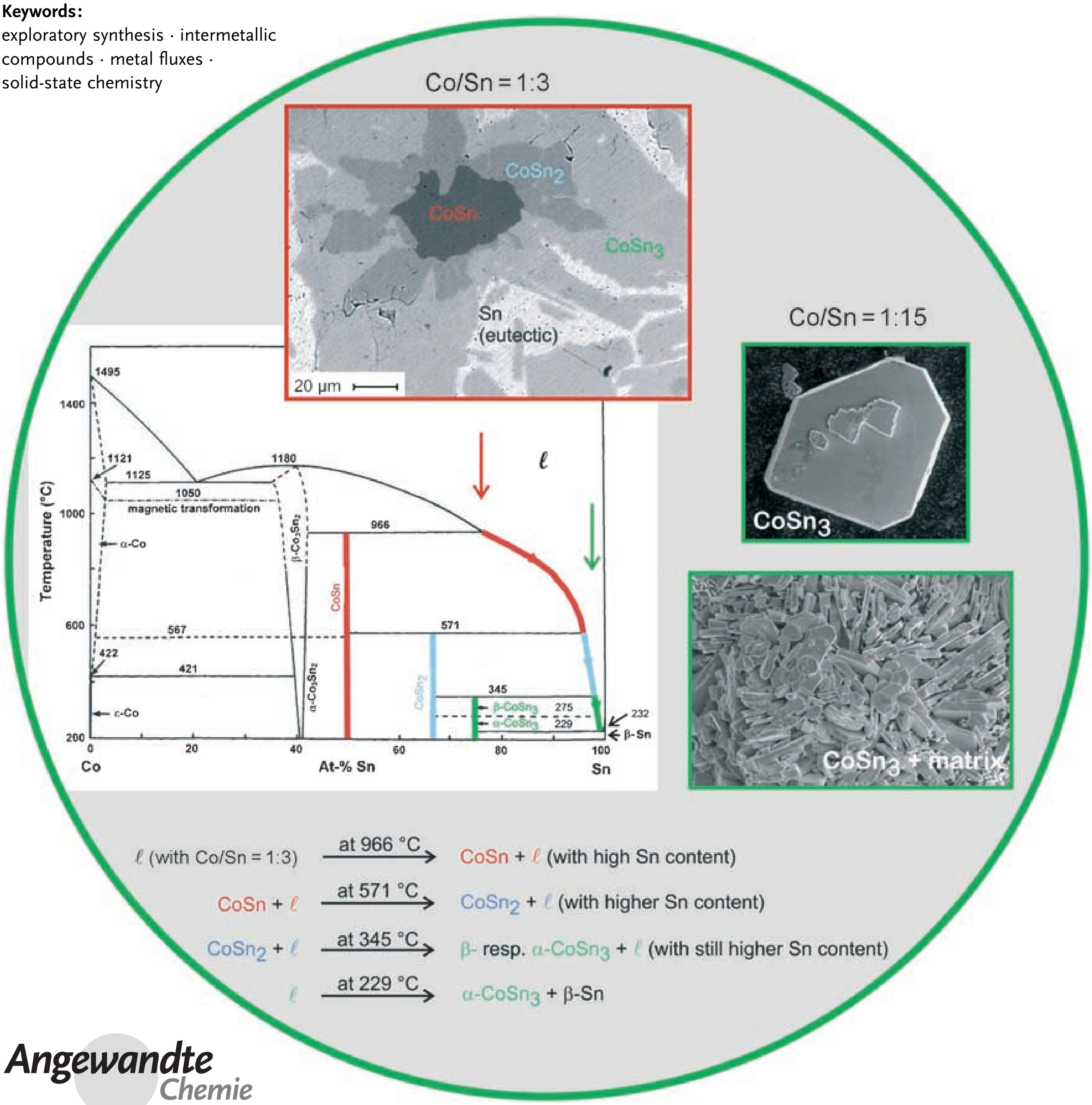
Keywords:
exploratory synthesis · intermetallic compounds · metal fluxes · solid-state chemistry



This review highlights the use and great potential of liquid metals as exotic and powerful solvents (i.e. fluxes) for the synthesis of intermetallic phases. The results presented demonstrate that considerable advances in the discovery of novel and complex phases are achievable utilizing molten metals as solvents. A wide cross-section of examples of flux-grown intermetallic phases and related solids are discussed and a brief history of the origins of flux chemistry is given. The most commonly used metal fluxes are surveyed and where possible, the underlying principal reasons that make the flux reaction work are discussed.

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1. Introduction

1.1. Intermetallic Phases in Science and Technology

Compounds containing exclusively two or more different kinds of metal (or metalloid) atoms are defined as intermetallic compounds. The difference between an intermetallic compound and a regular metal (e.g. a metallic element) is in the way the atoms bond. In metals, the bonding electrons distribute themselves throughout the material (i.e. the electrons are more delocalized), giving rise to predominantly nondirectional bonding in the solid. Intermetallic compounds, on the other hand, maintain a slight ionic and covalent character (i.e. the electrons are localized), and the atomic bonding becomes more directional. This difference in bonding character results in differences in material behavior. Chemists have often given secondary attention to intermetallic compounds as a class of materials, compared to the more ionic materials such as oxides, ceramics, chalcogenides, or halides. This lack of appeal may have been partly due to the difficulty in understanding some very basic characteristics of intermetallic compounds such as their compositions, bonding, and assignment of oxidation states for individual atoms. As a result, the bulk of synthetic activity and innovation in solid-state chemistry has focused primarily on the ionic type of materials, whereas typically the synthesis of intermetallic compounds has been carried out in only a few laboratories and requires very high temperature conditions which are achieved by the use of induction heating and arc melting.

Some important intermetallic compounds are aluminum-based and silicon-based materials. In commercial aluminum alloys (many of which also contain silicon), rare-earth or transition metals are included to improve the properties. A result of this approach is the formation of both known as well as yet unexplored multinary intermetallic compounds within the aluminum matrix.[1] The study of possible multinary compounds formed during the alloying process is vital to understand how to optimize the bulk material. Rare-earth-element-containing binary and ternary aluminides often have complex structures and interesting magnetic and electronic behavior.[2]

Silicides are both scientifically and industrially important,[3] and have been extensively studied during the past few decades. Because of their hardness, chemical stability, and high melting point, silicides are well known as high-temperature, oxygen-resistant structural materials which are used, for example, in making high-temperature furnaces[4] and for high-temperature coatings.[5] Transition-metal silicides are highly valued as electrical and magnetic materials, in addition to several new applications such as thermoelectric energy conversion,[6] and compatible electrode materials in electronics.[7] Some silicides are low-temperature superconductors.[8] Several reviews and papers regarding their preparation, properties, and crystal chemistry,[9] thermodynamics,[10] applications in silicon technology,[11] and materials aspects of silicides for advanced technologies[12] have been published.

Silicides are usually synthesized by direct reaction of the elements heated in vacuum or in an inert atmosphere. The

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required reaction temperatures are usually over 1000 °C necessitating the use of an arc welder or inductive furnace. Although single crystals sometimes can be obtained by annealing or quenching the product, in most situations only powder samples are obtained using these methods. This situation often makes crystal-structure determination difficult and limits proper characterization.

Of course there are many other important intermetallic compounds including nickel superalloys and titanium- and molybdenum-based systems which are remarkably heat and corrosion resistant, finding applications in jet engines, as coatings, as well as in the biomedical and automotive industries.[13] Many titanium-based alloys are also used in orthopedic applications owing to their good biocompatibility, appropriate mechanical properties, and excellent corrosion resistance. Advanced copper alloys are of interest for fusion-reactor applications and to aerospace engine makers (as liners for thrust cell combustion chambers and nozzle ramps).[14] A large number of intermetallic systems based on a variety of elements including Ti, Fe, Al, Ni, Ga, and Mn exhibit interesting shape-memory effects with implications in a number of important applications.[15] The remarkable compound Ti_3SiC_2 is damage tolerant, not susceptible to thermal shock, has excellent oxidation resistance, and is as readily machinable as graphite.[16] Single-crystalline samples of $MnNi_2Ga$ have been shown to produce close to 10% magnetic-field-induced strain.[17] Platinum intermetallic compounds are also of interest for use as catalysts[18] and for high-temperature applications such as inert coatings for titanium alloys.[19]

Traditionally, the study of intermetallic phases has been mainly the subject of metallurgists who have synthesized many of the known compounds. As a result, intermetallic compounds are critical as structural materials in technological applications. Many new applications, however, are emerging or envisioned, and to go forward, advances in the understanding and in the discovery of new intermetallic compounds are needed. Solid-state chemistry has a significant role to play in this regard.

1.2. The Flux Method in Solid-State Chemistry

The synthetic toolbox of the solid-state chemist contains several powerful and productive means, each with its unique capabilities, advantages, and disadvantages. For intermetallic compounds these techniques generally involve very high temperatures as for example arc-melting and radio frequency (rf or high frequency (hf)) induction heating. These methods are necessary because the starting materials employed in such reactions are usually solids themselves and very high temperatures are necessary to cause sufficient diffusion for a reaction to take place. Often even high temperatures alone are not enough to overcome these barriers and the samples need to be ground to powders several times during the synthesis to expose fresh surfaces on which reactions can occur. These high temperatures give rise to two important synthetic limitations. The reactions generally proceed to the most thermodynamically stable products; the high energies involved often leave little room for kinetic control. These thermodynamically stable products are typically the simplest of binary or ternary compounds, which because of their high structural stability can become synthetic roadblocks, and often are difficult to circumvent. In addition, the rapid cooling of reactants from high temperatures along with the repeated grinding of the samples, as mentioned above, do not create a favorable environment for crystal growth. Single crystals can sometimes form through extended annealing, and even then the growth of crystals large enough for physicochemical analysis is not always seen. Microcrystalline products can limit the proper characterization of the new material both

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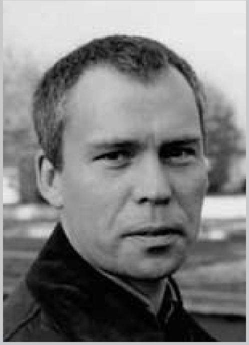

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structurally and physically, particularly when knowledge about anisotropic effects is desired, and may even prevent the proper identification of the products in extreme cases.

Methods that permit reactions to be carried out at lower temperature are likely to produce new phases. This thesis applies to all classes of compounds including intermetallic phases.[20–22] To increase the odds for new compound formation and avoid the thermodynamic traps, the reactant diffusion must be increased so that the activation energy barrier (associated with solid–solid reactions) is lowered. Under these conditions the reaction could proceed at lower temperatures to some other outcome. High diffusion rates (from a solid-state perspective) could be achieved by simply allowing soluble starting materials to react in a solvent.

To achieve enhanced diffusion of reactants in solid-state synthesis, molten solids can be used as solvents (i.e. fluxes). Such media (predominantly salts) have been employed for well over a 100 years for high-temperature single-crystal growth. Although many salts are high-melting species, eutectic combinations of binary salts and salts of polyatomic species often have melting points well below the temperatures of classical solid-state synthesis, making possible the exploration of new chemistry at intermediate temperatures. In many instances, these liquids act not only as solvents, but also as reactants, providing species which can be incorporated into the final product. In the latter case this is analogous to solvate formation or to cases where the solvent provides atoms to the compound being formed. Such a molten solvent is called a "reactive flux". Therefore, appropriate molten metals can act in such a fashion to become bona-fide solvents for synthesis. Lessons learnt from solution synthesis could be applied in this type of solid-state synthesis with, as we will show in this review, remarkable results.

2. Challenges in the Solid-State Chemistry of Intermetallic Compounds

Because the composition of most intermetallic compounds does not yield to the type of electron counting and oxidation-number analysis typically applied to more familiar solid-state compounds such as halides, oxides, and chalcogenides, it is very difficult to predict the type of composition that would be stable in a given system of metallic elements (except for special cases, such as Zintl, Laves, or Hume–Rothery phases). For example, whereas compositions of the type K_2MoO_4, Ag_2HgI_4, FeS_2, and Fe_2SnS_4 are well understood and can be predicted and therefore can be targeted for synthesis, the compositions $FeGa_3$, $YNiGe_2$, $RhSn_4$, Sm_2NiGa_{12}, or $SmNiSi_3$ appear totally strange to the average chemist. The situation is even more complicated when considering quaternary systems such as $Sm_2NiAl_7Si_5$ or $Sm_8Ru_{12}Al_{49}Si_{21}$. For intermetallics such stoichiometries are more the norm than the exception, whereas in more polar non-intermetallic compounds it is generally the other way around. Non-intermetallic compounds display more ionic character in their bonding, extensive charge transfer between different atoms, and as a result can be explained easily to a chemistry student, whereas this is difficult for intermetallic compounds. A different type of basic understanding and intuition is required, one that goes beyond the complexity of the electronic band-structure calculations usually done to deal with these kinds of compounds. How can such compositions be predicted, so they can be targeted for exploratory synthesis? Of course, the answer today is that they cannot be. Using liquid metals as fluxes, to carry out synthetic explorations, could serve as a great way to discovering (without having to predict) a large variety of intermetallic compounds.

Herein we present the use of liquid metals as reaction media to synthesize new classes of intermetallics and other non-oxidic solids, such as carbides, nitrides, and pnictides. The emphasis is placed on the utility of the fluxes to discover new materials rather than to grow large crystals of known materials. We highlight herein how the metal-flux technique is aimed at gaining control at lower temperatures and is a critical synthetic tool in the solid-state chemist's arsenal of methods. This review is not meant to be an exhaustive account of what has transpired since the first example of metal-flux synthesis was reported. Therefore a number of worthwhile reports may not be referenced. Instead our goal is to increase awareness of this synthetic approach by drawing attention to the possibilities it offers. This article is written from a solid-state chemist's point of view and we mainly focus on the recent literature with respect to the synthesis and crystal growth of new compounds.

3. Metallic Fluxes

The use of molten metals as media for the synthesis of new materials has been limited compared to the highly successful use of molten salts. In those cases where metallic fluxes have been used, new compounds have resulted that are interesting from the structural, physicochemical, and even the practical point of view. In the vast majority of cases, however, use of molten metals has been focused primarily on growing single crystals of known compounds, not for exploratory synthesis.[23,24] The purpose of this article is to give an overview of the known chemistry associated with exploratory synthesis using metallic fluxes and to highlight the potential of this approach.

Several key characteristics must be met for a metal to be a viable flux for reaction chemistry: 1) the metal should form a flux (i.e. a melt) at reasonably low temperatures so that normal heating equipment and containers can be used, 2) the metal should have a large difference between its melting point and boiling point temperatures, 3) it should be possible to separate the metal from the products, by chemical dissolution, filtration during its liquid state, or if necessary mechanical removal, 4) the metal flux should not form highly stable binary compounds with any of the reactants. This last point is critical.

4. Historical Perspective on the Preparation and Crystal Growth from Metallic Melts

Metallic fluxes were employed early on in the preparative chemistry of solids. Henri Moissan (1852–1907) tried to obtain diamonds in many experiments by rapidly quenching carbon containing (in homogeneous and heterogeneous form) liquid iron and other metals from high temperatures using the electric furnace that he developed.[25] In this way he had hoped to create the required high pressure within the contracting metal jacket. After dissolving the metallic matrices in acids he found tiny, very hard crystals, some with octahedral shape which burned and produced carbon dioxide. Moissan died believing that he had made diamonds. His experiments were reproduced and resulted in carborundum (SiC, with the mineral name moissanite). It is interesting that industrial diamonds were first successfully synthesized in 1954 in the laboratories of the General Electric Company at high pressure, again in the presence of liquid iron. Without the metallic flux, much higher pressure is required. Thus, this process, generally regarded only as a high-pressure synthesis, may also be quoted as a crystal growth from a metallic flux. Now it is estimated, that about one hundred tons of synthetic diamonds are produced annually by this process.[26]

At around 1900 Paul Lebeau, a co-worker of Moissan, prepared various silicides of late transition metals from a copper flux, and Jolibois of that school has to be credited for being the first to employ a tin flux to grow nickel phosphides.[27] In subsequent years such solution growth from metallic fluxes has variously been called menstruum technique, Lebeau method, auxiliary bath method (Hilfsmetallbadtechnik), and molten metal solution growth. Many borides, carbides, silicides, and nitrides of the early transition metals have been obtained this way in well-crystallized form, usually with higher purity than by direct reaction of the elemental components. Some of the early literature about metallic fluxes is cited in the introductory paragraphs of various papers reporting on the recrystallization of transition-metal borides (e.g., TiB_2, ZrB_2, VB, NbB_2, W_2B_5) using iron, copper, aluminum, tin, or lead as fluxes,[28–30] the preparation of the high-melting carbides (e.g., TiC, WC, UC) with iron, cobalt, nickel, or aluminum as fluxes,[31] and the preparation of various silicides of early transition metals (e.g., $TiSi_2$, $CrSi_2$, Mo_5Si_3, $MoSi_2$, W_5Si_3, WSi_2) employing mainly copper or tin as fluxes.[32,33] Deitch reviewed the early literature on the growth of semiconductors, e.g., Si, SiC, AlP, GaAs, ZnS, ZnTe, $ZnSiP_2$, $CdSiP_2$,[34] and Lundström summarized the literature on the preparation and crystal growth of non-oxidic refractories using molten metallic solutions.[35] The handbooks on crystal growth by Elwell and Scheel[24] and Wilke and Bohm[36] list more than 100 references on the growth of single crystals of various, mostly binary compounds from metallic fluxes.

By using a metallic flux, it is not necessary to completely dissolve the elemental components of the desired products. The flux may act as a transporting medium, which dissolves a component in one place and grows the product at another location of the sample container. Nevertheless, it is important for the flux to have reasonable solubilities for the components to avoid exceedingly long growth times. Gumiński has published a compilation of experimental solubilities of metals in liquid low-melting metallic fluxes, such as mercury, gallium, indium, tin, lead, and bismuth. He also gives some estimates for combinations of metallic elements, where no experimental data are available.[37] The solubilities of various industrially important transition-metal disilicides MSi_2 with M = Ti, V, Nb, Ta, Cr, Mo, and W in metallic fluxes have been investigated experimentally.[38] The monograph edited by Hein and Buhrig[39] gives an extensive treatment of such data both for equilibrium and non-equilibrium conditions, and also from a theoretical point of view.

5. Peritectic Reactions and Reactive Fluxes

Some terms, commonly known by metallurgists and crystal growers, may be less appreciated by preparative chemists. A compound formed by a *peritectic* reaction may be such a case. Consider the phase diagram of the binary system cobalt–tin (Figure 1).[40,41] The compound designated as β-Co_3Sn_2 melts congruently (that is, the solid and liquid have the same composition) at 1180 °C. In contrast, CoSn melts incongruently at 966 °C, forming solid β-Co_3Sn_2 and a liquid ℓ of a composition, which is indicated by the large down-pointing arrow in that phase diagram. Conversely, if a melt of that composition (with a Co:Sn ratio of approximately 1:3) is cooled, the liquidus line will be reached at 966 °C. On further cooling, the compound CoSn will crystallize until the sample reaches 571 °C. At that temperature solid CoSn will react with the liquid (by what is called a peritectic reaction) to form $CoSn_2$. The problem is, that this phase forms an envelope around the reactant CoSn. Thus, this (peritectic) reaction can now only proceed by diffusion through the solid envelope of $CoSn_2$. This diffusion process takes time and may not be finished before the sample reaches the next peritectic equilibrium temperature of 345 °C. At that temperature (the high-temperature modification) β-$CoSn_3$ is formed. The melt changes its composition continuously, following the red, then the blue, and finally the green liquidus curves. The remaining melt will solidify at the eutectic temperature of 229 °C.

A scanning electron micrograph of a sample with a slightly higher tin content (Co:Sn ratio 1:4) is shown in the lower part of Figure 1. The very light areas of the micrograph have the lowest cobalt content; they correspond to the tin-rich eutectic. Naturally it will be very difficult to isolate single crystals of (one or the other modification of) $CoSn_3$ from such a sample.

A single-phase sample of α- or β-$CoSn_3$ (depending on the relatively low annealing temperature above or below 275 °C) can be obtained from a solidified melt of that composition (1:3) only by annealing for a very long time, for example, for several weeks. However, the situation changes dramatically if a large excess of tin is used. In this case, well-developed crystals of $CoSn_3$ can be grown by slow cooling down to the eutectic temperature. The crystals of $CoSn_3$ are then embedded in a tin-rich matrix, which can be dissolved in diluted hydrochloric acid.

Herein we have described the preparation of single-phase $CoSn_3$ by using an excess of tin as—what may be called—a *reactive flux*, thus avoiding the very slowly proceeding peritectic reaction. Frequently the phase diagram is not known, and guess work or trial and error are required to find the excess of the reactive flux needed to crystallize the desired product. This of course will be the normal situation in

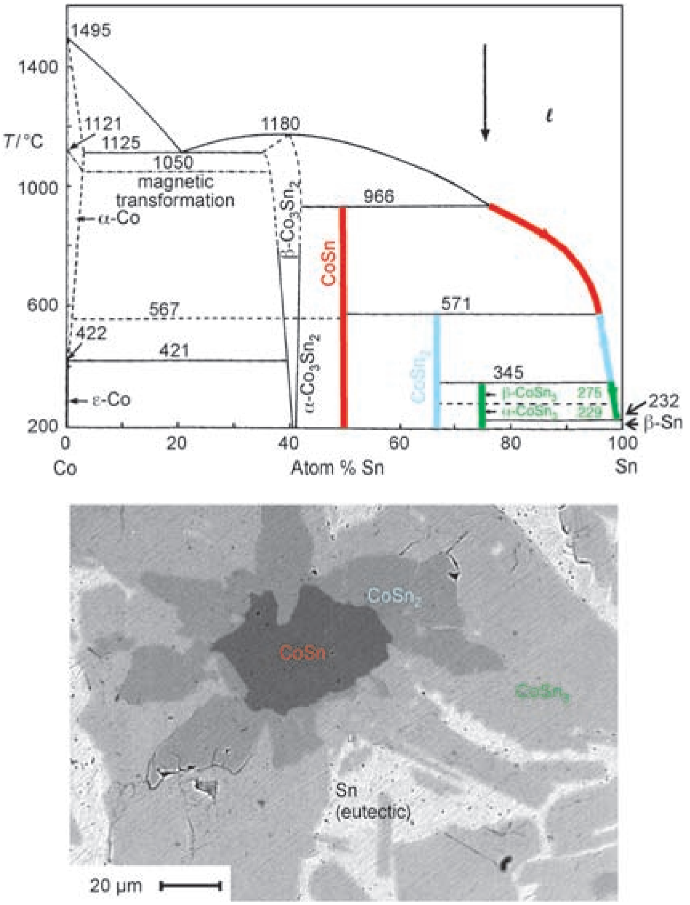

Figure 1. Peritectic reactions in the binary system Co–Sn. Top: the phase diagram of the Co–Sn system. By rapidly cooling a melt (liquidus, ℓ) of the approximate composition Co:Sn = 1:3 (large black arrow) crystals of composition CoSn are obtained first. Since these crystals have a higher Co content than the original melt, the liquid phase changes its composition on cooling along the red liquidus line. At 571 °C the crystals of CoSn start to react with the remaining melt, thereby forming a microcrystalline envelope of the compound $CoSn_2$. During this reaction, the liquid phase changes its composition along the blue line. After further cooling, at 345 °C, the melt, now with a Sn content of approximately 98 atom %, starts to react with $CoSn_2$ and forms another microcrystalline envelope this time of microcrystalline β-$CoSn_3$. Thereby the melt changes its composition along the green line. Finally, at 229 °C it solidifies, to form the eutectic, which consists of a matrix of a solid solution of Co in β-Sn with heterogeneous inclusions of α-$CoSn_3$. Bottom: A micrograph of a corresponding sample (with the slightly different overall composition Co:Sn = 1:4).[41] It is clear that well developed large crystals of α- or β-$CoSn_3$ cannot be grown by such a cascade of peritectic reactions. This sample has been cooled at the relatively slow rate of 100 °C h^{-1}. Nevertheless, it has not reached thermodynamic equilibrium. In its center it contains the remains of a primarily crystallized grain of CoSn, embedded in grains of $CoSn_2$. Before reaching equilibrium the sample had cooled to 345 °C, thus forming β-$CoSn_3$.

exploratory research, where the emphasis is on novel materials with potentially interesting properties. Such materials may contain several components and it may be impractical to work out the phase diagrams. However, it must be remembered, that the kind of the reaction product obtained will depend not only on the annealing conditions, but also on the amount of the reactive flux used.

When such transition metal stannide crystals are grown from a tin-rich flux, the solidified excess flux can be dissolved with hydrochloric acid, since the stannides are more stable than the flux. Figure 2 shows the experimental results for the preparation of $RhSn_4$ crystals. In the upper part of the Figure a partially dissolved matrix is shown, while one selected crystal is presented at the bottom.

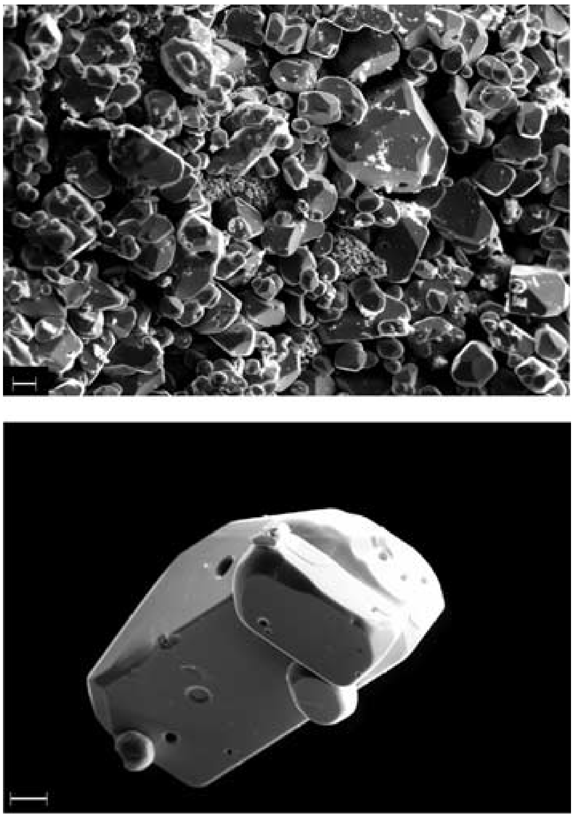

Figure 2. Single crystals of $RhSn_4$ grown in a tin flux. Top: the tin-rich matrix partially dissolved with diluted hydrochloric acid (scale bar 20 µm); bottom: a selected single crystal, with a few much smaller attached crystals (scale bar 10 µm)).

6. Experimental Techniques

To carry out exploratory reactions in a metallic flux, care must be taken to contain the liquid metal and prevent it from reacting with the container or evaporating. Therefore, the procedures and containers vary, depending on the liquid metal. Generally, liquid metals such as aluminum are highly reducing and react quickly with conventional container materials such as silica. Less reactive metals such as Sn, Ga, or In also react with silica if in contact for prolonged times and/or if the temperature is too high. A more attractive container material is alumina (Al_2O_3), which is inert to Al, Sn, or Ga. In this case alumina thimbles are used and are placed inside silica tubes, which are then sealed. Alternatively, for Sn or Ga fluxes graphite thimbles or crucibles can be used. Typically these are left open (i.e. without lid) because of the relatively low volatility of these metals at the temperatures used. Alumina and graphite, however, react with liquid alkali metals, and therefore are unsuitable when these are used as fluxes. In some cases glassy carbon can be used as container material. Most metal fluxes do not react with this rather inert material. For reactions at higher temperatures tubes or crucibles of high-melting metals (Nb, Ta, Mo, W) may be used. Indium flux reactions have often been carried out in ZrO_2 crucibles. An extensive discussion of experimental techniques and procedures has been published by Fisk and Remeika.[42] For experimental details we refer to the original literature.

After the reaction is finished, isolation is either by recovering the solid ingot which contains the products embedded in the flux, or by immersing the entire thimble inside a flux-dissolving solution such as hydrochloric acid or aqueous sodium hydroxide. More exotic combinations can be used to dissolve the metal flux such as organic solvents containing various oxidants such as Br_2, I_2, peroxides. In the case of gallium and tin fluxes, the centrifugation technique has successfully been used for the separation of the crystals from the excess flux.[43–45] In the following sections we summarize recent results categorized by the respective flux medium.

7. The Tin Flux

The chemical and physical databases reveal a huge amount of literature dealing with the development of tin-based low-melting alloys for welding and soldering applications. We do not refer to this literature herein. In the case of tin fluxes we focus only on the preparation of new compounds.

7.1. Binary Phosphides and Polyphosphides

Elemental tin as a flux has already been used by Jolibois[27] to prepare the phosphides NiP_2 and NiP_3 in well-crystallized form. Crystal-structure investigations, carried out much later, showed that these compounds have P–P bonds. Such compounds are called polyphosphides today. Phosphides with high phosphorus content are difficult to synthesize by direct reaction of the elemental components. At relatively low temperatures (e.g. 500 °C), the reactions are too slow, and at higher temperatures polyphosphides tend to decompose into lower phosphides and phosphorus vapor. With the tin-flux technique this difficulty can be overcome as long as the desired polyphosphides are thermodynamically more stable than the corresponding stannides. Thus, phosphides and polyphosphides of the Mn, Fe, and Co group can be prepared this way, while Pd, Pt, and the coinage metals under similar conditions frequently form the corresponding transition-metal stannides (Figure 3) or ternary polyphosphides such as Cu_4SnP_{10}.[46] This limitation can be overcome to some extent by increasing the phosphorus and decreasing the tin content of the sample.

Usually, after such reactions, the tin-rich matrix of the binary or ternary transition-metal phosphides and polyphosphides can be dissolved in hydrochloric acid. The extent to which the acid attacks the phosphides and polyphosphides depends on the reactivity of the transition metal. Thus, for instance, after dissolving their tin-rich matrix, crystals of MoP_2 show rounded-off edges, whereas crystals of ReP_4 appear practically unattacked (Figure 4).

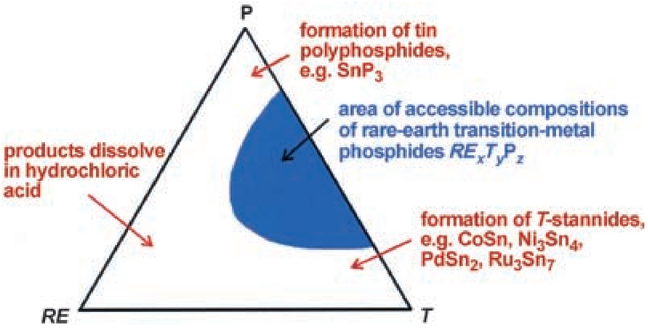

Figure 3. The use of a tin flux to prepare ternary phosphides of the type $RE_xT_yP_z$ (*RE* = rare-earth, *T* = transition-metal) Only phosphides within the blue area of the ternary phase diagram *RE*-*T*-P can be prepared well and isolated. Attempts to prepare samples with compositions which have high contents of phosphorus or with high contents of certain late transition metals may result in binary tin polyphosphides or transition-metal stannides, respectively. Ternary phosphides with a high content of rare-earth elements dissolve in hydrochloric acid and therefore are difficult to isolate from the tin-rich matrix.

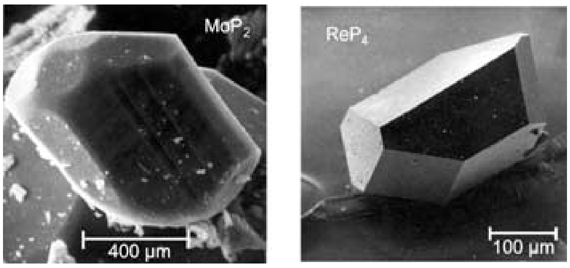

Figure 4. The appearance of the transition-metal polyphosphides MoP_2 and ReP_4 after their tin-rich matrix has been dissolved in diluted hydrochloric acid. Note that the edges of the MoP_2 crystal are rounded, while the crystal of ReP_4 has not been attacked by this acid.

Examples for binary phosphides and polyphosphides prepared in liquid tin are given in Table 1. It should be mentioned that the compounds SiP (sphalerite type),[47] *p*-SiP_2 (pyrite type),[47] CrP_4,[48] MoP_4,[48] and one modification of MnP_4[49]—subsequently called 8-MnP_4[50]—were first thought to be high-pressure compounds, because they could not be obtained by direct reaction of the elemental components at normal pressure. Their preparation by using a tin flux (for references see Table 1) showed that they must be considered as ambient-pressure compounds. In turn, the fact that these compounds could be prepared in the absence of tin, shows that they are not stabilized by small amounts of tin.

The preparation of binary rhenium phosphides and polyphosphides has been studied systematically, both using iodine as a mineralizer (somewhat similar to chemical vapor transport reactions, but over a shorter distance) or in a tin flux. As could have been expected, both preparation techni-

Table 1: Binary phosphides and polyphosphides prepared from a tin flux.

Compound	Sample composition Atomic ratio *M*:P:Sn	Typical preparation conditions[a]	Ref.
SiP	1:1:10	1150 °C → 10 °C h^{-1} → 300 °C	[51]
SiP_2	1:8:12	1000 °C → 10 °C h^{-1} → 300 °C	[52, 53]
CrP_4	1:10:15	1 day, 800 °C → 2 °C h^{-1} → 300 °C	[54]
MoP_2	1:10:6	10 days, 850 °C	[55]
MoP_4	1:10:6	10 days, 550 °C	[55]
α-WP_2	1:10:6	14 days, 750 °C	[55]
β-WP_2	1:10:6	7 days, 950 °C	[55]
2-MnP_4	1:10:20	21 days, 550 °C	[50, 56]
6-MnP_4	1:10:6	14 days, 600 °C	[50, 56]
8-MnP_4	1:10:15	1 day, 800 °C → 2 °C h^{-1} → 100 °C	[54]
Tc_3P	3:1:18	20 days, 950 °C	[57]
Tc_2P_3	1:3:6	20 days, 950 °C	[58]
TcP_3	2:9:12	20 days, 950 °C	[59]
TcP_4	1:10:6	20 days, 950 °C	[57]
Re_2P	2:1:12	7 days, 900 °C → 5 °C h^{-1} → 300 °C	[60]
Re_3P_4	1:1:6	7 days, 800 °C	[60]
Re_6P_{13}	1:4:8	7 days, 800 °C	[60, 61]
Re_2P_5	10:33:57, 8:42:50	7 days, 850 °C; 7 days, 950 °C	[60, 62]
ReP_3	2:9:12	14 days, 750 °C	[59, 60]
ReP_4	1:5:9	7 days, 800 °C	[60, 63]
α-FeP_4	1:5:40, 1:10:40	10 days, 650 °C → 5 °C h^{-1} → 200 °C	[64, 65]
RuP_2	1:2:100	3 days, 1200 °C → 25 °C h^{-1} → 300 °C	[66]
RuP_3	1:5:4	6 h, 1000 °C → 50 °C h^{-1} → 300 °C	[67]
α-RuP_4	1:8:10	7 days, 600 °C	[68, 69]
β-RuP_4	1:10:15	30 days, 700 °C	[68, 69]
α-OsP_4	1:12:20	10 days 700 °C	[68, 69]
β-OsP_4	1:10:40	30 days, 800 °C	[68, 69]
CoP_2	not stated	not stated	[70]
CoP_3	1:8:3	1 day, 450 °C; 7 days, 675 °C	[71]
RhP_3	1:3:80	1 day, 1150 °C → 5 °C h^{-1} → 550 °C	[72]
IrP_2	1:2:100	2 days, 1200 °C → 50 °C h^{-1} → 300 °C	[66]
NiP_2	1:2:40	1 day, 1150 °C → 5 °C h^{-1} → 550 °C	[27, 72]
NiP_3	1:6:7	7 days, 700 °C	[27, 71, 73]
PtP_2	1:15:30	1 day, 1200 °C → 5 °C h^{-1} → 550 °C	[74]
CuP_2	1:2:10	1 day, 1150 °C → 5 °C h^{-1} → 550 °C	[72, 75]

[a] **Caution**: Usually the less reactive modification of red phosphorus is used. Nevertheless, even this modification reacts violently with tin. Thus, care must be taken in heating the reactive mixtures of the elements. Frequently the samples are heated to the desired temperatures at very slow rates, for example, 5 °C h^{-1}. For detailed reaction conditions the original publications should be consulted.

ques yield essentially the same sequence of phases, however, the synthesis in the tin-flux proceeds faster and thermodynamic equilibria were reached at lower temperatures than in the reactions with iodine.[60] The compound Re_2P_5 was obtained only through the tin-flux synthesis. However, neither an energy dispersive X-ray fluorescence analysis, nor the structure determination gave any indication for it being stabilized by tin.[62] Furthermore, the structure of Re_2P_5 can be completely rationalized on the basis of a two-electron model, counting two electrons for each Re–Re, Re–P, and P–P interaction. In agreement with this extremely simple model, the compound shows semiconducting behavior. In contrast, the compound Re_6P_{13} with a very similar composition, prepared the same way by the tin-flux technique, lacks electrons to fill all the bonding states required according to the two-electron bond model. And in agreement with this result, its electrical conductivity is several orders of magnitude higher and has an inverse temperature dependence, thus indicating metallic behavior.[62] This result demonstrates not only the usefulness of the two-electron model for the rationalization of the physical properties of such transition-metal phosphides, but also that only insignificant amounts of tin were incorporated during the tin-flux syntheses of these compounds.

7.2. Ternary Phosphides and Polyphosphides of Rare-Earth and Transition Metals and Related Compositions

A large number of ternary rare-earth (*RE*) transition-metal (*T*) phosphides and polyphosphides were prepared by the tin-flux method. The polyphosphides with "filled" skutterudite type structure were the first to be investigated. They derive their name from the mineral $CoAs_3$ (Co_4As_{12}). Their crystal structure was determined for $LaFe_4P_{12}$. Some twenty phosphides are known to crystallize with this structure type, where iron may be substituted by its homologues ruthenium and osmium.[71,76] They were originally prepared from the elemental components in a tin flux with the atomic ratio $RE{:}T{:}\mathrm{P}{:}\mathrm{Sn} = 1{:}4{:}20{:}50$ in sealed silica tubes by slowly heating (to avoid violent reactions!) to 800 °C, annealing at that temperature for one week, followed by slow cooling (2 °C h^{-1}) to room temperature. After dissolving the tin-rich matrix in moderately diluted hydrochloric acid, crystals with diameters up to 2 mm can be obtained by this method.[77,78] As an example, we show a crystal of $NdFe_4P_{12}$ in Figure 5. In these compounds the *RE* components are usually the early-rare-earth elements from lanthanum to gadolinium. In addition, polyphosphides with the actinoids have also been synthesized from a tin flux: $ThFe_4P_{12}$,[79] $ThRu_4P_{12}$,[79] and UFe_4P_{12}.[80,81] The preparation of such polyphosphides without a tin flux has been successful mainly at high pressure (for references see ref. [82]). One exception is the sodium-containing filled skutterudite type polyphosphide $Na_{1+x}Fe_4P_{12}$ with excess sodium ($x \approx 1$), which has been prepared hydrothermally.[83] Another, very interesting exception is the series of metastable phosphides $Ln\mathrm{Fe_4P_{12}}$, where the *Ln* components are late-rare-earth elements. These were prepared by heating of multilayer precursors at the relatively low temperature of 200 °C.[84] Many of these polyphosphides with $LaFe_4P_{12}$-type structure have interesting physical properties, including superconductivity and heavy fermion behavior. The purity of such samples prepared from a tin flux can be judged from the fact, that the cerium compounds are semiconducting—clearly, all four

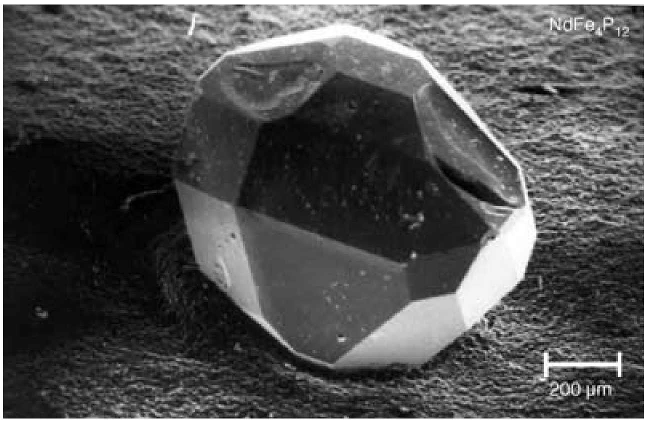

Figure 5. A crystal of $NdFe_4P_{12}$ with the cubic $LaFe_4P_{12}$ type structure grown from a tin flux.

valence electrons of the cerium atoms are involved in one way or the other in chemical bonding—whereas the skutterudite phosphides filled with the typically trivalent rare-earth elements are metallic conductors. The isostructural antimonides (RET_4Sb_{12}) have outstanding thermoelectric properties. Thus, the filled skutterudites have been studied by many research groups, details about their preparation can be found through the review articles.[82,85]

The ternary "filled" skutterudites RET_4P_{12} usually contain iron and its homologues ruthenium and osmium as the transition-metal components. When cobalt or its congeners rhodium and iridium are used as transition metals, the ternary compounds are nonstoichiometric with large defects at the RE positions, for example, $La_{0.2}Co_4P_{12}$ and $Ce_{0.25}Co_4P_{12}$.[86] With nickel as the transition metal the cubic compounds $Ln_6Ni_6P_{17}$ with $Ln =$ La, Ce, Pr are obtained. These form by reactions of the elemental components in tin fluxes of greatly varying compositions. For example $La_6Ni_6P_{17}$ could be isolated from samples with the atomic ratios La:Ni:P:Sn = 1:1:8:20 and 3:1:6:10.[87] With analogous reaction conditions, using palladium as the transition-metal component, the low-temperature modification of the binary palladium stannide $PdSn_2$ is obtained (Figure 3), although the intended palladium compounds $La_6Pd_6P_{17}$ and $Ce_6Ni_6P_{17}$ could be prepared in microcrystalline form by direct reaction of the elemental components.[88]

Another large series of ternary phosphides frequently prepared by the tin-flux method have the composition AT_2P_2, where A is a lanthanoid or actinoid and T a late transition metal. Most of these phosphides crystallize with a body-centered tetragonal structure, variously called $BaAl_4$- and $ThCr_2Si_2$-type structures after the first binary or ternary representatives, respectively. From a crystallographic point of view, this structure type is interesting, because it is the one with the highest number of representatives, some 800. While the many silicides with this structure are usually prepared by direct reaction of the elemental components, the phosphides are best obtained by the tin-flux route, although most of these compounds have also been prepared in the absence of tin. Most phosphides of the three series AFe_2P_2, ACo_2P_2, and ANi_2P_2 (where A is practically all of the lanthanoids, including cerium, europium, and ytterbium which frequently show mixed-valent behavior in these compounds) have first been prepared from idealized starting compositions A:T:P:Sn varying between 1:2:2:3 and 1:2:2:25.[89,90a,b,91] Later, when the physical properties of these phosphides were investigated, it became important to prepare samples with higher purity and the starting compositions of the melts were optimized by trial and error. Thus, for instance the series of the nickel containing compounds ANi_2P_2 ($A =$ Ca, La–Yb) were prepared with higher purity and yield from melts with the compositions A:Ni:P:Sn = 1.3:2:2.3:16.[92] Similar compositions have been used for the preparation of iron- and cobalt-containing phosphides with this structure.[93] Usually the mixtures of the elemental components are slowly heated (e.g. at a rate of 4 °C h^{-1}) to a temperature of between 850 and 950 °C, held at that temperature for one week, then quenched or slowly cooled to room temperature. After dissolving the tin-rich matrices, single crystals with edge lengths of up to 2 mm have been obtained from such fluxes (Figure 6).[94,95] Energy dispersive X-ray fluorescence analyses in scanning electron microscopes usually do not reveal any impurities such as tin or silicon (from the silica tubes) unless the reaction temperatures have been extremely high. However, heterogeneous inclusions of elemental tin have been observed in many cases, as concluded from the signals observed by difference scanning calorimetry at 232 °C, the melting point of tin.[96]

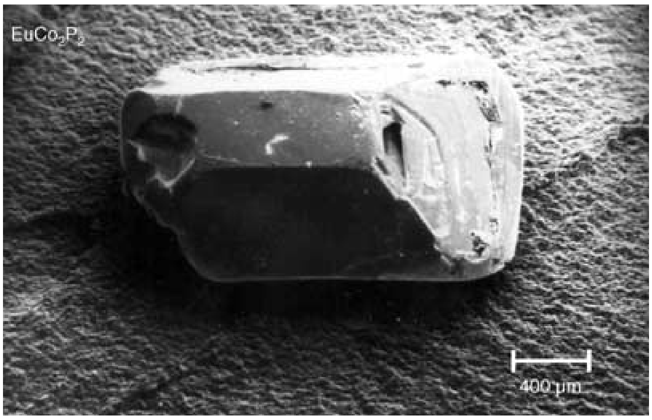

Figure 6. A 1.44 mm^3 single crystal of $EuCo_2P_2$ with the tetragonal $ThCr_2Si_2$ type structure grown from a tin flux.[95]

The phosphides with $ThCr_2Si_2$-type structure are known to crystallize with two different variants of this tetragonal structure with very different ratios of the unit cell dimensions c/a e.g., $EuCo_2P_2$ with $c/a = 3.01$ and $EuNi_2P_2$ with $c/a = 2.41$.[90] When the physical properties of these compounds became of interest, it was attempted to prepare samples of solid solutions between compounds with drastically different c/a ratios. Thus, the solid solutions $Ca_{1-x}Sr_xCo_2P_2$,[97] $LaCo_{2-x}Ni_xP_2$,[97] $LaFe_{2-x}Ni_xP_2$,[97] and $EuCo_{2-x}Ni_xP_2$[98] were investigated. More or less continuous changes in the c/a ratios were observed for $Ca_{1-x}Sr_xCo_2P_2$ between $x = 0.25$ and $x = 0.50$, for $LaCo_{2-x}Ni_xP_2$ between $x = 0.5$ and $x = 1.5$, and for $LaFe_{2-x}Ni_xP_2$ between $x = 1.0$ and $x = 2.0$. These samples were prepared by slowly heating powders in the ratio A-

(Ca,Sr,La):T(Fe,Co,Ni):P:Sn = 1.1:2:2:20 at a rate of 40 °C h^{-1} to 880 °C and annealing at that temperature for 10 days. In contrast, a discontinuous change of the c/a ratio was observed for $x = 1.0$ in the pseudobinary system $EuCo_{2-x}Ni_xP_2$. The samples for this latter investigation were prepared by mixing powders of the end-members $EuCo_2P_2$ and $EuNi_2P_2$, and annealing these mixtures for two weeks at 910 °C in the presence of a relatively small amount of tin (29 mol %). This reaction was termed activated solid-state synthesis.[98]

With ruthenium as the transition-metal component the series ARu_2P_2 (A = Ca, Sr, La–Yb) with $ThCr_2Si_2$-type structure have been prepared from tin fluxes with atomic starting ratios varying between A:Ru:P:Sn = 1:2:2:5, 1:2:2:20, and 3:2:2:15. Of these products, $LaRu_2P_2$ becomes superconducting with a critical temperature of $T_c = 4.1$ K.[99] The compound $BaRu_2P_2$ has not been obtained this way, although it could be prepared by direct reaction of the elemental components.[100] Similarly, the palladium-containing phosphides of the series APd_2P_2 (A = Ca, Sr, Y, La–Er, Yb) with $ThCr_2Si_2$-type structure were obtained only by reaction of the elements.[88] The ternary actinoid phosphides $AnCo_2P_2$ (An = Th and U) crystallize with a primitive tetragonal $CaBe_2Ge_2$-type structure, which is closely related to the body-centered tetragonal structure of $ThCr_2Si_2$. These phosphides were also prepared from a tin flux using atomic ratios close to An:Co:P:Sn = 1:2:2:25.[90b,93b,93d] An entirely different orthorhombic structure, closely related to those of $BaZn_2As_2$ and $BaCu_2S_2$, was found for the phosphides $ThRu_2P_2$ and URu_2P_2. For the preparation of these phosphides with a tin flux, the binary phosphide RuP and a prereacted heterogeneous binary alloy of the overall composition "$U_{1.3}Ru_2$" were used with the starting ratios for both Th:RuP:Sn and $U_{1.3}Ru_2$:P:Sn of 1:2:10.[101a] Two modifications of $ThNi_2P_2$ with $BaCu_2S_2$-type and $CaBe_2Ge_2$-type structures, were prepared in a tin flux by annealing at 850 and 1000 °C, respectively, both with the same starting composition Th:Ni:P:Sn = 8:13:13:66.[101b] The manganese-containing compounds $EuMn_2Pn_2$ (Pn = P, As, Sb) have a simple hexagonal structure first determined for Ce_2O_2S and $CaAl_2Si_2$.[102a] For the physical characterization of the phosphide $EuMn_2P_2$ the crystal growth of this compound from a tin flux was optimized. Relatively large crystals with diameters up to 2 mm were obtained from a melt in the atomic ratio Eu:Mn:P:Sn = 14:4:11:265 (≈90 atom % Sn). After slow heating, the sample was annealed at 1050 °C for 6 h, slow-cooled at 3 °C h^{-1} to 700 °C, and centrifuged at that temperature through silica wool into another vessel.[102b]

The uranium nickel phosphides UNi_3P_2,[103] $U_6Ni_{20}P_{13}$,[103] $U_2Ni_{12}P_7$,[103] and $U_3Ni_{3.34}P_6$[104] were prepared by reacting the elemental components in a tin flux with a tin content of 67 and 59 atom %, respectively. Two modifications of UCr_6P_4 were obtained by reactions of the binary uranium phosphide UP_2, phosphorus, and chromium in a tin flux of 70 atom %.[105]

A large family of closely related ternary rare-earth transition-metal phosphides has been found for compositions with a metal:phosphorus ratio of exactly or very close to 2:1. Most of the iron- and cobalt-containing compounds have been obtained in well-crystallized form with tin as a flux, while many of the corresponding nickel compounds were prepared in the absence of tin.[106] Nevertheless, the phosphides of the three series $RE_2Fe_{12}P_7$, $RE_2Co_{12}P_7$, and $RE_2Ni_{12}P_7$, were all prepared first using a tin flux with tin contents of between 70 and 80 atom % for the iron and cobalt containing compounds,[107] and between 25 and 35 atom % for the nickel compounds (note that the amount of tin flux tolerated for the nickel compounds is much lower, see Figure 3).[108] Needle-shaped crystals of $Tm_2Ni_{12}P_7$ with lengths of up to 2 cm were obtained by this preparation method.[109] The corresponding uranium compounds $U_2T_{12}P_7$ (T = Fe, Co, Ni) were also obtained this way.[110] Other compounds belonging to this structural family which were prepared by the tin flux technique include the two isotypic phosphides $LaNi_5P_3$ (La:Ni:P:Sn = 5:45:25:25)[91] and $EuNi_5P_3$ (Eu:Ni:P:Sn = 1:2:2:20),[111] the two isotypic series $RECo_5P_3$[112,113] and $REFe_5P_3$[107b] crystallizing with a different structure type, and the three isotypic phosphides $LaCo_8P_5$,[114,115] $PrCo_8P_5$,[115] and $EuCo_8P_5$.[115] In the case of the latter compounds the annealing was for 7 days at 880 °C, followed by controlled cooling (10 °C min^{-1}) to 600 °C and quenching. Crystals of the europium compound of up to 3 mm length and with diameters up to 1 mm were obtained this way. The barium nickel phosphide $BaNi_9P_5$ has also been prepared from a tin flux by slowly heating the components to 850 °C, and subsequent slow cooling at a rate of 2 °C h^{-1}. This resulted in equidimensional crystals with diameters of up to 3 mm.[116] The three series of phosphides $RECo_3P_2$,[113,117] $RE_5Co_{19}P_{12}$,[113,118] and $RE_6Co_{30}P_{19}$[119] were also prepared by the tin-flux technique, and they also belong to this large family of ternary structures with a metal/metalloid ratio of exactly or nearly 2:1. In this family the metalloid components are mainly silicon, phosphorus, and their homologues.[120]

The system scandium–cobalt–phosphorus contains the phosphides ScCoP, $ScCo_5P_3$, $Sc_2Co_{12}P_7$, and $Sc_5Co_{19}P_{12}$. They were all prepared using a tin flux of 80 atom %.[118] For the other ternary rare-earth–cobalt–phosphorus systems the phase equilibria, as far as they are accessible with a 75 atom % tin flux, have been investigated systematically for the sections at 850 °C. The samples were annealed for about two weeks, followed by quenching in air. Generally, between three and eight ternary phases were found in this way.[121] A remarkable result of this investigation is the fact that the sample composition required for the syntheses of certain isotypic phosphides, changes systematically with the rare-earth components. This situation is demonstrated in Figure 7 for three pairs of isotypic samarium and thulium phosphides with the three structure types first established for $Zr_2Fe_{12}P_7$,[122] YCo_5P_3,[112] and $HoCo_3P_2$.[117] It can be seen that higher phosphorus contents of the samples are needed for the synthesis of the thulium compounds than for the corresponding samarium compounds.

Ternary rare-earth and actinoid transition-metal phosphides prepared by the tin-flux technique with iron and nickel as the transition-metal components include the compounds $ScFe_4P_2$[123] and $ThFe_4P_2$,[124] which crystallize with two different structure types, $Th_5Fe_{19}P_{12}$[124] and isotypic $Yb_5Ni_{19}P_{12}$,[125] $ThFe_5P_3$,[126] $La_2Fe_{25}P_{12}$,[127] $Th_{11}Ni_{25}P_{20}$ and isotypic $U_{11}Ni_{25}P_{20}$,[128] $Yb_9Ni_{26}P_{12}$,[129] and $YbNi_5P_3$.[129] With chromium as the transition-metal component the compounds UCr_5P_3,[130] $A_2Cr_{30}P_{19}$ (A = U and Zr),[131,132] and $Zr_6Cr_{60}P_{39}$[133]

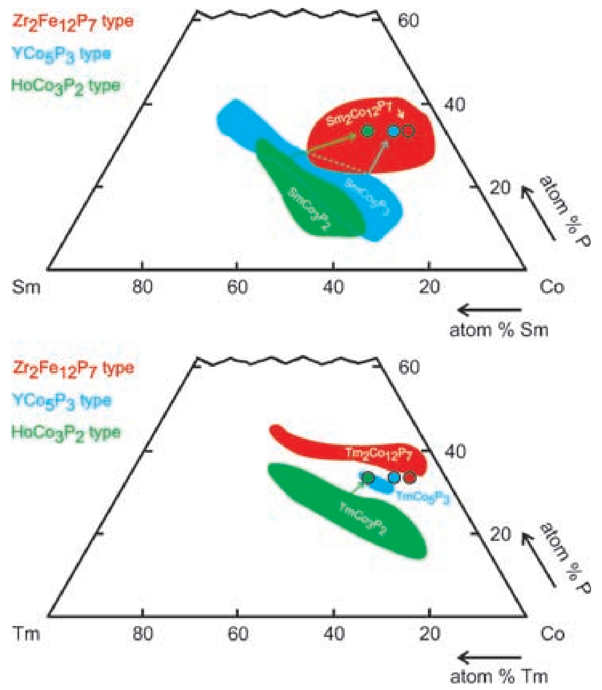

Figure 7. Sample compositions for the preparation of ternary Sm (top) and Tm (bottom) cobalt phosphides from a tin flux. All samples were prepared with 75 atom% tin as a flux. The diagrams indicate the ratio of the remaining 25% of the elements samarium, thulium, cobalt, and phosphorus. The phase diagrams contain several ternary phosphide phases. Only the sample compositions resulting in ternary phosphides with $Zr_2Fe_{12}P_7$-type,[107a] YCo_5P_3-type,[112] and $HoCo_3P_2$-type[117a] structures are shown. The compositions of the ternary phosphides are indicated by large colored dots. All samples were equilibrated for two weeks at 850 °C and the tin-rich matrix was dissolved in diluted hydrochloric acid.[117b]

were prepared in well-crystallized form from a tin flux. For the syntheses of corresponding molybdenum compounds (e.g. $U_2Mo_{30}P_{19}$[131] and $U_6Mo_{60}P_{39}$[134]), however, arc-melting of prereacted pellets of the elemental components turned out to be more successful.

7.3. Ternary Transition-Metal Polyphosphides

Generally, the use of a tin flux for the preparation of phosphides containing two different kinds of transition metals has been explored less systematically than the investigations for the syntheses of ternary phosphides containing lanthanoids or actinoids as one metal component and a transition-metal element as the other. Ternary phosphides with a relatively high metal content of two different transition-metal elements can be prepared well by arc melting of the prereacted components. Only some polyphosphides, which are difficult to prepare otherwise (e.g. at high pressure), have been synthesized with a tin flux. The first examples seem to have been the isotypic diamagnetic semimetals $MoFe_2P_{12}$ and WFe_2P_{12}. For their preparation the elemental components were allowed to react in the atomic ratio Mo(W):Fe:P:Sn = 1:2:12:20. The annealing was at 970 K, with subsequent quenching in air. Annealing at lower or higher temperatures (870 and 1170 K) resulted in the binary polyphosphides MoP_2 and α-FeP_4 or MoP_2 and FeP_2, respectively.[135] The metallic conductor $TiMn_2P_{12}$ has a different structure. It could be prepared from the elemental components in the presence of iodine. For its preparation with a tin flux only a relatively small amount of tin was used: Ti:Mn:P:Sn = 1:2:30:20.[136] With similar atomic ratios the $TiMn_2P_{12}$-type compounds $NbMn_2P_{12}$ (5:2:10:17), $MoMn_2P_{12}$ (1:2:30:20), and WMn_2P_{12} (1:2:15:20) were prepared from a tin flux.[137] For the syntheses of the polyphosphides $MoNiP_8$ and $WNiP_8$ the elements were allowed to react in the ratio Mo(W):Ni:P:Sn = 1:1:40:50.[138]

The preparation of the compound Ti_2NiP_5 by reaction of the elemental components in a tin flux failed. However, this compound could be prepared by using powders of the binary alloy of the composition TiNi in a tin flux with the ratio TiNi:P:Sn = 1:20:25. After slow heating (it is important to remember the violent reactivity of phosphorus) the annealing was for one month at 650 °C.[139] Apparently, when the metals Ti and Ni are used instead of the binary alloy TiNi, the binary phosphides of the transition metals are formed first. And at 650 °C these react too slowly to produce the intended ternary phosphide. Similarly, powders of the binary alloys were used for the preparation of the ternary polyphosphides VNi_4P_{16}, $NbNi_4P_{16}$, and WNi_4P_{16}.[140] Three stacking variants of the binary manganese polyphosphide MnP_4 are known: 2-MnP_4,[56] 6-MnP_4,[50] and 8-MnP_4.[49] The missing stacking variant 4-MnP_4 could only be prepared in form of a solid solution with chromium: $Cr_{1-x}Mn_xP_4$ with x having values between 0.3 and 0.7. Again, for the preparation of these samples in a tin flux powders of binary Cr/Mn alloys were used.[141]

Many of the compounds listed in Table 1 are polyphosphides of the late transition metals. With copper as the transition-metal component, only CuP_2 could be prepared from a tin flux, although with Cu_2P_7 a polyphosphide with a still higher phosphorus content has been obtained in well crystallized form using iodine as a mineralizer.[142] Apparently, the presence of tin reduces the chemical activity of phosphorus to the extent that the higher polyphosphides cannot be prepared (Figure 3) and the ternary compound Cu_4SnP_{10} is formed instead.[46,142] Similarly, no silver phosphide could be obtained from a tin flux, although the compounds AgP_2[142] and Ag_3P_{11}[143] could be prepared in the presence of iodine. With the subsequent elements gold, zinc, cadmium, and mercury the presence of tin prevents the formation of binary phosphides and the ternary compounds $M SnP_{14}$ (M = Zn, Cd, Hg) and $Au_{1-x}Sn_{1+x}P_{14}$ are obtained.[144,145] Also, apparently, in trying to optimize the preparation conditions for the binary nickel polyphosphide NiP_3[27,71,73] from a tin flux, the ternary compounds Ni_2SnP[146] and $Ni_{1.17}Sn_{0.69}P_{0.31}$[147] were obtained using atomic ratios Ni:Sn:P of 2:6:1 and 4:40:1, respectively, at well defined temperatures.

7.4. Borides, Silicides, and Further Pnictides from Liquid Tin

The excellent wettability of tin enables the preparation of a large variety of compounds. Besides the numerous phosphides reported in the previous sections, also some boron-rich solids such as YB_{25}[148] or the silicide boride $Er_8Si_{17}B_3$[149] have been synthesized in liquid tin. Binary silicides can be obtained in various metal fluxes. As discussed in Section 13, liquid copper has widely been used for the growth of such silicide crystals, but compounds such as V_3Si, V_5Si_3, VSi_2,[150] Mn_5Si_3, MnSi, or $Mn_{27}Si_{47}$[151] are also accessible from liquid tin.

In the case of ternaries, many compounds with two different main-group elements in ordered two- or three-dimensional networks have been synthesized. Single crystals of EuSnP[152] and Nb_5Sn_2Ga[153] can be obtained by the tin self-flux technique. The growth of larger crystals enables direction-dependent investigations of the physical properties. A larger family of compounds was observed for the silicon phosphides such as $ZnSiP_2$,[154] $Sn_{4.2}Si_9P_{16}$,[155] $T Si_4P_4$ (T = Fe, Ru, Os),[156] $RE Si_2P_6$ (RE = La, Ce, Pr, Nd),[157] $T Si_3P_3$ (T = Rh, Ir),[158] $PtSi_3P_2$, and $PtSi_2P_2$.[159] Owing to the similar X-ray scattering power, the correct determination of the silicon and phosphorus sites is the main problem for this interesting class of compounds. Also some of the quaternary phosphide oxides of the series REFePO, RERuPO, and RECoPO,[160] and $Th_4Fe_{17}P_{10}O_{1-x}$[126] were first obtained from tin fluxes. Later most of these materials were been synthesized in NaCl/KCl salt fluxes. Some more recent developments are referred to in a paper on $Pr_3Cu_4P_4O_{2-x}$.[161]

Liquid tin is also a suitable flux for the higher homologues arsenic and antimony. For example, the ternary arsenide $Ba_{0.8}Hf_{12}As_{17.7}$ was synthesized in a tin flux at 950 °C.[162] With antimony, several ternary alkaline-earth, rare-earth metal, or uranium-containing compounds such as RE_3TiSb_5 (RE = La, Ce, Pr, Nd, Sm),[163] La_3ZrSb_5, La_3HfSb_5, $LaCrSb_3$,[164] $Sr_{21}Mn_4Sb_{18}$,[165] $Eu_{10}Mn_6Sb_{13}$,[166] or U_3TiSb_5 and U_3MnSb_5[167] have been obtained in well crystallized form. For instance, the latter two antimonides were obtained with the atomic starting ratios U:Ti:Sb:Sn = 1:3:2:6 and U:Mn:Sb:Sn = 1:3:2:9 in alumina crucibles. The temperature was allowed to oscillate between 600 and 700 °C for one week. After quenching, the tin matrix was dissolved in diluted hydrochloric acid, which attacked the needle-shaped hexagonal crystals of U_3TiSb_5 and U_3MnSb_5 at a much slower rate. The fact that these antimonides were also prepared without the tin flux—albeit in microcrystalline form—shows that they are not stabilized by small amounts of tin. Containing two main-group elements, the Zintl phases $Ba_2Sn_3Sb_6$,[168] $EuSn_3Sb_4$,[169] $Ba_3Sn_4As_6$,[170] and $SrSn_3Sb_4$[171] are accessible by a tin flux.

7.5. Binary and Ternary Stannides

As already discussed for some of the Zintl phases in Section 7.4, liquid tin is often used as a self-flux. As examples, we have already mentioned above the growth of the binary cobalt stannides CoSn, $CoSn_2$, and $CoSn_3$ by peritectic reactions.[41] This preparation technique has widely been used also for binary stannides of the early transition metals such as Ti_2Sn_3,[172,173] VSn_2,[174] or $MoSn_2$.[175] Stannides with even higher tin contents are formed with the noble metals. Recent examples are Os_4Sn_{17},[176] Os_3Sn_7,[177] $RhSn_3$,[177] $RhSn_4$,[177] Ir_3Sn_7,[178] and two modifications of $IrSn_4$.[177,179] Furthermore, a variety of mixed transition-metal stannides have been prepared, for example AuMnSn[180] or $Co_{1-x}Ni_xSn_2$ ($0.23 < x < 0.59$).[181]

The largest families of stannides that can be prepared from liquid tin are alkaline-earth or rare-earth transition-metal stannides. A good overview on the manifold phase relationships and the crystal chemistry of these intermetallics has been given by Skolozdra.[182] Three recent examples for crystal growth are the stannides $RE Mn_6Sn_6$ (RE = Tb, Ho, Er, Tm, Lu),[183] ScPtSn,[184] and $La_{4.87}Ni_{12}Sn_{24}$.[185]

8. The Lead Flux

Tin is a well known flux medium for the growth of single crystals of metal-rich phosphides and arsenides with a metal:phosphorus (arsenic) ratio close to 2:1. In some cases better crystal-growth results have been obtained using a lead flux rather than tin, especially for compounds with the platinum metals, which form very stable stannides, as already pointed out above. Recent examples for products from such reactions are $Ca_2Ir_{12}P_7$, $Ca_5T_{19}P_{12}$ (T = Rh, Ir), or $Eu_6Rh_{30}As_{19}$,[186] $AE Ir_2P_2$ (AE = Ca, Sr, Ba),[187] $Sr_2Rh_7P_6$,[188] and $MgRh_6P_4$.[189] The elements can be treated with an excess of lead at 1100 °C in an alumina crucible that is sealed in a silica ampoule. A typical starting composition is approximately 60 equivalents of lead for one formula unit of the desired compound. A large advantage for crystal growth in the lead flux in these cases is the reduction of the reaction time. The conventional synthesis often requires repeated regrinding and annealing of the reaction components. The dissolution of the flux with hydrochloric acid is less suitable because lead chloride is only significantly soluble in hot water. In this case an elegant way to dissolve the flux is to use a mixture of concentrated acetic acid and H_2O_2 (30 %).

A lead flux was already used by Hittorf in 1865 for the recrystallization of elemental phosphorus. Some 50 years ago Krebs and co-workers reproduced these experiments.[190] They also used metallic fluxes, mostly lead, for the growth of polyphosphides with high phosphorus content, for example, CdP_4[191] and the compounds $M PbP_{14}$ (M = Zn, Cd, Hg).[192] Various other polyphosphides with $HgPbP_{14}$ type structure have been described later.[144,145] The polyphosphide Au_2PbP_2[193] was grown from a starting composition Au:Pb:P = 1:3:1. The sample was first heated to 400 °C within 20 min, held at that temperature for 16 h, heated to 800 °C at a rate of 5 °C h^{-1}, kept at that temperature for 100 h, and subsequently furnace-cooled.

Excellent crystals of the silicides $RE Mn_2Si_2$ (RE = Y, Tb–Lu) have been grown from molten lead under an argon atmosphere, Figure 8.[194,195] The rare-earth elements were mixed with manganese and lead in the ideal 1:2:2 atomic ratio and lead was added to these mixtures at a ratio of 3.8:1 in weight. This mixture was placed in a crucible of high-purity hexagonal boron nitride, annealed under argon at 1350 °C for 5 h, cooled to 800 °C at a rate of 50 °C h^{-1}, and finally quenched to room temperature. The excess lead had been dissolved in hydrogen peroxide and diluted acetic acid.

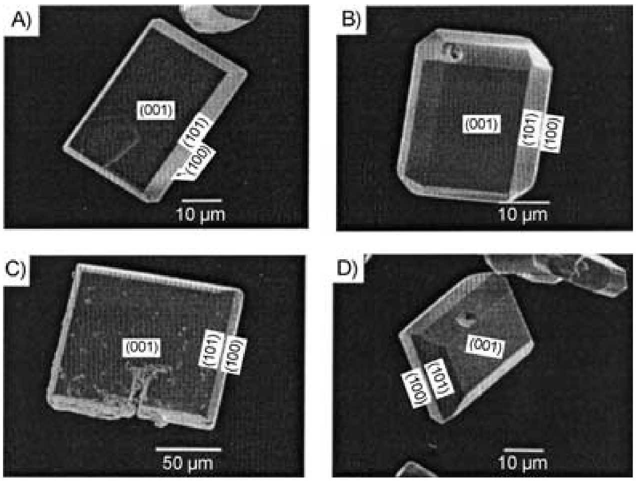

Figure 8. Scanning electron micrographs of $ErMn_2Si_2$ (A), $TmMn_2Si_2$ (B), $YbMn_2Si_2$ (C), and $LuMn_2Si_2$ (D) grown from a lead flux. From Okada et al.[195]

Lead fluxes have not had the type of extensive use in the syntheses of intermetallics as other fluxes described herein. In the examples cited, the reactions were run at rather high temperatures, many hundred degrees above lead's melting point, possibly because the solubility in lead of most elements is lower than that in tin. Nevertheless, it would be worthwhile to explore reactions in molten lead at lower temperatures as well, using longer annealing times.

9. Liquid Aluminum as a Flux

Aluminum melts at 660 °C and dissolves a large number of elements as can readily be seen from the extensive binary phase diagram information available in the literature.[40] Furthermore, it dissolves readily in non-oxidizing acids, for example, in hydrochloric acid. This property makes aluminum potentially a great flux system in which reactions can be carried out and indeed its utility as such has been demonstrated in the last few decades. A large variety of intermetallic aluminides have been prepared from liquid aluminum, many featuring fascinating new structures, and many being key components in advanced aluminum alloys.

9.1. Borides from an Aluminum Flux

Aluminum has been shown to be a useful flux in the synthesis of metal borides and ternary metal aluminides. Primarily Japanese, Swedish, and Russian groups have been active in boride synthesis using molten aluminum.[196] Some of the compounds reported include V_2B_3,[197a] Cr_3B_4, Cr_2B_3, and CrB_2,[197b] Ta_5B_6,[198a] Ta_3B_4, and TaB_2,[198b] LaB_6,[199a] LuB_4, $LuAlB_4$, and Lu_2AlB_6.[199b] Single crystals of TmB_4 and $TmAlB_{14}$ were obtained by the high-temperature aluminum-solution method using thulium powder and crystalline boron powder as starting materials. The optimum conditions required a temperature of 1500–1600 °C.[200] Crystals of the icosahedral B_{12} compounds $AlLiB_{14}$ and $AlMgB_{14}$[201] were grown from high-temperature aluminum solutions.

Also ternary transition-metal-containing borides can be prepared from liquid aluminum. MoAlB[202] and Fe_2AlB_2[203] were obtained from samples with starting compositions 1:6:1 and 35:35:30, respectively, were aluminum is used as a self-flux. These borides are stable in concentrated hydrochloric acid.

9.2. Binary and Ternary Aluminides

As is evident from the binary transition-metal–aluminum phase diagrams,[40] the aluminum self-flux technique is very useful for the preparation of binary aluminum-rich transition-metal aluminides. Some recent examples include Co_4Al_{13},[204] Re_4Al_{11}, $ReAl_6$,[205] $ReAl_{2.63}$,[206] and $IrAl_{2.75}$.[207]

Numerous ternary rare-earth– and actinoid–transition-metal aluminides have been prepared in recent years using an excess of aluminum as a reactive flux.[208a–o] Many of these have interesting magnetic properties.[208p–v] They crystallize with some ten different structure types sometimes in strange stoichiometries. For example, some 80 compounds have the compositions $A_6T_4Al_{43}$ (A = Y, La–Lu (with the exception of Eu), Th, and U; T = Ti, V, Nb, Ta, Cr, Mo, W, and Mn)[208a,b,r] and crystallize with a hexagonal structure which was determined for $Ho_6Mo_4Al_{43}$.[208a] The compounds of the series $RERe_2Al_{10}$ crystallize with four different structure types,[208i,k,n] one of which was determined some 20 years ago for $CaCr_2Al_{10}$.[209a] Some 20 isotypic aluminides have the general formula $RE_{7+x}T_{12}Al_{61+y}$ (T = Os and Re), where it could be shown for the rhenium compounds that their composition varies systematically between $Gd_{7.23}Re_{12}Al_{61.70}$ and $Lu_{7.61}Re_{12}Al_{61.02}$ depending on the size of the rare-earth atoms.[208d,n,p] Many representatives have been found for the compositions $A_2T_3Al_9$ (A = Lanthanoids and Actinoids, T = Co, Rh, Ir, and Pd),[208v] crystallizing with a structure first determined for $Y_2Co_3Ga_9$.[209b] Reactions in the systems RE–Au–excess Al (atomic ratio 1:1:10) produced low yields of $REAu_3Al_7$ with more prevalent products being $REAuAl_3$, and binary aluminides such as $REAl_3$. Increasing the amount of gold in the reaction (using a reactant ratio of 1:2:15) increased the yield of $REAu_3Al_7$.[210] Further preparation conditions of ternary aluminides grown from melts with an excess of aluminum can be found in the literature.[208]

9.3. Quaternary Compounds

The phase diagram of the binary system Al–Si shows that these elements form a eutectic system with a eutectic point at 577 °C and 12.2 mol % Si.[40] Aluminum melts dissolve some silicon, but they do not form any binary compounds. This situation is supported by the fact that silicon crystals are frequently found as by-products of reactions aimed at the synthesis and crystal growth of silicides. With rapid silicon diffusion in the melt, comes increased reactivity with the other metals which initiates phase formation. Most elements are to a certain extent soluble in aluminum and, in this sense, the flux reaction is not different from any conventional solvent.

There are few rare-earth aluminum silicides reported.[211] Most of them were synthesized as powders and their crystal structures have not been determined or refined. For Ho, Er, and Tm, only RE_6Al_3Si (RE = Ho, Tm)[212] and Er_4AlSi_3[213] have been reported.

In the late 1990s the first deliberate attempt was made to produce silicon intermetallics by reacting rare-earth elements with silicon in excess aluminum. Crystals of various metal–aluminum silicides grow easily in an aluminum melt below 900 °C, and a large number of such silicides has been identified. These reactions proceed rapidly; examples are the series $RE_2Al_3Si_2$ (RE = Ho, Er, Dy, Tm)[214] as well as the quaternary aluminum silicide $Sm_2Ni(Ni_xSi_{1-x})Al_4Si_6$. Crystals as long as 4 mm form readily in the aluminum flux. A crystal of $Ho_2Al_3Si_2$ grown in this fashion is shown in Figure 9. These compounds form with the late lanthanoids whereas the reactions with the mid and early lanthanoids, such as La, Ce, Nd, Sm, give REAlSi, and La, Sm, Tb, Yb give $REAl_2Si_2$. Neither of these two types of compounds has been found for Ho, Er, and Tm to date. Instead, the $RE_2Al_3Si_2$[214] and $REAl_{3-x}Si_x$[215,216] series seems to be favored. There are several old reports that claimed the production of binary silicides, such as $RESi_2$, $ThSi_2$, $MoSi_2$, and WSi_2 in molten aluminum. However, we find that most of these are in fact ternary metal aluminum silicides (e.g. REAlSi) rather than binary metal silicides.

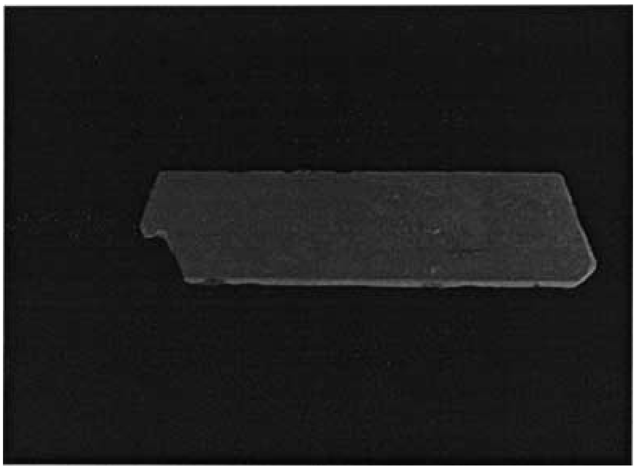

Figure 9. Scanning electron micrograph of a crystal of $Ho_2Al_3Si_2$ (length 0.5 mm).

The reaction of Sm, Ni, and Si in molten aluminum proceeds at approximately 750 °C to yield well-formed crystals of $Sm_2Ni(Ni_xSi_{1-x})Al_4Si_6$.[217] To obtain a single-phase product, it is necessary to use stoichiometric amounts of Sm, Ni, and Si with excess aluminum metal. To isolate the compound the excess aluminum metal was dissolved with NaOH (aq) because $Sm_2Ni(Ni_xSi_{1-x})Al_4Si_6$ ($x = 0.18$–0.27) decomposes in dilute hydrochloric acid and therefore its isolation in strong basic solution was important for its discovery.

The isostructural compounds $Dy_2Ni(Ni_xSi_{1-x})Al_4Si_6$, $Gd_2Ni(Ni_xSi_{1-x})Al_4Si_6$, and $Sm_{2-y}Y_yNi(Ni_xSi_{1-x})Al_4Si_6$ also form from an aluminum flux.[218] An intriguing observation in the structures of these compounds is the presence of certain crystallographic sites with mixed Ni/Si occupancy. Such mixed Ni/Si and Ni/Ge occupancies are often observed in RE/Ni/Si and RE/Ni/Ge phases. The really interesting part about these results is the complex stoichiometries of these compounds, which are unlikely to be discovered rationally by mixing these elements in direct-combination reactions. They are too difficult to guess. The flux chemistry leads to the most feasible result under the prevailing conditions of reactant ratio and concentration. In other words, it “finds” the accessible compositions regardless of complexity and this underscores the great potential of molten metals as reaction media for accessing novel multinary phases.

Many other RE/T/Al/Si phases were discovered in aluminum flux. An intriguing new compound is $Sm_5(Cu_{4.26}Si_{3.74})Al_8Si_2$,[218] which has a three-dimensional Cu/Al/Si framework with infinite zigzag silicon chains and crystallographic sites with extensive Cu/Si mixed occupancy, similar to the Si/Ni disorder described above. The zigzag silicon chains do not contain copper.

Additional examples include $RE_2NiAl_4Ge_2$,[219] $RENiAl_4Ge_2$, $RE_{1-x}T_2Al_{5-y}Si_y$, $RE_{2-x}T_2Al_4Tt_2(Al_{1-y}Tt_y)(Al_{1-z}Tt_z)_2$, ($RE$ = rare earth element; T = Ni, Co; Tt = Si, Ge)[220] $RE_4Fe_{2+x}Al_{7-x}Si_8$, and $REFe_4Al_9Si_6$. Along with the new structure types of these compounds, several isostructural analogues, such as $RENiAl_4(Si_{2-x}Ni_x)$ and $RENiAl_{6-x}Ge_{4-y}$, have also been synthesized. Explorations with 4d and 5d transition metals revealed intriguingly complex phases such as $Th_2[AuAl_2]_n(Au_xSi_{1-x})Si_2$,[221a] $Gd_{1.33}Pt_3Al_7Si$,[221b] and the series of the cubic compounds $RE_8Ru_{12}Al_{49}Si_9(Al_xSi_{12-x})$.[222] The latter feature unique $(Al/Si)_{12}$ cuboctahedral clusters. Figure 10 show several typical crystals of various compounds grown in liquid aluminum. Table 2 summarizes some of the ternary and quaternary compounds synthesized or discovered in aluminum flux.

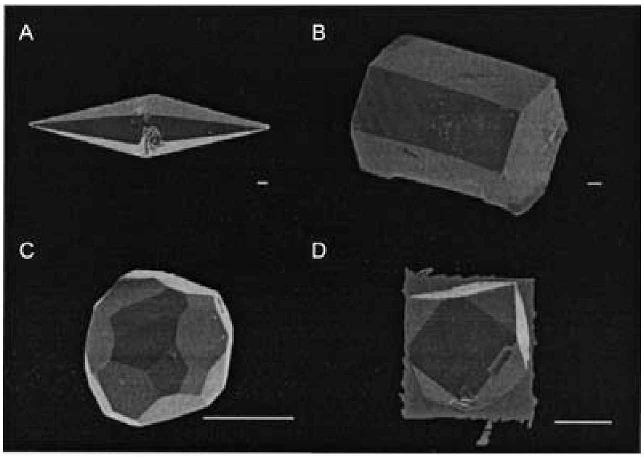

Figure 10. Typical crystals grown in liquid metals (scanning electron micrographs): A) $Sm_{2-x}Ni_2Al_4Si_2(Al_{1-y}Si_y)(Al_{1-z}Si_z)_2$, (from molten Al), B) $YNiAl_4Ge_2$, C) $CrSi_2$ (from molten In), and D) $RE_8Ru_{12}Al_{49}Si_9(Al_xSi_{12-x})$ (from molten Al). All the scale bars are 0.3 mm.

Table 2: Examples of ternary and quaternary compounds grown in liquid aluminum.

Compound	Composition (atomic ratio)	Typical preparation conditions [°C]	Reference
ternary			
RE$Al_{3-x}Ge_x$	2:15:2	50→1000 in 15 h, 3 days at 1000, 1000→650 in 36 h, 650→RT in 10 h	[216b]
RE$_2Al_3Si_2$ (*RE* = Tb–Tm)	1:10:1	50→1000 in 24 h, 5 days at 1000, 1000→300 in 96 h, 300→RT in 10 h	[214]
REAu_3Al_7 (all *RE* with the exception of La and Eu)	1:2:15	50→1000 in 12 h, 15 h at 1000, 1000→860 in 24 h, 60 h at 860, 860→RT in 72 h	[210]
$Gd_{1.33}Pt_3Al_8$ $Gd_{0.67}Pt_2Al_5$	1:1:12 0.33:1:12	50→1000 in 12 h, 15 h at 1000, 1000→860 in 24 h, 48 h at 860, 860→RT in 72 h	[221b]
quaternary			
RE$_2Ni(Ni_xSi_{1-x})Al_4Si_6$ (*RE* = Pr, Nd, Sm, Gd–Tb)	2:1:20:7	50→1000 in 12 h, 15 h at 1000, 1000→860 in 10 h, 96 h at 860, 860→360 in 5 h	[217]
$Sm_2Co(Co_xAl_{1-x})Al_4Ge_{6-y}$	2:1:20:7	50→1000 in 12 h, 15 h at 1000, 1000→860 in 10 h, 96 h at 860, 860→360 in 5 h	[220]
RE$NiAl_4(Si_{2-x}Ni_x)$ (*RE* = La–Nd, Eu) $CeCoAl_4Si_2$ *RE*$CuAl_4(Si_{2-x}Cu_x)$ (*RE* = La, Ce, Sm) $LaPdAl_4(Si_{2-x}Pd_x)$	1:1:10:2	50→1000 in 12 h, 8 h at 1000, 1000→860 in 10 h, 48 h at 860, 860→260 in 36 h, 260→50 in 6 h	[220]
RE$_2NiAl_4Ge_2$ (*RE* = Gd–Dy, Er) *RE*$_2CoAl_4Ge_2$ (*RE* = Sm, Gd, Tb)	2:1:10:2 2:1:10:2	50→1000 in 24 h, 48 h at 1000, 1000→500 in 48 h, 500→50 in 12 h	[220] [220]
RE$_2NiAl_{6-x}Ge_{4-y}$ ($x \approx 0.24$, $y \approx 1.33$; *RE* = La–Nd, Sm)	1:1:30:1	50→850 in 20 h, 96 h at 850, 850→500 in 72 h, 500→50 in 12 h	[220]
RE$NiAl_4Ge_2$ (*RE* = Y, Sm, Gd–Lu,)	1:1:15:5	50→800 in 20 h, 96 h at 800, 800→500 in 48 h, 500→50 in 9 h	[220]
RE$_{1-x}T_2Al_{5-y}Si_y$ (*RE*=Y, Nd, Sm, Tb, Tm, Yb; *T* = Ni, Pd)	1:2:20:2	50→1000 in 15 h, 5 h at 1000, 1000→850 in 2 h, 72 h at 850, 850→50 in 36 h	[220]
RE$_{2-x}TAl_4Tt_2(Al_{1-y}Tt_y)(Al_{1-z}Tt_z)_2$ (*RE*=Sm, Dy, Er; *T* = Ni, Co; *Tt* = Si, Ge)	3:4:20:6	50→1000 in 15 h, 5 h at 1000, 1000→850 in 2 h, 72 h at 850, 850→50 in 36 h	[219]
RE$_4Fe_{2+x}Al_{7-x}Si_8$ (*RE* = Ce–Nd, Sm)	1:2:15:4	50→850 in 20 h, 96 h at 850, 850→500 in 72 h, 500→50 in 12 h	[220]
RE$_4Mn_{2+x}Al_{7-x}Si_8$ (*RE* = Ce–Nd, Gd)	1:2:15:4	50→850 in 20 h, 96 h at 850, 850→500 in 72 h, 500→50 in 12 h	[220]
RE$Fe_4Al_9Si_6$ (*RE* = Gd–Er)	1:4:20:6	50→850 in 20 h, 96 h at 850, 850→500 in 72 h, 500→50 in 12 h	[220]
RE$_8Ru_{12}Al_{49}Si_9(Al_xSi_{12-x})$ (*RE* = Pr, Nd, Sm, Gd, Tb, Er)	6.5:10:100:8	50→1000 in 15 h, 15 h at 1000, 1000→860 in 10 h, 96 h at 860, 860→500 in 72 h	[222]
$Gd_{1.33}Pt_3Al_7Si$ $Gd_{0.67}Pt_2Al_4Si$	1:1:10:5 0.33:1:10:5	50→1000 in 12 h, 15 h at 1000, 1000→860 in 24 h, 48 h at 860, 860→RT in 72 h	[221b]
$Th_2AuAl_2Si_3$ $Th_2Au_3Al_4Si_2$	1:1:10:5	50→1000 in 12 h, 15 h at 1000, 1000→860 in 20 h, 48 h at 860, 860→RT in 72 h	[221a]

$Gd_{1.33}Pt_3Al_8$ was synthesized by the combination of Gd and Pt in liquid aluminum.[221b] Addition of silicon resulted in the incorporation of a small amount of this element into the material to form the isostructural compound $Gd_{1.33}Pt_3Al_7Si$. Both compounds grow as facetted hexagonal rodlike crystals (Figure 11). The rods also appear to have corrugated surfaces; the corrugation lines are perpendicular to the long direction, indicative of polysynthetic twinning. The related compounds $Gd_{0.67}Pt_2Al_5$ and $Gd_{0.67}Pt_2Al_4Si$ also form as hexagonal rods, but they are not characterized by the aforementioned uneven surfaces. These complex intermetallics only account for 10–20% of the solid isolated after removal of the flux. The remaining product consists of $GdAl_3$ needles, but also contains plate-like silicon crystals and crystals of $GdAl_2Si_2$. Evidently, in this case the flux does not completely meet criterion 4 mentioned in Section 3 and reacts to form undesirable phases.

Thorium metal reacts with gold and silicon in molten aluminum to give a mixture of the two quaternaries $Th_2AuAl_2Si_3$ (comprising about 40% of the solid product after soaking in NaOH) and $Th_2Au_3Al_4Si_2$ (40%), as well as small amounts of silicon crystals (10%) and $ThSi_2$ crystals (10%). The quaternary compounds are part of a homologous series of intermetallics, with the general formula $Th_2(Au_xSi_{1-x})[AuAl_2]_nSi_2$.[221a]

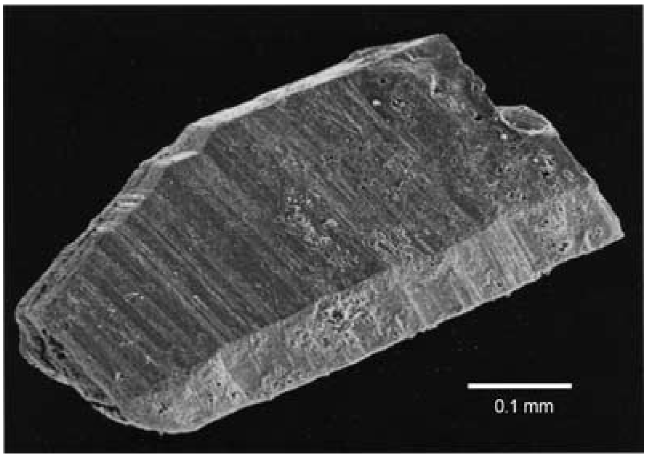

Figure 11. A representative crystal of $Gd_{1.33}Pt_3Al_7Si$, showing the typical shape of a polysynthetic twin.

10. Reactions in Liquid Gallium

Gallium has been relatively little utilized as a synthetic flux medium. The success of molten aluminum melts, however, to uncover new materials naturally stimulates inquiry into the related gallium system. The known binary and ternary compounds of gallium are numerous.[223] Most work on these systems, especially with the 3d transition metals was carried out by Grin and co-workers. Some ternary rare-earth–transition-metal gallides with ruthenium and osmium as the transition-metal components and a high content of gallium, for example, the series $RERu_2Ga_8$ or $REOsGa_4$, have recently been prepared by Schlüter and Jeitschko.[224] Reports on quaternary intermetallic phases, such as silicides and germanides, are still few. It would be interesting to assess the behavior of liquid gallium in light of that of aluminum, by performing corresponding experiments using gallium as the solvent. There are again two types of reactions, those in which gallium is incorporated into the compounds (reactive flux) and those in which it is not.

Interestingly, analogous reactions to those with aluminum that give rise to $RE_2Ni(Si_{1-x},Ni_x)Al_4Si_6$ do not yield analogous results. In the case of the quaternary system Sm/Ni/Si/Ga, phase separation results in the silicide $SmNiSi_3$,[225] and the gallide Sm_2NiGa_{12}.[226] The latter has a fascinating tetragonal structure with a three-dimensional gallium network. It is noteworthy that many *RE*/Ni/Ga phases have been known for some time[227,228] and the Sm/Ni/Ga phase diagram contains a striking number of phases: SmNiGa, $SmNiGa_2$, Sm_2Ni_2Ga, $SmNi_3Ga_2$, $Sm_3Ni_6Ga_2$, $SmNiGa_3$, Sm_2NiGa_3, $SmNiGa_4$, $Sm_{26}Ni_{11}Ga_6$, Sm_4NiGa_7, and $Sm_{17}Ni_{58}Ga_{25}$.[223] None of these materials was synthesized in a gallium flux. It is therefore rather remarkable that despite the great number of ternary compounds in this system Sm_2NiGa_{12} is a new addition. Another gallide that was discovered in this fashion was $SmNi_3Ga_9$, a hexagonal compound which adopts the $ErNi_3Al_9$ structure type.[215]

The use of molten gallium as a nonreactive solvent was demonstrated to give single crystals for the ternary silicides $RE_2Ni_{3+x}Si_{5-x}$ (*RE* = Sm, Gd, and Tb).[229] This allowed the structure of these compounds to be solved and refined with great accuracy. The structure is related to the $U_2Co_3Si_5$ structure type; however, the new studies suggested that the earlier crystallographic site assignments in $U_2Co_3Si_5$ were incorrect.

Table 3 summarizes some of the ternary and quaternary compounds synthesized or discovered with a gallium flux. The compounds $RE_4FeGa_{12-x}Ge_x$[230] were discovered during investigations of reactions in liquid gallium involving *RE*, *T*, and Ge, where *RE* = Y, Ce, Sm, Gd, Tb; and *T* = Fe, Co, Ni, or Cu. These systems were investigated at various metal ratios and different heating regimes. A heating regime with a shorter isothermal step was shown to favor the formation of the cubic phases $RE_4FeGa_{12-x}Ge_x$. For example, when a six-day isothermal step ($T = 850$ °C) was used in the system Tb/Fe/Ga/Ge, the products were Tb_4FeGe_8[231] and $Tb_2Ga_2Ge_5$,[232,239] along with the cubic phase as a minor product. Whereas a shorter isothermal step of three days at 850 °C produced the cubic phase in high yield. For *RE* = Sm, the situation was similar, as the six day isothermal heating gave rise to Sm_3Ga_9Ge as the major component, and the cubic phase, $FeGa_3$, and Ge as minor components. Reducing the time by half brought about an increase in the yield of the cubic phase. From this it can be concluded that the cubic phases are essentially a kinetic product of the reaction. Furthermore, it is clear that the time can be an important reaction parameter allowing the chemical reactivity of a system to be explored and access to kinetic and thermodynamic products. Large single crystals of $Tb_4FeGa_{12-x}Ge_x$, measuring up to 2 mm each side, could be grown from molten gallium (Figure 12). The incorporation of gallium in these phases shows that in this case the solvent is reactive. This situation is in contrast to the Sm/Ni/Ga/Si system in which the gallium-free $SmNiSi_3$ phase could be obtained.

It is interesting that isostructural phases to $RE_4FeGa_{12-x}Ge_x$ were not observed when iron was changed to Co, Ni, or Cu. Instead, a variety of other quaternary compounds arising form liquid gallium were detected.[232,235,236] In addition, the type of rare-earth metal appears to be important in phase formation. Thus, in the system *RE*/Fe/Ga/Ge, when *RE* was Y, Ce, or Gd, the RE_3Ga_9Ge phases were obtained.

Recent studies of the reactivity and phase formation in the systems *RE*/*T*/Ga/Ge, where *T* = Ni and Co, in liquid gallium showed that different compounds are obtained depending on the *RE*:*T* ratio. When the ratio $RE:T < 1$ the reactions resulted in the hexagonal compounds $RE_{0.67}T_2Ga_{5-x}Tt_x$, and $RE_{0.67}T_2Ga_{6-x}Tt_x$[235] (*Tt* = Si or Ge) that form readily within a rather broad range of synthetic conditions (time and temperature). However, ratios with $RE:T \geq 1$, give results that depend strongly on the nature of *RE*. For these ratios the chemistry is significantly more sensitive to the reaction conditions. For these studies the following compounds were obtained $RETGa_3Ge$, $RE_2TGa_9Ge_2$ (*RE* = Y, Sm, Tb, Gd, Er, Tm; *T* = Ni, Co), $RE_3Ni_3Ga_8Ge_3$ (*RE* = Sm, Gd), and $RE_4Ni_3Ga_6Ge_4$.[232]

There is an interesting contrast in the behavior of nickel and cobalt. When *T* = Ni the reaction of different lanthanoid elements under otherwise identical conditions results in $YNiGa_3Ge$, $Ce_2NiGa_9Ge_2$, $Gd_3Ni_3Ga_8Ge_3$, and $TbNiGa_3Ge$.

Table 3: Examples of ternary and quaternary compounds grown in liquid gallium.

Compounds (see Table 2)	Sample composition (atomic ratio)	Typical preparation conditions [°C]	Ref.
ternary			
RENiSi$_3$ (RE=Y, Sm)	RE:Ni:Ga:Si 1:1:15:3	50→1000 in 4 h, 1000→850 in 5 h, 4 days at 850, 850→150 in 4 days	[225]
Sm$_2$NiGa$_{12}$	Sm:Ni:Ga 2:1:18	50→900 in 12 h, 4 days at 900, 900→150 in 72 h	[226]
Sm$_2$NiGa$_{12-x}$Si$_x$	Sm:Ni:Ga:Si 2:1:10:4	50→1000 in 15 h, 5 h at 1000, 10 days at 1000, 1000→150 in 6 days	[226]
RE_2Ni$_{3+x}$Si$_{5-x}$ (RE=Sm, Gd, Tb)	RE:Ni:Ga:Si 1:2:30:2	50→1000 in 15 h, 5 h at 1000, 1000→600 in 16 h, 600→50 in 5 h	[229]
RE_4FeGa$_{12-x}$Ge$_x$ (RE=Y, Ce, Sm, Gd, Tb)	RE:Fe:Ga:Ge 4:1:30:3	50→1000 in 15 h, 5 h at 1000, 3 days at 850, 850→200 in 10 h	[230]
Tb$_4$FeGe$_8$	Tb:Fe:Ga:Ge 4:1:30:4	50→1000 in 15 h, 5 h at 1000, 6 days at 850, 850→200 in 3 days	[231]
RE_2Ga$_2$Ge$_5$ (RE=La, Sm, Tb)	Byproducts of RE:Fe:Ga:Ge 4:1:30:6	50→1000 in 15 h, 5 h at 1000, 6 days at 850, 850→200 in 3 days	[232]
RE_3Ga$_9$Ge (RE=Y, Ce, Gd)	RE:Ga:Ge 1:15:1	50→1000 in 15 h, 5 h at 1000, 6 days at 850, 850→200 in 3 days	[233]
Yb$_3$Ga$_4$Ge$_6$	Yb:Ga:Ge 1:10:2	50→1000 in 15 h, 5 h at 1000, 3 days at 850, 850→200 in 36 h	[234]
Yb$_2$Ga$_4$Ge$_6$	Yb:Ga:Ge 1:10:3	50→1000 in 15 h, 5 h at 1000, 3 days at 750, 750→200 in 36 h	[234]
quaternary			
$RE_{0.67}T_2$Ga$_{5-x}Tt_x$ (RE=Y, Sm, Gd–Tm; T=Ni, Co; Tt=Si, Ge)	RE:T:Ga:Tt 1:2:30:2	50→1000 in 15 h, 5 h at 1000, 3 days at 850, 850→200 in 36 h	[235]
$RE_{0.67}T_2$Ga$_{6-x}Tt_x$ (RE=Y, Sm, Gd–Dy; T=Ni, Co; Tt=Si, Ge)	RE:T:Ga:Tt 1:2:30:2	50→1000 in 15 h, 5 h at 1000, 3 days at 850, 850→200 in 36 h	[235]
RETGa$_3$Ge (RE=Y, Sm, Gd, Tb, Er, Tm; T=Ni, Co)	RE:T:Ga:Ge 1:1:15:1	50→1000 in 15 h, 5 h at 1000, 36 h at 850, 850→250 in 18 h	[236]
RE_2TGa$_9$Ge$_2$ (RE=Y, Sm, Gd, Tb, Er, Tm; T=Ni, Co)	RE:T:Ga:Ge 2:1:30:3	50→1000 in 15 h, 5 h at 1000, 6 days at 850, 850→250 in 75 h	[232]
RE_3Ni$_3$Ga$_8$Ge$_3$ (RE=Sm, Gd)	RE:T:Ga:Ge 1:1:15:1	50→1000 in 15 h, 5 h at 1000, 36 h at 850, 850→250 in 18 h	[236]
RE_4Ni$_3$Ga$_6$Ge$_4$ (RE=Y,Tb)	RE:T:Ga:Ge 1:1:15:1	50→1000 in 15 h, 5 h at 1000, 6 days at 850, 850→250 in 75 h	[232]
Tb$_{1.8}$Si$_8$C$_2$(B$_{12}$)$_3$	Tb:B:Ni:Si 1:6:1:1 + a 10-fold molar excess of Ga	50→1000 in 12 h, 96 h at 1000, 1000→500 in 60 h	[237]
β-SiB$_3$	B:Si:Cu:Ga 4:1:1:20	50→1000 in 12 h, 96 h at 1000	[238a]

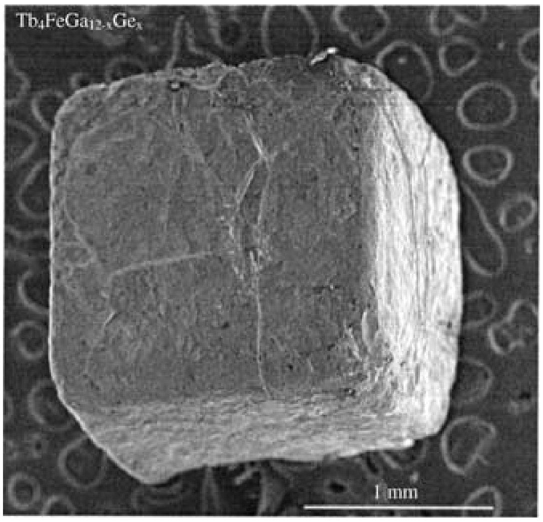

Figure 12. SEM image of a typical Ga-grown Tb$_4$FeGa$_{12-x}$Ge$_x$ crystal. The roughening of the surface is caused by an etching process during isolation.

The case is even more complicated for samarium, as up to three phases Sm$_2$NiGa$_9$Ge$_2$, SmNiGa$_3$Ge, and Sm$_3$Ni$_3$Ga$_8$Ge$_3$ could be observed. With Y and Tb, long reaction times (3–6 days) produced Y$_4$Ni$_3$Ga$_6$Ge$_4$ and Tb$_4$Ni$_3$Ga$_6$Ge$_4$, whereas shorter reaction times gave YNiGa$_3$Ge and TbNiGa$_3$Ge. Interestingly, when T=Co, the following phases form in quantitative yield: YCoGa$_3$Ge, Ce$_2$CoGa$_9$Ge$_2$, SmCoGa$_3$Ge, GdCoGa$_3$Ge, and ErCoGa$_5$. These phases probably have similar formation energies because they have common structural components.

The gallium flux medium works well for silicon/boron compounds probably because both silicon and boron are soluble in it and do not form binary compounds.[240] For example we have applied the gallium flux to RE/T/B/Si (borosilicides) in an attempt to produce lighter analogues of the RE/T/Al/Si compounds. We have shown that liquid gallium can provide an excellent route to complex quaternary silicon borides such as Tb$_{1.8}$Si$_8$C$_2$(B$_{12}$)$_3$ that cannot be formed using high-temperature techniques such as arc melting.[237] Boron-containing solids have acquired renewed interest because of the discovery of superconducting quaternary borocarbides[241] and the binary MgB$_2$, a well-known compound with a very simple structure, but only recently recognized as a high-temperature non-oxidic superconductor.[242]

A spectacular illustration of the ability of liquid gallium to stabilize phases that are inaccessible by conventional synthetic routes is the discovery of the binary boride β-SiB$_3$.[238a] This was a surprising discovery because a phase with a similar formula, Si$_{1-x}$B$_{3+x}$ (α-SiB$_3$)[238b] and a rhombohedral structure has been known for decades.[243] In contrast, β-SiB$_3$ has a new structure type with very different structural features, physical and electronic properties. It is significant that the synthesis of β-SiB$_3$ requires metallic flux conditions, which permit the total bypass of the rhombohedral compound α-SiB$_3$.

11. Indium Flux

Due to its low melting temperature of 157 °C, indium is an ideal metal for use as a reactive flux (self-flux condition). It has widely been used for the synthesis and crystal growth of indium-rich binary and ternary indides. In many cases, a slight excess of indium significantly increases the crystal growth. Good examples in the case of binary intermetallics are compounds such as $T\mathrm{In}_3$ (T = Co, Ru, Rh, Ir),[244,245] $\mathrm{Ti}_2\mathrm{In}_5$,[246] $\mathrm{Hf}_2\mathrm{In}_5$,[247] or IrIn_2.[248] In these cases, two strategies may be applied. Pure polycrystalline samples for physical-property measurements can be synthesized with the ideal starting composition, while high-quality single crystals for structure refinements can be grown from a flux with an indium excess. Indium has been exploited even less as a synthetic flux medium than aluminum and gallium. With indium there are again two types of reactions possible; those in which indium is incorporated in the products and those where it is acting strictly as a solvent. Its low melting point makes indium convenient for reaction chemistry at relatively low temperatures and facilitates its removal during isolation. Herein we will give some examples of phases crystallized in liquid indium.

11.1. Indium as a Reactive Flux

Besides the binary transition-metal–indium compounds, a large family of ternary rare-earth-metal–transition-metal indides has been synthesized in liquid indium. Several members of the compounds $\mathrm{Ce}T\mathrm{In}_5$ with HoCoGa_5-type structure and $\mathrm{Ce}_2T\mathrm{In}_8$ with $\mathrm{Ho}_2\mathrm{CoGa}_8$-type structure have been prepared in the form of relatively large single crystals for physical-property measurements.[249–252] Experimental details about the method are given in refs. [23,24]. In a typical experiment, cerium, the transition metal, and indium are mixed in the atomic ratio 1:1:20 and placed in an alumina crucible which is sealed in a silica tube to prevent oxidation. The sample is then heated over several hours to 1100 °C, kept at that temperature for 2 h, and then slowly cooled to 700 °C at a rate of $10\,^{\circ}\mathrm{C\,h^{-1}}$. At that temperature the excess indium is decanted in a centrifuge resulting in well-shaped single crystals with volumes up to 1 cm^3. The melt-centrifugation method has also been used by Boström[43,44] for the crystal growth of manganese gallides and by Nylén et al.[45] for the crystal growth of palladium stannides.

A variety of other rare-earth-based indides has been obtained by using an excess of indium. For the growth of CeNiIn_2 crystals, an arc-melted CeNiIn_2 sample can be recrystallized using an excess of about 10 wt % indium in a ZrO_2 crucible.[253] The temperature is first raised to 1200 °C, kept at that temperature for 6 h, cooled at a rate of $5\,^{\circ}\mathrm{C\,h^{-1}}$ to 600 °C, and quenched in air. Similar temperature profiles have been used for the synthesis of $\mathrm{Tb}_6\mathrm{Pt}_{12}\mathrm{In}_{23}$ and $\mathrm{Dy}_2\mathrm{Pt}_7\mathrm{In}_{16}$,[254] however in these cases, arc-melted precursor alloys TbPtIn_4 and $\mathrm{DyPt}_3\mathrm{In}_6$ were used for recrystallization from liquid indium. Selected single crystals of CeNiIn_2, $\mathrm{Tb}_6\mathrm{Pt}_{12}\mathrm{In}_{23}$, and $\mathrm{Dy}_2\mathrm{Pt}_7\mathrm{In}_{16}$ are shown in Figure 13.

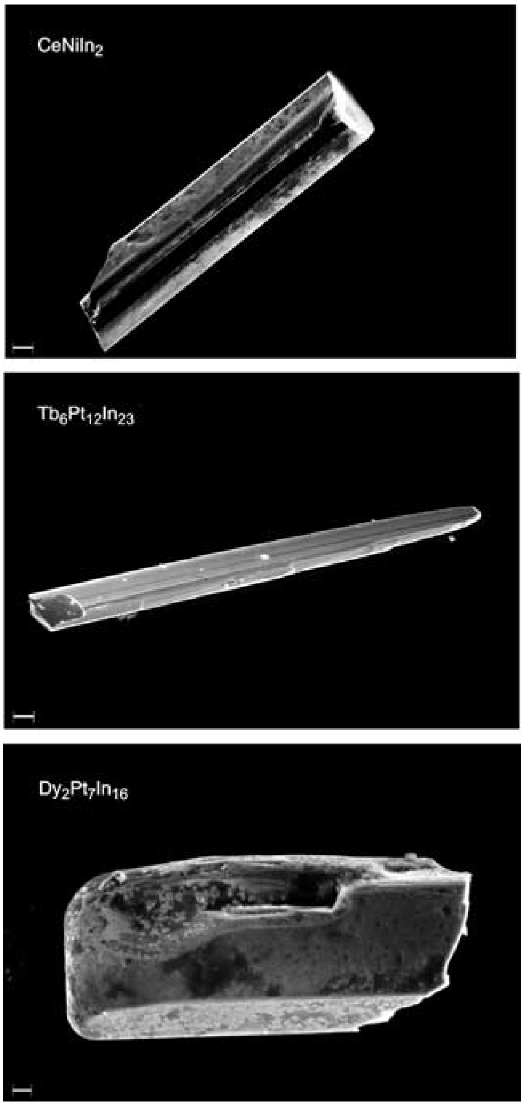

Figure 13. Scanning electron micrographs of CeNiIn_2 (scale bar 10 μm) $\mathrm{Tb}_6\mathrm{Pt}_{12}\mathrm{In}_{23}$ (scale bar 10 μm), and $\mathrm{Dy}_2\mathrm{Pt}_7\mathrm{In}_{16}$ (scale bar 3 μm) single crystals.

If only a small excess of indium is used for the self-flux technique, the melt-centrifugation technique cannot be applied. In this case it is better to dissolve the indium. This is a significant difference between indides and binary and ternary stannides, while most stannides resist 2 N hydrochloric acid, indides are often destroyed. The problem can be avoided by removing the melt with diluted acetic acid. The crystals shown in Figure 13 have been cleaned in this way. In most cases, the crystals have a thin indium coating which can easily be removed with diluted acetic acid.

The ytterbium based indides $\mathrm{Yb}T\mathrm{In}_5$ (T = Co, Rh, Ir) have been prepared from an indium flux with starting compositions Yb:T:In = 1:1:7.[255,256] Tantalum was used as crucible material and the samples were initially heated to 1050 °C, kept at that temperature for 6 h, and then cooled at a rate of $5\,^{\circ}\mathrm{C\,h^{-1}}$ to 400 °C, with subsequent quenching to room temperature. A different procedure was used for YbPtIn_4.[255] An arc-melted precursor alloy of approximate composition $YbPtIn_2$ was annealed with indium in the ideal ratio 1:2 in a molybdenum crucible. The initial step was rapid heating at 1100 °C, this temperature was maintained for 6 h, and then slow cooling at a rate of $5\,°C\,h^{-1}$ to room temperature. The four ytterbium compounds were thus obtained as well-shaped crystals with edge lengths larger than 200 μm. Interestingly, the heavy-rare-earth-containing series of compounds RE_2Cu_2In (RE = Gd–Lu, except Yb) were also grown in an indium flux despite their relatively low indium content.[257]

11.2. Indium as a Nonreactive Flux

Similar to molten aluminum and gallium, indium is also attractive for its capacity to dissolve Si, Ge, and a host of lanthanoid and transition metals, which results in highly reactive forms of the elements. Further, In does not form binary compounds with Ge or Si.[258] For example, reactions of Cr, W, V, and several rare-earth elements with silicon in indium flux at 800–900 °C result in well formed single crystals of the corresponding disilicides $CrSi_2$, WSi_2, VSi_2, and $RESi_2$.[259] No indium incorporation is observed. Also single crystals of the ternary compound $CeCu_2Si_2$ were grown from indium flux. However, in this case elemental analysis showed that small amounts of indium had entered into the compound.[260]

When a transition metal such as nickel is added to the reactions with rare-earth elements and germanium in indium flux, new forms of the compounds β-$RENiGe_2$ (RE = Dy, Er, Yb, Lu) are obtained which crystallize with the $YIrGe_2$ structure type.[261] This result is intriguing because phases with the same composition (α-$RENiGe_2$) have been known for some time, but crystallize in the $CeNiSi_2$ structure type. In fact, many germanides $RETGe_2$ with RE = Y, Tb–Lu, and T = Pd, Pt, Ir with the $YIrGe_2$-type structure are known, but phases containing first-row transition metals were not known till the indium flux was used.

It is of note that the formation of β-$RENiGe_2$ occurs exclusively in liquid iridium. The yields from these reactions range from 60 to 70 % (based on the RE), with approximately 70 % purity. The main impurities were the α-phase and recrystallized Ge. When other methods, such as arc-melting or radio-frequency furnace heating, were used to synthesize $RENiGe_2$ compounds they only led to the α-form. Furthermore when the reaction times were increased from 48 to 96 h the α-phase was the dominant fraction at approximately 65 %. Likewise, if the isotherm temperature for the reaction was increased from 850 to 1000 °C a larger fraction of the reaction product, approximately 50–60 %, crystallized as the α-form. Two other experiments were also conducted where the elements Dy or Er, Ni, Ge, and In were combined in a 1:1:2:10 ratio, and then were arc-melted for 3 min, or heated with a radio frequency furnace for 1 h. Both of these methods, which employ much higher temperatures than the flux reaction, yielded practically pure α-form despite using excess indium. These results indicate that a combination of low temperature and excess indium are needed to arrive at the β-form and suggests that the α-phase is thermodynamically the more stable form, and the β-form is the kinetically stable phase.

12. Lithium and Sodium Fluxes

Among the alkali metals, lithium has the highest melting (180.5 °C) and boiling (1374 °C) point.[258] This difference in temperatures is a good prerequisite for use as a metal flux. Jung and Diessenbacher[262] reported on the growth of single crystals of the boride $Sr_2Ru_7B_8$ in a lithium flux from the starting composition Li:Sr:Ru:B = 50:2.3:7:8. A sealed tantalum tube was used as a container material and the annealing temperature was 1100 °C for 4 days.

The same technique was subsequently used for the crystal growth of various rare-earth-metal–transition-metal carbides.[263] The lithium flux is especially useful for the synthesis of ytterbium-based carbides. Owing to the low boiling temperature of ytterbium (1193 °C) a synthesis of such carbides by arc-melting always results in large weight losses. In contrast, liquid lithium served as an excellent medium for the synthesis of $YbAl_3C_3$.[264] The elements were combined in the atomic ratio Yb:Al:C:Li = 1:3:3:30, sealed in an iron ampoule (tube volume ca. 4 cm^3), annealed for one day at 800 °C, and finally cooled at a rate of $7\,°C\,h^{-1}$ to room temperature. Lithium was dissolved in ethanol in an ultrasonic bath leaving silvery small hexagonal platelets. The single-phase reaction product was suitable for physical property investigations.

Iron or nickel ampoules can be used as container materials, since molten lithium reactively penetrates silica tubes. Typical tube sizes have an outer diameter of 10 mm and a wall thickness of 1 mm (100 mm length). The tubes are closed by 5-mm bolts that are sealed by arc-welding under an argon atmosphere.[265] For short reaction times (1–3 days) and moderate temperatures (< 500 °C), the metal ampoules can be annealed directly in a muffle furnace. For high-temperature annealing, the iron or nickel ampoules are sealed in silica tubes to prevent surface oxidation.

Using this experimental technique, the new carbides $Yb_2Cr_2C_3$,[266] $Yb_4Ni_2C_5$,[267] YbCoC,[268] and $Gd_{10.34}Mn_{12.66}C_{18}$[269] have been synthesized. At this point it is worth noting that an independent synthesis without lithium as flux medium is necessary to prove that lithium does not stabilize the respective structure. In all cases the carbides have independently been prepared by arc-melting, but these experiments did not result in single-phase samples.

The choice of the ampoule material is very important. Nickel, iron, and stainless steel are inexpensive, while niobium and tantalum are much more expensive. Especially iron and steel tubes contain small amounts of carbon which the liquid lithium is able to extract from the tube. Studies of recrystallizing praseodymium nickel arsenides in a lithium flux in steel tubes[270] resulted in well shaped single crystals of $PrNiC_2$.[271]

Besides lithium, the higher congener sodium has been widely used for the growth of crystals or fine powders for various industrially important nitrides such as BN, AlN, or GaN. A severe problem occurs for the production of aluminum nitride powder. Owing to the large heat of formation of AlN, the AlN particles already sinter and form agglomerates during the reaction. These preparative problems can easily be overcome by using a sodium flux.[272] Aluminum metal powder can be reacted with the azide NaN_3 in a sealed stainless steel ampoule. Thermal decomposition of NaN_3 at 300 °C provides pure N_2 and Na. The reaction mixture is heated to 600 °C for 12 h and then to 700 °C and 24 h. The furnace is then turned off and the tube cooled to room temperature within the furnace. The sodium metal, including the fine AlN powder, is allowed to react with isopropanol and then with ethanol. The product can be cleaned with ethanol in an ultrasonic bath and may be collected by centrifugation. Finally the products can be dipped into distilled water for 10–20 h to ensure the removal of all free sodium.

The sodium flux technique with the azide route was also used for the growth of *h*-BN and GaN crystals.[273] In these cases, at the final reaction temperature of 800 °C a nitrogen pressure of 100 atm was generated by the decomposition of sodium azide. Especially for GaN, the influence of the N_2 pressure and various Na–Ga melts as the staring flux material have been investigated in detail.[274–276]

As well as the Group III nitrides, complex alkaline-earth-metal–transition-metal nitrides and nitride oxides with peculiar new crystal structures have also been discovered. Sodium flux was used to generate new nitride compounds, such as Ba_2GeGaN and $(Ba_xSr_{1-x})_3Ge_2N_2$,[277] $Sr_3Ge_2N_2$ and Sr_2GeN_2,[278] $Ba_3Ge_2N_2$,[279] and $Ba_5Si_2N_6$.[280] Additional examples are Ba_3ZnN_2O,[281] $Sr_{39}Co_{12}N_{31}$,[282] Sr_2NiN_2,[283] or $Ba_{14}Cu_2In_4N_7$.[284] Niobium ampoules were used as a crucible material for the synthesis of Ba_3ZnN_2O and $Sr_{39}Co_{12}N_{31}$. $Ba_{14}Cu_2In_4N_7$ was prepared in a BN crucible which was placed in a stainless steel container, while the synthesis of Sr_2NiN_2 was carried out in a nickel ampoule. For all nitrides, the products within the crucibles or within the ampoules were washed with liquid ammonia using a special glass apparatus.[285] The nitrogen pressure in the ampoules was generated through decomposition of sodium azide.

Liquid sodium is also a very suitable flux for the growth of subnitride and suboxide crystals of the alkaline-earth elements.[286–288] Examples are the subnitride series $Na_xBa_{14}CaN_6$ ($x = 8,14,17,21,22$) with the new cluster type $[Ba_{14}CaN_6]$, the binary nitride Ba_3N, or the mixed oxide $NaBa_2O$, or the mixed nitride $NaBa_3N$.[286,288] The excess sodium can either be distilled away or it may be separated from the reaction product using a special press.[289]

13. Miscellaneous Metallic Fluxes and Materials

Many other fluxes have been reported for the preparation of peculiar compounds or for crystal growth starting from polycrystalline materials. It is impossible to list all the work herein. In this last section we summarize some of the most interesting results.

13.1. Copper and Cobalt Flux

Copper has been used sporadically in growing crystals of boride compounds with very interesting results. In 1973 Johnson described in detail how to grow well formed octahedral crystals of MnSi by reaction of Mn and Si in a copper flux. A mixture of Mn, Si, and excess Cu is heated to 1200 °C over a period of 12 h and then cooled to 500 °C at $10\,^{\circ}C\,h^{-1}$. The copper-rich Cu-Mn-Si matrix was dissolved in 8 N HNO_3 leaving octahedral crystals of MnSi.[290] More recently, the well-known silicide Mn_5Si_3 was reported to grow from liquid copper but interestingly no other known binaries such as $Mn_{27}Si_{47}$ formed under these conditions.[151]

Crystals of Cr_3Si and Cr_5Si_3 single crystals were prepared in copper flux using Cr and Si powders as starting materials in an argon atmosphere. The conditions for obtaining these crystals as single-phase materials and of a relatively large size were established.[291] Crystals of NbB, Nb_5B_6, Nb_3B_4, Nb_2B_3 (new phase), and NbB_2 were prepared similarly using Nb and B as starting materials in an argon atmosphere.[292] Crystals of W_2B, δ-WB, and WB_2 were prepared from copper solutions using tungsten metal and crystalline boron powders as starting materials under an argon atmosphere.[293]

Multinary boride compounds have been grown as well. The first such report involved the growth of the series $RERh_4B_4$ ($RE = $ Y, Sm, Gd–Tm, and Lu).[294] Later, Japanese workers confirmed these results and reported the additional boride series $RERh_3B_2$ ($RE = $ Gd, Dy, Er–Lu) and $RERh_3B$ ($RE = $ Sm, Gd, Er, Tm) as well as the two boride carbides $RERh_2B_2C$ with $RE = $ Er and Gd.[295a] The layered compound $PrRh_{4.8}B_2$ was obtained as hexagonal plates by a molten metal-flux growth method, using copper as a flux. The X-ray photoelectron spectroscopic study and electron probe microanalysis results showed the presence of a few monolayers of copper atoms between the crystals of $PrRh_{4.8}B_2$.[295b,c] Similarly, slow cooling molten copper solutions of the systems *RE*-Rh-B and *RE*-Rh-B-C gave single crystals of the above mentioned ternary borides $RERh_4B_4$, $RERh_3B_2$, and $RERh_3B$. Crystals of $ErRh_3B_2$ grew as hexagonal objects, crystals of $ErRh_4B_4$ were obtained as rectangular objects with a tetragonal structure, and single crystals of cubic $ErRh_3B$ were extracted as cubes. Single crystals of the new tetragonal compounds $RERh_2B_2C$ have been obtained as thin plates.[295] Clearly these results give a preview of what could be accomplished with copper.

The equiatomic transition-metal boride MoCoB[296] was prepared in a cobalt flux from a sample with the starting composition Mo:Co:B = 7:70:21. The excess cobalt was dissolved in concentrated hydrochloric acid, while the ternary boride is stable under these conditions.

13.2. Quasicrystals

Flux-growth techniques have been successfully applied by Canfield et al. for the preparation of several families of quasicrystals and related approximant phases. Large (up to 1 cm^3) single-grain samples have been obtained for icosahedral *RE*-Mg-Zn ($RE = $ Y, Gd–Er) and Al-Pd-Mn, decagonal

Al-Ni-Co, and other quasicrystals. Grown in a flux with a high content of magnesium and zinc by slowly cooling from 700 to 480 °C, the *RE*-Mg-Zn family of approximant phases (composition $\approx RE_9Mg_{34}Zn_{57}$) were the first rare-earth-containing quasicrystals that allowed the study of localized magnetic moments in a quasiperiodic environment (Figure 14).

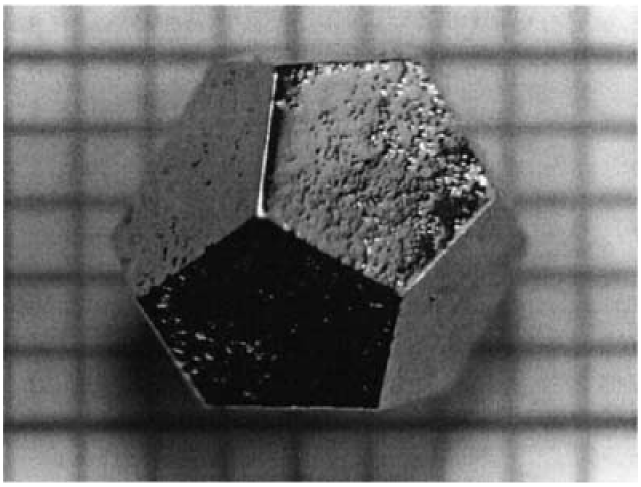

Figure 14. A well-formed Ho-Mg-Zn quasicrystal with dodecahedral morphology (mm grid) grown from a flux with a high content of magnesium and zinc.[297c]

Samples of the Al-Pd-Mn and the Al-Ga-Pd-Mn approximant phases were obtained by slowly cooling ternary (or quaternary) melts of a composition that intersects the primary solidification surface of the desired phase in the equilibrium ternary-alloy phase diagram. The metallic fluxes lead to almost strain-free quasicrystals and clearly allow the fascinating pentagonal growth habit to be revealed.[297]

13.3. Zinc Flux

Zinc is a metal with a comparatively low melting point (420 °C). Like for the preparation of binary stannides discussed in Sections 5 and 7, peritectic reactions are found also in the zinc-rich regions of the transition-metal–zinc systems.[40] Such reactions can occur when zinc coatings are used to protect iron- and steel-based materials. For this reason the Fe–Zn phase diagram has been investigated in detail.

The binary compounds Ti_3Zn_{22} and $TiZn_{16}$[298] have been prepared from samples of the starting compositions Ti:Zn 5:95 and 3:97, respectively. The 5:95 sample (silica tubes as crucible material) was first equilibrated for two days at 850 °C, then cooled at a rate of $5\,°C\,h^{-1}$ to 500 °C and quenched in air from that temperature. The final annealing temperature for the 3:97 sample was 455 °C. Large crystals with edge lengths up to 4 mm were obtained after dissolution of the matrix in hydrochloric acid. With similar preparation conditions well-developed crystals of the compounds Zr_5Zn_{39} and $ZrZn_{22}$ were obtained.[299] As a by-product of these reactions $Zr_6Zn_{23}Si$[300] with a "filled" Th_6Mn_{23}-type structure was observed, where the silicon content arises from the quartz tube. Subsequently this compound was also prepared in alumina containers, where the silicon had to be added deliberately. By slow cooling of melts with very high zinc contents (98 and 99 % Zn) the compounds $NbZn_3$, $NbZn_{16}$, and $MoZn_{20.44}$[301] were prepared in well-crystallized form. Also the rhodium-based compounds RhZn, Rh_2Zn_{11}, and $RhZn_{13}$ (Figure 15) are accessible in this way.[302]

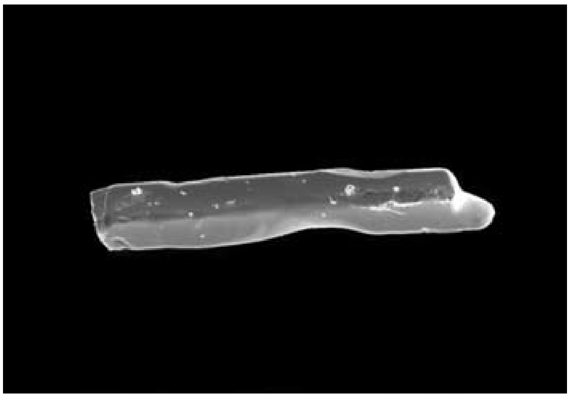

Figure 15. Scanning electron micrograph of a $RhZn_{13}$ single crystal (length ca. 0.2 mm).

Similar to the ternary aluminides reported in Section 9, ternary transition-metal–zinc compounds and rare-earth-metal–transition metal–zinc compounds can also be obtained from liquid zinc. Recent examples are the compounds RET_2Zn_{20} (T = Fe, Ru, Co, Rh, Ni),[303] TT'_2Zn_{20} (T = Zr, Hf, Nb; T' = Mn, Fe, Ru, Co, Rh, Ni),[304] or $RE_2T_3Zn_{14}$ (T = Fe, Co, Rh, Ni, Pd, Pt) with ordered Th_2Zn_{17} structure.[305] As an example a crystal of $HfRu_2Zn_{20}$ is shown in Figure 16. When carrying out reactions with zinc, care must be taken to control and handle the high vapor pressure of this metal at high temperatures.

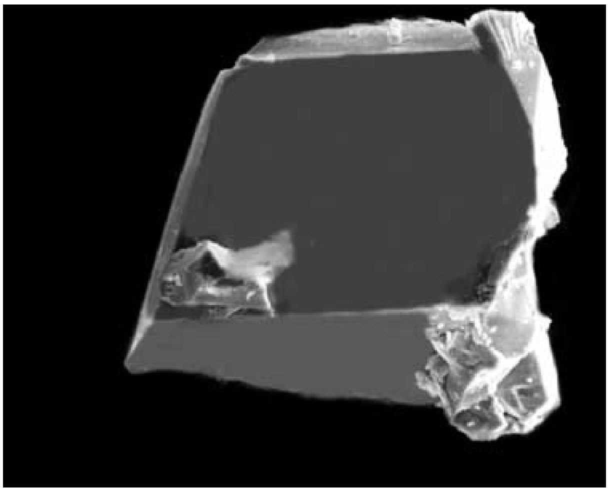

Figure 16. Scanning electron micrograph of a $HfRu_2Zn_{20}$ single crystal (length ca. 0.12 mm).

13.4. Mixed-Metal Fluxes

Almost all reactions reported in the previous sections used an excess of only one metal as flux. Even more preparation possibilities are available through multinary mixtures. An interesting approach by Hillebrecht and Gebhardt with different Cu–Al fluxes revealed a whole series of niobium boride carbides.[306] The molar ratios Cu:Al:B:C:Nb were 20:5:2:1:4 for Nb_3B_3C, 20:5:0.2:0.1:0.2 for $Nb_4B_3C_2$, 20:5:2:1:2 for $Nb_7B_6C_3$, and 20:5:0.1:0.1:0.2 for $Nb_7B_4C_4$. Alumina was used as crucible material with the following temperature program: room temperature to 1600 °C with 400 °C h^{-1}, 24 h holding, cooling to 1500 °C at a rate of 100 °C h^{-1}, to 1100 °C at a rate of 1 °C h^{-1}, and finally to room temperature at 150 °C h^{-1}. The metal excess was dissolved in half-concentrated nitric acid.

Reactions in combined Ga:Zn fluxes revealed a large series of compounds: $MoZn_6$, $NbZn_3Ga_3$, $TaZn_3Ga_3$, $MoZn_{4.5}Ga_{4.5}$, or $Mo_7Ga_9Zn_{43}$.[307] Such intermetallics show packings of polyhedra that resemble the structures of the metallic elements. Ti/Al/Sn fluxes have been used for the preparation of ternary titanium–aluminum–carbides.[308]

14. Concluding Remarks and Prospects and Opportunities for the Future

Fluxes are solvents in almost all respects and they have recently emerged as an important synthetic tool in solid-state chemistry for both crystal-growth studies and exploratory studies of new chemical systems. Because of the huge potential for new materials discovery in the realm of intermetallics, the molten metal-flux technique is proving to be an outstanding tool for preparation. The advantages of this method lie in the enhanced diffusion of the elements facilitated by the solvent and the lower reaction temperatures that can be tolerated. The latter allow better kinetic control that gives more flexibility for novel compositions and atomic arrangements to be adopted in the structure.

For the synthesis of intermetallic tetrelide (mainly Si and Ge containing) compounds, the option of molten metal fluxes presents a promising approach, particularly with the use of low melting metals of Group 13 (Al, Ga, and In). These metals have low melting points, large solubility limits for tetrelides at moderate temperatures, do not form binary compounds with tetrelides, and are easily isolable from the final products through either chemical or physical means.

Lower temperatures also facilitate the formation of kinetically derived materials that may not be accessible by traditional high-temperature synthetic methods, such as arc melting or radio-frequency heating. Even within the flux-growth scenario, variation of the reaction time and temperature can influence the product outcome within a system just as in any conventional solution-based process.

The results presented herein indicate that considerable advances in the discovery of novel and complex phases are achievable utilizing molten metal fluxes as solvents. The flux approach to exploratory synthesis is the solid-state equivalent of conventional synthetic approach in coordination chemistry. The underlying principal reasons that make the flux reaction work, are the lower temperatures and enhanced diffusion rates that become accessible. When the benefits of flux synthesis are combined with the constant need to explore the chemistry of most elements of the periodic table, we have a powerful means with which to grasp the potential for future inquiry in solid-state chemistry. Naturally, this type of research is largely synthetic in nature, but the results could affect both basic and applied chemistry as well as physics, since in the plethora of new compounds to be discovered, exciting materials are sure to exist that have a variety of interesting phenomena and applications.

The benefits of molten metal solvents are by no means limited to the liquid metals described herein. Many other metal fluxes, such as lead, indium, and bismuth, can be explored more systematically as elemental solvents with relatively low melting points. It is also easy to imagine the use of binary or ternary compositions with low melting temperatures as solvents for similar reactions, such as various eutectic compositions of Co, Ni, or Cu with boron.

The investigations at the WWU Münster have continuously been supported by the Degussa–Hüls AG and the Heraeus Quarzschmelze through generous gifts of noble metals and silica tubes. This work was financially supported by the Fonds der Chemischen Industrie and by the Deutsche Forschungsgemeinschaft. M.G.K. thanks the Alexander von Humboldt Foundation for allowing him an extended stay in Germany where this article was written. Research at Michigan State University was supported by the Department of Energy Office of Basic Energy Sciences.

Received: September 30, 2004
Revised: March 10, 2005

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