Binary immiscible metal systems for preparation of borides

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Abstract. The binary systems with the immiscibility in the liquid state are considered as a tool for synthesis and crystallization of borides. New preparation method using two solvents (immiscibility gap method) is compared with the conventional solution-melt method using one solvent (flux method). The appropriate systems are analyzed with respect to the temperature and concentration limits of the immiscibility gap, density ratio of solvents and reagents, interaction of reagents, formation and crystallization of compounds, and allocation of products in the metallic matrix.

1. Introduction

Recently, we reported first results on the new route of processing and investigation of interaction of elements in binary systems with immiscibility in the liquid state (immiscibility gap method) with respect to the synthesis and crystallization from two immiscible solvents L\textsubscript{1} and L\textsubscript{2} [1, 2]. In the present work, the immiscibility method was applied as the tool for synthesis of metal borides. Differences are discussed between the new and the conventional solution-melt method using one solvent L (flux method [3]). Experimental part has been already described in [2].

Analysis of the known phase diagrams [4] reveals five binary systems most suitable for experiments under ambient conditions: Ga/Pb, Cd/Ga, Al/Pb, Al/Cd and Pb/Zn. The system Ga/Pb has an immiscibility gap, but the upper immiscibility temperature (610 °C) is too low for synthesis of refractory compounds. The system Cd/Ga is unsuitable for immiscibility gap method because of very low temperatures (9 °C) and narrow concentration range of immiscibility (52.25 at% Ga). Remaining three - Al/Pb, Al/Cd and Pb/Zn - possess wide temperature and concentration ranges of immiscibility (table 1) and are the most suitable for synthesis and crystallization of refractory compounds. The basic differences between the flux and immiscibility gap methods are related to:

(i) temperature-concentration boundary conditions for the liquid phase;
(ii) presence of the immiscibility range bound to a binodal;
(iii) density ratios of the solvents and the reagents;
(iv) conditions for the chemical reaction of the reagents and formation of the compounds;
(v) conditions of crystallization and allocation of the products in the metallic matrix.
Figure 1. Generalized phase diagram with an immiscibility gap.

### Table 1. Temperature and concentration limits of the immiscibility gap in selected systems

| Binary system | $\Delta T_{L1+L2} = T_c - T_{mono}$ ($^\circ$C) | $\Delta C_{L1+L2} = C_{mono,ip} - C_{ip,mono}$ (at% of one component) |
|---------------|-----------------------------------------------|---------------------------------------------------------------|
| Al/Cd         | 370 = 1020 - 650                              | 93.14 = 94.9 - 1.76 (Cd)                                      |
| Al/Pb         | 907 = 1566 - 659                              | 97.71 = 97.91 - 0.19 (Pb)                                    |
| Cd/Ga         | 9 = 291 - 282                                 | 52.25 = 74.95 - 22.7 (Ga)                                     |
| Ga/Pb         | 297.4 = 610 - 312.6                           | 91.9 = 93.7 - 1.8 (Pb)                                       |
| Zn/Pb         | 380.2 = 798 - 417.8                           | 93.7 = 94 - 0.3 (Pb)                                         |

2. Temperature-concentration limits of the immiscibility gap

This condition is crucial taking into account the fact, that in such systems the reagents are dissolved in different solvents. They react at the immiscibility border of the solvents. The interaction is supported by the counter diffusion and convection of solvated particles of reagents within immiscible layers.

In a generalized phase diagram (figure 1) the immiscibility area is bound to a dome-shaped curve (a binodal) and its basis (monotectic horizontal). The temperature interval $\Delta T$ is defined by the monotectic temperature ($T_{mono}$) and the critical point of immiscibility ($T_c$). There are two types of the phase diagrams with an immiscibility range: systems with monotectic and inflection points and systems with two inflection points [5]. Thus, the concentration range $\Delta C$ is defined either by the monotectic point $C_{mono}$ and an inflection point $C_{ip}$, or by two points of an inflection [5]. For the elements with the melting temperature lower than $T_{mono}$, an eutectic ($T_e$, $C_e$) should be located below the monotectic reaction. In such systems preparation of compounds and their crystallization is possible in the temperature-concentration areas of $\Delta T = T_c - T_{mono}$ and $\Delta C = C_{mono,ip} - C_{ip,mono}$. The larger are $\Delta T$ and $\Delta C$, the more variable is the given system for synthesis in respect to the temperatures, solvent ratios L1 and L2, amounts of the dissolved reagents, and conditions for crystallization of products (e.g., more time for growth of the larger crystals with less defects).
3. Density ratio of the dissolved reagents and solvents

In addition to the immiscibility gap, selected solvents and reagents have to fulfill the following condition. The reagent dissolved in the upper layer should sink in the top liquid solvent, but not in the bottom liquid solvent. The bottom reagent should emerge in the bottom layer, but not in the top layer (figure 2a). Such density ratio allows the transport of the reagents and supports chemical reaction at the liquid phase boundary by counter diffusion and convection.

For the immiscibility gap preparation of the borides the key point is the selection of an appropriate solvent for boron. E.g., metals with low melting temperatures, such as Al (density 2.70 g cm\(^{-3}\)), Zn (7.14) and Cd (8.64), are heavier than B (2.34). Boron dissolves only partially in Al, and is almost insoluble in Zn or Cd. Therefore, the system Ca (1.55)/Ce(6.78) was chosen for synthesis of TiB\(_2\) (figure 3a). Here Ca is lighter than B and dissolves boron. Titanium (4.50) is soluble and emerges in liquid cerium, reacting with boron at phase boundary and forming refractory boride TiB\(_2\).

Syntheses in the system Ca(+B)/Ce(+Ti) were carried out in a sealed tantalum crucible. The obtained ingots were cut in two parts: one was used for metallographic characterization, another was dissolved in strongly diluted acids to isolate the crystalline products. Different shapes of crystals were observed: needles (figure 4a), isometric formations (figure 4b) or staples of plates (figure 4c). Please note that TiB\(_2\) prepared by usual flux method is usually obtained in form of thin hexagonal plates [3]. More detailed investigations on the origin of the different crystal shapes are in progress.

Another solvent for boron can be obtained by reducing of the density of the aluminium melt by adding a lighter metal, e.g., Mg (1.74). The Mg/Al ratio should be selected so that the density of the mixture is lower than the density of boron. So, for the target density of 2.2 g cm\(^{-3}\) the mass
ratio for the mixture is Al : Mg = 10 : 7. The so-obtained Al/Mg solvent forms an immiscibility gap system with Pb. It is possible to perform synthesis and crystallization of hexaborides of the rare-earth metals in this system despite formation of intermetallic compounds between Al and Mg and between Mg and Pb. These compounds decompose at the temperatures between 450 and 550 °C and do not hinder the formation of refractory rare-earth hexaborides at elevated temperatures. Based on these considerations, single crystals of solid solutions $La_{1-x}Nd_xB_6$ were obtained from the immiscibility system $(Al,Mg)(+B)/Pb (+La,Nd)$ in form of isometric crystals, needles and plates (figure 5).

Use of the mixed solvents in immiscibility systems has special aspects. Ideally, the component added to one solvent should form also a phase diagram with an immiscibility gap with the solvent.

Figure 3. Phase diagrams Ca/Ce and Al/Pb with immiscibility gaps, used for synthesis and crystallization of borides.
of the second layer. So, addition of well-soluble Ga to Al in the system Al/Pb will be in favor, because both Ga and Al form with Pb immiscibility systems having large $\Delta T$ and $\Delta C$. For the same reasons, an addition of Al to Ga in the immiscibility system Ga/Pb will be also in favor. To the best of our knowledge, this paper is the first report on the use of the mixed solvents for preparation and crystallization with the immiscibility gap method.

4. Allocation of the products in immiscibility systems

In general, several variants of synthesis and crystallization of compounds in immiscibility systems may be considered. In the first scenario, the reagents are soluble in different layers and the product is soluble in the top layer. The dissolved reagents meet at the immiscibility border and react, forming a compound with a density lower than the density of the bottom solvent and higher than the density of the top solvent. The product moves to the top layer. Under further cooling, the crystallization occurs close to the immiscibility border.

In the second scenario, one of the reagents is almost insoluble in the bottom solvent, but emerges in it (e.g., Co in Pb). In this case, the insoluble particles move to the immiscibility border by convection and react with the dissolved top reagent. The possibility of the crystal growth depends here on the solubility of the products in one of the layers. If they are insoluble
Figure 5. Single crystals of La$_{1-x}$Nd$_x$B$_6$ in different shapes, obtained from the system (Al,Mg)(+B)/Pb(+La,Nd).

in both solvents, a polycrystalline product is formed immediately at the immiscibility border. If the product is soluble in one of the layers, it crystallizes in the vicinity of the immiscibility border in the according layer. This was observed in the system Pb(+Co)/Zn(+Ge): insoluble in Pb cobalt reacts with Ge from the top layer, forming binary compound Co$_{61}$Ge$_{39} \approx$ Co$_3$Ge$_2$ (figure 6). In this case, the reaction is complicated by the formation of the ternary byproduct Co$_{10}$Zn$_{87+x}$Ge$_x$ with the solvent [2].

5. Separation of products of synthesis and crystallization
In accordance with the first scenario described above, the products in the form of crystals with different shapes concentrate in the bottom part of the top layer (figure 2). Their separation in many cases is easier and faster than in case of the usual flux method. The top layer of the solidified ingot can be cut off and dissolved in an appropriate solvent which removes the matrix and does not attack the target crystals. This reduces processing time and costs.
Figure 6. The microstructure of the ingot after immiscibility gap preparation in the system Pb(+Co)/Zn(+Ge). Formation of intermetallic compounds is observed in the vicinity of the immiscibility border in both layers together with the excess of elemental Ge crystallized by cooling from the Zn melt.

6. Conclusions
An appropriate choice of the binary systems with the immiscibility gap in the liquid state allows performing chemical reactions and crystallization of the products at the immiscibility border. Key requirements for this immiscibility gap method are solubility of the reagents in different layers and reasonable density ratio between the reagents and the solvents. The feasibility of the new preparation route is shown on example of synthesis and crystallization of refractory borides TiB$_2$ and La$_{1-x}$Nd$_x$B$_6$.

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References
[1] Burkhardt U, Boström M, Schnelle W, Hui Z, Grin Yu and Gurin V 2003 Proc. 9th Euro. Conf. Solid State Chem. (Stuttgart, Germany) p 204
[2] Burkhardt U, Gurin V N and Grin Yu 2006 Develop. Instit. Sci. Rep. (MPI CPfS, Dresden, Germany) p 246
[3] Gurin V N and Korsukova M M 1983 Prog. Cryst. Growth Charact. 16 59
[4] Massalski T B (ed) 1996 Binary Alloy Phase Diagrams 2nd ed (ASM International, The Materials Information Society) Vol. 1-3
[5] Anosov V Ya, Ozerova M I and Fialkov Yu Ya 1976 Principles of physical chemical analysis (Moscow, Nauka) p 140 (in Russian)