Synthesis, Crystal Structure Determination and Property Investigation of Intermetallic Phases as a Concerted Complex Process

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The synthesis and investigation of intermetallics in our group has led to the discovery of numerous new phases, most of which have unique crystal structures. The resulting structural models provide a good basis for an analysis of the chemical bonding and interpretation of physical properties. The use of state-of-the-art equipment allowed us to solve non-trivial tasks (e.g. resolving twinning) and interpret the real structure of the investigated phases (e.g. partial disorder as an incorporation of different structural motifs into the parent structure).

The structural chemistry of intermetallic compounds varies from a simple atomic arrangement containing 2 atoms in a unit cell (ScAl, space group $Pm\bar{3}m$, Pearson symbol $cP2$, CsCl type [1]) to quite complex structures with unit cell volumes up to thousands of cubic angstroms consisting hundreds or thousands of atoms ($Mg_{29}Pt_4$, space group $F\bar{4}3m$, Pearson symbol $cF391$ [2], β-Mg_2Al_3, Samson phase, space group $Fd\bar{3}m$, Pearson symbol $cF1168$ [3]). At first glance, the synthesis of intermetallic phases seems like a trivial task: joining two or more metal components by melting or sintering, for example. The task becomes much more complicated when metals with very different melting points are to be combined, or when many compounds with very similar compositions exist in the systems. In many cases, the compounds are not formed directly from the melt, but by a more complex process, such as a peritectic reaction. Typical for this class of the compounds is the existence of several temperature modifications as well as the formation of extended solid solutions. All this requires precise adherence to the synthesis conditions, and sometimes the use of auxiliary sources, e.g. flux.

All of the above issues often complicate the crystal structure determination. For example, insufficient heat treatment is often reflected in the poor quality of diffraction patterns, or the presence of several modifications results in the twinning of the investigated specimens used for single crystal investigations. Therefore, the study of crystal structure requires a combination of many methods, such as powder and single-crystal diffraction, using also synchrotron and neutron sources, metallography and microscopy (TEM), chemical or thermal analysis. Conversely, the structure investigations provide additional guidance for improving the synthesis conditions in order to obtain samples of higher quality. Precise structural information forms the basis for further investigation of the atomic interaction using the chemical bonding calculations.

The developed comprehensive approach to the matter allowed to synthesize numerous new intermetallic compounds, determine their crystal structure, investigate their physical properties and clarify bonding interactions between atoms. Among them are not only ternary and multicomponent compounds, but also a significant number of phases found in well-studied binary systems, or phases whose existence was reported earlier, but whose structure was not established due to the lack of a comprehensive approach to this problem.

Here are some interesting examples from the past and present: $YbAlB_4$ (complex atomic arrangement of $YCrB_4$ (majority) and $ThMoB_4$ (minority) structural motifs) [4]; Mn_6Ga_{29} (four modifications within a narrow temperature range of 100 − 500 K, α↔β phase transformation just above room temperature, complex structures, low symmetries (triclinic, monoclinic), systematic twinning of the investigated single crystal specimens) [5]; Ba_4Al_7 (new phase in the well-studied binary system, which forms peritectically within a narrow "peritectic temperature gap" around 15°C) [6]; $UHg_{6.4}$ (this phase was discovered about 50 years ago, but due to problems in synthesis, the crystal structure was not determined until our investigations) [7].

As examples, two investigations were selected for detailed discussion in this report. (a) compositional evolution of the $NaZn_{13}$ structure motif in the system La–Ni–Ga [8]; (b) synthesis, polymorphism, twinning, crystal structure determination and chemical bonding in $Ba_6Li_8Ga_8N$ [9].

A sequence of morphotropic phase transformations has been found in the series $LaNi1_{3-x}Ga_x$ resulting in five varieties of the $NaZn_{13}$ structure (Figure 1): the cubic phase with aristotype structure at $x = 2$ (space group $Fm\bar{3}c$, Pearson symbol $cF112$), two tetragonal phases at $x = 2.5 – 4.25$ (space group $I4/mcm$, Pearson symbol $tI56$-I) and 7 – 7.5 (space group $I4/mcm$, Pearson symbol $tI56$-II), both with an atomic arrangement of the

$CeNi_{8.5}Si_{4.5}$ type, and two orthorhombic phases at $x = 4.5 – 5.75$ ($LaNi_7In_6$ structure type, space group *Ibam*, Pearson symbol *oI*56) and $x = 6.37 – 6.87$ (a new derivative of the $NaZn_{13}$ prototype structure, space group *Fmmm*, Pearson symbol *oF*112). Complex twinned and multiple twinned (twinning of twins) domain structures, which are revealed for the tetragonal as well as both the orthorhombic phases, clearly indicate temperature-induced polymorphic phase transitions during the formation of these phases.

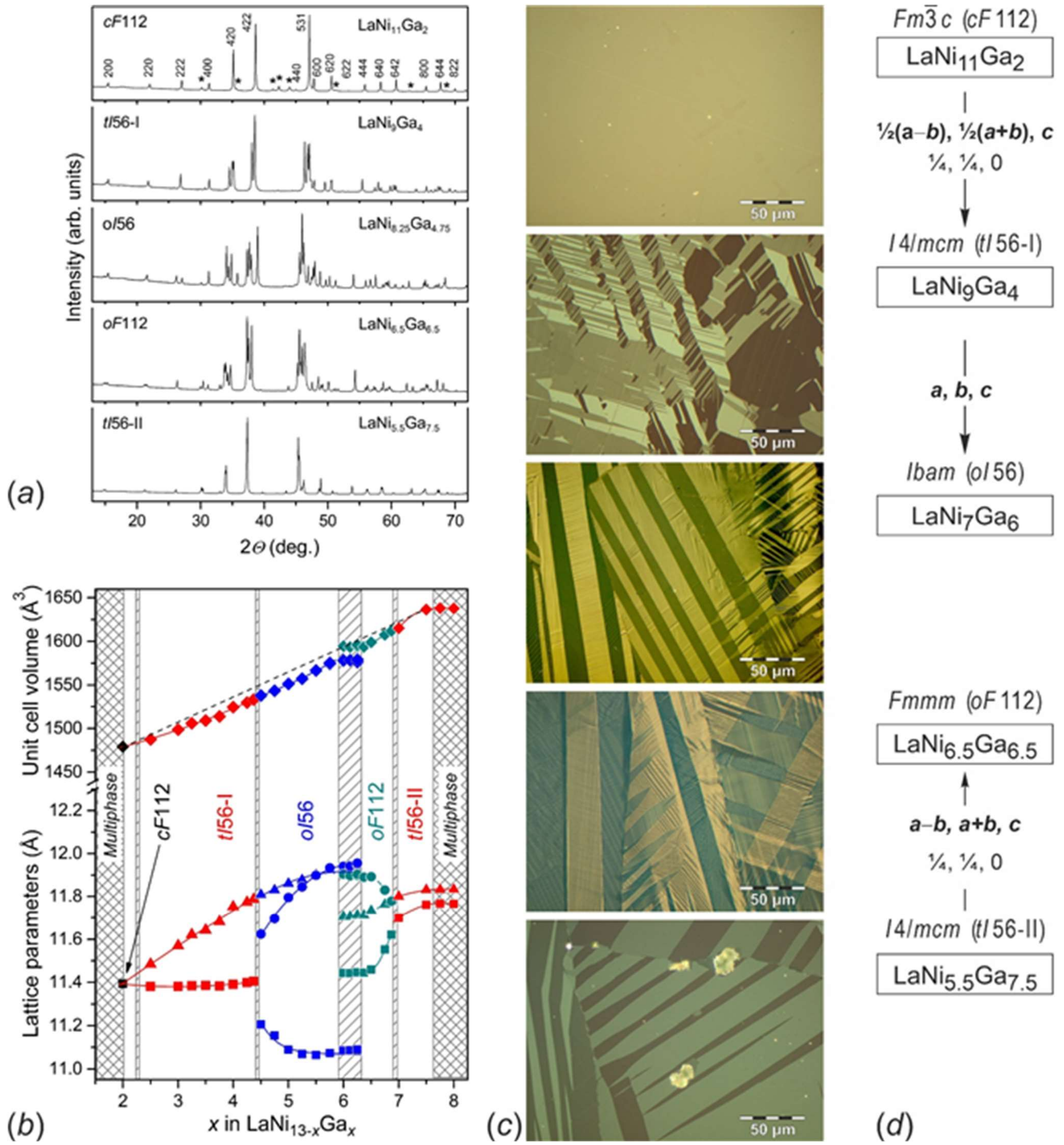

Fig. 1: $LaNi_{13-x}Ga_x$ series: (a) XRPD patterns of the selected samples with five different variants of the $NaZn_{13}$ related structures. Miller indices are given for the $NaZn_{13}$ aristotype. (b) Concentration dependence of the normalized unit cell dimensions a, b, c and volumes (squares, circles, triangles and diamonds respectively). (c) microstructure of the selected samples indicating complex twin formation. (d) group–subgroup relations in the Bärnighausen formalism.

This fact requires optimization of the synthesis process: long-term annealing at temperatures just below the melting point and slow cooling in order to stabilize the structure sufficiently. The multiple twinning makes it practically impossible to analyze this system using a single crystal method. In addition, the complexity of the powder diagrams requires the use of synchrotron radiation to successfully resolve the diffraction peaks in the resulting diffractograms.

The $LaNi_{13-x}Ga_x$ system with 5 varieties of the $NaZn_{13}$ structure is unique because the number of derivatives described for a particular binary or ternary system is usually limited to one or two derivatives. From this point of view, these results can be an insightful example for textbooks on crystal chemistry, since this description of morphotropic phase transformations is accompanied by a gradual change in symmetry and can be described by group-subgroup relationships.

Our studies on the influence of electronegativity difference between the constituent components (ΔEN) and the number of valence electrons per gallium atom (VEC_{Ga}) on the formation of isolated Ga_n clusters in the ternary AE–Li–Ga (AE = alkane earth metal or europium) systems resulted in a series with a variety of Ga_n motifs: isolated Ga atoms, dumbbells, triangles, tetrahedra, tetragonal pyramids, bell-like [Ga_5] clusters and truncated [Ga_9] icosahedra [10]. Moreover, we extended our study by introducing a second anion (N) into the system.

Using Ba, Li, Ga and Li_3N as starting materials, a new quaternary compound $Ba_6Li_8Ga_8N$ was synthesized. It was observed that the nitrogen concentration has an influence on the formed crystal structure of this compound. Thus, two almost identical structures can be formed in space groups $P6_3mc$ ($a = 9.8459(5)$ Å, $c = 6.7995(6)$ Å) and $Pmnn$ ($a = 9.8238(2)$ Å, $b = 17.0472(2)$ Å, $c = 6.449(1)$ Å) by varying the amount of nitrogen. To obtain a phase-pure hexagonal modification, the synthesis must be carried out under nitrogen deficiency conditions, i.e. with a lower concentration of lithium nitride, or with an increase in the amount of lithium. By applying stoichiometric amounts of starting materials, only the formation of the orthorhombic modification is observed.

While the refinement of the structure of the hexagonal modification was trivial and led to an ordered structural model with low residuals ($R1 = 0.033$, $wR2 = 0.077$), the determination of the orthorhombic structure was hampered by the systematic twinning of the investigated single crystals. The initially identified hexagonal metric of the investigated single crystal specimen ($a = 19.68$ Å, $c = 6.85$ Å) showed a discrepancy in the observed extinction conditions which were incompatible with any known space group. All this, together with the poor agreement of the intensities of the equivalent reflexes for any hexagonal (trigonal) symmetries (e.g. $R_{\mathrm{int}} = 0.90$ for Laue class $\bar{3}$), led to the conclusion about the multi-twinning of the unit cells with lower symmetry. The results of high-resolution powder diffraction by using a synchrotron source allowed us to finally confirm the orthorhombic metric of the investigated phase: a typical splitting of the diffraction peaks for such a kind of deformation was observed (Figure 2). Finally, the structure of the orthorhombic $Ba_6Li_8Ga_8N$ has been also successfully refined ($R1 = 0.039$, $wR2 = 0.121$) and resulted in a twin component ratio of 0.456(2) : 0.419 : 0.125.

The basic structural elements that define both modifications are Ga_4 tetrahedra and columns of face-linked Ba octahedra, every second of the latter is occupied by a nitrogen species. The two structures differ only in the orientation of their Ga_4 clusters in relation to the c axis: parallel for the hexagonal structure and antiparallel for the orthorhombic one (Figure 2). The Ga_4 tetrahedra are slightly compressed in the [001] direction, which is reflected in the Ga–Ga contacts of 2.789 Å and 2.798 Å in the base of the tetrahedron compared to the distances d(Ga–Ga) of 2.634 Å and 2.670 Å from the base to the top. Tetrahedra are isolated from each other, the closest distance between them is about 5 Å. Interestingly, despite the similarity of both structures, they do not have a direct group-subgroup relationship and are located on different branches of the “Bärnighausen tree“ originating from the $P6_3/mmc$ space group.

The analysis of the bonding situation was performed by considering the orthorhombic structure. The analysis carried out on the basis of the Zint-Klemm concept resulted in a comparatively good match, so that the structure can be regarded as almost electron-precise with an excess of only one electron: $[Ba^{2+}]_6[Li^{1+}]_8[(4b)Ga^{2-}]_8[N^{3-}]$ e. The effective charges determined as part of the electron density evaluation using the QTAIM technique initially confirm the presence of two types of anions in the form of gallium $[Ga_4]^{8-}$ and N^{3-}.

Thus, the study of intermetallic phases still leads to the discovery of unexpected structural and bonding features. We expect great potential in the discovery of new binary compounds, as well as in the further synthesis and study of gallium clusters, for example, in compounds with rare earth metals.

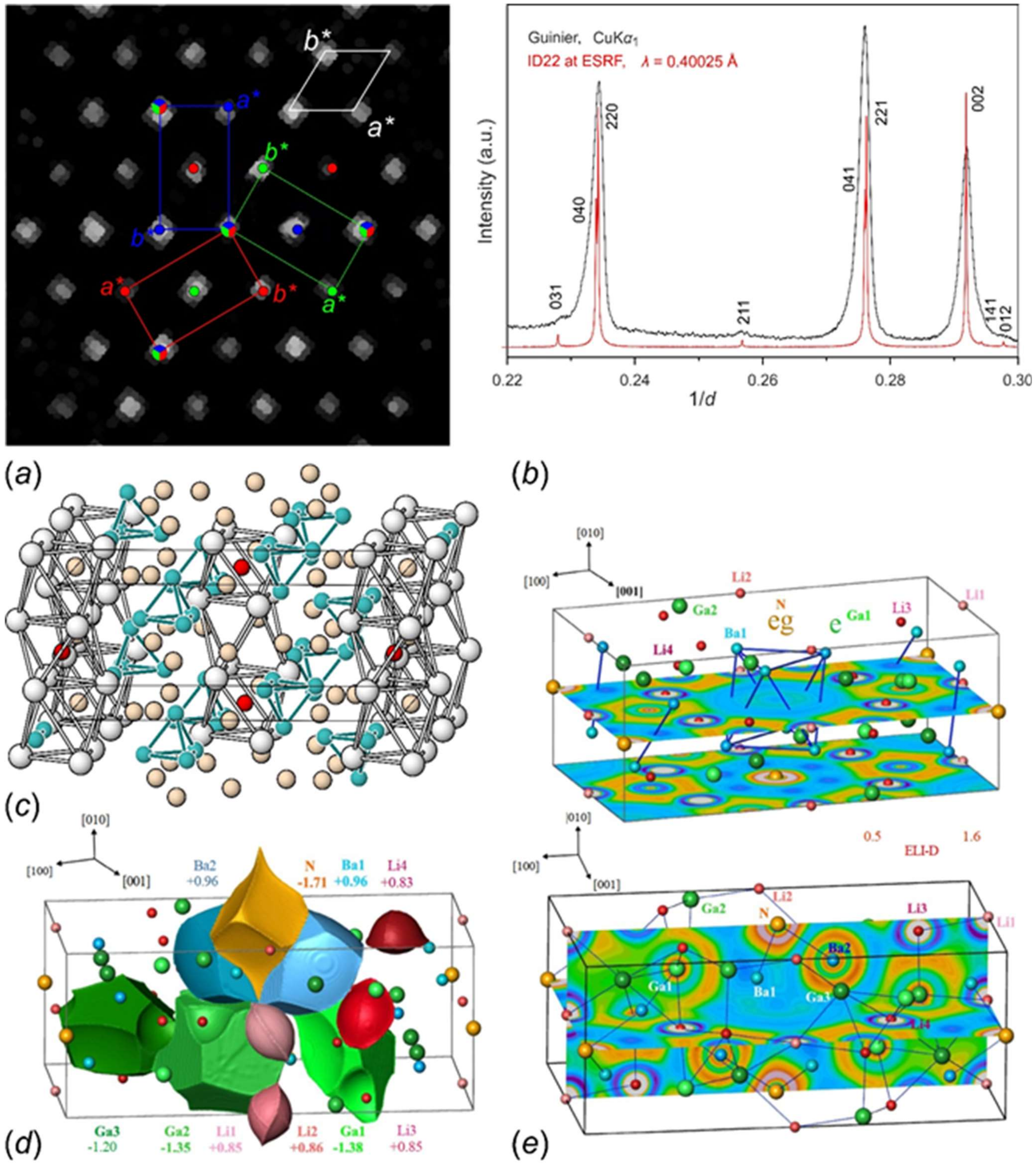

Fig. 2: Orthorhombic $Ba_6Li_8Ga_8N$ (Pmnn): (a) Reconstructed image of the reciprocal space in the projection along [001], the rectangles emphasize the arrangement of the twin domains; (b) Comparison of the powder diffraction patterns obtaining by laboratory and synchrotron sources; (c) crystal structure with emphasized [Ga_4] tetrahedra and columns formed by Ba_6 octahedra; (d) shapes and charges of the effective QTAIM atoms; (e) (Top) ELI-D distribution at planes (010) and (020); (Bottom) ELI-D distribution at planes (002) and (020).

External Cooperation Partners

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