Crystal Growth by Chemical Vapor Transport

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A large number of compounds from different classes – intermetallic phases, pnictides, oxides, chalcogenides, and halides have been crystallized by chemical vapor transport. A new research focus has recently been on intermetallic compounds that crystallize in the FeSi structure type. The obtained crystals were provided for various joint projects, in an effort to investigate their physical and chemical properties. The development of physical measurement methods to ever more sensitive systems opens up new perspectives for chemical transport. Materials that have previously been unsuitable for measurements due to their small size can now be characterized very precisely in terms of their physical properties. After 2018, monophosphides and -arsenides of niobium and tantalum became the subject of further publications.

Chemical vapor transport reactions represent an efficient method for the synthesis and crystal growth of a variety of inorganic and intermetallic compounds. With their help, single-phase products, in many cases as monocrystalline material of high purity, may be synthesized and/or crystallized with comparatively little effort. Well-developed individual crystals with readily identifiable crystallographic faces are frequently obtained. In the last few years, a number of intermetallic phases [1-3], pnictides [4-9], chalcogenides [10-13], oxides [14], and halides [15], have been crystallized by chemical vapor transport, thus contributing to the measurement of their physical, chemical and structural properties.

Chemical transport reactions are particularly suitable as an alternative to other methods of synthesis or crystallization in the following cases:

• One or more components of a compound have a high vapor pressure at the melting temperature;
• A phase exhibits a very high melting temperature;
• A compound decomposes, e.g. peritectically, before the melting temperature is reached;
• A phase has merely narrow regions of existence in the subsolidus region;
• A phase is not crystallizable from the melt, respectively a material shows one or more phase transitions before the melting temperature is reached (low-temperature modifications);
• Phases differ only slightly in their chemical composition, such as Magneli phases.

The chemical transport reactions can be described by thermodynamic laws, and thus it is possible to predict efficient transport means, optimal reaction conditions, the transported compound or compounds and their amounts of substances. The choice and control of the experimental parameters of the chemical transport experiment, both the chemical composition of the material and its amount of substance can be determined. The composition of the deposited crystals depends on the composition of the starting material, on the temperatures of source and sink, on the total pressure in the transport vial as well as on the amount of the starting material related to the amount of deposited crystals.

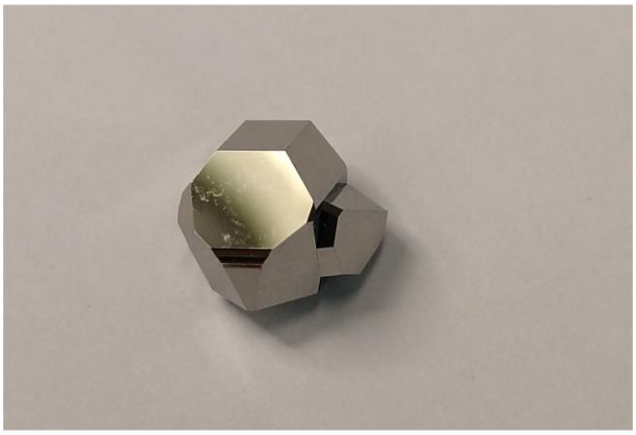

Fig. 1: NbP crystal (grown at conditions: ϑ_{source} = 900 °C, ϑ_{sink} = 1000 °C, size: approx. 8x8x8 mm).

Recently, a major focus of research has been on the study of compounds that crystallize in the FeSi structure type.
(https://www1.cpfs.mpg.de:2443/CMS_02)
The absence of centrosymmetry in this chiral and polar crystal structure is the reason for many interesting physical and chemical properties - unusual magnetic ordering (skyrmions), interesting catalytic activity, unconventional superconductivity, ferroelectricity, optical birefringence. A number of the FeSi type compounds were grown by CTR in the form of well-formed single crystals: e.g. FeSi, CoSi, FeGe and CrGe. Especially CrGe and FeGe are difficult to obtain as single crystals by other methods because they form in peritectic and peritectoid reactions, respectively, and in the case of FeGe, the FeSi type of structure is present in the low-temperature modification.

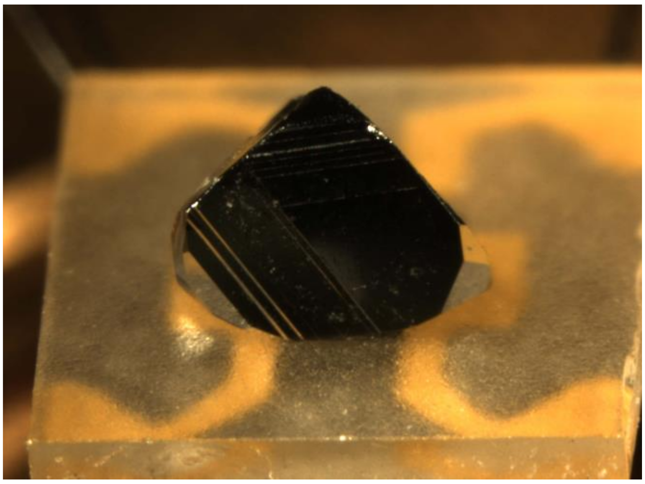

Fig. 2: FeGe crystal of the cubic low-temperature modification (grown at conditions: ϑ_{source} = 575 °C, ϑ_{sink} = 535 °C, size: approx. 1.6x1.6x1.6 mm).

References

[1]* *Absolute Structure from Scanning Electron Microscopy*, U. Burkhardt, H. Borrmann, P. Moll, M. Schmidt, Y. Grin, and A. Winkelmann, Sci. Rep. **10** (2020) 4065, doi.org/10.1038/s41598-020-59854-y

[2]* *Electronic band structure and proximity to magnetic ordering in the chiral cubic compound CrGe*, J. Klotz, K. Götze, T. Förster, J. A. Bruin, J. Wosnitza, K. Weber, M. Schmidt, W. Schnelle, C. Geibel, U. Rößler, and H. Rosner, Phy. Rev. B **99** (2019) 085130, doi.org/10.1103/PhysRevB.99.085130

[3]* *Chiral topological semimetal with multifold band crossings and long Fermi arcs*, N. Schröter, D. Pei, M. Vergniory, Y. Sun, K. Manna, F. de Juan, J. Krieger, V. Süß, M. Schmidt, P. Dudin et al., Nat. Phys. **15** (2019) 759, doi.org/10.1038/s41567-019-0511-y

[4]* *Orbital effect and weak localization in the longitudinal magnetoresistance of Weyl semimetals NbP, NbAs, TaP, and TaAs*, M. Naumann, F. Arnold, M. Bachmann, K. Modic, P. Moll, V. Süß, M. Schmidt, and E. Hassinger, Phys. Rev. Mater. **4** (2020) 034201, doi.org/10.1103/PhysRevMaterials.4.034201

[5]* *Strong anisotropy of the electron-phonon interaction in NbP probed by magnetoacoustic quantum oscillations*, C. Schindler, D. Gorbunov, S. Zherlitsyn, S. Galeski, M. Schmidt, J. Wosnitza, and J. Gooth, Phys. Rev. B **102** (2020) 165156, doi.org/10.1103/PhysRevB.102.165156

[6]* *Effect of uniaxial stress on the electronic band structure of NbP*, C. Schindler, J. Noky, M. Schmidt, C. Felser, J. Wosnitza, and J. Gooth, Phys. Rev. B **102** (2020). 035132, doi.org/10.1103/PhysRevB.102.035132

[7]* *Antiferromagnetic Ordering and Transport Anomalies in Single-Crystalline $CeAgAs_2$*, M. Szlawska, D. Gnida, P. Ruszala, M. Winiarski, M. Samsel-Czekala, M. Schmidt, Y. Grin, and D. Kaczorowski, Materials **13** (2020) 3865, doi.org/10.3390/ma13173865

[8]* *Pressure tuning of the electrical transport properties in the Weyl semimetal TaP*, M. Besser, R. dos Reis, F.-R. Fan, M. O. Ajeesh, Y. Sun, M. Schmidt, C. Felser, and M. Nicklas, Phys. Rev. Mater. **3** (2019) 044201, doi.org/10.1103/PhysRevMaterials.3.044201

[9]* *Extremely high conductivity observed in the triple point topological metal MoP*, N. Kumar, Y. Sun, M. Nicklas, S. Watzmann, O. Young, I. Leermakers, J. Hornung, J. Klotz, J. Gooth, K. Manna et al., Nat. Commun. **10** (2019) 2475, doi.org/10.1038/s41467-019-10126-y

[10]* *Selective Orbital Imaging of Excited States with X-Ray Spectroscopy: The Example of α-MnS*, A. Amorese, B. Leedahl, M. Sundermann, H. Gretarsson, Z. Hu, H. Lin, C. Chen, M. Schmidt, H. Borrmann, Yu. Grin et al., Phys. Rev. X **11** (2021) 011002, doi.org/10.1103/PhysRevX.11.011002

[11]* *Crystal Structure of $Fe_{1-x}Te$ (x=0.38)*, Y. Prots, L. Akselrud, M. Schmidt, U. Burkhardt, S. Rößler, Yu. Grin, and U. Schwarz, Z. Anorg. Allg. Chem. **647** (2021) 113, doi.org/10.1002/zaac.202000389

[12]* *Preparation and Crystal Growth of Transition Metal Dichalcogenides*, M. Schmidt, J. Gooth, and M. Binnewies, Z. Anorg. Allg. Chem. **646** (2020) 1183, doi.org/10.1002/zaac.202000111

[13]* *Two types of magnetic shape-memory effects from twinned microstructure and magneto-structural coupling in $Fe_{1+y}Te$*, S. Rößler, C. Koz, Z. Wang, Y. Skourski, M. Doerr, D. Kasinathan, H. Rosner, M. Schmidt, U. Schwarz, U. Rößler, and S. Wirth, Proc. Natl. Acad. Sci. USA **116** (2019) 16697, doi.org/10.1073/pnas.1905271116

[14]* *Multiple low-temperature skyrmionic states in a bulk chiral magnet*, L. J. Bannenberg, H. Wilhelm, R. Cubitt, A. Labh, M. Schmidt, E. Lelièvre-Berna, C. Pappas, M. Mostovoy, and A. Leonov, npj Quantum Materials **4** (2019) 11, doi.org/10.1038/s41535-019-0150-7

[15]* *Scale-invariant magnetic anisotropy in $RuCl_3$ at high magnetic fields*, K. Modic, R. McDonald, J. P. Ruff, M. Bachmann, Y. Lai, J. Palmstrom, D. Graf, M. Chan, F. Balakirev, J. Betts, et al., Nat. Phys. **17** (2021) 240, doi.org/10.1038/s41567-020-1028-0

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