How to Get High Quality, Single Crystalline Material with Well-Defined Crystallographic Orientation and Handedness

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High-purity and crystallographically well-characterized crystals or polycrystalline material are the basis for the experimental investigations of the structure-property relationships of the – predominantly – intermetallic phases at our institute. The CVT technique is a method for preparing high-quality crystals that has been well established at the institute for many years and is used with great success on known and new phases. The possibilities of sample preparation have been significantly expanded in recent years through the improvements of the microstructure analysis and micro-preparation. Spatially resolved crystallographic characterization of polycrystalline microstructures by the EBSD method and micrometer-precise cutting by means of the FIB techniques make it possible to obtain single crystals and microdevices with a defined crystallographic orientation and handedness from polycrystalline material. In a current project, we used these methods – CVT, EBSD and FIB – to investigate the twinning of the chiral phase CoSi with the aid of the TEM.

Chemical vapor transport - status and new developments

Chemical Vapor Transport (CVT) is an efficient method for synthesizing, and especially growing, crystals of a variety of inorganic compounds. It can be used to synthesize and/or crystallize single phase products, in many cases as single crystalline material of high purity. Well-formed single crystals with easily recognizable crystallographic surfaces are often obtained [1].

In recent years, a large variety of crystals have been synthezised by CVT to study their physical, chemical and structural properties. The development of increasingly sensitive measurement techniques and instrumentation has opened up new perspectives for chemical transport, as the resulting crystals, which were previously unsuitable for physical measurements due to their small size, can now be characterized very precisely. Recently, interest has shifted from the theory of chemical transport to its application, modification, and adaptation to current materials systems and problems. The CVT is an alternative to crystal growth from the melt or from solutions, especially for compounds with high melting temperatures and such that decompose during melting, or where one or more components have high decomposition pressures. This is also true for compounds that do not coexist with the melt (low-temperature modifications) or for compounds that differ only slightly in chemical composition, such as Magneli phases, where precise control of partial pressures (e.g. of $p(O_2)$) is essential for crystallization. The CVT can be described by thermodynamic data of the solid and gaseous species contained in the system. These data can be used to simulate the transport process. This makes it possible to calculate efficient transport agents, optimal temperature gradients and transport rates, and to predict the transported compound(s). By selecting and controlling the experimental conditions, both the chemical composition of the crystallized material and its amount can be determined. Both properties can be influenced specifically by the choice of transport additives, the composition of the starting material, the control of the source and sink temperatures, the total pressure and the reaction time. The chemical composition of the source material and the deposited crystals are not always the same.

Recently, our focus has been on growing crystals of compounds that crystallize in the FeSi structure type (B20) as well as well-formed homochiral single crystals of the element tellurium. In particular, single crystals of FeSi, CoSi, FeGe and CrGe have been grown by CVT. Specifically, the latter two are difficult to obtain as single crystals by any other methods because FeGe forms in a peritectoid reaction and CrGe forms in a peritectic one. In addition, in the case of FeGe, the interesting FeSi structure is present in the low-temperature modification. CoSi and FeGe (see Figure 1) were at first chemically transported conventionally, i.e. with a clear spatial separation of source and sink materials and a temperature gradient between 50 and 100 K. Subsequently, the compounds were also crystallized via short-distance transport using microdiffusion, i.e., the crystallization took place directly on the source material or in its immediate vicinity in a temperature gradient of less than 5 K with the addition of small amounts of transport agents. In contrast to conventional crystallization by chemical transport, which is based on the

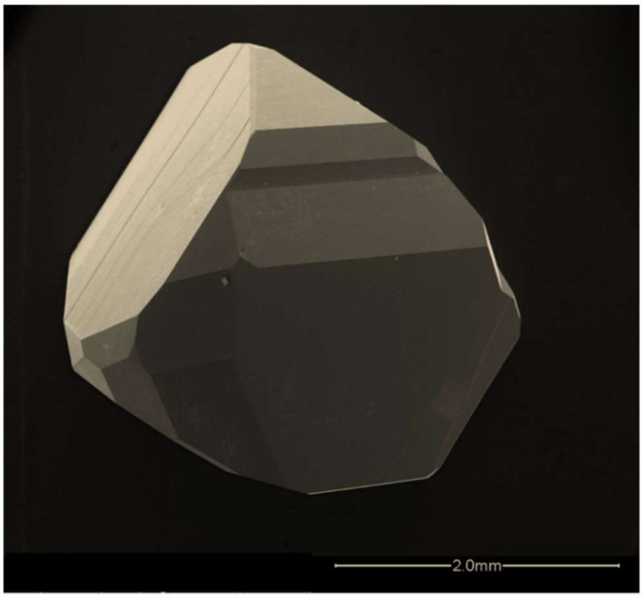

Fig. 1: FeGe (cubic modification) crystallite prepared by Chemical Vapor Transport (CVT) method.

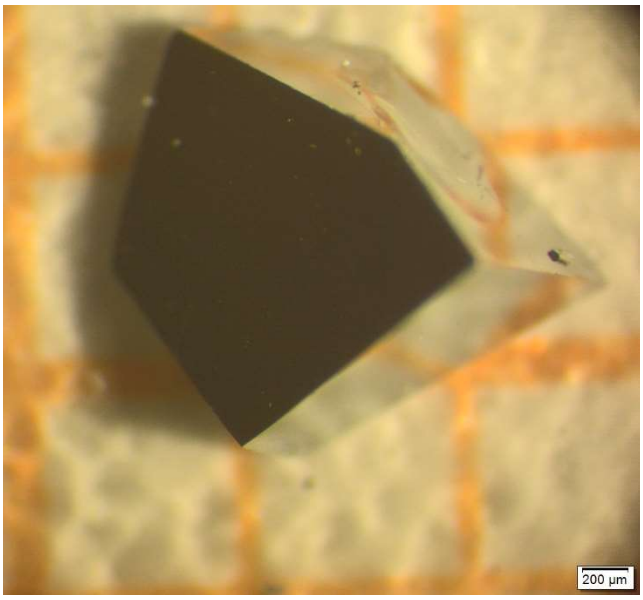

Fig. 2: Te crystal prepared by Chemical Vapor Transport (CVT) method using sulfur as transport agent.

different position of the transport equilibrium on the source and sink sides, the necessary partial pressure difference in short-distance transport results from the different free standard enthalpies of the source material before and after crystallization. Short distance transport is effective even with small partial pressure differences in the range of 10^{-6} bar. In contrast to conventional transport, where the focus is usually on crystallizing single crystals with as little growth disorder as possible, crystals with many domain boundaries have been grown using short-distance transport with the aim of structurally characterizing the transition between the domains.

In addition to the intermetallic compounds with B20 structure, the elements manganese (crystals not obtained by CVT), selenium and tellurium have also been studied with respect to the relationship between crystal structure – with a focus on chirality – and their physical properties. The tellurium crystals used were grown by different variants of chemical transport and under different conditions (transport agent, amount of transport agent, temperature gradient, ampoule geometry) with the aim of obtaining large crystals that are as homochiral and well-formed as possible. Tellurium can be chemically transported with both iodine and sulfur. The transport additive used has a significant influence on the habitus of the obtained crystals. The use of sulfur as a transport additive has proven to be particularly suitable, both in terms of the crystal habitus and the chemical purity of the deposited crystals (see Figure 2).

Scientific platform group metallography – status and new developments

The metallographic characterization of the microstructure of an alloy provides information on the chemical composition of the phases, the phase distribution, the size of the grains and their crystallographic orientation. It has been, and is used, in a variety of ways to assess sample quality, but is also important in recent projects for determining phase equilibria [2, 3], characterizing crystallization processes (**CMS_10_Antonyshyn**), structural phase transformations [4], **CMS_07_Prots**, and process-related microstructural changes (**COLL_03_Antonyshyn_Altendorf**).

The microstructure as it is investigated at the MPI-CPfS is examined mostly on embedded sample pieces, the surfaces of which are polished flat in several grinding and polishing steps. The finish is - if necessary - a chemical-mechanical polishing step with 0.25 µm oxide abrasive particles. Adapted grinding preparation agents and equipment are available for water- and air-sensitive substances. The microstructure is characterized using light and scanning electron microscopes. The EDX (energy dispersive X-ray spectroscopy) and WDX (wavelength dispersive X-ray spectroscopy) methods are used in the SEM (scanning electron microscope) to determine the local chemical composition. With good surface quality, the SEM based method EBSD (electron backscatter diffraction) provides information on the crystallographic orientation of the surface material at the location of the electron beam.

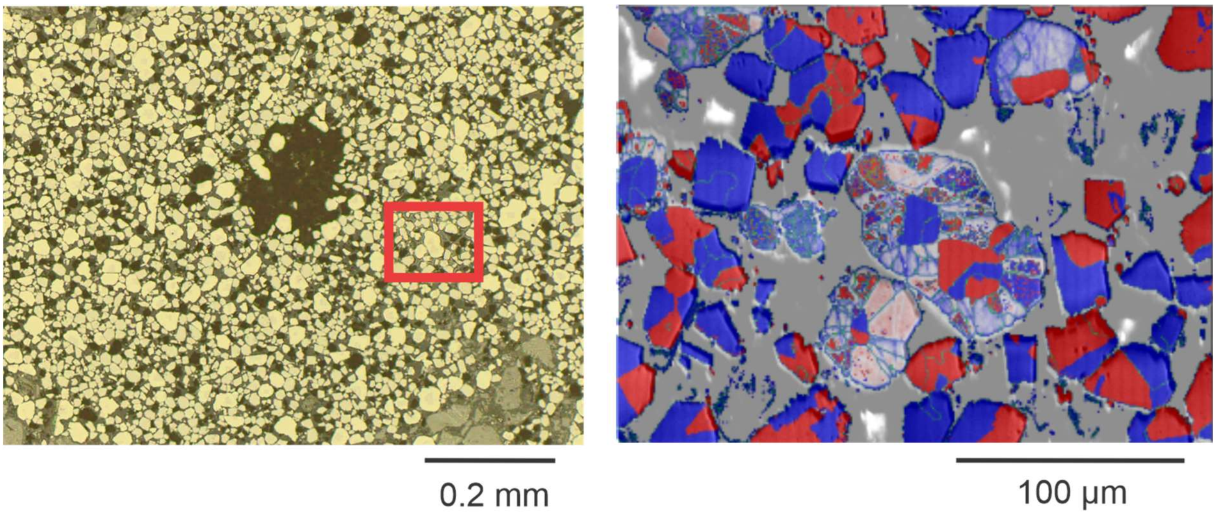

Fig. 3: (Left) CoSi crystallites prepared by the short distance Chemical Vapor Transport (CVT) method; (Right) enantiomorph distribution map showing A-form (red) and B-form (blue) overlayed to the SEM image of the selected area (left image: red frame); light domains are assigned to the Co_2Si phase.

Recent improvement in the EBSD pattern evaluation allows to distinguish between the pattern of both enantiomorphs of non-centrosymmetric phases [5]. EBSD can be carried out on metallographically prepared microstructures. In addition, this method features a good spatial resolution, allowing the determination of the distribution of enantiomorphic domains in polycrystalline materials.

Handedness analysis of the chiral phase CoSi on micro- and nanoscale

Intermetallic phases with a non-centrosymmetric crystal structure are currently in the focus of much scientific research due to their unusual physical and chemical properties. The absence of the inversion center of the crystal structure can lead to unusual magnetic order, may cause unusual superconducting states and is associated with special catalytic properties of these materials. The determination of the absolute structure, as in the case of phases with the chiral B20 crystal structure (FeSi type), is therefore of particular interest. The EBSD method is a comparatively simple method with which the handedness of single crystals as well as polycrystalline materials can be determined in a scanning electron microscope. The method is based on the quantitative comparison (cross correlation method) between the experimental and calculated EBSD patterns of both enantiomorphs. The better understanding of the dynamic electron multiple scattering processes allows the accurate calculation of EBSD patterns that reveal handedness-dependent contributions in the case of chiral crystal structures. Consequently, the match with the experimental EBSD patterns are different and allow the reliable assignment of handedness. This method can be used to evaluate complete EBSD mappings and to determine the distribution of enantiomorphs in a polycrystalline material. It has been shown that crystals prepared by the CVT method provide particularly good EBSD patterns without any surface treatment. For polycrystalline materials, the usual metallographic grinding and polishing methods are often sufficient to achieve the necessary surface quality. A first application for the EBSD-based, spatial resolved chirality assignment is our investigation of CoSi crystallites [6] prepared by the short distance CVT method. The EBSD based enantiomorph distribution map for a great number of CoSi crystals (s. Figure 3) shows that almost all crystals consist of several domains of different handedness. In contrast, conventional long distance CVT results in high quality CoSi single crystals with well-defined handedness [5]. The identification of homochiral domains in a crystallite by the enantiomorph distribution map enabled the target preparation of the interface between domains of different chirality (see Figure 4 *left*). After the lift-out and suitable FIB (focused ion beam) thinning and polishing, the interface was suitable for investigations by means of the transmission electron microscopy. The HR-STEM images show that the atomic arrangement at the interface is very similar to the undisturbed crystal structure (Figure 4 right; **CMS_05_Simon**). The derived model describes the atomic arrangement as a stacking fault of almost undisturbed planes of CoSi crystal structure which leads to a change in handedness on both sides of the interface. Quantum chemical calculations show the altered chemical bonding at the interface [6].

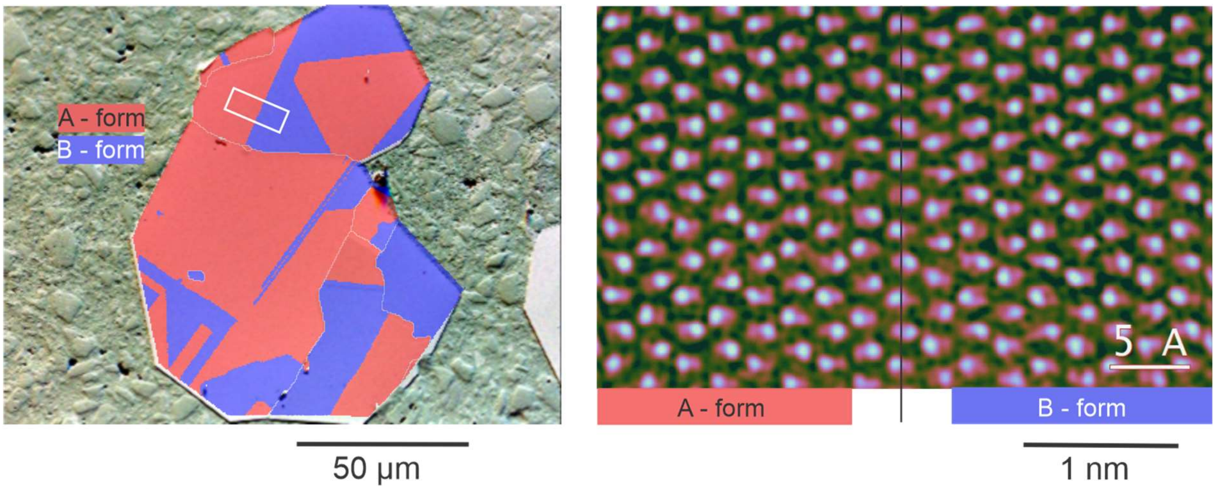

Fig. 4: (Left) CoSi crystallite with A-form (red) and B-form (blue) domains of different handedness; the TEM lamellae at the interface (white frame) are cut by FIB technique; (Right) HR-STEM image along [010] at the interface between the A- and B-form (cf. CMS_05_Simon).

Currently, we investigate the influence of handedness on the physical and chemical properties of selected intermetallic phases. The EBSD method provides the determination of the handedness of individual single crystals or can be used to create enantiomorph distribution maps of a polycrystalline material. The development of the FIB based micro-preparation technique enables individual grains or areas with a defined crystallographic orientation and handedness to be cut out of a microstructure with micrometer precision. For example, single crystals of the chiral high-temperature phase β-Mn with defined handedness were cut from polycrystalline material. A unique feature in this context is the determination of the handedness of crystals of elements with a chiral crystal structure. The EBSD pattern simulation provide chirality-dependent differences in the EBSD pattern for the element structures β-Mn, Te and γ-Se [7, 8]. In contrast, the determination of the handedness by X-ray diffraction experiments is not possible due to vanishing differences in the intensities of the Friedel pairs. The FIB cuts for this and other related projects are realized in close cooperation with the department PQM. The preparation of enantiopure samples from a microstructure opens up many possibilities for systematic investigations of handedness-dependent properties.

External Cooperation Partner

A. Winkelmann (AGH University of Science and Technology, Kraków, Poland).

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