

THE ATOMIC-SCALE ASPECTS OF TWINNING AND POLYTYPOISM IN MINERALS

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Abstract

Phase transformations in minerals are important indicators of geochemical and thermodynamic changes during crystal growth. Initial stages of phase transformations can be recognized by the formation of thermodynamically or chemically induced planar defects, such as twin, antiphase, or inversion boundaries in the affected crystals. Based on the principles of crystal chemistry, some early scientists suggested that the atomic structure of the twin boundary must be related to the existing polymorphic modification of the major phase. The confirmation of this hypothesis was not possible until the development of modern electron microscopy techniques, which enabled a direct insight into the local structure and chemistry of twin boundaries at the atomic scale. Our studies of twins and other translational defects in minerals have shown that their formation is chemically induced by specific dopants that stabilize the particular polytypic structure. Inherent anisotropy imposed by the chemically induced transformation fault (*e.g.* growth twin) causes exaggerated growth of the crystal parallel to the fault plane as long as geochemical and thermodynamic conditions favour the formation of faulted stacking. These initial growth stages dictated by the growth of the chemically induced fault are clearly reflected in the final morphology of the crystals and can be recognized by the so-called twin-plane re-entrant angles and the additional symmetry elements that can be observed on such crystals. Because of commonly complex geochemical conditions minerals incorporate an assortment of foreign elements that are present during crystal growth, only one of these elements, however is responsible for the faulted stacking (*e.g.* twinning). In order to identify the elements that trigger twinning in minerals we developed new techniques that enable atomic-scale determination of the interfacial crystal chemistry. The investigations of twinning in minerals represents one of the fundamental scientific challenges that offers possibilities for true understanding of the basic building principles of solids and fundamentals of phase transformations in minerals.

Keywords: twinning, phase transformations, sphalerite, spinel, pyrite, bixbyite, perovskite, rutile.

Introduction

In prevalently ionic compounds, like some oxides, chalcogenides and halides, one of the species (often anionic) constitutes close-packed layers of atoms. The layers can then be stacked in either cubic (*ccp*) or hexagonal (*hcp*) sequence, or even some more complex structures can be built by varying the two stackings. A hexagonal sequence is built by stacking the layers in two (out of three) unique positions (*A* and *B*) along the plane normal, coinciding with the hexagonal *c*-axis. If however, the close-packed layers are stacked in all three positions (*A*, *B* and *C*) the resulting sequence is cubic, and when repeated, identical stacking is observed in four directions coinciding with $\langle 111 \rangle$ directions of the cubic structure. $\{111\}$ planes of *ccp* structures and $\{0001\}$ planes of their *hcp* analogues are thus aligned parallel with the rudimentary close-packed layers. The rest of the atomic species (*e.g.* cations) occupy the interstitial sites available between any two closed-packed layers of anions. Three basic types of interstitials exist: (i) lower tetrahedral Type-I (at $\frac{1}{3}$ of the interlayer distance), (ii) central octahedral (at $\frac{1}{2}$ of the height) and (iii) upper tetrahedral Type-II (at $\frac{2}{3}$ of the height). While the stacking of the close-packed layers defines the common sub-lattice framework, discrete structures emerge by specific occupancy of the available intersti-

tials. For example, a rock-salt structure is obtained when all octahedral sites in anionic *ccp* sublattice are occupied by cations. Typical representatives of this structure are periclase (MgO), galena (PbS) and halite (NaCl). If however anionic close-packed layers are stacked in an *hcp* sequence, and occupied interstices remain octahedral, we get nickeline, a hexagonal analogue of the rock-salt structure. Typical representatives of this structure are troilite (FeS) and nickeline (NiAs). Another set of correlated structure types is produced if one set of tetrahedral sites is occupied instead of the octahedral ones. This produces sphalerite (*ccp*) and wurtzite (*hcp*) structure types, named after the cubic and hexagonal polymorphs of ZnS. These structures in particular are very prone to polymorphism and other phase transformations between the two (cubic and hexagonal) endmembers. For example, zincite (ZnO) crystallizes in wurtzite (*hcp* sub-lattice; Type-I tetrahedral interstices occupied), sphalerite (*ccp* sub-lattice; Type-I tetrahedral interstices occupied), as well as in the rock-salt (*ccp* sub-lattice; octahedral interstices occupied) structure type. The largest variety of anion sub-lattice types are found in moissanite (SiC). It does not occur only in form of simple cubic and hexagonal polymorphs, but it exists in several intermediate repeat sequences, known

as polytypes. In a similar way more complex structures can be built within the common structural sub-lattices. For example, in spinel (AB_2O_4) all three types of interstitials are partially occupied, in perovskite (ABO_3)

cation A lies in the anionic sublattice and $\frac{1}{4}$ of the available octahedral sites are occupied by cations B, and all these structures have polymorphic counterparts or even form polytypes.

Polymorphic phase transitions and twinning in minerals

Each polymorph (or polytype) is stable at different p-T conditions. Quite often however, different polytypes coexist, for example sphalerite *ccp* layers in *hcp* wurtzite, or *hcp* enargite in *ccp* luzonite, *etc.* (PÓSFÁI & BUSECK, 1997). This can happen when the minerals pass through the phase transformation temperature so fast, that there is not enough time to completely establish the new equilibrium structure. Another possibility is chemical stabilization of high-temperature polymorphs, so that they can form at much lower temperatures, as long as the particular dopant is available during crystal growth. For example, in HgS the transformation temperature is lowered by the presence of Zn (DICKSON & TUNELL, 1959), whereas in ZnS it is lowered under S-deficient environment (AKIZUKI, 1981). Phase transformations in minerals are therefore important marker of thermodynamic, as well as geochemical conditions during crystal growth. Polytypic sequences are rarely fully evolved and periodic. They may form irregular modular structures or even appear in form of isolated planar faults that have a stacking of a higher-temperature polymorph. As for the polytypes, the cause for the formation of polytypic faults can either be kinetic or thermodynamic. They form as a consequence of mechanical stress, rapid changes of p-T conditions, incorporation of dopant elements, *etc.* While kinetically induced defects can easily be translated through the crystal and even annealed out by suitable thermal treatment, chemically induced faults are thermodynamically stable and can not be moved. Kinetic defects are dislocations, stacking faults (*e.g.* *hcp* SFs in sphalerite, or *ccp* SFs in zincite) and deformation twins (*e.g.* rutile), while chemically induced faults are growth twins, antiphase and inversion boundaries (REČNIK *et al.*, 2001). The most significant difference between the kinetic and thermodynamic defects is that the latter have changed chemistry compared to that of the hosting crystal. The presence of growth twin, antiphase or inversion boundaries is also clearly reflected in crystal morphology (exaggerated growth along the fault planes, the presence of twin-plane re-entrant angles, *etc.*). Therefore they are usually easily distinguished from the kinetic defects.

Chemically induced faults are growth defects that nucleate in the initial stages of crystal growth. They are result of structurally confined 2D chemical reaction between the dopant and the major phase (REČNIK *et al.*, 2001). In the nucleation stage, dopant atoms are chemisorbed (react) to specific crystallographic planes of the host in highly ordered manner, controlled by the surface structure. Chemisorption does not take place

with any alien species, but only with those, which can form a chemical bond to given structural environment (common sub-lattice framework) in a similar way as the atoms of the hosting structure. Most of the alien atoms do not cause any larger disruption to the structure (they form solid solution), but some however, impose an irreparable fault in the stacking (*e.g.* *hcp* instead of *ccp*) of otherwise uniform sub-lattice framework. This has a remarkable effect on the next layers that are built in. By introducing a sub-lattice fault, all new layers of the growing host crystal are symmetrically translated by the imposed crystallographic operation. Once such 2D cluster is formed it will persist to grow as long the conditions permit its formation. As the crystals always tend to overgrow defects or inclusions, in the same propensity they try to overgrow the inherent fault. However, because of the imposed symmetry, crystal domains on both sides of the fault are equally successful in this attempt, so instead of overgrowing the fault, they assist its growth. In this way, the dopant atoms that caused the sub-lattice fault will continue to produce the faulted layer (where they are most easily accommodated) while the host crystal is rushing to heal the defect. Thermodynamic stability of the growing 2D structure in most cases is orders of magnitude higher than that of the hosting crystal (REČNIK *et al.*, 2012). This has dramatic effects on crystal morphology. In the initial stages of growth, crystals infected with thermodynamically stable faults grow exaggeratedly along the fault plane forming unusual plate-like crystals with distinct tabular morphology (*e.g.* contact twins), if the faults are grown in more equivalent directions the host crystal grows in all these directions (*e.g.* interpenetration twins). In the later stages, when thermodynamic or geochemical conditions change to an extent that the nucleation of the faulted layer is stopped, crystal domains continue to overgrow the inherent fault, which causes development of twin-plane re-entrant angles, characteristic not only for chemically induced twin boundaries, but also other chemically induced faults such as antiphase and inversion boundaries.

In general, there is not much known about the origin of thermodynamic faults. While there is a lot of knowledge about the morphology and crystallography of growth twins, their local structure and chemistry have rarely been assessed quantitatively on the atomic scale. From the recent studies of growth twin, antiphase and inversion boundaries in perovskite (REČNIK *et al.*, 2001), zincite (REČNIK *et al.*, 2001), sphalerite (ŠROT *et al.*, 2003), pyrite (DANEU *et al.*, 2005), spinel

(DANEU *et al.*, 2007), bixbyite (KLEEBE *et al.*, 2008) and rutile (DANEU *et al.*, 2007) it is evident that the local structure in most cases is rather trivial, whereas their local chemistry can be more challenging, especially in natural minerals, due to complex geochemical conditions during crystal growth. Out of all foreign elements that can be present near the twin boundary, only one is actually responsible for the formation of faulted stacking. In all cases studied so far, it appears that the local chemistry and structure of these interlayers is closely correlated to the first binary compound that exists between the host phase and the dopant. These 2D phases can never exist stand-alone and can be understood as the preparatory stage of the binary phase formation. They nucleate in those planes of the host phase (preferably close-packed planes, or other high density planes) that most efficiently accommodate the dopant

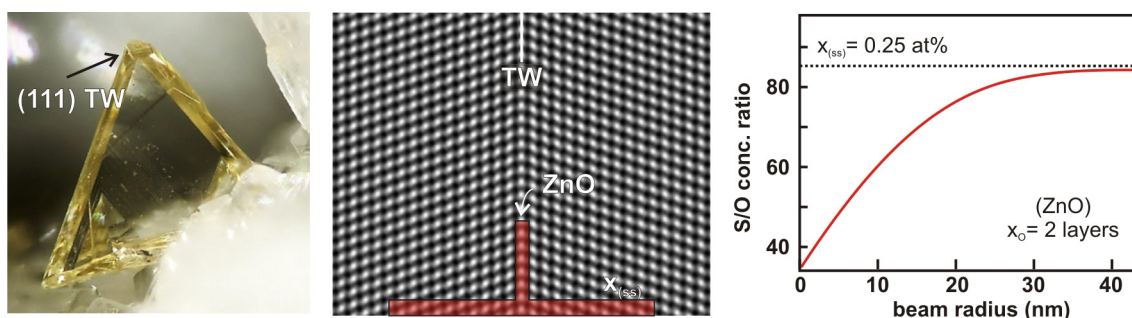
element. As opposed to the pure phase, crystals with these defects more efficiently lower the total free energy (they are thermodynamically more stable than the major phase), which is reflected in exaggerated growth. In systems that are prone to the formation of chemically induced faults, a binary phase (between the major phase and the dopant) would form at elevated temperatures. In binary phase diagrams, where available, these phases are polytypoidic incongruent-melting compounds with modular structures comprising structural elements of both end-phases. Similar structural features as found in these compounds, can be observed in chemically induced faults that nucleate at lower temperatures. Local chemistry is therefore the most important indicator of the origin of growth faults. In the following, few examples of chemically induced twinning in natural minerals are presented.

(111) twins of sphalerite and their relation to zincite

The first systematic nanostructural analysis of growth faults in natural minerals was performed on sphalerite (ZnS) crystals from Trepča in Kosovo (ŠROT *et al.*, 2003). The crystals display characteristic twin-plane re-entrant angles, which indicate the presence of {111} twin boundaries. HRTEM analysis revealed that the local stacking across the twin boundary changes from cubic (*ccp*) to hexagonal (*hcp*). It was shown that the twin boundaries are significantly enriched in oxygen, which triggers local sphalerite-to-wurtzite transformation. The local chemistry and the stacking at the twin boundaries in sphalerite is similar to that of zincite, the stable polymorph of ZnO, which crystallizes in the

wurtzite structure. From the structural and compositional point of view, (111) twin plane is nothing but (0001) layer of zincite, coherently intergrown within the sphalerite structure.

In addition to twin boundaries, sphalerite crystals are densely populated by *hcp* stacking faults (SFs) extending in {111} planes. In contrast to twin boundaries, SFs show no change of chemistry, neither they have any effect on the morphology of the crystals. The increased concentration of other elements (Mn, Fe and Cu) in the vicinity of the twin boundary is a consequence of segregation (also a kinetic effect) to the twin boundary during cooling.



(111) twins of spinel and their relation to chrysoberyl

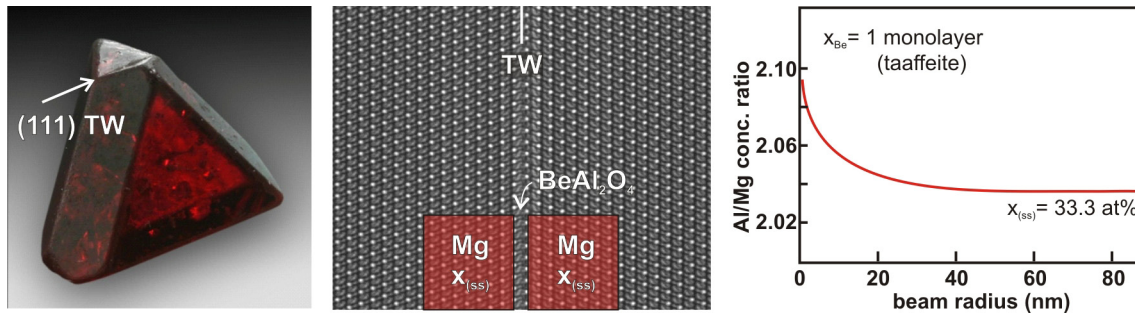
Another fine example of chemically induced twinning are (111) twins of spinel (MgAl_2O_4), after which the spinel-law of twinning received its name. For this study, simple contact twins of spinel from the Mogok metamorphic belt in Burma were used (DANEU *et al.*, 2007). The translational state observed on these twins can be best described by a 180° rotation around [111]-axis in oxygen sub-lattice after the so-called kagome

layer of the structure. This operation produces a local *hcp* stacking, which is the basic twin element in an otherwise cubic structure.

To identify the cause of the observed stacking disorder, we used a combination of TEM-based analytical techniques. Results of concentric electron probe (CEP) method (REČNIK *et al.*, 2001) indicated a sharp drop of Mg^{2+} concentration at the twin boundary, implying that

Mg^{2+} ions are not present in the boundary tetrahedral sites. In addition no other impurity element measurable by EDS, showed a corresponding increase. In order to maintain the local charge balance the only candidate to occupy the available tetrahedral interstices was Be^{2+} . The most closely related *hcp* analogue of the *ccp* sublattice of the spinel structure is chrysoberyl ($BeAl_2O_4$). This was an important finding, which indicated that the twin formation in spinel is related to the formation of polytypoidic series that exist between spinel and chry-

soberyl, of which taaffeite ($BeMg_3Al_8O_{16}$) is one of the most characteristic representatives. And indeed, *ccp-hcp* modules of the taaffeite structure closely resemble the structural configuration at (111) twin boundaries in spinel, while Be^{2+} ions in taaffeite occupy the tetrahedral sites adjacent to *hcp* layers of the structure. Like all growth twins (chemically induced!), the morphology of spinel crystals reflects the initial exaggerated growth along the twin boundary and a subsequent overgrowth producing characteristic twin-plane re-entrant angles.

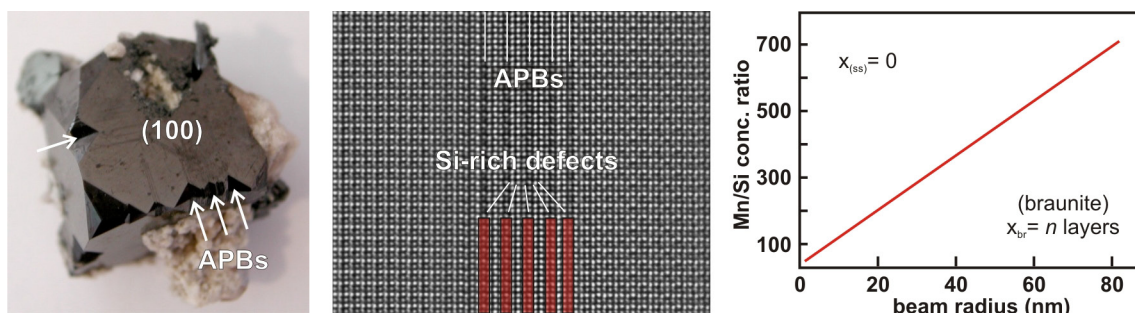


{100} antiphase boundaries in bixbyite and their relation to braunite

And sometimes twins are not twins in spite of all external signs that suggest twinning. Thomas Mountain Range in Utah is famous for splendid crystals of bixbyite ($MnFeO_3$). They occur in rhyolite vugs in a form of black lustrous crystals with marked re-entrant angles at halfways of the cube edges. According to these morphological features, such crystals could be considered {100} twins; however, any crystallographic operation on {100} planes of a centrosymmetric cubic structure such as bixbyite, would produce an untwinned crystal (KLEEBE & LAUTERBACH, 2008).

So, if they are not twins, what they could possibly be? HRTEM study revealed that the crystals are densely intersected by a 3D network of planar faults running along {100} planes of the structure. The highest density

of these faults is near the centre of the crystal, where they form ordered lamellas with evident polytypoidic structure, similar to {100} antiphase boundaries reported in synthetic perovskite crystals (REČNIK *et al.* 2001). Chemical analysis showed that faults as well as ordered lamellas are Si-rich, whereas their local structure is closely related to mineral braunite (Mn_7SiO_{12}). Topotaxial intergrowth of (001) braunite layers with {100} planes of bixbyite is the main cause for the apparent bixbyite morphology. A braunite core formed already in the nucleation stage. It caused a 3D exaggerated growth of topotaxial bixbyite crystal along {100} planes. In the final stages of growth the conditions for the formation of intrinsic braunite layers ceased and re-entrant angles developed with bixbyite overgrowth.

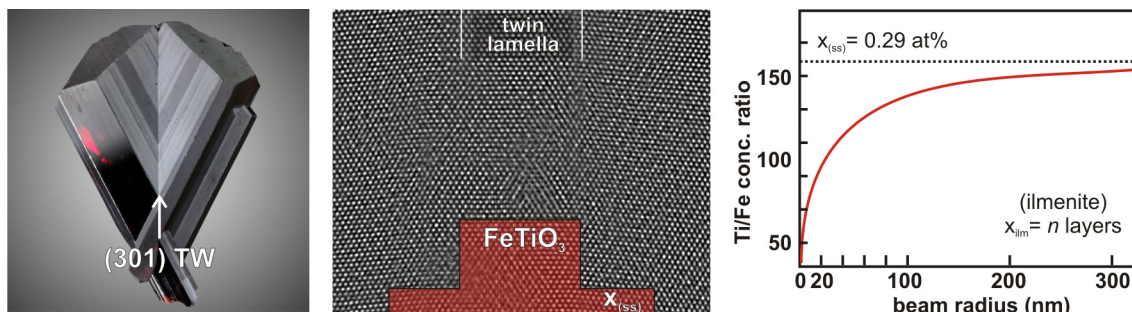


{301} and {101} twins of rutile in relation to ilmenite and corundum

Every now and then the twins can be a result of a whole series of recrystallization processes. This was best demonstrated on {301} and {101} twins of rutile (TiO_2) from Diamantina, Brazil (DANEU *et al.*, 2007). TEM study of (301) rutile twins from this locality revealed that the twin boundary comprises a few nanometers thick Fe-rich lamella with a corundum-type structure. Chemical and structural analysis showed that this internal twin-lamella consists of Al-rich ilmenite (FeTiO_3). The orientation relationship between the ilmenite lamella and the epitaxial rutile domains is $(01\bar{1}0)[0001]_I \parallel (301)[010]_R$. Both ilmenite-rutile interfaces are atomically sharp and devoid of misfit dislocations that would compensate for the lattice mismatch between the two structures. The structural mismatch is compensated by incorporation of Al into the ilmenite structure. A detailed HRTEM analysis of the ilmenite lamella revealed goethite-related reflections and presence of nano-twins. This was an important hint to resolve the whole crystallization sequence that led to the formation of these twins. The ilmenite lamella formed during a thermally-induced dehydration process from twinned tivanite-like Fe-Ti-Al oxy-hydroxide precursor. Tivanite (400) planes are mirror twin planes for the common anion sub-lattice and are parallel to the (301) planes of rutile. It is expected that under the inflow of

acidic Ti-rich solutions rutile started to grow epitaxially on twinned tivanite-like precursor mineral. This was accompanied by dehydration process, under which an equilibrium boundary was formed between the internal lamella and the epitaxial rutile. In this process, the composition of the lamella reached equilibrium close to the stoichiometry of ilmenite. In order to reduce the lattice mismatch with respect to the epitaxial rutile a sufficient amount of Al^{3+} ions was incorporated into the ilmenite structure to reduce the pertinent unit-cell dimensions.

Our recent study of (101) twin in rutile from the same locality have shown a similar configuration, except that in this case the interface is decorated with precipitates of Ti-rich corundum (Al_2O_3). In this case the orientation relationship between the two phases is identical as in the case of (301) twins, except that the interface is different. The formation of these precipitates is yet unknown, but it seems that they formed in a similar way, from an Al-rich oxy-hydroxide precursor (e.g. diaspore), and after dehydration corundum precipitates formed and retracted to equidistant locations along the (101) twin boundary of rutile. The reason why corundum does not form a continuous layer lies in the large lattice mismatch between $\{21\bar{1}0\}$ planes of corundum and $\{101\}$ planes of rutile.



Conclusions

The described analyses show that the formation of transformation faults and intergrown topotaxial structures is always chemically triggered. During their growth, natural minerals are exposed to incomparably more unpredictable thermodynamic conditions and geochemical environments than the minerals synthesized in laboratory. Therefore we can observe the consequences of sequential phase transformations in natural minerals that evidence the dynamics of the geochemical surrounding in which they were formed. In nature we

find many examples of transformation faults, polytypic structures and epitaxial overgrowths of minerals and the reasons for their formation are mostly unknown. Based on nanostructural investigations of these planar defects and precipitates in minerals we are able to reconstruct the geochemical conditions in the time of their formation. This knowledge is not only the basis for the explanation of their formation and growth, but is also a rich source of information about regional rock-forming and tectonic processes during their growth.

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