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A crystal growth scenario from HREM studies of pinakiolite related oxyborates

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Résumé. — Les défauts de Wadsley d'oxyborates de type pinakiolite ($M_3O_2BO_3$, $M = Mg, Mn, Fe, Al, Sb, Ti$) ont été étudiés par microscopie électronique haute résolution et microanalyse X. Des images de structure de cristaux de ludwigite à l'aluminium montrent de larges lamelles de chestermanite avec une forte concentration d'antimoine. De telles variations chimiques liées au changement structural et la nature des défauts locaux suggèrent un modèle de croissance cristalline incluant le maclage chimique et un front de croissance cristalline parallèle à la surface (100). Un nouveau composé de synthèse de la famille de pinakiolites avec une séquence maclée d'une répétition régulière de structures de type ludwigite et clustermanite a été identifié.

Abstract. — The Wadsley defects of pinakiolite related oxyborates ($M_3O_2BO_3$, $M = Mg, Mn, Fe, Al, Sb, Ti$) have been studied with high resolution transmission electron microscopy (HREM) and microanalysis (EDX). Structure images of Al-ludwigite crystals show broad slabs of chestermanite with a higher content of antimony. Such chemical variations of structure changes and the nature of local defects support a suggested crystal growth model, including chemical twinning and a crystal growth front parallel to the (100) surface. A new synthetic member of the pinakiolite family, with a twin sequence of regular repeat of ludwigite- and chestermanite-like structures, was identified.

1. Introduction.

The pinakiolite family of minerals has thirteen known members. The general formula for the members is $M_3O_2BO_3$. M can be both divalent as Mg^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} or Ni^{2+} and/or trivalent as Mn^{3+} , Fe^{3+} , and Al^{3+} , but also tetra- and pentavalent as Sn^{4+} , Ti^{4+} and Sb^{5+} . It is possible to synthesize most of the members of the family and as the structure type is able to host ions of different valence of the same element, members of the pinakiolite family are potential catalysts. Preliminary tests show catalytic activity in total oxidation of hydrocarbons.

The structure family can be considered as built up by chemical twinning [1] of the parent structure pinakiolite (or hulsite) [2] (cf. Fig. 1a). The metal ions are octahedrally coordinated to oxygen

atoms and the octahedra are linked together by edgesharing to form flat walls, F walls (cf Fig. 1a), and zig-zag walls. With the notation of Takéuchi [2], the central columns of octahedra through the zig-zag walls are denoted C walls and those at the corners of these walls S columns (cf Fig. 1a). Structural investigations of synthetic Mg-Mn orthopinakiolite (Norrestam *et al.*, to be published), disordered pinakiolite [3] and of the minerals takéuchiite [4] and blatterite [5] have shown that the presence of considerable amount of Mn^{3+} causes structural disorder in the C walls (cf Figs. 1a and 1b) so every second of the octahedra rows, in the c-axis direction, is disordered. This is illustrated by the X-ray and HREM investigations of pinakiolite (Norrestam & Bovin, to be published) shown in figures 1a and b.

Fig. 1. — a) Polyhedra drawing of the pinakiolite structure viewed along the c-axis. The F and C walls and S columns are marked with arrowheads. b) A HREM structure image of a pinakiolite crystal, $\text{Mg}_{1.82}\text{Mn}_{1.13}\text{Fe}_{0.04}\text{O}_2\text{BO}_3$, recorded along [001] at Scherzer focus and with 400 keV (JEM-4000EX). One of the disordered octahedra rows of the C-walls is marked with arrowheads in a and b.

The first chemical twin member of the pinakiolite family, ludwigite, has two layers of octahedra between the twin planes and is denoted 2t2t2t2 . The second member, orthopinakiolite or chestermanite, has the twin sequence 4t4t4t4 . Two more members, takéuchiite and blatterite with the sequence 6t6t6t6 and 8t8t8t8 (cf Fig. 2), are known.

HREM studies of minerals of the family, pinakiolite [6] ludwigite [7] orthopinakiolite [8] chestermanite (Alfredsson *et al.*; to be published), takéuchiite [4,9] and blatterite [5] as well as synthetic members [10, 11], have shown many different structural defects. The Wadsley defects found early on predicted new members of the family and later takéuchiite and blatterite were found and their structures determined [4, 5, 9] from HREM images and single crystal X-ray diffraction.

This paper will, with the discovery of the two Al-rich members chestermanite and ludwigite crystallized in the same paragenesis, show that the distance between the twin planes depends on chemical variations during the crystal growth.

Fig. 2. — HREM structure image of a blatterite, $\text{Mg}_{1.33}\text{Mn}_{1.44}\text{Fe}_{0.05}\text{Sb}_{0.17}\text{O}_2\text{BO}_3$, crystal recorded along [001] with JEM-4000EX and at an underfocus of 430 Å. A polyhedra drawing of the structure is matched into the image and the chemical twin planes of the structure are marked with lines. The white arrow marks the disordered C-wall.

2. Experimental.

2.1 HREM METHOD. — Thin crystal fragments of each mineral were collected on holey carbon films for atomic resolution HREM studies. The work was performed with a JEM-4000EX, equipped with a high resolution pole piece ($C_s = 1 \text{ mm}$), operated at 400 keV. The vacuum in the specimen chamber is at the best $5 \times 10^{-6} \text{ Pa}$. The structural resolution was determined, by optical diffraction of micrographs of amorphous carbon with Au-crystals as internal standard, to be 0.16 nm. A SIT TV-system, Gatan 622, is connected by way of optical fibers to the bottom of the microscope viewing chamber. The oxyborates are slightly beam sensitive, so weak beam techniques were used. Image processing for noise reduction, contrast enhancements and frame grabbing was performed with a digital video processor, Quantex DS-30. Image simulations, using the microscope optical parameters, were computed with an updated local version of the SHRLI programs.

2.2 MICROANALYSIS. — Small defect areas, down to a diameter of 30 nm, were analysed at 200 keV with a JEM-2000FX equipped with a Link AN10000 energy dispersive X-ray detector system. The EDX spectra were processed by the computer program ZAF/PB [12] for quantitative evaluation.

3. Results and discussion.

Even if the X-ray structure determination of Al-ludwigite indicated well ordered atom arrangements [7], the HREM structure images showed several planar defects parallel to the *a*- and *b*-axes. The defects along [100] were of the same type as reported before i.e. intergrowth of slabs of structures belonging to the other members of the pinakioite family. This is clearly shown in figure 3 where a crystal fragment of the single crystal used in X-ray diffraction study [7] is imaged with the electron beam slightly off the *c*-axis. The Al-ludwigite structure of the image is marked with L, while the defect part down to the left shows a two unit cell wide orthopinakioite (chestermanite) like structure image. It is obvious from this image (and from many others [8, 9]) that the same crystal fragment can change from one structure to another (with a new twin sequence), without any local structure distortions, in the [100] direction. The crystal structure does not usually fit so well in the (010) plane, as can be seen in the heavily disordered local areas marked with D-arrows. Occasionally, the boundary can be a (010) plane, with an unknown local (ordered ?) structure, as in the right hand part of the image where the ludwigite structure is facing a chestermanite structure.

Fig. 3. — An Al-ludwigite crystal with planar defects and disorder (D) is imaged with the electron beam (200 keV) close to parallel with the *c*-axis. The area with ludwigite like structure image is marked L and the chestermanite like ones C.

The fundamental idea of chemical twinning [1] is that chemical variations (including impurities) during the crystallization can be accommodated by changing the twin mechanism and/or periodicity. It has never been possible to experimentally analyse two different structures with different twin periodicity in the same crystal, in order to verify the chemical twin concept. There is no confident analysis method for determine the composition of one single twin plane. EDX-analysis of a slab of ten or more twin units of chestermanite is though possible if it is grown onto Al-ludwigite. The variation in elemental composition can be detected and compared to the contents of the basic structure. This is clearly illustrated in figure 4 where an Al-ludwigite crystal is imaged with a 18 nm broad defect of a twin repeat distance of two times the basic structure. The electron beam (200 keV) was focused down to a diameter of 30 nm (circle A) and the EDX-spectrum was collected for 400 sec. (cf. spectrum A in Fig. 4). Image simulations of TEM images of the Al-ludwigite structure with the optical parameters of the microscope showed that the contrast of the crystal edge, imaged in figure 4, can be interpreted so that its thickness is less than 20 nm. The beam spread in the crystal thus must be negligible for the beam area shown at A and B. An

EDX-spectrum was recorded under the same conditions at the area B (cf. Fig. 4). It is clear by comparison of the two spectra that the area A has a higher antimony content than B. ZAF/PB calculations gave the chemical composition :

Further EDX-analyses of areas with many defects show an average analysis given by the formula :

For comparison the data from EDX-analysis of bulk samples are :

Fig. 4. — Microanalysis of a thin (< 20 nm) Al-ludwigite crystal (the same as in Fig. 3) with defect slabs. The image was recorded at 200 keV with the beam parallel to the c-axis. EDX-spectra are shown for a counting time of 400 sec. and recorded with an electron beam diameter (30 nm) corresponding to the circles A and B.

For the structure image in figure 4 the change from $\text{--}2t2t2t\text{--}$ twin repeat of ludwigite to $\text{--}4t4t4t\text{--}$ repeat appears without any sign of structural disorder; only by change of unit cell and increase of antimony content. This means the crystal has most likely been growing by adding atom planes to the (100) surface of the crystal.

In order to investigate defects of the internal and successive (100) crystal planes of $(\text{Mg}_x\text{Mn}_y\text{Sb}_z)_3\text{O}_2\text{BO}_3$ (Sb_z , $0.05 < z < 0.10$), synthetic crystals were prepared. The mixing of the initial metal oxides was not done well so the crystal growth could proceed with local variations in antimony (and also Mg and Mn) concentration.

Many of the crystals grown in this way showed extensive disorder in the *a*-axis direction but in some cases a crystal could be imaged with broad slabs of ordered structures. Even new phases were identified in this way and one common structure is shown in figure 5. The new phase called N-phase could be determined to have an ordered intergrowth sequence of ludwigite- and chestermanite (orthopinakiolite)-like structures. The chemical twin repeat can be written $\text{--}4t4t2t2t4t\text{--}$, with an *a*-axis of the unit cell of three times the *a*-axis of ludwigite i.e. $a = 2.76$, $b = 1.25$ and $c = 0.6$ nm. These are the same parameters as for the takéuchiite structure, but that one has the twin repeat $\text{--}6t6t6t\text{--}$.

Fig. 5. — A structure image of a synthetic crystal, $(\text{Mg}_x\text{Mn}_y\text{Sb}_z)_3\text{O}_2\text{BO}_3$ ($z = 0.07$), recorded at 200 keV with the electron beam close to parallel to the *c*-axis. The unit cell of a new phase, with the chemical twin plane sequence $\text{--}4t4t2t2t4t\text{--}$, is marked with N. The unit cell of the ludwigite-like structure is marked with L.

If the growth direction along the *a*-axis of the crystal imaged in figure 5, is assumed to be from right to left, it has started to grow with adding on atom planes with the structure of the N-phase. Arriving at the (100) plane marked with the arrow A the chemical composition of the melt surrounding the crystal must have reached such a concentration level of the cations (perhaps of the antimony ions) so it must change the chemical twin sequence from that of the N-phase to that of ludwigite (marked L in Fig. 5). The crystal growth process has then proceeded by adding 6 more unit cell layers of the ludwigite like structure to the (100) surface. Adding on the ludwigite layer marked with arrow 1 it is still elements of the right concentration around for the $-2t2t2t2-$ twin repeat. When the layers of atoms, constituting the two unit cell broad ludwigite layers marked with the arrows 2 and 3, reach half the way the concentration most likely has changed because the growth continues with the twin sequence belonging to the N-phase. The structure becomes disordered (broad dark area in the image) for a distance of about 2.5 nm because of the misfit of twin planes in the *b*-axis direction. The structure adjusts for the disorder and continues with the N-phase twin repeat. Note that the $-2t2-$ unit repeat of L can be the start of the N-phase unit cell (marked above the disordered area) in such a way that the twin sequence becomes $-2t2t4t4-$. During the growth of the rest of the crystal atoms are added to the (100) surface so the twin repeat of the N-phase is generated.

Fig. 6. — A synthetic crystal, $(\text{Mg}_x\text{Mn}_y\text{Sb}_z)_3\text{O}_2\text{BO}_3$ ($z = 0.07$), with epitaxial growth of four different phases in the *a*-axis direction. The crystal is imaged with the electron beam (200 keV) parallel to the *c*-axis. The chestermanite part is marked with C, ludwigite with L, takéuchiite with T and the new phase (cf Fig. 5) with N.

In some of the crystals the new N-phase could be found together with several of the known members of the pinakiolite family. In the crystal fragment imaged in figure 6, from the right, the following phases can be identified; three unit cells of the N-phase, four takéuchiite-like ($-6t6t6t6-$)

unit cells, one unit of -4t2t2t2t4- , ten unit cells of a ludwigite-like structure followed by five unit cells of a chestermanite (orthopinakiolite)-like structure. This crystal very nicely shows that the epitaxial growth of different pinakiolite related structures occurs adding new atom layers to the (100) surface of the crystal.

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