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## Electron Microscopy of Oxyborates.

### II. Intergrowth and Structural Defects in Synthetic Crystals

BY JAN-OLOV BOVIN\* AND M. O'KEEFFE

*Chemistry Department and Center for Solid State Science, Arizona State University, Tempe, Arizona 85281, USA*

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#### Abstract

Crystals of composition  $Mg_3Mn_3B_2O_{10}$ ,  $Mg_{3-1}Mn_{2-9}B_2O_{10}$  and  $Mg_3(Mn_{2.4}Fe_{0.6})B_2O_{10}$  have been prepared at 1270 K in air and investigated by high-resolution transmission electron microscopy. Almost all crystals showed structural defects. The most common type of defect was a variation in period of chemical twinning. Slip planes and single twin planes were also found. Many crystals also showed mixed intergrowth of several structure types. Thus  $Mg_3Mn_3B_2O_{10}$  crystals contained mixed intergrowth of ludwigite-, pinakiolite- and orthopinakiolite-like structures.  $Mg_{3.1}Mn_{2.9}B_2O_{10}$  crystals contained mostly the ludwigite structure but also new long-period (82.3 Å) structures.  $Mg_3(Mn_{2.4}Fe_{0.6})B_2O_{10}$  crystals had mainly

the orthopinakiolite structure with intergrowth of ludwigite. Several new phases were identified in the electron micrographs.

#### Introduction

Synthetic compounds with the composition  $M_3BO_5$ , where  $M$  stands for different combinations of the ions  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{3+}$  and  $Fe^{3+}$  have been reported (Bertaut, 1950; Nielsen, Sotofte, Thorup & Norrestam, 1978) to have the ludwigite structure [cf. Fig. 1(b) in the previous paper by Bovin, O'Keefe & O'Keefe, 1981 (paper I)]. No synthetic compounds with pinakiolite, orthopinakiolite or takéuchiite structures have been reported. This investigation of synthetic members of the pinakiolite family was undertaken in order to reveal the 'true' structure of crystals prepared with different cation concentrations. From the structural

\* Permanent address: Inorganic Chemistry 2, Chemical Centre, PO Box 740, S-220 07, Lund 7, Sweden.

relations described in paper I it is obvious that there are a great number of possibilities for intergrowth between the different members of the family. Not many examples of such defects were found in crystals of the minerals but they could possibly be more frequent in synthetic crystals where time for reaching equilibrium is limited and where a rapid cooling could be affected. The nature of the cations in the crystals is probably the key to nature's choice of structure type. To gain some insight into this we have studied, by electron microscopy, crystals of three compositions:  $\text{Mg}_3\text{Mn}_3\text{B}_2\text{O}_{10}$ ,  $\text{Mg}_{3.1}\text{Mn}_{2.9}\text{B}_2\text{O}_{10}$  and  $\text{Mg}_3(\text{Mn}_{2.4}\text{Fe}_{0.6})\text{B}_2\text{O}_{10}$ .

### Experimental

The three types of compounds were prepared by heating pressed pellets containing well-mixed stoichiometric amounts of  $\text{MgO}$ ,  $\text{MnO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{B}_2\text{O}_3$  at 1270 K in air. Under these conditions  $\text{Mn}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  are the stable oxides (Hahn & Muan, 1960). Powder X-ray films recorded for the different compositions showed no lines from the starting materials. No attempt was made to determine the ratio of  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$  ions in the crystals. All crystals were found to contain a considerable number of structural defects and that would have been difficult to determine if the defects were caused by the ratio of oxidation states or *vice versa*.

The high-resolution transmission electron microscopy study was carried out in the same way as described in paper I (Bovin, O'Keeffe & O'Keeffe, 1981).

### Structural defects

Each composition  $\text{Mg}_3\text{Mn}_3\text{B}_2\text{O}_{10}$ ,  $\text{Mg}_{3.1}\text{Mn}_{2.9}\text{B}_2\text{O}_{10}$  and  $\text{Mg}_3(\text{Mn}_{2.4}\text{Fe}_{0.6})\text{B}_2\text{O}_{10}$  produced crystals containing different kinds of defects in the dominating structure (Table 1) and results for each group will therefore be presented separately.

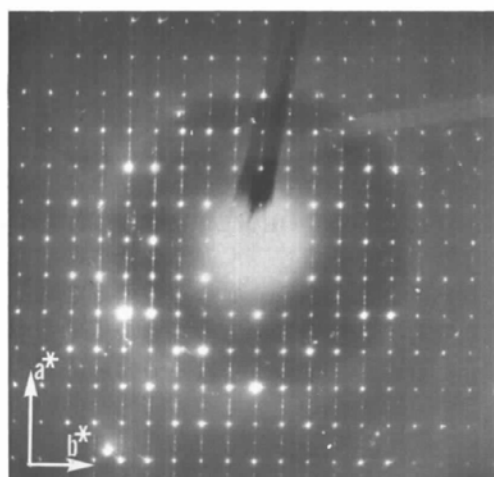
#### (a) $\text{Mg}_3\text{Mn}_3\text{B}_2\text{O}_{10}$

Crystals prepared with this composition usually showed very complicated intergrowth patterns of different structures. A typical electron diffraction

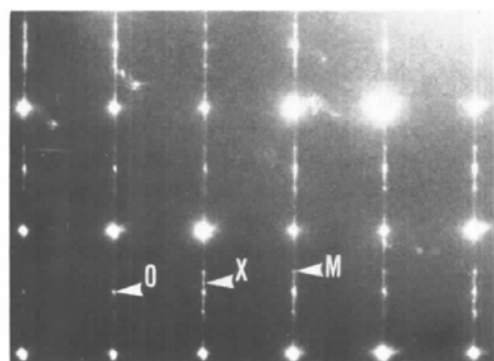
Table 1. Structure types, pinakiolite (*P*), ludwigite (*L*), orthopinakiolite (*O*) and new (*X*), found in synthetic oxyborates of different composition

Composition	Dominating structure	Intergrowth structures
$\text{Mg}_3\text{Mn}_3\text{B}_2\text{O}_{10}$	<i>L</i>	<i>P</i> + <i>O</i> + <i>X</i>
$\text{Mg}_{3.1}\text{Mn}_{2.9}\text{B}_2\text{O}_{10}$	<i>L</i>	<i>O</i> + <i>X</i>
$\text{Mg}_3(\text{Mn}_{2.4}\text{Fe}_{0.6})\text{B}_2\text{O}_{10}$	<i>O</i>	<i>L</i> + <i>X</i>

pattern is shown in Fig. 1(a) and (b). The strong reflections in the pattern correspond to the ludwigite structure [*cf.* Fig. 12(a) in paper I] but between these reflections there are several sets of superstructures in the *a*-axis direction. One set [marked *O* in Fig. 1(b)] indicates an *a* axis approximately twice as long as the *a* axis of ludwigite (9.14 Å): 18.32 Å. This value is in good agreement with the *a* axis of the mineral orthopinakiolite. Reflections marked *M* in Fig. 1(b) must belong to an *a*-axis repeat of 27.57 Å which is very close to the *a* axis of the mineral takéuchiite. However, the intensities of the reflections are different from those of takéuchiite [*cf.* Fig. 12(c) in paper I] indicating another structure with the same unit cell. It is also possible to distinguish reflections corresponding to a repeat of 55.14 Å [marked *X* in Fig. 1(b)] but this repeat was not found in any image recorded from the crystal.



(a)



(b)

Fig. 1. (a) Electron diffraction pattern of  $\text{Mg}_3\text{Mn}_3\text{B}_2\text{O}_{10}$  crystal with ludwigite structure dominating. (b) Magnification of part of the pattern in (a) showing reflections corresponding to 18.32 Å (marked *O*), 27.57 Å (*M*) and 55.14 Å (*X*). Images from the same crystal as this are shown in Fig. 2 through Fig. 5.

A low-resolution image of the crystal corresponding to the diffraction pattern in Fig. 1(a) and (b) is shown in Fig. 2. The dominating structure is ludwigite (label 11) but here and there interrupted by single or double bands of defects (13) sometimes terminated in the structure (12). The ludwigite structure grows coherently with another structure at 10. The structure in the lower left corner has a unit-cell repeat in the  $a$ -axis direction of twice that of ludwigite. A high-resolution image of the same boundary is shown in Fig. 3. The contrast in the image to the left can be interpreted as the orthopinakiolite structure [cf. Fig. 10 in paper I]. The crystal is thick in this region and the image has reverse contrast. The image of the ludwigite structure to the right is close to the image of the upper part of Fig. 13 in paper I. The structural change at the boundary involves a change in twin repeat and can be written symbolically:  $-4t4t4t2t2t2t-$ . It has been suggested (Takeuchi, 1978) that the twin repeat is a function of the  $Mn^{3+}/Mn^{2+}$  concentration. Indeed the only reasonable variation in species concentration (in this case no  $Fe^{3+}/Fe^{2+}$  is involved) during the growth of the crystals is the  $Mn^{2+}$  ions competing with the  $Mg^{2+}$  ions to occupy the octahedra and in this way changing the concentration of  $Mn^{3+}$  ions. Local faults in the twin period were commonly found in the crystals of ludwigite and Fig. 4 shows in high resolution how such defects even terminate in the crystal. The defect marked 13 is an orthopinakiolite slab that is two unit cells wide, grown into the ludwigite structure. The slab can be written as  $-2t2t4t4t4t4t2t2t-$ . This interpretation is based on the similarities between the magnified image of Fig. 4(b) and the image of the thick part of the

crystal in Fig. 14 of paper I. The intergrowth of orthopinakiolite can thus be understood as four missing twin operations. The terminated defects marked with arrows in Fig. 4(a) show a somewhat different behavior compared with the terminated defect observed in the mineral orthopinakiolite (cf. Fig. 16 in paper I). The two parts of the ludwigite crystal on each side of the defect are not displaced along  $b$  [cf. Fig. 4(b)] because two or four twin operations are missing. In the case of two missing operations one is clockwise and the other anticlockwise removing the misfit arising from one twin operation. It is most likely that the missing twin operations occur due to a local change in concentration of one or more of the ions centering the octahedra. The gradual change in contrast, shown as long dark bands parallel to  $b$ , indicates a stress in the structure.

The crystal structure corresponding to the  $a$ -axis repeat of  $27.57 \text{ \AA}$  given in the electron diffraction pattern of Fig. 1(b) is shown in the image of Fig. 5. In the upper part of the image the ludwigite structure can be identified [cf. Fig. 13 in paper I]. The image in the lower part can best be interpreted on the basis of a structure generated by the new twin operation sequence

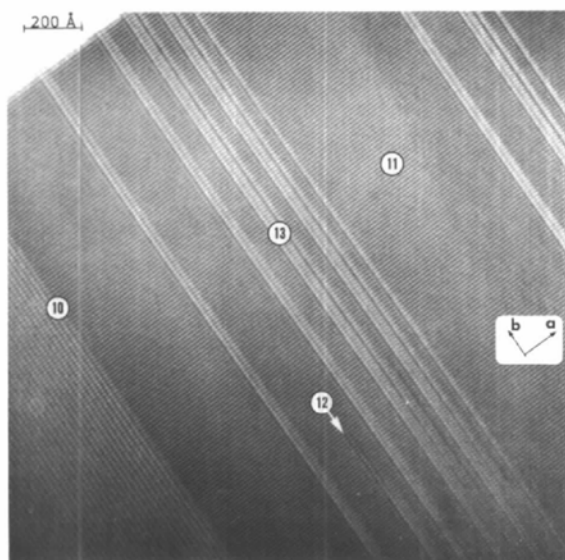


Fig. 2. Low-magnification electron micrograph of a  $Mg_3Mn_3B_2O_{10}$  crystal recorded with the beam parallel to  $c$ . The notations on the image mark the defect types shown in Figs. 3 and 4.

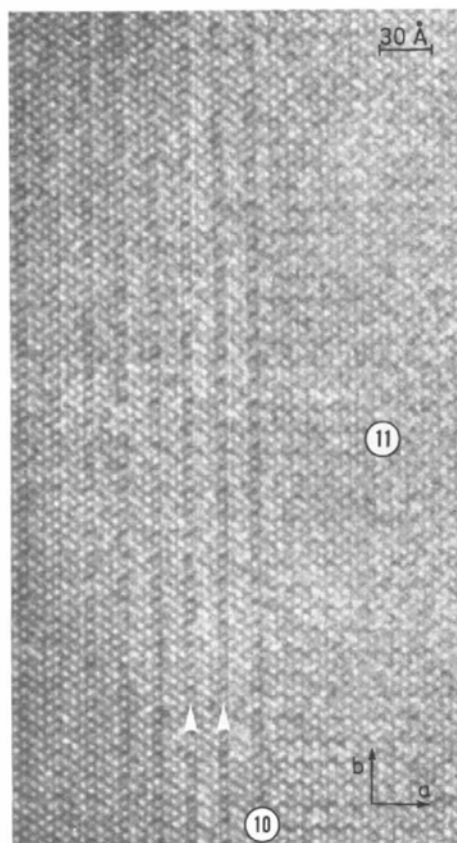
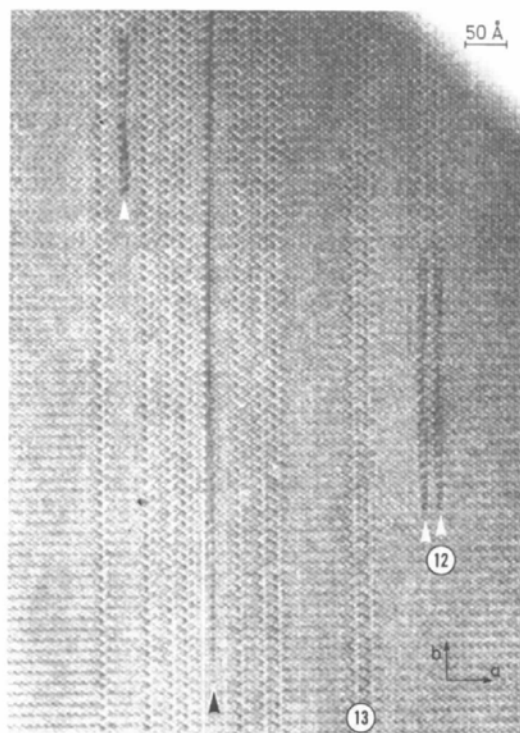


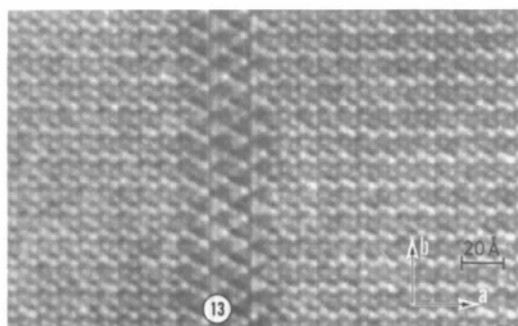
Fig. 3. High-resolution image of the structure boundary marked 10 in Fig. 2. The white arrows mark the periodicity ( $18.32 \text{ \AA}$ ) of the orthopinakiolite structure.

$-2t2t4t4t2t2t4t4t-$ , in other words, an ordered intergrowth of the ludwigite structure and the orthopinakiolite structure. This structure is not known as a mineral but could well be a new member of the pinakiolite mineral family. The unit cell would be the same as for takéuchiite but the symmetry would be different.

The crystals of composition  $Mg_3Mn_3B_2O_{10}$  were dominated by the structure of ludwigite but in some crystals those of pinakiolite and orthopinakiolite were found to grow together with ludwigite, as in the crystal



(a)



(b)

Fig. 4. (a) High-resolution image of the orthopinakiolite intergrowth (13) in ludwigite and the terminated (12) defects also shown in Fig. 2. (b) Orthopinakiolite intergrowth in ludwigite shown at high magnification. Compare the image of the defect with the right part of the image of orthopinakiolite shown in Fig. 1(b).

shown in Fig. 6. The part shown in the image gives a representative illustration of the different kinds of defects and intergrowth patterns found in other crystals. The image in Fig. 6 is dominated by the pinakiolite structure (marked 21). The defect marked *T* is a twin boundary like the one shown in the polyhedral drawing of Fig. 9(b) in paper I. The defect marked *S* can be explained as a slip as in Fig. 6(c) of paper I. Both structure building operations relating the parent structure of pinakiolite to the other structures of the family are here represented in one crystal. The slip defect shows a 'knee' at the arrow – a feature difficult to understand structurally.

The image within the white rectangle of Fig. 6 includes a boundary between the structures of orthopinakiolite (marked 18) and pinakiolite. The change from the structure of orthopinakiolite to that of pinakiolite is simple to understand as a sudden lack of twin operations. The structure of the boundary is illustrated in the polyhedral drawing of Fig. 7. The same intergrowth in the *a*-axis direction can of course exist between the structures of ludwigite and pinakiolite as can be seen between the images marked 11

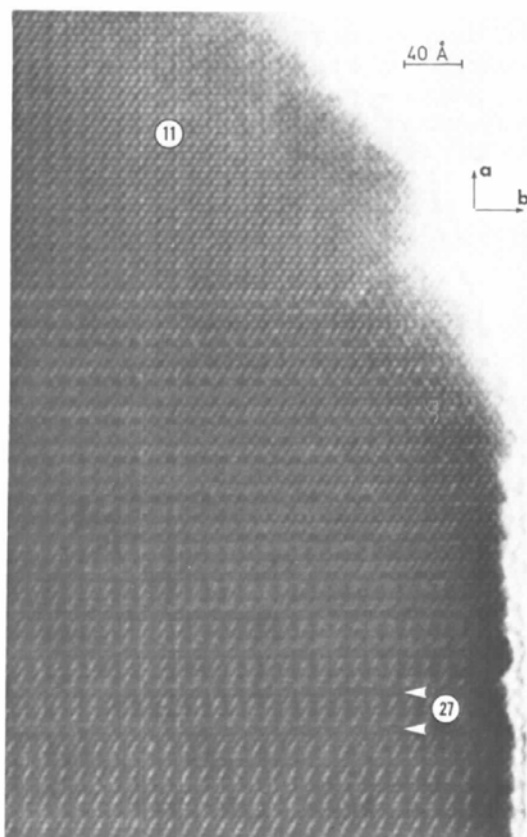


Fig. 5. Electron micrograph showing a thick part of the same crystal which gave the electron diffraction pattern in Fig. 1. The unit-cell repeat (27.57 Å), marked with arrows, corresponds to an ordered intergrowth of ludwigite and orthopinakiolite.





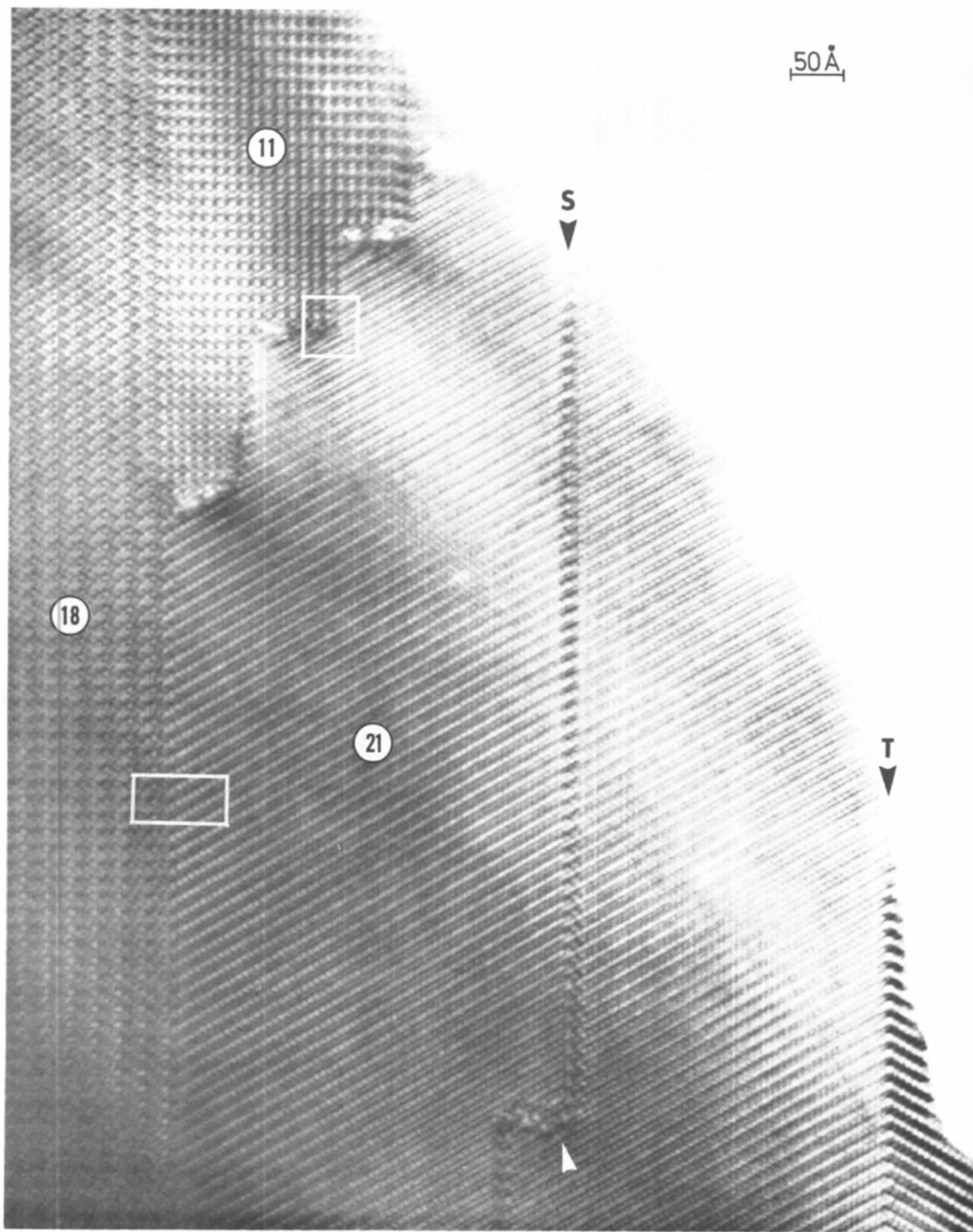


Fig. 6. Electron micrograph of a  $\text{Mg}_3\text{Mn}_3\text{B}_2\text{O}_{10}$  crystal showing a mixed intergrowth of ludwigite (11), orthopinakiolite (18) and pinakiolite (21). Arrows marked *S* and *T* indicate a slip boundary and twin boundary respectively in pinakiolite. The white rectangle indicates an area corresponding to the drawing in Fig. 7. The structure of the area within the white square is in principle given in Fig. 8.



Fig. 14. Electron micrograph of a  $\text{Mg}_3(\text{Mn}_{2.4}\text{Fe}_{0.6})\text{B}_2\text{O}_{10}$  crystal with mainly orthopinakiolite structure. The arrows mark a defect boundary where twin slabs of different width meet.

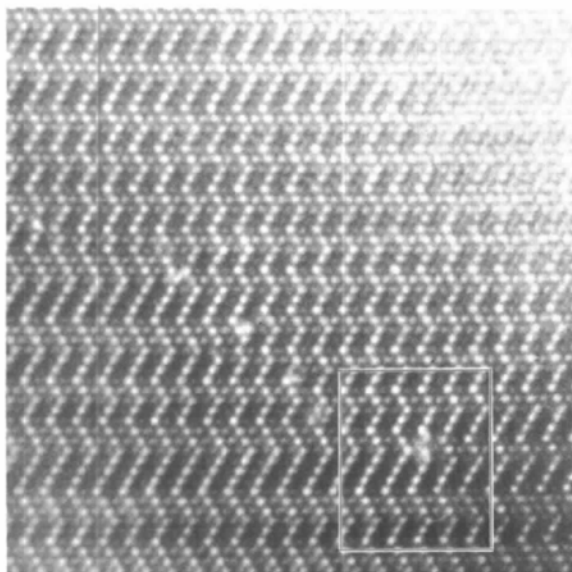


Fig. 15. High-resolution image of part of the defect boundary in Fig. 14. The image contrast can be compared with the thick crystal region in Fig. 14 (paper I). The underfocus is not the same in Figs. 14 and 15. The structure of the area within the white rectangle is shown in Fig. 16.

misfits at the boundary as expected even if the two structures fit surprisingly well in some parts (marked with a small arrow). A crystal with unidentified structure ( $X$ ) is growing incoherently at the surface of the orthopinakiolite crystals. The image repeats in this projection are  $a = 6.25$  and  $c = 9.4$  Å with  $\beta \approx 127^\circ$ . No borate compound with this monoclinic unit cell has been reported in the literature.

Crystals prepared with the composition  $\text{Mg}_3(\text{Mn}_{2.4}\text{Fe}_{0.6})\text{B}_2\text{O}_{10}$  showed a new type of defect not seen before in the oxyborates. In areas of mainly orthopinakiolite structure there were often twin-period defects combined with a defect boundary. The defect boundary did not show any preferred crystallographic orientation. A typical crystal with such a defect boundary (marked with arrows) is shown in Fig. 14. Twin slabs of different width meet each other in the defect boundary causing local distortions of the structure at the boundary. A possible structure of such a distortion can be deduced by matching the different twin slabs together in a polyhedral model. For a more detailed study the image within the white rectangle of Fig. 15 is chosen. The image is recorded with another underfocus and therefore differs from Fig. 14. The image looks similar to the thick part of the crystal in Fig. 14 of paper I. By combining the different twin slabs within the rectangle of Fig. 15 the structure shown in Fig. 16 is obtained. The only defect part of the structure is marked with blue and green octahedra where the coordination of the cations must be very distorted. This corresponds to the diffuse area of the image.

## Conclusions

The simple scheme of variation of cations used in the synthesis of the oxyborates gives some clues to the stability of the different structures of the pinakiolite family. The ludwigite structure dominates for crystals prepared without the Fe ions but it also occurs when Fe is present. It is well known that ludwigite is a very stable structure type, tolerating a great number of different cations like Fe, Co, Ni and Cu (Bertaut, 1950). Ludwigite as a mineral never shows any structural defects and one nickel-containing ludwigite,  $\text{Ni}_4\text{Fe}_2\text{B}_2\text{O}_{10}$ , prepared during this investigation showed no structural defects or intergrowth defects either. Pinakiolite was found to be a rather common phase in crystals with the composition  $\text{Mg}_3\text{Mn}_3\text{B}_2\text{O}_{10}$ . There has been no report on synthetic pinakiolite before. As soon as there was an excess of Mg, no crystals were found to contain pinakiolite. Orthopinakiolite was found in crystals of all compositions but when Fe ions were present it became the dominating phase. It is evident that Fe ions play a role in stabilizing that structure; it is known that the mineral contains approximately 5% Fe.



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## Electron Microscopy of Oxyborates. III. On the Structure of Takéuchiite

BY JAN-OLOV BOVIN,\* M. O'KEEFFE AND M. A. O'KEEFFE†

*Chemistry Department and Center for Solid State Science, Arizona State University, Tempe, Arizona 85281, USA*

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#### Abstract

The crystal structure of the new mineral takéuchiite,  $\text{Me}_3\text{BO}_3$  (Me = Mg,  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ti}^{4+}$ ), has been derived by matching experimentally obtained high-resolution transmission electron microscope images with computed ones. The crystals are orthorhombic *Pnnm* or *Pnn2*, with  $a = 27.50$  (1),  $b = 12.614$  (2) and  $c = 6.046$  (1) Å and  $Z = 24$ . The structure can be described as a periodic chemical twinning of the parent structure of pinakiolite, and is thus closely related to the other known chemical twins of pinakiolite, *viz* ludwigite and orthopinakiolite.

#### Introduction

The new mineral takéuchiite was found in a specimen from Långban mine, Sweden (Bovin & O'Keeffe, 1980). The specimen (Smithsonian Institute no. 138548) was labeled orthopinakiolite but was found, during a high-resolution electron transmission microscopy study of synthetic and natural oxyborates (Bovin, O'Keeffe & O'Keefe, 1981; Bovin & O'Keeffe,

1981), to contain only crystals of the new mineral imbedded in dolomite and calcite.

The group of mineral structures closely related to those of pinakiolite (Takéuchi, Watanabé & Ito, 1950; Moore & Araki, 1974) and hulsite (Yamnova, Simonov & Belov, 1975; Konnert, Applemen, Clark, Finger, Kato & Miura, 1976), comprise ludwigite (Takéuchi *et al.*, 1950), vonsenite (Takéuchi, 1956) and orthopinakiolite (Takéuchi, Haga, Kato & Miura, 1978). All these structures can be described as chemical twinings (Andersson & Hyde, 1974) of the parent structure of pinakiolite (hulsite). Takéuchi (1978) predicted the existence of the new mineral, and by comparing the metal-atom occupancies in the structures of pinakiolite and orthopinakiolite he also suggested a model for the metal occupancies in the structure of the new mineral.

Using the Cowley–Moodie multislice formulation (Cowley & Moodie, 1957) it is possible to compute the electron microscope image to be expected from the structural model given by Takéuchi and to compare it with the experimentally obtained one. Thus it is possible to make a 'structure determination', not with the classical X-ray accuracy but accurately enough for determination of structure type and structural relations.

#### Structure model

The structural model used for takéuchiite can be derived by the structure building operation of chemical twinning on the unit-cell level (Andersson & Hyde, 1974).

\* Permanent address: Inorganic Chemistry 2, Chemical Centre, PO Box 740, S-220 07, Lund 7, Sweden.

† Present address: University of Cambridge, Department of Physics, Old Cavendish Laboratory, Cambridge CB2 3RQ, England.