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An Electron Microscope and X-Ray Diffraction Study of Some Synthetic $(Mg,Mn)_3BO_5$ Oxyborates

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The phase region surrounding the composition $(Mg,Mn)_3BO_5$, the nominal formula of the phases ludwigite, orthopinakiolite, takéuchiite, and pinakiolite, has been investigated by powder X-ray diffraction and transmission electron microscopy. It has been found that in samples prepared at 1000°C or higher the phases lie in the sequence ludwigite, takéuchiite, and orthopinakiolite as the composition increases in oxygen and Mn^{3+} content. All compounds appear to be nonstoichiometric and the composition $(Mg,Mn)_3BO_5$ has no special significance at 1000°C. The commonest defect microstructures observed were wider or narrower than normal twin plane spacings and coherent intergrowths of one structure type in another. Pinakiolite only formed at temperatures up to approximately 900°C. An alternative twinned form of pinakiolite, utilizing (100) twin planes, not previously observed before in synthetic material, has been characterized. It is suggested that takéuchiite is correctly regarded as a 1 : 1 intergrowth of ludwigite and orthopinakiolite and that pinakiolite and ludwigite are high and low temperature polymorphs with similar compositions. © 1992 Academic Press, Inc.

Introduction

The phases ludwigite, orthopinakiolite, and takéuchite are members of the pinakiolite family of oxyborate minerals. All have the same idealized formula M_3BO_5, where the metal M is usually a combination of octahedrally coordinated Mg, Mn, and Fe. Crystallographic studies (*1–14*) have shown that their structures can be generated by regular twinning of the parent pinakiolite phase. The phases vary from each other by having dissimilar twin plane repeat distances. In order of increasing twin plane density the structural series can be written pinakiolite, takéuchite, orthopinakiolite, and ludwigite. The structures represented in this way are shown in Fig. 1.

The chemical reasons for a structure to twin have been set out by Hyde *et al.* (*15*). Major factors of importance were considered to be stoichiometry changes and the generation of new cation sites. In terms of these criteria the reasons for twinning in the pinakiolite series of oxyborates are not obvious. The idealized formula is constant and no sites are created or destroyed by the twinning operation.

To date the only plausible explanation as to why these twinned phases should form has been given by Takéuchi (*16*), who noted that the compositions of mineral specimens of ludwigite, orthopinakiolite, and pinakiolite were $M_{3.00}BO_5$, $M_{2.95}BO_5$, and $M_{2.90}BO_5$, respectively. X-ray diffraction

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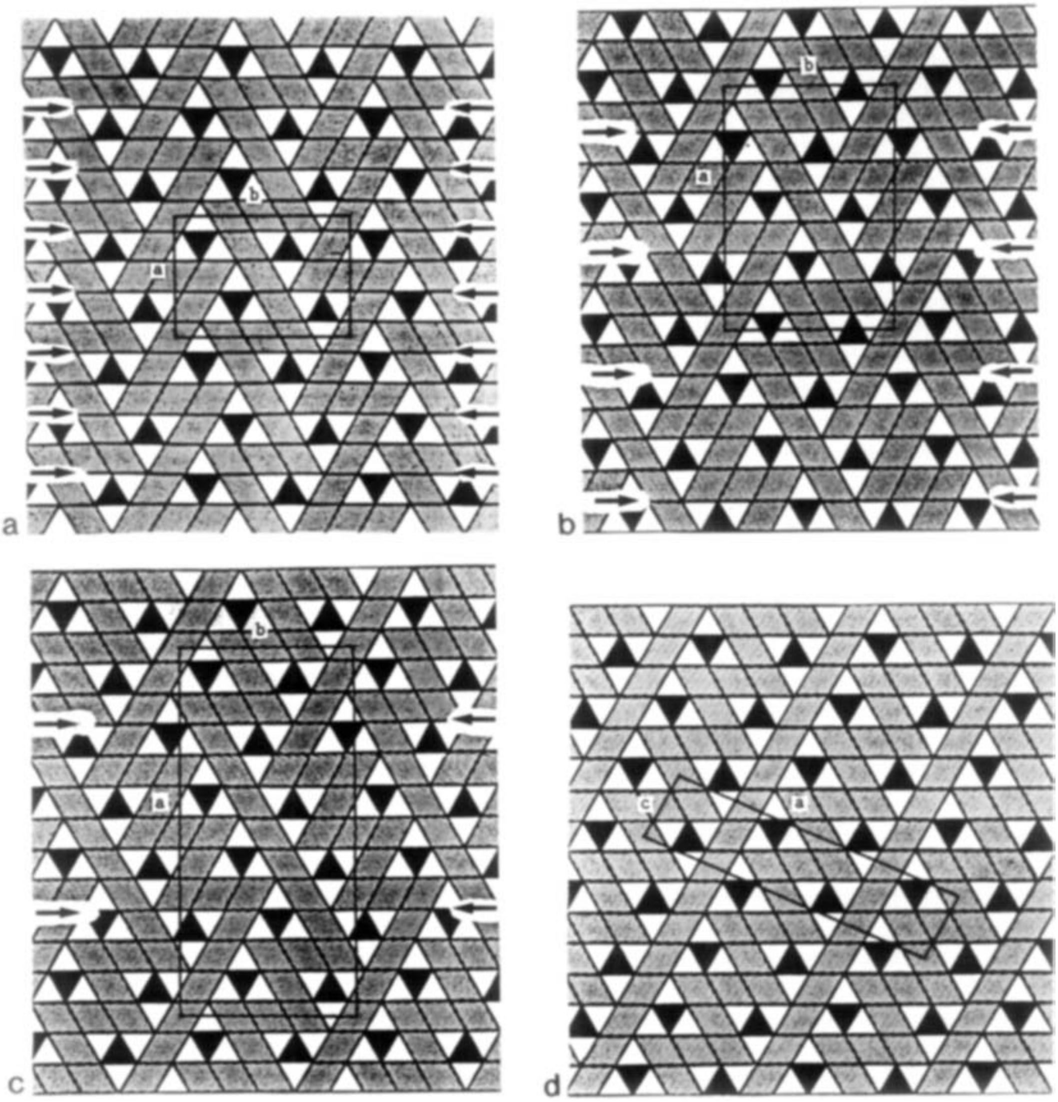


FIG. 1. Idealized polyhedral representation of the structures of (a) ludwigite; (b) orthopinakiolite; (c) takéuchiite; and (d) pinakiolite. The shaded diamonds represent MO_6 octahedra and the closed triangles BO_3 groups. The unit cells are outlined. In (d) the unit cell is that of the mineral form of pinakiolite. The arrows show the glide-twin planes needed to derive these structures from that of pinakiolite.

studies (*3*, *9*) had revealed that the departures from the idealized composition were associated with the existence of cation vacancies at octahedral sites in a part of the structure called a C-wall. Takéuchi assumed that the number of cation vacancies that could be accommodated depended upon the relative size of the C-walls. Twinning reduces the size of the C-walls and thus a high vacancy concentration will drive the structure toward untwinned pinakiolite while a low vacancy concentration will result in the formation of the most heavily twinned phase, ludwigite.

According to this idea there should be a direct correlation between composition and twin plane density. However, the correctness of this hypothesis is open to some doubt. The composition of mineral specimens of takéuchiite lies between that of ludwigite and orthopinakiolite rather than between orthopinakiolite and pinakiolite, as twin plane density would require. Additionally, Bovin *et al.* and Bovin and O'Keefe (*5–7*), who examined both synthetic and mineral specimens of oxyborates, observed that the structure formed was more dependent upon the Fe:Mn ratio than upon oxygen-to-metal stoichiometry. The aim of the study reported here was to try to clarify the situation by investigating the relationship between structure and stoichiometry in more detail than reported previously.

Experimental

All samples were prepared from "Specpure" quality MgO, Mn, MnO_2, B_2O_3 supplied by Johnson Matthey Ltd, each of which had a quoted total metallic impurity of less than 10 ppm. The boric oxide used was reported to have a water content of less than 200 ppm and was stored in a dessicator until used. The manganese oxides used in the preparations, Mn_2O_3 and Mn_3O_4, were prepared from MnO_2 powder which was heated in a Pt crucible at temperatures of 800 or 1000°C in air for 24 hr, followed by rapid quenching into liquid nitrogen. Under these conditions only the desired oxides formed, as was confirmed by weight loss measurements and powder X-ray diffraction.

Appropriate quantities of these materials were ground together in an agate mortar, formed into pellets, sealed into platinum tubes using a plasma microwelder and heated for the temperatures and times detailed in Tables I–III below. After reaction the tubes were quenched into liquid nitrogen.

The phases produced were identified by powder X-ray diffraction with a Guinier–Hägg focusing camera employing strictly monochromatic Cr$K\alpha_1$ radiation and KCl (a_0 = 0.62929 nm) as an internal standard. Films were measured with respect to a scale exposed on the film prior to development. Unit cell dimensions were refined using standard computer routines (*17*).

Samples were examined by transmission electron microscopy to assist in phase analysis and to characterize defect microstructures. For microscopy, small quantities of the samples were crushed under *n*-butanol. A drop of the resulting suspension was then placed on a holey carbon film and allowed to dry before examination in a JEOL 200CX transmission electron microscope fitted with a top entry goniometer stage and operated at 200 kV. Only suitably aligned crystal fragments with thin edges projecting over holes in the support film were examined in detail.

Results

X-Ray Diffraction

Phases found at 1000°C. Three series of preparations lying on the $MgO–Mn_3O_4–B_2O_3$ composition plane were designed to investigate the changes brought about by varying the boron content, $(Mg,Mn)_3B_xO_5$, the (Mg,Mn) content, $(Mg,Mn)_xBO_5$, and the oxygen content, $(Mg,Mn)_3BO_x$. The results are given in Table I and shown in Fig. 2. This figure is not intended to be an accurate phase diagram but does map out the succession of structures found and the approximate range of composition over which they occurred.

In the composition region closest to MgO an (Mg,Mn)O solid solution, *M*O, was identified. Preparations richer in Mn often contained a spinel solid solution $(Mg^{2+},Mn^{2+})Mn_2^{3+}O_4$ (M_3O_4), a warwickite solid solution $(Mg,Mn)^{2+}Mn^{3+}BO_4$ (M_2BO_4), and occasionally Mn_2O_3. The M_3BO_5 oxyborate

TABLE I

PREPARATIONS ON THE $MgO–B_2O_3–Mn_3O_4$ PLANE[a]

MgO	Mn_3O_4	B_2O_3	Formula	O/M	Products[b]	No.
0.0	1.0000	0.333	$M_3B_{0.667}O_5$	1.3635	M_3O_4, W, O	
0.375	0.8750	0.375	$M_3B_{0.75}O_5$	1.3333	M_3O_4, W	
0.645	0.7850	0.405	$M_3B_{0.81}O_5$	1.3123	M_3O_4, W, O	
0.9375	0.6875	0.4375	$M_3B_{0.875}O_5$	1.2903	M_3O_4, O	
1.1265	0.6245	0.4585	$M_3B_{0.917}O_5$	1.2765	M_3O_4, O, N*	
1.5	0.5000	0.5000	M_3BO_5	1.2500	L, T	
1.95	0.3500	0.5500	$M_3B_{1.1}O_5$	1.2195	L	1
0.0	0.875	0.5	$M_{2.625}BO_5$	1.3793	Mn_2O_3, W	
0.1	0.85	0.5	$M_{2.65}BO_5$	1.3699	Mn_2O_3, W	
0.3	0.8	0.5	$M_{2.7}BO_5$	1.3514	M_3O_4, W	
0.5	0.75	0.5	$M_{2.75}BO_5$	1.3333	M_3O_4, W	
0.7	0.7	0.5	$M_{2.8}BO_5$	1.3158	M_3O_4, W, O	
0.9	0.65	0.5	$M_{2.85}BO_5$	1.2987	O	
1.1	0.6	0.5	$M_{2.9}BO_5$	1.2821	O, T	
1.3	0.55	0.5	$M_{2.95}BO_5$	1.2658	T	5
1.5	0.5	0.5	M_3BO_5	1.2500	T, L	
1.7	0.45	0.5	$M_{3.05}BO_5$	1.2346	L	3
1.9	0.4	0.5	$M_{3.1}BO_5$	1.2195	L, MO	
2.1	0.3	0.5	$M_3BO_{4.8}$	1.2000	L, MO	
1.8	0.4	0.5	$M_3BO_{4.9}$	1.2250	L,	2
1.5	0.5	0.5	$M_3BO_{5.0}$	1.2500	T, L	
1.2	0.6	0.5	$M_3BO_{5.1}$	1.275	T,	6
0.9	0.7	0.5	$M_3BO_{5.2}$	1.3000	M_3O_4, W, O	
0.6	0.8	0.5	$M_3BO_{5.3}$	1.3250	M_3O_4, W, O	
0.3	0.9	0.5	$M_3BO_{5.4}$	1.3500	M_3O_4, W	
0.0	1.0	0.5	$M_3BO_{5.5}$	1.375	Mn_2O_3, W	

[a] All samples were heated for 1 week at 1000°C in sealed Pt tubes.

[b] W, warwickite; O, orthopinakiolite; L, ludwigite; T, takéuchiite; P, pinakiolite; N, new material; *, disordered phase; M_3O_4, $(Mg^{2+},Mn^{2+})Mn_2^{3+}O_4$; MO, $(Mg^{2+},Mn^{2+})O$.

phases which formed were in the sequence ludwigite, takéuchiite, and orthopinakiolite as the oxygen and Mn^{3+} content increased. Additionally some new oxyborate phases occurred. These compounds, labeled N in Fig. 2 and the tables, were described in an earlier publication (*18*).

A series of preparations with compositions lying on the $Mg_{1.5}Mn_{1.5}BO_x$ line which passed through the $MgO–Mn_3O_4–B_2O_3$ plane toward the oxygen corner of the phase diagram gave the results recorded in Table II. The sequence of oxyborate phases encountered as the oxygen content increased was ludwigite, takéuchiite, and orthopinakiolite.

Temperature variation. The reaction series used to explore phase existence as a function of temperature are listed in Table III. The trends noted as samples were heated at lower temperatures were as follows. Ludwigite evolved into takéuchiite or disordered pinakiolite containing isolated twin planes depending upon the temperature of reaction. Takéuchiite evolved via orthopinakiolite to M_3O_4 or M_2BO_4. In some series a highly disordered material containing a considerable number of planar defects parallel to (100) planes formed, designated as L* in Table III. This phase could equally well be considered a very disordered ludwigite or very disordered pinakiolite. In compositions M_4BO_6 the new phases N and MO solid solutions were also found.

Ludwigite. At a synthesis temperature of 1000°C reactions 1, 2, 3, and 4 yielded monophasic ludwigite. The composition variation was from $Mg_{1.95}Mn_{1.05}B_{1.1}O_5$ ($M$$O_{1.2195}$), reaction 1, $Mg_{1.80}Mn_{1.20}BO_5$ ($M$$O_{1.2250}$), reaction 2, $Mg_{1.70}Mn_{1.35}BO_5$ ($M$$O_{1.2346}$), reaction 3, to $Mg_{1.50}Mn_{1.50}BO_5$ ($M$$O_{1.2375}$), reaction 4. The unit cell dimensions of a ludwigite sample produced via reaction (1) were a = 0.9231 nm, b = 1.2519 nm, and c = 0.6044 nm, which compare favorably with those of the Fe-containing ludwigites studied by Takéuchi (*1*), viz. a = 0.914 nm, b = 1.245 nm, and c = 0.305 nm with the exception that the c-axis of the synthetic material is approximately double that of the mineral. The doubled axis is consistent with an ordered distribution of Mg and Mn atoms as is found in other oxyborate minerals. The composition range was accompanied by a lattice parameter variation in which ludwigite samples with higher concentrations of manganese had increased unit cell dimensions.

Takéuchiite. At 1000°C takéuchiite was observed in samples which contained significantly higher concentrations of Mn^{3+} and oxygen than those which gave rise to ludwigite. Three samples, reactions 5, 6, and 7, produced only takéuchiite at this temperature. The composition variation was

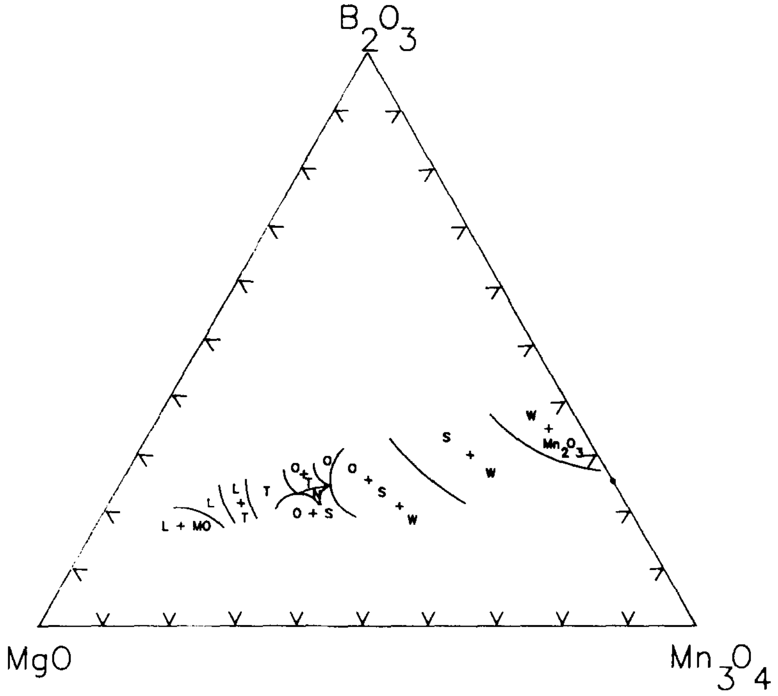


FIG. 2. The existence regions for phases found in preparations at 1000°C lying on the $MgO-Mn_3O_4-B_2O_3$ plane. MO, rock-salt type; L, ludwigite; T, takéuchiite; O, orthopinakiolite; S, spinel, M_3O_4; W, warwickite, M_2BO_4, N, new materials.

from $Mg_{1.30}Mn_{1.655}BO_5$ ($MO_{1.2658}$), reaction 5, $Mg_{1.20}Mn_{1.80}BO_{5.1}$ ($MO_{1.2750}$), reaction 6, to $Mg_{1.50}Mn_{1.50}BO_{5.05}$ ($MO_{1.2625}$), reaction 7. Takéuchiite was also produced alone from reaction 5 at 1100°C and reaction 8, $Mg_{0.90}Mn_{1.95}BO_5$ ($MO_{1.2987}$), at 1200°C. At 1000°C the $O:M$ ratio tolerated by takéuchiite extended above the $MgO-Mn_3O_4-B_2O_3$ plane. The limited amount of data at other temperatures suggested that the composition of takéuchiite moved toward higher Mn^{3+} and oxygen contents as the temperature increased.

The refined powder X-ray diffraction data for takéuchiite produced by reaction 5 at 1000°C gave unit cell dimensions $a = 2.7677$ nm, $b = 1.2580$ nm, and $c = 0.6094$ nm, which compare favorably with those determined by Bovin and O'Keefe (*4*), $a = 2.750$ nm, $b = 1.2614$ nm, and $c = 0.6046$ nm, for a mineral specimen. X-ray diffraction patterns produced from the takéuchiite specimen prepared from reaction 7 showed a shift in the positions of the diffraction maxima toward higher Bragg angles compared with those from the takéuchiite samples produced from mixtures lying on the $MgO-Mn_3O_4-B_2O_3$ plane, providing further evidence of the existence of a composition range for takéuchiite.

Orthopinakiolite. In general orthopinakiolite formed in specimens which had higher Mn^{3+} concentrations than those which produced takéuchiite at 1000°C. Single phase orthopinakiolite was produced by reaction 8, with composition $Mg_{0.90}Mn_{1.95}BO_5$ ($MO_{1.2987}$), between 900 and 1100°C and by reaction 5, with composition $Mg_{1.30}Mn_{1.655}BO_5$ ($MO_{1.2658}$), at 900°C. As with takéuchiite, the limited temperature information

TABLE II

PREPARATIONS ON THE $Mg_{1.5}Mn_{1.5}BO_x$ LINE[a]

MgO	Mn_3O_4	Mn_2O_3	Mn	B_2O_3	Formula	O/M	Products[b]	No.
1.5	0.4625	0.0	0.1125	0.5	$M_3BO_{4.85}$	1.2125	L, N*	
1.5	0.4875	0.0	0.0375	0.5	$M_3BO_{4.95}$	1.2375	L	4
1.5	0.5	0.0	0.0	0.5	M_3BO_5	1.2500	L, T	
1.5	0.4	0.15	0.0	0.5	$M_3BO_{5.05}$	1.2625	T,	7
1.5	0.2	0.45	0.0	0.5	$M_3BO_{5.15}$	1.2875	T, M_3O_4	9
1.5	0.0	0.75	0.0	0.5	$M_3BO_{5.25}$	1.3125	T, O	

[a] All samples were heated for 1 week at 1000°C in sealed Pt tubes.

[b] W, warwickite; O, orthopinakiolite; L, ludwigite; T, takéuchiite; P, pinakiolite; N, new material; *, disordered phase; M_3O_4, $(Mg^{2+},Mn^{2+})Mn_2^{3+}O_4$; MO, $(Mg^{2+},Mn^{2+})O$.

available suggests that the more oxygen rich composition is preferred at higher temperatures.

The refined X-ray diffraction data for orthopinakiolite produced via reaction 8 at 1000°C gave unit cell dimensions of a = 1.840 nm, b = 1.2598 nm, and c = 0.6156 nm, which are in good agreement with the data reported by Takéuchi (*1*), viz. a = 1.8357 nm, b = 1.2591 nm, and c = 0.6068 nm, for a mineral specimen. Some variation in the unit cell dimensions of the synthetic orthopinakiolite samples was observed, indicating a variable composition for this phase.

Pinakiolite. In contrast to the frequent occurrence of the other oxyborate phases, pinakiolite was produced in only a few cases and no pinakiolite was ever produced at temperatures above 900°C. No compositional variations were discovered. Monophasic pinakiolite was only obtained in reaction 9 at 900°C, with a composition of $Mg_{1.50}Mn_{1.50}BO_{5.15}$ ($MO_{1.2875}$). Only one other preparation contained pinakiolite, reaction 3 at 800°C.

The refined X-ray data for pinakiolite obtained from reaction 9 heated at 900°C gave unit cell dimensions of a = 1.0443 nm, b = 0.6041 nm, c = 0.5441 nm, and β = 96.03°, which compare favorably with those of the mineral pinakiolite with unit cell dimensions a = 2.179 nm, b = 0.5977 nm, c = 0.5341 nm, and β = 95.83° (*9*). The a-axis of the synthetic counterpart is approximately half that of the mineral sample. The doubled a-axis dimension is due to the C-face centering of the lattice which would cause absences whenever the values of $h + k$ are odd. These absences do not occur in our samples and we have preferred the smaller unit cell.

Electron Microscopy

Planar faults. Crystals of orthopinakiolite, takéuchiite, and ludwigite produced in this study often showed variations in the twin repeat distance. These were revealed as planar faults which are seen in electron micrographs as either wider (in the case of ludwigite) or narrower than normal lamellae of the pinakiolite type between the twin planes. These defects were found to lie parallel to the twin planes, that is, perpendicular to the [100] direction of each structure. In many instances these faults were terminated abruptly within the crystal lattice. As similar structures have been illustrated before (*5–7, 18–20*) they are not shown here.

Intergrowth structures. Intergrowths between different members of the structural series were often observed within the same crystal fragment. The boundary planes were parallel to the twin planes in both phases.

TABLE III

PREPARATIONS AT DIFFERING TEMPERATURES[a]

						Heating			
MgO	Mn_3O_4	Mn_2O_3	Mn	B_2O_3	Formula	°C	days	Product[b]	No.
1.7	0.45	0.0	0.0	0.5	$M_{3.05}BO_5$	1100	5	L	3
1.7	0.45	0.0	0.0	0.5	$M_{3.05}BO_5$	1000	7	L	3
1.7	0.45	0.0	0.0	0.5	$M_{3.05}BO_5$	900	10	L*	3
1.7	0.45	0.0	0.0	0.5	$M_{3.05}BO_5$	800	20	N*, P*	3
1.5	0.5	0.0	0.0	0.5	M_3BO_5	1200	5	L	
1.5	0.5	0.0	0.0	0.5	M_3BO_5	1100	5	L	
1.5	0.5	0.0	0.0	0.5	M_3BO_5	1000	7	L, T	
1.5	0.5	0.0	0.0	0.5	M_3BO_5	900	10	L*	
1.3	0.55	0.0	0.0	0.5	$M_{2.95}BO_5$	1200	5	L, T	5
1.3	0.55	0.0	0.0	0.5	$M_{2.95}BO_5$	1100	5	T	5
1.3	0.55	0.0	0.0	0.5	$M_{2.95}BO_5$	1000	7	T	5
1.3	0.55	0.0	0.0	0.5	$M_{2.95}BO_5$	900	10	O	5
1.3	0.55	0.0	0.0	0.5	$M_{2.95}BO_5$	800	20	L*, M_3O_4	5
0.9	0.65	0.0	0.0	0.5	$M_{2.85}BO_5$	1200	5	T	8
0.9	0.65	0.0	0.0	0.5	$M_{2.85}BO_5$	1100	5	O	8
0.9	0.65	0.0	0.0	0.5	$M_{2.85}BO_5$	1000	7	O	8
0.9	0.65	0.0	0.0	0.5	$M_{2.85}BO_5$	900	10	O	8
0.9	0.65	0.0	0.0	0.5	$M_{2.85}BO_5$	800	20	W, M_3O_4	8
1.5	0.2	0.45	0.0	0.5	$M_3BO_{5.15}$	1000	7	T, M_3O_4	9
1.5	0.2	0.45	0.0	0.5	$M_3BO_{5.15}$	900	10	P*	9
1.5	0.75	0.0	0.25	0.5	M_4BO_6	1200	7	N	
1.5	0.75	0.0	0.25	0.5	$M_{44}BO_6$	1100	7	N*, L	
1.5	0.75	0.0	0.25	0.5	M_4BO_6	1000	7	N*, L	
2.5	0.5	0.0	0.0	0.5	M_4BO_6	1200	7	L, MO	
2.5	0.5	0.0	0.0	0.5	M_4BO_6	1100	7	L, MO	
2.5	0.5	0.0	0.0	0.5	M_4BO_6	1000	7	L, MO	

[a] All samples were heated in sealed Pt tubes.

[b] W, warwickite; O, orthopinakiolite; L, ludwigite; T, takéuchiite; P, pinakiolite; N, new material; *, disordered phase; M_3O_4, $(Mg^{2+},Mn^{2+})Mn_2^{3+}O_4$; MO, $(Mg^{2+},Mn^{2+})O$.

No mismatch at the boundary planes between each component was ever evident, indicating coherency between the different regions. In general only two phases were found intergrown in any crystal, these corresponding to the phases present in the sample as indicated by X-ray diffraction. As similar structures have been illustrated before (*5–7, 19–21*) they are not shown here.

Defects in pinakiolite. Fragments of pinakiolite often contained isolated twin planes, parallel to the (201) planes referred to the mineral unit cell (or (101) referred to the unit cell of our synthetic samples), distributed randomly throughout the crystal as shown in Fig. 3. The diffraction patterns from such crystals, shown in Fig. 3b, were typical of those from twinned crystals.

An alternative type of twinning, on (100) planes, was also found in these synthetic samples. Fig. 4a shows a crystal fragment containing such a twin plane. The electron diffraction pattern from the fragment, Fig. 4b, confirms that the crystal is twinned. From the contrast at the thin edge of the crystal it is apparent that the twin operation occurs at one of the flat walls of the edge

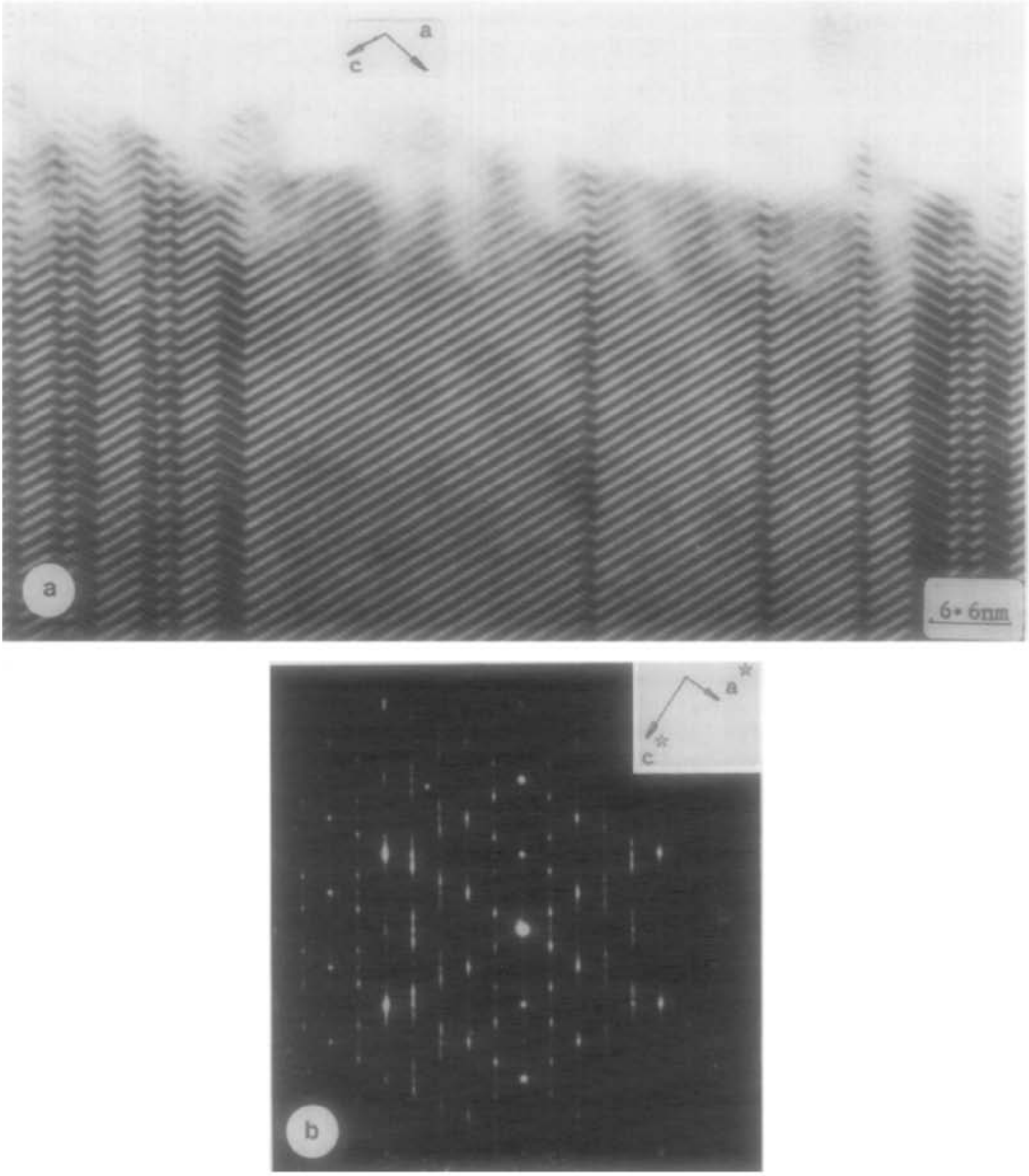


FIG. 3. Electron micrograph (a) and electron diffraction pattern (b) of a pinakiolite crystal containing disordered (101) twin planes. These are seen running from top to bottom in (a); the structure being mirrored on either side of each twin boundary.

sharing octahedra. A schematic drawing of the twin plane is shown in Fig. 5.

Many crystal fragments of pinakiolite were observed in which defects lying on (100) planes were more or less disordered. Figure 6a is a lattice image of these defects. The micrograph shows rows of white spots lying parallel to the *c*-axis and is typical of high resolution images of pinakiolite. At the defect boundaries the rows of spots are dis-

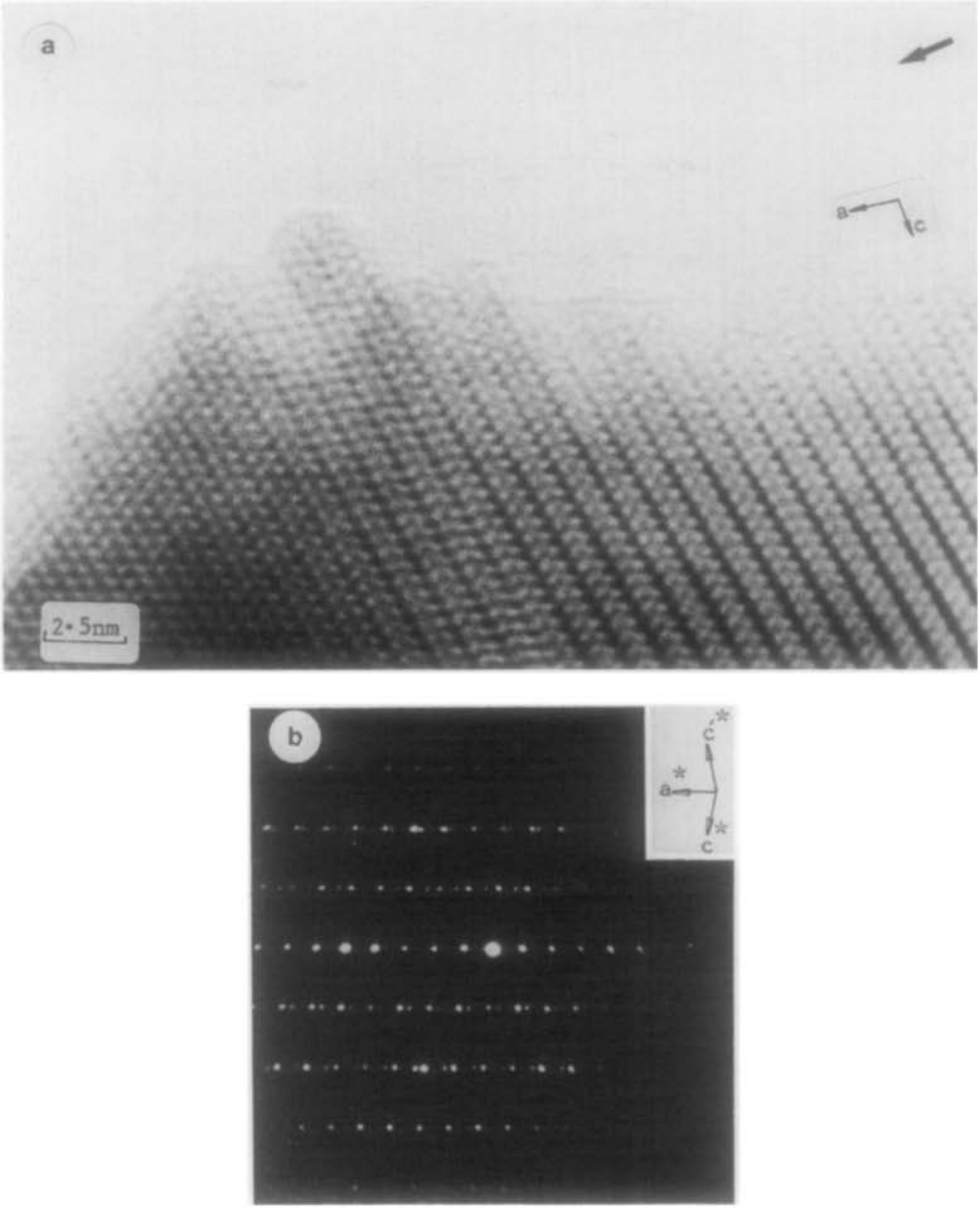


FIG. 4. Electron micrograph (a) and electron diffraction pattern (b) of a twinned pinakiolite crystal. The twin planes lie parallel to (100) planes and are best seen by viewing the micrograph at grazing incidence in the direction of the arrow.

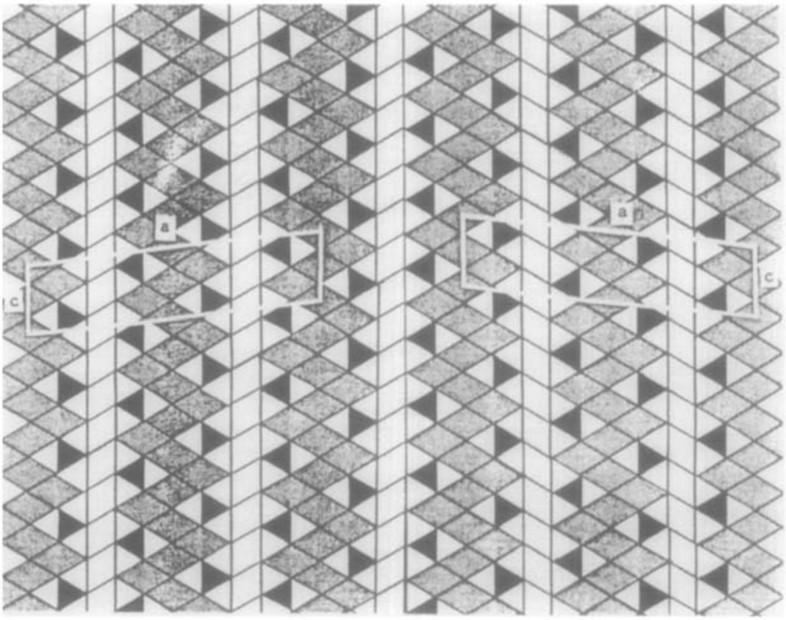


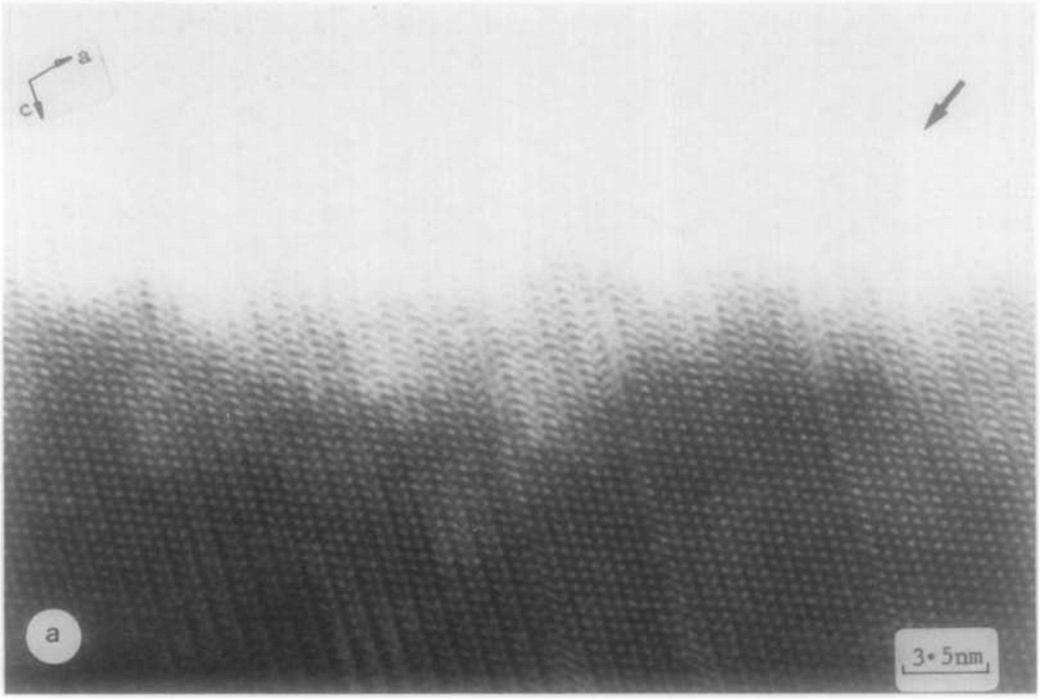
FIG. 5. An idealized polyhedral daigram representing a possible (100) twin boundary in pinakiolite. The fault plane lies in the central flat wall of octahedra and the twinning operation involves a displacement along the *c*-axis direction. The unit cells marked correspond to the mineral form of pinakiolite.

placed by approximately half the repeat distance along [001]. Since the structure of pinakiolite is known and as the image at the crystal edge in Fig. 6a bears a direct correspondence to this structure it is possible to interpret the image contrast in the defect planes with confidence. A plausible structural model for the defects is shown in Fig. 6b. Defects of this type are similar, and may be identical, to those observed in a natural specimen of an antimony-rich pinakiolite, reported by Hansen *et al.* (*21*).

Discussion

The results have shown that the structure of the nominally M_3BO_5 oxyborate phase formed in the Mg–Mn–B–O system is dependent upon both composition and temperature of preparation. The composition M_3BO_5 itself had no special significance; at 1000°C, for example, mixtures of ludwigite and takéuchiite were formed. The phase domains of the oxyborates produced at 1000°C are summarized in Fig. 2. Ludwigite was observed to form with an overall O : M ratio of between 1.2195 and 1.2375, takéuchiite with a ratio of between 1.2625 and 1.2750, and orthopinakiolite with a ratio of 1.2987 at 1000°C. These data do not indicate the precise limits of each structure type as careful equilibration was not carried out. The lattice parameter changes observed, however, do indicate that these phases possess extended composition ranges.

There is a close relationship between the types of defect found and the gross composition of the initial oxide mixtures. In most of the single phase samples the crystal fragments were generally well ordered, exceptions being found most often in low temperature preparations. Intergrowths were mainly found in those samples which were biphasic. For example, intergrowths in the



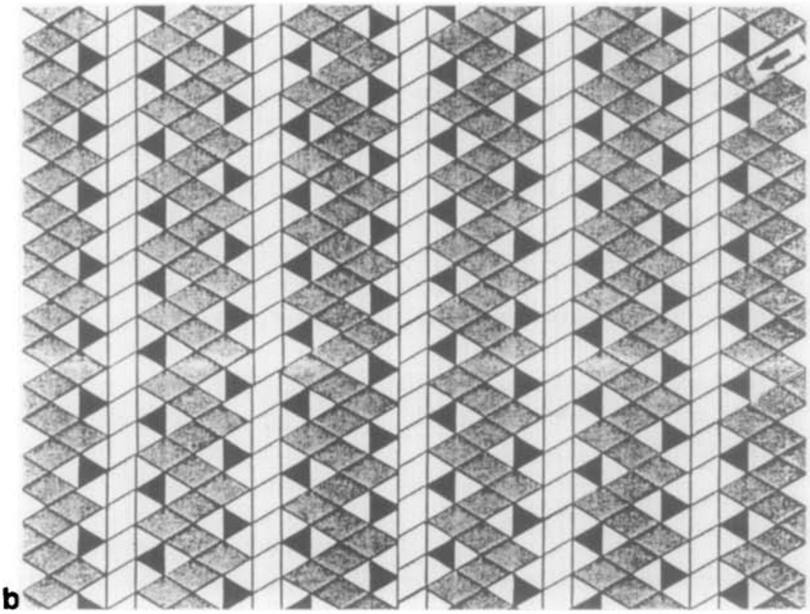


FIG. 6. (a) Electron micrograph of a pinakiolite crystal containing faults on (100) planes. These are best seen by viewing the micrograph at grazing incidence in the direction of the arrow. (b) A plausible structural model for the defects seen in (a). The fault plane, which lies in the central wall of octahedra, can be best seen by viewing the diagram along the arrowed direction. This direction is the same as that marked on the micrograph.

samples between M_3BO_5 and $M_{2.9}BO_5$ consisted of ludwigite and takéuchiite or takéuchiite and orthopinakiolite, depending on the exact preparation conditions.

From a structural viewpoint the twin plane density decreases in the order ludwigite, orthopinakiolite, and takéuchiite. The succession of structures which form as a function of oxygen or Mn^{3+} content at 1000°C is, on the other hand, ludwigite, takéuchiite, and orthopinakiolite. The results clearly indicate that takéuchiite always forms between the composition ranges of ludwigite and orthopinakiolite. Thus the premise outlined in the Introduction, that there should be a smooth progression from ludwigite via orthopinakiolite, takéuchiite, and ultimately pinakiolite as a function of composition, has been shown to be incorrect. The twin plane repeat distance emphasised in earlier studies is not a correct indicator for the structure–composition relations in this series.

An alternative explanation for the sequence found can be obtained by a consideration of Fig. 7. This shows the idealized structures of ludwigite and orthopinakiolite with the unit cell slabs highlighted. Examination of this figure makes it clear that takéuchiite can be considered an ordered intergrowth of unit cell thick slabs of ludwigite and orthopinakiolite. It is then understandable that takéuchiite falls between ludwigite and orthopinakiolite in composition. From this perspective it is of interest to inquire whether intergrowths other than the 1 : 1 ludwigite : orthopiniakolite could form. None have been observed in this study.

The composition variations across the composition range from ludwigite to orthopinakiolite require changes in the Mn^{3+}-to-Mn^{2+} ratio. As the twin planes do not alter the composition of the matrix the change in structure with composition must be due to other factors. A reasonable suggestion is that the structures form so as to minimize the elastic strain energy in the crystals. The origin of the elastic strain energy is likely to be the Jahn–Teller distortions of the Mn^{3+}-containing octahedra. This usually takes the form of two long bonds and four shorter bonds, causing the surrounding oxygen octahedron to adopt a tetragonal form. The crystallographic studies detailed in Refs. (*1–15*) show that such distortions occur in all of the Mn^{3+}-containing oxyborates. It would therefore appear that, for preparations at 1000°C, the structure adopted when the amount of Mn^{3+} or elastic strain is lowest is ludwigite and the structure adopted when the amount of Mn^{3+} or elastic strain is highest is orthopinakiolite.

The Jahn–Teller distortion is temperature dependent and in general it has been found that the distortions decrease with temperature. Thus one would expect that the low strain form, ludwigite, would tend to dominate at higher temperatures. This is in accord with the observations. However, the degree to which distortions can be quenched in depends upon structure, and in the present case the conversion of one structure type to another requires considerable atom movement (*19, 20*). It is therefore not clear how easily the structure which is formed during reaction at 1000°C, which presumably would be the one which minimizes strain energy at that temperature, will transform on cooling. Careful annealing experiments or high temperature X-ray studies will be needed to resolve this question.

The pinakiolite structure appears to be preferred to the ludwigite structure at temperatures below 900°C. This suggests that pinakiolite is also a low strain structure and that ludwigite and pinakiolite are not at the extreme ends of a series related by cation vacancy concentrations but instead are low and high temperature phases. This is consistent with the fact that hulsite, an Fe-containing pinakiolite, forms without any Mn^{3+} present. As the Mn^{3+} content increased in the preparations made at 800°C

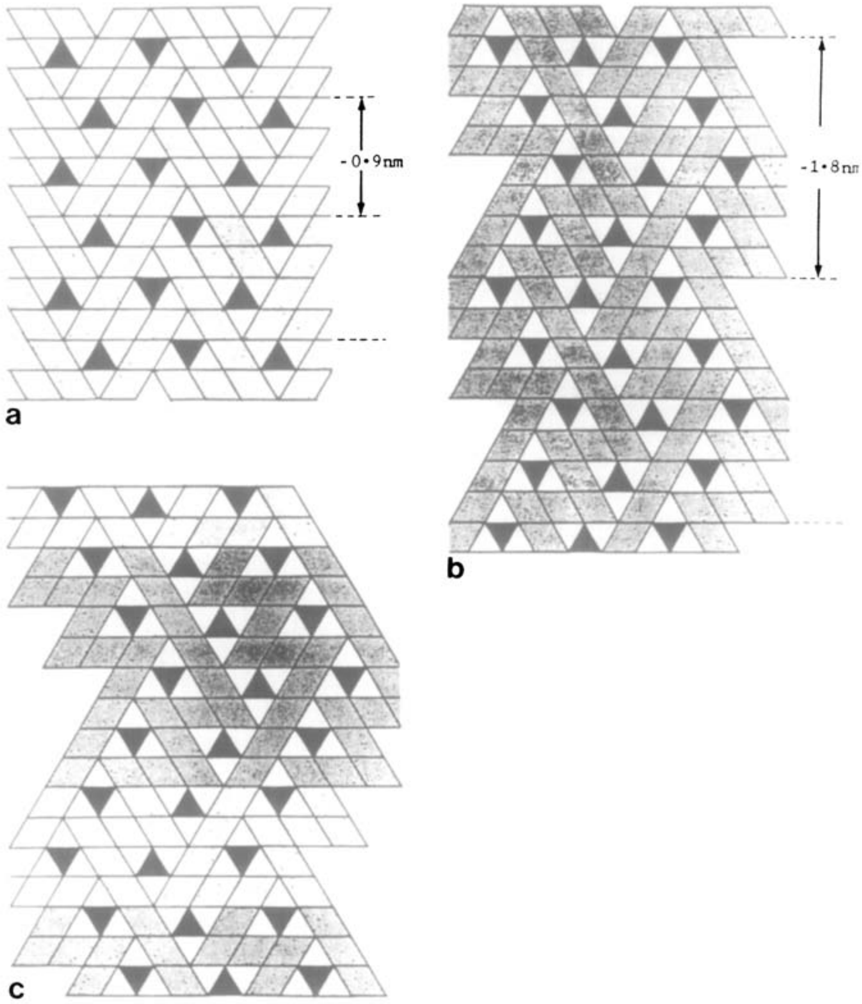


FIG. 7. Idealized polyhedral representations of the structures of (a) ludwigite and (b) orthopinakiolite. The length of the unit cells parallel to *a* are shown. The structure of takéuchiite (c) can be regarded as a 1 : 1 intergrowth of ludwigite and orthopinakiolite.

pinakiolite was replaced by warwickite rather than by any of the twinned phases and it is not clear that pinakiolite does exist in the presence of twinned phases apart from in a disordered state which may be indicative of nonequilibrium. Further experiments will be needed to clarify this matter.

The (100) twinning observed suggests that a new series of oxyborate structures may form under some experimental conditions. These new materials would also be related to the parent pinakiolite structure by regular twinning. The twin planes would, however, lie on the (100) planes in pinakiolite as opposed to the (201)/(101) planes and the various homologues would be generated by regular twin plane separations given by some multiple of the pinakiolite *a*-axis repeat distance. Further study is needed to explore this possibility.

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References

1. Y. Takéuchi, *Mineral. J.* **2,** 19 (1956).
2. Y. Takéuchi, T. Watanabe, and T. Ito, *Acta Crystallogr.* **3,** 98 (1950).
3. Y. Takéuchi, N. Haga, T. Kato, and Y. Miura, *Can. Mineral.* **16,** 475 (1978).
4. J. O. Bovin and M. O'Keeffe, *Am. Mineral.* **65,** 1130 (1980).
5. J. O. Bovin, M. O'Keeffe, and M. A. O'Keefe, *Acta Crystallogr. A* **37,** 28 (1981).
6. J. O. Bovin and M. O'Keeffe, *Acta Crystallogr. A* **37,** 35 (1981).
7. J. O. Bovin, M. O'Keeffe, and M. A. O'Keefe, *Acta Crystallogr. A* **37,** 42 (1981).
8. J. A. Konnert, D. E. Appleman, J. R. Clark, L. W. Finger, T. Kato, and Y. Miura, *Am. Mineral.* **61,** 116 (1976).
9. P. B. Moore and T. Araki, *Am. Mineral.* **59,** 985 (1975).
10. R. Norrestam and J.-O. Bovin, *Z. Kristallogr.* **18,** 135 (1987).
11. J.-O. Bovin and R. Norrestam, *Inst. Phys. Conf. Ser.* **2**(93), 555 (1988).
12. R. Norrestam, S. Dahl, and J.-O. Bovin, *Z. Kristallogr.* **187,** 201 (1989).
13. R. Norrestam, K. Neisen, I. Sotofte, and N. Thorup, *Z. Kristallogr.* **189,** 33 (1989).
14. R. Norrestam and S. Hansen, *Zeit. Kristallogr.* **191,** 105 (1990).
15. B. G. Hyde, S. Andersson, M. Bakker, C. M. Plug, and M. O'Keeffe, *Prog. Solid State Chem.* **12,** 273 (1979).
16. Y. Takéuchi, *Recent Prog. Nat. Sci. Jpn.* **3,** 153 (1978).
17. B. G. Brandt and A. G. Nord, *Chem. Commun. Univ. Stockholm* **5** (1970).
18. J. J. Cooper and R. J. D. Tilley, *J. Solid State Chem.* **63,** 129 (1986).
19. J. J. Cooper and R. J. D. Tilley, *J. Solid State Chem.* **58,** 375 (1985).
20. J. J. Cooper and R. J. D. Tilley, *J. Solid State Chem.*, in press.
21. S. Hansen, U. Hålenius, and B. Lindqvist, *Neues Jahrb. Mineral. Monatsh.* **5,** 231 (1988).