JOURNAL OF SOLID STATE CHEMISTRY **58**, 375–382 (1985)

Direct Observation of the Transformation of Ludwigite to Orthopinakiolite

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Received October 5, 1984; in revised form December 14, 1984

Crystals with the composition $Mg_{1.5}Mn_{1.5}BO_5$ prepared at 1300°C in sealed platinum tubes were studied by high-resolution electron microscopy. The crystals were found to possess the ludwigite structure with very few inherent planar defects. After heating in the electron beam the electron diffraction patterns and electron micrographs showed that the ludwigite structure had rearranged to the orthopinakiolite structure. Two possible mechanisms for such a transformation have been described.

Introduction

The oxyborate family of minerals related to pinakiolite have the nominal formula $M_x BO_5$ ($2.9 \leq x \leq 3.0$) where the metal ion M is usually a combination of the atoms Mg, Mn, and Fe. The real formula of the minerals is, however, complex and for the two phases of interest in this report, ludwigite and orthopinakiolite, formulae of $(Mg,Fe)_2^{2+}Fe^{3+}BO_5$ (*1*) and $Mg^{2+}_{1.42}Mn^{2+}_{0.43}Mn^{3+}_{0.88}Fe^{3+}_{0.22}BO_5$ (*2*), respectively, have been cited. Besides these materials, the related oxyborate minerals pinakiolite (*1*, *3*), hulsite (*4*), vonsenite (*5*), and takéuchiite (*6*) have been characterised by X-ray diffraction studies. In addition Bovin and O'Keeffe (*8*) and Bovin *et al.* (*6*, *7*) have studied mineral samples of pinakiolite, ludwigite, orthopinakiolite and takéuchiite plus a few synthetic samples of these compounds by high-resolution electron microscopy.

Although the formulae of all these minerals is very similar, their structures are different. The relationships between these structures have been discussed in terms of cation ordering, especially of populations of Mn^{2+} and Mn^{3+} by Takéuchi (*9*) and Moore and Araki (*3*). Bovin and O'Keeffe (*8*) and Bovin *et al.* (*6*, *7*) have discussed the various structures in terms of chemical twinning. However, to date there is no convincing explanation of why so many structure types occur in these closely related oxyborates, or whether one structure can transform to another, although intergrowths between the structure types have been observed (*6*–*8*). Because of this we have started a careful investigation of the structure-composition relations in synthetic oxyborates. During this investigation we have observed the transformation of $Mg_{1.5}Mn_{1.5}BO_5$ with the ludwigite structure directly to orthopinakiolite, also with the same nominal stoichiometry, during electron microscope examination. As these observations are new we report them in this paper.

0022-4596/85 $3.00

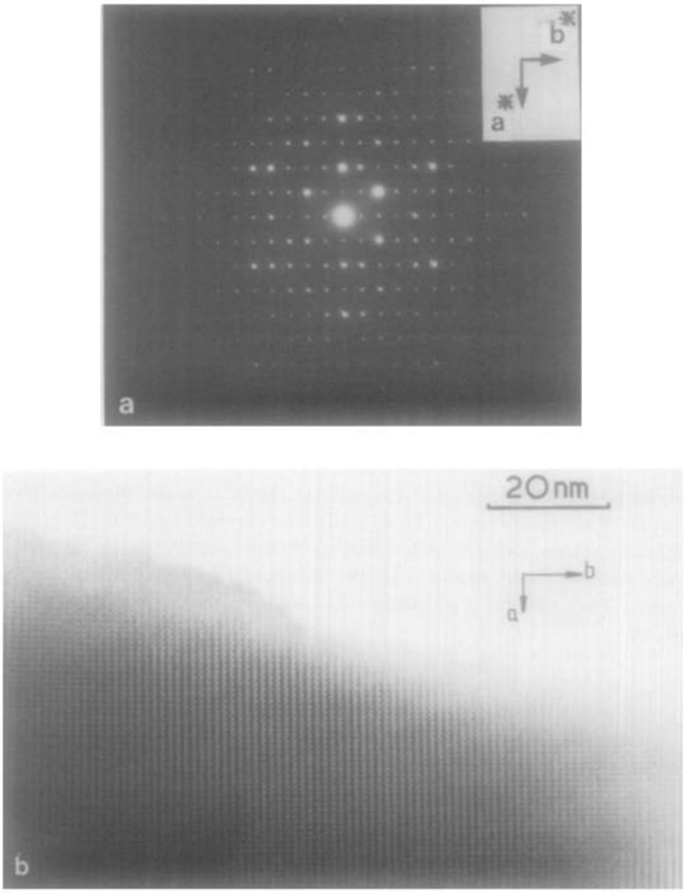

FIG. 1. (a) Electron diffraction pattern of a $Mg_{1.5}Mn_{1.5}BO_5$ crystal with the ludwigite structure photographed with the electron beam parallel to *c*. (b) Electron micrograph of a $Mg_{1.5}Mn_{1.5}BO_5$ ludwigite-type crystal recorded with the beam parallel to *c*.

Experimental

Oxyborate crystals of composition $Mg_{1.5}Mn_{1.5}BO_5$ were prepared by heating pressed pellets containing well-mixed stoichiometric amounts of MgO, Mn_3O_4, and $B_2O_3 \cdot xH_2O$ at 1300°C in sealed platinum tubes. The water content of the $B_2O_3 \cdot xH_2O$ was determined from microbalance studies and the resulting formula used to give the required amount of boron for the preparation. Small quantities of the resulting pellets were crushed under butanol in an agate mortar and then placed on a holey carbon film for examination in a JEOL 100B electron microscope operated at 100 kV. Crystal fragments with thin edges were aligned so that the beam was parallel to the shortest unit cell axis. The resulting electron diffraction and high-resolution images were then photographed using a low incident beam intensity. The crystals were then heated by increasing the beam intensity and gradually condensing the electron beam over a period of a few hours. During this operation the crystal was continually realigned and the resulting diffraction pattern and images were recorded in the normal way.

Results

Crystal fragments were identified as being of the ludwigite structure by observation of the electron diffraction pattern. A typical example is shown in Fig. 1a. In this it should be noted that the systematic absences of the reflections do not agree with those of the mineral ludwigite reported in the structure determination by Takéuchi *et al.* (*1*). However, our diffraction patterns are identical to those for ludwigite shown by Bovin *et al.* (*7*) and can only be indexed in terms of the ludwigite unit cell. It is certain, therefore, that the structure of the fragments is of the ludwigite type.

In general the fragments were stable in the electron beam under normal imaging conditions, that is, using a low beam intensity. Very few defects were identified in these crystals, and no faulting was found. A typical fragment is shown in Fig. 1b.

Examination of these same crystal fragments using a higher beam intensity caused decomposition to take place. This was often uncontrolled and lead to a microcrystalline product forming. Sometimes, however, this severe decomposition was limited to the edge of the crystal even after prolonged heating. This reaction will not be considered further here.

Of more interest was the fact that planar faults were often observed to form at the thin edges of the fragments and propagate into the thicker parts of the crystal in a controlled reaction sequence. The planar faults were always parallel to (100) planes and usually appeared singly at the start of the reaction. Continued beam heating, however, caused the original faults to broaden out and produce wider or narrower areas of faulted crystal. Observations of the faults at high magnification showed that they were not single fault planes such as antiphase boundaries, twin boundaries or crystallographic shear planes but narrow lamellae 2 ludwigite unit cells wide in the [100] direction. These lamellae grew wider simply by the addition of further slabs to either side of the initial fault to produce hybrid crystals with less and less ludwigite structure matrix as the reaction proceeded. Crystal fragments in the course of reaction and representative of this process are shown in Fig. 2.

The diffraction patterns from such partly reacted crystals showed varying degrees of streaking along the a^* direction. Initially the streaking was of low intensity and continuous, but as the fault density increased the streaking developed a prominent maximum of intensity midway between the ludwigite spots. These maxima evolved into reasonably sharp reflections themselves via a stage in which the ludwigite matrix spots appeared sharp and the new spots alone were streaked. This progression is shown in Fig. 3.

A comparison of the final diffraction patterns obtained in this sequence with those expected from other oxyborates and those illustrated by Bovin *et al.* (*7*) shows categorically that the final product is of the orthopinakiolite structure. It is clear, therefore, that the ludwigite structured $Mg_{1.5}Mn_{1.5}BO_5$ is transforming to the orthopinakiolite structure under the influence of the electron beam.

Discussion

Bovin and O'Keeffe (*8*) observed crystals of the ludwigite structure which contained thicker or thinner lamellae of the orthopinakiolite structure and which are very similar in appearance to the partly reacted crystals described here. However, they did not observe the transformation of one structure into another, and did not describe a mechanism by which such a transformation could take place. They did, however, describe a mechanism for the transformation of the pinakiolite structure

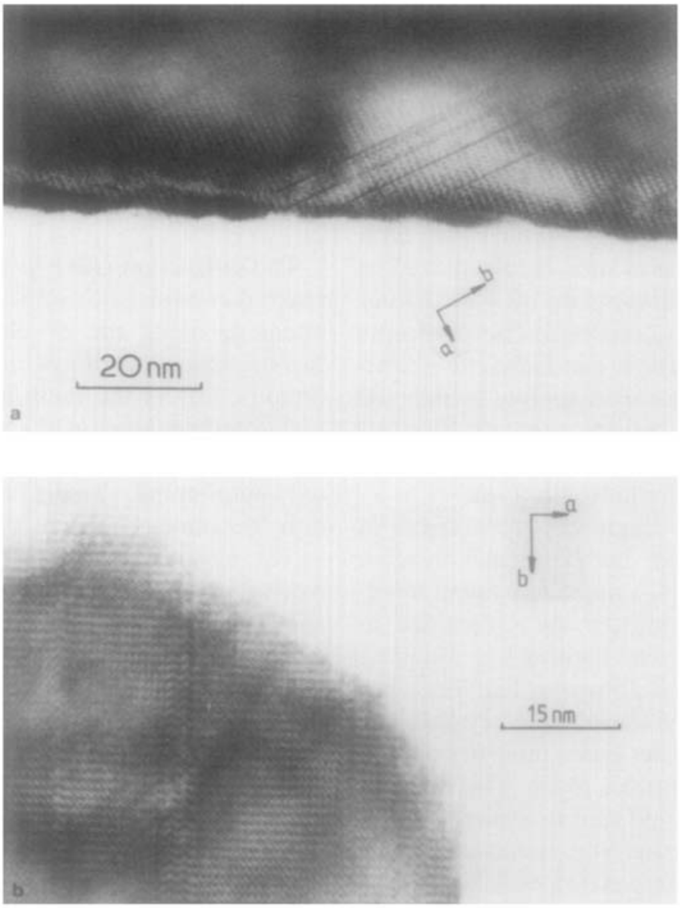

FIG. 2. (a) Low magnification electron micrograph of a ludwigite crystal showing planar faults parallel to (100) planes produced by heating fragments in the electron beam. (b) After further reaction slabs of the orthopinakiolite structure are seen despite the degradation in resolution due to beam damage.

to the ludwigite structure by way of a slip operation. The way in which the lamellae of orthopinakiolite grew into the ludwigite matrix is very reminiscent of the growth of crystallographic shear planes into tungsten trioxide *(10)* and suggests that shear or slip may be in operation here.

A plausible mechanism is shown in Fig. 4. In Fig. 4a the slightly idealised ludwigite structure is shown. It is seen to consist of zig–zag ribbons of edge-shared Mg and Mn octahedra, which contain B in threefold coordination in the triangular tunnels so formed. Also shown in Fig. 4a are two slip vectors marked **S1** and **S2**. If the slip operation marked **S1** is performed (by scissors on a drawing, if necessary) the structure in Fig. 4b is formed. The operation **S2** performed on the structure in Fig. 4b leads to that shown in Fig. 4c. A unit jump of Mg or Mn cations into neighbouring sites, indicated by the curved arrows in Fig. 4c results in the structure shown in Fig. 4d. This, in fact, represents a lamella of the orthopinakiolite structure coherently intergrown within a ludwigite matrix, as can be

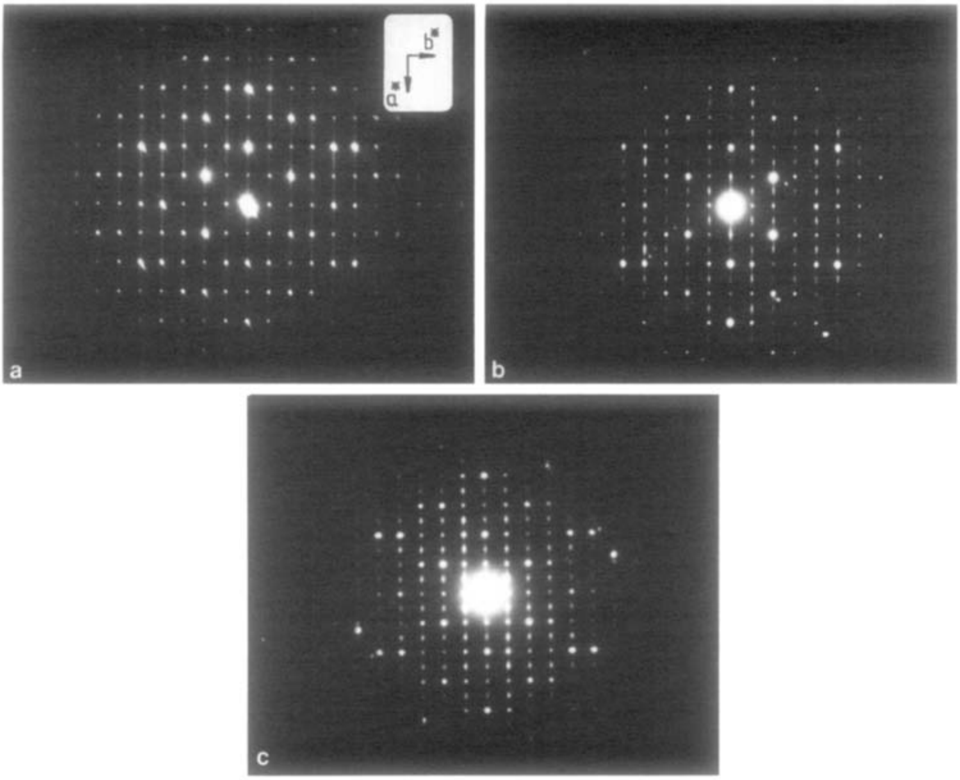

FIG. 3. (a) Electron diffraction pattern from a partly reacted crystal of $Mg_{1.5}Mn_{1.5}BO_5$. After slight decomposition the streaking along the a^* direction is seen, consistent with the formation of (100)-type faults within the ludwigite matrix. (b) After further reaction the streaking is tending to coalesce into discrete spots. (c) With prolonged heating the streaking has progressed to give reasonably sharp reflections midway between the ludwigite spots due to the formation of the orthopinakiolite structure type.

seen by comparing Fig. 4d with Fig. 4e, the orthopinakiolite structure. Repetition of the slip process will produce wider lamellae of orthopinakiolite. This mechanism is in accord with the experimental observations, and would reproduce exactly the form of the diffraction pattern observed during the reaction. The mechanism, of course, is not likely to operate sequentially as it has been described here, but **S1** and **S2** are likely to take place simultaneously. This may be termed "synchroslip" as it bears some resemblance to the mechanism "synchroshear" proposed by Hornstra to account for deformation in materials with the spinel structure (*11*). The synchroslip mechanism has the advantage that the dislocated region at the tip of the orthopinakiolite lamella is small and is unlikely to set up enormous strain in the surrounding matrix.

The propagation of a thin lamella of orthopinakiolite in ludwigite can also be envisaged in terms of a small set of atom jumps or diffusion. These are illustrated in Fig. 5. In Fig. 5a we show the probable geometry of a termination of such a lamella as the real geometry of such a termination is not yet known. The small arrows in Fig. 5a detail the diffusion that must take place to produce the structure shown in Fig. 5b.

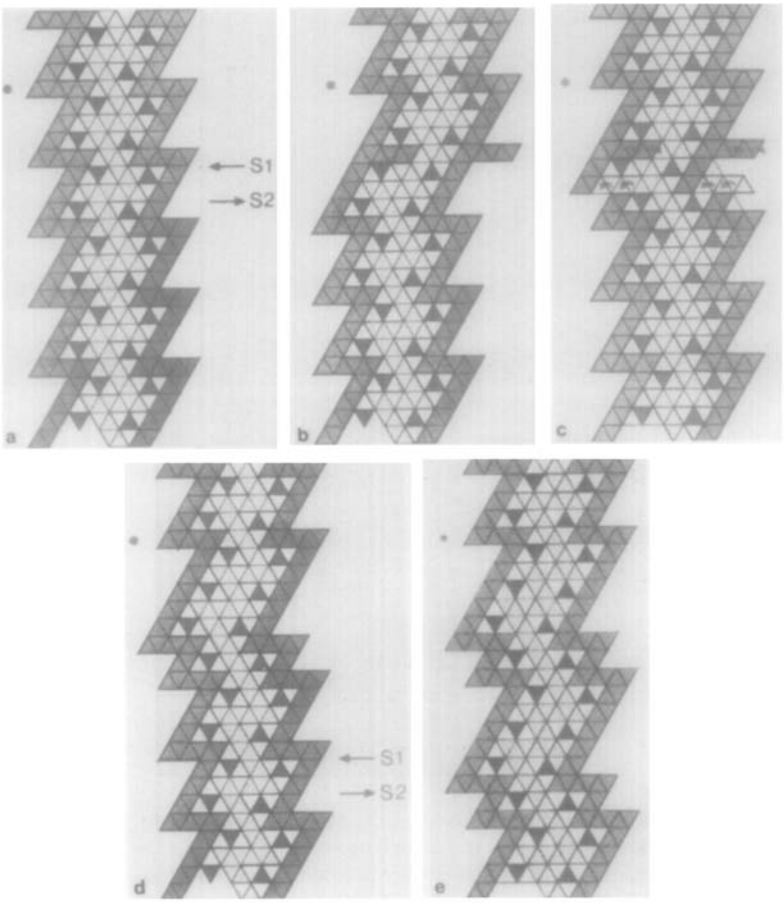

FIG. 4. Slightly idealized drawings of the structure of ludwigite projected along *c* showing a possible transformation mechanism by the action of slip vectors **S1** and **S2** producing the ludwigite to orthopinakiolite transition. The arrows in (c) show the cation movements necessary to complete the transformation and the asterisk marks the same reference point in all figures.

Similarly, the series of arrows marked in Fig. 5b yield the structure shown in Fig. 5c, which is simply an extension of the lamella of orthopinakiolite into the ludwigite matrix. The two diffusion chains are akin to the synchroslip operations described. As in this latter case, the operation of both diffusion rings simultaneously will reduce the overall distortion in the tip and hence the strain of the surrounding matrix.

It should be noted that the operation of one slip operation on ludwigite will produce takéuchiite. Gentle heating conditions may allow this reaction to proceed but we have not yet observed it. Experiments to test this idea as well as beam-heating experiments using takéuchiite crystals as starting materials are in progress.

The reasons for the beam-heating reaction to take place is not completely clear. From the literature evidence it would seem that both synthetic ludwigite and orthopinakiolite have the same composition, i.e., $Mg_{1.5}Mn_{1.5}BO_5$. The transformation observed would then be classified as a structural transformation at constant composi-

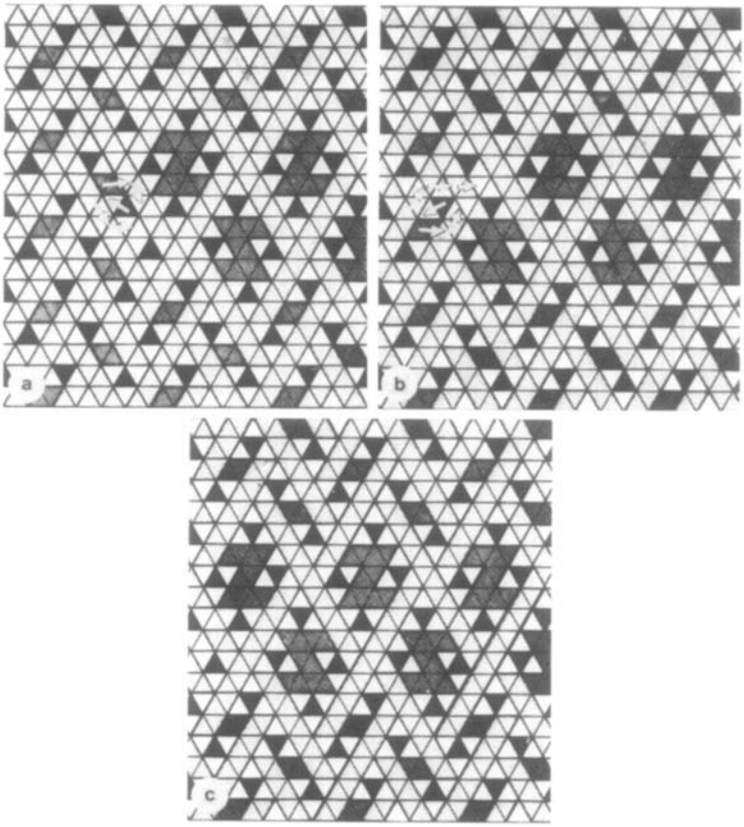

FIG. 5. Slightly idealized drawings of the structure of ludwigite showing a plausible mechanism by which an intergrown slab of orthopinakiolite may extend throughout a crystal matrix with the ludwigite structure. In (a) and (b) a slab of orthopinakiolite extends into a ludwigite matrix from the right. The arrows in both diagrams show the cation jumps necessary to extend the slab by one unit cell to produce the structure shown in (c).

tion. However, such transformations, if initiated solely by heating, tend to be reversible. In fact, most beam-induced reactions reported in the past involve a change in composition of the crystal fragments examined under the combined influence of the electron beam and the surrounding vacuum of the electron microscope column. For fairly refractory oxides this takes the form of oxygen loss. Oxygen loss would necessarily change the Mn^{2+} to the Mn^{3+} ratio in the crystals and this itself may be of importance in stabilising the structures observed. Such a proposal has been made by Takéuchi (*9*), who stressed the role of Mn^{3+} concentration rather than overall oxygen-to-metal stoichiometry. The two are clearly linked, but the nature of any defects to account for such changes in metal to oxygen ratio has not yet been clarified.

Acknowledgment

J. J. Cooper is indebted to ICI. Limited for financial support.

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