Journal of Crystal Growth **21** (1974) 17–22 © *North-Holland Publishing Co.*

A NEW TYPE OF TWIN IN AN AlN CRYSTAL

SHIGEO HORIUCHI and TOSHIHIKO ISHII

National Institute for Researches in Inorganic Materials, Kurakake, Sakura-mura, Niihari-gun, Ibaraki, Japan, 300–31

and

KENTARO ASAKURA

Department of Metallurgy, Faculty of Engineering, University of Tokyo, Hongo 7, Bunkyo-ku, Tokyo, Japan, 113

Received 17 April 1973; revised manuscript received 25 September 1973

Plate-like crystals of aluminium nitride, prepared by a sublimation method at 1800 °C, are examined by means of transmission electron microscopy. Each crystal of about 100 µm in size is divided by a twin boundary. When the crystal is thin, it is $(10\bar{1}1)$ plane with an angle 63° to the $(1\bar{1}00)$ crystal surface, but as the thickness is increased it bends and changes to $(11\bar{2}2)$ plane, which is perpendicular to the surface. A growth mechanism is proposed in the conjunction with the bending of the twin boundary and the morphological aspects of the crystal.

1. Introduction

Single crystals of AlN (wurtzite type) are synthesized by a sublimation method[1–6]. Their morphology depends mainly on the preparation temperature and impurities: whiskers or needle crystals are grown at temperatures of 1150 to 1700 °C and plate crystals at temperatures of 1800 to 2000 °C[1–5].

The following information is reported concerning the twins in AlN: Witzke observed that twinned crystals are formed when coalescence occurs. In this case the boundary is a $(11\bar{2}1)$ plane perpendicular to a $(10\bar{1}0)$ crystal surface[2]). Gindt and Kern observed two types of twin[7]). In one of them ("contact twin") the boundary is a $(10\bar{1}\bar{3})$ plane, which is normal to a $(\bar{1}2\bar{1}0)$ crystal surface. In another type ("penetration twin") the $(10\bar{1}\bar{2})$ is the twin boundary.

In the present study a new type of twin in a plate-like crystal of AlN is found. The structure of the twinned crystal is examined by a transmission electron microscopy. The emphasis is placed on clarifying the relationship between the twin boundary and the growth mechanism.

2. Preparation of AlN crystals

AlN powder was prepared by means of arc discharge between aluminium electrodes in a purified nitrogen atmosphere[1]). Oxygen of 0.2 wt% was detected as an impurity in the powder. The AlN was pressed in the form of a square prism (10 × 10 × 30 mm) at room temperature. The prism was put on a graphite susceptor and heated for 5 hr at 2050 °C in a high frequency induction furnace. The AlN crystals, examined in the present study, were formed by sublimation on a part of the susceptor, whose temperature was estimated to be about 1800 °C.

3. Results and discussion

The AlN thin crystals are transparent and have no colour. Fig. 1 shows the transmission optical micrograph. They are of a kite form. The size of the plates is 50 to 200 µm. Each crystal contains a line mark, which runs from one corner having an angle of about 60° to the opposite one with about 120°. The observation using a polarizing microscope reveals that two regions, separated by the line mark, bear a twin relationship to each other. The other corners, facing to it, make a right angle in small crystals. In large ones the edges are usually zigzag with an angle of 90°. They make an angle of about 30° or 60° to the line of the twin boundary in both ones.

It is observed that the crystals touch to the susceptor at the corner having an angle of about 60°: each crystal starts to grow at this corner. Dark particles are attached to this corner. The rest of the crystal is clean (fig. 1).

Fig. 1. An optical micrograph of AlN.

The crystals were examined by electron microscopy (accelerating voltage: 100 or 150 kV). Fig. 2a is a transmission micrograph. A broad line due to a twin boundary is observed at the central part of the crystal. The electron diffraction pattern shown in fig. 2b is obtained from a selected area A of about 1 μm. The main diffraction spots (open and filled circles in fig. 2c) can be identified with two groups of ($1\bar{1}0$) reciprocal lattice section, which are rotated 64° to each other about the [$1\bar{1}00$] axis. Two 112 reciprocal lattice points are common to the two groups of the section and the 112 reciprocal lattice vector is normal to the line of the twin boundary. The edges of the crystal are parallel to the *c* axes and make an angle 32° with the line due to the twin boundary, being nearly parallel to the [$\bar{1}\bar{1}25$] direction. The two regions, separated by the boundary, are therefore related to each other by the 180° rotation about the [$11\bar{2}2$] direction. Extra diffraction spots in fig. 2b (half-filled circles in fig. 2c) occur by the double diffraction. The lattice parameters are determined as $a = 3.12$ Å and $c = 5.00$ Å.

The fact that the line due to the twin boundary is broad suggests that it is inclined to the incident electron beam. Its projection along the direction of the electron beam is examined by tilting the specimen in the electron microscope. It is concluded that the twin boundary inclines about 63° to the crystal surface, i.e. ($10\bar{1}1$) plane. The double diffraction spots (half-filled circles in fig. 2c) in fig. 2b can be explained by the wedge thus formed. Two (0002) reflected beams marked 1 and 2 in fig. 2c are due to the upper crystal. They act as a source for the diffraction in the lower crystal. The thickness of the crystal is estimated to be about 4000 Å in this case and varies step-wise from position to position. The steps are often parallel to the *c* axis, or the *a* axis normal to the *c* axis.

The other weak extra spots, appeared at the midpoints between the direct spot and 0002 spots (open and filled triangles in fig. 2c) and between the direct and $11\bar{2}2$ spots (half-filled triangles) in fig. 2b, can not be explained by the double diffraction. The fact suggests the formation of a superstructure. The details of the superstructure are not clear in this study.

At the corner of the crystal in fig. 2a, where the crystal starts to grow, moiré patterns are observed. The electron diffraction pattern (fig. 2d) obtained from the part B in fig. 2a reveals that the twin relation mentioned above is already formed at the early stage of the growth, although the structure is complicated. Two diffraction rings ($d = 2.14$ and 1.24 Å) in fig. 2d are identified to graphite having such an orientation that the *c* axes are nearly parallel to the electron beam. Presumably, the graphite particles are formed by sublimation and correspond to the dark ones observed under an optical microscope (fig. 1).

Fig. 3 shows the corner having an angle of about 120°. The broad line due to the twin boundary bisects the corner. The thickness of the crystal near the twin

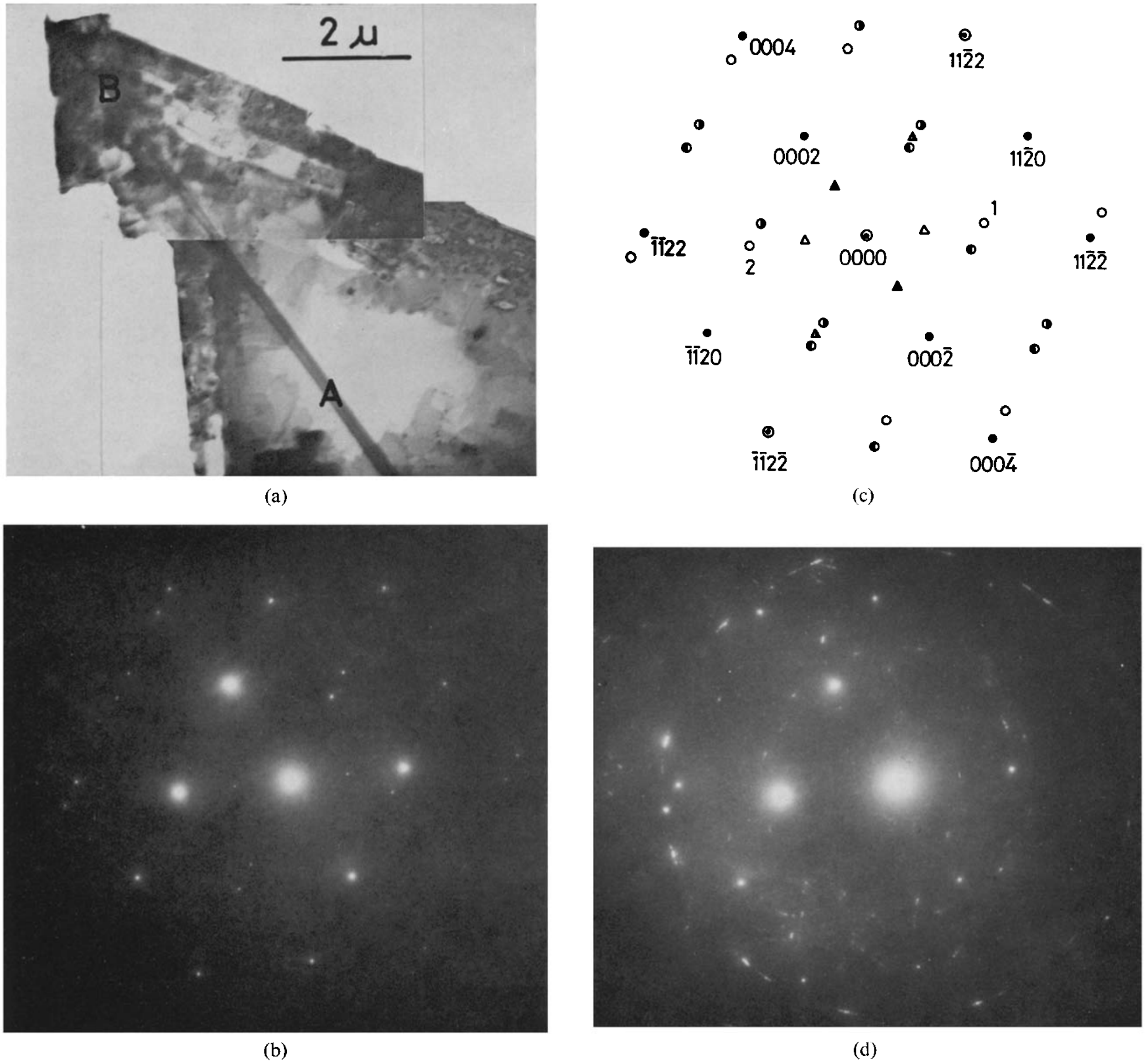

Fig. 2. (a) A transmission electron micrograph of AlN. The twin boundary is observed as a broad line AB. (b) The selected-area electron diffraction pattern for the position A of (a). (c) Indexing for the diffraction pattern (b); open and filled circles indicate the normal reflection spots for each twinning crystal; the spots marked 1 and 2 play the role of the source for the doubly diffracted spots (half-filled circle) of the crystal below the twin boundary. (d) Selected-area diffraction pattern from the area B in (a); the two diffraction rings are due to graphite crystals.

boundary is about 4000 Å and decreases in the region far from it. This indicates that the central region, including it, has first formed and afterwards the rest of the crystal grows. Thickness steps observed in the latter region are nearly parallel to the *c* axis.

Fig. 4a and b are the dark field electron micrographs with an accelerating voltage of 1000 kV of a thick twinned crystal. The incident electron beam is almost perpendicular to the crystal surface. Equal-thickness fringes, which are difficult to observe on the bright field images, appear along the twin boundary, which is parallel to $(10\bar{1}1)$. The crystal was then tilted 8.5° about an axis DE. Narrower fringes newly appear on one or both sides of the initial twin boundary (fig. 4c). They show that the boundary is bent from the $(10\bar{1}1)$ to the $(11\bar{2}2)$ plane in the thick crystal, the $(11\bar{2}2)$ plane

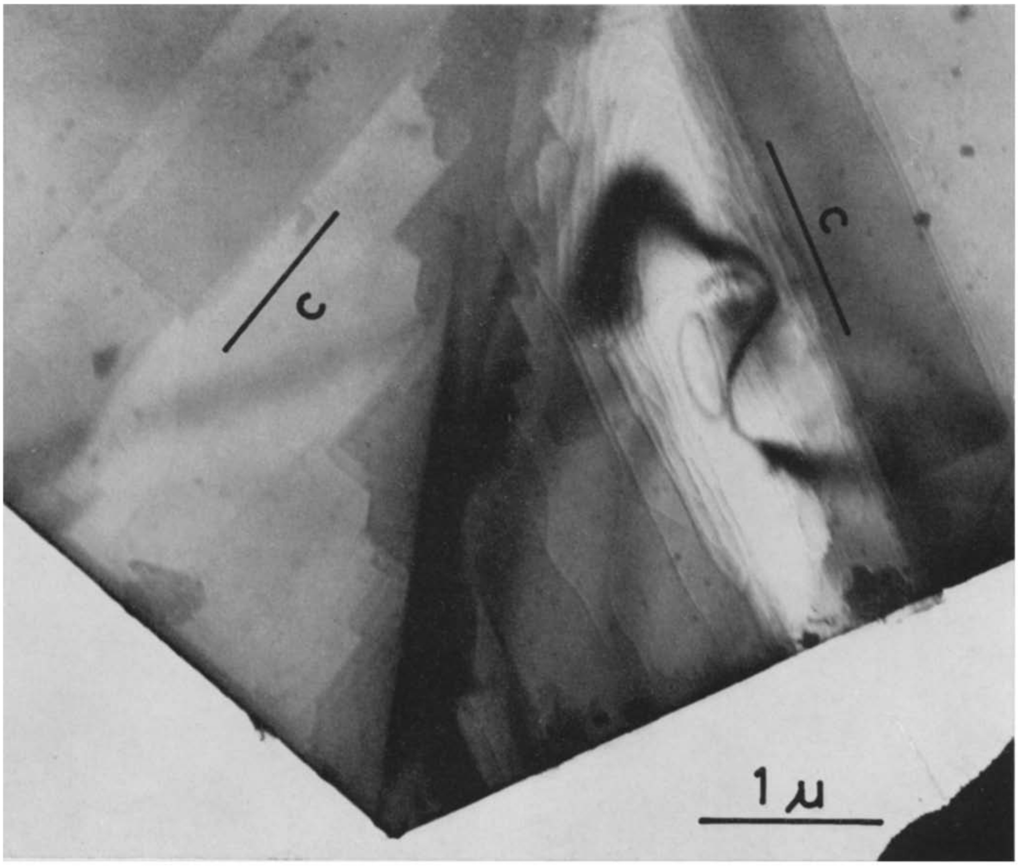

Fig. 3. The electron micrograph of the 120° corner.

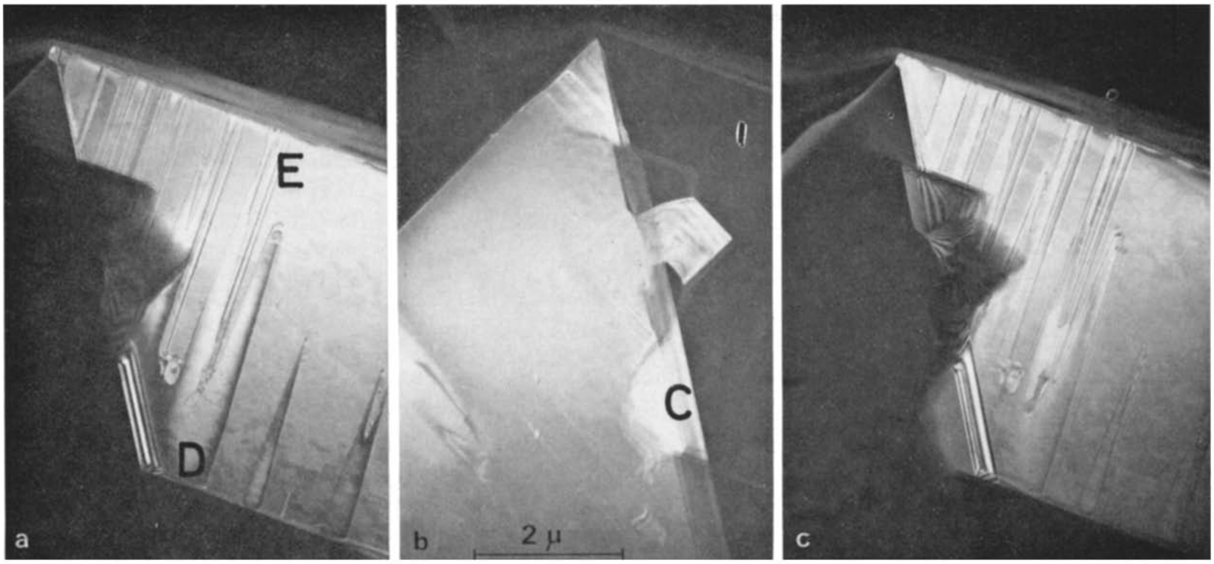

Fig. 4. (a) A dark-field electron micrograph with 0002 reflection of one member of a thick twinning crystal. (b) Another member of the crystal. (c) After tilting the crystal by 8.5° about an axis DE.

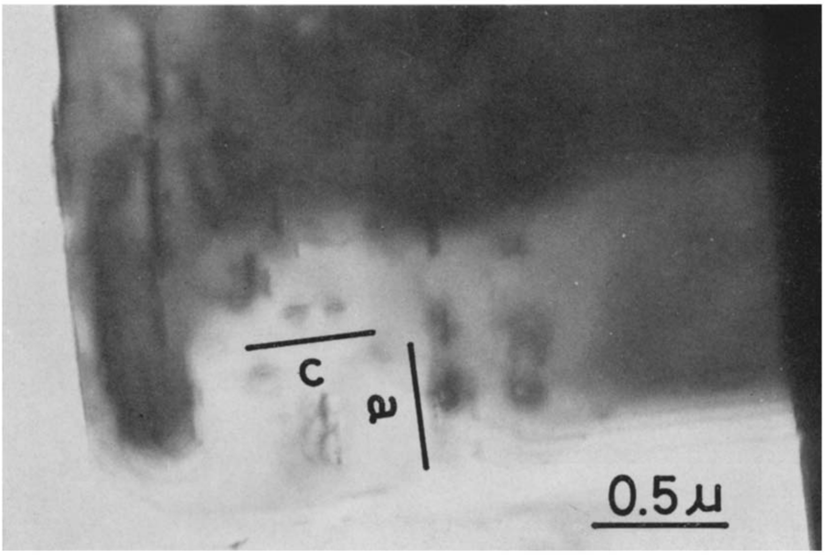

Fig. 5. Island crystals on the surface of a relatively thick crystal.

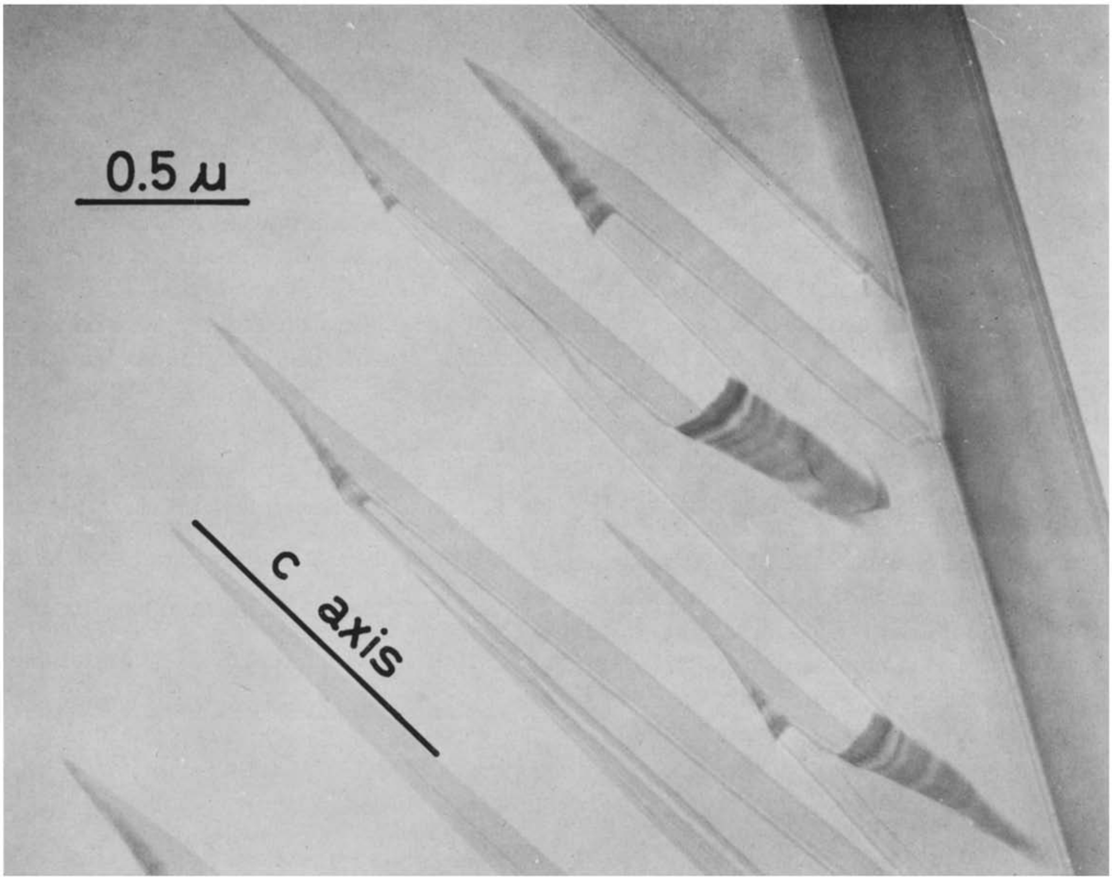

Fig. 6. A dark field electron micrograph of a thick crystal. The specimen is tilted about 10°.

being perpendicular to the crystal surface. The fact that they are observed in the region C (fig. 4b) only on the right-hand side of the initial twin boundary is related to the fact that the growth increasing the thickness takes place only on the bottom surface of the plate. The analysis of the fringes in this region indicates that the thickness of the crystal parts divided by the $(11\bar{2}2)$ boundary and the initial $(10\bar{1}1)$ boundary is about 5000 Å respectively in this particular case.

Small crystals ("islands") are observed locally on the surface of relatively thick crystals (fig. 5). They elongate often in the ***a*** axis direction and occasionally in the ***c*** axis direction, some of them have a very narrow width. They are considered to act as nuclei in the growth increasing the thickness.

In fig. 6 several elongated crystals are observed to nucleate at the large step, formed at the intersection of the crystal surface with the $(10\bar{1}1)$ twin boundary. They grow in the ***c*** direction. The analysis of the fringes, which are observed by tilting the specimen, shows that the new crystals are about 6000 Å in thickness in this case. Each elongated crystal is not uniform in width but very sharp at the tip. In fig. 4 similar elongated crystals, which have grown larger than those in fig. 6, are observed.

4. Summary

The growth mechanism of AlN twinned crystals of a kite form is proposed as follows: first, a twinned crystal rod is formed on a graphite suceptor. Next, the crystal extends along the $(1\bar{1}00)$ plane to become a kite form. The twin plane inclines with an angle 63° to the extended surface. The growth increasing the thickness then takes place as illustrated in the series of fig. 7; usually, a surface nucleation occurs on one half of a kite crystal. The steps from the nuclei move on the crystal surface mainly in the ***c*** direction and the crystal gains thickness. The movement of the steps is inhibited by the outcrop of the initial twin boundary (fig. 7a). A large step is formed as a number of steps arrive there (fig. 7b). A nucleation-and-growth occurs at the large step (fig. 7c) on the other half of the kite crystal. The orientation of the crystal is the same as that of the substrate. The boundary becomes normal to the crystal surface.

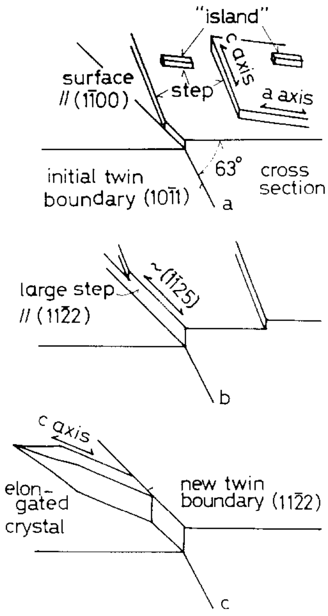

Fig. 7. A schematic representation of the mechanism of the growth increasing the thickness.

Acknowledgment

The authors wish to express their deep gratitude to Dr. M. Iwata and Mr. T. Sato for their valuable discussions and to Dr. S. Yamaguchi (NIRIM) for his encouragement. They thank Dr. H. Akahori and Mr. T. Kamino (Hitachi Ltd.) for the help in the electron microscopic experiment using HU 1000.

References

1) T. Ishii, T. Sato and M. Iwata, Mineral. J. **6** (1971) 323.
2) H. D. Witzke, Freiberger Forschungsh. C **195** (1965).
3) A. Kato, Denki Kagaku **40** (1972) 743.
4) J. Pastrňák and L. Roskovcová, Phys. Status Solidi **7** (1964) 331.
5) T. Ishii, T. Sato and M. Iwata, J. Mineral. Soc. Japan **11** (1973) 127.
6) C. M. Drum and J. W. Mitchel, Appl. Phys. Letters **4** (1964) 164.
7) R. Gindt and R. Kern, Bull. Soc. Franc. Miner. Crist. **81** (1958) 266.