The Formation of κ- and κ'-Al_2O_3 from the Dehydration of Tohdite $5Al_2O_3 \cdot H_2O$

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The dehydration of tohdite $5Al_2O_3 \cdot H_2O$ is well followed by means of the single-crystal electron-diffraction patterns, the X-ray powder patterns, differential thermal analysis, and the measurement of the density. Thermogravimetric measurements were also performed, both under a normal atmosphere and in a high vacuum. Just after the dehydration, an unstable intermediate phase was obtained; it was denoted as κ'-Al_2O_3 (from tohdite). The mechanism of the transformation series:

$$\text{tohdite} \rightarrow \kappa'\text{-}Al_2O_3 \rightarrow \kappa\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3$$

was discussed, and some basic data to serve as clues to elucidate the crystal structure of κ'- and κ-Al_2O_3 were obtained.

In 1966, Krischner reported an investigation into the thermal dehydration of tohdite $5Al_2O_3 \cdot H_2O$ (Al_2O_3-K1, according to his notation) by the electron-diffraction method.[1] In his work, fine-grained hexagonal plates of tohdite, with a particle size of about 1 micron, which had been obtained by the hydrothermal treatment of bayerite, were heated by means of an electron beam in an electron microscope, and electron-diffraction patterns were obtained at various reaction stages. Since the incident beam was parallel to the *c*-axis, all the patterns obtained in his work represent the reciprocal *a-b* plane. No experimental results to elucidate the atomic arrangement along the *c*-axis were obtained in his work. Therefore, it is difficult to determine the crystal structure of dehydration products of tohdite from his experimental results only.

Furthermore, Krischner's experimental results were insufficient to elucidate the transformation mechanism, because his experiment was limited to the method of comparing the electron-diffraction patterns of the materials heated by an electron beam at uncertain temperature.

The present study has aimed at elucidating the thermal dehydration and transformation mechanism in more detail, and at obtaining basic data to serve as clues to elucidate the atomic arrangement of dehydration products. For this purpose, differential thermal analysis, thermogravimetric measurements under both a normal atmosphere and in a high vacuum, an X-ray powder diffraction experiment, and density measurements were performed. A single-crystal electron-diffraction experiment was also performed for the needle-like crystals in order to obtain information on the atomic arrangement along the *c*-axis as well as for the hexagonal-plate crystals.

Experimental Procedure

Specimen Preparation. In previous paper,[2,3] detailed conditions for tohdite formation were discussed. It was established that the addition of certain mineralizers favers the formation of tohdite. The specimen of tohdite used in this experiment was prepared as follows.

(a) A sample of η-Al_2O_3 obtained from the dehydration of bayerite at 800°C in air was inverted to tohdite by heating it hydrothermally at 460°C, 300 atm, without any mineralizer. The tohdite thus obtained was in the form of hexagonal plates with a particle size of about 1 micron and will be denoted as "tohdite(η)."

(b) Gibbsite was heated hydrothermally at 480°C, 800 atm in the presence of aluminium fluoride. The tohdite thus obtained was in the form of hexagonal plates with a particle size of about 1 micron and will be denoted as "tohdite(F)." It contains about 0.3% fluorine ion in the crystal structure.

(c) Gibbsite was heated under hydrothermal conditions of 500°C, 1000 atm, by adding $Ti(SO_4)_2$ as a 3—4% aqueous solution. The tohdite thus obtained was in the form of needle-like crystals about 10 micron in size and will be denoted as "tohdite(Ti)."

Differential Thermal Analysis and Thermogravimetric Measurements. The differential thermal analysis and thermogravimetric measurements were performed simultaneously under a normal atmosphere and at a heating rate of 5°C/min using a simultaneous thermobalance analyser.

Thermogravimetric measurements in a high vacuum (10^{-4} mmHg) were also performed using a silica spring thermobalance (Fig. 1).

Electron-diffraction Procedure. Single-crystal electron-diffraction patterns were obtained by means of a Hitachi electron microscope, Type HU-11DS. All the specimens were dispersed with water on a folmbar film attached to the sample grid and were observed at a 100 kV accelerating potential.

X-Ray Powder Measurements. X-Ray powder diffraction patterns were obtained by means of a Rigaku-Denki diffractometer using Ni-filtered Cu$K\alpha$ radiation.

Density Measurements. The density of the dehydrated materials of tohdite was measured using the Archimedian principle. The buoyance of the materials (about 1 g) in toluene was measured with a highly-sensitive ($\pm$0.01 mg) microbalance, and the density was calculated. In order to increase the accuracy of measurement, the specific gravity of toluene (about 0.89) was checked at every measurement with a standard material of a piece of pure gold (99.99%).

1) H. Krischner, *Ber. Deut. Keram. Ges.*, **39**,1366_(1966).

2) G. Yamaguchi, H. Yanagida, and S. Ono, *J. Ceram. Assoc. Japan*, **74**, 84 (1966).

3) S. Ono, G. Yamaguchi, and H. Yanagida, *ibid.*, **77**, 126 (1969).

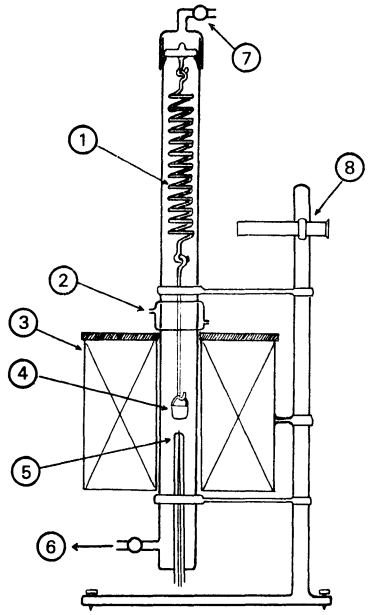


Fig. 1. High vacuum TGA instrument.

1 silica spring
2 water jacket
3 heater
4 sample holder (silica basket)
5 thermo couple
6 diffusion pump
7 leak valve
8 cathetometer

Experimental Results

Differential Thermal Analysis and Thermogravimetric Data. The DTA and TGA curves at a normal atmosphere are shown in Fig. 2. A single endotherm was observed in the temperature range of 700—800°C, and there was a large weight loss. As can be seen in Fig. 2, the dehydration of tohdite is completed in a single step at this temperature range. After dehydration, no further change in DTA and TGA curves occurred until about 1000°C.

At about 1000°C an exotherm was observed ((a), (c) diffuse, (b) sharp). The X-ray powder diffraction patterns of the materials after exothermic reaction are the same as that of α-Al_2O_3.

The X-ray powder diffraction pattern of the material heated in the 700—1000°C temperature range, which corresponds to the temperature range between the endothermic and exothermic peaks, is very similar to the pattern of κ-Al_2O_3, which is one of the dehydration products of gibbsite. Therefore, this material will be denoted as "κ-Al_2O_3 (from tohdite)."

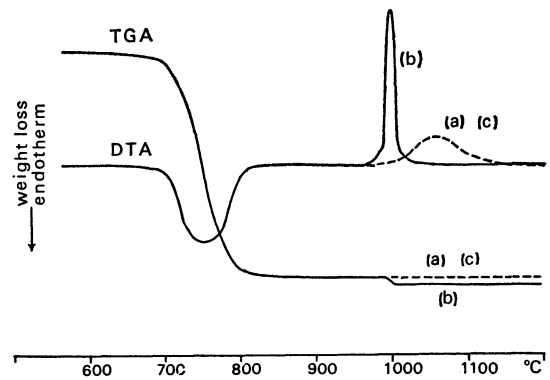


Fig. 2. DTA and TGA curves of tohdite.
(a) tohdite(η), (b) tohdite(F), (c) tohdite(Ti).

The dehydration of tohdite in a high vacuum also proceeded in a single step. Dehydration was observed at a lower temperature range (650—750°C) because of the rapid water loss in a high vacuum, the X-ray diffraction pattern of the dehydrated material is unlike the pattern of κ-Al_2O_3 (from tohdite) and this material will be denoted as "κ'-Al_2O_3 (from tohdite)." As κ'-Al_2O_3 (from tohdite) is an unstable intermediate phase, it can easily be transformed into κ-Al_2O_3 (from tohdite) by further heating both in a high vacuum and under a normal atmosphere. The stabilities of κ'-Al_2O_3 are, however, slightly different according to their starting materials, tohdite(η), tohdite(F), and tohdite(Ti). The κ'-Al_2O_3 obtained from tohdite(η) is more unstable than the κ'-Al_2O_3(from tohdite(F)) and the κ'-Al_2O_3 (from tohdite(Ti)); therefore, it is not easy to obtain κ'-Al_2O_3 (from tohdite(η)) crystal as as single phase without κ-Al_2O_3 crystals.

X-Ray Powder Data. The X-ray powder patterns of tohdite and its dehydration products κ'-Al_2O_3 (from tohdite) and κ-Al_2O_3 (from tohdite) are shown in Fig. 3. An important feature of the pattern of κ'-Al_2O_3 is that it resembles the pattern of tohdite itself, though it is rather more simple.

The tohdite reflections to which the oxygen atoms do not contribute decrease in intensity, while the reflections due mainly to the oxygen atoms remain to form the main part of the κ'-Al_2O_3 (from tohdite) pattern. The contribution of oxygen atoms to the intensity of the tohdite reflections was calculated; it is illustrated in Fig. 3, with sign + and −.

The reflections of κ'-Al_2O_3 (from tohdite) can be well indexed on the basis of the hexagonal unit cell of tohdite, which contains 5⅓ formulas of Al_2O_3. The propriety of employing this unit cell will be discussed later. The unit-cell dimensions of κ'-Al_2O_3 (from tohdite(F)) calculated from the X-ray data are shown in Table 1.

Table 1. Cell dimensions (in Å)

Tohdite(η)	$a=5.575$, $c=8.761$
Tohdite(F)	$a=5.577$, $c=8.774$
κ'-Al_2O_3 (from tohdite(F))	$a=5.544$, $c=9.024$
κ-Al_2O_3 (from tohdite(F))	$a=9.599$, $c=9.015$

The similarity between κ'- and κ-Al_2O_3 (from tohdite) was also seen (Fig. 3). The additional reflections of κ-Al_2O_3 (from tohdite) are probably caused by the distribution of aluminium atoms. The reflections are indexed on the basis of hexagonal unit cell with $a \approx \sqrt{3}a$ of tohdite, $c \approx c$ of tohdite. These cell dimensions were calculated from the X-ray data; they are also listed in Table 1.

Electron-diffraction Data. Electron-diffraction patterns were obtained for the following specimen series (the dehydration products have the same particle size and shape as the starting tohdite):

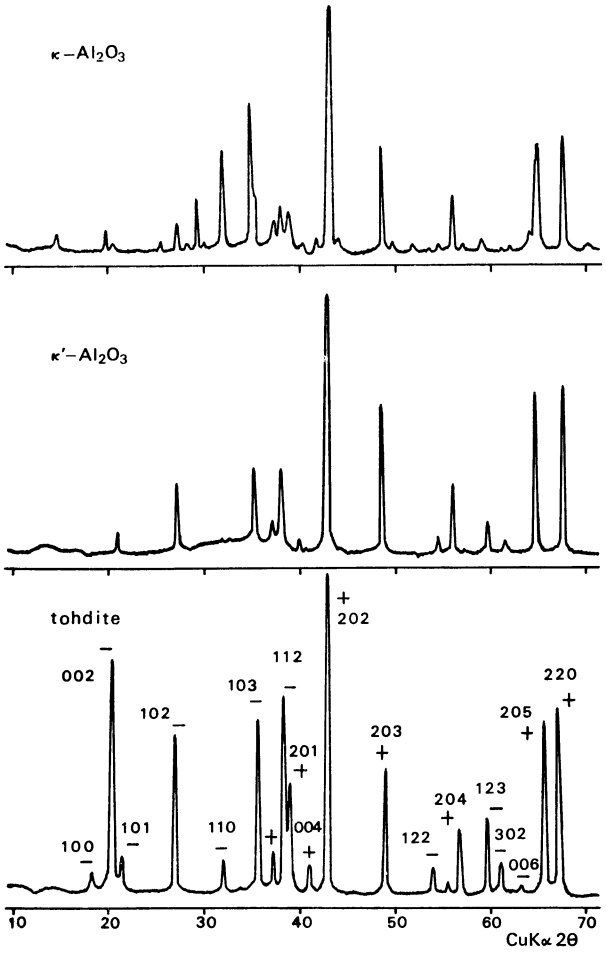


Fig. 3. X-Ray diffraction pattern of tohdite(F), κ'-Al_2O_3 (from tohdite(F)) and κ-Al_2O_3 (from tohdite(F)). The contribution of oxygen atoms on the intensity of tohdite is calculated.
+: reflection which is due mainly to the oxygen atoms
−: reflection for which oxygen atoms do not contribute

(a) tohdite(η) $\xrightarrow{900°C \text{ in air}}$ κ-Al_2O_3 (from tohdite(η))

These specimens correspond to the KI and KII of Krischner's study.

(b) tohdite (F) $\xrightarrow[(10^{-4} \text{ mmHg})]{750°C \text{ in vacuum}}$ κ'-Al_2O_3 (from tohdite(F))

$\xrightarrow{900°C \text{ in air}}$ κ-Al_2O_3 (from tohdite (F))

(c) tohdite (Ti) $\xrightarrow[(10^{-4} \text{ mmHg})]{750°C \text{ in vacuum}}$ κ'-Al_2O_3 (from tohdite(Ti))

$\xrightarrow{900°C \text{ in air}}$ κ-Al_2O_3 (from tohdite(Ti))

Patterns:

(a) The electron diffraction pattern of κ-Al_2O_3 (from tohdite(η)) agrees with that of KII described by Krischner. As has also been described by Krischner, this pattern agrees with the pattern, "(D)," of the dehydration product of gibbsite described by Brindley and Choe.[4]

(b) The electron-diffraction patterns of this series specimen are shown in Figs. 4, 5, and 6. The pattern of κ-Al_2O_3 (from tohdite(F)) is the same as that of κ-Al_2O_3 (from tohdite(η)).

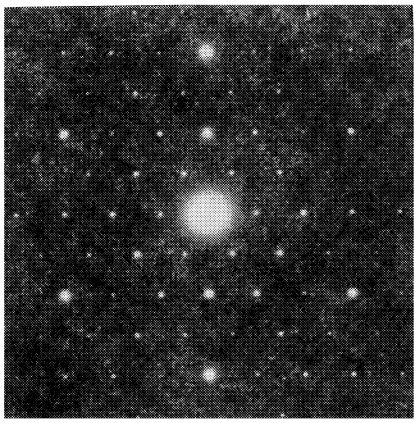


Fig. 4. Electron diffraction pattern of tohdite(F).

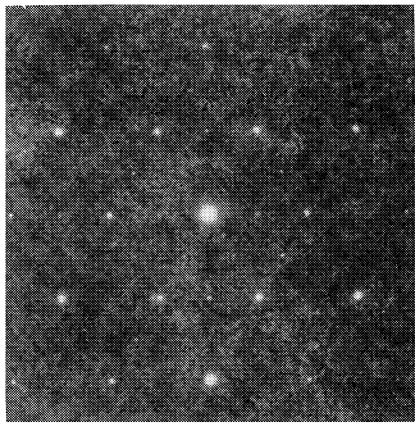


Fig. 5. Electron diffraction pattern of κ'-Al_2O_3 (from tohdite(F)).

Fig. 6. Electron diffraction pattern of κ-Al_2O_3 (from tohdite(F)).

The pattern of κ'-Al_2O_3 (from tohdite(F)) resembles that of tohdite, though the intensity distribution is different. Therefore, the reflections of this pattern are indexed on the basis of the unit cell of tohdite.

(c) The electron-diffraction patterns of needle-like crystals evaporated with aluminium metal were also obtained (Figs. 7—10). These patterns represent $(h, k, \overline{h+k}, l)$ reflections of the materials, where h and k are integers which should be determined from the

4) G. W. Brindley and J. O. Choe, *Amer. Mineral*, **46**, 771 (1961).

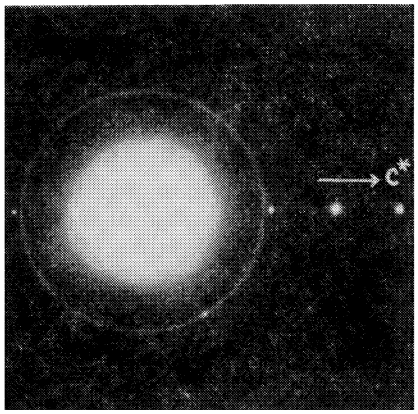


Fig. 7. The electron diffraction pattern of needle like crystal tohdite(Ti). (The electron beam $\perp$ c-axis.)
The strongest ring is that of the 111 reflection of aluminium metal (d=2.338 Å).

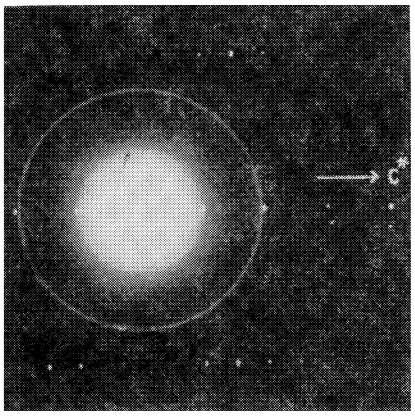


Fig. 8. The electron diffraction pattern of needle like crystal κ'-Al_2O_3 (from tohdite(Ti)).

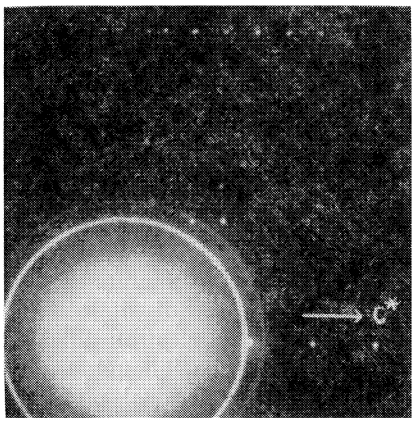
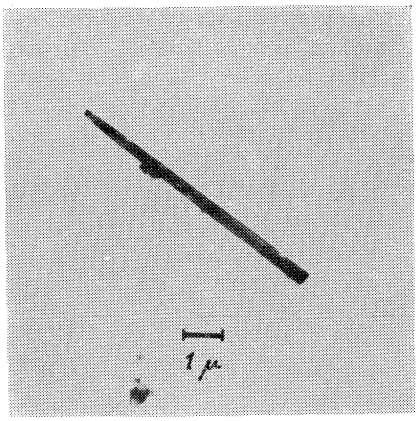
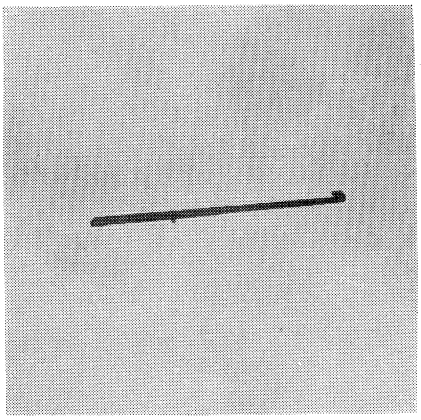


Fig. 9. The electron diffraction pattern of needle like crystal κ-Al_2O_3 (from tohdite(Ti)).

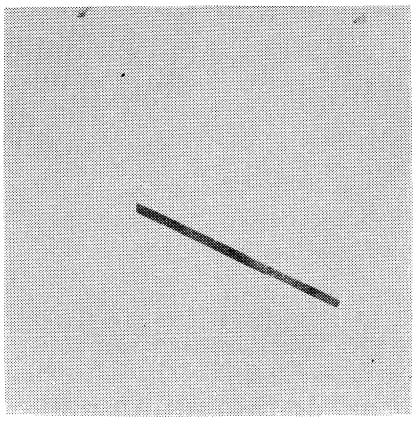
atomic netplane parallel to the electron beam. Whatever value h and k may have, a row of (000l) reflection spots can be found in the pattern. The interval between the (000l) spots of tohdite was calculated as 4.4 Å from the pattern. This agrees with the values of $c/2$=4.38 Å calculated from the X-ray data; the spots are indexed as (0002), (0004), *etc.* This indexing can also be expected from the crystal structure of tohdite,



(a)



(b)



(c)

Fig. 10. Needle like crystal. (a) tohdite(Ti), (b) κ'-Al_2O_3 and (c) κ-Al_2O_3 (from tohdite(Ti)).

which was determined from the X-ray powder data.[5,6] However, in some patterns of tohdite(Ti), the (000l) l=odd reflections were observed to have a very weak intensity, indicating a small deviation from the ideal structure of tohdite ($P6_3mc$). This deviation may be caused by the impurity titanium atoms contained in tohdite(Ti) (about 3%).

5) G. Yamaguchi, H. Yanagida, and S. Ono, *ibid.*, **37**, 752 (1964).
6) G. Yamaguchi, M. Okumiya, and S. Ono, *ibid.*, **42**, 2247 (1969).

By comparing the pattern of κ-Al_2O_3 (from tohdite (Ti)) with the pattern of tohdite(Ti), the following results are obtained. The row of (000l) spots is of the same type as that of tohdite(Ti), and the interval between the spots is 4.5 Å. From this value, the c-axis of κ-Al_2O_3 (from tohdite(Ti)) is calculated as 9.0 Å. In some patterns of κ-Al_2O_3 (from tohdite (Ti)), very weak (000l) l=odd reflections were also observed as in the case of tohdite(Ti), but no evidence was found that the c-axis of κ-Al_2O_3 (from tohdite (Ti)) was twice as large as that of tohdite(Ti).

The pattern of κ'-Al_2O_3 (from tohdite(Ti)) resembles that of κ-Al_2O_3 (from tohdite(Ti)). The cell dimension of c=9.0 Å which was calculated from the electron-diffraction patterns agrees with that of c= 9.015 Å calculated from the X-ray powder diffraction data.

Density Measurements. It is difficult to obtain the absolute value of the density of the fine-grained materials with a high accuracy. In the present work, it is important to compare the density of the dehydration products with that of the starting tohdite. For this purpose, the specimen series (b) was used, because the specimens of this series were easily obtained in a large amounts as a single phase. The average values of five measurements and their standard deviation are shown in Table 2. The measured valued of the density are as follows:

tohdite(F)<κ'-, κ-Al_2O_3 (from tohdite(F))<α-Al_2O_3

Table 2. Density of tohdite, κ'-, and κ-Al_2O_3 (from tohdite)

	Measured density with their standard deviations	Calculated density[a)]
Tohdite(F)	3.63 (0.006)	3.72
κ'-Al_2O_3 (from tohdite(F))	3.68 (0.002)	3.76
κ-Al_2O_3 (from tohdite(F))	3.67 (0.008)	3.77
α-Al_2O_3 (from tohdite(F))	3.96 (0.008)	4.00

a) These value are calculated from unit cell dimensions listed in Table 1 and formula unit per unit cell. The formula units are assumed as follows.
tohdite(F): $5Al_2O_3 \cdot H_2O$
κ'-Al_2O_3 (from tohdite(F)): $5\frac{1}{3}Al_2O_3$
κ-Al_2O_3 (from tohdite(F)): $16Al_2O_3$

Discussion

Krischner concluded, on the basis of their experimental results on electron diffraction, that the basic lattice of oxygen atoms is preserved during the transformation from tohdite to κ-Al_2O_3 (from tohdite), while the cations move to make the symmetry of κ-Al_2O_3 (from tohdite). However, their conclusion for the crystal structure of κ-Al_2O_3 (from tohdite) was that 30 formulas Al_2O_3 exist in a hexagonal unit cell with the cell dimensions of a=9.71 Å, and c=17.86 Å. This indicates a non-close-packed oxygen arrangement. He said that the measured density of 3.5 g/cm^3 agrees well with the value calculated from this unit cell and 30 formulas Al_2O_3. However the experimental results of the present work show that the measured density of κ-Al_2O_3 (from tohdite) (the value for κ-Al_2O_3 (from tohdite(F)), 3.67 g/cm^3), which has a close-packed oxygen arrangement in the crystal structure. Therefore, the present authors consider that the oxygen arrangement of κ-Al_2O_3 (from tohdite) is a close-packed one, as is that of κ'-Al_2O_3 (from tohdite) (the measured density for κ'-Al_2O_3 (from tohdite(F)) is 3.68 g/cm^3).

However, his experimental results on electron diffraction seem important in support the idea of the preservation of the oxygen lattice. This was confirmed by various methods in the present work. We will now consider the mechanism of the transformation and the crystal structure of the dehydration products on the basis of this idea.

Just after the 100% water loss, aluminium atoms are distributed at random in octahedral and tetrahedral positions between the oxygen layers, which are unchanged during the transformation. This atomic arrangement may give the X-ray and electron diffraction pattern of κ'-Al_2O_3 (from tohdite). The impurity atoms which are considered to distributed at random in the crystal structure of the starting tohdite stabilize the κ'-phase. As κ'-Al_2O_3 is an unstable intermediate phase, the κ'-Al_2O_3 (from tohdite) obtained by quenching has a "freezed" crystal structure.

The experimental results can be explained well by this consideration. Therefore, it is proper to employ a unit cell with cell dimensions of a=5.544 Å, and c= 9.024 Å, and which contains a non-integer unit formula of 5⅓ Al_2O_3 and an ABAC stacking sequence of oxygen layers for κ'-Al_2O_3 (from tohdite).

The electron-diffraction pattern of the material identified as "Bild 7" in the Krischner paper is very similar to that of κ'-Al_2O_3 (from tohdite) (Fig. 6). The cell dimensions calculated from "Bild 7" have been reported to include a=from 5.56 to 5.54 Å. This value agrees well with the cell dimension of κ'-Al_2O_3 (from tohdite), a=5.54 Å, calculated from the X-ray powder diffraction data. Therefore, the material, "Bild 7", which was obtained by heating tohdite quickly by an electron beam in an electron microscope may correspond to κ'-Al_2O_3 (from tohdite).

At higher temperatures aluminium atoms are allowed to move more freely and are distributed in a symmetry which gives the X-ray and electron-diffraction patterns of κ-Al_2O_3 (from tohdite). Though the oxygen position may deviate from the ideal position of tohdite, it is proper to assume that the oxygen arrangement of κ-Al_2O_3 (from tohdite) is an ABAC-type closed packing and that the unit cell dimensions are a=9.60 Å, and c=9.02 Å.

Over a temperature of 1000°C, a large-scale oxygen rearrangement takes place and the ABAC stacking sequence changes into the ABAB of α-Al_2O_3. The sharp exothermic peak for the specimen series (b) (Fig. 2) can be explained as follows. Since tohdite (F) is obtained by hydrothermal treatment with aluminium fluoride as a miniralizer, it is expected that this specimen will contain fluorine ions as impurities in

the crystal of tohdite. Furthermore, it can be assumed that fluorine ions, the ion radius of which is comparable to that of oxygen, exist in the oxygen sub-lattice of tohdite and remain in the oxygen sub-lattice of κ-Al_2O_3 (from tohdite(F)). The transformation reaction to α-Al_2O_3, which takes place through the rearrangement of oxygen stacking, is accelerated by the dissociation of the impurity fluourine ions from the oxygen sub-lattice, causing a sharp exotherm (Fig. 2). The dissociation of fluourine ions, which was observed as a slight weight loss (about 0.3%) in the thermogravimetric measurements (Fig. 2), was confirmed by the following analysis. The fluorine gas dissociated from the crystal was captured by a wet nitrogen flow which was introduced into a NaOH aqueous solution, and the photometric determination was performed with an alizarin complexon.

Conclusions

(1) The transformation series:

tohdite $\rightarrow$ κ'-Al_2O_3 (from tohdite)
$\rightarrow$ κ-Al_2O_3 (from tohdite) $\rightarrow$ α-Al_2O_3

was confirmed.

(2) Density measurements and electron-diffraction and X-ray diffraction experiments showed that the oxygen arrangements of both κ'- and κ-Al_2O_3 (from tohdite) are close-packed ones, with the oxygen sub-lattice kept unchanged. No evidence was found that the c-axis was twice as large as that of tohdite, in spite of Krischner's assumption. Therefore, it is proper to assume that the stacking sequence of oxygen layers is ABAC and a close-packed one.

(3) For κ'-Al_2O_3 (from tohdite), the hexagonal unit cell containing $5\frac{1}{3}$ Al_2O_3 non-integer unit formulas was employed. The cell dimensions were $a=5.544$ Å, and $c=9.015$ Å. The unit cell of κ-Al_2O_3 (from thodite) is hexagonal, with cell dimensions of $a=9.599$ Å, and $c=9.024$ Å.

On the basis of this conclusion, a crystal structure analysis of κ'- and κ-Al_2O_3 (from tohdite) is now being perfomed. The results will be published later.