

Crystallization of anorthite from CaO–Al₂O₃–SiO₂ glasses

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SUMMARY. The X-ray powder diffraction pattern of synthetic anorthite crystallized from a CaO–Al₂O₃–SiO₂ glass having the anorthite (1:1:2) molar ratio is identical with that reported in the literature, and also with that of a natural Japanese anorthite specimen. Increasing the CaO or SiO₂ content of the parent glasses used for crystallization studies has no measurable effect on that portion of the powder pattern attributable to anorthite. However, glasses containing an excess of Al₂O₃ ranging from 5 to 10 mol % gave, after crystallization at temperatures below *c.* 1150 °C, a distinctively different powder pattern. Several powder reflections that are normally strong, such as $\bar{2}20$, $1\bar{1}2$, etc., were found to be virtually absent. Moreover, the chemical excess of Al₂O₃ did not appear as a separate alumina-bearing phase. Upon reheating these anorthites to temperatures above 1200–50 °C, or upon crystallizing a fresh portion of alumina-rich glass above 1200–50 °C, only the normal anorthite powder X-ray pattern was obtained; the pattern also contained some reflections due to corundum (α -Al₂O₃). Examination of the anomalous low-temperature anorthite by electron diffraction shows that the apparent absence of some powder lines is caused by both albite and Carlsbad twinning, which occur on an intimate scale not exceeding a few unit cell repeats. From the unique manner of its occurrence, the twinning is believed to be associated with the inclusion of an excess of Al³⁺ in the anorthite.

Experimental. CaO–Al₂O₃–SiO₂ glasses were prepared as starting materials, using the general procedure given by Rankin and Wright (1915). They used glass starting materials for this first thorough study of phase equilibrium relations in this system. In the present study, ‘Analar’ grades of CaCO₃ and Al₂O₃ were used; SiO₂ was added as a very pure crushed quartz crystal, which was supplied by Thermal Syndicate Ltd. Weighed amounts of the three components were intimately mixed and finally fused in platinum crucibles in an electrically heated muffle capable of attaining 1600 °C. The composition and homogeneity of each glass was checked by measuring the absolute value of its refractive index, as well as looking for inhomogeneities within each glass sample. The absolute values of refractive indices agreed with those given by Rankin and Wright to within ± 0.002 , although several firings were often necessary to produce a homogeneous glass.

Other mixtures or glasses containing proportions of CaO, Al₂O₃, and SiO₂ differing slightly from the anorthite composition were prepared in two ways: First a weighed excess of either CaO (weighed as CaCO₃), Al₂O₃, or SiO₂ was added to a powdered anorthite glass, and the entire batch re-melted until a homogeneous glass was produced. In the second method, a weighed quantity of CaCO₃, Al₂O₃, or SiO₂ was added to the powdered anorthite glass, and this was ground and intimately mixed. The first method of preparation yielded a homogeneous product; the second, a two-phase mixture of glass plus one crystalline phase—either calcite, α -Al₂O₃, or quartz.

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Portions of these starting materials were reheated in quenching or muffle furnaces. The temperatures recorded were accurate to $\pm 5^\circ\text{C}$. At the end of a run, the products were examined at ambient temperatures, using petrographic techniques and by X-ray powder diffraction. Powder patterns were obtained on a Nonius-Guinier camera using $\text{Cu-K}\alpha$ radiation.

Electron-diffraction patterns were obtained on an A.E.I. type EM-3 microscope equipped with a rotating and tilting goniometric stage designed by one of us (J. A. G.). Later, an A.E.I. type EM-802 instrument became available, and was also used for

TABLE I. *Results of crystallizing $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ compositions. Geh, gehlenite*

Temp. ($^\circ\text{C}$)	Time (h)	Phases present	Temp. ($^\circ\text{C}$)	Time (h)	Phases present
<i>Glass: 20.16 % wt CaO; 36.65 Al_2O_3; 43.19 SiO_2</i>					
900	72	An	1150	48	An
950	72	An	1250	48	An
1050	48	An	1330	48	An
<i>Glass: 23.72 CaO; 35.01 Al_2O_3; 41.27 SiO_2</i>					
860	41	Glass	1000	48	An+Geh
900	24	Glass	1110	68	An+Geh
900	72	An	1200	192	An
900	168	An+Geh			
<i>Glass: 18.58 CaO; 41.60 Al_2O_3; 39.82 SiO_2</i>					
800	168	Glass	1050	600	An $^\circ$
860	41	Glass	1100	24	An $^\circ$
900	24	Glass	1100	68	An $^\circ$
900	72	trace of An	1275	24	An+ α - Al_2O_3
900	168	An $^\circ$			
<i>Glass: 19.20 CaO; 34.90 Al_2O_3; 45.90 SiO_2</i>					
900	24	Glass	1000	48	An
900	72	trace of anorthite	1100	116	An
900	168	An	1200	192	An

An $^\circ$: anorthite giving the powder pattern of fig. 1c.

both micrographs and diffraction measurements. Samples were crushed and dispersed in isopropyl alcohol, and drops of the dispersion were transferred to a specimen grid carrying a carbon film. Specimens intended for electron diffraction were lightly coated with evaporated gold, which served as an internal standard for measuring d -spacings. Most electron-diffraction photographs were also duplicated from a crystal of natural anorthite placed in the corresponding orientation, in order to permit a direct comparison of the observed diffraction effects.

Results. The time and temperature of runs together with the composition of starting materials used are shown in table I, as well as the products identified by petrographic and X-ray examination. The results shown are typical of compositions containing an excess of either CaO , Al_2O_3 , or SiO_2 and the individual runs are selected to show the

range of times and temperatures used. Crystallized glasses of the anorthite composition, or those containing an excess of either CaO or SiO₂, gave a powder pattern that was identical to that of natural anorthite. At the lowest temperatures at which crystallization could be induced to occur in reasonable time (typically, 24–100 h) the anorthite powder pattern was generally diffuse, as would normally be expected for a very fine-grained product. However, at devitrification temperatures of 1050–1100 °C or higher, the patterns were sharp. Compositions containing excess SiO₂ gave powder patterns that also showed the strongest lines of cristobalite; correspondingly, gehlenite was usually detected amongst the crystallization products of the higher-lime glasses. Results obtained from compositions prepared from the mechanical mixtures of a

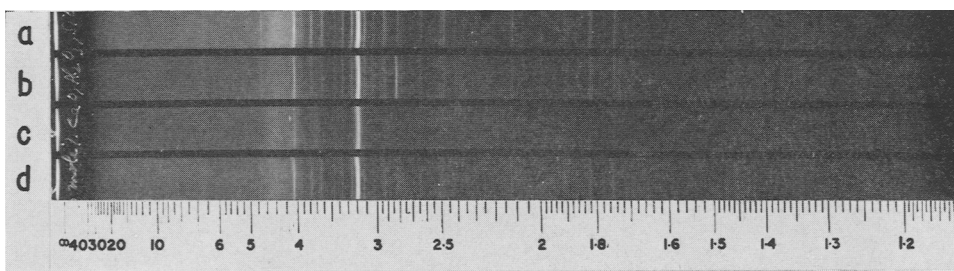


FIG. 1. X-ray powder diffraction photographs of some crystallized CaO–Al₂O₃–SiO₂ glasses: *a*, CaO·Al₂O₃·2SiO₂ glass; *b*, glass on the join: CaO·Al₂O₃·2SiO₂–CaO (23.72 wt % CaO); *c*, glass on the join: CaO·Al₂O₃·2SiO₂–Al₂O₃ (41.60 wt % Al₂O₃); *d*, glass on the join: CaO·Al₂O₃·2SiO₂–SiO₂ (45.90 wt % SiO₂).

glass having the anorthite composition plus either CaCO₃ or SiO₂ were identical with those obtained from initially homogeneous glasses. Accordingly, these runs have not been included in table I, although each run shown for a homogeneous glass was also duplicated using mechanical mixtures.

The most interesting observations related to the devitrification of initially homogeneous compositions containing excess Al₂O₃. The mechanical mixtures of anorthite glass plus α -Al₂O₃ crystallized at temperatures above 950 °C to give anorthite plus α -alumina (corundum). The α -Al₂O₃ powder lines could be detected visually at a calculated excess of 5 mol % Al₂O₃: the occurrence of a chemical excess of Al₂O₃ as corundum would be predicted from the phase diagram. This may be contrasted with the results obtained by crystallizing initially homogeneous glasses, containing an excess of Al₂O₃, at temperatures below \sim 1150 °C. Powder lines of α -Al₂O₃, or indeed any lines other than those due to anorthite, could not be detected in X-ray photographs from glasses containing up to 10 mol % Al₂O₃, after apparently complete crystallization at temperatures below 1150 °C. Crystallization for several weeks at 1150 °C, or for shorter periods at higher temperatures, produced an independent α -Al₂O₃ phase, which could readily be detected by X-rays. Fig. 1 shows a series of powder patterns, in which the marked changes in appearance of the anorthite portion of the powder pattern should be noted. All four of these exposures were recorded simultaneously on the same film, hence they are closely comparable. The anorthite made in the presence

of either excess CaO or SiO₂ is essentially identical with that crystallized from a glass of the anorthite composition (top). A few extra weak lines present in fig. 1*b* and in fig. 1*d* are due to gehlenite and cristobalite, respectively. However, in the photograph fig. 1*c*, which was obtained from a homogeneous glass containing excess alumina that had been crystallized at 1100 °C, a number of reflections were apparently missing from

TABLE II. X-ray powder data for anorthites

<i>hkl</i> †	Anorthite		Al-rich product*	<i>hkl</i> †	Anorthite		Al-rich product*
	<i>d</i>	<i>I</i>			<i>d</i>	<i>I</i>	
$\bar{1}\bar{1}1$	6.807 Å	8	U	130	3.620	33	{A
$\bar{1}10$	6.522	8	U	$\bar{1}\bar{3}2$	3.603		{A
020	6.420	4	U	$\bar{1}32$	3.510	4	U
1 $\bar{1}1$	5.118	2	U	$\bar{1}\bar{3}1$	3.476	14	{U
$\bar{1}\bar{2}1$	5.002	1	U	$\bar{1}\bar{1}4$	3.459		{U
0 $\bar{2}2$	4.690	14	A	$\bar{2}\bar{2}2$	3.403	7	A
003	4.240	2	U	$\bar{1}14$	3.362	25	U
$\bar{2}02$	4.039	48	U	$\bar{2}20$	3.261	52	A
1 $\bar{1}2$	3.916	11	A	040	3.210	63	U
$\bar{1}30$	3.783	28	{A	$\bar{2}04$	3.194	100	U
$\bar{1}\bar{3}1$	3.767		{U§	004	3.180	91	U
112	3.756	19	A	220	3.122	39	A
				$\bar{1}\bar{3}2$	3.042	18	A

* Obtained by crystallizing a glass containing 18.58 % (wt) CaO, 41.60 % Al₂O₃, 39.82 % SiO₂ at 1000 °C for 48 h.

† X-ray *d*-spacings, intensities, and indexing are taken from Borg and Smith (1968).

‡ Intensities are designated U where visual comparison showed them to be essentially unchanged from those of natural or synthetic anorthite. Reflections essentially absent are designated A.

§ Indicates that the reflection was probably present with unchanged intensity but that it was partially overlapped by adjacent reflections.

A comparison of the patterns extended to smaller *d*-spacings results in more ambiguity in attempting to index the missing reflections. Those that were apparently missing, and to which indices could be assigned, include: $\bar{2}\bar{2}2$, *d* = 2.559; 310, *d* = 2.384; $\bar{3}32$, *d* = 2.323; and 152, *d* = 2.095 Å. In addition, one or more reflections in each of the following groups are probably apparently absent: [0 $\bar{4}2$, 0 $\bar{2}4$, $\bar{2}\bar{2}4$], [132, $\bar{1}\bar{3}4$], and [222, $\bar{3}10$].

the powder pattern. These reflections are ordinarily present both in natural anorthite and in the other synthetic samples containing excess Al₂O₃, but crystallized at higher temperatures. A list of these apparently missing reflections, taking natural anorthite as the standard of comparison, is shown in table II. Because of the difficulty in resolving all the powder reflections, it is not possible to index all the apparently missing reflections uniquely: nevertheless some of the absent reflections can be assigned indices without ambiguity. Where possible, these are indicated in table II. Most of the missing reflections lie on either the *hko* or *hk2* zones of the reciprocal lattice. Thus $\bar{2}20$ (*I* = 52), 220 (*I* = 39), and $\bar{1}\bar{3}2$ (*I* = 18) are missing (the intensities shown are for natural anorthite). However, these reflections are partially overlapped by a strong triplet of reflections; thus, the 040 (63), $\bar{2}04$ (100), and 004 (91) reflections all lie between the

expected positions of the $\bar{2}20$ and 220 reflections and to some extent, overlap both. Similar considerations apply in deciding if other apparently missing reflections are genuinely absent, or merely very weak and diffuse. It was first supposed that the reflections were genuinely missing, and that this was due to a change in symmetry of the anorthite. However, the pattern of missing reflections does not correspond to any that has been previously reported for natural plagioclases and, in any event, the complex symmetry changes noted for calcic feldspars are generally associated with an appreciable Na^+ content and are thus confined to members containing at least 10–20 % albite. It was then supposed that the product might be one of the other known ‘anorthite’ modifications. However, the powder data bear an obvious and close relationship to that of natural anorthite, whereas the hexagonal and orthorhombic ‘anorthites’ of Davis and Tuttle (1952) are structurally unrelated to anorthite and hence have no similarity in X-ray powder patterns.

Microscopic examination showed that the low-temperature devitrification of these glasses yields very fine-grained products, and it was not possible to make detailed optical measurements on the anomalous anorthite crystallites. The mean refractive index of the anorthite crystallized from the alumina-rich glasses was slightly higher than that of anorthite itself, by *c.* 0.005–0.007. Attempts were made to grow larger crystallites of this modified anorthite, but neither long annealing nor addition of fluxes (such as 0.1–0.5 wt % Na_2O) to the parent glass produced crystals larger than a few micrometres; the small crystallites were usually anhedral, approximately equidimensional, and exhibited undulose extinction. It was hypothesized that the apparently missing reflections might be greatly weakened because of preferred orientation. However, a 6-cm powder photograph taken on a full-plate film showed the complete powder arcs over a considerable angular range, which included the zone of several of the missing reflections. It failed to show any trace of preferred orientation.

A series of electron-diffraction patterns was taken of the anomalous anorthite prepared from the glass containing 41.6 % Al_2O_3 , crystallized at 950 °C for 72 h. Four sections of the reciprocal lattice are shown in electron-diffraction plates, fig. 2. In spite of the accurate crystallographic data given in the literature for anorthite, considerable difficulty was experienced in indexing the patterns fully, both on account of the large numbers of reflections and triclinic symmetry, and also because of the fortuitous similarity in *d*-spacings of many reflections. A crystal of natural anorthite was always photographed in a corresponding orientation as an additional check on the indexing. In the synthetic product, rows of reflections containing streaked multiple reflections were often encountered; such sections always contained a *oko* row in which the multiplicity of the reflections (compared with natural anorthite) lay parallel to *oko*. Several crystals were then tilted around *b** in order to obtain sets of reciprocal lattice sections, and in this way, the full reciprocal lattice was reconstructed from seven different orientations. The ‘extra’ spots that were encountered in the patterns of the devitrified synthetic product suggest that a phase having an apparently body-centred real cell with *c* \simeq 7.1 Å is intergrown with the ‘normal’ cell. However, all these extra reflections could also be indexed in the normal reciprocal lattice of anorthite on the assumption that all reflections of anorthite were duplicated by mirror

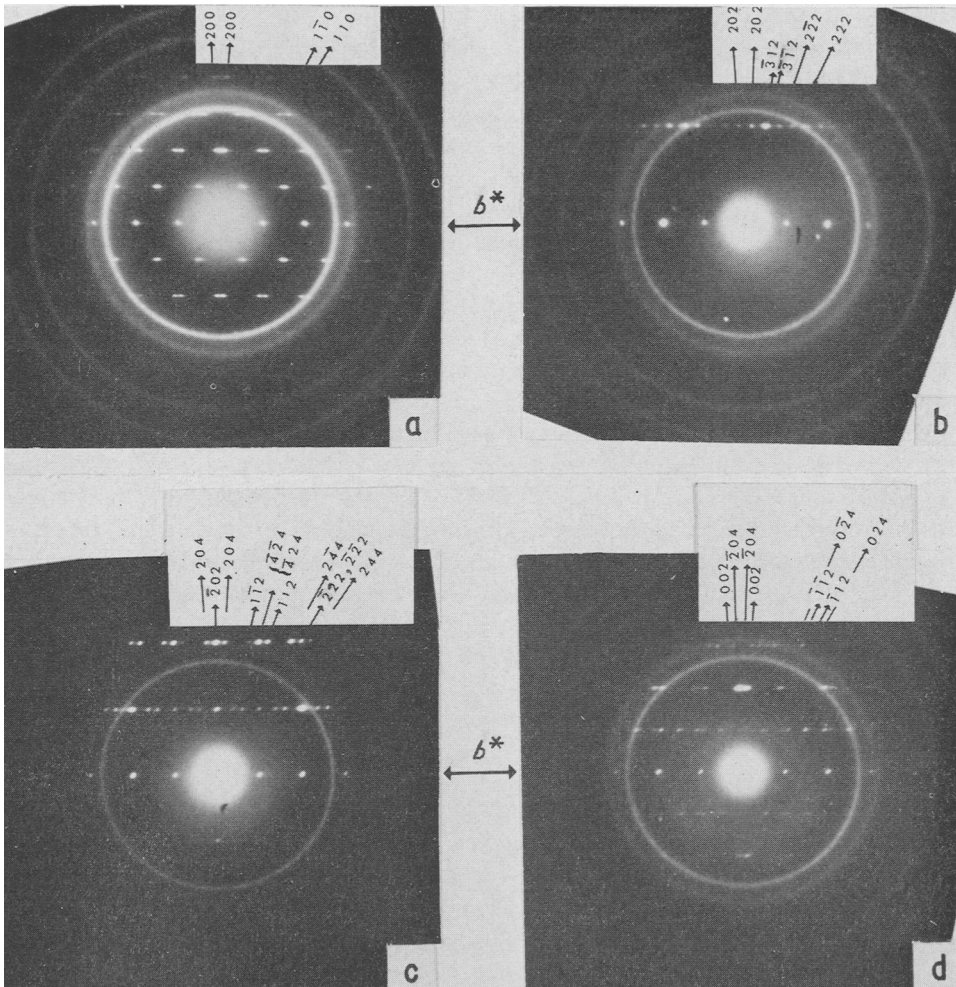


FIG. 2. Electron-diffraction patterns recorded with the A.E.I. type EM-3 microscope from fragments of anorthite crystallized from a $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ glass containing 41.60% Al_2O_3 (table I) at *c.* 950 °C. *hkl* indices are given for the reflection with the longest *d*-spacing in the direction of each arrow. Zone axes oriented parallel to the electron beam for each Carlsbad twin are shown below; P and C indicate whether the network of reflections is primitive or centred, respectively: *a*, [001] C for both twins; *b*, [203] C and [10 $\bar{1}$] P; *c*, [101] P and [20 $\bar{1}$] C (the pattern for the former orientation is almost exactly rhombic, hence the groups of three spots); *d*, [201] C and [100] P. The rings are from gold (2.355, 2.040, 1.443, 1.230 Å).

imaging across both the planes (010) and (100). This mirroring effect is caused by albite and Carlsbad twinning, respectively. Identical reciprocal lattice sections may be obtained from the same flake in different orientations; this again indicates twinning. Both twins have (010) as the composition plane. All the reflections seen are explained by this twinning. For example, in fig. 2c, one set of reflections is arranged on a rhombic net, so that these, when doubled by mirror imaging across (010), coincide so

as to give single reflections. This accounts for the groups of three reflections in the second row (e.g. 224 , $\bar{4}24$, and $\bar{2}2\bar{4}$), for while the $\bar{4}k4$ and $4k\bar{4}$ reflections coincide, $2k4$ and $\bar{2}k\bar{4}$ do not. All reflections seen in the electron-diffraction photographs can thus be accounted for on the basis of combined albite and Carlsbad twinning. All electron-diffraction plates obtained from the alumina-rich anorthite showed the twinning. It was not possible to examine areas small enough to contain only a single twin domain. This suggests that the scale of the twinning must be very small. Thus although the Japanese anorthite used as a standard was seen to be microscopically twinned, this was not observed in any of the small flakes examined by electron diffraction. Indeed, it was very unlikely that the area selected for diffraction would be positioned on a twin boundary. Further direct evidence for the intimate scale of the twinning in these synthetic specimens is, of course, present in the electron-diffraction patterns. Groups of twinning reflections are seen to be notably streaked in the b^* direction; the photographs shown here are selected as comparatively sharp examples. The degree of streaking along b^* was observed to vary from crystal to crystal within the same preparation, but in general the streaking was most conspicuous in samples that had been crystallized at the lowest temperatures *c.* 950°C . The electron-diffraction evidence, therefore, shows that the symmetry of the anorthite remains unchanged and that the apparently missing powder X-ray reflections must be merely grossly broadened.

Re-examination of the X-ray photographs confirms this interpretation. At about 1150°C , the powder pattern of aluminous anorthite will again become normal upon prolonged (1–2 weeks) heat treatment. A succession of powder photographs taken at 24-h intervals show that after 24 h the glass has crystallized to anorthite, and that a number of powder reflections still appear to be missing. After 48 h, these can definitely be detected but are very diffuse. After 72 h at 1150°C the reflections are sufficiently sharp so that a half-breadth can be measured. The mean size of the twin lamellae normal to the b direction can then be calculated approximately from the relation $T = \lambda/\beta \cos \theta$, where T is the thickness of the lamellae, β the intrinsic breadth of the reflection, λ the wavelength (in this instance, 1.54 \AA), and θ the Bragg angle. Several different reflections give values for T of approximately $75\text{--}90 \text{ \AA}$. As the breadth of the twin domains increases, the X-ray powder patterns also show that $\alpha\text{-Al}_2\text{O}_3$ appears. Thus, at or below approximately 1150°C , the initial crystallization of alumina-rich compositions gives, as the first product of crystallization, an anorthite solid solution. Upon continued isothermal treatment at 1150°C the twin lamellae coarsen and the apparently missing set of X-ray reflections gradually appear, diffuse at first. As they sharpen, $\alpha\text{-Al}_2\text{O}_3$ is also crystallized out. At lower temperatures, the $\alpha\text{-Al}_2\text{O}_3$ is not readily exsolved; for example, at 1050°C , even a run of 600 h duration gave only a modified anorthite powder pattern.

A series of electron micrographs have been taken to further confirm the nature of this recrystallization. Fig. 3*a* shows the appearance of an anorthite crystal containing 10 mol % excess Al_2O_3 . The powder pattern obtained from this preparation contains a number of apparently missing reflections; it is identical with that shown in fig. 1*c*. The very fine scale of the twinning is shown directly in fig. 3*a*, in which the thinness

of the individual twin lamellae is best measured by examination of the original plate with a low-power magnifying glass. Fig. 3*b* shows the corresponding micrographs obtained by reheating crystals from this preparation to 1340° for 24 h. The pattern obtained from this reheated material is interpreted as comprising a mixture of ordinary anorthite plus Al₂O₃. The flake shown in fig. 3*b* is an anorthite crystal; corundum is not visible. Compared with fig. 3*a*, the twinning is seen to have coarsened considerably. Electron-diffraction patterns are now completely free from streaking in the *b** direction, indicating that the individual lamellae are now much broader, but

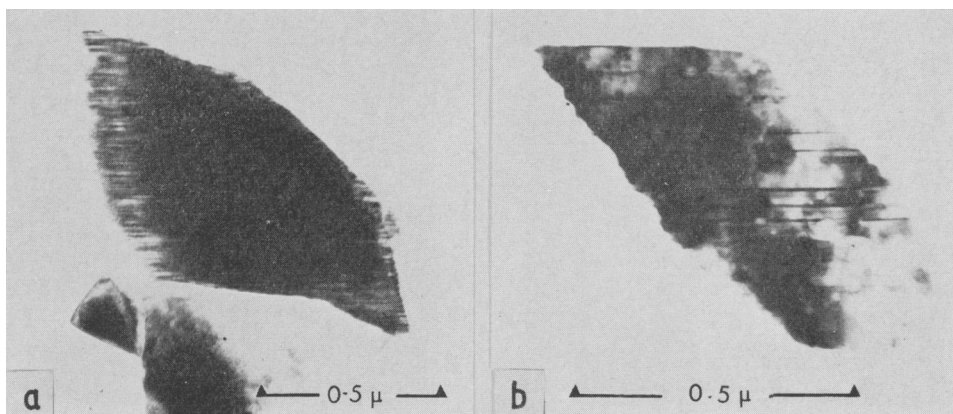


FIG. 3. Electron micrographs taken in bright field of anorthite fragments crystallized from a CaO–Al₂O₃–SiO₂ glass containing 41.60 % Al₂O₃: *a*, heated 18 h at 1270 °C; the twin lamellae are often 25 or 50 Å wide, i.e. two- or four-unit cell *b*-dimensions. In *b* the same sample was reheated to 1370 °C for 18 h; the lamellae have broadened to several hundred Å. The (010) composition plane was oriented parallel to the electron beam and is horizontal in the figures.

both types of twin are still present; see fig. 4. Because the structural misfit between Carlsbad domains is so large, rearrangement of these domains is energetically difficult. Rearrangement of the albite domains, however, involves only a very small displacive change. It is therefore suggested that an important feature of the structural changes upon annealing is an increase in the width of the albite domains within each Carlsbad domain. An unexpected feature of these photographs is the strength of the reflections that double the *c* axis repeat to *c*. 14 Å. These extra reflections are enhanced in electron diffraction.

Discussion. Results of the present study show that ‘anorthite’ can probably take approximately 10 mol % Al₂O₃ into solid solution. These solid solutions are created by crystallization of an initially homogeneous glass starting-material at comparatively low temperatures. The solid solutions, once formed, decompose upon reheating to higher temperatures. The evidence suggests, therefore, that the solid solutions are thermodynamically metastable. Although the idea of an appreciable homogeneity region for anorthite may seem surprising, other feldspathoid phases, such as nepheline, are known to have a range of homogeneity within the Na₂O–Al₂O₃–SiO₂ system, and

moreover these aluminous solid solutions are presumed to be thermodynamically stable. Nevertheless, the exact method by which a chemical excess of Al^{3+} is incorporated into either the feldspar or feldspathoid structures is still unknown. If it is assumed that the oxygen framework of the solid solutions remains essentially unchanged, and that each atom has its normal oxidation state, the number of possibilities for solution of excess Al^{3+} is limited. There are several possible mechanisms for the solid solution of Al^{3+} in anorthite:

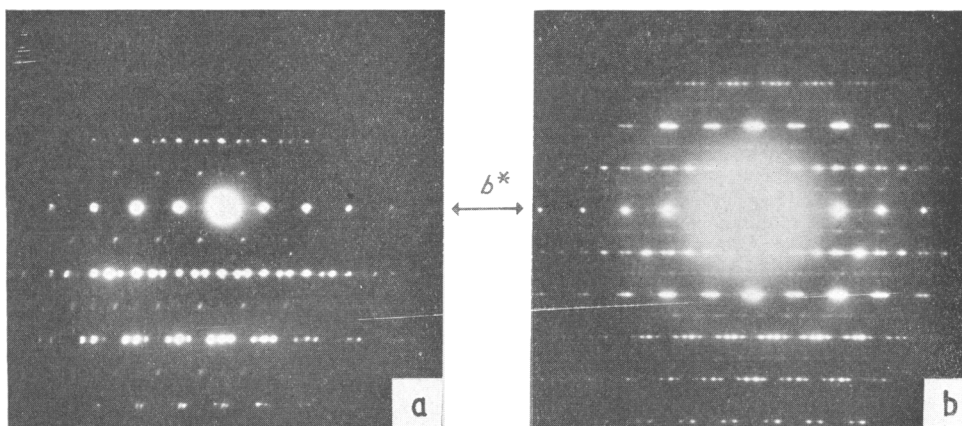


FIG. 4. Electron-diffraction patterns of anorthite crystallized from glass above 1270°C , showing complete zones of reflections with l odd, indicating ordered distribution of Al and Si atoms. a and b have the same orientations as figs. 2 c and d respectively; odd- l spots are present in the $[101]$ zone of fig. 4 a , and in the $[100]$ zone of fig. 4 b . Recorded with an A.E.I. type EM-802 microscope.

Al^{3+} may replace Si^{4+} with concomitant stuffing of excess Al^{3+} . The type formula of the solid solutions then becomes $\boxed{\text{Al}}_1\text{Ca}_8\text{Al}_{16}(\text{Si}_{13}\text{Al}_3)\text{O}_{64}$ where $\boxed{\quad}$ denotes a structural site that is normally vacant in anorthite itself.

Al^{3+} may replace Si^{4+} with concomitant stuffing of excess Ca^{2+} to yield a solid solution of the type $\boxed{\text{Ca}}_{1.5}\text{Ca}_{8.0}\text{Al}_{16}(\text{Si}_{13}\text{Al}_3)\text{O}_{64}$.

Or Al^{3+} may replace Ca^{2+} with the excess positive charge balanced by omission of Ca^{2+} . This yields a solid solution of the type $(\text{Ca}_{6.5}\text{Al}_{1.0})\text{Al}_{16}\text{Si}_{16}\text{O}_{64}$.

These formulae are given in terms of unit cell contents and represent compositions lying near the experimentally observed limits of solid solution. The proper use of these different formulae is to show, firstly that a number of different mechanisms of solid solution might be possible, and secondly that these mechanisms would not necessarily yield the same end-member formula. In fact, the third mechanism predicts a rather high ratio of Si:Al in the solid solutions and the first two mechanisms provide a more reasonable fit to the experimental observations. Before attempting to choose between them, it would be as well to explain why solid solution mechanisms that involve anion stuffing have been ruled out. X-ray powder data show that the Al-substituted anorthites must have a unit cell volume that differs little from that of anorthite itself;

this appears to be a common feature of these 'hybrid' solid solutions, which Donnay (1965) found to occur between diopside and forsterite. Therefore, if the excess of charge caused by stuffing of excess Al^{3+} into anorthite is to be balanced by concomitant stuffing of O^{2-} , the density of the solid solutions and their mean refractive index should rise very rapidly, as more atoms are being stuffed into essentially the same volume: this is not observed. In the $\text{Li}_2\text{Si}_2\text{O}_5$ - SiO_2 solid solutions studied by Glasser (1967) it could be proved that the oxygen framework remained essentially unchanged. Translating the mechanism used to explain these solid solutions to the present case would suggest that the mechanisms given above, which do not involve oxygen stuffing, are likely ones. However, at least one other type of mechanism should be considered. This mechanism envisages that oxygen is omitted as Al^{3+} is substituted for Si^{4+} , yielding a solid solution of the type $\text{Ca}_{8.0}\text{Al}_{16}\text{Si}_{14}\text{Al}_2\text{O}_{63}$.

An oxygen-omission solid solution might inherit its structure from the liquid or glass. Thus it is probable that the short-range structural ordering of a glass of the anorthite composition resembles that of anorthite itself. If a slight excess of Al^{3+} is dissolved in the liquid at high temperatures, at least some of the added Al^{3+} replaces Si^{4+} in tetrahedral sites. For each Si^{4+} replaced, an unbalanced charge would be created, which might be compensated by omission of oxygen. At low (several mol %) Al^{3+} contents, this would lead to creation of network 'defects' rather than to catastrophic depolymerization or disruption of the network. In supercooling of the liquid these postulated defects would be preserved, and during subsequent crystallization would be incorporated into the growing crystals as sites that are energetically suitable for the relief of strain energy, and hence for twin formation. In this view, the excess Al^{3+} would be localized on the composition planes of the twin domains.

Further speculation concerning the nature of these aluminous solid solutions must await more experimental data. An electron-probe analysis of the anomalous anorthite crystallites would be helpful in providing additional proof that a large excess of alumina can be put into solid solution, but this type of analysis is not, in itself, sufficient to choose between the different solid solution mechanisms that have been discussed.

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REFERENCES

- BORG (I. Y.) and SMITH (D. K.), 1968. *Amer. Min.* **53**, 1709.
DAVIS (G. L.) and TUTTLE (O. F.), 1952. *Amer. Journ. Sci.* **Bowen vol.** 107.
DONNAY (G.), 1965. *Acta Cryst.* **19**, 283.
GLASSER (F. P.), 1967. *Physics Chem. Glasses*, **8**, 224.
RANKIN (G. A.) and WRIGHT (F. E.), 1915. *Amer. Journ. Sci.* ser. 4, **39**, 1.

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