SOME CHARACTERISTICS OF SYNTHETIC INTERMEDIATE ALBITE

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The albite synthesized from the gels of NaAlSi3O8 composition in the system Na2O-Al2O3-SiO2-H2O-CO2 has been investigated. The obliquity 2θ(131)-2θ(131) indicated that all the synthetic albites are of intermediate type according to the definition of albite polymorph given by Martin (1969). X-ray powder patterns for synthetic intermediate albite are reported for the first time. Some of synthetic albites are produced as single crystals, with which the intensity of reflection was measured by means of four-circle diffractometer. The RF value; F1ko-F1ko/F1ko+F1ko proposed here seems convenient to characterize the structural state of albite polymorph. The IR spectra of these intermediate albites and its glass are reported in detail. In the DTA curve of high albite, an intersection point 1116±7°C of the endothermic peak shows a striking similarity to the melting point, 1118±3°C, of albite suggested by Schairer and Bowen (1956). Polymorphism of the intermediate albite is discussed on the basis of the fact that some of natural and synthetic intermediate albites deviate from the linear trend between obliquity and their cell parameters.

INTRODUCTION

Natural intermediate albites have been described by the following workers; Baskin (1956), Callegari and Depieri (1971), and Desborough (1975); they mainly reported their lattice parameters. Most of albites synthesized under hydrothermal conditions have the structural state corresponding to a partially-ordered albite (MacKenzie, 1957; Trembath, 1973). Raase and Kern (1969) synthesized intermediate albites, by heating an albite glass containing 0.19% Fe2O3. Nearly all crystals they synthesized were Albite-twinned, mostly with fine lamellae, but at the lower temperature tufts of non-repeated Albite twins occurred often. Afterwards Martin (1970) presented the data for cell parameters of high to low albites hydrothermally synthesized from the albite glass.

In spite of many studies on the synthesis of albite, there have been only a few reports on the system Na2O-Al2O3-SiO2-H2O-CO2. Koster van Groos and Wyllie (1968) showed that albite is the main silicate phase at low H2O contents, while cancrine is the main silicate phase at high H2O content. From a viewpoint of the obliquity in albite, Martin (1969) suggested that Na2CO3 does lead to shorter obliquity than in the system albite water through analyzing the synthetic albite, but the data have not been published.

The definition of low, intermediate, and high albites was given by Martin (1969), according to whose definition the term "intermediate albite" (2θ(131)-2θ(131)
1.17~1.94) was used in the present paper.

**PREPARATION OF SYNTHETIC ALBITE**

Reagent-grade chemicals used are sodium carbonate, alumina and silica gels which were dried at 120°C for seven days. Each chemical reagent was ground to pass 250 mesh, and a mixture with the chemical composition of albite was prepared and mixed in an agate mortar, which was used as the starting material. All runs were made in an autoclave without quenching technique. Bulk compositions were made by injecting a distilled water in a silver tube, and successively by adding the starting material, and both ends of the tube were sealed by fusion welding. The autoclaves used are of the Morey-type with 50 ml content, and temperature measurements are believed accurate to ±5°C; pressure, measured with commercial bourdon-type gauges, is accurate to within 10 kg/cm².

**RESULTS AND DISCUSSION**

Table 1 summarizes the data obtained in the present study, together with the obliquity data. The products were examined under the microscope and identified by X-ray powder diffraction patterns. The measurement of obliquity followed the same method adopted by Martin (1969). The partial pressure of CO₂ was calculated on the assumption that neither H₂O nor CO₂ are present in the synthetic crystals and real gas solutions are ideal solution (Garrels and Christ, 1965). As is evident from Table 1, all of the albites synthesized in the present experiments have intermediate structural state in Al/Si distribution. Under the conditions of temperature 450 to 400°C and pressure 400 kg/cm², the effect of amount of water or CO₂

![Table 1. Results of synthetic experiments on intermediate albite.](image)

* Weight ratio: Water/Starting material.  
  Ab=albite, Qt=quartz, Anl=Analcime. 
  The analcime synthesized is very scarce.
partial pressure on obliquity was examined, but no appreciable relation was noted.

**X-ray ANALYSIS**

The X-ray powder patterns of the synthetic albites were compared with those of natural intermediate albite (Desborough, 1975), which is shown in Table 2. The X-ray reflections observed with CuKα (λ = 1.5418 Å) radiation were identified using calculated powder patterns for high and low albite (Ferguson et al., 1958); peaks for intermediate albite were identified by interpolating values for high and low albite. The (031) and (142) reflections in the pattern indexed by Desborough (1975) are inadequate to the space group CI of albite structure. The cell parameters and constants, determined by the refinement of X-ray diffractometer data using a silicon internal standard and the modified UNICS RSLC-3 computer program (Sakurai, 1967) are, with standard errors in parentheses, given in Table 3 including those of cleavelandite albite and the heated one. These cell parameters, as well as the positions of the (201), (060), and (204) X-ray spacings, also indicate that these albites are non-ordered (Wright, 1968: Wright and Stewart, 1968).

Single crystals of intermediate albite were synthesized under the condition of Run no. 4313. The largest crystals (up to 2.0 × 0.4 × 0.3 mm³ in size) with simple twinning were of light whitish colour and transparent. Fig. 1 gives the 0-layer Weissenberg photograph of this albite with the rotation axis [100]. The observed reflections have hkl with h+k=2n, indicating the space group CI. Oscillation and Weissenberg photographs made with long exposures showed no reflection due to superstructure. The relative intensity of pair spots, such as (045) and (045), (061) and (061), (025) and (025), (046) and (046), suggested that c*
Table 3. Lattice parameters of albite polymorphs.

<table>
<thead>
<tr>
<th>1)</th>
<th>2)</th>
<th>3)</th>
<th>4)</th>
<th>5)</th>
<th>6)</th>
<th>7)</th>
<th>8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>8.141(5)</td>
<td>8.166(9)</td>
<td>8.160(5)</td>
<td>8.147(4)</td>
<td>8.130(7)</td>
<td>8.114(4)</td>
<td>8.145(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>7.161(3)</td>
<td>7.143(4)</td>
<td>7.116(3)</td>
<td>7.158(5)</td>
<td>7.135(2)</td>
<td>7.145(2)</td>
<td>7.141(4)</td>
</tr>
<tr>
<td>α (°)</td>
<td>94.33(4)</td>
<td>93.91(6)</td>
<td>93.43(4)</td>
<td>94.18(7)</td>
<td>94.26(3)</td>
<td>94.09(6)</td>
<td>93.85(5)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>116.57(5)</td>
<td>116.58(5)</td>
<td>116.41(5)</td>
<td>116.54(5)</td>
<td>116.31(2)</td>
<td>116.46(3)</td>
<td>116.46(4)</td>
</tr>
<tr>
<td>θ (°)</td>
<td>87.65(4)</td>
<td>88.96(5)</td>
<td>90.25(5)</td>
<td>88.13(3)</td>
<td>88.74(5)</td>
<td>88.79(5)</td>
<td>88.99(5)</td>
</tr>
<tr>
<td>v(Å³)</td>
<td>665.2(5)</td>
<td>666.2(6)</td>
<td>668.4(4)</td>
<td>666.8(3)</td>
<td>667.0(3)</td>
<td>666.5(4)</td>
<td>666.0(5)</td>
</tr>
<tr>
<td>obliquity</td>
<td>1.08</td>
<td>1.46</td>
<td>1.98</td>
<td>1.27</td>
<td>1.36</td>
<td>1.51</td>
<td>1.59</td>
</tr>
</tbody>
</table>

1) natural cleavelandite albite (low albite),
2) the authigenic albite reported by Desborough (1975)
3) cleavelandite albite heated for 2184 hours at 1055°C (high albite),
4)–8) Run no. 4906, 4703, 5004, 4313, 4910.

crystals has substantially the same unit cell, that is, the structural state partially disordered in the same degree, because it was confirmed under the microscope that a simple twin boundary occurs: the resulting reciprocal lattice shows two sets of spots which overlap completely in the direction normal to the twin boundary. In Albite twinning the angular misfit between the two individuals on either side of the twin plane is the angle between [010] and the b crystallographic axis, and is designated φ. The value of φ can be calculated from the following expression;

\[
\cos \phi = \sin \alpha \times \sin \gamma.
\]

In the present albite \(\phi = 3.922\) was calculated by using the lattice parameters (Table 3), while Starkey (1967) reported that for maximum ordered and maximum disordered albites \(\phi\) become 4.362 and 2.460, respectively. It is interesting to note that the “intermediate” state for this albite may be also inferred from \(\phi\).

It is also examined whether the intensity differences for high- and low-albite proposed by Laves and Chaisson (1950) would give the characterization of an intermediate structural state or not. Here, through the application to the difference of the structure factor between the \((hk0)\)
and (h0k0) reflections, the author suggests the following equation:

\[ RF = \frac{F_{h0k0} - F_{hk0}}{F_{h0k0} + F_{hk0}}. \]

Intensity data for the synthetic albite were collected using a computer-controlled Rigaku four-circle diffractometer with Nb-filtered and graphite monochromatized MoKa radiation. The observed intensities were corrected for Lorentz and polarization effects, and back ground effect depending upon the conditions that the corrected intensity (IN) is given by the following equation: \[ IN = IP - \frac{TP}{2 \cdot TB} (B1 + B2), \] where IP; the intensity of each reflection, TP; scanning time for each reflection, TB; counting time for the background, B1 and B2; each intensity of higher and lower angle back ground measurements, respectively. An absorption correction was neglected, since the linear absorption coefficient of this albite for MoKa radiation is small, 9.17 cm⁻¹. The structure factors of the reflections (h0k0) and (hk0) were calculated on the basis of the corrected intensities. As an example, the results obtained for (1k0) and (1k0) reflections are tabulated (Table 4) with those of high and low albites reported by Ferguson et al. (1958). Summation of the RF values obtained agrees well with the assumption of an intermediate structural state of this albite.

**INFRARED ABSORPTION DATA**

The infrared sample was prepared by the KBr disk method. The measurements were made with a Japan Spectroscopic IRG double beam spectrophotometer in the frequency range from 1400 to 400 cm⁻¹, which is shown in Fig. 2. The correction of the frequency was made by reference to the polystyrene absorption bands at 537, 907, 1028 and 1154 cm⁻¹. As compared with the spectra of high and low albite reported by Laves and Hafner (1956), it is evident Spectra 1), 2) and 3) for the synthetic albites show the transitional state between broad bands in high albite and well-resolved, sharp bands in low albite. This figure also shows the spectrum of the albite glass produced after heating up to 1200°C of D.T.A., and the main characteristic of this spectrum is the elimination of the absorption bands from 650 to 500 cm⁻¹ corresponding to O-Si(Al)-O bending assigned by Iiishi et al. (1971). This elimination implies that AlO₄ tetrahedron might be deformed and SiO₄ tetrahedron would be distributed at random.

**THERMAL STUDY**

New data for DTA and TG curves of albite polymorphs, especially synthetic intermediate albite and high albite transformed by heating natural low albite, were obtained in air with a Rigaku thermostx under the following condition: thermocouple, Pt-PtRh; reference, Al₂O₃; mean heating rate, 10°C/min; sensitivity (DTA), ±250μV; sensitivity (TG), 5 mg; sample
Fig. 2. Infrared absorption spectra of synthetic intermediate albites and the glass. The spectra are arranged in order of increasing obliquity.
1) Run no. 4703 2) 4313 3) 4910 4) the glass of 4910 produced after D.T.A. up to 1200°C.

weight, about 30 mg; size fractions, minus 300 mesh, while for synthetic albite, the size insensible to the finger tip. The results of D.T.A. are given in Table 5. In the TG curves no weight loss was noticed from room temperature to 1200°C for nearly all the
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Table 5. Results of differential thermal analysis.

<table>
<thead>
<tr>
<th>specimen</th>
<th>temperatures of intersection points (°C)</th>
<th>run times</th>
<th>errors (°C)</th>
<th>products observed after D. T. A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-Ab</td>
<td>1121</td>
<td>4</td>
<td>±3</td>
<td>low albite, glass</td>
</tr>
<tr>
<td>H-Ab</td>
<td>1116</td>
<td>6</td>
<td>±7</td>
<td>glass, high albite tr.</td>
</tr>
<tr>
<td>4703</td>
<td>1132</td>
<td>3</td>
<td>±4</td>
<td>glass, quartz tr.</td>
</tr>
<tr>
<td>4313</td>
<td>1129</td>
<td>4</td>
<td>±6</td>
<td>glass, quartz tr.</td>
</tr>
<tr>
<td>4910</td>
<td>1136</td>
<td>3</td>
<td>±4</td>
<td>glass.</td>
</tr>
</tbody>
</table>

L-Ab: natural cleavelandite albite (low albite).
H-Ab: cleavelandite albite heated for 2184 hours at 1055°C (high albite).

albite polymorphs examined. Exothermic peaks cannot be seen at all, but only one sharp endothermic peak at about 1200°C resulted from the melting of the crystals to form a glass, whose existence is confirmed by X-ray powder patterns and microscope. In the case of low albite, however, its structure remains without the appreciable change of its obliquity after D.T.A., which shows that the remaining low albite was not produced through the process of cooling after melting. Accordingly it can be said positively that the crystal of low albite exhibits the superheating phenomenon, and this is supported by Dietz et al. (1970). These facts conclusively demonstrate that the endothermic peak reported by Köhler and Weiden (1954) might be due to impurity in albite.

Parts of DTA curves are shown in Fig. 3. An intersection point of one peak (Nomenclature Committee of the ICTA, 1972) is very close to the temperature representing the transition of one phase, which has found general acceptance. An intersection point of the peak in high albite is situated at lower temperature, 1116±7°C, than those in other albites, which suggests that the melting of high albite is easier to occur. It is a noteworthy point that an intersection point of high albite is very close to the melting temperature, 1118±3°C, reported by Schairer and Bowen (1956). Intersection points of synthetic albites exist toward higher temperature, which might be due to the sharpening of the peak because
Fig. 4. b-axis of albites plotted with respect to obliquity. The straight line was calculated by Martin (1970) through least squares regression and dashed line shows its standard deviation. Symbols: ◊ cleavelandite albite; □ synthetic albites (this paper); △ natural intermediate albite (Baskin, 1956; Callegari and Depieri, 1967; Desborough, 1975); ◈ low and high albites (Ferguson et al., 1958); □ "highly metastable" synthetic albites (Martin, 1970); □□ synthetic albite (Raase, 1971); × synthetic albite (Grundy and Brown, 1969). The size of the symbols reflects the standard deviation.

Fig. 5. Unit cell parameter, γ angle as a function of obliquity of albite polymorph. Comments and symbols as in Fig. 4.
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of the difference of size fraction and crystallinity and so on.

Polymorphism of intermediate albite

Cell parameters of natural intermediate albites agree poorly with the data on synthetic albites, as pointed out by Martin (1970), but he could not solve the questions concerning this lack of agreements. The addition of the recent data to them summarized by Martin (1970) is represented in Fig. 4 and Fig. 5. Some of synthetic albites as well as natural intermediate ones tend to deviate from the belt proposed by Martin (1970). This deviation is thought to be caused by the followings;

1) the effect of nonstoichiometric property of albite,
2) the existence of silicic albite, e.g. Na_{0.75}Al_{0.15}Si_{1.15}O_{6}, in somewhat exaggerated expression,
3) the effect of very small An and Or amounts in natural intermediate albite,
4) the variety of Al/Si distribution in the intermediate structural state with the same obliquity.

In pure natural albite, the case 1), namely, nonstoichiometric property regarding only Na, Al, and Si atoms has never been confirmed on the basis of reliable data, and so has the case 2). And then with due consideration for An and Or amounts of natural intermediate albite, that is, natural albite of obliquity 1.69 with Ab_{0.67}An_{0.15}Or_{0.18} and of 1.16 with Ab_{0.61}An_{0.03}Or_{0.36} (Callegarini and Depieri, 1967), and CaO<0.05 and K2O<0.06 weight percent of natural intermediate albite (Desborough, 1975), it is of no logic to think that such small Or and An compositions have considerable effect on the difference in cell parameters. As to the case 4), since NaAlSi_3O_8 has a continuum of structural states between high and low albites, four tetrahedral sites T_{1}(O), T_{1}(m), T_{2}(O), and T_{2}(m) (Megaw, 1954) are occupied by Al and Si atoms, bearing the relation that the summation of Al ratio in each site is constantly unity. Thereupon it is reasonable to think that intermediate albite can have various Al/Si distributions in four tetrahedral sites because of its metastability. This means that two intermediate albites with the same obliquity do not necessarily have the same mode of Al/Si distribution in four tetrahedral sites, that is, there can be polymorphs among the intermediate albite with the same obliquity except for low and high albites. If this is the case, polymorphism of intermediate albite can lucidly explain the following observations;

1) one obliquity produces different cell parameters among intermediate albites.
2) there was seen the difference of wave-number in the bands of infrared absorption spectra — which Iiishi et al. (1971) assigned to O-Si(Al)-O band (about 645 cm\(^{-1}\)) and coupling between O-Si-O deformation and Na-O stretching (about 535 cm\(^{-1}\)) — between ordering and disordering process of albite as shown by Martin (1970).
3) the anomalies between obliquity and \(2\theta (201)_{\text{Ab}}-2\theta (101)_{\text{KBrO}}\), were found by Hamilton and Edgar (1969). No evidence against this interpretation has come to my attention but polymorphism of intermediate albite is confirmed by high-precision crystal structure analysis of such intermediate albites as having the same obliquity and yielding under different environments.

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REFERENCES