SYNTHESIS OF DUMORTIERITE IN THE SYSTEM $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3\text{-H}_2\text{O}$

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Synthesis of dumortierite indicates that stoichiometric dumortierite is unstable. Compositional variation of synthetic dumortierite is almost absent regardless of wide range of synthetic temperature and difference in coexisting minerals. Substitutions of $\text{Al-O} \rightleftharpoons \text{Al-OH}$ and $\text{AlO}_6 \rightleftharpoons \text{BO}_6$ in dumortierite are revealed by chemical analyses and infrared spectroscopic study.

INTRODUCTION

Crystallochemical formula of dumortierite is considered as $\text{Al}_7\text{O}_3(\text{BO}_3)(\text{SiO}_4)_3$. However, chemical analyses of natural dumortierite show small amounts of H_2O (Claringbull and Hey, 1958). Sum of weight percentages of Al_2O_3 and SiO_2 of any dumortierite from the Ryoke pelitic gneisses are considerably small as compared with ideal composition, $\text{Al}_7\text{O}_3(\text{BO}_3)(\text{SiO}_4)_3$ (Ono, 1977). Synthesis of dumortierite was carried out to elucidate these problems.

Fig. 1 Structure of dumortierite.

CRYSTAL STRUCTURE

Dumortierite is a nesosubsilicate consisting of isolated SiO_4 tetrahedra, with BO_3 triangles as additional anions. The SiO_4 tetrahedra are held together by Al ions in octahedral site (Fig. 1). Viewing down the $[001]$ direction, the crystal can be considered as consisting of channels with AlO_3 octahedra and BO_3 triangles (Wyckoff, 1968).

Table 1. Chemical compositions of the starting materials

	a	d
SiO_2	30.10	25.53
Al_2O_3	59.59	54.24
B_2O_3	5.81	11.39
H_2O	4.50	8.84
Total	100.00	100.00

METHOD OF SYNTHESIS

Starting materials were prepared by mixing mechanically SiO_2 , Al_2O_3 and H_3BO_3 .

SiO_2 and Al_2O_3 were prepared from H_2SiO_3 and $\text{Al}(\text{OH})_3$ at 1500°C . Table 1 shows the chemical compositions of the starting materials. Chemical composition "a" in Table 1 corresponds to the stoichiometric formula $\text{Al}_7\text{O}_3(\text{BO}_3)(\text{SiO}_4)_3$. "d" in Table 1 is B_2O_3 -excess as compared with synthetic dumortierite. Mixture of "d" and SiO_2 are also used as a starting material in a few experimental runs.

The synthesis of dumortierite was carried out by Boyd-England type single stage piston cylinder apparatus of 12.75 mm in diameter designed by O. Fukunaga. NaCl with 5% MoS_2 , pyrex glass and Alsimag ceramics were used as the pressure medium. Pressure values are uncorrected data of the nominal pressure. Chromelalumel thermocouples were used in all runs for the temperature measurements. The duration of experimental runs was 1 to 95 hours. Starting materials were sealed in platinum tube with no water added. The products of the runs were identified by X-ray diffraction patterns, optical properties and chemical compositions analyzed by an electron probe microanalyzer.

ANALYTICAL METHOD

Synthetic dumortierite were analyzed by an electron probe microanalyzer. Analyti-

cal procedures are as follows: 1) determination of apparent concentrations of SiO_2 and Al_2O_3 . 2) ZAF correction procedure was carried out. Dumortierite was treated as the ternary system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3$. Apparent boron content was assumed so as to attain 100 per centage in sum of oxide components after the ZAF correction. 3) Chemical compositions obtained by this procedure are different from the ideal composition of $\text{Al}_7\text{O}_3(\text{BO}_3)(\text{SiO}_4)_3$. Boron atom per formula unit on the basis of 18 oxygen always exceeds 1.5. Occupancy of Al atom in the tetrahedral Si positions is significant. Thus, charge neutrality is only achieved by exceeding the seven positions of Al octahedral sites available in the crystal structure. 4) We propose, therefore, the following chemical formula for dumortierite crystal.

$\text{Al}_6(\text{B}_x, \text{Al}_{1-x})\text{O}_3(\text{BO}_3)[(\text{Si}_{3-y}, \text{Al}_y)\text{O}_{12-y}](\text{OH})_y$
Chemical compositions of dumortierite were recalculated so as to support the above chemical formula. In this recalculation, the Al_2O_3 and SiO_2 contents were not changed, and the B_2O_3 contents were subtracted and the H_2O contents were added. Because the amount of H_2O content is very small, this procedure may be correct. New chemical formula is based on supposing substitution of oxygen (O(1) and O(2) after Wyckoff (1968)) by OH.

Fig. 2 Infrared spectrum of dumortierite.

INFRARED SPECTROSCOPY

Synthetic dumortierite were purified by dissolving out impurities with HF-HCl acid. KBr pellets containing small amount of acid treated dumortierite were prepared by the ordinary method, and a vibrational spectrum of OH near 3600 cm^{-1} was measured by an IR spectroscopy.

Fig. 2 shows a result of the measurements. A weak absorption peak is present at 3500 cm^{-1} . The peak width is about 25 cm^{-1} . This is an evidence of OH in dumortierite crystal. Same peak is present in two natural dumortierite examined. The peak is present after heat treatment at 860°C in air.

EXPERIMENTAL RESULTS

Results of experimental runs are shown in Fig. 3. Representative runs are listed in Table 2 together with experimental con-

Fig. 3 P-T range of synthesis of dumortierite
Dumortierite-out line is shown in the figure.

ditions. Vapor phase is present in all experimental runs, therefore vapor blew out from platinum tube when Pt-capsules were

Table 2 Results of representative experimental runs

Chemistries of the starting materials "a" and "d" are given in Table 1. All experiments used by starting material "a" are listed in this Table.

sample	temp °C	press kb	time hours	starting material	products
3	870	11.6	46	a	d + qtz + cor + b + v
25	780	14.5	32	a	qtz + cor + b + v
27	840	11.6	74	a	qtz + cor + b + v
34	830	18.8	49	a	d + qtz + cor + b + v
43	805	17.7	1	d	d + cor + b + v
31	840	9.4	95	d	cor + qtz + b + v
15	840	12	48	d+SiO ₂	d + qtz + v
56	950	11	7	d	d + cor + glass + v
57	980	9.9	7	d	cor + qtz + glass + v
60	920	10	8	d	cor + qtz + b + v
53	920	11.2	21	d	d + cor + glass + v
52	1030	13	5	d	cor + sill + glass + v
48	900	11.6	7	d	d + cor + b + v

d: dumortierite, cor: corundum, qtz: quartz, sill: sillimanite,
b: brown material, v: vapor

cut out after experimental runs. Dumortierite could not be produced below 10 kb, 870°C. Corundum, quartz and brown material are present instead of dumortierite. Brown material is partly soluble in water, and tiny crystals of H_3BO_3 were formed after evaporation of water. Brown material may be rich in B_2O_3 component. Brown color is due to translucent nature of fine aggregate of crystals. Absence of dumortierite in low pressure experimental runs does not mean unstability of dumortierite in low pressure. Corundum, quartz and brown material may be a metastable mineral assemblage. Coexistence of corundum and quartz is surely metastable with respect to sillimanite.

Dumortierite synthesized below 870°C and above 10 kb coexist with small amount of corundum and brown material. Dumortierite coexisting with quartz were synthesized from the starting material added by considerable amount of SiO_2 . Above 900°C transparent glasses are present together with corundum and dumortierite. Amount of glass increase with increasing temperature. Dumortierite is absent in high temperature side of line shown in Fig. 3 where corundum, sillimanite and glass occur.

At high pressure, dumortierite was formed after one hour. The rapid reaction rate suggests that large dumortierite crystals of longer run durations synthesized at high pressure may be in equilibrium with other phases.

Dumortierite could not be produced from the starting material of "a" at 840°C, 11.6 kb. At higher temperature and pressure, dumortierite were synthesized together with considerable amount of corundum and quartz.

It is noteworthy that metastable assem-

Table 3 Chemical compositions of synthetic dumortierite.

sample	1	5	10	3	14	15	56
temp °C	850	810	840	880	815	840	950
press kb	11	16	12	11.6	16	12	11
SiO_2	28.28	28.15	28.32	28.63	28.59	28.61	27.96
Al_2O_3	61.43	60.92	61.56	61.73	61.16	61.32	61.70
B_2O_3	9.73	10.33	9.57	9.14	9.73	9.56	9.73
H_2O	0.56	0.59	0.55	0.49	0.51	0.50	0.61
Total	100.00	99.99	100.00	99.99	99.99	99.99	100.00
Si	2.648	2.629	2.654	2.688	2.677	2.681	2.618
Al IV	0.352	0.371	0.346	0.312	0.323	0.319	0.382
B	1	1	1	1	1	1	1
Al VI	0.428	0.334	0.452	0.518	0.427	0.454	0.427
B	0.572	0.666	0.548	0.428	0.573	0.546	0.573
Al	6	6	6	6	6	6	6
OH	0.350	0.370	0.345	0.310	0.321	0.317	0.380

Fig. 4 Phase relations of the examined system at 850°C

a, d: starting materials (see Table 1), A: synthetic dumortierite, b: brown material (fine-grained undetermined material).

blage of corundum+quartz occurs at low pressure and/or low temperature region, and synthesis of dumortierite depends on bulk composition of starting materials.

Analytical results of dumortierite are given in Table 3. Chemistry of dumortierite is similar with each other regardless of wide

range of synthetic temperature and difference of coexisting minerals. Fig. 4 shows relationships between chemical compositions of starting materials and products in sub-solidus temperature region. Corundum, dumortierite and brown material are produced from the starting material "d". Brown material may be SiO_2 -rich and Al_2O_3 -poor in chemical composition as shown in Fig. 4. Starting material "a" is on a line connecting sillimanite and dumortierite.

NATURAL DUMORTIERITE

Dumortierite occur commonly in the Ryoke pelitic gneisses. Chemical compositions of these dumortierite may be different from those of synthetic ones, because condition of formation is greatly different from each other. Examination of natural dumortierite revealed the following facts. 1) Infrared absorption peak of OH vibration is present. 2) B_2O_3 content of dum-

ortierite is similar to that of synthetic one. 3) Appreciable amount of Mg replaces Al. These data suggest substitutions of $\text{Al}-\text{O} \rightleftharpoons \text{Al}-\text{OH}$ and $\text{AlO}_6 \rightleftharpoons \text{BO}_6$.

X-ray structural analysis based on $\text{Al}_7\text{O}_3(\text{BO}_3)(\text{SiO}_4)_3$ composition indicates that temperature factors of Al(1), O(1) and O(2) are very large (Okamura and Ono, 1978). This supports presence of the substitutions described above.

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Al_2O_3 - SiO_2 - B_2O_3 - H_2O 系におけるデュモティエライトの合成

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デュモティエライトの高圧合成と分析結果によると、従来考えられてきた理想化学式のものは合成できなかった。広い温度範囲に渡って、また共存する鉱物（石英やコランダム）の種類に関係なく、合成結晶の固溶範囲は小さい。分析値は B_2O_3 が 9% を超え、これは Al のサイトに B が置換していることを示す。また $\text{SiO}_4 \rightleftharpoons \text{AlO}_4$ の置換もみとめられる。赤外吸収スペクトルによると、 3500cm^{-1} に OH の振動による吸収ピークが認められた。これは Si と 6 配位の Al を結びつけている酸素が OH に置換されていることを示す。天然のデュモティエライトにおいても同様の事柄が認められた。