

Interpretation of the Crystal Structure of Synthetic Kaliophilite from the Domain Structure of Kalsilite

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The syntheses of kaliophilite have been carried out from the starting materials of near kalsilite compositions (KAlSiO_4), of which the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio is greater than 1/2. The X-ray powder diffraction pattern fit well to those of previous investigators. The crystal structure of synthetic kaliophilite was proposed by using the model consisting of four different types of kalsilite structure. The positions and intensities of the X-ray powder pattern were able to be explained on the basis of these four domains, belonging to the twinning by merohedry. As a result of the conditions of the syntheses, it may be supposed that the violation of the Al-O-Al avoidance rule can possibly exist along the domain boundaries.

Keywords: kaliophilite, kalsilite, syntheses, domain boundary

1 Introduction

Kalsilite (KAlSiO_4) is one of the representative mineral in nepheline-kalsilite group, whose crystal structure has been assumed to be those having tridymite-like frameworks. An accurate structure determination of natural kalsilite was carried out by Perrota and Smith (1965). They proved that the space group of kalsilite was $P6_3$ and the crystal structure was derived from that of tridymite.

Dollase and Freeborn (1977) produced kalsilite from nepheline by alkali exchange in molten KCl. The refinement of alkali-exchanged kalsilite gave essentially the same structure as natural kalsilite. But they observed that intensities of the reflections ($h\bar{h}l, l - \text{odd}$) were different from one crystal to another, and they found one crystal, in which the reflections ($h\bar{h}l, l - \text{odd}$) were not observed. They interpreted that the alkali-exchanged kalsilite consisted of domains in two orienta-

tions related by mirror planes perpendicular to the *a*-axis with each other and the domain structure yielded the positional disorder of oxygen atoms situated on the three fold rotation axes and, in the case that the two domains have equal volumes in each other, no reflections ($h\bar{h}l, l - \text{odd}$) were observed.

Andou and Kawahara (1982) assumed that the domain structure of kalsilite was considered to be caused by the displacive transformation on the analogy of the generation of twins in low quartz. They confirmed the existence of high-low inversion of kalsilite at 875°C by means of high temperature X-ray powder methods, and presented the structural model of high temperature form of kalsilite.

Kawahara, Andou, Okuno and Marumo (1987) confirmed the drastic disappearance of the reflection, $h\bar{h}l, l - \text{odd}$ above the inversion temperature 875°C by means of high temperature single crystal diffractometry.

In addition to kalsilite, five modification of KAlSiO_4 composition have been reported: natural kaliophilite, anomalous natural kaliophilite, synthetic kaliophilite and two types of orthorhombic KAlSiO_4 .

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Natural kaliophilite is an extremely rare mineral and two types are known. Bannister (1931) studied the first type of them by means of chemical, optical and X-ray methods and compared it with nepheline, and proposed that kaliophilite has the same hexagonal symmetry as nepheline with planes of symmetry, but the unit cell of kaliophilite ($a=27.0$, $c=8.6$ Å) is much larger than that of nepheline ($a=10.4$, $c=8.5$ Å). The comparison of the a -axis of both minerals indicated that the larger unit cell and symmetry planes of kaliophilite could be explained by a three fold twinning or parallel growth of the nepheline cell and that the occupancy of the large potassium atoms in the hole of this structure might produce the distortion enough to build up the larger cell without varying the c -axis.

Lukesh and Buerger (1942) described the crystallographic data of kaliophilite ($a=26.94$, $c=8.55$ Å, space group $P6_322$), and Claringsbull and Bannister (1948) suggested that the crystal structure of kaliophilite is a multiple of kalsilite structure and that the smaller value of c -axis for kaliophilite than that for kalsilite indicates slight flexing of the linkage between T-O bonds along the c -axis.

The second type of natural kaliophilite, which gives anomalous X-ray reflections, is considered to be the disorder type of natural kaliophilite. The anomalous natural kaliophilite has diffuse reflections with $k=3n$, while the normal natural kaliophilite has sharp ones. Both the normal and the anomalous natural kaliophilite are discovered only in volcanic rocks.

Thugutt (1937) reported to have synthesized kaliophilite. But it is not certain whether the materials obtained is really natural kaliophilite or not, because the X-ray data of them were not presented in his paper. According to the papers so far published, the synthesized crystals as natural kaliophilite may not have been synthesized.

Rigby and Richardson (1947) produced a new phase of composition KAlSiO_4 at temperature of 900°C , which shows hexagonal symmetry and have powder patterns related to the natural kaliophilite. Smith and Tuttle

(1957, 1958) synthesized this new phase under hydrothermal conditions ($1,000 \sim 1,100^\circ\text{C}$ at 500 kg/cm^2 water vapor pressure). The X-ray powder patterns of the new phase were able to be indexed on the basis of the unit cell of natural kaliophilite, and they suggested that this synthetic materials may be a disordered form of the natural kaliophilite, so it was named 'synthetic kaliophilite'.

As mentioned above, minerals with KAlSiO_4 composition has been interpreted by several authors, and some structures of kaliophilite derived from kalsilite were proposed. But any structural models which interpret the positions and the intensities of X-ray powder patterns have not been so far proposed.

For the purpose of the studies about the structure of kalsilite and its analogous substances, the authors have been synthesized several specimens of kalsilite by hydrothermal methods (Andou and Kawahara, 1982, 1984; Kawahara et al., 1987) and constructed several models of the domain structure of kalsilite and its analogous structures. Unexpectedly the authors succeeded to make a model on the basis of the domain structures of four kinds of kalsilite, which could explain exactly the powder diffraction pattern of synthetic kaliophilite. In this case, the extinction rule $h\bar{h}l, l\text{-odd}$ can not be checked because the experiments were carried out by X-ray powder diffractometry. But even if the above extinction rules can not be checked, in the case that the observed reflections coincides with the calculated ones from domain models in powder patterns, the hypothetical domain model is considered to be completely demonstrated,

The present paper reports the result of the syntheses and the structural models of synthetic kaliophilite by means of X-ray powder methods.

2 Synthesis of kaliophilite

Hydrothermal methods have been tried to synthesize kaliophilite phases but they have not been succeeded. After several preparatory experiments, the synthesis of kaliophilite was succeeded by heating the starting materials

without the intervention of water phases. The starting materials consist of a reagent mixture of activated alumina(Al_2O_3), silica gels(SiO_2), and K_2CO_3 . These starting materials were put in the porcelain boats. These boats were put in the electric furnace and were heated at the range of temperatures from 800°C to $1,250^\circ\text{C}$, and quenched after holding for 2 hours at the temperature mentioned above. The conditions of the syntheses are shown in Table 1.

Two kinds of crystalline product were obtained through this syntheses. However, any large crystals appropriate for the single crystal method were not obtained. As a result of the X-ray powder method, one of them is synthetic kaliophilite and another is orthorhombic KAlSiO_4 as reported by Smith and Tuttle (1957).

As shown in the Table 1, kaliophilite was produced at lower temperature from the mixture containing higher contents of aluminum, while at higher temperatures orthorhombic KAlSiO_4 was produced.

The results of the X-ray powder diffraction pattern of synthetic kaliophilite and orthorhombic KAlSiO_4 are given in Table 2 and Table 3 respectively. The cell dimensions of orthorhombic KAlSiO_4 were calculated on the basis of the data obtained by X-ray powder methods by mixing a small amount of silicon powder as an internal standard. The results are: $a=9.01(1)$, $b=15.60(2)$, $c=8.53(4)\text{\AA}$. The d values of synthetic kaliophilite are preliminary indexed by using the cell dimensions of kalsilite ($a=5.17(1)$, $c=8.49(3)\text{\AA}$)

Table 1.

The conditions of the syntheses. The symbols, Gl, Sk and Or in the last column correspond to glass, synthetic kaliophilite and orthorhombic KAlSiO_4 , respectively.

Starting materials $\text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{K}_2\text{CO}_3$	Heating Temperature $^\circ\text{C}$	Product
1.0 : 0.8 : 1.5	800	Gl
1.0 : 0.8 : 1.5	900	Gl
1.0 : 0.8 : 1.5	1,000	Gl
1.0 : 0.8 : 1.5	1,100	Sk
1.0 : 0.8 : 1.5	1,200	Sk
1.0 : 0.8 : 1.5	1,250	Sk
1.0 : 0.9 : 1.5	800	Gl
1.0 : 0.9 : 1.5	900	Gl
1.0 : 0.9 : 1.5	1,000	Gl
1.0 : 0.9 : 1.5	1,100	Sk
1.0 : 0.9 : 1.5	1,200	Sk
1.0 : 0.9 : 1.5	1,250	Sk
1.0 : 1.0 : 1.5	800	Gl
1.0 : 1.0 : 1.5	900	Gl
1.0 : 1.0 : 1.5	1,000	Sk
1.0 : 1.0 : 1.5	1,100	Sk
1.0 : 1.0 : 1.5	1,200	Or
1.0 : 1.0 : 1.5	1,250	Or
1.0 : 1.1 : 1.5	800	Gl
1.0 : 1.1 : 1.5	900	Sk
1.0 : 1.1 : 1.5	1,000	Or
1.0 : 1.1 : 1.5	1,100	Sk
1.0 : 1.1 : 1.5	1,200	Or
1.0 : 1.1 : 1.5	1,250	Or
1.0 : 1.2 : 1.5	800	Gl
1.0 : 1.2 : 1.5	900	Gl
1.0 : 1.2 : 1.5	1,000	Sk
1.0 : 1.2 : 1.5	1,100	Sk
1.0 : 1.2 : 1.5	1,200	Or
1.0 : 1.2 : 1.5	1,250	Or
1.0 : 1.3 : 1.5	800	Gl
1.0 : 1.3 : 1.5	900	Sk
1.0 : 1.3 : 1.5	1,000	Sk
1.0 : 1.3 : 1.5	1,100	Or
1.0 : 1.3 : 1.5	1,200	Or
1.0 : 1.3 : 1.5	1,250	Or
1.0 : 1.4 : 1.5	800	Gl
1.0 : 1.4 : 1.5	900	Sk
1.0 : 1.4 : 1.5	1,000	Sk
1.0 : 1.4 : 1.5	1,100	Or
1.0 : 1.4 : 1.5	1,200	Or
1.0 : 1.4 : 1.5	1,250	Or
1.0 : 1.5 : 1.5	800	Gl
1.0 : 1.5 : 1.5	900	Sk
1.0 : 1.5 : 1.5	1,000	Or
1.0 : 1.5 : 1.5	1,100	Or
1.0 : 1.5 : 1.5	1,200	Or
1.0 : 1.5 : 1.5	1,250	Or

Table 1. (continue)

Starting materials Al ₂ O ₃ : SiO ₂ : K ₂ CO ₃	Heating Temperature °C	Product
1.0 : 1.6 : 1.5	800	Gl
1.0 : 1.6 : 1.5	900	Sk
1.0 : 1.6 : 1.5	1,000	Or
1.0 : 1.6 : 1.5	1,100	Or
1.0 : 1.6 : 1.5	1,200	Or
1.0 : 1.6 : 1.5	1,250	Or
1.0 : 1.7 : 1.5	800	Gl
1.0 : 1.7 : 1.5	900	Gl
1.0 : 1.7 : 1.5	1,000	Or
1.0 : 1.7 : 1.5	1,100	Or
1.0 : 1.7 : 1.5	1,200	Or
1.0 : 1.7 : 1.5	1,250	Or
1.0 : 1.8 : 1.5	800	Gl
1.0 : 1.8 : 1.5	900	Gl
1.0 : 1.8 : 1.5	1,000	Gl
1.0 : 1.8 : 1.5	1,100	Or
1.0 : 1.8 : 1.5	1,200	Or
1.0 : 1.8 : 1.5	1,250	Or
1.0 : 1.9 : 1.5	800	Gl
1.0 : 1.9 : 1.5	900	Gl
1.0 : 1.9 : 1.5	1,000	Gl
1.0 : 1.9 : 1.5	1,100	Or
1.0 : 1.9 : 1.5	1,200	Or
1.0 : 1.9 : 1.5	1,250	Or
1.0 : 2.0 : 1.5	800	Gl
1.0 : 2.0 : 1.5	900	Gl
1.0 : 2.0 : 1.5	1,000	Gl
1.0 : 2.0 : 1.5	1,100	Or
1.0 : 2.0 : 1.5	1,200	Or
1.0 : 2.0 : 1.5	1,250	Or
1.0 : 2.1 : 1.5	800	Gl
1.0 : 2.1 : 1.5	900	Gl
1.0 : 2.1 : 1.5	1,000	Gl
1.0 : 2.1 : 1.5	1,100	Gl
1.0 : 2.1 : 1.5	1,200	Or
1.0 : 2.1 : 1.5	1,250	Or
1.0 : 2.2 : 1.5	800	Gl
1.0 : 2.2 : 1.5	900	Gl
1.0 : 2.2 : 1.5	1,000	Gl
1.0 : 2.2 : 1.5	1,100	Gl
1.0 : 2.2 : 1.5	1,200	Or
1.0 : 2.2 : 1.5	1,250	Or

Sk : synthetic kaliophilite
 Or : orthorhombic KAlSiO₄
 Gl : glass

Table 2. The X-ray powder data of synthetic kaliophilite

$d(obs.)$ [Å]	$I(obs.)$	$h k l$	$d(calc.)$ [Å]
4.507	8	1 0 0	4.477
4.271	20	0 0 2	4.245
3.082	100	1 0 2	3.081
2.572	41	1 1 0	2.585
2.186	11	1 1 2	2.208
2.096	12	0 0 4	2.122

Table 3. The X-ray powder data of orthorhombic KAlSiO₄ (Or)

$d(obs.)$ [Å]	$I(obs.)$	$h k l$	$d(calc.)$ [Å]
5.799	7	0 2 1	5.756
		1 1 1	5.757
4.521	9	2 0 0	4.505
		1 3 0	4.504
4.267	13	0 0 2	4.265
3.990	6	2 0 1	3.984
		1 3 1	3.983
3.860	12	2 1 1	3.860
3.541	28	2 2 1	3.548
		0 4 1	3.547
3.400	29	2 3 0	3.405
3.291	7	1 4 1	3.300
3.152	8	2 3 1	3.162
3.082	100	1 3 2	3.097
		2 0 2	3.097
2.934	8	2 4 0	2.949
		3 1 0	2.949
2.770	37	2 4 1	2.787
		3 1 1	2.787
3.644	13	0 2 3	2.671
		1 1 3	2.671
2.578	74	3 3 0	2.601
		0 6 0	2.600
2.221	8	2 6 0	2.252
		4 0 0	2.253
2.188	16	3 3 2	2.221
		0 6 2	2.220

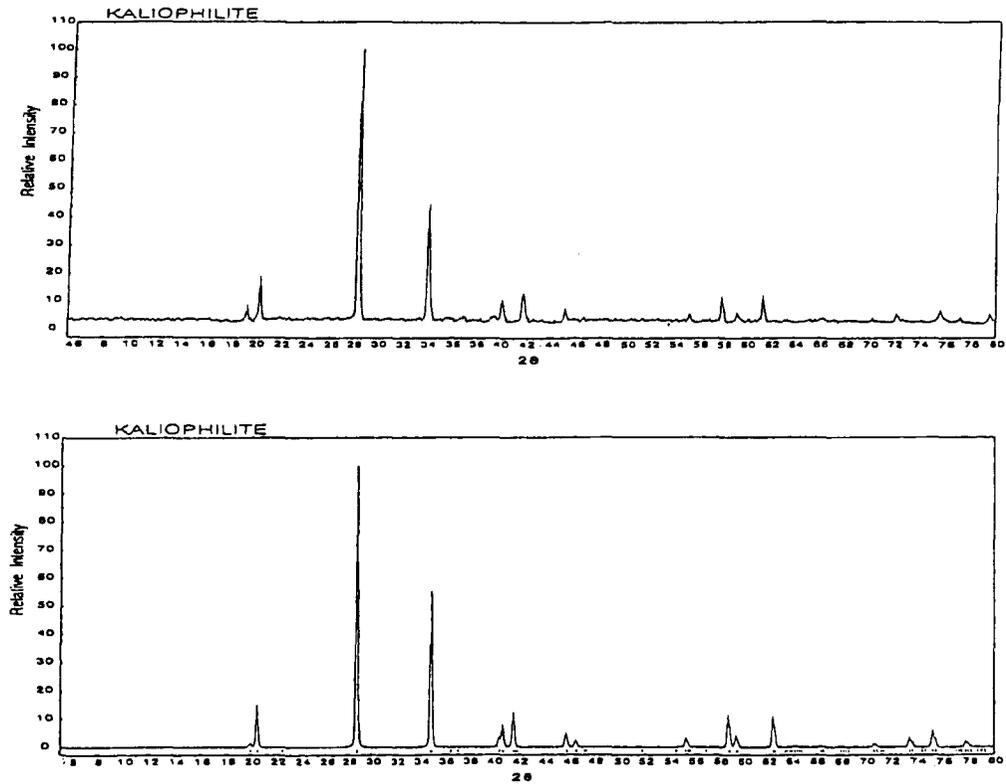


Fig. 2 Powder pattern of synthetic kaliophilite and its simulate model. The background levels were corrected according to the method by Sonneveld and Visser (1975).

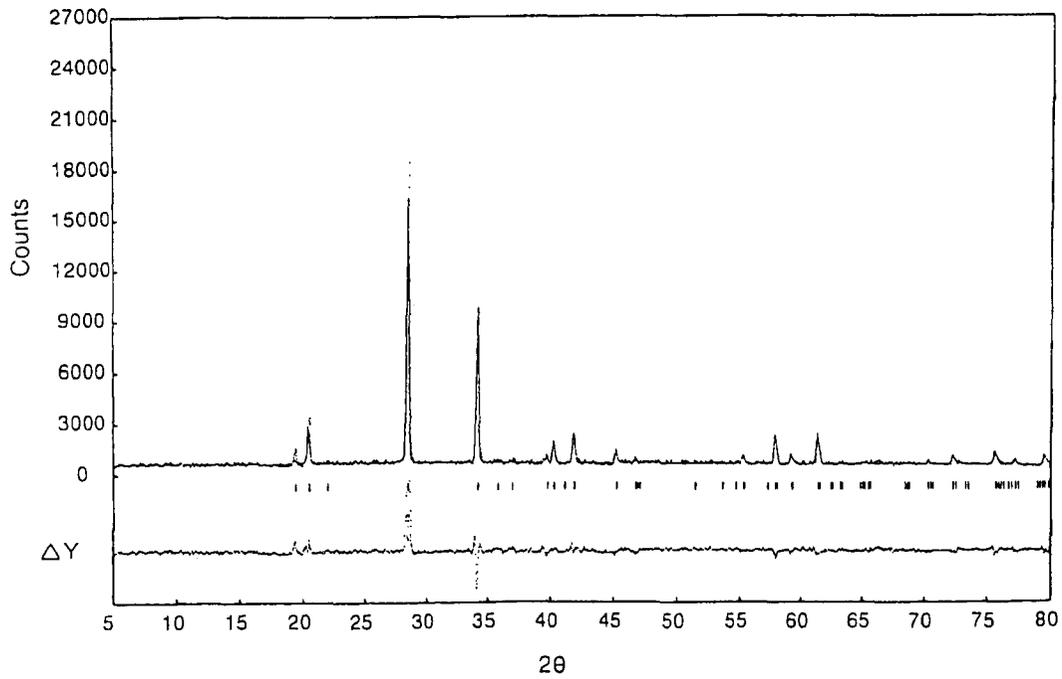


Fig. 3 Pattern fitting between the observed and the calculated for synthetic kaliophilite.

3 Assumption of the structure

Synthetic kaliophilite was reported to be a disordered form of natural kaliophilite, because the X-ray powder pattern of synthetic one could be indexed on the basis of the unit cell of natural specimens. However, the *a*-axis of synthetic kaliophilite (5.2 Å) is much smaller than that of natural kaliophilite (26.9 Å), and is close to that of kalsilite (5.2 Å).

The main peaks of kalsilite in X-ray powder diffraction were maintained up to about 1,100°C. It is confirmed from these experiments that the framework of kalsilite-like structure is not destroyed up to these temperatures. Also, the structure of synthetic kaliophilite can be produced only by quenching below about 1000°C. According to these facts, the authors have been assumed that the structure of synthetic kaliophilite can be thought to be a distorted form of kalsilite and the probable domain models have been adopted in the assumption of the structure of kaliophilite. After many trials of the presumed structures, the existence of the four types of kalsilite structure which scatters X-rays coherently come to their mind, and tried to make a calculation. One of these results correspond exactly to the results of X-ray powder patterns of synthetic kaliophilite.

Fig.1 shows these four possible types of the kalsilite structure, whose unit cells are expressed according to different orientations. Type(a) and (b), or type(c) and (d), have the mirror-equivalent positions respectively and have the relations to form the domain structure (Dollase & Freeborn, 1977, Andou & Kawahara, 1984). Type(a) and (d), or type(b) and (c), are the quite identical structure, but they are translated by a half period to the *c*-axis each other. The geometrical relationship of these four domains belongs to the twinning by merohedry after the definition proposed by Friedel (1926).

The model above mentioned was considered as a disordered form of kalsilite, where the four structural units are almost equivolume and distributing randomly and reflecting X-

rays coherently.

The simulated powder pattern was compared with that obtained from experiments. The background levels of the experimental pattern were corrected according to the method by Sonneveld and Visser (1975). The result is illustrated in Fig.2. The pattern of the simulated model is perfectly agreed with that of synthetic kaliophilite.

4 Refinement and discussion

On the assumption of the four types of domains of kalsilite the refinement of synthetic kaliophilite was carried out using the program of Rietveld method, Rietan (Izumi, 1993), where the values of positional parameters were used from those of synthetic kalsilite (Andou and Kawahara, 1984). The calculation were done on the basis of overlapping of four types of structures based on the domain structure model using the space group, $P6_3mc$.

In the course of refinement, all positional and thermal parameters of every atoms were fixed, while the other pattern fitting parameters were moved in each cycle. After nine cycles of the least squares refinement, the structure of synthetic kaliophilite was converged to the final *R*-value of 0.121 giving equal weights to all reflections. The positional and thermal parameters of each atom together with those of refined cell parameters are shown in Table 4. The atomic parameters are all the same as those of kalsilite refined by Andou and Kawahara (1984). The pattern fitting obtained between observed and calculated one is shown in Fig.3. The rather high *R*-value may be ascribed to the disorderness due to the boundaries of the domain structure.

Synthetic kaliophilite was produced from the mixture containing higher contents of aluminum more than equivalent contents of aluminum and silicon (Si : Al = 1 : 1), which was necessary for producing $KAlSiO_4$ compounds. As a result of these conditions of the syntheses, the aluminum atoms may encourage the construction of the domain structure and may be concentrated near the domain boundary. Therefore the violation of the Al-O-Al avoid-

ance rule can possibly exist along the boundaries of four different domains.

According to the results mentioned above, synthetic kaliophilite is considered to be the agglomerates of the domains of kalsilite without destroying the tridymite T-O frameworks. Though details about the structure are future problems, the determination of the synthetic kaliophilite structure might supply a great deal of information in order to presume the unknown structure of such minerals as natural kaliophilite, orthorhombic KAlSiO_4 , and so on, which belong to the system NaAlSiO_4 - KAlSiO_4 .

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