The existence of high-low inversion point of kalsilite

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Abstract

Kalsilite shows the domain structure corresponding to the disordered oxygen atoms at two mirror equivalent sites. The domain structure was considered to be due to the high-low inversion, and the structural model of the high-form was constructed. The heating experiment was carried out, which revealed that the X-ray powder pattern changes at 1138 K. It was confirmed that kalsilite undergoes a displacive transformation like quartz and tridymite. The high-form is hexagonal, probably $P6_3mc$, with $a=5.30(1)$, $c=8.65(1)$ Å. The high-form was also considered to be divided into two groups, high-kalsilite ($P6_3mc$) and disordered high-kalsilite ($P6_3/mmc$). The Zellengleichen subgroup relations are found among these three polymorphs.

Introduction

Dollase and Freeborn (1977) investigated the structure of kalsilite (KAlSiO_4) produced from natural nepheline by alkali exchange methods, and showed that the specimen revealed the same structure as natural kalsilite but had the domain structure corresponding to the oxygen atoms splitted into two mirror-equivalent sites. The present authors also refined the structure of kalsilite synthesized by hydrothermal methods (Andou and Kawahara, 1981), and they showed the same domain structure as investigated by the previous authors.

In view of the examples of quartz, tridymite, leucite and others, the present authors thought that the domain structure of kalsilite was considered to be ascribed to the displacive high-low transition of the structure. But no papers have been found about this subject up to the present.

The present paper reports the results of experiments by high-temperature X-ray powder methods, which revealed the existence of high-low inversion point of this specimen at 1138 K. The topological structure of high temperature form was also determined by X-ray powder methods.

The calculation necessary for this investigation was carried out at the Computer Center of Okayama University using the modified programs of UNICS (Sakurai, 1971). The X-ray powder pattern simulation program was written by the present authors.

Experimental

The high temperature X-ray powder photographs were taken with a Weissenberg camera in which a small electric furnace was set up, using $\text{CuK}\alpha$ radiation. The powder specimen of kalsilite, which was synthesized hydrothermally (873 K, 1000 kg/cm², 7 days) from mixtures of SiO_2 , Al_2O_3 and K_2CO_3 , was sealed in a thin quartz glass capillary ($\phi=0.5$ mm), and fixed on a goniometer head using a small amount of silicon cement. The temperature was measured by using chromel-alumel thermocouples, whose scales of the millivoltmeter were calibrated by the melting point of Zn(692 K) and Ag(1234 K) metals.

The measurement was carried out from room temperature up to 1273 K. No changes of the powder pattern were observed from room temperature to 1138 K except those due to the thermal expansion. But above 1138 K, the pattern shows some changes. The heating and cooling experiments were repeated on the same powder specimen in the temperature range above mentioned. The change of the pattern was reversible, and the inversion point at 1138 K was confirmed.

The specimen which shows high temperature X-ray powder pattern above 1138 K was named high-kalsilite.

In order to obtain the cell dimensions and the parameters of the structure of high-kalsilite, the X-ray powder diffractometer was used at 1073 K and 1173 K using a small amount of silicon powder as an internal standard.

Assumption and confirmation of the structure of the high temperature form

The structure of high-kalsilite was assumed from that of the low-form by rotating the tetrahedra in (001) layers from ditrigonal ring configurations to hexagonal ones. The space group was changed from $P6_3$ to $P6_3mc$. Especially, the space group became $P6_3/mmc$, if the random distribution of Si and Al atoms were considered.

Lattice dimensions of the high-form were assumed by considering the average interatomic distances of Si(Al)-O (1.67 Å), and K-O (3.22 Å): $a=5.49$ and $c=8.68$ Å.

The atomic parameters of the structure were determined geometrically by considering the symmetry of the space group $P6_3mc$ or $P6_3/mmc$. Here, for convenience, the random distribution of Si and Al atoms were considered.

In order to confirm the structure of the high-form assumed above, the X-ray powder diffraction patterns of the low- and high-form were compared. Fig. 1 shows the observed powder patterns at 1073 K and 1173 K, together with those simulated by the computer, using the atomic parameters of the low-form

FIG. 1. The comparison of the observed and calculated powder patterns at 1073 K and 1173 K. The pattern of the high-form lacks hhl , l -odd reflections.

and those of the high-form listed in Table 1. The program used for the calculation is written by the present authors. Since the space group changed from $P6_3$ to $P6_3mc$ or $P6_3/mmc$, the pattern of the high-form lacks hhl reflections having l -odd; in fact, the peak of 111 is absent in the observed pattern. There was a perfect correspondence between these observed and calculated

TABLE 1. Atomic parameters of high-kalsilite assumed from the symmetry of the space group $P6_3mc$ and $P6_3/mmc$. These values were confirmed by the structure factor calculations.

	X	Y	Z	B
K	0.0	0.0	1/4	17.0
Si(Al)	1/3	2/3	1/16	3.0
Si(Al)	1/3	2/3	7/16	3.0
O(1)	1/2	0.0	0.0	5.0
O(2)	1/3	2/3	1/4	5.0

powder patterns.

Refinement of the lattice dimensions and structure factor calculations

The lattice dimensions were refined by the program RSLC3 of UNICS (Sakurai, 1971) using 13 peaks obtained by a high temperature powder diffractometer. The instrumental errors of the diffractometer were corrected by using the NBS standard silicon powder ($a=5.43088 \text{ \AA}$). The values of $a=5.30(1)$ and $c=8.65(1) \text{ \AA}$ were obtained.

The integrated intensities were measured on the 20 peaks obtained from the powder method. These values were corrected to the structure factors by applying the Lorentz-polarization correction. The structure factors were calculated, where the values of isotropic temperature factors of 17.0, 3.0, 3.0 and 5.0 were attributed to the K, Al, Si and O atoms, respectively, by making reference to the values investigated by Foreman and Peacor (1970). The R was 0.15. The atomic parameters of the high-form thus determined are listed in Table 1.

Description of the structure and discussion

The schema of the structure of high-kalsilite is shown in Fig. 2, right, together with that of low-form for comparison. As shown in the figure, O(1) atoms whose positions are splitted in low-kalsilite, occupy the positions on mirror planes parallel to the c -axis. The two kinds of Si-O and Al-O tetrahedra are arranged orderly in the low-form. If the transition from the low- to high-form causes only the slight rotation of Si(Al)-O tetrahedra and the displacement of O(1) atoms, the distribution of Si-O and Al-O tetrahedra is also ordered in the high-form. In this case, the space group symmetry of high-form is $P6_3mc$. When many structural misfits parallel to the (001) plane exist in the low-form, and the considerable amount of domain parts suffer the rotation of 60° about

three-fold axes at the time of inversion, the space group of high-form becomes $P6_3/mmc$, which corresponds the symmetry of disordered high-kalsilite.

The values of interatomic distances of the high-kalsilite is shown in Table 2. The values of interatomic distances calculated from the parameters determined by the present method does not clarify whether Si-O and Al-O tetrahedra are ordered. The K atoms are surrounded by three O(2) (3.1 Å) and twelve O(1) (3.4 Å), and the coordination number becomes fifteen. The electrostatic valence sums were calculated according to the values of Brown and Wu (1976). The results are satisfactory for all atoms.

Fig. 3 shows the subgroup relation diagram (Neubüser and Wondratschek, 1966) of kalsilite. As shown in the figure, $P6_3$ (low-kalsilite), $P6_3mc$ (high-kalsilite) and $P6_3/mmc$ (disordered high-kalsilite) are in the relation of Zellen-gleichen subgroups. The number of equivalent positions are doubled, when the transition occurs from one state to the other. On the other hand, Gottardi (1979) divided the symmetry of kalsilite into three kinds: topologic symmetry (TS): $P6_3/mmc$, topochemical symmetry (TCS): $P6_3mc$ and real symmetry (RS): $P6_3$. This classification of Gottardi corresponds exactly to those of three types of the above mentioned modification of kalsilite. In order to clarify whether the space group of highkalsilite is $P6_3mc$ or $P6_3/mmc$, the high temperature single

FIG. 2. The schema of the structure of high-kalsilite, right, together with that of low-form for comparison, left, a and b.

TABLE 2. Interatomic distances of high-kalsilite.

K-O(1)	3.42 Å (×12)	Si(Al)-O(1)	1.62 Å (×3)
K-O(2)	3.06 (×3)	Si(Al)-O(2)	1.62 (×1)
Mean K-O	3.35

FIG. 3. The subgroup relation diagram of kalsilite. The numbers of equivalent positions are doubled, when the transition occurs from one state to the other.

crystal intensity measurements would be necessary. The research is now in progress.

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