Study of Coordination Number of Al^{3+} by Wave Length Shift of AlKα Radiation in a Clinopyroxene $CaFe^{3+}AlSiO_6$

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Abstract

Clinopyroxene with a composition of $CaFe^{3+}AlSiO_6$ has been synthesized from glass and its wave length shift of emitting AlKα radiation was studied by the X-ray fluorescence spectroscopy with reference to aluminum metal, anorthite, orthoclase, corundum and jadeite. The result shows that Al^{3+} ions occupy not only the site of 4-fold coordination but also the site of 6-fold coordination.

1. Introduction

It has been noticed that wave length shift of emitting characteristic X-ray is affected in small degrees by the chemical environment in solid targets. This phenomenon designated as wave length shift or displacement is widely applied, especially for rapid determination of the coordination numbers of aluminum ions in aluminates and aluminosilicates.1)~6)

Three types of Tschermak's molecules are known in clinopyroxene, i. e. $CaAl(AlSi)O_6$ molecule,7)~12) $CaFe^{3+}(Fe^{3+}Si)O_6$ molecule13) and $CaFe^{3+}AlSiO_6$ molecule14). Though the former two molecules do not form clinopyroxenes at atmospheric pressure, the last molecule $CaFe^{3+}AlSiO_6$ can exist as clinopyroxene, forming a complete solid solution series with $CaMgSi_2O_6$ molecule at atmospheric pressure14). However, as for the coordination number of Al^{3+} in this clinopyroxene, it has not been clearly determined whether Al^{3+} takes both 4-fold and 6-fold coordination sites or either one of them. In this paper this problem was studied by means of the wave length shift of emitting AlKα radiations, with special reference to the possibility of the X-ray fluorescence analysis for determination of the sites of Al^{3+} ions.

2. X-ray fluorescence spectroscopy

Wave length shift of AlKα radiation in a synthetic clinopyroxene with composition of $CaFe^{3+}AlSiO_6$ was measured with reference to standard specimens, anorthite (Al^{IV})**, orthoclase (Al^{IV}), diopside solid solution containing 15 percent of $CaAl(AlSi)O_6$ (abb. $Di_{85}Ca\text{-}Ts_{15}$) ($Al^{IV,VI}$), corundum (Al^{VI}) and jadeite (Al^{VI}). Rigakudenki GF-SI X-ray fluorescence analyser, with wolfram target at 40KV and 20mA, EDDT analysing crystal 0.45mm soller slit and gas flow proportional counter was used at a scanning speed of 0.25°(2θ)/min. and a chart speed of 2 cm/min.. At least three measurements were made for specimens with high concentration of aluminum with experimental errors less than 0.005°(2θ). For specimens with low concentration of aluminum, especially for $Di_{85}Ca\text{-}Ts_{15}$, however, repeated

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** Roman numerals denote coordination numbers.

measurements were made at various scale factors with time constant fixed, with an error of 0.01°(2θ). Pure aluminum metal was used as relative standard material. Specimens are all synthetic except orthoclase and jadeite.

3. Preparation of specimen minerals

Reagent grade chemicals, $CaCO_3$, MgO*, Fe_2O_3** and pure quartz weighed to get 10 gram glasses of desired composition were ground in an agate mortar with ethyl alcohol three times. Then, the mixture was transfered to a platinum crusible and ignited at 1450-1600°C for 2-3 hours. Glasses obtained by quenching the crusible in water were crushed in a steel mortar. Contaminating iron particles were eliminated by a hand magnet. Then the glasses were pulverized in the agate mortar and their homogenity was examined under the microscope. Finally they were crystallized at temperatures ranging from 1200° to 1300°C for 20 hours to 40 hours. The conditions were 1300-20, 1200-30 and 1200°C-40 hours, respectively to anorthite, $Di_{85}Ca$-Ts_{15} and present specimen in question. The ignited chemical of Al_2O_3 was used as the specimen of corundum. All synthetic and natural minerals were found to be pure by the polarizing microscope and the X-ray diffractometer.

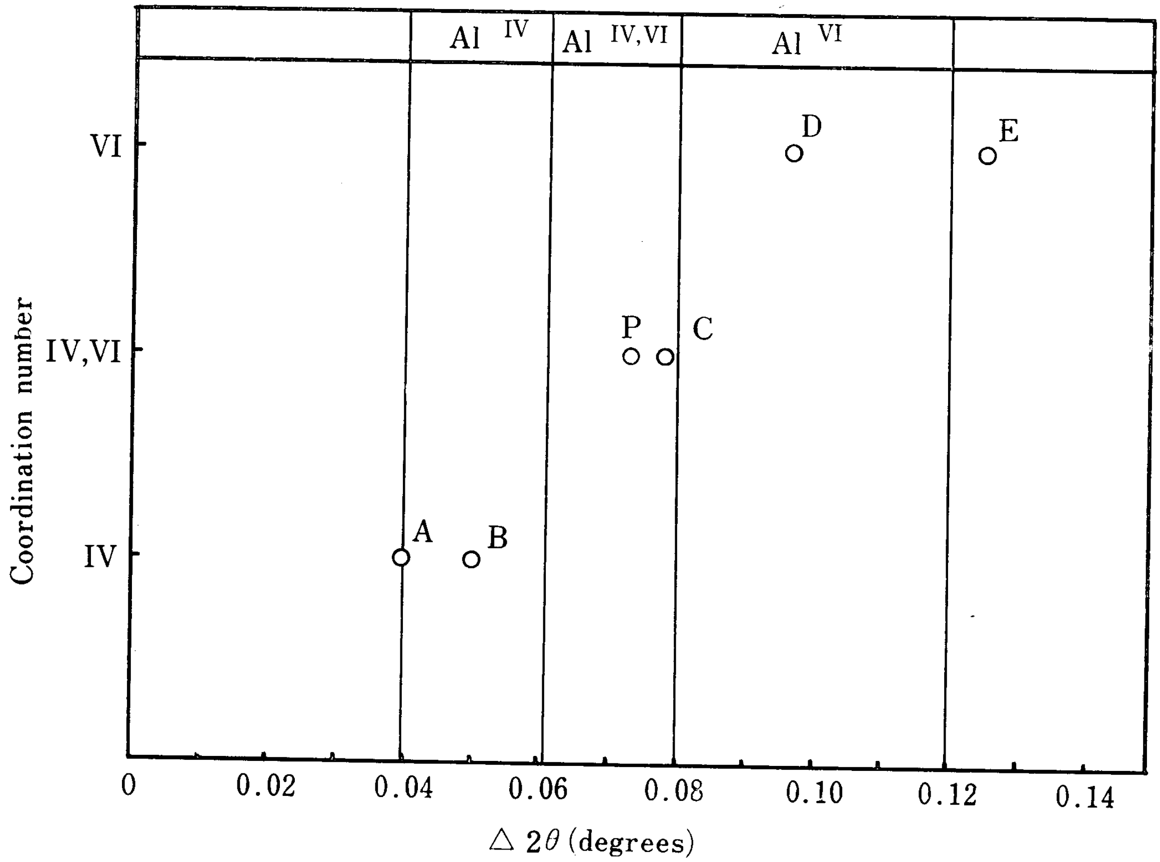

Fig. 1 Shifts of AlKα radiation from the relative standard material of Al metal.
Wolfram target ; 40KV and 20mA. Analysing crystal ; EDDT.
Specimens ; A (Anorthite) B (Orthoclase) C ($Di_{85}Ca$-Ts_{15}) D (Corundum)
E (Jadeite) P ($CaFe^{3+}AlSiO_6$, present specimen in question)
Vertical lines ; boundary of Al^{IV}, $Al^{IV,VI}$ and Al^{VI} (Day, 1963)3)

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* Preignited at 1450°C for 2 hours before use.

** Decomposed ferrous oxalate at 800°C in air.

4. Result and discussion

Wave length shift of AlKα radiation were determined with reference to the standard samples. The results are plotted against $\Delta 2\theta$ (in degrees) versus coordination number in Fig. 1. It is observed that the amounts of shifts increase with increasing coordination numbers of aluminum ions. Day[3] gave empirical value of 0.040-0.061 for Al^{IV} and 0.080-0.120 for Al^{VI}. He also found the intermediate values which indicate the shift caused by more than two kinds of coordination site of aluminum ions, generally by both Al^{IV} and Al^{VI}. Present data show good agreement with those reported previously within the experimental error. It is confirmed from Fig. 1 that Al^{3+} ions are present in both 4-fold and 6-fold coordination sites in $CaFe^{3+}AlSiO_6$. This means that the clinopyroxene $CaFe^{3+}AlSiO_6$ can be expressed by $Ca(Fe^{3+}{}_{1-x}Al_x)(Fe_xAl_{1-x}Si)O_6$, $0<x<1$. This result agrees well with that obtained by the Mössbauer spectroscopy[15]. In diopside solid solution bearing only Ca-Tschermaks's molecule, on the other hand, it is evident that Al^{3+} ions are distributed in both 4-fold and 6-fold coordination sites in equal amount. Therefore, judging from the present data, it may be expected that Al^{3+} ions in the $CaFe^{3+}AlSiO_6$ clinopyroxene have nearly the same site occupancy. However, the Mössbauer spectra on this pyroxene synthesized by oxide sintering technique at about 1300°C showed 27 percent of Fe^{IV} and 73 percent of Fe^{VI}, i.e., 73 percent of Al^{IV} and 27 percent of Al^{VI}. No temperature dependence of the occupancy was observed (Ōhashi, personal comm., and Shinno, personal comm.).

5. Conclusion

In the clinopyroxene $CaFe^{3+}AlSiO_6$ obtained by the crystallization of a glass with stoichiometric composition at 1200°C, the Al^{3+} ions occupy the sites of both 4-fold and 6-fold coordination, when the disorder of cation distribution between 8-fold and 6-fold coordination sites, if any, as reported on the hedenbergite solid solution by the Mössbauer spectroscopy[16] is disregarded. The measurement of wave length shift of AlKα radiation is helpful not only to the study of coordination number of Al^{3+} in silicates rich in Al^{3+}, but to silicate solid solutions with low content of Al^{3+}, just as the Mössbauer spectroscopy in the case of ferrous and ferric ions.

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