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UNIT-CELL DIMENSIONS OF THE CLINOPYROXENES ALONG THE JOIN $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFe}^{3+}\text{AlSiO}_6$

by

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(with 2 Text-Figures)

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Abstract

The clinopyroxenes in 10 mole per cent intervals between the two end members along the join $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFe}^{3+}\text{AlSiO}_6$ have been synthesized, and their unit-cell dimensions have been determined by X-ray powder method. The variation of unit-cell dimensions of these clinopyroxenes is as follows: a -dimension increases regularly from Di_{100} (9.745Å) to CF_{100} (9.783Å), b -dimension decreases lineally from Di_{100} (8.925Å) to CF_{100} (8.787Å), c -dimension and cell volume increase from Di_{100} (5.250Å, 439.2Å³) to CF_{100} (5.372Å, 444.3Å³) and β -dimension increases from Di_{100} (105.87°) to $\text{Di}_{80}\text{CF}_{20}$ or $\text{Di}_{70}\text{CF}_{30}$ (106.04°) and then decreases to CF_{100} (105.82°) with increasing $\text{CaFe}^{3+}\text{AlSiO}_6$ molecule in diopside.

It is considered that the substitution of Al for Si in tetrahedral site is more effective for the increase of a -dimension of these clinopyroxenes than the substitution of Fe^{3+} for Mg, and that Fe^{3+} ion replaced for Mg contributes to increase of c -dimension as well as Al for Si. Judging from the linear changes of unit-cell dimension and calculated densities of the clinopyroxenes along this join, this series of clinopyroxenes form a complete series of solid solutions.

Several effects of the ionic substitution along this join are discussed as compared with that along the two joins $\text{CaMgSi}_2\text{O}_6$ - $\text{CaAl}_2\text{SiO}_6$ and $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFe}^{3+}_2\text{-SiO}_6$.

Introduction

There are several series of solid solutions with a coupled substitution of ions for Mg and Si in diopside; that is, AlAl , GaAl , Cr^{3+}Al , $\text{Fe}^{3+}\text{Fe}^{3+}$ etc. for MgSi . Among them, SAKATA (1957) investigated the unit-cell dimensions of diopside solid solutions along the join $\text{CaMgSi}_2\text{O}_6$ - $\text{CaAl}_2\text{SiO}_6$ up to 20 weight per cent of $\text{CaAl}_2\text{SiO}_6$. He mentioned that the data are in harmony with the theoretical consideration; that is, a - and b -dimensions decrease by the substitution of smaller Al for Mg in octa-

hedral site and *c*-dimension increases by the substitution of larger Al for smaller Si in tetrahedral site with increasing $\text{CaAl}_2\text{SiO}_6$.

CLARK (1962) reported that the join $\text{CaMgSi}_2\text{O}_6$ – $\text{CaAl}_2\text{SiO}_6$ forms complete solid solutions at 20 kb. The variation of unit-cell dimension along the join obtained by CLARK is in good agreement with the results by SAKATA up to 20 weight per cent of $\text{CaAl}_2\text{SiO}_6$, and the unit-cell dimension of the end member ($\text{CaAl}_2\text{SiO}_6$) of the join agrees well with that obtained by HIJIKATA and YAGI (1967).

The clinopyroxene of the composition CaGaAlSiO_6 , which is considered an end member of the substitution GaAl for MgSi in $\text{CaMgSi}_2\text{O}_6$ was synthesized at 10 kb and 1100°C by means of a girdle type high pressure apparatus (HIJIKATA, 1966 unpublished). The unit-cell dimensions of this clinopyroxene has a similar relation to that of $\text{CaAl}_2\text{SiO}_6$; *a*- and *b*-dimensions are smaller, but *c*-dimension is larger than those of diopside.

COLEMAN (1962) determined the unit-cell dimensions of the series of clinopyroxenes along the join $\text{CaMgSi}_2\text{O}_6$ – $\text{CaFe}^{3+}\text{AlSiO}_6$ up to about 10 mole per cent of $\text{CaFe}^{3+}\text{AlSiO}_6$.

The object of the present investigation lies in the synthesis of the clinopyroxene of the composition $\text{CaFe}^{3+}\text{AlSiO}_6$ (abbreviated CF), which is an end member of the join $\text{CaMgSi}_2\text{O}_6$ – $\text{CaFe}^{3+}\text{AlSiO}_6$, as well as in the investigation on the effect of the ionic substitution of Fe^{3+} Al for MgSi. For this purpose the clinopyroxenes along the join $\text{CaMgSi}_2\text{O}_6$ – $\text{CaFe}^{3+}\text{AlSiO}_6$ in 10 mole per cent intervals between the two end members have been synthesized, and their unit-cell dimensions have been determined. They were compared with those of the clinopyroxenes along the joins, $\text{CaMgSi}_2\text{O}_6$ – $\text{CaAl}_2\text{SiO}_6$ and $\text{CaMgSi}_2\text{O}_6$ – $\text{CaFe}^{3+}_2\text{SiO}_6$ (HUCKENHOLZ, SCHAIRER, and YODER, 1968). Several effects of the ionic substitution on the clinopyroxene solid solution are also discussed.

Preparation of the samples

Homogeneous glasses were prepared in 10 mole per cent intervals between the two end members, except compositions $\text{Di}_{10}\text{CF}_{90}$ and CF_{100} , by melting pure chemicals in a platinum crucible at about 1400°C. Reagent grade chemicals CaCO_3 , Al_2O_3 , Fe_2O_3 , MgO and pure quartz were used. The crushed glasses, heated at subsolidus temperature of 1200°C for 2 days, were found to consist of minute granular crystals of clinopyroxene. For the compositions $\text{Di}_{10}\text{CF}_{90}$ and CF_{100} , sintering technique instead of melting was used, because it was impossible to make the glasses of those compositions owing to the separation of iron oxides in the liquid state. The chemicals, which were carefully weighed stoichiometric to each composition of CF_{100} and $\text{Di}_{10}\text{CF}_{90}$, were ground well in an agate mortar with pure ethyl alcohol. The mixture was first ignited at 1200°C for 2 hours in a platinum crucible to form a sintered cake. They were crushed and ground again in the agate mortar.

The well-mixed powder, transferred into a platinum crucible, was heated again at 1250°C for 3 hours. After repeating the treatment of sintering for five times, almost homogeneous crystals, except a trace of hematite included, were obtained.

These crystals prepared either from crystallization of glasses or by sintering of oxide mixtures were found optically or by X-ray powder pattern to consist of a single phase of clinopyroxene.

X-ray method.

X-ray powder diffraction patterns of the clinopyroxenes along the join $\text{CaMgSi}_2\text{O}_6\text{--CaFe}^{3+}\text{AlSiO}_6$ were obtained by the diffractometer (Rigaku Denki, Tokyo Japan) with a crystal monochromator, using CuK_α radiation at 35 KV and 20 mA.

The clinopyroxene crystals ground until the grain size of powder becomes under 300 mesh in an agate mortar, were pressed in an aluminum sample holder with an open window. The surface of the holder was polished by fine alumina powder in order to obtain a completely flat surface of the pressed cake.

After complete patterns were taken with a scanning speed of 1° per minute from 70° to 20° in 2θ , special reflections of 002, 022, $53\bar{1}$, 600, 060 and 531 by which the unit-cell dimensions were determined, were obtained by scanning speed of 1/8° per minute. Measurement of 2θ was made to $\pm 0.005^\circ$ and reproducibility for the 2θ measurements in triplicate was found to be $\pm 0.01^\circ$. Pure quartz powder was used as an external standard.

Indexed powder pattern of pure diopside was compared with patterns obtained on the clinopyroxenes along the join. Each peak of these clinopyroxenes corresponds to that of pure diopside but its position shifts regularly as a function of the composition. The diffraction data of Di_{100} , Di_{50} , CF_{50} and CF_{100} are given in Table 1.

Results and discussions

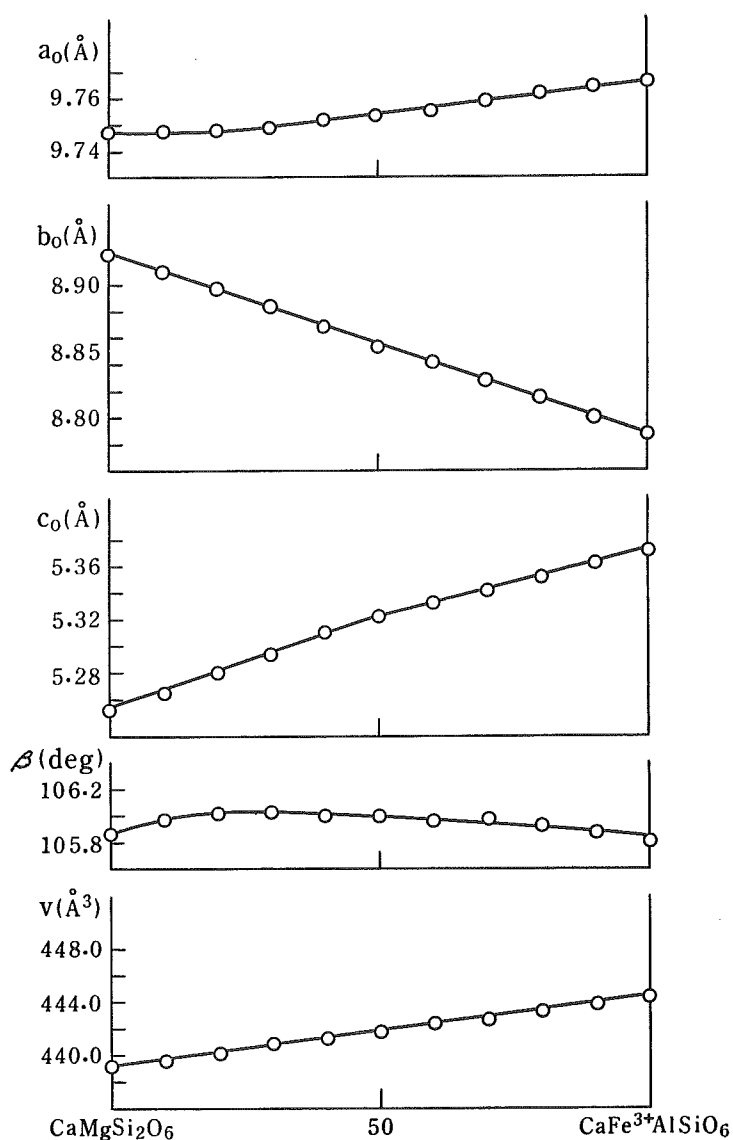
The unit-cell dimensions of the clinopyroxenes along the join $\text{CaMgSi}_2\text{O}_6\text{--CaFe}^{3+}\text{AlSiO}_6$ listed in Table 2 are believed to be accurate to $\pm 0.003\text{\AA}$ for a and c , $\pm 0.002\text{\AA}$ for b , $\pm 0.03^\circ$ for β , and $\pm 0.4\text{\AA}^3$ for cell volume. Calculated densities of these clinopyroxenes are also listed in Table 2. The variation of unit-cell dimensions and calculated densities of the clinopyroxenes along the join is shown in Fig. 1.

b-dimension: There is a linear decrease of *b*-dimension from Di_{100} to CF_{100} . The rate of decrease of *b*-dimension for every 10 mole per cent of $\text{CaFe}^{3+}\text{AlSiO}_6$ in $\text{CaMgSi}_2\text{O}_6$ is 0.0138\AA . The substitution of smaller ions such as Al, Fe^{3+} and Ti^{4+} for Mg in diopside causes generally a reduction of *b*-dimension. The rate of decrease of *b*-dimension resulting from the substitution of Al for Mg along the

Table 1. X-ray powder diffraction data of the clinopyroxenes, $\text{CaMgSi}_2\text{O}_6$, $(\text{CaMgSi}_2\text{O}_6)_{50}(\text{CaFe}^{3+}\text{AlSiO}_6)_{50}$ and $\text{CaFe}^{3+}\text{AlSiO}_6$

hkl	$\text{CaMgSi}_2\text{O}_6$		$(\text{CaMgSi}_2\text{O}_6)_{50}$ $(\text{CaFe}^{3+}\text{AlSiO}_6)_{50}$		$\text{CaFe}^{3+}\text{AlSiO}_6$	
	d (Å)	I	d (Å)	I	d (Å)	I
020	4.46	1	4.44	1	4.43	1
021	3.35	2	3.34	1		
220	3.23	4	3.22	2	3.21	2
22 $\bar{1}$	2.991	10	2.990	10	2.986	10
310	2.952	4	2.947	4	2.954	4
31 $\bar{1}$	2.893	5	2.898	3	2.904	2
13 $\bar{1}$	2.566	4			2.546	4
002	2.525	8	2.556	8	2.580	4
22 $\bar{1}$	2.514		2.516	6	2.523	5
131	2.388	1				
311	2.302	3	2.309	2	2.320	1
112	2.214	2	2.233	2	2.253	1
022	2.198	2	2.212	1	2.224	1
330	2.155	2	2.145	3	2.139	1
33 $\bar{1}$	2.133	4	2.127	2	2.120	3
42 $\bar{1}$	2.107	2	2.106	2	2.107	2
041	2.040	4			2.021	2
402	2.015	2	2.029	3		
240	2.009	2			2.037	2
13 $\bar{2}$	1.969	2	1.975	1	1.977	1
331	1.858	1				
510	1.833	2	1.837	1	1.840	1
132	1.813	1				
150	1.753	3	1.743	2	1.727	2
042	1.671	1			1.685	1
31 $\bar{3}$	1.657	1	1.674	2	1.673	1
22 $\bar{3}$	1.625	5	1.638	2	1.650	2
53 $\bar{1}$			1.623	2	1.622	2
440			1.612	1	1.605	1
530	1.586	1				
600	1.562	1	1.563	1	1.569	1
350	1.550	1	1.542	1	1.543	1
60 $\bar{2}$	1.528	1	1.532	1	1.534	1
402	1.523	2	1.527	1	1.530	1
13 $\bar{3}$	1.503	2	1.514	2	1.522	2
060	1.487	1	1.476	1	1.464	1
531	1.422	3	1.422	2	1.425	2
35 $\bar{2}$	1.407	2	1.408	2	1.403	2
223	1.390	1				
24 $\bar{3}$	1.374	1				

Intensities were determined by the relative value of peak height.

**Fig. 1**

The changes of unit-cell dimensions of the clinopyroxenes along the join $\text{CaMgSi}_2\text{O}_6$ – $\text{CaFe}^{3+}\text{AlSiO}_6$

join $\text{CaMgSi}_2\text{O}_6$ – $\text{CaAl}_2\text{SiO}_6$ is larger than that by the substitution of Fe^{3+} for Mg along the present join. This fact shows that the ionic radius of Al (0.50Å) or Fe^{3+} (0.64Å) in octahedral position has a direct influence on the b -dimension in

Table 2. Unit-cell dimensions and calculated densities of the clinopyroxene along the join $\text{CaMgSi}_2\text{O}_6\text{-CaFe}^{3+}\text{AlSiO}_6$

	Di_{100}	$\text{Di}_{80}\text{CF}_{10}$	$\text{Di}_{60}\text{CF}_{20}$	$\text{Di}_{40}\text{CF}_{30}$	$\text{Di}_{20}\text{CF}_{40}$	$\text{Di}_{10}\text{CF}_{50}$
a_0 (Å)	9.745	9.746	9.746	9.749	9.753	9.758
b_0 (Å)	8.925	8.912	8.897	8.883	8.869	8.855
c_0 (Å)	5.250	5.265	5.280	5.293	5.308	5.319
β (deg)	105.87	105.99	106.04	106.04	106.01	106.01
V (Å ³)	439.2	439.6	440.1	440.7	441.3	441.8
D (g/cc)	3.274	3.317	3.360	3.401	3.442	3.484

	$\text{Di}_{40}\text{CF}_{60}$	$\text{Di}_{30}\text{CF}_{70}$	$\text{Di}_{20}\text{CF}_{80}$	$\text{Di}_{10}\text{CF}_{90}$	CF_{100}
a_0 (Å)	9.762	9.768	9.773	9.779	9.783
b_0 (Å)	8.841	8.828	8.813	8.800	8.787
c_0 (Å)	5.330	5.340	5.351	5.362	5.372
β (deg)	105.95	105.96	105.91	105.89	105.82
V (Å ³)	442.3	442.7	443.2	443.8	444.3
D (g/cc)	3.526	3.568	3.610	3.651	3.692

(CF : $\text{CaFe}^{3+}\text{AlSiO}_6$ mole per cent)

these two series of clinopyroxenes. Since, however, the rate of change of b -dimension along the join $\text{CaMgSi}_2\text{O}_6\text{-CaFe}^{3+}\text{AlSiO}_6$ is larger than in the case of the join $\text{CaMgSi}_2\text{O}_6\text{-CaFe}^{3+}_2\text{SiO}_6$ (HUCKENHOLZ et al., 1968), the difference in the rates of decrease in b -dimension along these two joins should be ascribed to the substitution of Al or Fe^{3+} for Si in tetrahedral position. The substitution of Al or Fe^{3+} for smaller Si in tetrahedral position contributes to an increase in b -dimension, whereas the substitution of Al or Fe^{3+} for larger Mg in octahedral position contributes to a decrease in b -dimension.

In the case of clinopyroxene solid solutions of the joins $\text{CaMgSi}_2\text{O}_6\text{-CaTiAl}_2\text{O}_6$ and $\text{CaMgSi}_2\text{O}_6\text{-CaMgTi}_2\text{O}_6$, the b -dimension of diopside decreases with increasing $\text{CaTiAl}_2\text{O}_6$ and increases with increasing $\text{CaMgTi}_2\text{O}_6$. The substitution of smaller Ti^{4+} for Mg contributes more to the decrease in b -dimension than the increase of b -dimension resulting from the substitution of Al for Si. In the clinopyroxenes along the join $\text{CaMgSi}_2\text{O}_6\text{-CaMgTi}_2\text{O}_6$, b -dimension increases with increasing number of Ti^{4+} in tetrahedral position, as described elsewhere (ONUMA, HIJIKATA, and YAGI 1969).

a-dimension: The a -dimension of the clinopyroxenes along the present join slightly increase (0.0063 Å per 10 mole per cent of $\text{CaFe}^{3+}\text{AlSiO}_6$ in $\text{CaMgSi}_2\text{O}_6$) from Di_{100} to $\text{Di}_{70}\text{CF}_{30}$ and increases lineally from $\text{Di}_{70}\text{CF}_{30}$ to CF_{100} with increasing $\text{CaFe}^{3+}\text{AlSiO}_6$ molecule. The rate of increase of a -dimension from $\text{Di}_{70}\text{CF}_{30}$ to

CF_{100} for every 10 mol per cent of $\text{CaFe}^{3+}\text{AlSiO}_6$ in $\text{CaMgSi}_2\text{O}_6$ is 0.0027\AA . The $a \sin \beta$ decreases from Di_{100} to $\text{Di}_{80}\text{CF}_{20}$ and increases from $\text{Di}_{80}\text{CF}_{20}$ to CF_{100} , having a minimum at the composition of $\text{Di}_{80}\text{CF}_{20}$. It is, however, unknown why the minimum exists at this composition.

The decrease of a -dimension is expected generally by the substitution of smaller Fe^{3+} for Mg, but nevertheless in both cases of the joins $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFe}^{3+}\text{AlSiO}_6$ and $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFe}^{3+}_2\text{SiO}_6$ a -dimension increases with increasing $\text{CaFe}^{3+}\text{AlSiO}_6$ or $\text{CaFe}^{3+}_2\text{SiO}_6$ in $\text{CaMgSi}_2\text{O}_6$. This apparent discrepancy may be explained by the assumption that the substitution of Al or Fe^{3+} for Si in tetrahedral position is more effective to the increase of a -dimension than the contraction of octahedra resulting from the substitution of Fe^{3+} for Mg.

c-dimension: The c -dimension increases from Di_{100} to CF_{100} with increasing $\text{CaFe}^{3+}\text{AlSiO}_6$. The rates of increase of c -dimension for every 10 mole per cent of $\text{CaFe}^{3+}\text{AlSiO}_6$ in $\text{CaMgSi}_2\text{O}_6$ are 0.0138\AA from Di_{100} to $\text{Di}_{50}\text{CF}_{50}$ and 0.0106\AA from $\text{Di}_{50}\text{CF}_{50}$ to CF_{100} . It is generally expected that the c -dimension of this type of clinopyroxene solid solution increases with increasing number of larger ions, such as Al, Fe^{3+} , Ti^{4+} , replacing smaller Si in tetrahedral sites of the clinopyroxene chain. The maximum value of c -dimension in the series of $\text{CaMgSi}_2\text{O}_6$ - CaFe^{3+} - AlSiO_6 is about 0.1\AA greater than the value of the clinopyroxene $\text{CaAl}_2\text{SiO}_6$. The c -dimensions of the three clinopyroxene solid solutions, that is $(\text{CaMgSi}_2\text{O}_6)_{80}(\text{CaAl}_2\text{SiO}_6)_{20}$ (SAKATA, 1957), $(\text{CaMgSi}_2\text{O}_6)_{80}(\text{CaFe}^{3+}\text{AlSiO}_6)_{20}$ and $(\text{CaMgSi}_2\text{O}_6)_{79.3}(\text{CaFe}^{3+}_2\text{SiO}_6)_{20.7}$ (HUCKENHOLZ et al., 1968) are 5.266\AA , 5.280\AA and 5.293\AA respectively. From these data, if Si is replaced only by Al, but not by Fe^{3+} , in the substitution of Fe^{3+}Al for MgSi , the increase of c -dimension of the clinopyroxene along the join $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFe}^{3+}\text{AlSiO}_6$ should be regarded as the results of not only the substitution of Al for Si, but of Fe^{3+} for Mg in octahedral sites.

According to the study by PEACOR (1967) on the crystal structure of a pyroxene of formula $\text{M}_\text{I}\text{M}_\text{II}(\text{Si}_{1.5}\text{Al}_{0.5})\text{O}_6$, Al substitutes for Si in a ratio of about 1:3, and about a half of M_I sites (octahedral site) are occupied by Mg and the other half by Fe^{2+} , Al, Fe^{3+} or Ti^{4+} . Thus this pyroxene corresponds to $\text{Di}_{50}\text{CF}_{50}$ with respect to the ratio of Si and Al in tetrahedral positions. The c -dimension (5.319\AA) of this pyroxene is in good agreement with the value (5.319\AA) of $\text{Di}_{50}\text{CF}_{50}$.

Cell volume: Cell volume of the clinopyroxene along the present join increases linearly from Di_{100} to CF_{100} with increasing $\text{CaFe}^{3+}\text{AlSiO}_6$. The rate of increase of cell volume for every 10 mole per cent of $\text{CaFe}^{3+}\text{AlSiO}_6$ in $\text{CaMgSi}_2\text{O}_6$ is 0.51\AA^3 . The increasing tendency of cell volume is also found in the clinopyroxene along the join $\text{CaMgSi}_2\text{O}_6$ - $\text{CaTiAl}_2\text{O}_6$ (ONUMA, HIJIKATA and YAGI, 1969). The expansion

of tetrahedra resulting from the substitution of Al for Si is considered more effective to increase the cell volume of these series of clinopyroxene solid solutions than the contraction of octahedra resulting from the substitution of Fe^{3+} and Ti^{4+} for Mg.

COLEMAN's (1962) data along the join $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFe}^{3+}\text{AlSiO}_6$ show the same tendency but a large discrepancy from the data of the present investigation.

The linear decrease of b -dimension, the linear increase of c -dimension, cell volume and calculated density shown in Fig. 2 and regular increase of a -dimension

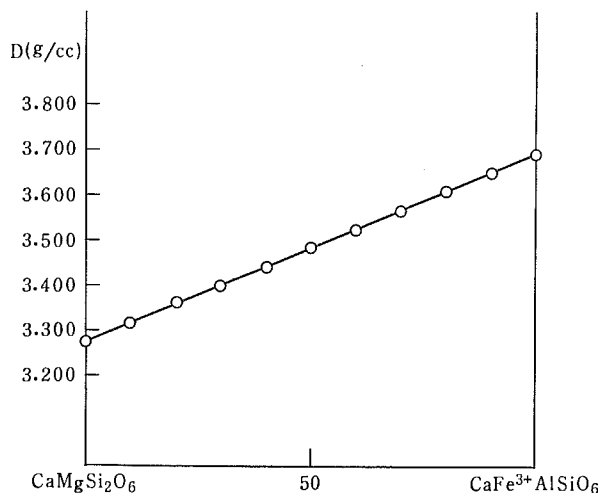


Fig. 2

The change of the calculated densities of the clinopyroxenes along the join $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFe}^{3+}\text{AlSiO}_6$

with increasing $\text{CaFe}^{3+}\text{AlSiO}_6$ molecule indicate that the join $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFe}^{3+}\text{AlSiO}_6$ forms a complete series of solid solutions, and X-ray powder patterns of these clinopyroxenes also show that all of them belong to a same space group $C2/c$.

The structural analysis of these clinopyroxenes is expected to throw more light on the problems of clinopyroxene solid solution.

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