Analysis of a Magnesium-containing β-Eucryptite Solid Solution by the Lattice Constant Method and Its Application[1,2]

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An X-ray diffraction method has been developed for the determination of the composition of a magnesium-containing β-eucryptite solid solution which consists of a pseudo-ternary system, SiO_2–$Mg_{1/2}AlO_2$–$LiAlO_2$. Standard samples of the solid solution within the range of 60—75 mol% SiO_2 and 0—15 mol% $Mg_{1/2}AlO_2$ were prepared from high-purity materials by the "glass-crystallization" technique. The diffraction angles of the (206) and (212) planes were measured from the center of gravity of the profile recorded on a chart by a counter diffractometer. After having been corrected for various systematic errors, both angles were used for the calculation of the lattice constants. It was found that $Mg_{1/2}AlO_2$ and $LiAlO_2$ contributed similarly to a_0, but in a different way to c_0. The composition of the solid solution in a commercial glass-ceramic could be determined from the correlation between the composition and the lattice constants. The standard deviation of the determination from one measurement was about 0.2—0.4 mol%, and the time required for analysis was about 30 min.

Low-thermal-expansion glass-ceramics contain a β-spodumene solid solution ($Li_2O \cdot Al_2O_3 \cdot nSiO_2$, $n>3$) or a β-eucryptite solid solution ($Li_2O \cdot Al_2O_3 \cdot nSiO_2$, $n \geq 2$), and their properties, such as the thermal expansion, depend not only on the content, but also on the composition of the solid solution. Therefore, the determination of the composition of the solid solution in the glass-ceramics is very important for the quality control and the study of the glass-ceramics; it is possible, however, only by the X-ray diffration method, as has been described in our previous papers.[1,3] The application of this method to a β-spodumene solid solution and a β-eucryptite solid solution has already been reported by us.[1,3] A magnesium-containing β-eucryptite solid solution consists of Li_2O, MgO, Al_2O_3, and SiO_2, and the number of moles of Li_2O plus that of MgO is equal to that of Al_2O_3. Therefore, the solid solution can be expressed as a pseudo-ternary system, SiO_2–$Mg_{1/2}AlO_2$–$LiAlO_2$. Since the solid solution is a hexagonal crystal, it is expected that the composition can be determined by measurements of the lattice constants, a_0 and c_0, if the three components contribute to a_0 and c_0 in any different manner. In the present paper, the analysis of a magnesium-containing β-eucryptite solid solution in glass-ceramics will be described on the basis of measurements of the two lattice constants.

Experimental

Apparatus. A Rigaku X-ray diffractometer with a proportional counter was used for this study. The glass samples were prepared by the use of an electric furnace with a silicon carbide heating element. A nichrome wire furnace was used for the crystallization of the glass. A Nippon Jarrell-Ash atomic-absorption and flame-emission spectrophotometer, AA-500, was used to check the lithium contents in the prepared samples.

Preparation of Standard Samples. Standard samples of the magnesium-containing β-eucryptite solid solution were prepared from lithium carbonate of a guaranteed reagent grade (min. 99.0%, Kanto Chemicals) and high-purity magnesium oxide (99.9% nominal, High Purity Chemical Laboratory), aluminum oxide (99.9—99.99% nominal, Iwatani & Co.), and silicon dioxide (min. 99.8%, Nissan Rare Elements). The magnesium oxide was heated in a platinum dish for 1.5 hr by means of a Mecker burner to dehydrate it. The aluminum oxide and silicon dioxide were similarly heated for 1 hr. The raw materials were weighed out by the amounts calculated for the intended compositions of the solid solution within the range of 60—75 mol% SiO_2 and 0—15 mol% $Mg_{1/2}AlO_2$ (the residual was $LiAlO_2$). The lithium carbonate was weighed out by the 3% excess of the calculated amount, considering a partial loss of lithium due to evaporation.[1] The materials weighed were mixed in an agate mortar for about 30 min, loaded into a platinum crucible, and heated at 1430 °C for 3 hr in the electric furnace. The melt was quenched in water, together with the crucible. The resultant glass was dried in an electric drying oven and subsequently powdered in an alumina mortar. The glass powder (48—200 mesh) was placed in a platinum crucible and then kept at a constant temperature in the range of 670 to 900 °C for 2—96 hr. When a glass or β-spodumene solid solution which is stable at higher temperatures was found by means of the X-ray diffraction method, a different condition of heat-treatment was used to obtain a sample containing the β-eucryptite solid solution only. In order to check the lithium content of the prepared sample, the sample was decomposed with hydrofluoric acid, perchloric acid, and nitric acid, and the lithium content was determined by flame photometry.

Measurement of Interplanar Spacings. Since the concentrations of any two components of the solid solution vary independently, at least two diffraction lines must be measured. The lines must not overlap with any other line. In addition, it is preferable for the lines to satisfy the following requirements: (1) one of these lines be that from a plane nearly perpendicular to the c axis, and the other be that from a plain nearly parallel to the c axis, because the analysis is based on the different contributions of the three components of the solid solution to a_0 and c_0 ; (2) the diffraction angles of the lines shift as much as possible with the change in the composition; (3) the intensities of lines be as high as possible. From these requirements, the (212) and (206) lines were selected as the best lines; and each line was measured three times under the conditions shown in Table 1. In order to compensate for any slight misalignment of the goniometer, (311) and (400) lines of a high-purity, sintered silicon plate (an external standard) were measured under the same conditions before and after the measurements of the lines of the solid solution. The internal standard technique was not adopted, because the diffraction lines of any internal standard and those of the solid solution were liable to overlap.

The diffraction profiles obtained by the use of the Cu$K\alpha_1$ ($\lambda = 1.54051$Å) and $K\alpha_2$ ($\lambda = 1.54433$Å) radiations overlapped in part. The profiles of thirteen samples of the solid solution were separated into α_1- and α_2-components on the charts on the basis of the intensity ratio and the degree of the α_1-α_2 angular separation. The diffraction angle obtained from the center of gravity of the triangle approximating the α_1-component was compared with the $K\bar{\alpha}$-diffraction angle obtained in a similar way from the intact profile. The difference agreed, within the limits of experimental error, with the angular separation calculated from the wavelengths of Cu$K\alpha_1$ and $K\bar{\alpha}$ (λ=1.54178 Å). For economy of time, therefore, the interplanar spacings of the other samples of the solid solution were obtained by the latter method, *i.e.*, by $K\bar{\alpha}$ angle measurements. Each profile of the (400) and (311) lines of the silicon standard was measured about ten times, and separated into α_1- and α_2-components. The difference was calculated between the angle obtained from the center of gravity of the triangle approximating the α_1-component and that obtained from the midpoint of the width at two-thirds of the maximum intensity of the intact profile. The reproducibility of the difference was good. Consequently, the diffraction angles of the silicon standard were obtained from the midpoint of the two-thirds-width of the intact profile, and corrected for the above difference.

TABLE 1. EXPERIMENTAL CONDITION

X-ray tube		Cu
Filter		Ni
Tube voltage (kV)		35
Tube current (mA)		15
Divergence and scatter slit (°)		2
Receiving slit (mm)		0.3
Time constant (s)		4
Scanning speed (°/min)		1/4
Chart speed (mm/min)		40
Silicon standard		
For (212)	Line	(311)
	2θ (°)[a]	56.122
For (206)	Line	(400)
	2θ (°)[a]	69.130

a) Diffraction angle of Cu$K\alpha_1$ corrected for systematic errors.

The diffraction angles thus obtained still include the systematic errors due to the diffraction at the inner parts of specimens, the use of flat specimens, and the divergence of the primary beam perpendicular to the plane of Bragg

TABLE 2. RESULTS OF ANALYSIS OF LITHIUM AND CONDITIONS OF CRYSTALLIZATION OF GLASSES

Sample no.	Intended composition (mol%) SiO$_2$	Mg$_{1/2}$AlO$_2$	LiAlO$_2$	Intended Li$_2$O (wt%)	Analyzed Li$_2$O (wt%)	Crystalliz. cond. Temp. (°C)	Time (hr)
M60- 0[a]	60.0	0.0	40.0	—	—	—	—
2.5	60.0	2.5	37.5	9.0	9.0	750	24
5	60.0	5.0	35.0	8.3	8.3	750	24
10	60.0	10.0	30.0	7.1	6.9	750	24
15	60.0	15.0	25.0	5.9	6.0	750	24
M62.5- 0[a]	62.5	0.0	37.5	—	—	—	—
2.5	62.5	2.5	35.0	8.4	8.5	750	24
5	62.5	5.0	32.5	7.8	7.8	750	24
7.5	62.5	7.5	30.0	7.2	7.2	750	24
12.5	62.5	12.5	25.0	5.9	6.0	750	24
M65- 0[a]	65.0	0.0	35.0	—	—	—	—
5	65.0	5.0	30.0	7.2	7.2	750	6
10	65.0	10.0	25.0	6.0	6.0	750	24
15	65.0	15.0	20.0	4.8	4.8	750	72
M67.5- 0[a]	67.5	0.0	32.5	—	—	—	—
2.5	67.5	2.5	30.0	7.2	7.3	750	24
7.5	67.5	7.5	25.0	6.0	6.0	750	24
12.5	67.5	12.5	20.0	4.8	4.6	800	24
M70- 0[a]	70.0	0.0	30.0	—	—	—	—
5	70.0	5.0	25.0	6.0	6.0	750	48
7.5	70.0	7.5	22.5	5.4	5.3	800	24
10	70.0	10.0	20.0	4.8	5.0	800	24
15	70.0	15.0	15.0	3.6	3.6	800	48
M72.5- 0[a]	72.5	0.0	27.5	—	—	—	—
2.5	72.5	2.5	25.0	6.0	6.2	850	24
7.5	72.5	7.5	20.0	4.8	4.8	850	24
12.5	72.5	12.5	15.0	3.6	3.6	900	36
M75- 0	75.0	0.0	25.0	6.1	5.9	700	4
5	75.0	5.0	20.0	4.8	4.7	850	24
10	75.0	10.0	15.0	3.6	3.5	850	24
15	75.0	15.0	10.0	2.4	2.4	900	48

a) Although the samples of these compositions were not prepared, these samples will be also discussed in the study by the use of the diffraction data from the preceding paper.[1]

focusing. These errors were compensated for on the basis of the equation given by Willson and Pike.[4)]

Results and Discussion

Magnesium-containing β-Eucryptite Solid Solution. Table 2 shows the conditions of crystallization and the results of the analysis of lithium. The intended and analyzed Li_2O contents agreed well, and no impurity was detected by the X-ray diffraction method. These results indicate that the prepared samples were pure enough for this study. The crystallization required higher temperatures as the content of SiO_2 or $Mg_{1/2}AlO_2$ increased.

Correlation between the Composition and the Lattice Constants. The interplanar spacings and lattice constants of the solid solution are shown in Table 3. The relation between the composition and lattice constants is shown in Fig. 1. The results can be summarized as follows: (1) when $LiAlO_2$ or $Mg_{1/2}AlO_2$ was substituted for SiO_2, a_0 increased markedly; (2) when $LiAlO_2$ was substituted for SiO_2, c_0 hardly changed at all, or even decreased somewhat, in the low-lithium region, and increased in the high-lithium region; (3) when $Mg_{1/2}AlO_2$ was substituted for SiO_2, c_0 decreased markedly except in the high-lithium region.

TABLE 3. INTERPLANAR SPACINGS (d) AND LATTICE CONSTANTS OF MAGNESIUM-CONTAINING β-EUCRYPTITE SOLID SOLUTION

Sample no.	d (Å)		Lattice const. (Å)	
	(212)	(206)	a_0	c_0
M60- 0[a)]	1.6370	1.4218	5.241	10.945
2.5	1.6371	1.4204	5.242	10.925
5	1.6369	1.4187	5.243	10.904
10	1.6348	1.4147	5.237	10.860
15	1.6326	1.4111	5.232	10.822
M62.5- 0[a)]	1.6345	1.4192	5.233	10.923
2.5	1.6350	1.4182	5.236	10.907
5	1.6333	1.4162	5.231	10.887
7.5	1.6319	1.4142	5.227	10.868
12.5	1.6298	1.4108	5.221	10.833
M65- 0[a)]	1.6315	1.4173	5.223	10.912
5	1.6303	1.4143	5.221	10.877
10	1.6270	1.4108	5.210	10.847
15	1.6227	1.4065	5.197	10.810
M67.5- 0[a)]	1.6283	1.4157	5.212	10.907
2.5	1.6281	1.4148	5.212	10.895
7.5	1.6239	1.4105	5.199	10.860
12.5	1.6214	1.4073	5.192	10.827
M70- 0[a)]	1.6250	1.4144	5.201	10.906
5	1.6225	1.4113	5.193	10.876
7.5	1.6199	1.4088	5.185	10.856
10	1.6189	1.4072	5.182	10.839
15	1.6155	1.4038	5.172	10.810
M72.5- 0[a)]	1.6211	1.4129	5.187	10.906
2.5	1.6200	1.4112	5.184	10.888
7.5	1.6155	1.4073	5.170	10.858
12.5	1.6127	1.4042	5.161	10.830
M75- 0	1.6155	1.4109	5.167	10.907
5	1.6135	1.4077	5.162	10.874
10	1.6106	1.4044	5.153	10.844
15	1.6068	1.4012	5.141	10.821

a) The data obtained from the preceding paper.[1)]

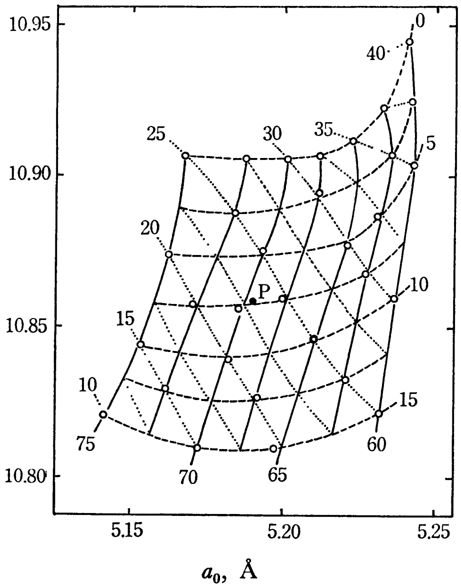

Fig. 1. Correlation between composition and lattice constants of the solid solution.
——: Line on which mol% of SiO_2 is equal.
----: Line on which mol% of $Mg_{1/2}AlO_2$ is equal.
······: Line on which mol% of $LiAlO_2$ is equal.
Numbers in the figure indicate mol% of each component.
P: The solid solution in the glass-ceramic described in the text.

These facts may be explained as follows on the basis of the crystal structure of the solid solution. The crystal structure was determined by Chi-Tang Li[5)] for the composition of 66.7 mol% SiO_2 and 33.3 mol% $LiAlO_2$. The solid solution consists of the SiO_4 and AlO_4 tetrahedra arranged along a hexagonal screw axis parallel to the c axis in double helical fashon, and of the lithium and magnesium ions on the interstitial sites along the hexagonal screw axis. The lithium or magnesium ion compensates for the deficiency in the positive charge due to the substitution of an aluminum ion for a silicon ion, and is coordinated by four oxygen ions. This LiO_4 or MgO_4 tetrahedron shares two edges with the two opposite $Al(Si)O_4$ tetrahedra. The shared edges are the shortest for both the $Li(Mg)O_4$ and $Al(Si)O_4$ tetrahedra; they have a slope of about 45° to the c axis. Two of the unshared edges of the $Al(Si)O_4$ tetrahedron lie on the $(00l)$ planes, while the others have a slope of about 45° to the c axis.[5)] When $LiAlO_2$ or $Mg_{1/2}AlO_2$ is substituted for SiO_2, the lithium or magnesium ion wedges itself in the hexagonal screw. The shortest distance between a lithium (or magnesium) ion and an aluminum (or silicon) ion lies on a $(00l)$ plane and is very short (about 2.58 Å for the composition of 75 mol% SiO_2 and 25 mol% $LiAlO_2$). Therefore, the screw may be compelled to widen by the repulsive force between

Table 4. Comparison of lattice constants of magnesium-containing β-eucryptite solid solution with data of several other authors

Author	Composition (mol%)			Lattice const. (Å)		Lattice const. (Å) in this work[a)]	
	SiO_2	$Mg_{1/2}AlO_2$	$LiAlO_2$	a_0	c_0	c_0	a_0
Ray and Muchow	60.0	8.0	32.0	5.240	10.876	5.240	10.877
	66.7	6.7	26.6	5.210	10.868	5.209	10.866
	71.4	5.7	22.9	5.172	10.824	5.183	10.868
Petzoldt	66.1	15.0	18.9	5.18	10.85	5.193	10.810
	70.2	4.4	25.4	5.19	10.90	5.199	10.894

a) Obtained from Fig. 1 for the composition.

the lithium (or magnesium) ion and the aluminum (or silicon) ion, and hence a_0 increases. On the contrary, the effect of the Li(Mg)–Al(Si) repulsive force on c_0 may be small, because the shortest Li(Mg)–Al(Si) distance lies on a (00*l*) plane, and the next shortest distance is relatively long and has a large slope to the c axis. Since the Li–Li distance along the c axis is long in the low-lithium region, the Li–Li repulsive force may be weak. In the high-lithium region, the distance is short; hence, the repulsive force may be strong enough to increase the c_0. Since the magnesium ion has a stronger polarizing power than the lithium ion, the Mg–O bond is stronger and more covalent than the Li–O bond. Therefore, the edges of the $Al(Si)O_4$ tetrahedra shared by the MgO_4 tetrahedra may be shorter than those of the $Al(Si)O_4$ tetrahedra shared by the LiO_4 tetrahedra. As can be seen from the orientation of the $Al(Si)O_4$ tetrahedra described above, this effect may decrease c_0 of the magnesium-containing solid solution. However, it may not decrease a_0, because the unshared edges may be elongated and counteract the contraction of the shared edges. Since the Mg–O bond is more covalent than the Li–O bond, the effective charge of the magnesium ion may be relatively small. Moreover, the number of the magnesium ions introduced is half of that of the lithium ions. Therefore, the Mg–Mg repulsive force along the c axis may be smaller than the Li–Li repulsive force. Consequently, the c_0-decreasing effect may overcome the c_0-increasing effect; hence, c_0 may be decreased by introducing magnesium ions. In the high-lithium region, though, c_0 is hardly decreased at all by introducing magnesium ions, because the Li–Li repulsive force may increase considerably.

In any case, the data indicate that the composition of the solid solution can be determined by the measurements of a_0 and c_0, because the contributions of the three components to a_0 and c_0 were markedly different.

Application to a Glass-Ceramic Sample. In the preceding paper, it was found that slightly different values of the SiO_2 content of a β-eucryptite solid solution in a glass-ceramic were obtained depending on the diffraction line used. This phenomenon was presumed to result from the partial substitution of the magnesium ion for the lithium ion. Therefore, the present method was applied to this glass-ceramic sample. The P point ($a_0=5.190$ Å, $c_0=10.858$ Å) in Fig. 1 shows the solid solution in the sample. The concentration between adjacent lines of Fig. 1 can be considered to be approximately proportional to the distance from each line. Therefore, the composition could be obtained as follows: 69.5 mol% SiO_2, 7.3 mol% $Mg_{1/2}AlO_2$, and 23.2 mol% $LiAlO_2$.

Comparison with the Data of Several Other Authors. Table 4 compares the lattice constants of the solid solution with the data reported by several other authors.[6,7] Two of Ray and Muchow's data agreed well with ours, but one disagreed. When we compare the disagreeing datum with the tendency of the composition *vs.* lattice constant curves of their paper,[6] it seems that their value is too low. Petzoldt used lower diffraction angles for the measurement of the lattice constants, and so that precision of his measurement was only ±0.005 Å for a_0.[7] In addition, the authors of both papers did not consider the possibility of the evaporation of lithium during the sample preparation. In this study, the evaporation of lithium was taken into account, and higher diffraction angles were used and corrected for the systematic errors. The standard deviation of the data was 0.0005 Å for a_0. Moreover, a large number of data were accumulated. Therefore, it seems that the data of the present paper are more reliable.

Error in the Determination. The precision of the present method was as follows. The standard deviations of 2θ, a_0, and c_0 on one measurement were about 0.01°, 0.0008 Å, and 0.0025 Å respectively. The corresponding standard deviations of the analytical values of each component varied somewhat depending on the composition region. For example, in the neighborhood of the composition of 70 mol% SiO_2, 7.5 mol% $Mg_{1/2}AlO_2$, and 22.5 mol% $LiAlO_2$, the standard deviations of SiO_2, $Mg_{1/2}AlO_2$, and $LiAlO_2$ were 0.20, 0.39, and 0.28 mol% respectively. For the weight percentage, the standard deviations of SiO_2, MgO, Li_2O, and Al_2O_3 were 0.19, 0.13, 0.07, and 0.39 wt% respectively. For the purpose of obtaining the absolute composition by the use of Fig. 1, the errors of the equi-concentration lines in the figure must also be taken into account. These errors consist of the deviations of the compositions and the errors of the lattice constants of the standard samples. Since the lattice constants were obtained from the average of three measurements, the variances of the lattice constants were one-third of those described above.

The systematic errors of the lattice constants were compensated for; hence, they are negligible here. The deviation of the composition in Fig. 1 could be estimated as follows from the errors of weighing in sample preparation, the variations of impurities of the raw materials, and the permitted differences between the intended and determined lithium contents: SiO_2 0.3 mol% or less, $Mg_{1/2}AlO_2$ 0.1 mol% or less, and $LiAlO_2$ 0.4 mol% or less as the standard deviations. Then the errors of the equi-concentration lines were calculated: SiO_2 0.32 mol% or less, $Mg_{1/2}AlO_2$ 0.25 mol% or less, and $LiAlO_2$ 0.43 mol% or less as the standard deviations. Consequently, the absolute composition of the solid solution can be obtained by the use of Fig. 1 with the following maximum errors from one measurement in the neighborhood of the above composition: SiO_2 0.38 mol%, $Mg_{1/2}AlO_2$ 0.46 mol%, $LiAlO_2$ 0.51 mol%; SiO_2 0.37 wt%, MgO 0.15 wt%, Li_2O 0.12 wt%, and Al_2O_3 0.56 wt%.

The correlation between the lattice constants and the composition has been exclusively discussed for general use. The correlation between the composition and interplanar spacings or diffraction angles of (206) and (212), however, can also be used; its use is recommended for routine work because of the simplicity of calculation. The time required for analysis was about 30 min by the use of a desk electronic computer.

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