Unit cell dimensions of some synthetic olivine group solid solutions

YOSHITO MATSUI¹ and YASUHIKO SYONO²

Institute for Thermal Spring Research, Okayama University, Misasa,
Tottori-ken¹, and Institute for Solid State Physics, University of
Tokyo, Minato-ku, Tokyo², Japan

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Abstract—Two series of solid solutions of olivine structure, $(\text{Mg}, \text{Co})_2\text{SiO}_4$ and $(\text{Mg}, \text{Ni})_2\text{SiO}_4$, were synthesized at 1,400°C, and their unit cell parameters were measured at room temperature. It was found that deviations from Vegard's law increase according to the order $(\text{Mg}, \text{Fe})_2\text{SiO}_4$, $(\text{Mg}, \text{Co})_2\text{SiO}_4$ and $(\text{Mg}, \text{Ni})_2\text{SiO}_4$. This order coincides with the order of octahedral crystal field stabilization energies of transition metal ions. It was suggested that the site preference of Mg and transition metal ions over M_I and M_{II} sites is most pronounced in the case of $(\text{Mg}, \text{Ni})_2\text{SiO}_4$ solid solution series.

INTRODUCTION

Considerable attention has been paid in recent years as to the site preference of divalent cations in the ferromagnesian minerals (GHOSE, 1962, 1965; MUELLER, 1962; MATSUI and BANNO, 1965; BANNO and MATSUI, 1966; EVANS *et al.*, 1967; BANCROFT *et al.*, 1967). Thermodynamic considerations indicate that solid solutions with site preference phenomena become necessarily nonideal, primarily because of reduced entropy of mixing of constituent particles (BANNO and MATSUI, 1967).

Crystal structure of olivine provides two kinds of non-equivalent sublattice sites for cations, *i.e.*, M_I which is larger and slightly more distorted octahedral (sixfold-coordinated) site of point symmetry m , corresponding to Ca position of monticellite CaMgSiO_4 , and M_{II} which is smaller and more regularly sixfold-coordinated site of point symmetry $\bar{1}$, corresponding to Mg position of monticellite. In this circumstance it can be expected that there is site preference over M_I and M_{II} for Mg and Fe. GHOSE (1962) has supposed concentration of Fe in M_I , from the consideration of sizes of both ions and sublattice sites. However, no direct measurement of Fe and Mg distribution over two sites has been reported yet.

Another controlling factor for cation distribution among non-equivalent sublattice sites in addition to the size effect is a stabilization energy due to crystal field effect in the case of transition metal ions. If the site preference is controlled predominantly by the crystal field stabilization energies, the ordered configuration of cations in the olivine solid solutions may become more pronounced according to the order $(\text{Fe}, \text{Mg})_2\text{SiO}_4$, $(\text{Co}, \text{Mg})_2\text{SiO}_4$ and $(\text{Ni}, \text{Mg})_2\text{SiO}_4$, since octahedral stabilization

energies increase in the order Fe^{2+} , Co^{2+} and Ni^{2+} , and possibly the differences of site occupancy energies between M_I and M_{II} follow the same order. It can be expected that various properties of solid solutions, such as unit cell volumes and unit cell edges, are affected by the degree of site preference. To test this expectation, we measured unit cell dimensions of nickel and cobalt olivine solid solution series with magnesium olivine.

SAMPLE PREPARATIONS AND X-RAY MEASUREMENTS

Three end members, Mg_2SiO_4 , Co_2SiO_4 and Ni_2SiO_4 were synthesized from mixtures of reagent grade oxides by subsolidus solid reactions without use of any mineralizers. Powder mixtures were intimately mixed, and pressed into pellets in a steel die. Both Mg_2SiO_4 and Co_2SiO_4 specimens were sintered in air at 1,500 and 1,400°C respectively for more than 20 hr and abruptly cooled. These end members were examined to be in a single phase olivine by usual X-ray technique and microscopic observation. Synthesis of a single phase Ni_2SiO_4 is rather difficult, since nickel olivine undergoes subsolidus decomposition to NiO and SiO_2 at temperatures above 1,500°C. Sintering at temperatures below 1,500°C requires more than 100 hr to obtain a single phase nickel olivine.

Solid solutions of $(\text{Co}, \text{Mg})_2\text{SiO}_4$ and $(\text{Ni}, \text{Mg})_2\text{SiO}_4$ were prepared for every *ca.* 25 mole%, except for magnesium rich side of $(\text{Ni}, \text{Mg})_2\text{SiO}_4$, where solid solutions were made for every *ca.* 12.5%. Specimens were fired at 1,400°C for more than 8 hr and quenched to room temperature. Formation of uniform solid solutions was judged from well defined X-ray diffraction peaks. Composition of the products was determined chemically by chelatometric titration for Mg, Co and Ni.

Unit cell dimensions were determined from X-ray powder diffraction data

Table 1. Examples of *d*-spacing calculation

Specimen	Mg 8		Co 4		Co 8		Ni 4		Ni 8	
Composition	Mg_2SiO_4		$\text{Co}_{0.98}\text{Mg}_{1.02}\text{SiO}_4$		Co_2SiO_4		$\text{Ni}_{0.98}\text{Mg}_{1.02}\text{SiO}_4$		Ni_2SiO_4	
<i>hkl</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>d</i> _{obs}	<i>d</i> _{calc}
222	1.7480	1.7484	1.7536	1.7536	1.7580	1.7580	1.7414	1.7420	1.7349	1.7349
241	1.6694	1.6697	1.6770	1.6766	1.6824	1.6823	1.6653	1.6657	1.6582	1.6583
061	1.6349	1.6349	1.6431	1.6431	1.6514	1.6512	1.6324	1.6322	1.6224	1.6222
133	1.6176	1.6174	1.6212	1.6213	1.6258	1.6261	1.6103	1.6101	1.6018	1.6017
152	1.5886	1.5883	1.5952	1.5946	1.6009	1.6010	1.5842	1.5839	1.5751	1.5751
004	1.4957	1.4955	1.4975	1.4974	1.5011	1.5009	1.4865	1.4867	1.4787	1.4788
062	1.4777	1.4777	1.4838	1.4841	1.4906	1.4907	1.4740	1.4741	1.4652	1.4653
312	1.3877	1.3876	1.3921	1.3918	1.3950	1.3949	1.3833	1.3828	1.3780	1.3781
322	1.3506	1.3506	1.3545	1.3549	1.3581	1.3581	1.3459	1.3461	1.3414	1.3413
134	1.3152	1.3155	1.3181	1.3182	1.3217	1.3218	1.3089	1.3089	1.3021	1.3021

measured at room temperature, using a Rigaku Denki Model DM 3 diffractometer equipped with a Geiger-Müller tube as a counting head. Calibration of goniometer was carried out using high purity silicon as an external standard. Goniometer scanning speed was $0.5^\circ 2\theta$ per minute. Iron $K_{\alpha 1}$ radiation was used throughout.

Calculation of lattice parameters was performed by the least square technique, in which square sum of difference in $1/d^2$ was the quantity to be minimized. Ten diffraction lines of (222), (241), (061), (133), (152), (004), (062), (312), (322) and (134) were used, whose 2θ angles range from 66° to 97° . In Table 1 the results of d -spacing calculations for Mg_2SiO_4 , Co_2SiO_4 , Ni_2SiO_4 , $\text{Co}_{0.98}\text{Mg}_{1.02}\text{SiO}_4$ and $\text{Ni}_{0.98}\text{Mg}_{1.02}\text{SiO}_4$ are shown as examples.

RESULTS AND DISCUSSION

Data of unit cell dimensions of $(\text{Co}, \text{Mg})_2\text{SiO}_4$ and $(\text{Ni}, \text{Mg})_2\text{SiO}_4$ are compiled in Table 2 and are shown graphically in Figs. 1 and 2. Unit cell dimensions of $(\text{Fe}, \text{Mg})_2\text{SiO}_4$ solid solution system are also reproduced in Fig. 3 from AKIMOTO and FUJISAWA (1968). (The data were partly corrected owing to the further refinement of cell parameters and the redetermination of chemical composition on a few members (AKIMOTO, private communication)).

Cell parameters of three end members are compared with those reported by previous investigators in Table 3. Values for Mg_2SiO_4 are in an excellent agreement with those by YODER and SAHAMA (1957) and AKIMOTO and FUJISAWA (1968). The lattice parameters of Co_2SiO_4 are also in reasonable agreement with those found in an ASTM card (No. 15-865), in RINGWOOD (1963) and in AKIMOTO *et al.* (1965). However, the values of cell dimensions of Ni_2SiO_4 are a little larger than those reported by PISTORIUS (1963). We repeated thrice the synthesis of this compound

Table 2. Cell constants and unit cell volumes of synthetic olivine group solid solutions (at room temperature)

Specimen	Molar % of Mg_2SiO_4	a (Å)	b (Å)	c (Å)	V (Å ³)
Mg 8	100	4.7553 ± 0.0006	10.1977 ± 0.0014	5.9820 ± 0.0007	290.09 ± 0.11
Co 2	75	4.7638 ± 0.0007	10.2255 ± 0.0016	5.9846 ± 0.0008	291.52 ± 0.13
Co 4	51	4.7720 ± 0.0008	10.2522 ± 0.0019	5.9896 ± 0.0009	293.03 ± 0.15
Co 6	25	4.7779 ± 0.0004	10.2799 ± 0.0009	5.9961 ± 0.0004	294.51 ± 0.07
Co 8	0	4.7823 ± 0.0003	10.3044 ± 0.0008	6.0036 ± 0.0004	295.85 ± 0.06
Ni 1	90	4.7523 ± 0.0007	10.2008 ± 0.0016	5.9726 ± 0.0008	289.54 ± 0.13
Ni 2	76	4.7485 ± 0.0004	10.1988 ± 0.0010	5.9627 ± 0.0005	288.77 ± 0.08
Ni 3	63	4.7444 ± 0.0009	10.1939 ± 0.0020	5.9534 ± 0.0010	287.93 ± 0.15
Ni 4	51	4.7422 ± 0.0008	10.1843 ± 0.0018	5.9467 ± 0.0009	287.20 ± 0.14
Ni 6	26	4.7345 ± 0.0010	10.1539 ± 0.0025	5.9290 ± 0.0012	285.03 ± 0.19
Ni 8	0	4.7287 ± 0.0003	10.1214 ± 0.0006	5.9153 ± 0.0003	283.11 ± 0.05

Fig. 1. Composition dependence of unit cell parameters a , b and c and unit cell volume V of $(\text{Co}, \text{Mg})_2\text{SiO}_4$ solid solutions with olivine structure.

from the different lots of starting reagents and obtained the almost identical values. Chemical analysis of our products revealed the molar ratio of Ni to Si to be 2 : 1 within the analytical uncertainty. We searched further for possible impurities such as Mg, Co, Fe, Mn, Ca and Zn by emission spectrography and atomic absorption

Fig. 2. Composition dependence of unit cell parameters a , b and c and unit cell volume V of $(\text{Ni}, \text{Mg})_2\text{SiO}_4$ solid solutions with olivine structure.

flame photometry, but could not detect in effect these contaminants. The reason for this discrepancy is not clear at the present stage.

As is seen from Figures, unit cell volumes are linear function of molar composition within experimental error in $(\text{Co}, \text{Mg})_2\text{SiO}_4$, whereas in $(\text{Ni}, \text{Mg})_2\text{SiO}_4$ slightly positive excess volume of mixing is observed. The situation is very critical in the case of $(\text{Fe}, \text{Mg})_2\text{SiO}_4$. A very small positive anomaly could be justified

Fig. 3. Composition dependence of unit cell parameters a , b and c and unit cell volume V of $(\text{Fe, Mg})_2\text{SiO}_4$ solid solutions with olivine structure,

Table 3. Comparison of cell constants of three end members as reported by several authors

	a (Å)	b (Å)	c (Å)	V (Å ³)	Reference
Mg ₂ SiO ₄	4.756 ±0.001	10.197 ±0.001	5.982 ±0.001	290.1	AKIMOTO and FUJISAWA (1968)
	4.756 ±0.005	10.195 ±0.005	5.981 ±0.010	290.0	YODER and SAHAMA (1957)
	4.7553±0.0006	10.1977±0.0014	5.9820±0.0007	290.09±0.11	Present study
Co ₂ SiO ₄	4.779	10.340	5.996	296.3	RINGWOOD (1963)
	4.781 ±0.003	10.289 ±0.007	5.993 ±0.003	294.8	AKIMOTO <i>et al.</i> (1965)
	4.778	10.301	6.005	295.6	PISTORIUS (1963)
	4.7823	10.310	6.0074	296.20	ASTM index card No. 15-865*
	4.7823±0.0003	10.3044±0.0008	6.0036±0.0004	295.85±0.06	Present study
Ni ₂ SiO ₄	4.725 ±0.004	10.118 ±0.008	5.908 ±0.004	282.5	PISTORIUS (1963)
	4.7287±0.0003	10.1214±0.0006	5.9153±0.0003	283.11±0.05	Present study

* Data by the U. S. National Bureau of Standards.

which is not inconsistent with the previous report (FISHER, 1967).

As to the cell edges, some anomalies can be detected in a - and c -axes in (Co, Mg)₂SiO₄. Strictly speaking, thermodynamics itself tells nothing about unit cell edges. Nevertheless we may expect that, so far as the mixing of cations is completely random, lengths of cell edges are very nearly linear functions of composition; *i.e.*, Vegard's law may result. If this statement is correct, it follows that even in the system Co₂SiO₄-Mg₂SiO₄, there exists ordered structure to some degree, probably due to site preference of Co and Mg over two sites. This view seems plausible, for the anomalous deviation is maximum around Co : Mg = 1 : 1, which coincides with the ratio of sublattice points, $M_I : M_{II}$, in the olivine structure. One may safely conclude that the anomaly in the unit cell volume is fortuitously cancelled out as a result of positive and negative anomalies in a and c axes.

Cell edge lengths of (Fe, Mg)₂SiO₄ also deviate but slightly from Vegard's law. However, in this system deviations are all positive except for some ambiguous values. This can partly be explained by considering that, if excess volume of mixing is very small, cell edges are to vary as functions of cube root of molar composition. Thus the anomalies in the cell parameters of (Fe, Mg)₂SiO₄ are not warranted.

Anomaly in the system Ni₂SiO₄-Mg₂SiO₄ appears more remarkable and complicated in nature. The existence of excess volume of mixing presents decidedly the proof of its nonideality. Moreover, as is seen from the peculiar shape of cell edge curves, it seems that this system can be more properly understood by supposing that the system comprises two solid solution series, *i.e.*, Ni₂SiO₄-NiMgSiO₄ and NiMgSiO₄-Mg₂SiO₄. (Note that the cell constants show no anomalous features in the range Ni : Mg > 1.). In other words, cation distribution in NiMgSiO₄ is highly ordered, presumably Mg²⁺ and Ni²⁺ occupying M_I and M_{II} , respectively.

Considerations given above indicate definitely that degree of site preference increases in the order just as has been expected in the introductory section, *i.e.*, $(\text{Fe}, \text{Mg})_2\text{SiO}_4$, $(\text{Co}, \text{Mg})_2\text{SiO}_4$ and $(\text{Ni}, \text{Mg})_2\text{SiO}_4$. NAFZIGER and MUAN (1967) and KITAYAMA and KATSURA (1968) has reported that the system Fe_2SiO_4 - Mg_2SiO_4 is not ideal, but positively deviates from Raoult's law at 1,200°C, the activity coefficient of Fe_2SiO_4 for half formula unit being *ca.* 1.4 in the range of $\text{Fe}/(\text{Fe}+\text{Mg}) \leq 0.1$. On the other hand, the system Ni_2SiO_4 - Mg_2SiO_4 is also nonideal as is shown above, presumably with highly ordered cation distribution. Highly ordered solid solutions are expected to be nonideal, negatively deviating from Raoult's law (BANNO and MATSUI, 1967). It is highly probable that this system is the case, at least qualitatively. The system Co_2SiO_4 - Mg_2SiO_4 may possibly be an intermediate case. In this system deviation from Raoult's law may be less positive than that of $(\text{Fe}, \text{Mg})_2\text{SiO}_4$ and less negative than that of $(\text{Ni}, \text{Mg})_2\text{SiO}_4$.

Since the degree of site preference may certainly be altered with temperature, unit cell parameters of solid solutions of the present type cannot be determined uniquely, unless conditions at which solid solutions have been formed are specified. This is another topic which will be treated in a separate report.

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