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Solid Solubility and Cation Distribution in the System Co_2GeO_4–Mg_2GeO_4

M. INAGAKI, T. OZEKI, H. FURUHASHI, AND S. NAKA

Synthetic Crystal Research Laboratory, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464, Japan

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In the system Co_2GeO_4–Mg_2GeO_4, solid solubilities in spinel and olivine structures were studied on samples prepared by solid state reaction at temperatures of 1000–1300°C. The solubility limits were determined from the identification by X-ray powder pattern and the change of the lattice constant of spinel with composition. The relation between temperature and the free energy difference ΔG° which was estimated from the solubility limits agreed qualitatively with the fact that the spinel phase of Mg_2GeO_4 is stable at low temperatures under atmospheric pressure. The spinels were also synthesized at 800°C under the pressure of 20 kb. Over the whole range of composition, the cation distribution was found to be normal with $u = 0.375$. Above 1000°C under 20 kb in the presence of water, the spinels, except Co_2GeO_4, were found to react with water to form enstatite and probably magnesium hydroxide in an amorphous state.

Introduction

We have been interested in the cation distribution in spinel-type oxides. Previously (*1*), we proposed a modified X-ray method for its determination and showed experimentally that Co_2GeO_4 has an exactly normal distribution of cations, $(Ge)_{tetra}[Co_2]_{octa}O_4$, with the ideal cubic close packing of oxygen atoms, $u = 0.375$. The same method was applied to the solid solutions in the system Co_2GeO_4–$CoAl_2O_4$ (*2*). The results showed that the coexistence of germanium and cobalt ions in the same tetrahedral sites is unfavorable.

In the present work, solid solubilities in the spinel and olivine structures were investigated in the system Co_2GeO_4–Mg_2GeO_4. Since Mg_2GeO_4 was obtained in the spinel structure under high pressure (*3*) or as poorly crystalline precipitates followed by long-time annealing at 650°C (*4*), the synthesis of the spinel solid solutions was carried out not only under normal pressure but also under a pressure of 20 kbar. Thermodynamic considerations were applied to the solubilities of spinel and olivine structures. The cation distribution and stability under hydrothermal conditions were also examined on the spinel phases.

Experimental

The solid solutions in the system Co_2GeO_4–Mg_2GeO_4 were synthesized from a mixture of CoO, MgO, and GeO_2 by solid state reactions at temperatures of 1000, 1100, 1200, and 1300°C under the atmospheric pressure of air. The heating was repeated in a platinum envelope with tightly folded edges, until no changes in X-ray powder pattern, positions, and relative intensities of diffraction lines were detected. After the final heating the samples were quenched in water. The syntheses of spinel solid solutions were carried out also under 20 kb at 800°C for 3 hr by using a girdle-type high-pressure apparatus (*5*). For the samples thus prepared, the existing phases were identified from the X-ray powder patterns. For the spinel phases, the lattice constant a_0 was determined from 533 reflection ($2\theta = 90^\circ$) by referring to an internal standard

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of silicon and the cation distribution was measured by using the method proposed previously (*1*).

The stability of spinels was also examined under 20 kb in the presence of water. The phases formed were identified from their powder pattern.

Results and Discussion

1. Phase Relation

In the present system, the phases identified and the lattice constant a_0 of the spinel phase are shown as a function of composition x in (Ge) $[Co_{1-x}Mg_x]_2O_4$ in Fig. 1. The phase boundary on the spinel side in Fig. 1a is drawn on the basis of the change in the lattice constant with composition (Fig. 1b).

The phase boundaries obtained in the present work converge to the estimated point of phase transition for Mg_2GeO_4 from spinel to olivine (*3*) under atmospheric pressure. The phase relation observed in the present work is a little different from that reported by Navrotsky below 1100°C (*6*). In the present work, the samples were heated at 1100°C for 10 days and at 1000°C for 20 days. At the beginning of the heat treatment, the spinel solid solution, which has a small value of x (estimated from the lattice constant), and the olivine solid solution were formed and both reacted gradually with each other by the continuation of the heat treatment. Below 1100°C and at compositions with $x < 0.6$, the lattice constant of the spinel solid solution decreased slowly with the heat treatment and finally reached the values shown in Fig. 1b. At $x = 0.7$, a very small amount of olivine phase was observed even after heating for 20 days at 1000°C.

We tried to obtain the equilibrium phases at 900°C in air. However, the reaction rate was so slow that the equilibrium phases could not be obtained even after 40 days. We tried to get them by using a mineralizer LiF, but without success even after 30 days.

Under the pressure of 20 kbar at 800°C, the spinel solid solutions were obtained in the single phase over the whole composition range. The relation between lattice constant a_0 and composition x is linear and agrees with that obtained under atmospheric pressure as shown in Fig. 1b.

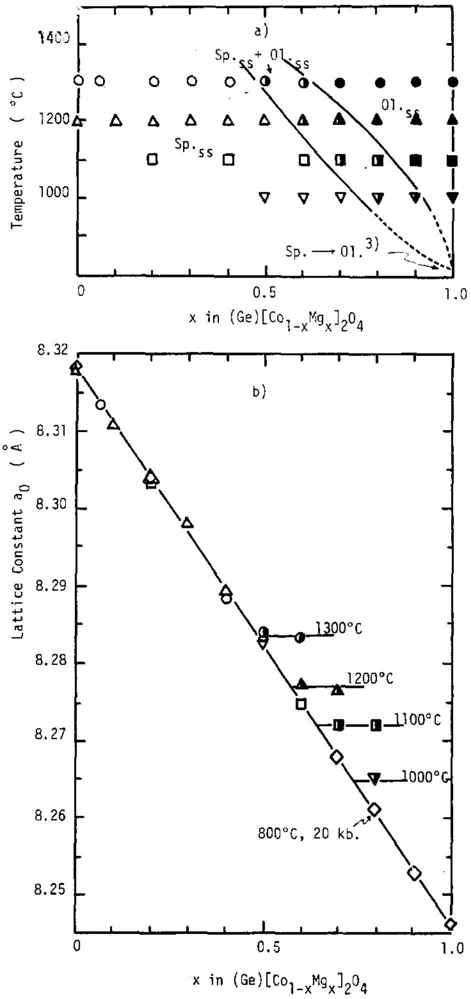

FIG. 1. Phase relation and lattice constant change in the Co_2GeO_4–Mg_2GeO_4 system. The results at different temperatures are plotted by different marks. The open mark stands for the single phase with spinel structure, the filled mark for the single phase with olivine structure, and the half-filled mark for the coexistence of two phases. The lattice constant a_0 for the spinel solid solutions obtained at 800°C under 20 kb is also plotted (◇).

2. Thermodynamic Considerations

A crude estimation of the free energy differences $\Delta G°$ for the transitions of Mg_2GeO_4 from olivine (Ol.) to spinel (Sp.) and also of Co_2GeO_4 from spinel to olivine was made at

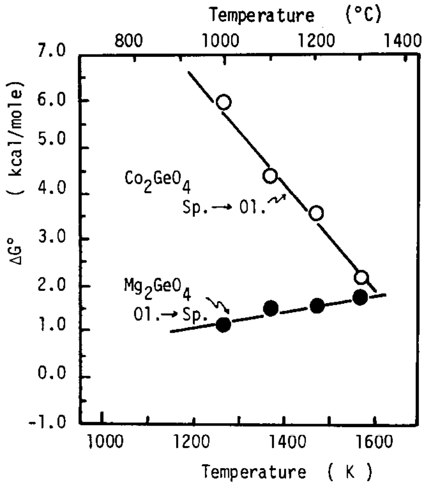

FIG. 2. Free energy differences $\Delta G°$ as a function of temperature.

different temperatures by the calculation of the activity coefficient from the solubility limits which were obtained under atmospheric pressure, according to the same procedure as Navrotsky (*6*, *7*). The $\Delta G°$ values obtained from the present data were plotted as a function of temperature in Fig. 2.

For the transition Mg_2GeO_4 (Ol.) → Mg_2GeO_4 (Sp.), the obtained values of $\Delta G°$ showed the stability of the olivine structure at the temperatures examined and at 1200°C the same value of $\Delta G°$ was obtained as reported by Navrotsky (*6*). The value of $\Delta G°$ tends to decrease with decreasing temperature and this tendency agrees qualitatively with the fact that the spinel structure becomes stable at low temperatures (*3*).

The high value $\Delta G°$ for the transition of Co_2GeO_4 (Sp.) to Co_2GeO_4 (Ol.) suggests that the stability of the spinel structure in the temperature range examined is high. It tends to decrease with increasing temperature.

3. Cation Distribution

The cation distribution was measured on the spinel solid solutions prepared at 800°C under 20 kb and on some prepared under atmospheric pressure. The present results indicate that Ge^{4+} ions always occupy the tetrahedral sites. All solid solutions in the present system have the cation distribution of (Ge) $[Mg_xCo_{1-x}]_2O_4$ with $u = 0.375$.

It has been shown by the same method that Co_2GeO_4 is normal spinel (*1*) and that the coexistence of Ge^{4+} and Co^{2+} ions in the same tetrahedral sites is unfavorable (*2*). On the spinel Mg_2GeO_4, two distinct results have been reported, inversed (*3*) and normal (*4*, *8*, *9*), on the basis of X-ray intensities and infrared spectrum. The present result shows that Mg_2GeO_4 is normal with $u = 0.375$.

4. Stability under Hydrothermal Condition

Under high pressure a small amount of water has been known to accelerate solid state reactions. In the present system, the same effect was observed at temperatures below 1000°C. However, the decomposition was also observed at high temperatures. The experimental results are summarized in Table I. Below 800°C, the spinel phase is stable over the whole composition range of the present system, even in the presence of water. The spinels obtained in the presence of water have the same lattice constant as shown in Fig. 1b. Above 1000°C, however, the decomposition of the spinel phase is observed by detecting extra phases; one was identified as enstatite from the powder pattern and another was estimated as an amorphous phase (Am.) because of the halo at low diffraction angles. The amorphous phase was difficult to detect at 1000°C, probably because of its small amount, even though it was formed in the specimen. Without water, such decomposition of spinel was not observed even at 1200°C (Table 1). No decomposition of Co_2GeO_4 spinel was observed even with water at 1200°C. In the specimens (3 mm in diameter and 10 mm long) of the spinel solid solutions heat treated above 1200°C under pressure, a distribution in color along the radial direction was observed; the periphery changing to white, the central part remaining pink (the color of spinel phase), and the middle part having a dark pink color. The enstatite phase was preferentially observed in the middle part in addition to the original spinel phase and the amorphous phase in the peripheral white part. Any appreciable change in the lattice constant of the spinel phase was not detected even after

TABLE I

EXPERIMENTAL RESULTS UNDER HIGH PRESSURE

Starting material	T(°C)	P(kb)	t(hr)	Water(wt%)	Phase identified[a]
Mg_2GeO_4 (Ol.)	600	20	5	10	Sp. ($a_0 = 8.241$ Å)
	800	20	24	10	Sp.
	1000	20	24	10	Sp. + En.
	1100	20	24	10	Sp. + En.
	1200	20	24	10	Sp. + En. + Am.
	1300	20	24	10	Sp. + En. + Am.
$Co_{0.2}Mg_{1.8}GeO_4$ (Ol.)	800	20	5	10	Sp. ($a_0 = 8.253$ Å)
	1000	20	5	10	Sp. + En.
	1200	20	5	10	Sp. + En. + Am.
$Co_{0.4}Mg_{1.6}GeO_4$ (Ol.)	800	20	5	10	Sp. ($a_0 = 8.261$ Å)
	1200	20	24	10	Sp. + En. + Am.
	1200	20	24	0	Sp.
$Co_{0.5}Mg_{1.5}GeO_4$ (Ol.)	1200	20	24	10	Sp. + En. + Am.
Co_2GeO_4 (Sp.)	800	20	5	10	Sp. ($a_0 = 8.318$ Å)
	1200	20	24	10	Sp.

[a] Ol.: olivine, Sp: spinel, En.: enstatite, Am.: amorphous.

starting the decomposition. From these results, we propose the following decomposition reaction for Mg_2GeO_4 spinel,

$$Mg_2GeO_4\,(Sp.) + H_2O \rightarrow MgGeO_3\,(En.) + Mg(OH)_2\,(Am.).$$

This decomposition reaction probably occurs due to the high basicity of the Mg^{2+} ion. For the spinel solid solutions, it seems likely that the Mg^{2+} ions are preferentially extracted from the spinel structure by water and the Co-containing enstatite phase is formed.

The present results agree with those by Ringwood and Seabrook (*10*) which show the stability of $MgGeO_3$ (En.) and Co_2GeO_4 (Sp.) under high pressure.

References

1. H. FURUHASHI, M. INAGAKI, AND S. NAKA, *J. Inorg. Nucl. Chem.* **35**, 3009 (1973).
2. H. FURUHASHI, M. INAGAKI, AND S. NAKA, *J. Inorg. Nucl. Chem.* **35**, 3707 (1973).
3. F. DACHILLE AND R. ROY, *Amer. J. Sci.* **258**, 225 (1960).
4. P. TARTE, *Spectrochim. Acta* **19**, 23, 49 (1963).
5. S. NAKA, T. HANAWA, AND T. NODA, *Nippon Kagaku Kaishi*, 722 (1972).
6. A. NAVROTSKY, *J. Solid State Chem.* **6**, 21 (1973).
7. A. NAVROTSKY, *J. Solid State Chem.* **6**, 42 (1973); **12**, 12 (1975).
8. A. DURIF-VARAMBON, E. F. BERTAUT, AND R. PAUTHENET, *Ann. Chim.* **13**, 525 (1956).
9. D. REINEN, *Z. Anorg. Allg. Chem.* **356**, 172 (1968).
10. A. E. RINGWOOD AND M. SEABROOK, *J. Geophys. Res.* **68**, 4601 (1963).