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Thermodynamic Relations among Olivine, Spinel, and Phenacite Structures in Silicates and Germanates. IV. The System ZnO–MgO–GeO_2

A. NAVROTSKY

Department of Chemistry, Arizona State Unviersity, Tempe, Arizona 85281

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Phase relations in the system ZnO–MgO–GeO_2 were determined at 1200°C in air. Subsolidus phase relations along the pseudobinary join Zn_2GeO_4–Mg_2GeO_4 were determined between 700 and 1200°C, the portion below 900°C was obtained hydrothermally. Only one spinel phase is formed at low temperatures; this phase extends from Mg_2GeO_4 to $(Mg_{0.73}Zn_{0.27})_2GeO_4$ at 820°C. Its highest temperature of stability is 880°C, with a composition of $(Mg_{0.75}Zn_{0.25})_2GeO_4$. The free energies of transformation from the olivine to the phenacite structures at 1200°C are estimated to be $+6 \pm 1.0$ kcal/mole and -10 ± 1.5 kcal/mole for Mg_2GeO_4 and Zn_2GeO_4, respectively.

I. Introduction

In previous communications (*1–3*) we reported subsolidus phase equilibrium studies of the systems CoO–MgO–GeO_2, NiO–MgO–GeO_2, CoO–ZnO–GeO_2, NiO–ZnO–GeO_2, and CuO–MgO–GeO_2. Phase relations in these systems were used to calculate approximate activity–composition relations along the orthogermanate pseudobinary joins and to estimate the free energies of olivine–spinel and phenacite–spinel transformations in the M_2GeO_4 end-members. The present work extends such studies to the system MgO–ZnO–GeO_2, which is interesting in several respects. Firstly, because Mg_2GeO_4 is dimorphic (*4*) (olivine above 810°C, spinel below) while Zn_2GeO_4 has the phenacite structure, one expects each of these 3 phases to have some temperature–composition field of stability along the Mg_2GeO_4–Zn_2GeO_4 join at atmospheric pressure, making this system rather unusual among silicates and germanates. Study of phase relations and thermodynamics might be expected to provide semiquantitative estimates of the relative stability of these three structures as a function of composition. Secondly, a second distinct spinel phase, probably with an "inverse" action distribution, $Zn(MGe)O_4$ is found in the cobalt- and nickel-containing systems near $X_{Zn_2GeO_4} = 0.5$ (*2*). Its possible existence in the analogous magnesium-containing system should be investigated. Thirdly, the corresponding silicate sgstem, MgO–ZnO–SiO_2 has been studied (*5*, *6*), and rather large terminal solubilities have been found between Mg_2SiO_4 and Zn_2SiO_4, making the comparison of silicate and germanate interesting. Lastly, since $ZnSiO_4$, and $ZnGeO_3$ exist only at high pressures (*7*), study of the $(MgZn)GeO_3$ partial solid solution may offer an alternative way of estimating the free energy of formation of $ZnGeO_3$.

This study, then, presents an isothermal section of the MgO–ZnO–GeO_2 phase diagram at 1200°C. At this temperature approximate activity–composition relations in the bonding MgO–ZnO system are known (*8*). In addition, we have studied the Mg_2GeO_4–Zn_2GeO_4 join as a function of temperature to map out the existence of the low temperature spinel phase(s).

2. Experimental

The procedures used were essentially the same as those described previously (*1–3*). Starting materials were reagent grade MgO, ZnO, and GeO_2, dried at 1000°C before use.

Approximately 1 g samples of appropriate compositions were weighed out, ground together under acetone, prereacted for 48 hr at 1000°C and ground again. Small samples of this prereacted material were equilibrated in air in a globar quench furnace for runs above 1000°C and in sealed 70Ag–30Pd capsules hydrothermally at 0.5 kbar water pressure for the experiments below 1000°C. Phases were identified by X-ray diffraction and the attainment of equilibrium was checked as before. The typical duration of a run was 3–5 days at temperatures above 850°C and 7–14 days at the lower temperatures.

TABLE I

EXTENT OF TERMINAL SOLID SOLUTIONS IN SYSTEMS ZnO–MgO–GeO_2 AND ZnO–MgO–SiO_2 AT 1200°C

	ZnO–MgO–GeO_2, 1200°C, this work		ZnO–MgO–SiO_2 1200°C, Sarver and Hummel	
	(a)[a]	(b)[b]	(a)[a]	(b)[b]
MO	0.04	0.28	0.04	0.34
M_2XO_4	0.31	0.12	0.39	0.21
MXO_3	—	0.05	—	0.32

[a] $\left(\frac{Mg}{Zn + Mg}\right)$ in Zn-rich phase: zincite or phenacite.

[b] $\left(\frac{Zn}{Zn + Mg}\right)$ in Mg-rich phase: rocksalt, olivine, or pyroxene.

3. Results and Discussion

3.1. *Isothermal Section in the System MgO–ZnO–GeO_2 at 1200 ± 2°C*

This section of the ternary phase diagram is shown in Fig. 1. A comparison with the data of Sarver and Hummel (5) for the system ZnO–MgO–SiO_2 shows that terminal solubility in the ternary phases is significantly smaller in the GeO_2-containing system (see Table I). For the join ZnO–MgO, our data are in fair agreement with those of Sarver and Hummel, although we find the solubility of ZnO in MgO to be somewhat smaller (28 mole%) than they report (34 mole%). The very small extent (5% $ZnGeO_3$) of the pyro-

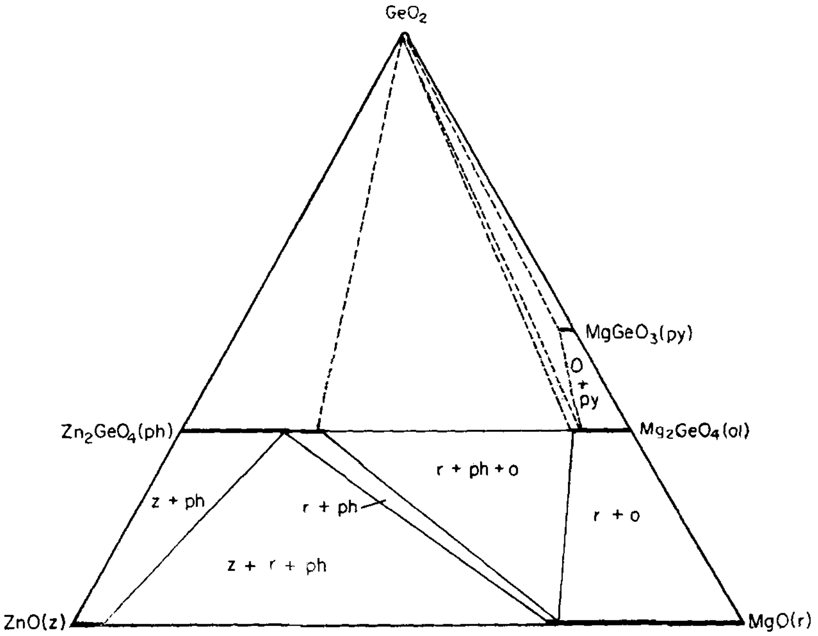

FIG. 1. Isothermal section of the system ZnO–MgO–GeO_2 at 1473°K. A liquid rich in GeO_2 is present in assemblages with $X_{GeO_2} > 0.5$. Symbols: z = zincite, r = rocksalt, ph = phenacite, o = olivine, py = pyroxene.

xene solid solution in the germanate contrasts with the incorporation of 32% $ZnSiO_3$ into $MgSiO_3$. A possible explanation for this difference may be as follows. $ZnSiO_3$ pyroxene is stable above about 30 kbar pressure (*7*). In the ZnO–GeO_2 system, an ilmenite polymorph of $ZnGeO_3$ appears at high pressure, but no pyroxene is formed (*7*). It is possible that the pyroxene form of $ZnGeO_3$ is considerably less stable than the ilmenite, which would be consistent with a small solubility of $ZnGeO_3$ in $MgGeO_3$.

The small variation of lattice parameter within the olivine, phenacite, and rocksalt phases precluded the accurate determination of tie lines within each 2 phase region. Therefore, the calculation of activity–composition relations along the pseudobinary join Mg_2GeO_4– Zn_2GeO_4 is not possible. A crude estimate of the free energy of transformation of Zn_2GeO_4 to the olivine and Mg_2GeO_4 to the phenacite structure can be made if one assumes that, within each single phase region, the solute obeys Henry's Law and the solvent obeys Raolt's Law.

Then

$$\gamma_{ZnG_{0.5}O_2} \text{ (in olivine)} = \text{constant} = \frac{X_{Zn_2GeO_4(ph)}}{X_{Zn_2GeO_4(ol)}} = \frac{0.69}{0.12} = 5.75 \qquad (1)$$

and

$$\gamma_{MgGe_{0.5}O_2} \text{ (in phenacite)} = \text{constant} = \frac{X_{Mg_2GeO_4(ol)}}{X_{Mg_2GeO_4(ph)}} = \frac{0.88}{0.31} = 2.84, \qquad (2)$$

where the mole fraction, X, refers to terminal solubilities, and γ is the activity coefficient of the solute. Then, for the reaction

$$Zn_2GeO_4(ph) \rightarrow Zn_2GeO_4(ol)$$

$$\Delta G^\circ = 2RT \ln \gamma_{ZnGe_{0.5}O_2(ol)}$$
$$= 10._2 \text{ kcal/mole } (\pm \sim 1.5 \text{ kcal/mole}) \qquad (3)$$

and for

$$Mg_2GeO_4(ol) = Mg_2GeO_4(ph)$$

$$\Delta G^\circ = 2RT \ln \gamma_{MgGe_{0.5}O_2(ph)}$$
$$= 6._1 \text{ kcal/mole } (\pm \sim 1.0 \text{ kcal/mole}). \qquad (4)$$

The uncertainties in these values are hard to assess quantitatively, but estimated limits of error are given above.

These values, although very approximate, appear reasonable when compared with previous work. We found, for the reaction $Mg_2GeO_4(ol) \rightarrow Mg_2GeO_4(sp)$ at 1473°K, $\Delta G^\circ = +1.6$ kcal/mole (1). Thus, the phenacite structure lies considerably above the olivine and spinel structures in free energy for Mg_2GeO_4. For Zn_2GeO_4, the olivine and spinel structures lie at rather comparable (free) energies above the phenacite (10.2 kcal at 1473°K and 12.6 kcal at 1323°K (2), respectively).

3.2. The System Zn_2GeO_4–Mg_2GeO_4 as a Function of Temperature

The results are shown in Fig. 2. The runs at 1000°C and above were carried out in air,

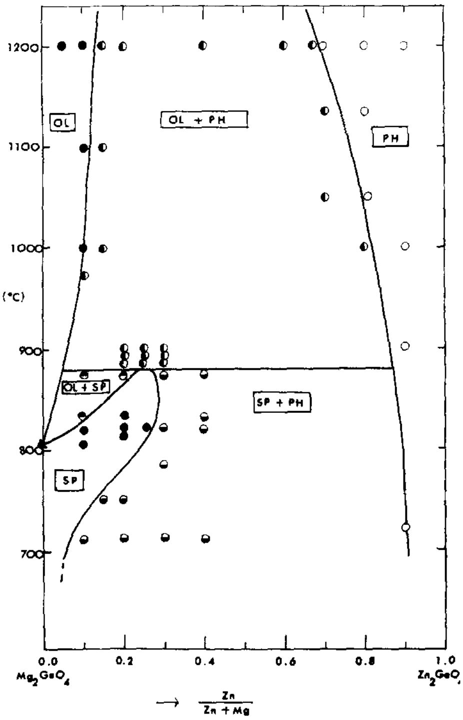

FIG. 2. Subsolidus phase relations in Zn_2GeO_4–Mg_2GeO_4. Points above 900°C determined in air, points below 900°C determined hydrothermally at 0.5 kbar water pressure. Symbols: filled circles = spinel or olivine; open circles = phenacite; vertically divided circles = olivine plus phenacite; horizontally divided circles = spinel plus olivine or spinel plus phenacite.

those below 900°C were done hydrothermally at 0.5 kbar water pressure. For this discussion we shall neglect the small effect of the difference in pressure on the phase diagram.

As seen from Fig. 2, at low temperatures, only one spinel phase is formed; that is the one derived from Mg_2GeO_4 by zinc substitution. There is no evidence for a second spinel near $X_{Zn_2GeO_4} = 0.5$, such as is formed in the analogous cobalt and nickel systems. The reason for this difference is not known. The substitution of zinc into the spinel phase permits the retention of a stability field for that structure up to about 880°C, as compared to 810°C for the olivine–spinel transition in Mg_2GeO_4 (4). This would suggest either that Zn_2GeO_4 spinel is somewhat more stable than Zn_2GeO_4 olivine (which our data at 1200°C do not seem to support) or that the spinel phases of intermediate composition are stabilized, such as by additional configurational disorder involving Zn, Mg, and Ge, relative to Zn-substituted olivines.

Acknowledgments

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