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Thermodynamic Relations Among Olivine, Spinel, and Phenacite Structures in Silicates and Germanates: II. The Systems NiO–ZnO–GeO_2 and CoO–ZnO–GeO_2

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Activity–composition relations along the orthogermanate joins of the systems NiO–ZnO–GeO_2 and CoO–ZnO–GeO_2 at 1050°C have been determined from the phase diagrams and the location of conjugation lines between oxide and orthogermanate phases. In each system, a second distinct spinel phase near $X_{Zn_2GeO_4} = 0.5$ is observed in addition to the terminal spinel and phenacite solid solution. The free energies of transformation from the spinel to the phenacite structure are estimated to be +23, +12.7, and −12.6 kcal/mole for Ni_2GeO_4, Co_2GeO_4, and Zn_2GeO_4, respectively.

Introduction

The preceding paper in this series presented experimental phase equilibrium data on the systems NiO–MgO–GeO_2 and CoO–MgO–GeO_2 (*1*) as part of a systematic study of stability relations among olivine, spinel, and phenacite structures in germanates and silicates of the stoichiometry A_2XO_4. The present communication deals with the systems NiO–ZnO–GeO_2 and CoO–ZnO–GeO_2, in which both phenacite and spinel structures appear at atmospheric pressure, and from which the free energy of the spinel → phenacite transition in the three end-members Ni_2GeO_4, Co_2GeO_4, and Zn_2GeO_4 can therefore be estimated.

Previous work related to these systems includes the measurement of the enthalpies of formation of the three orthogermanates (*3*), the determination of activity–composition relations and of free energies of transformation from rocksalt to zincite structures in the binary systems NiO–ZnO and CoO–ZnO (*4*), and the transformation of Zn_2GeO_4 at high pressures from the phenacite to both a distorted and a cubic spinel modification (*5*, *6*). The pseudobinary systems Ni_2GeO_4–Zn_2GeO_4 and Co_2GeO_4–Zn_2GeO_4 have been studied by Reinen (*7*), who found considerable solid solubility of Zn_2GeO_4 in the terminal spinel phases and, in addition, a second spinel phase of some width near $X_{Zn_2GeO_4} = 0.50$ in both systems, which was separated from the terminal spinel phase by a distinct two-phase region. This second spinel had significantly larger lattice constants than the terminal spinel and was postulated by Reinen (*7*) to have a cation distribution approximately $Zn[GeA]O_4$ as compared to $Ge[A_{2-x}Zn_x]O_4$ for the zinc-poor spinel. Substantial solubility of Co_2GeO_4, but not of Ni_2GeO_4, in Zn_2GeO_4 was found.

The present work examines these zinc-containing germanate systems in more detail. Subsolidus isothermal sections at 1050°C of the two ternary systems have been determined. Compatibility relations and several conjugation lines in the two phase regions in the AO–ZnO–A_2GeO_4–Zn_2GeO_4 quadrilateral were found. From these relations and from the previously determined activity–composition curves in the binary AO–ZnO systems (*4*), activity–composition relations along each A_2GeO_4–Zn_2GeO_4 join have been calculated and the few energies of structural transformation estimated.

Experimental

The temperature of 1050°C was chosen because the zinc-containing systems were found to reach equilibrium rapidly, because loss of zinc

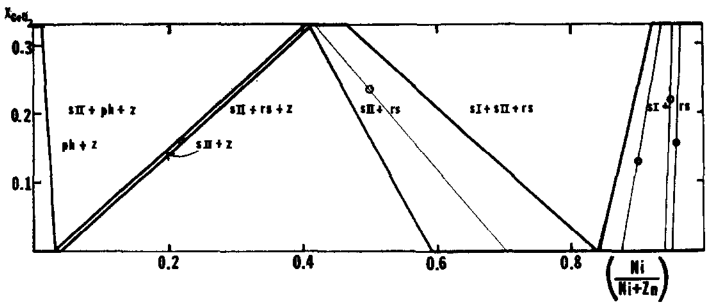

FIG. 1. Isothermal section at 1050°C in air of NiO–ZnO–Ni$_2$GeO$_4$–Zn$_2$GeO$_4$ quadrilateral. Open circles indicate compositions of samples used to find conjugation lines in the two-phase regions.

through vaporization in air was negligible, and because the binary activity–composition relations had already been determined at that temperature. Starting materials were reagent grade NiO, ZnO, Co$_3$O$_4$, and hexagonal GeO$_2$, all dried at 850°C before use. The preparation, equilibration, quenching, and phase determination of samples were done as before (*1*). All experiments were performed in a kanthal-wound vertical tube furnace at 1050 ± 2°C in air. Equilibration times were 48–72 hr, and the attainment of equilibrium was checked as previously (*1*). The compositions of coexisting spinel and rocksalt phases were established by measurement of the lattice parameters of the rocksalt phase.

Results

Phase Relations

Isothermal sections at 1050°C in the quadrilaterals NiO–ZnO–Ni$_2$GeO$_4$–Zn$_2$GeO$_4$ and CoO–ZnO–Co$_2$GeO$_4$–Zn$_2$GeO$_4$ are shown in Figs. 1 and 2. The existence and extent of the two distinct spinel phases present in each system and labeled SI and SII agree with the observations of Reinen (*7*). The solubility of Ni$_2$GeO$_4$ in the phenacite structure is much smaller than that of Co$_2$GeO$_4$, just as the solubility of NiO in ZnO is smaller than that of CoO. The solubility of Co$_2$GeO$_4$ in Zn$_2$GeO$_4$ (~19 mole% at 1050°C) is substantially less than in the corresponding silicate system, where the solubility of Co$_2$SiO$_4$ (olivine) in Zn$_2$SiO$_4$ (phenacite) is close to 50 mole% at 1300°C (*8*). This probably reflects the difference in the structures of Co$_2$GeO$_4$ and Co$_2$SiO$_4$ at atmospheric pressure and also the fact that the enthalpy of formation of Co$_2$GeO$_4$ (sp) is some 3.5 kcal more *negative* than that of Zn$_2$GeO$_4$ (ph), while that of Co$_2$SiO$_4$ (ol) is some 3.5 kcal/mol more *positive* than that of Zn$_2$SiO$_4$ (*3*).

Lattice Parameters

The variation of lattice constant with composition in both spinel phases in each system is shown in Table I. These data agree well with those of Reinen (*7*). The small extent of each spinel phase does not permit an accurate extrapolation of lattice parameters to $X_{Zn_2GeO_4} = 1$, but if one dares such an extrapolation, the values shown are obtained, which give, for the spinel form of Zn$_2$GeO$_4$, an average value of a_0 equal to 8.35 ± 0.01 Å. The cubic spinel phase characterized by Syono et al. (*2*) has $a_0 = 8.350$ Å, with which these extrapolations are in fortuitously good agreement. It is interesting that, within the rather large limits of error here, the extrapolations from the spinel I and spinel II phases give the

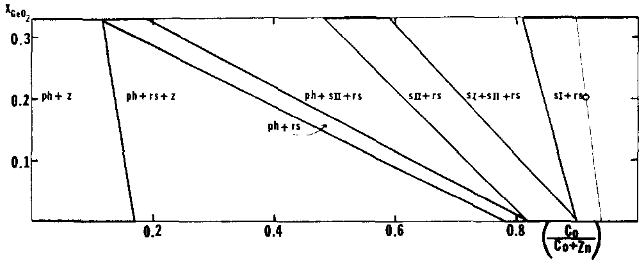

FIG. 2. Isothermal section at 1050°C in air of CoO–ZnO–Co$_2$GeO$_4$–Zn$_2$GeO$_4$ quadrilateral.

TABLE I

LATTICE PARAMETERS OF SPINELS IN SYSTEMS A_2GeO_4–Zn_2GeO_4[a]

$X_{Zn_2GeO_4}$	Phase(s)	a_0 (Å)
	Ni_2GeO_4–Zn_2GeO_4	
0.000	SI	8.221
0.035	SI	8.225
0.065	SI	8.230
0.200	SI + SII	8.231, 8.309
0.550	SII	8.310
0.600	SII + tr ph	8.312
1.000	—	8.36_2[b]
1.000	—	8.34_5[c]
1.000	—	8.350[d]
	Co_2GeO_4–Zn_2GeO_4	
0.000	SI	8.317
0.100	SI	8.319
0.200	SI + tr SII	8.321
0.400	SI + SII	8.321, 8.348
0.500	SII	8.350
0.700	SII + ph	8.353
1.000	—	8.33_8[b]
1.000	—	8.35_0[c]

[a] A = Ni, Co.

[b] Extrapolated from variation of lattice constant with composition in SI.

[c] Extrapolated from variation of lattice constant with composition in SII.

[d] Measured on high pressure phase, Ref. (*11*).

same value of a_0. If SI and SII indeed differ in their distribution of Zn^{2+} and Ge^{4+} among octahedral and tetrahedral sites, then these data would point to a very small volume change on disordering.

The lattice parameters in the rocksalt phases (NiZn)O and (CoZn)O have been discussed previously (*4*).

Thermodynamic Calculations and Discussion

Activity–Composition Relations

The equilibrium between oxide and orthogermanate at constant temperature and pressure may be written:

$$(AO)_{ss} + (ZnGe_{0.5}O_2)_{ss} = (ZnO)_{ss} + (AGe_{0.5}O_2)_{ss}, \quad (1)$$

where A = Ni or Co. Then

$$-2.3\,RT\log K = \tfrac{1}{2}(\Delta G^\circ_{A_2GeO_4\,(sp)} - \Delta G^\circ_{Zn_2GeO_4\,(ph)}), \quad (2)$$

and $\log K$ may be expressed as

$$\log K = \log C + \log \gamma_{AGe_{0.5}O_2} - \log \gamma_{ZnGe_{0.5}O_2}, \quad (3)$$

where

$$C = a_{ZnO} X_{AGe_{0.5}O_2} / a_{AO} X_{ZnGe_{0.5}O_2}. \quad (4)$$

Values of C are calculable from the measured coexisting compositions (conjugation lines) of orthogermanate plus oxide samples and the previously determined activity–composition relations in the binary systems AO–ZnO (*4*). The results are shown in Table II. In the NiO-containing system, the spinel II phase ($X_{Ni_2GeO_4} = 0.40_5$–0.45_5) participates in three 3-phase and two 2-phase regions, and the accuracy with which its composition at each boundary can be determined is limited by the narrow range of composition of the spinel. However, a rather large number of samples run in that region has permitted these boundaries to be drawn as shown, and consistent values of $\log C$ have been obtained. Several conjugation lines in two phase regions involving the (NiZn)O rocksalt phase could easily be determined because of the substantial variation of lattice parameter in that phase (*4*), while the much smaller variation of lattice constant in (CoZn)O (*4*) greatly limited the possibility of accurate tie line measurement.

Activity–composition relations in the orthogermanates were calculated by methods described previously (*1*, *9*). The appropriate equations in this case are

$$\log \gamma_{AGe_{0.5}O_2} = -(1 - X)\log C + \int_X^1 \log C\, dX, \quad (5)$$

and

$$\log \gamma_{ZnGe_{0.5}O_2} = X \log C - \int_0^X \log C\, dX, \quad (6)$$

where $X = X_{AGe_{0.5}O_2}$.

The integrations are made somewhat more complicated by the existence of a number of two-phase regions: rocksalt plus zincite, spinel II plus spinel I, and spinel II plus phenacite. These calculations, using the smoothed values of $\log C$ and composition increments shown, are summarized in Table III. The resulting activity–composition relations are plotted in Figs. 1 and 2. Activities in the single phase regions of (CoZn)-$Ge_{0.5}O_2$ are shown as dashed curves because of the previously mentioned difficulty in getting accurate conjugation lines.

TABLE II

CALCULATION OF LOG *C* FROM CONJUGATION LINES

$X_{AGe_{0.5}O_2}$[a]	Phases	X_{AO}[a]	a_{AO}[b]	a_{ZnO}[b]	C[c]	$\log C$
	$(NiO)_{ss} + (ZnGe_{0.5}O_2)_{ss} = (ZnO)_{ss} + (NiGe_{0.5}O_2)_{ss}$, 1050°C, air					
0.01	sII + ph + z	0.02_7	0.79	0.97_3	0.012	−1.90[d]
0.40_5	sII + ph + z	0.02_7	0.79	0.97_3	0.838	−0.078[e]
0.41_0	sII + rs + z	0.03, 0.59	0.82	0.97	0.825	−0.083[e]
0.41_5	sII + rs	0.70	0.83	0.94	0.804	−0.094[e]
0.45_5	sII + sI + rs	0.84	0.89	0.78	0.731	−0.134[e]
0.92_5	sII + sI + rs	0.84	0.89	0.78	10.7	+1.03[f]
0.93_7	sI + rs	0.88	0.92	0.68	11.0_5	+1.04[f]
0.95_8	sI + rs	0.94	0.96	0.47	11.0	+1.04[f]
0.96_7	sI + rs	0.95_5	0.96_2	0.41	12.2	+1.09[f]
	$(CoO)_{ss} + (ZnGe_{0.5}O_2)_{ss} = (ZnO)_{ss} + (CoGe_{0.5}O_2)_{ss}$, 1050°C, air					
0.12	ph + rs + z	0.17, 0.78	0.87	0.83	0.129	−0.888[d]
0.19	sII + ph + rs	0.82	0.90	0.74	0.193	−0.714[d]
0.48	sII + ph + rs	0.82	0.90	0.74	0.760	−0.120[e]
0.59	sII + sI + rs	0.90	0.92	0.52	0.814	−0.086[e]
0.81	sII + sI + rs	0.90	0.92	0.52	2.41	+0.382[f]
0.90	sI + rs	0.94	0.95	0.43	3.20	+0.600[f]

[a] Coexisting compositions determined from lattice parameters.

[b] From Ref. (*4*).

[c] $C = a_{ZnO}a_{AGe_{0.5}O_2}/a_{AO}a_{ZnGe_{0.5}O_2}$.

[d] In phenacite phase.

[e] In spinel II.

[f] In spinel I.

TABLE III

ACTIVITY COEFFICIENTS IN SYSTEMS A_2GeO_4–Zn_2GeO_4 (A = Ni, Co) at 1050°C

$X_{AGe_{0.5}O_2}$	$\log C$[d]	$\log \gamma_{ZnGe_{0.5}O_2}$	$\log \gamma_{AGe_{0.5}O_2}$	$\log K$
	Ni_2GeO_4–Zn_2GeO_4, 1050°C, air			
0.00[a]	(−1.90)	0.00	(1.89)	−0.01
0.01[a]	−1.90	0.00	1.89	−0.01
0.405[b]	−0.08	0.22	0.28	−0.02
0.420[b]	−0.10	0.21	0.29	−0.02
0.440[b]	−0.12	0.20	0.30	−0.02
0.455[b]	−0.13	0.20	0.31	−0.02
0.925[c]	+1.03	1.06	0.002	−0.02
0.950[c]	+1.05	1.06	0.001	−0.01
0.975[c]	+1.08	1.07	0.000	+0.01
1.000[c]	(+1.10)	1.10	0.000	±0.00
	Co_2GeO_4–Zn_2GeO_4, 1050°C, air			
0.00[a]	(−1.18)	0.00	1.05	−0.13
0.12[a]	−0.89	0.02	0.79	−0.12
0.19[a]	−0.71	0.03	0.61	−0.13
0.48[b]	−0.12	0.22	0.21	−0.13
0.59[b]	−0.09	0.24	0.21	−0.14
0.81[c]	+0.38	0.57	0.06	−0.13
0.90[c]	+0.60	0.73	0.01	−0.14
1.00[c]	(+0.84)	0.99	0.00	−0.15

[a] In phenacite.

[b] In spinel II.

[c] In spinel I.

[d] Smoothed values.

Free Energies of Transformation Among Spinel and Phenacite Structures in Ni_2GeO_4, Co_2GeO_4, and Zn_2GeO_4

The limiting activity coefficients of Ni_2GeO_4 and Co_2GeO_4 in the phenacite phase and of Zn_2GeO_4 in the terminal spinel can be used, as before, to estimate their free energies of transformation to those structures. Thus for the reaction

$$Ni_2GeO_4\ (sp) = Ni_2GeO_4\ (ph), \qquad (7)$$

$$\Delta G^\circ = 2 \times 2.3\,RT \log \gamma^\circ_{NiGe_{0.5}O_2} = 23\ \text{kcal}, \qquad (8)$$

which for

$$Co_2GeO_4\ (sp) = Co_2GeO_4\ (ph), \qquad (9)$$

$$\Delta G^\circ = 2 \times 2.3\,RT \log \gamma^\circ_{CoGe_{0.5}O_2} = 12.7\ \text{kcal}. \qquad (10)$$

The much larger value for Ni_2GeO_4 than for Co_2GeO_4 is readily understood, since in the phenacite structure all cations are tetrahedrally coordinated. For both these compounds the phenacite structure is energetically considerably less favorable than the olivine (*1*), while the spinel is by far the most stable structure, especially for Ni_2GeO_4. For the transition

$$Zn_2GeO_4\ (ph) = Zn_2GeO_4\ (sp), \qquad (11)$$

$$\Delta G^\circ = 2 \times 2.3\,RT \log \gamma^\circ_{ZnG_{0.5}O_2}. \qquad (12)$$

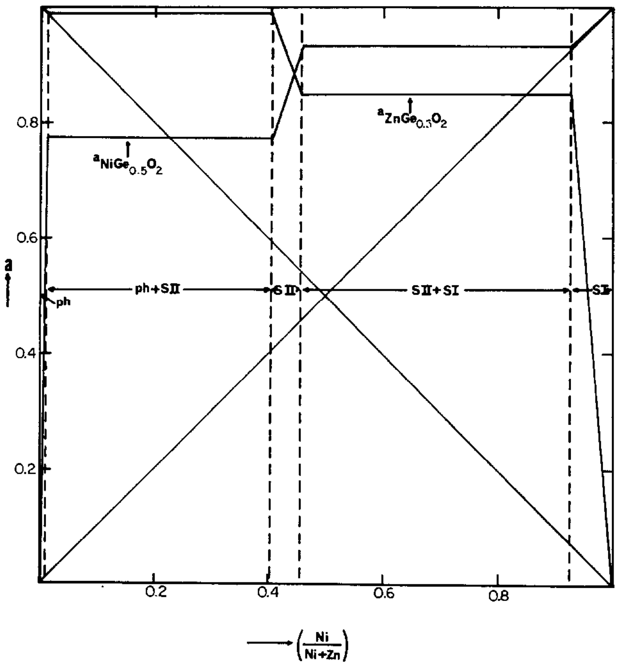

FIG. 3. Activity–composition relations in system Ni_2GeO_4–Zn_2GeO_4 at 1050°C.

From the system NiO–ZnO–GeO_2, $\log\gamma^{\circ}_{ZnGe_{0.5}O_2} = 1.10$ and $\Delta G^{\circ} = 13.4$ kcal, while from CoO–ZnO–GeO_2, $\log\gamma^{\circ}_{ZnGe_{0.5}O_2} = 0.99$ and $\Delta G^{\circ} = 11.8$ kcal. The agreement between these two values is satisfactory when one considers the inaccuracies inherent in both sets of data. An average value of

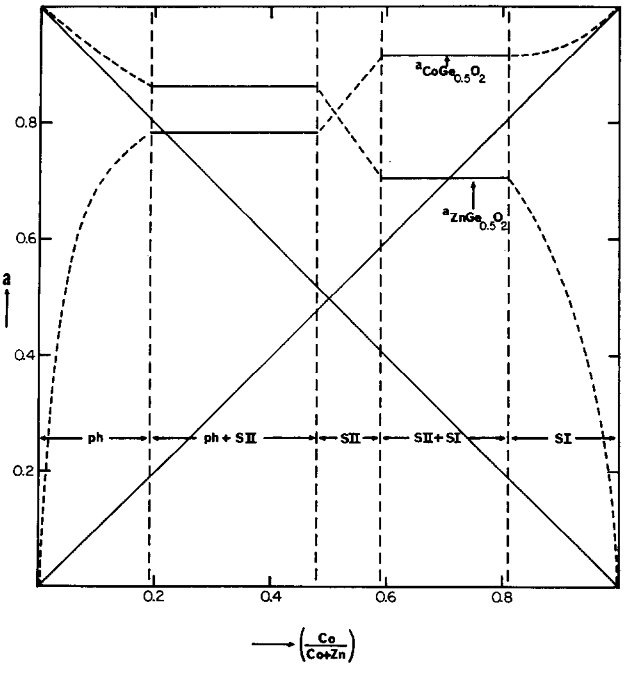

FIG. 4. Activity–composition relations in system Co_2GeO_4–Zn_2GeO_4 at 1050°C.

12.6 ± 1 kcal will be considered in further discussions. This value refers to the formation of the normal spinel, $Ge[Zn_2]O_4$.

We have recently calculated (*3*) a value of 11.6 kcal from the high pressure data of Rooymans (*5*). This is in general agreement with the present values, though our average value is perhaps somewhat higher. It is possible that the high-pressure modification of Zn_2GeO_4 may indeed be the "spinel II" or inverse spinel, $Zn[ZnGe]O_4$. This is suggested by the observation both by Ringwood and Major (*6*) and by Syono et al. (*2*) of a tetragonally distorted spinel at lower temperatures in the high pressure experiments. This distortion might be attributed to the ordering of Zn^{2+} and Ge^{4+} on octahedral sites, which could not occur in a normal spinel. Thus it appears probable that the normal and inverse spinel forms of Zn_2GeO_4 are very similar in energy, with the inverse modification being perhaps slightly more stable. A random or highly disordered cation distribution would seem very likely, then, for any samples prepared at high temperature. These data would lead us to suggest that, in the spinel structure, the octahedral site preference energies (*10*) of Zn^{2+} and of Ge^{4+} are quite similar.

It is instructive to compare these observations with those of Syono et al. (*2*) on the zinc silicates, and to concur with those authors that the similarity in the behavior of germanates and silicates breaks down in the case of zinc. The complex behavior of the zinc silicates at high pressures presumably results because Si^{4+} is too small to favorably occupy the tetrahedral sites in the spinel structure, while it has too great a preference, energetically speaking, for tetrahedral coordination to occupy the octahedral sites.

Free Energies of Formation of Germanates

Once more (*1*), only relative values of the free energies of formation from the oxides can be estimated. From the data in Table III and Eq. (2), we get

$$\Delta G^\circ_{Ni_2GeO_4\,(sp)} - \Delta G^\circ_{Zn_2GeO_4\,(ph)} = +0.1 \text{ kcal}, \quad (13)$$

and

$$\Delta G^\circ_{Co_2GeO_4\,(sp)} - \Delta G^\circ_{Zn_2GeO_4\,(ph)} = +1.6 \text{ kcal}. \quad (14)$$

The latter value, in particular, is to be regarded as only approximate, as are the activity–composition relations in the cobalt-containing system.

Acknowledgments

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