Acta Chemica Scandinavica, 1996: 50: 1102–1107
Printed in UK – all rights reserved

ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

Phase Relations and Activities of (Mn, Ni)-Olivine Solid Solution in the Ternary System $MnO–NiO–SiO_2$

Jian-Hong Huang, Dan Boström and Erik Rosén*

Department of Inorganic Chemistry, Umeå University, S-901 87 Umeå, Sweden

Huang, J.-H. Boström, D. and Rosén, E., 1996. Phase Relations and Activities of (Mn, Ni)-Olivine Solid Solution in the Ternary System $MnO–NiO–SiO_2$. – Acta Chem. Scand. 50: 1102–1107. © Acta Chemica Scandinavica 1996.

Phase relations involving tie-lines between (Mn, Ni)O and $(Mn, Ni)_2SiO_4$ solid solutions in the ternary system $MnO–NiO–SiO_2$ have been studied experimentally at 1310 K. A great number of mixtures, with various constitutions, were equilibrated and the compositions of coexisting solid-solution phases were determined by inductively coupled plasma (ICP) analysis as well as X-ray *d*-spacing measurements. The olivine phase $(Mn_{1-y}, Ni_y)_2SiO_4$ and SiO_2 occur together at compositions $0.27 \leqslant y \leqslant 1$, and the pyroxene phase $(Mn_{1-z}, Ni_z)SiO_3$ exists only in the composition range $0 \leqslant z \leqslant 0.08$. The activities in the (Mn, Ni)-olivine solid solution were derived from the tie-line data obtained at 1310 K. By using the solid-state EMF method, the activities of Ni-olivine solid solution were also determined at several compositions, $0.27 \leqslant y \leqslant 1$, in the temperature range 1140–1395 K. The activities obtained from both methods show significant positive deviations from ideality.

A ternary system $AO–BO–SiO_2$, in which AO and BO are oxides with divalent cations, such as $A = Mg^{2+}$ or Mn^{2+} and $B = Fe^{2+}$, Co^{2+} or Ni^{2+}, forms three different solid-solution series at high temperatures:[1–5] the complete series (A,B)O, with NaCl structure, and $(A,B)_2SiO_4$, with olivine structure, as well as the limited series $(A,B)SiO_3$ with pyroxene structure. For a better understanding of these multicomponent silica systems, which are frequently encountered in the field of ceramics, as well as in the processes of metallurgy, mineralogy and petrology, it is important to know the reliable phase relations and thermodynamic properties of the various phases. Concerning the ternary system $MnO–NiO–SiO_2$, activity–composition relations of the (Mn, Ni)O solid solution have been determined in the binary sub-system MnO–NiO,[6–9] whereas investigations dealing with the phase relations in this ternary system as well as activities of the olivine and pyroxene solid solutions are lacking in the literature. Therefore, it seemed of considerable interest to carry out studies on these aspects.

The aim of the present study was: (*i*) to delineate the phase relations for the system $MnO–NiO–SiO_2$ at a selected temperature, 1310 K. Specifically, the aim was to establish the tie-lines between the oxide (Mn, Ni)O and the olivine $(Mn, Ni)_2SiO_4$ solid solutions, as well as the stability range for the phase assemblage $(Mn, Ni)_2SiO_4 + SiO_2$. (*ii*) to determine activities in (Mn, Ni)-olivine from tie-line data as well as from the equilibrium oxygen partial pressures of the redox reactions

$$2Ni(s) + SiO_2(s) + O_2(g) \rightleftharpoons Ni_2SiO_4(s) \quad (I)$$

$$2Ni(s) + SiO_2(s) + O_2(g) \rightleftharpoons Ni_2SiO_4(ss) \quad (II)$$

through solid-state EMF measurements in the temperature range 1140–1395 K.

Experimental

Chemicals. The starting chemicals used in the present work were Ni, Fe, Si, Fe_2O_3 (Merck *p. a.*), as well as $MnCO_3 \cdot xH_2O$ (Merck *p. a.*), $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ and $SiO_2 \cdot aq$ (Fluka *p. a.*). Accurate amounts of Mn^{2+}, Ni^{2+} and SiO_2 present in the three latter chemicals were carefully determined by heating them separately in air at 1073 K several times until a constant weight was achieved, and then evaluation from the obtained weights of their respective products Mn_2O_3, NiO and SiO_2. The oxide NiO was synthesized from $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ by heating at 1173 K in air for 24 h, and amorphous SiO_2 was obtained by decomposition of $SiO_2(\cdot aq)$ at 1273 K in air for about 170 h. The wüstite phase 'FeO' was prepared with special care by heating a mixture of Fe and Fe_2O_3 in an evacuated Al_2O_3 tube at 1273 K for 48 h. Before use, Fe and Fe_2O_3 powders were dried at 473 and 1073 K, respectively.

All the phase identities were confirmed by means of X-ray powder diffraction.

* To whom correspondence should be addressed.

Phase relation studies. To establish the phase relations in the ternary system MnO–NiO–SiO_2 at 1310 K, a great number of equilibrated samples, as well as the separated oxide, olivine and pyroxene solid solutions, were prepared directly from the starting chemicals $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$, $MnCO_3 \cdot xH_2O$ and $SiO_2(\cdot aq)$ by mixing about 2 g of these chemicals in appropriate proportions. After that, the mixtures were finely ground in a vibration mill for 20 min and pelletized to 10 mm diameter at about 10 MPa in a steel die. The pellets were then placed in a platinum crucible, covered with a Pt foil, and heated in an 600 mm long closed-end Al_2O_3 tube at 1173 K for 48 h under reducing conditions, which was provided by flowing argon gas (1 ppm O_2) through the Al_2O_3 tube containing 5 g oxygen buffer mixture of Ni/NiO at the bottom. After this treatment, the samples were rapidly quenched to room temperature, ground, re-pelletized, and heated again at 1310 K for about 96 h in an evacuated Al_2O_3 tube with the Ni/NiO buffer mixture inside, generating an oxygen pressure of about 10^{-10} bar.[10] This procedure was checked in a preliminary run, and it was found that there was no change in composition of the phases when the total equilibrating time was more than 144 h. The furnace temperature was kept constant within 1 K in a 30 mm long zone by an electronic temperature controller Eurotherm 818. The temperature was measured with a Pt/Pt (10 mass% Rh) thermocouple. All separated solid solutions, and the phases present in the equilibrated and quenched samples, were analysed by X-ray powder diffraction using a Rigaku D/Max IIA diffractometer with filtered Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). Diffraction intensities were collected in the 2θ-range 5–90° with a scanning speed of 0.15° min^{-1}. The methods of producing and analysing X-ray powder diffraction patterns, using pure silicon ($a = 5.43088$ Å) as internal standard, were the same as those described previously.[11,12]

The compositions of the various separated solid solutions were determined by ICP (inductively coupled plasma) analysis. The values obtained were plotted against *d*-spacing data for the oxide and olivine solid solutions (Fig. 1), in which the reflections (220) and (222) were used, respectively. These 'calibration curves', which show significant negative deviations from linearity, were used to determine the compositions of the oxide and olivine solid solution phases present in the equilibrated samples. For the pyroxene solid solution with a limited composition range, due to the instability of $NiSiO_3$ at normal pressure, the (*d*-spacing)–composition relation was derived as follows: (*i*) Values of *d*(240), 2.7489 and 2.7431 Å were determined for pure $MnSiO_3$ and for solid solution $(Mn_{1-z}, Ni_z)SiO_3$ with $z = 0.05$, respectively. (*ii*) A straight line was drawn through the measured points.

Activity measurements. The activity of the Ni-olivine component in $(Mn, Ni)_2SiO_4$ solid solution was experimentally determined using the oxygen concentration cells

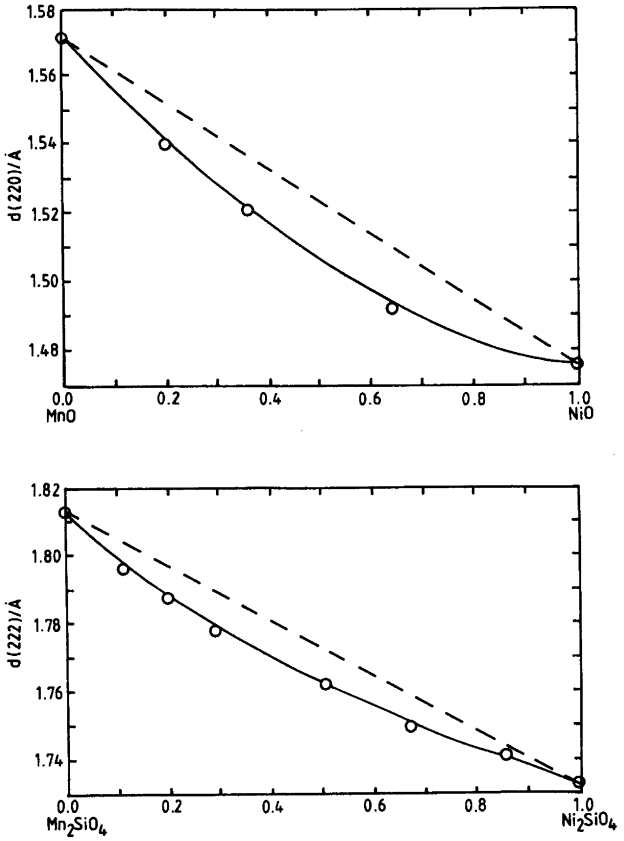

Fig. 1. Diagrams showing *d*(220) and *d*(222) values as a function of the compositions of the $(Mn_{1-x}, Ni_x)O$ and $(Mn_{1-y}, Ni_y)_2SiO_4$ solid solutions, respectively. The solid curves are drawn to fit the experimental data, given as circles; the broken lines represent the linear relationships according to Vegard's law.

with calcia-stabilized zirconia (CSZ) as the solid electrolyte. The cell configurations can be written:

Pt, O_2(g), Ni(s), SiO_2(s), Ni_2SiO_4(s) |CSZ|

reference system, O_2(g), Pt (A)

Pt, O_2(g), Ni(s), SiO_2(s), Ni_2SiO_4(ss) |CSZ|

reference system, O_2(g), Pt (B)

where Ni_2SiO_4(ss) represents the $(Mn, Ni)_2SiO_4$ solid solution with various compositions to be investigated. The reference systems used in the measurements were Fe/FeO or Ni/NiO. Two different cell arrangements were used, the 'double-tube cell' (DTC)[13] and the 'zero-point cell' (ZPC).[14] Generally, the ZPC arrangement involving Fe/FeO as reference system was found to be more advantageous. The principle of the ZPC arrangement is schematically shown in Fig. 2 (details are described in Ref. 14). As can be seen from the figure, the sample and reference systems were kept in two electrolyte tubes. To avoid any oxygen permeation through the wall of the electrolyte tube, containing the sample mixture, the oxygen pressures on both sides should be equal. This can be achieved by adjusting the ratio H_2/CO_2 of the

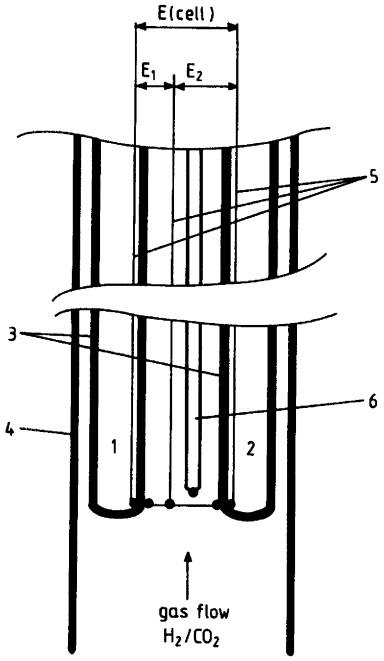

Fig.2. Principal sketch of the ZPC arrangement. (1) sample cell, (2) reference cell, (3) CSZ electrolyte tube, (4) furnace tube (Al_2O_3), (5) Pt-wire, (6) thermocouple [Pt–Pt(10 mass% Rh)].

incoming gas to generate the desired oxygen pressure. This means that $E_1 \approx 0$ (Fig. 2).

The sample mixture Ni + SiO_2 + olivine was prepared by mixing the components in an equimolar ratio, and the reference system Fe + FeO with molar ratio of 4:1. The mixtures were then placed inside the electrolyte tubes, and both cells were evacuated before a run. It should be mentioned that for the ZPC, the sample and the reference cells were also filled with some Ar gas after the evacuation to generate a total pressure in the cells of about 1 bar at high temperatures to reduce the risk for permeation of H_2 gas into the electrolyte tubes.

The cells were then heated in a vertical resistance furnace with non-inductively wound Kanthal A-1 as heating element. This furnace is also equipped with a ground-steel foil to shield the measuring equipment from electromagnetic noise. The EMF and temperature voltages were recorded by a Solartron 7075 digital voltmeter with a high impedance (10^{10} Ω).

A typical run was started at 1320 K and the cell was kept at this temperature for about 190 h to ensure equilibrium conditions to be attained. The temperature was then increased and decreased in steps of 20–40 K in several cycles in the measuring temperature range, which in general was limited to the upper working temperature (ca. 1400 K) of the furnace, and to a lower temperature of about 1150 K due to the low rate of the redox reactions. The EMF values were collected every 10 min by an automatic measurement and control system. The equilibration times were always longer than 170 h, and reproducible EMF values were obtained by approaching a temperature from both directions.

After each run, the composition of the olivine solid solution phase in the sample mixture was checked by X-ray powder diffraction. Initial olivine composition was found to be unchanged during the measurements.

Results and discussion

Phase relations. The experimentally determined phase relations in the ternary system MnO–NiO–SiO_2 at 1310 K are given in Table 1 and shown in Fig. 3. Two series of mixtures were equilibrated, one series at the mole fraction level, $X(SiO_2) = 0.58$, with two samples within the three-phase region, SiO_2 + olivine(ss) + pyroxene(ss), and the second series at the level, $X(SiO_2) = 0.18$, containing seven samples within the two-solid solution field, oxide(ss) + olivine(ss). The mole fraction of Ni^{2+} in the olivine $(Mn_{1-y}, Ni_y)_2SiO_4$ coexisting with SiO_2 varies from $y = 1.0$ to $y = 0.27$ (point A in Fig. 3), whereas the Ni^{2+} content in the pyroxene phase $(Mn_{1-z}, Ni_z)SiO_3$ covers the range from $z = 0$ to $z = 0.08$ (point B in Fig. 3). Between these two regions, there is a three-phase field containing the phases olivine, with the composition $(Mn_{0.73}, Ni_{0.27})_2SiO_4$, pyroxene, with the composition $(Mn_{0.92}, Ni_{0.08})SiO_3$, and pure SiO_2. It should be mentioned that the a couple of samples were also equilibrated at a lower temperature (1230 K) and at a higher temperature (1380 K) to determine the compositions of the points A and B. The following values were obtained: $y = 0.29$ and 0.26, $z = 0.07$ and 0.10, respectively. This indicates a slight tendency to narrow the stability range for the three-phase assemblage,

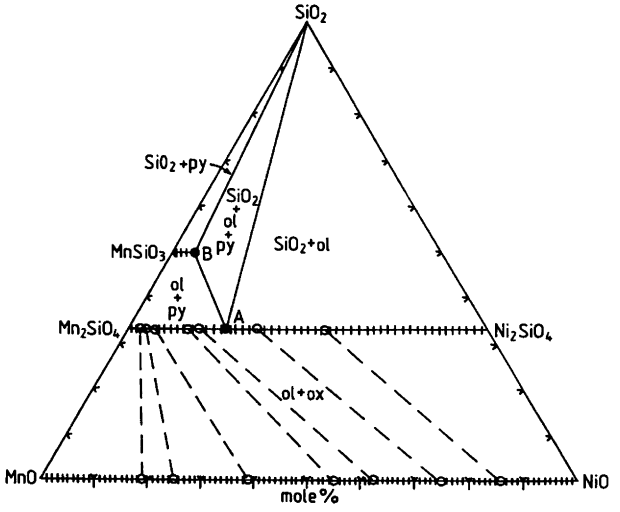

Fig. 3. Isothermal section showing phase relations at 1310 K in the ternary system MnO–NiO–SiO_2. Broken lines are tie-lines determined for coexisting solid solution phases; the hatched lines show the extent of solid solution between the two end-members. The abbreviations used in the diagram have the following meanings: ol, olivine(ss); py, pyroxene(ss); ox, oxide(ss).

Table 1. Equilibrium data obtained for coexisting oxide and olivine solid solutions at 1310 K under reducing conditions (O_2 pressure $\approx 10^{-10}$ bar).

	$(Mn_{1-x}, Ni_x)O$		$(Mn_{1-y}, Ni_y)_2SiO_4$			
No.	$d(220)$/Å	x	$d(222)$/Å	y	$a(MnSi_{0.5}O_2)$	$a(NiSi_{0.5}O_2)$
1	1.4804	0.86	1.7579	0.55	0.694	0.643
2	1.4852	0.75	1.7715	0.36	0.822	0.527
3	1.4937	0.62	1.7855	0.20	0.894	0.426
4	1.5010	0.55	1.7896	0.17	0.911	0.391
5	1.5185	0.39	1.8007	0.07	0.943	0.302
6	1.5353	0.25	1.8038	0.05	0.960	0.228
7	1.5428	0.19	1.8069	0.03	0.970	0.190

(Mn, Ni)O + (Mn, Ni)SiO_3 + (Mn, Ni)$_2SiO_4$, at increasing temperatures.

The tie lines between the oxide and the olivine solid solutions are slanted towards the end-members NiO and Mn_2SiO_4. This can clearly be seen in Fig. 4, where the Mn^{2+}-content in the olivine phase, $(1-y)$, is plotted against that in the oxide phase, $(1-x)$. By way of example, at the oxide composition $x=0.50$, the corresponding Mn^{2+} content of the olivine phase is 0.86.

Activities. Activities in (Mn, Ni)-olivine solid solution at 1310 K, calculated from the tie-line data as well as from the EMF measurements, are summarized in Fig. 5.

(1) Calculation from tie-line data. In the phase assemblage $(Mn_{1-x}, Ni_x)O + (Mn_{1-y}, Ni_y)_2SiO_4$, the cations Mn^{2+} and Ni^{2+} are distributed between the olivine and the oxide phases. The equilibrium conditions can be denoted according to

$$MnO(ss) + NiSi_{0.5}O_2(ss) \rightleftharpoons NiO(ss) + MnSi_{0.5}O_2(ss) \quad \text{(III)}$$

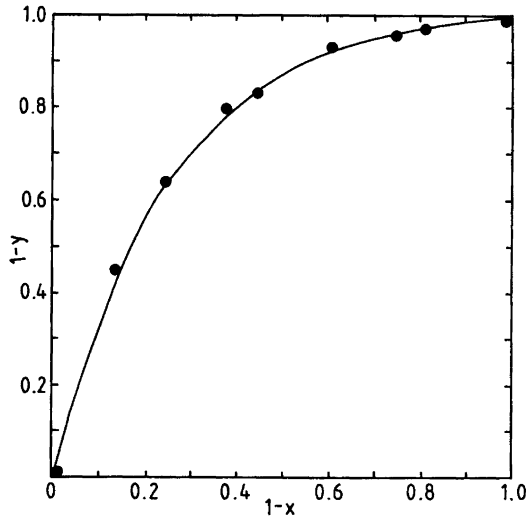

Fig. 4. Equilibrium distribution of Mn^{2+}-contents (mole fraction) between the oxide $(Mn_{1-x}, Ni_x)O$ and the olivine $(Mn_{1-y}, Ni_y)_2SiO_4$ solid solutions at 1310 K. Solid circles represent the experimental values and the curve is drawn to fit these data.

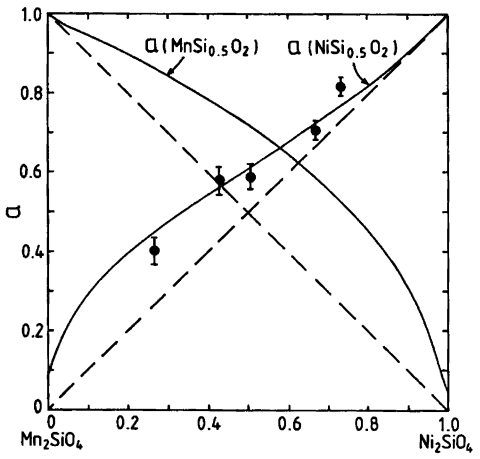

Fig. 5. Activity–composition (mole fraction) relations in the (Mn, Ni)-olivine solid solution at 1310 K. The curves represent activity values obtained from tie-line determinations; solid circles represent $a(NiSi_{0.5}O_2)$ values determined from EMF measurements and estimated uncertainties are indicated by the vertical lines.

where the olivine phases are written in the form $NiSi_{0.5}O_2$ and $MnSi_{0.5}O_2$, indicating that the total number of cation sites is equal to 1 in the olivine solid solution per formula unit. The activities (a) in the olivine solid solution are related to the cation compositions in the coexisting solid solutions as well as to the activity coefficients (γ) in the oxide (Mn, Ni)O solid solution. General equations for calculation of activity coefficients from tie-line data at a certain temperature have been derived by Jacob and Jeffes[15] and used to compute the activities in the olivine $(Mg,Co)_2SiO_4$.[5] Similar relationships have been used in the present study, given as follows:

$$\ln \gamma(NiSi_{0.5}O_2) = \int_0^{y'} -(1-y)\, d \ln \{[y(1-x)/x(1-y)] \times [\gamma(MnO)/\gamma(NiO)]\} \quad (1)$$

$$\ln \gamma(MnSi_{0.5}O_2) = \int_0^{y'} y\, d \ln \{[y(1-x)/x(1-y)] \times [\gamma(MnO)/\gamma(NiO)]\} \quad (2)$$

The activity coefficients $\gamma(NiSi_{0.5}O_2)$ and $\gamma(MnSi_{0.5}O_2)$

were calculated from eqns. (1) and (2) by using coherent composition values (x and y) of the two solid solutions, as given in Fig. 4, as well as known values of γ(NiO) and γ(MnO) reported by Paulsson and Rosén.[8] To carry out the integration of eqns. (1) and (2), the following relationship was derived through a least-squares treatment

$$y = 1.1137 - 0.74734\ W + 0.35034\ W \ln W \quad (3)$$

where W represents the term $\ln\{[y(1-x)/x(1-y)] \times [\gamma(\mathrm{MnO})/\gamma(\mathrm{NiO})]\}$. The activities were then evaluated using the equations

$$a(\mathrm{NiSi_{0.5}O_2}) = \gamma(\mathrm{NiSi_{0.5}O_2})y \quad (4)$$

$$a(\mathrm{MnSi_{0.5}O_2}) = \gamma(\mathrm{MnSi_{0.5}O_2})(1-y) \quad (5)$$

The activity–composition relations thus obtained for the (Mn, Ni)-olivine at 1310 K are given in Table 1 and shown in Fig. 5 by the two curves, where one represents $a(\mathrm{NiSi_{0.5}O_2})$ and the other $a(\mathrm{MnSi_{0.5}O_2})$. Both components exhibit significant positive deviations from ideality.

(2) Evaluation from EMF measurements. The EMF values obtained from the measurements of cells (A) and (B) for the various olivine compositions $(\mathrm{Mn_{1-y}},\mathrm{Ni_y})_2\mathrm{SiO_4}$ are summarized in Table 2. Totally about 100 data points (E/mV, T/K) were measured in the temperature range 1140–1395 K. The $E(T)$ relationships and the standard deviations of the fit (σE) were calculated by a least-squares treatment.

Systems containing solid SiO_2 as a component mostly react quite sluggishly. Special measures must therefore be taken to be able to study equilibrium conditions. In the present work, long equilibration times (5–15 d) were necessary, and it was found favorable to use the 'zero-point cell' (ZPC) arrangement to obtain stable EMF values. To check the reliability of the present results, a comparison can be made for the composition $y=1$ corresponding to the redox equilibrium reaction (I), which was previously studied by Boström and Rosén[16] and by O'Neill,[17] using the solid-state EMF technique. The Gibbs energy value, ΔG°(I), calculated at 1350 K with EMF values from the present study, amounts to $-242\,600 \pm 200$ J mol^{-1}. The corresponding values derived from the previous investigations are: $-242\,900 \pm 500$ J mol^{-1} according to Ref. 16, and $-243\,640 \pm 200$ J mol^{-1} according to Ref. 17. In fact, all values are in good agreement, especially between the present result and that obtained by Boström and Rosén.[16]

By appling the law of mass action to the equilibria (I) and (II), the following expressions are obtained:

$$K(\mathrm{I}) = 1/p(\mathrm{O_2},\mathrm{I}) \quad (6)$$

$$K(\mathrm{II}) = a(\mathrm{Ni_2SiO_4})/p(\mathrm{O_2},\mathrm{II}) \quad (7)$$

where $p(\mathrm{O_2},\mathrm{I})$ and $p(\mathrm{O_2},\mathrm{II})$ are the oxygen pressures generated in the equilibria (I) and (II), respectively. As the equilibrium constants K(I) and K(II) are equal, the activity of Ni_2SiO_4 can be calculated according to

$$a(\mathrm{Ni_2SiO_4}) = p(\mathrm{O_2},\mathrm{II})/p(\mathrm{O_2},\mathrm{I}) \quad (8)$$

and the activity of the Ni-olivine can be written in the form $NiSi_{0.5}O_2$

$$a(\mathrm{NiSi_{0.5}O_2}) = [p(\mathrm{O_2},\mathrm{II})/p(\mathrm{O_2},\mathrm{I})]^{1/2} \quad (9)$$

The ratio of the oxygen partial pressures, $p(\mathrm{O_2},\mathrm{II})/p(\mathrm{O_2},\mathrm{I})$, is calculated using the measured values, given in Table 1, according to the equation

$$\ln[p(\mathrm{O_2},\mathrm{II})/p(\mathrm{O_2},\mathrm{I})] = -(4F/R)[\Delta E/T] \quad (10)$$

where F and R are the Faraday and the gas constants, respectively, and ΔE represents the EMF difference

$$\Delta E = E(\mathrm{B}) - E(\mathrm{A}) \quad (11)$$

in the cases where the same reference systems were used.

Considering eqns. (9) and (10), the following expression is derived:

$$\ln a(\mathrm{NiSi_{0.5}O_2}) = -(2F/R)(\Delta E/T) \quad (12)$$

The calculated activity–temperature relationships are presented in Table 3, where the estimated uncertainties are also given. To compare with the results determined by the tie-line method, the calculated activities of $NiSi_{0.5}O_2$ at 1310 K are plotted in Fig. 5. Considering all the uncertainties involved in the experimental studies, the agreement between the results from the two different methods is quite satisfactory.

Acknowledgement. This work was financially supported by the Swedish Natural Science Research Council.

Table 2. $E(T)$ relationships as well as the calculated standard deviations of the fit (σE/mV), obtained for the $(\mathrm{Mn_{1-y}},\mathrm{Ni_y})_2\mathrm{SiO_4}$ solid solution at different compositions from cells (A) and (B).

	$E = a + bT$					
y	$-a$	$-b$	$\sigma(E)$	No. of measured points	T-range/K	Cell used
0.27	10.141	0.16435	±0.82	34	1205–1390	ZPC (Fe/FeO)
0.43	47.752	0.15117	±0.82	15	1265–1385	ZPC (Fe/FeO)
0.51	−174.98	0.10117	±0.55	5	1140–1325	DTC (Ni/NiO)
0.67	16.969	0.18315	±1.20	14	1170–1395	ZPC (Fe/FeO)
0.73	79.186	0.14158	±0.69	13	1160–1340	ZPC (Fe/FeO)
1.00	43.273	0.17788	±0.55	11	1230–1390	ZPC (Fe/FeO)
1.00	−53.581	0.03136	±0.41	8	1230–1355	DTC (Ni/NiO)

Table 3. Activity ln $a(NiSi_{0.5}O_2)$ as a function of temperature in $(Mn_{1-y}, Ni_y)_2SiO_4$ solid solution at different olivine compositions.

	ln $a(NiSi_{0.5}O_2) = c + d/T$			
y	c	d	Uncertainty in $a(NiSi_{0.5}O_2)$ at 1310 K	T-interval/K
0.27	−0.3140	−768.97	±0.010	1205–1390
0.43	−0.6199	103.95	±0.014	1265–1385
0.51	1.6202	−2817.57	±0.010	1140–1325
0.67	0.1223	−610.49	±0.022	1170–1395
0.73	−0.8425	833.51	±0.018	1160–1340

References

1. Muan, A. *Am. Mineral. 52* (1967) 797.
2. Riboud, P. V. and Muan, A. *Trans. AIME 224* (1962) 27.
3. Biggers, J. V. and Muan, A. *J. Am. Ceram. Soc. 50* (1967) 230.
4. Campbell, F. E. and Roeder, P. *Am. Mineral. 53* (1968) 257.
5. Jacob, K. T., Mukhopadhyay, S. and Shukla, A. K. *J. Am. Ceram. Soc. 75* (1992) 3081.
6. Seetharaman, S. and Abraham, K. P. *Trans. Inst. Min. Metall., Ser. C 77* (1968) 209.
7. Cameron, D. J. and Unger, A. E. *Metall. Trans. 1* (1970) 2615.
8. Paulsson, H. and Rosén, E. *Chem. Scr. 11* (1977) 204.
9. Catlow, C. R. A., Fender, B. E. F. and Hampson, P. J. *J. Chem. Soc., Faraday Trans. 73* (1977) 911.
10. Pejryd, L. *Acta Chem. Scand. Ser. A 38* (1984) 241.
11. McMurdie, H. F., Morris, M. C., Evans, E. H., Paretzkin, B., Wong-Ng, W. and Hubbard, C. R. *Powder Diffract. 1* (1986) 40.
12. Wong-Ng, W. and Hubbard, C. R. *Powder Diffract. 2* (1988) 242.
13. Pejryd, L. *Ph.D. Thesis*, Umeå University, Umeå, Sweden 1985.
14. Boström, D., Lindblom, B., Rosén, E. and Söderlund, M. *High Temp. Sci. 28* (1990) 235.
15. Jacob, K. T. and Jeffes, J. H. E. *High Temp.-High Press. 4* (1972) 177.
16. Boström, D. and Rosén, E. *Acta Chem. Scand. Ser. A 42* (1988) 149.
17. O'Neill, H. St. C. *Am. Mineral. 72* (1987) 280.
18. Alcock, C. B. and Zador, S. *Electrochim. Acta 12* (1967) 673.
19. Huang, J.-H. and Rosén, E. *Phys. Chem. Miner. 21* (1994) 228.

Received January 29, 1996.