Zeitschrift für Anorganische und
Allgemeine Chemie

Solid Solutions in the System Fe_{1-x}O -ZnO at Low Oxygen Partial Pressure

Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.201000084.R1
Wiley - Manuscript type:	Article
Date Submitted by the Author:	09-Mar-2010
Complete List of Authors:	Mader, Werner; University of Bonn, Chemistry Moll, Sebastian; University of Bonn, Institute of Inorganic Chemistry Weber, Sven-Ulf; Technische Universität Braunschweig, Institut für Physikalische und Theoretische Chemie Becker, Klaus-Dieter; Technische Universität Braunschweig, Institut für Physikalische und Theoretische Chemie
Keywords:	Ferrous oxide, Zinc oxide, Solid solution, Lattice parameters

ARTICLE

DOI: 10.1002/zaac.200((will be filled in by the editorial staff))

Solid Solutions in the System Fe_{1-x}O -ZnO at Low Oxygen Partial PressureSebastian Moll,^[a] Sven-Ulf Weber,^[b] Klaus-Dieter Becker,^[b] and Werner Mader^[a]*Dedicated to Professor Bernd Harbrecht on the Occasion of His 60th Birthday***Keywords:** Ferrous oxide; Zinc oxide; Solid solution; Lattice parameters;

The maximum solubilities of Zn^{2+} in Fe_{1-x}O and of Fe^{2+} in ZnO at temperatures from 1173 – 1473 K in the presence of metallic iron were determined. Mixed crystals $\text{Fe}_{1-x-z}\text{Zn}_z\text{O}$ with $0.04 \leq z \leq 0.19$ were prepared at 1273 K. All samples were characterised by X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy. The solubility of Fe^{2+} in wurtzite ZnO as well as the lattice parameter a of $\text{Zn}_{1-y}\text{Fe}_y\text{O}$ increases with reaction temperature whereas c remains virtually constant. The solubility of Zn^{2+} in Fe_{1-x}O increases with temperature. The lattice parameter a of $\text{Fe}_{1-x-z}\text{Zn}_z\text{O}$ for $0.04 \leq z \leq 0.13$ increases with Zn content. For $0.13 \leq z \leq 0.19$ a is constant,

whereas for higher Zn contents a decreases. Mössbauer spectroscopy of the mixed crystal $\text{Fe}_{1-x-0.09}\text{Zn}_{0.09}\text{O}$ yields a reduced amount of 6 % Fe^{3+} compared to wüstite $\text{Fe}_{1-0.04}\text{O}$ with 9 % Fe^{3+} . Such reduction of Fe^{3+} content was previously observed in the mixed crystal systems Fe_{1-x}O -MgO and Fe_{1-x}O -MnO too. The increase of the lattice parameter a of $\text{Fe}_{1-x-z}\text{Zn}_z\text{O}$ for low concentrations is explained by removal of Fe^{3+} ions. At higher Zn contents the occupation with Zn^{2+} ions – with smaller radius than Fe^{2+} – balances or exceeds the effect of Fe^{3+} removal.

* Prof. Dr. W. Mader

Fax: +49-288-734205

E-Mail: mader@uni-bonn.de

[a] Institut für Anorganische Chemie, Universität Bonn,
Römerstrasse 164
53117 Bonn, Germany

[b] Institut für Physikalische und Theoretische Chemie
Technische Universität Braunschweig
Hans-Sommer-Str. 10
38106 Braunschweig, Germany

Introduction

Despite zinc oxide (ZnO) has already many industrial applications owing to its physical and chemical properties, there is renewed interest and wide research activities in the past decade, e.g. on nanometre-sized ZnO crystals and on the electrical conductivity of the optically transparent oxide. Also, any doping of ZnO with other metal oxides to eventually implement ferromagnetism to the semi-conducting oxide is of high interest [1]. Recently, vast quantity of research is performed on ZnO systems with small dimensions and as thin films with various additions. In most cases, these systems are produced at low temperature and are thus far from equilibrium. Basic studies on equilibrium systems of ZnO with other oxides were usually made in the past, and this was the motivation to revisit the system zinc oxide – wüstite. The composition and structure of wüstite is still a matter of research documented in an immense number of studies in the literature.

Ferrous oxide is known as wüstite which crystallises in the rock salt crystal structure. Wüstite is non-stoichiometric, and it is deficient in iron which is represented by the chemical formula Fe_{1-x}O , with x between 0.04 and 0.15 determined by temperature and oxygen partial pressure [2]. Caused by the non-stoichiometry, part of the iron is high spin $d^5 \text{Fe}^{3+}$ which occupies tetrahedral as well as octahedral sites. Fe^{3+} in

tetrahedral sites tends to form defect clusters together with vacancies at immediate neighbouring octahedral cation sites [3]. Foster and Welch [4] realised that the lattice parameter a of wüstite depends on its composition, i.e. a increases with increasing Fe content which is equivalent to the decrease of Fe^{3+} . In recent years, Hayes, Jak, and Pelton [5, 6] studied the phase diagram of the system Fe-Zn-O. At low oxygen partial pressures the wüstite type mixed crystal $\text{Fe}_{1-x-z}\text{Zn}_z\text{O}$ with zinc solute is in equilibrium with the zinc rich wurtzite type phase $\text{Zn}_{1-y}\text{Fe}_y\text{O}$ across the two-phase region. They measured the solid solubility limits in the reaction products of ZnO which is confined in a metallic iron container [6]. However, the experimental setup did not allow obtaining further results. Claude et al. [7] studied Fe_{1-x}O with varying additions of ZnO at 1173 K, and they observed an increase of the lattice parameter with zinc content.

In a chemical vapour transport experiment Locmelis et al. [8] obtained zincite crystals containing different amount of Fe. They observed an increase of the lattice parameter a with increasing Fe content while c remains virtually constant.

In this study we present results of a systematic investigation of the system Fe-Zn-O in the presence of metallic iron, where we determine solubilities, lattice parameters, and in a case study the Fe^{3+} vs. Fe^{2+} content in the wüstite type phase.

Experimental Section

ZnO (99.999 % Sigma Aldrich), Fe_2O_3 (99.999 % Acros Organics) and Fe (99 % Fluka) were mixed in an agate mortar and pressed to pellets. Throughout, Fe_2O_3 and Fe were chosen in molar ratio of 1:1 to obtain wüstite with a small remainder of iron. The pressed mixtures were sealed in fused silica tubes (40-50 mm in length, 6 mm in diameter; filled with 10^{-2} mbar Ar) and heated in a tube furnace. The composition of the mixtures and the reaction

temperatures and times are given in table 1. After reaction the silica tubes were quenched in water.

Table 1. Composition of starting mixtures, reaction parameters and determined compositions of wüstite-type phase.

Sample no.	FeO / ZnO in starting mixtures	<i>T</i> [K]	Reaction time [h]	Ratio Fe / Zn Wüstite Phase
1	50 / 50	1173	192	-
2	50 / 50	1223	168	-
3	50 / 50	1273	168	-
4	50 / 50	1323	120	-
5	50 / 50	1373	168	-
6	50 / 50	1423	168	-
7	50 / 50	1473	96	-
8	95 / 5	1273	72	96 / 4
9	90 / 10	1273	72	91 / 9
10	86 / 14	1273	72	89 / 11
11	85 / 15	1273	72	88 / 12
12	84 / 16	1273	72	87 / 13
13	83 / 17	1273	72	86.5 / 13.5
14	82 / 18	1273	72	85 / 15
15	81 / 19	1273	72	84 / 16
16	80 / 20	1273	72	83 / 17
17	79 / 21	1273	72	82 / 18
18	78 / 22	1273	72	81 / 19

Powder X-ray diffraction data were obtained on a digitised Philips PW1050 (Co K_α radiation), Bragg-Brentano geometry, and post specimen monochromator. The powder diffraction diagrams were analyzed with the Diffrakt97 program package [9] which serves as user interface for e.g. the Treor90 [10] program for indexing and for the Rietveld algorithm based on the program LHPM1 [11]. Phase identification was carried out by comparison with the JCPDS-ICSD database cards.

The chemical composition of individual micro-crystals was determined by energy dispersive X-ray spectrometry (EDXS) conducted on a Philips CM30 transmission electron microscope operated at 300 kV. Quantitative microanalysis was based on experimentally determined calibration factors derived from standards. Micro-crystals for transmission electron microscopy (TEM) were obtained by grinding the reaction products in an agate mortar. The crystals were dispersed in ethanol and were deposited on a carbon-coated copper grid (Quantifoil R 1.2/1.3, 200 mesh).

Mössbauer measurements were performed in transmission geometry using a microcomputer-controlled spectrometer in constant acceleration mode using a ⁵⁷Co/Rh γ-ray source. The velocity scale was calibrated relative to ⁵⁷Fe in Rh. The transmitted γ-radiation was detected by means of a proportional counter. "Recoil" spectral analysis software [12] was used for the quantitative evaluation of the Mössbauer spectra.

Results and Discussion

Phase Diagram of Zn-Fe-O-System with Metallic Iron

The Phase diagram of the Zn-Fe-O system in the presence of metallic iron is known to consist of the iron rich wüstite phase with rock salt structure and the zinc rich wurtzite type phase separated by a two-phase field. Thus, in equilibrium an equal amount of Fe_{1-x}O and ZnO as starting mixture will yield a two phase product with maximum solute content of

either Zn in the wüstite type phase or Fe in the wurtzite type phase. The presence of these two oxide phases and some small amount of α-iron (less than ca. 5 at% of the iron content) could be verified in all the X-ray powder diffraction (XRD) diagrams collected from samples no. 1 to 7 (see table 1).

Individual single crystals on the supporting carbon film were analysed (i) by electron diffraction to identify the crystal structure and (ii) by EDXS to analyse the ratio of cations, respectively. Only crystals with either NaCl structure or with wurtzite structure having high iron content or high zinc content, respectively, were observed, and 10 to 20 crystals of any phase and reaction temperature (1173 to 1473 K) were analysed. The compositions of the phases at the two-phase field, i.e. the solubility limits, are listed in Table 2 and are visualised in the phase diagram in Figure 1.

Table 2. Solubility limits of Fe in Zn_{1-y}Fe_yO and of Zn in Fe_{1-x}Zn_xO as function of temperature.

Sample no.	<i>T</i> [K]	[Fe] / [Fe + Zn] %	[Zn] / [Fe + Zn] %
1	1173	16 (1)	18 (2)
2	1223	19 (1)	19 (1)
3	1273	20 (1)	20 (1)
4	1323	22 (1)	22 (1)
5	1373	24 (1)	22.5 (9)
6	1423	25 (1)	23 (2)
7	1473	26 (1)	25 (1)

The phase with wurtzite structure, Zn_{1-y}Fe_yO, as well as the wüstite type phase, Fe_{1-x}Zn_xO, exhibits increasing solute content of Fe and Zn, respectively, with increasing temperature, attributed to the increase of entropic factors in Gibbs free energy. The solubility limits are consistent with the ones reported by Jak and Hayes [6] despite the different materials preparation and the different methods for chemical analysis. The oxygen partial pressure in the presence of metallic iron varies from 10⁻⁹ to 10⁻¹³ mbar in the reaction temperature range [13].

Figure 1. Phase diagram of the system Zn-Fe-O in presence of metallic iron. Error bars of solubility limits represent standard deviations of EDXS measurements.

Wurtzite Type Zn_{1-y}Fe_yO

As result of Rietveld refinements the lattice parameters a and c of the hexagonal phase $\text{Zn}_{1-y}\text{Fe}_y\text{O}$ with maximum iron content at the chosen reaction temperatures are given in Table 3. The lattice parameter a increases linearly with increasing Fe content. However, the lattice parameter c appears to be widely invariant with compositional variations of the samples. As a result the c/a ratios of the mixed crystals vary from 1.589 to 1.594 between highest and lowest Fe content, respectively. Because the c/a ratio of ZnO is 1.602, substitution of Zn by Fe lowers the c/a ratio of the mixed crystals even more away of the ideal value of 1.633.

Table 3. Lattice Parameters of hexagonal $\text{Zn}_{1-y}\text{Fe}_y\text{O}$ with maximum Fe content (see Table 2).

Sample no.	a [Å]	c [Å]	GOF / %	R_B / %
1	3.2656(1)	5.2055(1)	7.9	3.1
2	3.2686(2)	5.2049(3)	12.1	1.9
3	3.2687(1)	5.2039(2)	9.7	5.7
4	3.2700(1)	5.2049(1)	8.8	6.6
5	3.2719(1)	5.2052(1)	8.9	1.1
6	3.2734(1)	5.2040(2)	12.1	9.0
7	3.2742(1)	5.2026(2)	8.8	2.7

The lattice parameters a and c of $\text{Zn}_{1-y}\text{Fe}_y\text{O}$ are plotted versus the Fe content in the wurtzite structure of ZnO in Figure 2. The increase of unit cell volume with increasing Fe content clearly indicates a solid solution of Fe in ZnO which is expected from the ionic radii. The radius of 4-fold coordinated Fe^{2+} is 0.77 Å compared to 0.74 Å of Zn^{2+} (Table 6). Additionally, there is experimental evidence that only Fe^{2+} is substituting zinc in ZnO at conditions used in the present study: (i) Mössbauer spectroscopy of $\text{Zn}_{0.89}\text{Fe}_{0.11}\text{O}$ produced by chemical vapour transport revealed predominantly Fe^{2+} [8]. (ii) Even little amounts of Fe^{3+} in ZnO produce typical inversion domains and related boundaries [14] which are readily detected in the electron microscope. However, none of such defects were observed in the $(\text{Zn}_{1-y}\text{Fe}_y)\text{O}$ mixed crystals studied here. Also, the observed tendency of lattice parameter variation of $(\text{Zn}_{1-y}\text{Fe}_y)\text{O}$ with Fe content is reported in the literature [8].

Figure 2. Lattice parameter a (triangles) and c (rectangles) of $\text{Zn}_{1-y}\text{Fe}_y\text{O}$ plotted vs. Fe content. Error bars show standard deviation.

Wüstite Type $\text{Fe}_{1-x-z}\text{Zn}_z\text{O}$

In order to study in detail the substitution of Fe with Zn^{2+} a series of mixed crystals $\text{Fe}_{1-x-z}\text{Zn}_z\text{O}$ with $0.04 < z < 0.19$ was prepared at 1273 K for 72 h. The starting materials and the resulting compositions of the products are listed in Table 1, samples no. 8 to 18. The standard deviation of the composition of wüstite products given in Table 1 is throughout less than 1 % (see also Figure 3). The refinement results of the lattice parameter a subject to the amount of Zn^{2+} ions built in the wüstite crystal are listed in Table 4. To better visualise the tendency, in Figure 3 the lattice parameter a is plotted over the composition. An unusual behaviour of the size of the unit cell is observed: while a increases with Zn content up to ca. 13 at. % of cations (regime I), a remains virtually constant at higher Zn contents (regime II).

Table 4. Refined lattice parameter a of $\text{Fe}_{1-x-z}\text{Zn}_z\text{O}$ as function of composition (see Table 1).

Sample no.	a [Å]	GOF / %	R_B / %
8	4.3137(1)	11.9	1.8
9	4.3162(1)	8.3	1.4
10	4.3170(1)	11.1	2.8
11	4.3180(1)	16.5	7.4
12	4.3184(1)	12.8	5.2
13	4.3191(1)	11.6	2.2
14	4.3191(1)	8.6	2.9
15	4.3190(1)	8.9	2.2
16	4.3188(1)	10.3	3.9
17	4.3189(1)	8.4	4.1
18	4.3190(1)	7.7	2.7

To understand and discuss the increase of the lattice parameter a in regime I the two possible sites for Zn^{2+} substitution, tetrahedral or octahedral, have to be considered. Tetrahedrally coordinated Zn^{2+} as interstitial in the sodium chloride structure of wüstite requires removal of four neighbouring Fe^{2+} ions, and substitution of other Fe^{2+} ions by Fe^{3+} because of charge balance. A single Zn^{2+} ion in tetrahedral site affords the substitution of 6 Fe^{2+} ions in octahedral sites by Fe^{3+} . The principle of occupying Zn^{2+} ions in tetrahedral sites is the same as for the defect clusters in wüstite, such as the prominent Koch-Cohen cluster with four Fe^{3+} ions in tetrahedral sites and 14 additional Fe^{3+} ions in octahedral sites. A structural equivalent cluster with four Zn^{2+} ions would even require 18 Fe^{3+} ions in octahedral sites. On the other hand, substitution of Fe^{2+} by Zn^{2+} on octahedral sites does not cause structural and charge problems and may not affect the amount of Fe^{3+} in wüstite.

Hence, the amount of Fe^{3+} in wüstite with zinc solute is the appropriate quantity to provide information on the preferred sites of Zn^{2+} . The ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ was determined with Mössbauer spectroscopy in the sample no. 9 with composition $\text{Fe}_{0.91}\text{Zn}_{0.09}\text{O}$. The resulting spectrum is shown in Figure 4. Its doublet structure consists of three doublets: doublets 1 and 2 are assigned to Fe^{2+} , and doublet 3 is assigned to Fe^{3+} . Small amounts (5%) of metallic iron produce a weak sextet whose outer lines are out of the range of Figure 4. The interpretation of the Mössbauer spectrum is summarized in Table 5. The analysis results in 93 % of Fe^{2+} and in 6.5 % of Fe^{3+} of the iron content in $\text{Fe}_{0.91}\text{Zn}_{0.09}\text{O}$. The amount of Fe^{3+} is thus lower than in wüstite (9 % Fe^{3+}) produced at similar conditions. As a consequence, the Zn^{2+} ions preferentially must occupy octahedral sites in the wüstite host crystal.

Figure 3. Lattice parameter a of the wüstite type ($\text{Fe}_{1-x}\text{Zn}_x\text{O}$) as function of Zn content. Error bars show standard deviation.

Figure 4. Mössbauer spectrum of sample $\text{Fe}_{0.91}\text{Zn}_{0.09}\text{O}$ measured in the velocity range ± 3 mm/s.

Table 5. Results of Mössbauer Spectra of Sample ($\text{Fe}_{0.91}\text{Zn}_{0.09}$)O.

Site	IS [mm/s] ^[a]	QS [mm/s] ^[b]	Relative Area (%) Total Iron	Relative Area (%) Oxide only
$\text{Fe}^{2+}_{\text{oct}}$	0.95(1)	0.85(3)	34(6)	36(6)
$\text{Fe}^{2+}_{\text{tet}}$	1.03(1)	0.39(2)	54(6)	57(6)
Fe^{3+}	0.37(3)	0.40(5)	6.1(5)	6.5(5)
Fe^0	0.0	--	5(2)	--

[a] isomeric shift, [b] quadrupolar splitting

At first sight, substitution of Fe^{2+} by Zn^{2+} with smaller ionic radius should yield a smaller unit cell volume (see Table 6). However, the lattice parameter measured clearly shows the opposite in regime I for small zinc contents. Thus the increase of cell volume has to be attributed to the decrease of Fe^{3+} in the mixed crystals $\text{Fe}_{1-x}\text{Zn}_x\text{O}$. The same tendency of lattice parameter increase is observed in the system $\text{Fe}_{1-x}\text{O-MgO}$ which exhibits complete solid solubility of the crystals $\text{Fe}_{1-x}\text{Mg}_x\text{O}$ [15, 16]. $\text{Fe}_{1-x}\text{Mg}_x\text{O}$ shows a pronounced deviation from Vegard's law, i.e. the cell parameter is clearly exceeding Vegard's line $\text{Fe}_{1-x}\text{O-MgO}$ in the Fe rich region [16]. Additionally, Mössbauer spectroscopy revealed a strong decrease of the relative amount of Fe^{3+} in particular at low solute content of MgO content. In the system $\text{Fe}_{1-x}\text{O-MnO}$ this observations is quite similar: the amount of Fe^{3+} decreases by substituting Fe^{2+} with Mn^{2+} [17]. In the system $\text{Fe}_{1-x}\text{O-ZnO}$ a Vegard's line can be drawn if the cell parameter $a = 4.28$ Å for ZnO is used which is obtained from high pressure ZnO with NaCl structure [18]. Hence, we observe a drastic deviation from Vegard's law in the mixed crystals $\text{Fe}_{1-x}\text{Zn}_x\text{O}$.

In wüstite with additions of oxides with two-valent cations considered here, the following may be summarized: substitution of Fe^{2+} by Mg^{2+} and Zn^{2+} ions on octahedral sites in the wüstite lattice result in an increase of the lattice constant larger than predicted by Vegard's law. This is a direct consequence of the removal of Fe^{3+} on octahedral and tetrahedral sites and implies a diminished amount of defect clusters compared to wüstite.

Table 6. Ionic radii of Fe, Zn, Mn and Mg in fourfold and sixfold coordination [19].

Coordination	Fe^{2+} r [Å]	Fe^{3+} r [Å]	Zn^{2+} r [Å]	Mg^{2+} r [Å]	Mn^{2+} r [Å]
tetrahedral	0.77	0.63	0.74	0.71	0.80
octahedral	0.92	0.785	0.88	0.86	0.97

$\text{Fe}_{1-x}\text{Zn}_x\text{O}$ with High Zinc Content

As shown in Figure 3, the lattice parameter of the mixed crystals $\text{Fe}_{1-x}\text{Zn}_x\text{O}$ with high concentrations of Zn^{2+} ($0.13 < x < 0.18$) remains constant. Obviously, in this regime II of higher zinc content the increase of lattice parameter due to removal of Fe^{3+} and its decrease by occupying Zn^{2+} cations in octahedral sites balances.

Even higher contents of Zn^{2+} are realised in crystals prepared at temperatures above 1300 K at the solubility limit (see Table 2). The corresponding lattice parameters are listed in Table 7 and are visualised and plotted versus the zinc content (Figure 5). As expected from the smaller ionic radius of Zn^{2+} compared to Fe^{2+} the lattice parameter decreases with increasing zinc content. For such high zinc content the impact of the occupation of small Zn^{2+} ions exceeds the effect of removal of Fe^{3+} ions.

Table 7. Lattice Parameter of cubic ($\text{Fe}_{1-x}\text{Zn}_x$)O with high Zn content (see Table 2).

Sample no.	a [Å]	GOF [%]	R_B [%]
1	4.3200(1)	7.9	1.05

2	4.3198(1)	12.2	0.56
3	4.3179(1)	9.7	2.23
4	4.3195(1)	8.8	3.4
5	4.3192(1)	8.9	0.78
6	4.3190(1)	12.1	2.2
7	4.3179(1)	8.8	5.0

Figure 5. Lattice parameter *a* of the wüstite phase (Fe_{1-*x-z*}Zn_{*x*})O vs. Zn content. Error bars show standard deviation.

Conclusions

In our systematic study the maximum solid solubilities of Fe and Zn in the phases Zn_{1-*y*}Fe_{*y*}O and Fe_{1-*x-z*}Zn_{*x*}O, respectively, were found to be substantial, and *y* and *z* exceed 0.25 at 1473 K. With increasing content of Fe²⁺ the *a* axis of the phase with wurtzite structure increases while the *c* axis slightly decreases. Thus, the *c/a* ratios of the mixed crystals are even further away from the ideal value.

Surprisingly, small amounts of Zn²⁺ ions at octahedral sites result in an increase of the lattice parameter in the series of mixed crystals Fe_{1-*x-z*}Zn_{*x*}O. This increase is the result of substituting Fe³⁺ at octahedral sites by Zn²⁺, which – because of charge balance arguments – leads to removal of Fe³⁺ at tetrahedral sites. Finally, the amount of defect clusters, compared to wüstite, is diminished. Such behaviour is also observed in the systems Fe_{1-*x*}O-MgO and Fe_{1-*x*}O-MnO with a smaller ionic radius and a larger ionic radius of M²⁺ ions than Fe²⁺, respectively. These observations lead us to the conclusion that dilution of Fe²⁺ by any appropriate addition of two-valent ions to wüstite reduces the necessity of formation of Fe³⁺ and hence of defect cluster creation. At higher ZnO contents Fe²⁺ is substituted by smaller Zn²⁺ ions at octahedral sites thus balancing or even reversing the effect of Fe³⁺ substitution.

Acknowledgments

We would like to acknowledge Dr. Wilfried Assenmacher and Dr. Klemens Kelm for their help in experimental work and for fruitful discussions.

[1] Ü. Özgür, *J. Appl. Phys.* **2005**, 98, 041301-1–103.

[2] a) R.M. Hazen, R. Jeanloz, *Rev. Geophys. Space Phys.* **1984**, 22, 37–46; b) L. Minervini, R.W. Grimes, *J. Phys. Chem. Solids* **1999**, 60, 235–245; c) W. Schweika, A. Hoser, M.

Martin, A.E. Carlsson, *Phys. Rev. B* **1995**, 51, 15771; d) R.W. Grimes, A.B. Anderson, A.H. Heuer *J. Am. Chem. Soc.* **1986**, 69, 619-623.

[3] F. Koch, J.B. Cohen, *Acta. Cryst.* **1969**, B 25, 275–287.

[4] P.K. Foster, A. J. E. Welch, *Trans. Faraday Soc.* **1956**, 52, 1626–1635.

[5] a) S.A. Degterov, E. Jak, P.C. Hayes, A.D. Pelton, *Metall. Mat. Trans. B* **2001**, 32B, 643-657; b) R. Hansson, P.C. Hayes, E. Jak, *Metall. Mat. Trans. B* **2005**, 36B, 179–185; c) R. Hansson, P.C. Hayes, E. Jak, *Scand. J. Metall.* **2004**, 33, 294-304; d) R. Hansson, P.C. Hayes, E. Jak, *Trans. Inst. Min. Metall. C* **2005**, 114, 141-146.

[6] E. Jak, B. Zhao, P.C. Hayes, *Metall. Mat. Trans. B* **2000**, 31B, 1195-1201.

[7] J.M. Claude, M. Zanne, C. Gleitzer, J. Aubry, *Mem. Scient. Rev. Metall.* **1977**, 229-236.

[8] S. Locmelis, M. Binnewies, *Z. Anorg. Allg. Chem.* **1999**, 625, 1573–1577.

[9] T. Degen, Diffrakt 97, V0.99, *Programm zur Auswertung von Pulverdaten* **1998**.

[10] P.E. Werner, L. Eriksson, M. Westdahl, *J. Appl. Cryst.* **1985**, 18, 267.

[11] R. J. Hill, C.J. Howard, LHPM, *A Computer Program for Rietveld Analysis of Fixed-Wavelength X-Ray and Neutron Diffraction Patterns*. Australian Atomic Energy Commission (now Ansto) Report No. M112. Lucas Height Research Laboratories, New South Wales, Australia. **1986**.

[12] K. Lagarec, D.G. Rancourt, *Recoil – Mössbauer Spectral Analysis Software for Windows, version 1.02.* **1998**, Department of Physics, University of Ottawa, Ottawa.

[13] E. Fromm, E. Gebhardt in *Gase und Kohlenstoff in Metallen*, Springer-Verlag, Berlin, **1976**, vol. 1, p. 601.

[14] O. Köster-Scherger, H. Schmid, N. Vanderschaeghe, F. Wolf, W. Mader, *J. Am. Ceram. Soc.* **2007**, 90, 3984–3991.

[15] a) I. Srećec, A. Ender, E. Woermann, W. Gans, E. Jacobsson, G. Eriksson, E. Rosén, *Phys. Chem. Min.* **1987**, 14, 492–498; b) In-Ho Jung, S.A. Decterov, A.D. Pelton, *J. Phys. Chem. Sol.* **2004**, 65, 1683–1695.

[16] H.St.C. O’Neil, M.I. Pownceby, C.A. McCammon, *Contr. Min. Petr.* **2003**, 146, 308-325.

[17] T. Sano, M. Tsuji, Y. Tamaura, *Solid State Ionics*, **1997**, 104, 311–317.

[18] C.H. Bates, W.B. White, R. Roy, *Science*, **1962**, 137, 993.

[19] R.D. Shannon, C.T. Prewitt, *Acta Chryst.* **1969**, B25, 925–946.

Received: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

244x160mm (300 x 300 DPI)

297x209mm (300 x 300 DPI)

127x135mm (300 x 300 DPI)

218x160mm (300 x 300 DPI)

256x160mm (300 x 300 DPI)