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Solid State Electrochemical Study of the Phase Diagram and Thermodynamics of the Ternary System Cu–Ge–O

W. WEPPNER, CHEN LI-CHUAN,* AND A. RABENAU

Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, FRG

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Coulometric titrations using solid zirconia ionic conductors have been employed to determine the phase diagram of the ternary system Cu–Ge–O in the temperature range from 750 to 950°C. $CuGeO_3$ was found to be the only existing ternary compound in the system. It is in equilibrium with Cu_2O, CuO, GeO_2, and oxygen of atmospheric pressure. Cu and Cu_2O may coexist with GeO_2. The standard Gibbs energy of formation of $CuGeO_3$ was found to be ΔG_f° ($CuGeO_3$) = −424.5 kJ/mole at 900°C. The standard enthalpy and entropy of formation are $\Delta H_f^0 = -756.8$ kJ/mole and $\Delta S_f^\circ = -283$ J/mole·K, respectively.

Introduction

The present knowledge of phase diagrams and thermodynamic data of oxides composed of three and more components is generally rather poor in spite of their technological importance. Only a relatively small number of systems has been studied completely and in detail with regard to the exact phase ranges and the equilibrium oxygen partial pressures.

A recently developed electrochemical technique (*1, 2*) is quite promising as a generally applicable and experimentally very tractable tool to obtain both phase diagram and thermodynamic information in one set of experiments. It is not necessary to quench the samples after equilibration and only a small number of samples has to be prepared with different ratios of the nonoxygen components because the oxygen content may be varied by coulometric titration. In addition, the resolution is extremely high, exceeding that of any other method.

This technique has been employed to study the ternary system Cu–Ge–O in the temperature range from 750 to 950°C. Only one ternary compound, $CuGeO_3$ (copper metagermanate), has been reported to date and structurally investigated (3–8). GeO_4 tetrahedra are linked by common O atoms and form linear chains in this material. But there have been repeated speculations about other phases, e.g., "Cu_3GeO_4" or "Cu_2GeO_4" ("copper orthogermanate"). This was usually based upon a comparison with other systems, e.g., Cu–Ti–O (*9, 10*) or orthogermanates which are formed with other oxides of divalent elements (*11, 12*). From a practical point of view, the phase diagram of Cu–Ge–O is of interest because of the use of copper germanium oxides as a sintering aid (*13*). No information about the ternary phase diagram is available from the literature up to now and only fragmentary thermodynamic data are reported (*14*).

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* On leave from the Institute of Physics, Academia Sinica, Peking, China.

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General and Theoretical Considerations

The investigated ternary oxide is employed as electrode in the solid state galvanic cell which is schematically shown in Fig. 1. Stabilized zirconia is a pure oxygen anion conductor in the investigated oxygen partial pressure and temperature range (*15–19*). A two-phase mixture of Cu and Cu_2O or air with the electronic contact provided by porous platinum acts as reference electrode and relatively unpolarizable ionic source or sink.

The galvanic cell has two different objectives. The oxygen content of the sample can be changed by well-defined amounts by coulometric titration (*20*) and it allows the determination of the corresponding equilibrium oxygen partial pressure of the sample. Both data are readily and precisely measurable by electrical quantities, i.e., the electrical current which has passed the cell for a certain amount of time and the steady-state cell voltage according to Nernst's law. Any composition of the sample may be obtained which lies on the straight line going through the starting composition, which is defined by the preparation and the pure oxygen corner of the ternary Cu–Ge–O Gibbs triangle. According to the phase rule, no degrees of freedom other than the temperature and the total pressure are available within three-phase regions and the cell voltage is invariant with composition. On the other hand, in one- and two-phase regions the oxygen partial pressure will change with stoichiometry. The extent of the various phase regions may be determined precisely in this way along the line of accessible compositions. By employing several samples of different Cu:Ge ratios, the entire phase diagram may be investigated. Compared to techniques in which the specimens are annealed in a sealed system and analyzed after quenching, a much smaller number of samples has to be prepared, the composition is much better defined, and problems due to phase changes during the quenching are eliminated, because the oxygen partial pressure is determined *in situ*. Compared to thermogravimetric techniques, the dependent and independent variables, i.e., oxygen partial pressure and mass change of the sample, are interchanged. Since singularities exist for the oxygen activity in the three-phase region, in practice no such field may be observed in thermogravimetric experiments under equilibrium conditions. Furthermore, the precision of weight measurements is much smaller than that of electrical measurements: The easily measurable charge of 1×10^{-5} A sec corresponds to merely 8×10^{-10} g oxygen.

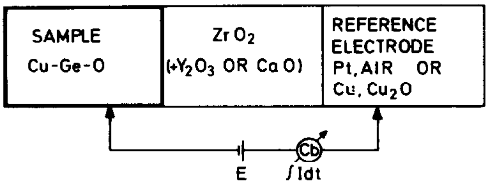

FIG. 1. Galvanic cell employed for the study of the ternary phase diagram and the thermodynamic investigation of the system Cu–Ge–O.

The charges that must pass through the cell to accomplish equidistant changes of sample composition along the composition path in the ternary phase diagram are dependent on position due to the fact that atomic percentages of the three components are plotted in such diagrams. If the starting composition is indicated by the formula $Cu_\alpha Ge_\beta O_\gamma$, one obtains for the charge Q (A sec) necessary to change the oxygen content of the sample from x_1 to x_2 atomic% oxygen, according to Faraday's law,

$$Q(x_1\rightarrow x_2)=\int I\,dt$$
$$=\frac{200\,mF(\alpha+\beta)(x_2-x_1)}{(100-x_1)(100-x_2)}\times[\alpha\cdot 63.54+\beta\cdot 72.59+\gamma\cdot 16]\;C, \quad (1)$$

where F (C) is Faraday's constant and m (g) is the mass of the sample with starting composition.

The EMF E of the galvanic cell is related to the change of the Gibbs (free) energy accompanying the chemical reaction which takes place upon a virtual current flux. Instead of considering the explicit reaction equation for the various positions in the phase diagram in detail, such as the identity of the phases involved, their molar numbers, and their stoichiometries, it is more convenient for systems of three or more components to make use of generally applicable equations which have been recently derived (*1, 2*). They are the result of a general consideration of the Gibbs reaction energy upon the addition of one of the components in multicomponent systems. The relation to the o.c. cell voltage E is then found in the usual way by Nernst's equation,

$$E = -\frac{\Delta G}{2q} = -\frac{kT}{4q} \ln \frac{p_{O_2}(\text{sample})}{p_{O_2}(\text{ref. electrode})}, \tag{2}$$

where ΔG, q, k, and T are the change of the Gibbs energy upon the addition of one O atom, the elementary charge, Boltzmann's constant, and the absolute temperature, respectively. The cell voltage E versus a standard oxygen reference electrode (atmospheric oxygen partial pressure) at the right-hand side of the galvanic cell for the case of the ternary Cu–Ge–oxides in a three-phase region, in which the phases $Cu_{\alpha_1}Ge_{\beta_1}O_{\gamma_1}$, $Cu_{\alpha_2}Ge_{\beta_2}O_{\gamma_2}$, and $Cu_{\alpha_3}Ge_{\beta_3}O_{\gamma_3}$ are in equilibrium, is given by

$$E = \frac{1}{2qd} \sum_{i=1}^{3} (-1)^i d_{i3} \Delta G_f^\circ (Cu_{\alpha_i}Ge_{\beta_i}O_{\gamma_i}). \tag{3}$$

Here d, d_{i3}, and ΔG_f° are the determinant formed by the stoichiometric numbers of the three coexisting phases,

$$d = \begin{vmatrix} \alpha_1 & \beta_1 & \gamma_1 \\ \alpha_2 & \beta_2 & \gamma_2 \\ \alpha_3 & \beta_3 & \gamma_3 \end{vmatrix}, \tag{4}$$

the minors which are formed by eliminating the third row (i.e., the stoichiometric numbers of the electroactive component) and the ith line of the determinant, and the standard Gibbs energy of formation (per molecule) from the pure elements, respectively. A verification of Eq. (3) may be seen by the fact that it describes the proper cell reaction in the phase field under consideration.

It should be noted that the stoichiometric numbers in Eqs. (3) and (4) correspond to the compositions at the three corners of the three-phase triangle. They may deviate from the numbers usually employed to describe the compounds. An advantage of this approach is the fact that this necessary additional information may be obtained in the same experiment.

If one side of the three-phase region can be assumed to be part of either of the legs of the Gibbs triangle formed by the Cu–O and Ge–O binary systems, the amount of the third phase does not change with the addition or deletion of oxygen. Only two phases are then involved in the reactions, and their Gibbs energies of formation determine the cell voltage.

Experimental Considerations

The flat closed ends of approximately 10-mm-wide gas-tight tubes and crucibles made from $ZrO_2 + 10\,\text{mole}\%\,Y_2O_3$ and $ZrO_2 + 15\,m/o$ CaO (Zircoa Corp. of America, Solon, Ohio), respectively, have been used as solid oxygen electrolytes. The atmospheres both inside and outside the tubes could be controlled separately and completely sealed. In the case of the crucibles, molten AR glass was used to form a liquid seal. Direct contact between the glass and the sample was avoided by use of a platinum disk, which acted simultaneously as the electronic lead, and an aluminum oxide cylinder. The gas space was thereby kept small. This is illustrated in Fig. 2. In this way, transport of

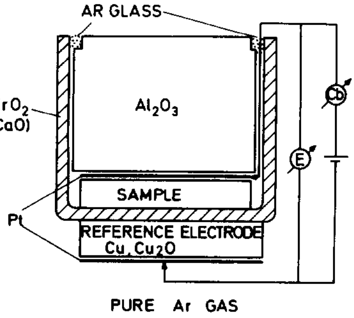

FIG. 2. Schematic representation of the experimental arrangement of the galvanic cell using a zirconia crucible as solid O^{2-} electrolyte and a Cu, Cu_2O reference electrode. Oxygen loss or gain through the gas phase is prevented for the sample by a gas-tight AR–glass seal.

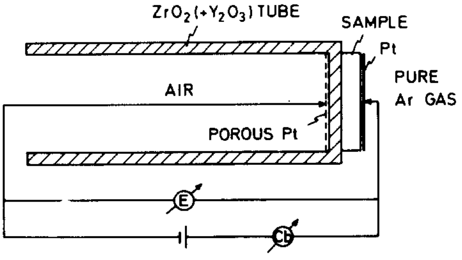

FIG. 3. Schematic representation of the experimental galvanic cell arrangement employed as an alternative to the cell shown in Fig. 2 for the phase diagram and thermodynamic investigation of the ternary system Cu–Ge–O. An air electrode ($p_{O_2} = 21$ kPa) is used for reference, being separated from the sample by an impervious zirconia tube which simultaneously acts as an oxygen electrolyte.

oxygen via the gas phase from one electrode to the other, which would not be measured electrochemically by an electric current through the cell, is avoided in both experimental arrangements. The crucible technique was advantageous at high oxygen partial pressures, when the uptake of oxygen by the gas phase requires an especially small gas volume.

Pellets pressed from two-phase mixtures of Cu and Cu_2O of defined oxygen partial pressure were generally used as kinetically rapid reference electrodes. They were typically four to five times as large as the samples, thus providing a sufficiently large reservoir for oxygen. Use of this reference electrode reduces to a minimum the oxygen permeation through the electrolyte due to electronic leakage (*16–19*), which would not be indicated by charge flux in the external electric circuit.

In some experiments, an air reference electrode with porous platinum as electronic contact was also used for comparison. This is schematically shown in Fig. 3. In order to avoid oxygen partial pressure gradients inside the 30- to 40-cm-long tubes, it was found necessary to provide a good circulation of air inside the tube.

The samples were pressed powder pellets of mixtures at appropriate ratios of CuO and GeO_2 (both from Alfa Ventron, ultrapure). In some experiments mixtures of metallic Cu and Ge (both also from Alfa Ventron, metallic purity > 99.999%) were also used as starting materials. The samples were typically 6 to 10 mm in diameter and 0.5 to 2 mm in thickness. Both electrodes were spring-loaded against the electrolyte.

High-purity argon gas was further purified in the laboratory and passed at atmospheric pressure and low flow rates over the cell. The purity was carefully maintained by using copper tubes, connections developed for a vacuum apparatus, and double-walled quartz tubes whose space in between was also flushed by Ar gas. Temperatures were automatically controlled within 1°C and measured by Pt, Pt 10% Rh thermocouples.

Time-independent charge fluxes (1–100 mA/cm^2) were usually employed for the coulometric titrations. A Knick (Type J 400) current source was used, or a Jaissle (Type 100 mA/cm^2) were usually employed for the galvanostat. Charges were determined by a Jaissle (Type M50T) coulometer. The cell voltages were measured by high-impedance Keithley electrometers (Type 616, $R > 2 \times 10^{14}\,\Omega$) and monitored by slow-speed recorders for observation of equilibrium conditions. The necessary time to achieve equilibrium over the sample after each titration was typically 1–4 hr.

Results and Discussion

In order to relate the observed experimental data to standard conditions, the cell voltages have to be corrected to give the value that would be observed when an oxygen reference electrode of atmospheric pressure ($p_{O_2} = 101.3$ kPa) is employed. In the case of Cu, Cu_2O reference electrodes, a voltage of

$$E(\mathrm{V}) = 0.865 - 3.66 \times 10^{-4} \cdot T(\mathrm{K}) \quad (5)$$

has to be added to the measured electromotive force. This is a result of a critical evaluation of literature data on the standard Gibbs energy of formation, ΔG_f°, of cuprite (Cu_2O) by Pyun and Müller (*21*):

$$\Delta G_f^\circ(Cu_2O)\,(\mathrm{J/mole}) = -1.6695 \times 10^5 + 70.65 \cdot T(\mathrm{K}). \quad (6)$$

A larger number of runs along lines of fixed Cu : Ge ratios has been studied in the phase diagram and thermodynamic studies of the ternary Cu–Ge–O system described here than necessary, if all rules are taken into consideration. This was due to the fact that the electrochemical technique employed was used here for the first time. The experiments have been performed in the temperature range between 750 and 950°C. The results obtained at 900°C with samples having Cu : Ge ratios of 4 : 1, 3 : 2, 1 : 1, and 1 : 3 are shown in Fig. 4. The voltages are plotted relative to a reference electrode with oxygen of atmospheric pressure. Different symbols are used for the various Cu : Ge compositions. The two- and one-phase regions which are observable by composition-dependent voltage ranges are negligibly small compared to the three-phase regions. The voltages corresponding to two-phase equilibria of the two binary systems Cu–O and Ge–O are also indicated in the diagram. The values for the Ge–GeO_2 (tetr.) equilibrium were calculated from thermodynamic tables (*22*) which are based on data confirmed by different authors (*23, 24*), whereas the Cu–Cu_2O and Cu_2O–CuO data are the result of Refs. (*21*) and (*25*), respectively. Only one voltage plateau is observed at all Cu : Ge compositions which does not coincide with any of the two-phase equilibrium voltages of the binary oxides. This shows that there is only one three-phase region in the ternary Cu–Ge–O system which does not have any of its sides in common with the binary Cu–O or Ge–O legs of the Gibbs triangle. Since that specific plateau is observed for all investigated compositions, it extends over the entire width of the diagram, i.e., a ternary compound is in equilibrium with a binary copper oxide and a binary germanium oxide. A voltage plateau corresponding to the Cu_2O–CuO equilibrium is not observed for Cu : Ge ratios equal to and smaller than 1. That means that both Cu_2O and CuO may not simultaneously coexist with a phase in the binary Ge–O system.

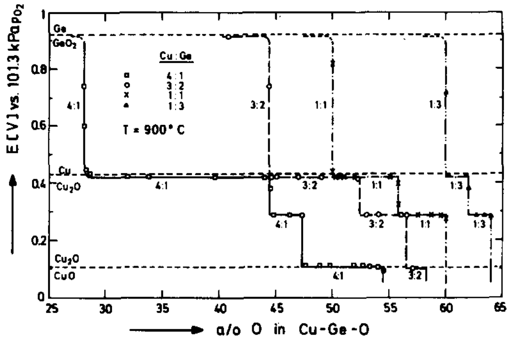

FIG. 4. Results of the coulometric titrations in the ternary system Cu–Ge–O along the lines in the Gibbs triangle with the Cu : Ge ratios 4 : 1, 3 : 2, 1 : 1, and 1 : 3, as indicated by different symbols, at 900°C. The o.c. equilibrium cell voltages which were observed following the partial titration steps are plotted versus the atomic percentages of oxygen. For comparison, the binary two-phase equilibria of Cu–O and Ge–O are also shown.

From these results, the ternary phase diagram shown in Fig. 5 has been constructed. Identical symbols are used for the various Cu : Ge : O ratios which show the same galvanic cell voltage. The two-phase

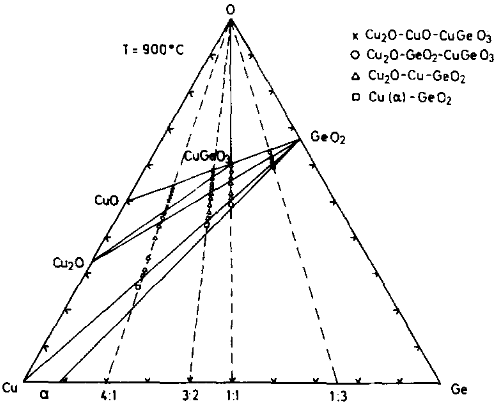

FIG. 5. Ternary phase diagram of Cu–Ge–O as determined from the coulometric titrations along the lines with the Cu : Ge ratios 4 : 1, 3 : 2, 1 : 1, and 1 : 3. Identical cell voltages for various compositions are indicated by the same symbol (which should not be confused with those in Fig. 5). At other temperatures in the range from 700 to 950°C, merely the widths of the Cu(α) and the liquid phase are changed.

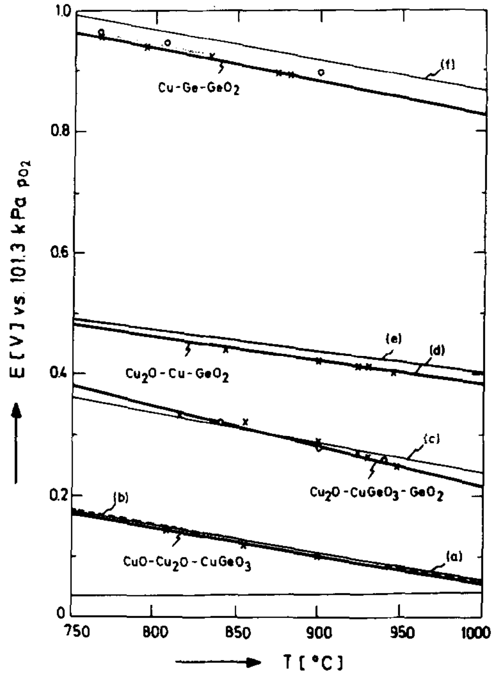

FIG. 6. Representation of the temperature dependence of the equilibrium cell voltages for the various three-phase regions. For comparison, the equilibria of the binary two-phase systems Cu–O and Ge–O as well as data calculated from the literature for the equilibrium Cu_2O–GeO_2–$CuGeO_3$ are also shown by finer lines. The references are: (a) (*25*); (b) (*22*); (c) ΔG_f° ($CuGeO_3$) (*14*), ΔG_f° (CuO) (*25*), ΔG_f° (GeO_2) (*22*); (d) this work, (*25*); (e) (*21, 22*); (f) (*22*). In addition, the lowest straight line shows the voltage of an air electrode versus oxygen of atmospheric pressure.

equilibria are readily obtained as lines separating the various fields. Only one ternary compound, $CuGeO_3$, exists at all temperatures investigated. The ranges of the Cu(α) phase and the liquid state in the binary Cu–Ge system were taken from the literature (*26*).

The temperature dependences of the voltages relating to the various three-phase regions of the ternary system are plotted in Fig. 6. In addition, data calculated from the literature for the binary systems Cu–O (*21, 22, 25*) and Ge–O (*22*) are given, as well as those determined from the Gibbs energies of formation of the pure phases of the compounds which contribute to the three-phase equilibrium Cu_2O–$CuGeO_3$–GeO_2 (*14, 22, 25*) according to Eq. (3). The somewhat lower cell voltages observed in the case of the presence of three components compared to binary two-phase equilibria is due to the partial solubility of the third compound in one or both phases which lie on the legs of the Gibbs triangle. On the contrary, one may conclude that the solubility, i.e., the width of one- and two-phase regions, is small if nearly identical voltages are observed. There obviously exists a solution of GeO_2 in Cu and/or Cu_2O, of Cu in Ge and/or GeO_2, and of $CuGeO_3$ in CuO and/or Cu_2O. It should be noted that the spacings between the straight lines are not necessarily an indication of the phase widths.

The slope of the straight line observed for the Cu_2O–$CuGeO_3$–GeO_2 equilibrium is quite different from the one calculated from literature data (*14, 21, 22, 25*). However, the agreement in the magnitude is very good. The standard Gibbs energy of formation of the ternary compound $CuGeO_3$ which resulted from this investigation is listed in Table I.

The formula employed is

$$\Delta G_f^\circ(\mathrm{CuGeO_3}) = -\mathrm{Eq} + \tfrac{1}{2}\Delta G_f^\circ(\mathrm{Cu_2O}) + \Delta G_f^\circ(\mathrm{GeO_2}). \qquad (7)$$

For ΔG_f° (Cu_2O) the results as expressed by Eq. (6) and for ΔG_f° (GeO_2) data taken from thermodynamic tables (*22*) have been considered. From the temperature dependence of ΔG_f° ($CuGeO_3$), the following standard entropy of formation is obtained:

$$\Delta S_f^\circ(\mathrm{CuGeO_3}) = -283\ \mathrm{J/mole\cdot K} \quad (800 \leq T \leq 950^\circ\mathrm{C}).$$

The standard enthalpy of formation, $\Delta H_f^\circ = \Delta G_f^\circ + T\Delta S_f^\circ$, is then given by

$$\Delta H_f^\circ(\mathrm{CuGeO_3}) = -756.8\ \mathrm{kJ/mole} \quad (800 \leq T \leq 950^\circ\mathrm{C}).$$

For comparison, the Gibbs formation energy of $CuGeO_3$ which was determined by calorimetric measurements (*14*) of the reaction $CuO + GeO_2 = CuGeO_3$ using the same thermodynamic data for Cu_2O and GeO_2 as above and Tretyakov's results (*25*) for the equilibrium oxygen partial pressure between CuO and Cu_2O is also listed. The formation entropy which results from those data is approximately 10% larger in its absolute value than the one obtained in this work.

Parallel to this work, some conventional annealing experiments under defined oxygen partial pressure conditions have been performed in our laboratory to investigate the question of the existence of further ternary compounds in the system Cu–Ge–O (*27*). These experiments did not result in any indication of other previously unknown ternary compounds at about 900°C.

It may be concluded from the present results that the electrochemical technique employed here is a very powerful tool for the simultaneous determination of the complete phase diagram of multicomponent systems and the thermodynamics of the formation of their phases. A considerably higher resolution is attainable with regard to both properties than with other techniques. Similar investigations may also be performed with other ternary oxides or systems having electroactive components other than oxygen. Investigations of the ternary system Fe–Y–O have also been performed (*28, 29*).

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TABLE I

STANDARD GIBBS ENERGY OF FORMATION OF $CuGeO_3$ AS DETERMINED ACCORDING TO EQ. (7)[a]

		kJ/mole			
T (°C)	E(V) vs 101.3 kPa (this work)	ΔG_f° (Cu_2O) (*21*)	ΔG_f° (GeO_2) (*22*)	ΔG_f° ($CuGeO_3$) (this work)	ΔG_f° = ($CuGeO_3$) (cal. from Refs. *14, 21, 22*)
800	0.347	−91.14	−373.7	−452.8	−450
850	0.314	−87.61	−364.6	−438.7	−437
900	0.280	−84.07	−355.4	−424.5	−424
950	0.247	−80.54	−346.2	−410.3	−411

[a] The employed Gibbs energies of formation of Cu_2O and GeO_2 are also listed, as well as the Gibbs energy of formation of $CuGeO_3$ calculated from calorimetric measurements as reported in the literature.

References

1. W. Weppner, C. Li-chuan, and W. Piekarczyk, submitted for publication.
2. C. Li-chuan and W. Weppner, *Naturwissenschaften* **65**, 595 (1978).
3. Y. Ginetti, *Bull. Soc. Chim. Belg.* **63**, 209 (1954).
4. E. I. Speranskaya and I. B. Barskaya, *Izv. Akad. Nauk SSSR Otd. Chim. Nauk* 1447 (1959).
5. E. I. Speranskaya, *Izv. Akad. Nauk SSSR Neorg. Mater.* **3**, 1271 (1967).
6. F. Liebau, *Z. Phys. Chem. (Leipzig)* **206**, 73 (1956).
7. H. Strunz, *Naturwissenschaften.* **47**, 154 (1960).
8. H. Völlenkle, A. Wittman, and H. Nowotny, *Monatsh. Chem.* **98**, 1362 (1967).
9. N. G. Schmahl and F. Müller, *Z. Anorg. Allg. Chem.* **332**, 12 (1964).
10. D. Hennings, *J. Solid State Chem.* **31**, 275 (1979).
11. W. L. W. Ludekens, *J. Inorg. Nucl. Chem.* **3**, 281 (1956).
12. A. Durif-Varambon, E. F. Bertaut, and R. Pauthenet, *Ann. Chim.* **1**, 525 (1956).
13. D. Hennings, *Ber. Dt. Keram. Ges.* **55**, 359 (1978).
14. A. Navrotsky, *J. Solid State Chem.* **11**, 10 (1974).
15. C. Wagner, *Naturwissenschaften* **31**, 265 (1943).
16. J. W. Patterson, E. C. Bogren, and R. A. Rapp, *J. Electrochem. Soc.* **114**, 752 (1967).
17. L. D. Burke, H. Rickert, and R. Steiner, *Z. Phys. Chem. N.F.* **74**, 146 (1971).
18. W. Weppner, *Z. Naturforsch.* **31a**, 1336 (1976).
19. W. Weppner, *J. Solid State Chem.* **20**, 305 (1977).
20. C. Wagner, *J. Chem. Phys.* **21**, 1819 (1953).
21. S. Pyun and F. Muller, *High Temp. High Press.* **9**, 111 (1977).
22. I. Barin and O. Knacke, "Thermochemical Properties of Inorganic Substances," Springer-Verlag, Berlin (1973); I. Barin, O. Knacke, and O. Kubaschewski, "Supplement," Springer-Verlag, Berlin (1977).
23. M. M. Faktor and J. I. Carasso, *J. Electrochem. Soc.* **112**, 817 (1965).
24. R. J. L. Andon and K. C. Mills, *J. Chem. Thermodyn.* **3**, 583 (1971).
25. Yu. D. Tretyakov, V. F. Komarov, N. A. Prosvirnina, and I. B. Kutsenok, *J. Solid State Chem.* **5**, 157 (1972).
26. H. Hansen, "Constitution of Binary Alloys," 2nd ed., p. 585, McGraw-Hill, New York (1958).
27. V. S. Stubican, private communication.
28. W. Piekarczyk, W. Weppner, and A. Rabenau, *Mat. Res. Bull.* **13**, 1077 (1978).
29. W. Piekarczyk, W. Weppner, and A. Rabenau, *Z. Naturforsch.* **34a**, 430 (1979).