

Ternary Chlorides in the Systems $ACl/TmCl_3$ ($A = Cs, Rb, K$)

Chagoui Zheng

Peking University, Beijing, China

and

Hans J. Seifert¹

Inorganic Chemistry, University Gh Kassel, Heinrich-Plett-Str. 40, D-34109 Kassel, Germany

Received March 27, 1997; in revised form August 14, 1997; accepted September 5, 1997

The phase diagrams of the systems $ACl/TmCl_3$ ($A = Cs, Rb, K$) were investigated by DTA and XRD. Compounds A_3TmCl_6 , A_2TmCl_5 , ATm_2Cl_7 , and $Cs_3Tm_2Cl_9$ exist. Rb_2TmCl_5 is the first 2:1 compound in the series La to Lu crystallizing in the Cs_2DyCl_5 structure with connected $[TmCl_6]$ octahedra. By emf vs T measurements in galvanic chlorine cells for solid electrolytes for all compounds, ATm_2Cl_7 excepted, the thermodynamic functions for the formation from the compounds adjacent in the phase diagrams could be determined. © 1998 Academic Press

Key Words: ternary thulium chlorides; phase diagrams; thermodynamic properties.

1. INTRODUCTION

In connection with our research on ternary lanthanide chlorides, we have investigated the pseudobinary systems of thulium(III) chloride with the alkali metal chlorides CsCl, RbCl, and KCl. Hitherto, only the unit cells of those compounds that could be prepared directly from melts were determined by Meyer (1) with X-ray powder patterns.

Our special interests were pointed to the question of whether the systematic rules found from the investigations of the analogous systems with $DyCl_3$ (2), $HoCl_3$ (3), and $ErCl_3$ (4) are continued, particularly, whether compounds A_2TmCl_5 with $A = Rb$ and K exist.

Furthermore, we have determined the mutual stability of the compounds ($\Delta_{syn}G^\circ$ values) in a system by means of emf measurements in galvanic cells for solid electrolytes.

2. EXPERIMENTAL

Materials

$TmCl_3$ was prepared either by dehydration of $TmCl_3 \cdot 6H_2O$, as described in detail for $DyCl_3$ (2), or by heating thulium formate in an HCl stream to 280–320°C. $Tm(HCOO)_3$ was obtained by boiling $TmCl_3 \cdot 6H_2O$ in formic acid (10 g in 50 ml), passing inert gas through the solution. The formate was formed as a colorless, nonhygroscopic precipitate. $TmCl_3 \cdot 6H_2O$ was obtained from a solution of Tm_2O_3 (99.99%; Zhujiang Refin. Guangzhou/China) in hydrochloric acid.

Differential Thermal Analysis (DTA)

The DTA measurements were performed in a home-built device for samples (~0.5 g) in vacuum-sealed quartz ampoules. If necessary, the material could be annealed after melting with a gas flame and homogenizing by shaking and quenching. In general, heating curves were measured (heating rate 2°C min⁻¹).

X-Ray Powder Patterns

Powder patterns were taken at ambient temperature with a Philips PW 1050/25 goniometer equipped with a proportional counter and a vacuum attachment. During exposure ($CuK\alpha$ radiation), the samples were kept under a helium atmosphere. For dynamic high-temperature photographs, the Guinier–Simon method was applied. Corundum ($a = 475.92$ pm, $c = 1299.00$ pm) was used as an internal standard.

Emf Measurements (5)

For the formation of the compound A_3TmCl_6 from ACl and A_2TmCl_5 , for example, the setup of the cell was

¹ To whom correspondence should be addressed.

(graphite + Cl₂)/ACl/A⁺-conducting diaphragm/A₂TmCl₅ (+ A₃TmCl₆)/(graphite + Cl₂)/temperature range 300–400°C.

The collected emf vs *T* values were subjected to a linear regression analysis.

Measurements of solution enthalpies, which need at least 5 g of each compound, were not performed as for the former systems because of the restricted amount of thulium oxide.

3. RESULTS

Ternary Chlorides from Solutions

Some ternary chlorides could be prepared conveniently from aqueous solutions or from acetic acid, provided they are congruently soluble in these solvents.

In the case of aqueous solutions, ACl and Tm₂O₃ were dissolved with the correct molar ratio in hydrochloric acid. These solutions were evaporated to dryness at temperatures of 100–120°C. The following compounds could be prepared: Cs₄TmCl₇ [the crystal structure could be solved by single-crystal measurement, as previously described (6)]; Cs₃TmCl₆ [orthorhombic modification, space group *Pbcm* (7)]; and Cs₂TmCl₅·H₂O [erythro-siderite structure (space group *Pnma*, *Z* = 4); the orthorhombic cell parameters are *a* = 1460.4(3), *b* = 1049.4(4), and *c* = 753.0(2) pm]. Cs₂TmCl₅·H₂O can be dehydrated by heating in an HCl stream at slowly rising temperature from 200 to 300°C.

From acetic acid, the compounds Cs₃TmCl₆ and Rb₃TmCl₆, both crystallizing with the Cs₃BiCl₆ structure (space group *C2/c*), could be precipitated with HCl gas. K₃TmCl₆ (space group *P2₁/c*) could be obtained only together with KCl. The solutions were prepared from TmCl₃·6H₂O and alkali metal carbonate in the correct molar ratio.

Phase Diagrams and Crystal Structures

Figure 1 illustrates the results of the DTA measurements on the systems ACl/TmCl₃ (*A* = Cs, Rb, K). Phase transitions below 350°C are not included in the diagrams.

As already found for ErCl₃, melts of TmCl₃ also react slowly with quartz. Therefore, the melting point was measured in a corundum crucible. The measured value of 1094 K (821°C) agrees well with that recently found by Gaune-Escard (8).

In the system CsCl/TmCl₃ four compounds were found: two congruently melting ones (Cs₃TmCl₆ and CsTm₂Cl₇) and two incongruently melting ones (Cs₂TmCl₅ and Cs₃Tm₂Cl₉). Cs₃TmCl₆ is the first tetramorphic tricesium hexachloro compound of the lanthanides: besides *L*-Cs₃TmCl₆ with the Cs₃BiCl₆ structure, the *H*-modification in the cubic elpasolite type, and orthorhombic Cs₃TmCl₆ from aqueous solution, a fourth modification exists between 376 and 409°C with a still unknown space group. For

CsTm₂Cl₇ two phase transitions were found: one at 172°C and a second at 432°C.

In the system RbCl/TmCl₃ two congruently melting compounds—Rb₃TmCl₆ and RbTm₂Cl₇, both dimorphic—and the incongruently melting Rb₂TmCl₅ with the Cs₂DyCl₅ structure exist.

The system KCl/TmCl₃ contains three compounds as in the RbCl system. However, KTm₂Cl₇ is now incongruently melting. K₂TmCl₅ is the first member of a new structure family, which is actually investigated with the isotypic compound K₂YbCl₅; probably the space group is *P2₁/c*. The third compound, K₃TmCl₆, has in addition to the cubic high-temperature and the monoclinic low-temperature modifications a middle-temperature phase above ~120°C. The correct structure (*Cmmm*?) is not yet proved; however, it can be described with a pseudomonoclinic cell with *a* = *c*.

The unit cells of the majority of the found compounds already have been determined by Meyer and co-workers from powder patterns: CsTm₂Cl₇ and RbTm₂Cl₇: RbDy₂Cl₇ type, space group *Pnma* (9); KTm₂Cl₇: KDy₂Cl₇ type, space group *P2₁/c* (9); Cs₃Tm₂Cl₉: Cs₃Tl₂Cl₉ type, space group *R $\bar{3}c$* (10); Cs₂TmCl₅ and Rb₂TmCl₅: Cs₂DyCl₅ type, space group *Pbnm* (id. *Pnma*) (10); *L*-Rb₃TmCl₆: Cs₃BiCl₆ type, space group *C2/c* (11). The unit cells of the compounds listed in Table 1, were still unknown; the lattice parameters for Cs₃Tm₂Cl₉ are refined.

A synopsis of the structures of all ternary lanthanide halides, including the fluorides, bromides, and iodides, which were known in 1982 was given by Meyer (1). According to this summary, the Cs₂DyCl₅ type and the structure for the compounds *ALn₂Cl₇* are originally determined by Meyer himself. The elpasolite type, which is the aristotype for all 3:1 compounds, and the structure of enneachlorides are well known. The K₂PrCl₅ type is identical with the Y₂HfS₅ structure, solved by Jeitschko (13).

Results of emf Measurements

Emf values were measured for the formation of each compound from ACl and the adjacent TmCl₃-richer compound in the temperature range ~300–400°C. In this range, the dependence of emf on *T* was linear. Thus, the equations for the regression lines could be transformed by multiplication with $-nF$ to the Gibbs–Helmholtz equation $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$.

Emf measurements could not be performed for the ErCl₃-richest compounds ATm₂Cl₇. According to our present experience, the emf cells break down for emf values higher than ~500 mV.

In the following, the Gibbs–Helmholtz equations for the reaction in the cell ($\Delta_r G^\circ$) are listed together with the temperature ranges of the measurements. The range of error was smaller than 1 kJ mol⁻¹ for the energy values and 0.8J K⁻¹ mol⁻¹ for the entropies.

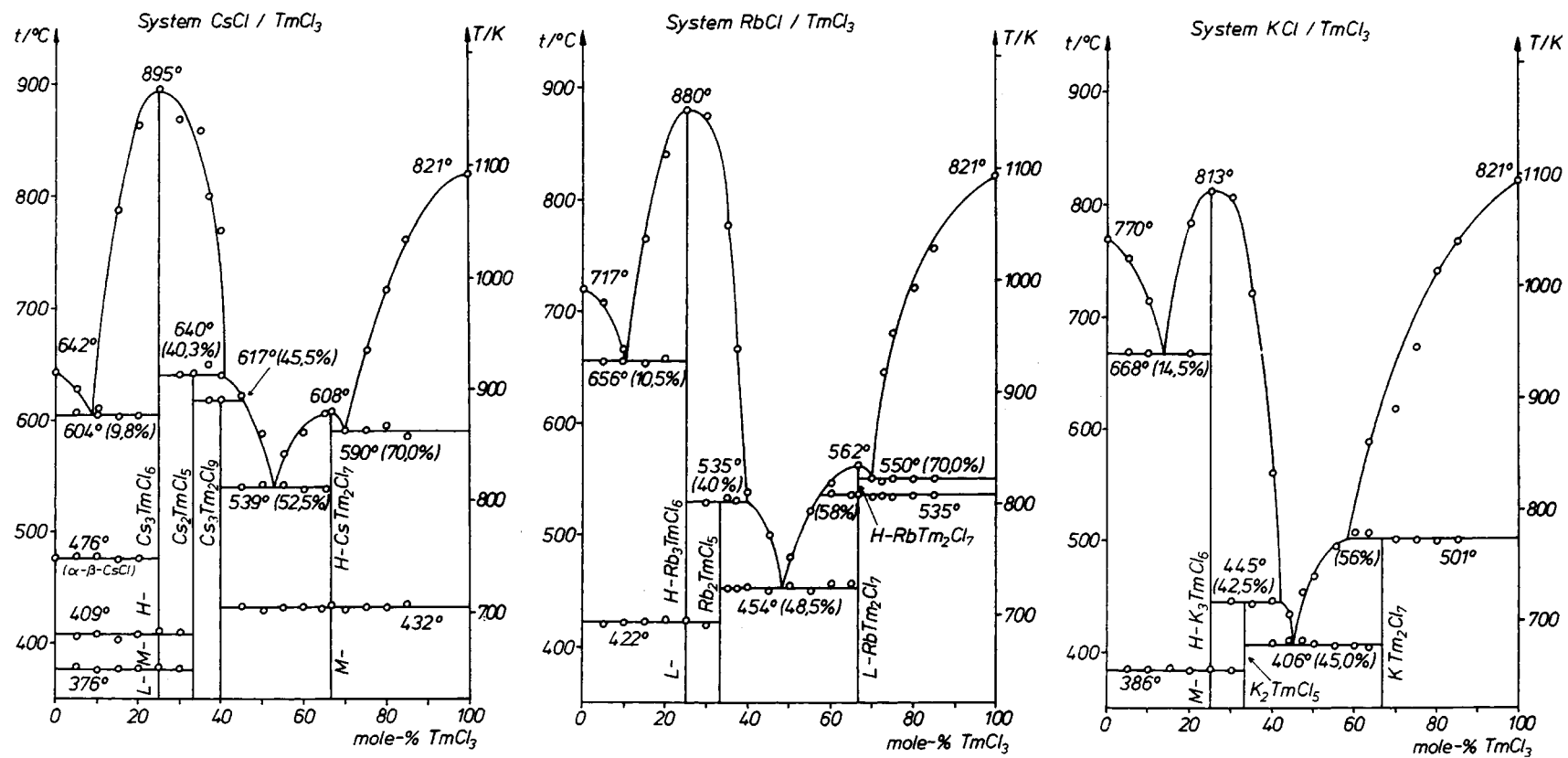
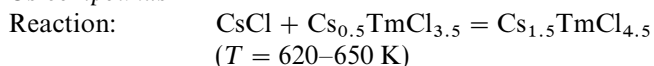

 FIG. 1. Phase diagrams of the systems $ACl/TmCl_3$.

TABLE 1
Hitherto Unknown Unit Cell Parameters of Ternary Thulium Chlorides

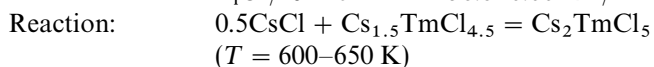
Compound	Space group	Z	a (pm)	b (pm)	c (pm)	β (deg)
Cs ₄ TmCl ₇	R $\bar{3}m$	3	768.2(2)		2621.4(6)	
Cs ₃ TmCl ₆ (aq soln)	<i>Pbcm</i>	8	811.5(2)	1304.3(3)	2636.6(7)	
<i>L</i> -Cs ₃ TmCl ₆	<i>C2/c</i>	8	2685.1(8)	811.5(2)	1308.9(6)	100.14(3)
<i>H</i> -Cs ₃ TmCl ₆ (500°C)	<i>Fm$\bar{3}m$</i>	4	1156.0(2)			
Cs ₃ Tm ₂ Cl ₉	<i>R$\bar{3}c$</i>	6	1299.7(2)		1827.4(5)	
<i>H</i> -Rb ₃ TmCl ₆ (500°C)	<i>Fm$\bar{3}m$</i>	4	1110.3(2)			
<i>L</i> -K ₃ TmCl ₆	<i>P2₁/c</i>	4	1307.6(3)	771.5(2)	1256.7(2)	109.96(2)
<i>M</i> -K ₃ TmCl ₆	pseudo- <i>P2₁/c</i>	4	1302.0	751.4	1302.0	109.46
<i>H</i> -K ₃ TmCl ₆ (500°C)	<i>Fm$\bar{3}m$</i>	4	1090.1(2)			
(K ₂ TmCl ₅)	<i>P2₁/c</i>	4	1134.5	1009.7	822.4	104.0)

Cs compounds



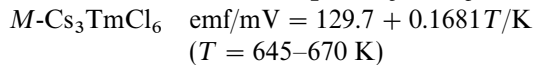
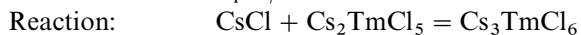
$$\text{emf/mV} = 402.0 + 0.0252T/\text{K}$$

$$\Delta_r G^\circ/\text{kJ mol}^{-1} = -38.8 - 0.0024T/\text{K}$$



$$\text{emf/mV} = 225.6 + 0.0796T/\text{K}$$

$$\Delta_r G^\circ/\text{kJ mol}^{-1} = -10.9 - 0.0038T/\text{K}$$



$$\Delta_r G^\circ/\text{kJ mol}^{-1} = -12.5 - 0.0162T/\text{K}$$

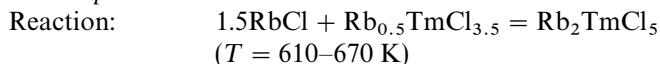


$$\Delta_r G^\circ/\text{kJ mol}^{-1} = -16.8 - 0.0095T/\text{K}$$

$$\Delta_r G^\circ(L) = \Delta_r G^\circ(M) \text{ at } 645 \text{ K } (372^\circ\text{C})$$

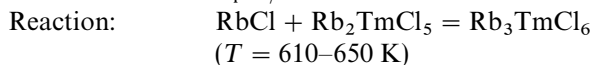
[from DTA: 376°C]
Transition enthalpy = 4.3 kJ mol⁻¹,
transition entropy = 6.7 J K⁻¹ mol⁻¹

Rb compounds



$$\text{emf/mV} = 216.1 + 0.1184T/\text{K}$$

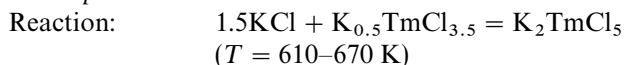
$$\Delta_r G^\circ/\text{kJ mol}^{-1} = -31.3 - 0.0171T/\text{K}$$



$$\text{emf/mV} = 259.8 + 0T/\text{K}$$

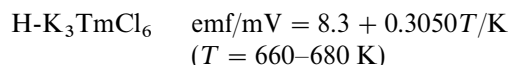
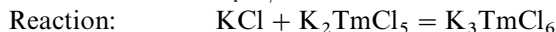
$$\Delta_r G^\circ/\text{kJ mol}^{-1} = -25.1$$

K compounds

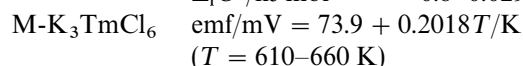


$$\text{emf/mV} = 159.4 + 0.1280T/\text{K}$$

$$\Delta_r G^\circ/\text{kJ mol}^{-1} = -23.1 - 0.0177T/\text{K}$$



$$\Delta_r G^\circ/\text{kJ mol}^{-1} = -0.8 - 0.0294T/\text{K}$$



$$\Delta_r G^\circ/\text{kJ mol}^{-1} = -7.3 - 0.0195T/\text{K}$$

$\Delta_r G^\circ(M) = \Delta_r G^\circ(H)$ at 659 K (386°C)
[From DTA: 386°C]

Transition enthalpy = 6.5 kJ mol⁻¹,
Transition entropy = 9.9 J K⁻¹ mol⁻¹

In a (pseudo)binary system a compound is stable in competition with all other existing compounds when the free enthalpy for the formation from its two adjacent compounds in the phase diagram—the free enthalpy of syn-reaction, $\Delta_{\text{syn}}G^\circ$ —is negative. We have calculated such $\Delta_{\text{syn}}G^\circ$ equations for all compounds for which $\Delta_r G^\circ$ values could be measured; these are all compounds between *ACl* and *A*_{0.5}TmCl_{3.5}, which are used as references. Compounds are stable at temperatures higher than 0 K when their syn-reaction enthalpies are negative. If these enthalpies are endothermic, they must be compensated in the Gibbs–Helmholtz equations $\Delta_{\text{syn}}G^\circ = \Delta_{\text{syn}}H^\circ - T\Delta_{\text{syn}}S^\circ$ by a sufficiently high $T\Delta_{\text{syn}}S^\circ$ term.

Gibbs–Helmholtz equations for $\Delta_{\text{syn}}G^\circ$

$$\frac{1}{3}\text{Cs}_{0.5}\text{TmCl}_{3.5} + \frac{2}{3}\text{Cs}_2\text{TmCl}_5$$

$$= \text{Cs}_{1.5}\text{TmCl}_{4.5} \quad \Delta_{\text{syn}}G^\circ/\text{kJ mol}^{-1} = -5.7 + 0.0017T/\text{K}$$

$$\frac{2}{3}\text{Cs}_{1.5}\text{TmCl}_{4.5} + \frac{1}{3}\text{L-Cs}_3\text{TmCl}_6$$

$$= \text{Cs}_2\text{TmCl}_5 \quad = -1.7 + 0.0006T/\text{K}$$

$$\text{CsCl} + \text{Cs}_2\text{TmCl}_5 = \text{L-Cs}_3\text{TmCl}_6 \quad = -16.8 - 0.0095T/\text{K}$$

$$0.4\text{Rb}_{0.5}\text{TmCl}_{3.5} + 0.6\text{Rb}_3\text{TmCl}_6$$

$$= \text{Rb}_2\text{TmCl}_5 \quad = 2.4 - 0.0068T/\text{K}$$

$$\Delta_{\text{syn}}G^\circ = 0 \text{ at } 353 \text{ K } (80^\circ\text{C})$$

$$\text{RbCl} + \text{Rb}_2\text{TmCl}_5 = \text{Rb}_3\text{TmCl}_6 \quad = -25.1$$

$$0.4\text{K}_{0.5}\text{TmCl}_{3.5} + 0.6\text{M-K}_3\text{TmCl}_6$$

$$= \text{K}_2\text{TmCl}_5 \quad = -4.8 + 0.0046T/\text{K}$$

$$\text{KCl} + \text{K}_2\text{TmCl}_5 = \text{M-K}_3\text{TmCl}_6 \quad = -7.3 - 0.0195T/\text{K}$$

4. DISCUSSION

The main result of these investigations is that the thulium systems are analogous to the systems with erbium (4) and holmium (3): there are existing compounds A_3LnCl_6 , A_2LnCl_5 , ALn_2Cl_7 , and $Cs_3Ln_2Cl_9$. In the group ALn_2Cl_7 , the lanthanide ion has the CN 7; the other compounds are built up by $[LnCl_6]$ octahedra, isolated in the 3:1 compounds, connected in the other families. This seems to hold for K_2TmCl_5 , too, the structure of which is correlated with that of K_3TmCl_6 .

For compounds A_2LnCl_5 two structure families exist. For the K_2PrCl_5 type the CN is 7 for the Ln^{3+} and (8 + 1) for the alkali metal ions. In the second group—the Cs_2DyCl_5 type (space group $Pnma$)—the lanthanide ions are octahedrally coordinated, the CN for the alkali metal ions is 10/11. It must be pointed out that the interstices for the A^+ ions are more spacious in the Cs_2DyCl_5 type than in the K_2PrCl_5 type.

With the large ions Ln^{3+} from La^{3+} to Nd^{3+} , for all A^+ the K_2PrCl_5 structure exists. The Cs_2DyCl_5 type with the smaller CN for Ln^{3+} begins for the Cs compounds with samarium, and for the Rb compounds with holmium.

Rb_2TmCl_5 is the only ternary thulium chloride with an endothermic $\Delta_{syn}H^\circ$ of 2.4 kJ mol^{-1} with a corresponding formation temperature of 353 K. Rb_2ErCl_5 is stable above 593 K ($\Delta_{syn}H^\circ = 6.0 \text{ kJ mol}^{-1}$), and Rb_2HoCl_5 has only a small range of existence between 687 and 785 K. For the K compounds the $\Delta_{syn}H^\circ$ values are -22.2 (K_2HoCl_5) and -4.8 kJ mol^{-1} (K_2TmCl_5).

Rb_2LnCl_5 -compounds with Tb^{3+} ($r = 0.923 \text{ \AA}$) and Dy^{3+} ($r = 0.908 \text{ \AA}$) do not exist: Here the 10/11 interstices

generated by the $[LnCl_6]$ octahedra are still too big for Rb^+ and also for K^+ . Beginning with Ho^{3+} ($r = 0.894 \text{ \AA}$), they are of the appropriate size for Rb^+ , but not yet for the smaller K^+ . Thus, K_2HoCl_5 crystallizes with the K_2PrCl_5 structure. A compound K_2ErCl_5 does not exist.

ACKNOWLEDGMENTS

Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. C.Z. thanks the Deutsche Akademische Auslandsamt for a research grant.

REFERENCES

1. G. Meyer, *Progres. Solid State Chem.* **14**, 141 (1982).
2. H. J. Seifert, and R. Krämer, *Z. Anorg. Allg. Chem.* **620**, 1543 (1994).
3. M. Roffe, and H. J. Seifert, *J. Alloys Compd.* **257**, 128 (1997).
4. D. Büchel, J. Krok-Kowalski, and H. J. Seifert, *Thermochim. Acta* **282/283**, 297 (1996).
5. H. J. Seifert and G. Thiel, *J. Chem. Thermodyn.* **14**, 1159 (1982).
6. G. Reuter, J. Sebastian, and G. Frenzen, *Acta Crystallogr., C* **52**, 1859 (1996).
7. G. Reuter, and G. Frenzen, *J. Solid State Chem.* **116**, 329 (1995).
8. M. Gaune-Escard, L. Rycerz, W. Szczeniowski, and A. Bogacz, *J. Alloys Compd.* **204**, 193 (1994).
9. G. Meyer, P. Ax, A. Cromm, and H. Linzmeier, *J. Solid State Chem.* **98**, 323 (1984).
10. G. Meyer and A. Schönemund, *Mater Res. Bull.* **15**, 89 (1980).
11. G. Meyer, J. Soose, A. Moritz, V. Vitt, and T. Holljes, *Z. Anorg. Allg. Chem.* **521**, 161 (1985).
12. H. Mattfeld and G. Meyer, *Z. Anorg. Allg. Chem.* **618**, 13 (1992).
13. W. Jeitschko and P. C. Donohue, *Acta Crystallogr., B* **31**, 1890 (1975).