Inorg. Chem. **1991**, *30*, 4789–4794

Contribution from the Department of Chemistry and Ames Laboratory—DOE,[1]
Iowa State University, Ames, Iowa 50011

Syntheses and Structures of $LaGe_{2-x}$ and LaAlGe: Interrelationships among the α-$ThSi_2$, α-$GdSi_2$, and LaPtSi Structure Types

Arnold M. Guloy and John D. Corbett*

Received March 22, 1991

α-$LeGe_{2-x}$ has been synthesized by powder sintering and shown to have the composition range $0.33 \le x \le 0.40$ and the orthorhombic α-$GdSi_2$-type structure (*Imma*, $Z = 4$) with deviations from near-tetragonal dimensions that increase with decreasing x. The structure of $LaGe_{1.60(1)}$ at 20 °C was refined from single-crystal data ($a = 4.2680$ (7), $b = 4.2735$ (6), $c = 14.404$ (1) Å; R, R_w = 2.5%, 2.3%) with the germanium deficiency predominantly on one of two independent non-metal sites. The allowed second-order phase transition of α-$LaGe_{2-x}$ to the β-form in the tetragonal α-$ThSi_2$-type structure ($I4_1/amd$) has been observed by powder diffractometry over the range of 425–635 °C with decreasing x. The structural nature of the transition is described. The $TbGe_{1.67}$ superstructure reported in space group *Fdd*2 is noted to also be consistent with a second-order transition from a high-temperature α-$ThSi_2$-type structure. The fully stoichiometric Zintl phase LaAlGe was synthesized and shown to exist in the ordered LaPtSi version of the $ThSi_2$ structure ($I4_1md$; $Z = 4$; $a = 4.336$ (1), $c = 14.828$ (5) Å; R, R_w = 3.2%, 2.1%). The stability of tetragonal, fully stoichiometric $LaAl_xGe_{2-x}$ extends well into the ternary system to $x \le 0.2$. Oxygen has a similar effect and stabilizes tetragonal $LaGe_{2-x}(O)$ (with small x) at room temperature.

Introduction

Research on rare-earth-metal carbides and silicides has been extensive, mainly because of their importance in high-technology applications.[2–4] Although the germanides offer a wider variety of electronic and optical properties of importance to modern engineering, very little research has been done on them, and data are comparatively sparse.[3–6] Interest in rare-earth-metal disilicides and digermanides has been furthered by their electrical and magnetic properties.[7–10] Seven different structure types have been reported for these,[11–15] all related to either AlB_2-type or α-$ThSi_2$-type structures. Most of these have been found to be nonstoichiometric,[5,6] but the stoichiometry ranges have not been well determined. Structures of the digermanides of the larger elements La–Sm are reported to be only of the tetragonal α-$ThSi_2$ or the related orthorhombic α-$GdSi_2$ type.[16] Additional AlB_2-related structures occur for the smaller rare-earth-metal (Gd–Lu, Y) digermanides and disilicides. The digermanides of the divalent metals (Eu, Yb) have structures related to the $CaSi_2$ type.[16]

Our research on the La–Ge binary system was prompted by our interest in the interstitial chemistry of La_5Ge_3.[17] The binary phase diagrams for the La–Ge system by Gladyshevskii[18] and by Lyutaya and Goncharuk[19] show several uncertainties. These indicate α and β phases around $LaGe_{1.67}$ without specifying the corresponding structures for each, and they also have an unspecified phase breadth around $LaGe_{1.60}$. The two phases have been reported by others to have the α-$ThSi_2$[11,12] and α-$GdSi_2$[13] structures (above), the former being stable at higher temperatures.[5] It has also been suggested, but not confirmed, that these two structures are related by a "polymorphic transformation", although another report indicated only the former tetragonal form existed.[18] A point of concern is that the purities of the starting rare-earth metals used in the earlier research ranged from only 94.6% to 99%. On the basis of our experience, the effects of impurity oxygen, carbon, or both may be considerable.[17]

In contrast, other authors have reported that stoichiometric $LaGe_2$ can be achieved via La_2O_3–Ge reactions as well as by arc-melting of the elements.[18,20,21] A similar situation also exists with the analogous Ce, Nd, and Pr germanides.[4] These seemingly conflicting observations and uncertainties led us to reinvestigate this portion of the La–Ge system. Our studies have established both the phase relationships present in the stoichiometry range $LaGe_{1.5}$–$LaGe_2$ and the structural and bonding relationships between α- and β-$LaGe_{2-x}$. We also report on the synthesis and crystal structure of the analogue LaAlGe.

Experimental Section

Materials. The lanthanum metal was obtained from Ames Laboratory in the form of a rod (99.999%), with the following principal impurities (ppm atomic): O, 190; N, 128; C, 34; F, 80; Fe, 7.6. The rod was cut into small pieces and kept in a He-atmosphere glovebox. Electronic grade germanium chunks obtained from Johnson-Matthey had a quoted electrical resistivity of 50 Ω cm at 20 °C (two-point method). High-purity aluminum granules were obtained from United Mineral and Chemical.

Syntheses. Containers made from $^3/_8$ in o.d. tantalum tubing and melting reactions were found suitable for all of the La–Ge and La–Ge–Al compositions studied. A mixture of weighted reagents with the desired stoichiometry was cold-pressed into a pellet within the glovebox and welded within a Ta container. This was then heated in a high-temperature high-vacuum furnace from room temperature to 1150 °C over 2 days. The temperature was then increased to 1350 °C for 1 day, after which it was slowly decreased to 1150 °C over 2 days and back to room temperature over 5 days.

The high-temperature high-vacuum furnace used is an Astro 1000A graphite resistance furnace modified to avoid carbon contaminants and to maintain a high vacuum in the reaction chamber. The furnace was divided into two sections by a muffle tube of impervious alumina, and

---

(1) Ames Laboratory—DOE is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Materials Sciences Division.

(2) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984; pp 427–465.

(3) *Kirk-Othmer Encycl. Chem. Technol., 3rd Ed.* **1980**, *11*, 791–802.

(4) Samsonov, G.; Bondarev, V. *Germanides*; Consultants Bureau: New York, 1969.

(5) (a) Gokhale, A. B.; Abbaschian, G. J. *Bull. Alloy Phase Diagr.* **1989**, *10*, 385. (b) Massalski, T. B., Ed. *Binary Alloy Phase Diagrams*, 2nd ed. American Society for Metals: Metals Park, OH, 1990.

(6) Eremenko, V. N. *Physical Chemistry Of Condensed Phases*: *Refractory Materials and their Grain Boundaries*; Naukova Dumka: Kiev, **1975**; pp 191–201.

(7) Sekizawa, K.; Yasukochi, K. *J. Phys. Soc. Jpn.* **1966**, *21*, 274.

(8) Hasegawa, A.; Yanase, A. *J. Phys. Soc. Jpn.* **1985**, *54*, 3833.

(9) Sekizawa, K. *J. Phys. Soc. Jpn.* **1966**, *21*, 1137.

(10) Matthias, B. T.; Corenzwit, E.; Zachariasen, W. H. *Phys. Rev.* **1958**, *112*, 89.

(11) Brauer, G.; Mitus, A. *Z. Anorg. Chem.* **1942**, *249*, 325.

(12) Brown, A. *Acta Crystallogr.* **1961**, *14*, 860.

(13) Perri, J. A.; Banks, E.; Post, B. *J. Phys. Chem.* **1959**, *63*, 616, 2073.

(14) Lyutaya, M. D.; Goncharuk, A. B. *Izv. Akad. Nauk SSSR, Neorgan. Mater.* **1965**, *1*, 326.

(15) Mayer, I. P.; Banks, E.; Post, B. *J. Phys. Chem.* **1962**, *66*, 693.

(16) Villars, P.; Calvert, L. D. *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*; American Society for Metals: Metals Park, OH, 1985; Vols. 1–3.

(17) Guloy, A.; Corbett, J. D. Unpublished research.

(18) Gladyshevskii, E. I. *J. Struct. Chem.* (*Engl. Transl.*) **1964**, *5*, 523.

(19) Lyutaya, M. D.; Goncharuk, A. B. *Inorg. Mater.* **1965**, *1*, 326.

(20) Lynchak, K. A.; Kosolapova, T. Ya. *Poroshk. Metall.* (*Kiev*) **1967**, *No. 11*, 195.

(21) Lynchak, K. A.; Kosolapova, T. Ya.; Kuz'ma, Yu, B. *Poroshk. Metall.* (*Kiev*) **1968**, *No. 2*, 54.

Table I. Selected Data Collection and Refinement Parameters for LaGe$_{1.60(1)}$ and LaAlGe

	LaGe$_{1.60}$	LaAlGe
space group, Z	*Imma* (No. 74), 4	*I*4$_1$*md* (No. 109), 4
a, Å[a]	4.2680 (7)	4.336 (1)
b, Å	4.2735 (6)	4.336 (1)
c, Å	14.404 (1)	14.828 (5)
V, Å^3	262.72 (4)	278.8 (1)
2θ max, deg	65	55.5
abs coeff (Mo Kα), cm^{-1}	400.9	257.8
transm coeff range	0.840–1.23	0.840–1.63
no. of indep refl	154	126
R,[b] %	2.5	3.2
R_w,[c] %	2.3	2.1

[a] Guinier data, $\lambda = 1.540\,56$ Å. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$; $w = [\sigma(F)]^{-2}$.

the inner reaction chamber was kept evacuated by a turbo-molecular pump to a working pressure of 10^{-6}–10^{-7} Torr. The outer section with the graphite heaters was evacuated by a roughing pump to 10^{-3} Torr, and a Ta sheet wrapped around the alumina tube protected the tube from heater radiation. The sealed Ta reaction containers were enclosed in a capped tantalum canister for further protection. Temperatures in the reaction chamber were measured by a W–Re thermocouple that was in contact with the bottom of the Ta canister.

For quenching experiments, the reactions were first either arc-melted or heated in an induction furnace. Samples in the latter were heated to about 1450 °C for 3 days; then the power was turned off and the sample quenched by promptly sucking some liquid N_2 into the vacuum chamber. Arc-melting reactions were done with a Centorr 5SA single-arc furnace under an Ar atmosphere. Reactor grade zirconium buttons were used as getters, and the reaction buttons were turned over and remelted several times to ensure homogeneity.

Powder X-ray Diffraction. Initial phase analyses of the products were based on X-ray powder patterns obtained from powdered samples mounted between pieces of cellophane tape within a Guinier camera (Enraf-Nonius, Cu Kα radiation, $\lambda = 1.540\,56$ Å) with silicon powder (NIST Standard Reference Material 640a) as an internal standard. The 2θ values of the standard reference lines were fitted to a quadratic in their positions on the film, and the lattice parameters of the sample were calculated by least-squares fit to the 2θ values of the indexed reflections.

High-Temperature X-ray Diffraction. The structures and phase transitions were studied using a Rigaku θ–θ powder diffractometer equipped with a Bühler sample chamber and controlled power supply for heating.[22] The sample chamber consisted of a cylindrical, double-walled, water-cooled chamber made of stainless steel with a beryllium window and a lid holding a rod heater. A Mo sample holder in direct contact with the heater was heated by direct means and by radiation. A W–Re thermocouple attached to the sample holder measured temperatures.

The residual pressure inside the sample chamber was held at about 10^{-6} Torr using a turbo-molecular pump that was attached as close as possible to the sample chamber for maximum efficiency. The sample chamber was also connected through a large valve to a N_2-filled glovebox in order to mount air-sensitive samples. Cu Kα radiation and a graphite monochromator were used.

Single-Crystal X-ray Diffraction. Single-crystal structural analyses were carried out on two samples, LaGe$_{1.6}$ and LaGeAl. Diffraction data were collected at room temperature with the aid of a Rigaku AFC6R single-crystal diffractometer and monochromated Mo Kα radiation, and refinements were done using the TEXSAN crystallographic package.[23] Reflections were measured with ω–2θ scans in both cases. Some details on the data collections and refinements are given in Table I.

LaGe$_{1.60}$. Black, metallic-looking, gemlike crystals obtained from a stoichiometric reaction that had been slowly cooled from 1150 °C were isolated in the glovebox and loaded into thin-walled glass capillaries, which were then sealed off. The candidate crystals were checked with oscillation photographs, and one crystal measuring 0.15 × 0.15 × 0.4 mm was selected for indexing and data collection. The 25 reflections found using SEARCH yielded a body-centered cell with orthorhombic lattice parameters that were close to tetragonal.

The first 200 reflections were taken with no restrictions to test the presence of an $h + k + l = 2n$ condition. After the body-centering condition had been confirmed, the exclusion was applied to the rest of the data collection. Three standard reflections showed an average intensity variation of only 0.01% over a total exposure time of 52 h. A close inspection of the diffraction data showed systematic absences consistent with the *Imma* and *Im*2*a* space groups. This Laue class was confirmed by the subsequent data averaging ($R(I)$ = 4.2%, 13.7%, and 14.4% for *mmm*, 4/*m*, and 4/*mmm*, respectively) and by refinement after absorption correction with DIFABS.[24] Of the two possible space groups, the centric *Imma* was chosen and shown to be correct.

Table II. Positional Parameters for LaGe$_{1.60(1)}$ and LaGeAl[a]

	x	y	z	B_{eq},[b] Å^2	occ
			LaGe$_{1.60}$ (*Imma*)		
La	0	$^1/_4$	0.3750 (1)	0.23 (7)	1.0
Ge1	0	$^1/_4$	0.7923 (3)	0.9 (2)	0.901 (6)
Ge2	0	$^1/_4$	0.9591 (3)	1.5 (2)	0.698 (6)
			LaGeAl (*I*4$_1$*md*)		
La	0	0	0	0.43 (3)	
Ge	0	0	0.4160 (3)	0.89 (6)	
Al	0	0	0.5823 (4)	0.85 (8)	

[a] 23 °C. [b] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\vec{\mathbf{a}}_i\vec{\mathbf{a}}_j$.

Table III. Important Interatomic Distances (Å) and Angles (deg) in LaGe$_{1.60}$ and LaAlGe

	LaGe$_{1.60}$		
La–Ge2 (×4)	3.204 (4)	Ge1–Ge2 (×1)	2.402 (4)
La–Ge1 (×4)	3.221 (4)	Ge1–Ge1 (×2)	2.458 (4)
La–Ge1 (×2)	3.246 (1)	Ge2–Ge2 (×2)	2.440 (4)
La–Ge2 (×2)	3.254 (1)		
Ge1–Ge2–Ge2	118.9 (1)	Ge1–Ge1–Ge1	120.5 (3)
Ge2–Ge1–Ge1	119.7 (2)	Ge2–Ge2–Ge2	122.2 (3)
	LaAlGe		
La–Ge (×2)	3.280 (3)	Ge–Al (×2)	2.470 (7)
La–Ge (×4)	3.310 (2)	Ge–Al (×1)	2.498 (7)
La–Al (×6)	3.300 (6)		
Al–Ge–Al	119.8 (3)	Al–Ge–Al	120.5 (5)

The application of direct methods (SHELXS 76[25]) gave three atom positions close to those known for α-GdSi$_2$.[13] Subsequent least-squares refinement and difference Fourier syntheses did not reveal other significant peaks. Refinement with isotropic thermal parameters proceeded to R = 7.4% with the thermal parameter of one Ge atom unusually larger than for the other. Refinement of the multiplicities of both germanium atoms resulted in lower residuals (R = 4.8%, R_w = 5.0%). The final anisotropic refinement converged at R = 2.5%, R_w = 2.3%, and GOF = 1.18 and a refined stoichiometry of LaGe$_{1.60(1)}$. The multiplicity of lanthanum did not deviate from unity by more than 1% when a single cycle was done on all variables (except scale). The largest residual peak in the final difference map, 1.8 e/Å^3, was 1.0 Å from La.

LaAlGe. Black gemlike single crystals were selected from the products of a reaction with a loaded stoichiometry of LaAlGe that had been slowly cooled from 1200 °C in the high-temperature vacuum furnace. The powder pattern could be entirely indexed with a body-centered tetragonal cell, as expected. The crystals were inspected with the aid of oscillation photographs, and one crystal with the dimensions 0.05 × 0.05 × 0.07 mm was selected for data collection. The 25 reflections found by random search were indexed to a body-centered cell and, on the basis of this and the powder pattern, the body-centering condition was imposed during data collection. Three standard reflections showed negligible intensity variation for the total exposure time of 34 h. After an empirical absorption correction based on three ψ-scans, the diffraction data were found to show systematic absences that corresponded to the centrosymmetric cell *I*4$_1$/*amd* known for α-ThSi$_2$. Preliminary refinement using those parameters[11] as the input model together with mixed occupation of the Si site 8e by equal proportions of Ge and Al resulted in a high residual, 0.26. Moreover, the statistics of the normalized structure factors indicated the absence of a center of symmetry. This was taken as an indication that the Al and Ge network was ordered, in analogy to LaPtSi.[26] This model in the related acentric space group *I*4$_1$*md* with La, Ge, and Al in special positions 4a proved to be correct. Reflection data for the space group *I*4$_1$*md* differ from those of *I*4$_1$/*amd* by the general systematic absence of *hk*0 with $h, k \neq 2n$ for the former. However, with all the atoms in the 4a sites, the special condition *hkl* with $2h + l = 4n$

---

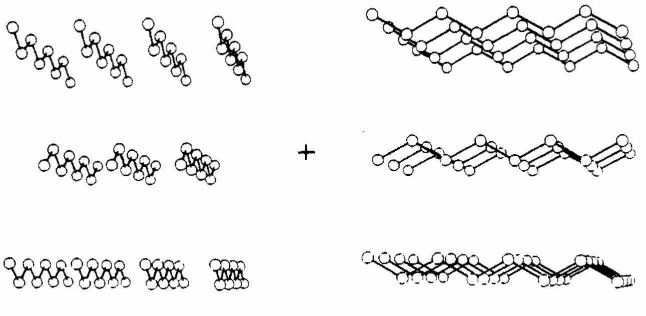
(22) Kim, S.-J. Ph.D. Dissertation, Iowa State University, 1988.

(23) *TEXSAN Structure Analysis Software, Version 5.0*; Molecular Structure Corp: The Woodlands, TX, 1989.

(24) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

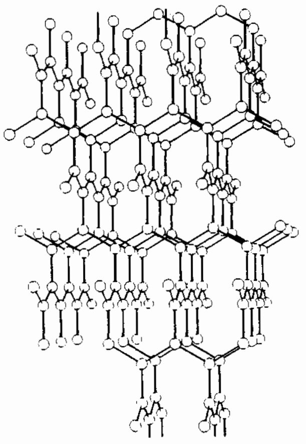
(25) Sheldrick, G.; Egert, E. SHELXS 76. Institut für Anorganische Chemie der Universität, Göttingen, FRG.

(26) Klepp, K.; Parthé, E. *Acta Crystallogr.* **1982**, *B38*, 1105.



Ge1 network

Ge2 network



Ge network in $LaGe_{2-x}$

Figure 1. Construction of the germanium network in $LaGe_{2-x}$ (α-$GdSi_2$-type) (bottom) from alternate stacking of independent zigzag chains of germanium parallel to $\vec{a}$ and $\vec{b}$ (top).

already provides for the absence of $h(k) \neq 2n$. Thus both α-$ThSi_2$ and LaGeAl have the same extinction conditions.

Least-squares refinement and difference Fourier syntheses did not yield other significant peaks. Isotropic and anisotropic refinement proceeded smoothly to $R = 4.2\%$, 3.2% and $R_w = 4.4\%$, 2.1%, respectively. Refinement of the occupancy of the Ge and Al positions did not result either in a significant improvement of the residuals or in occupancies that varied by more than 2% or 3σ from unity. The largest residual peak (3.1 e/Å^3) was <1 Å from La. The other enantiomer gave significantly higher residuals.

Structural parameters for both structures are listed in Table II, while important distances and angles are given in Table III. Other data, anisotropic displacement parameters, and scattering factor results are included in the supplementary material.

Results and Discussion

The $LaGe_{1.6}$ Structure. The general features of this structure are two independent slabs of parallel zigzag chains of germanium atoms that run parallel to the *a* or *b* axis, as shown at the top of Figure 1. The distances between atoms in different parallel chains are about 4.28 Å. These slabs of chains are stacked alternately along the *c* axis, and the atoms in each zigzag chain are alternately connected to the adjoining layers below and above by slightly shorter axial bonds. The result is a three-dimensional network of three-bonded Ge atoms that gives a general impression of 12- (and 10-) membered puckered rings interconnected at every position when viewed along $\vec{a}$ and $\vec{b}$, as shown at the bottom of Figure 1. The lanthanum atoms fill the channels formed by the Ge network (Figure 2), where they have 12-coordination and no close (<4.0 Å) La–La separations. The La–Ge distances of 3.22–3.26 Å are comparable to those of La_5Ge_3 and La_4Ge_3.[17]

The $LaGe_{1.6}$ structure is of the α-$GdSi_2$ type[13] and can be described as a slight orthorhombic distortion of the tetragonal α-$ThSi_2$ type. (The α identifications will be dropped hereafter.) The difference between $GdSi_2$ (*Imma*) and $ThSi_2$ ($I4_1/amd$) is the crystallographic equivalence of the Ge atoms in the latter, so that there are only two Ge–Ge bond distances: one axial (along $\vec{c}$) and one within the chains parallel to *a* and *b*. Breaking the 4-fold symmetry that accompanies the $ThSi_2 \rightarrow GdSi_2$ transformation leads to two inequivalent non-metal sites and two types of chains running perpendicular to one another. These have unequal refined occupancies, 90 (1)% for Ge1 and 70 (1)% for Ge2, giving the composition $LaGe_{1.60(1)}$.

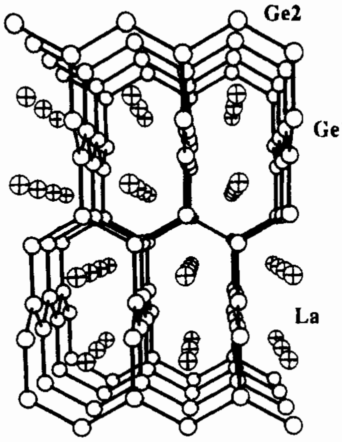


Figure 2. Approximate [010] view of the orthorhombic $LaGe_{2-x}$ structure with $\vec{c}$ vertical and lanthanum as crossed spheres.

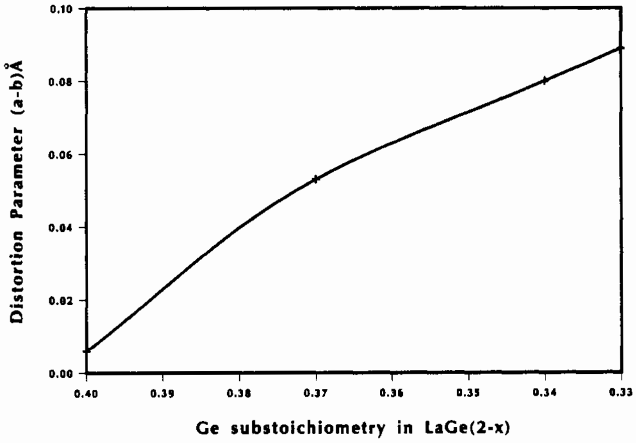


Figure 3. Orthorhombic distortion parameter $a - b$ for $LaGe_{2-x}$ at room temperature as a function of stoichiometry.

In a future article,[27] we will show that the alteration of bond lenths in and occupancies of the two chains can be traced with the aid of band structure calculations on $LaGe_{2-x}$ to p_z orbitals perpendicular to the zigzag plane of the chains that are π-bonding within the chains but σ-antibonding with respect to parallel chains. This effect was alluded to by Zheng and Hoffmann[28] in explaining the bonding of $ThSi_2$ vs AlB_2 structure types, but they did not elaborate further or note the relationship to $GdSi_2$.

Phase Relationships and Transformations. Our powder X-ray diffraction data for samples in the stoichiometry range $LaGe_{1.5}$–$LaGe_{2.0}$ coupled with the single-crystal study on $LaGe_{1.6}$ show that the system is orthorhombic and homogeneous in the range $LaGe_{2-x}$, $0.33 \leq x \leq 0.40$, at as low an effective temperature as can be achieved by slow cooling. This range compares with *x* limits of 0.34 and 0.41 reported earlier.[5,6] The phase at the limits is in equilibrium with Ge or LaGe, respectively. Moreover, no tetragonal phase was observed at room temperature throughout the homogeneity range regardless of the synthetic procedures, including quenching. Instead, the lattice parameters (Table IV) become only pseudotetragonal at the germanium-poor limit, the orthorhombic distortion increasing with an increase in the germanium content. This is illustrated in Figure 3 in terms of the distortion parameter $a - b$. This observation led us to investigate the system by high-temperature X-ray powder diffractometry to

---

(27) Guloy, A.; Corbett, J. D. To be submitted for publication.

(28) Zheng, C.; Hoffman, R. *Inorg. Chem.* **1989**, *28*, 1074.

Table IV. Formation of $LaGe_{2-x}$ Phases

loaded compn La:Ge	T, °C	product phases	lattice parameters, Å *a*	*b*	*c*
		Room-Temperature Diffraction: Orthorhombic $LaGe_{2-x}$[a]			
1:1.50	1100	$LaGe_{1.60}$ + LaGe (trace)	4.266 (1)	4.273 (1)	14.406 (1)
1:1.60	1100	$LaGe_{1.60}$	4.2680 (7)	4.2735 (6)	14.404 (1)
1:1.60	1050	$LaGe_{1.60}$	4.268 (1)	4.270 (1)	14.405 (1)
1:1.63	1100	$LaGe_{1.63}$	4.2898 (8)	4.3401 (6)	14.297 (1)
1:1.66	1100	$LaGe_{1.66}$	4.3071 (7)	4.3872 (6)	14.222 (1)
1:1.67	1100	$LaGe_{1.67}$	4.3125 (7)	4.4066 (6)	14.186 (1)
1:1.67	1050	$LaGe_{1.67}$	4.312 (1)	4.408 (1)	14.188 (1)
1:1.70	1100	$LaGe_{1.67}$ + Ge (trace)	4.312 (1)	4.407 (1)	14.187 (1)
1:2.0	1100	$LaGe_{1.67}$ + Ge	4.313 (1)	4.406 (1)	14.188 (1)
		High-Temperature Diffraction: Tetragonal $LaGe_{2-x}$[b]			
1:1.60	450	$LaGe_{1.60}$	4.274 (1)		14.389 (2)
1:1.63	575	$LaGe_{1.63}$	4.342 (1)		14.262 (2)
1:1.66	650	$LaGe_{1.66}$	4.379 (1)		14.210 (2)
1:1.67	675	$LaGe_{1.67}$	4.400 (1)		14.175 (2)

[a] Samples prepared by pressed-pellet reactions at T and slowly cooled, except that 1050 °C reactions were quenched. [b] Prereacted $LaGe_{2-x}$ (above) used in high-temperature diffractometer.

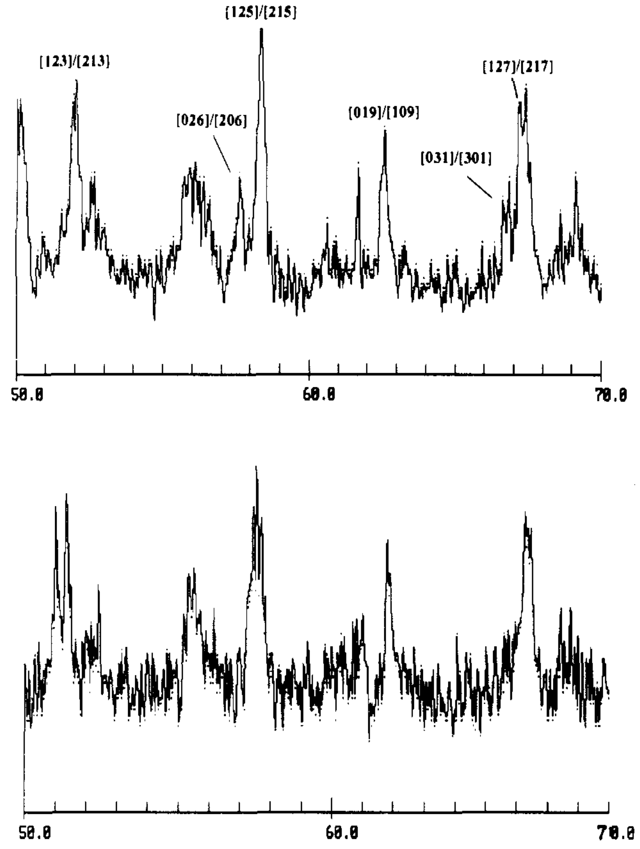


Figure 4. Portions of the powder diffraction patterns of $LaGe_{1.60}$ at 450 °C (top) and 25 °C (bottom) (Cu Kα).

see whether a tetragonal phase could be observed.

Orthorhombic to tetragonal phase transitions on heating were examined at temperatures between 350 and 650 °C, increasing with decreasing x in $LaGe_{2-x}$. Lattice parameters at temperatures where the transitions were judged to be complete are given in Table IV. Evidence for the phase transitions were noted especially well in the higher angle reflections, which merged at high temperatures and broadened or split into two lines on cooling. Intermediate portions of the patterns for $LaGe_{1.60}$ at 25 and 450 °C are shown in Figure 4. The splitting of the peaks at room temperature was imperceptible at low angles, but the (213) reflection split into (213) and (123) near $2\theta = 52°$, (217) yielded (217) and (127) near $2\theta = 66°$, and (312) → (312) and (132) at ~70°. The same treatment applied to samples with La:Ge ratios of 1:1.63, 1:1.66, and 1:1.67 gave similar results, with the changes in the reflections becoming more pronounced as $a - b$ increased. The deduced dependence of the phase transition temperature on germanium content is shown in Figure 5. The temperature range found, from 425 to 635 °C, is far greater than the range 420–455 °C determined earlier by thermal analysis.[5,6] The relative stabilization of the tetragonal form for germanium-richer samples in the older studies as well as their high-temperature lattice constants is consistent with the apparent effect of oxygen on the system (below).

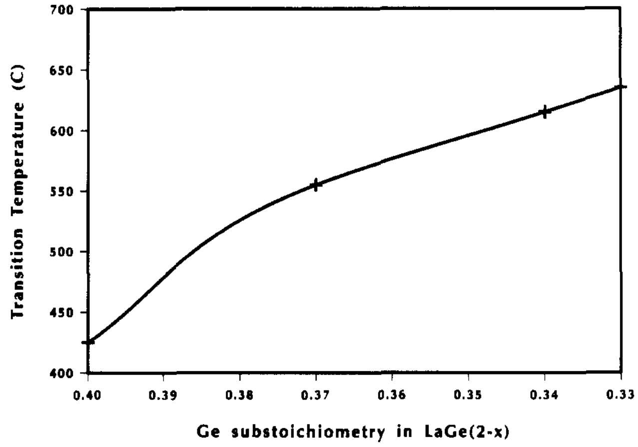


Figure 5. Orthorhombic (α-$GdSi_2$-type) to tetragonal (α-$ThSi_2$-type) transition temperatures in $LaGe_{2-x}$ as a function of x.

These phase transitions, that is, the degree of line broadening or splitting, were also observed to be continuous, their *apparent* breadth increasing with germanium content and $a - b$. At no time did the orthorhombic and the tetragonal phases coexist after the 15-min time window required for temperature equilibration near the transition temperature. The tetragonal to orthorhombic transition in $LaGe_{2-x}$ therefore satisfies all of Landau's conditions for a second-order phase transition,[29,30] as follows: (1) the space groups of the two structures involved in the transition are related by a group–subgroup relationship; (2) the transformation corresponds to a single irreducible representation of the space group of higher symmetry; (3) there is evidently no third-order term in the Gibbs free energy; (4) the space lattice of the lower symmetry structure is locked in by symmetry. This particular transition occurs without loss of translational symmetry (at Γ, $k = 0$).[30]

Most of the rare-earth-metal disilicides and digermanides have been reported[16] to be nonstoichiometric and to occur in both the

---

(29) Toledano, J. C.; Toledano, P. *The Landau Theory of Phase Transitions*; World Scientific Publishing Co.: Singapore, 1987.

(30) Franzen, H. F. *Chem. Mater.* **1990**, *2*, 486.

(31) Kovalev, O. V. *Irreducible Representations of the Space Groups*; Gordon and Breach Science Publishers, Inc.: New York, 1965.

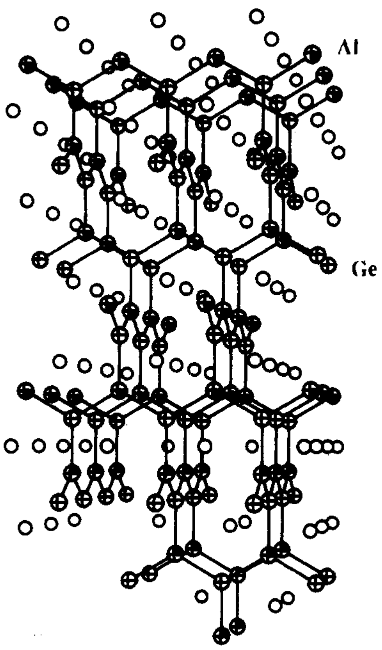


Figure 6. Off-[010] view of the tetragonal LaAlGe structure with Al as shaded, Ge as crossed, and La as open symbols.

$ThSi_2$- and $GdSi_2$-type structures, but with only limited[13] correlation between them. The results of this study suggest that the second-order relationship will probably exist for many of these and that the transition parameters will be dependent on composition.

A rather interesting result of the Landau analysis of the tetragonal $ThSi_2$ structure is the fact that another space group also satisfies the conditions for a second-order transition, *Fdd*2. A recent article on a neutron powder diffraction study of the structure of $TbGe_{1.67}$ (Tb_3Ge_5) reports a 6-fold superstructure cell of the α-$ThSi_2$ structure in the *Fdd*2 space group.[32] The Tb_3Ge_5 structure arises from the ordering of vacancies and positional displacements of the germanium atoms in a $GdSi_2$-like array. These authors also indicated that no tetragonal phase was found at room temperature, regardless of the heat treatment applied (annealing at different temperatures). A second-order transition relationship will fit these observations, and high-temperature diffractometry presumably would confirm this hypothesis. This structure has also been suggested for Y_3Ge_5.[32] There were no signs of a Tb_3Ge_5-like superstructure in the La–Ge binary system. The different sizes of the elements involved may be a factor.

An interesting result from the single-crystal analysis of $LaGe_{1.60}$ is evidence for a differentiation of the vacancies in the Ge network. The Ge2 sites with the shorter intrachain distances are less occupied, 69.8 (6)%, than those with longer Ge separations, 90.1 (6)%. A very recent neutron diffraction study on $TbSi_{2-x}$, which also has the $GdSi_2$ structure (or a subgroup thereof, *Im*2*b*), shows that the silicon vacancies qualitatively also show a strong preference for one site.[33] A partial ordering does not require an orthorhombic distortion, since the tetragonal space group $I4_1md$ also allows for inequivalence of the non-metal sites. This possibility has also drawn us to investigate the substitution of aluminum for germanium in $LaGe_{2-x}$ in order to stabilize a tetragonal phase (below).

Other relevant observations are the reported syntheses of stoichiometric, tetragonal $LaGe_2$ or $LaGe_{2-x}$ from germaniothermal reactions,[4,20,21] that is, from reactions of La_2O_3 and Ge in which gaseous GeO is a byproduct. The reported lattice parameters do not agree with our values for the binary phases, suggesting that oxygen may stabilize a tetragonal phase with a wider range of composition. This will be further considered later. We note that the supposed La_5Ge_3 made in the same way clearly has the lattice constants of La_5Ge_3O instead.[17]

Table V. Formation of $LaAl_xGe_{2-x}$ Phases

loaded compn La:Al:Ge	T,[a] °C	products (lattice type)	lattice parameters, Å	
			a	c
1:2:0	1150	$LaAl_2$ ($MgCu_2$)	8.147 (1)	
1:1:75:0.25	1150	$LaAl_{1.75}Ge_{0.25}$ (AlB_2)	4.402 (1)	4.401 (1)
1:1.5:0.5	1150	$LaAl_{1.5}Ge_{0.5}$ (AlB_2)	4.361 (1)	4.397 (1)
1:1.25:0.75	1150	$LaAl_{1.25}Ge_{0.75}$ (AlB_2)	4.350 (1)	4.390 (1)
1:1.0:1.0	1150	LaAlGe (LaPtSi)	4.3364 (4)	14.8278 (6)
1:1.0:1.0	1050	LaAlGe (LaPtSi)	4.333 (2)	14.825 (1)
1:0.75:1.25	1150	$LaAl_{0.75}Ge_{1.25}$ (tetragonal[b])	4.395 (1)	14.682 (2)
1:0.5:1.5	1150	$LaAl_{0.5}Ge_{1.5}$ (tetragonal)	4.403 (1)	14.600 (2)
1:0.25:1.75	1150	$LaAl_{0.25}Ge_{1.75}$ (tetragonal)	4.406 (1)	14.506 (2)
1:0.2:1.8	1150	$LaAl_{0.2}Ge_{1.8}$ (tetragonal)	4.410 (1)	14.498 (3)

[a] Pressed-pellet reactions at T, slowly cooled except for the one at 1050 °C, which was quenched. [b] The observed LaPtSi and the disordered $ThSi_2$ type could not be readily distinguished in this region.

LaAlGe. The newly synthesized compound LaAlGe is found to be isostructural with LaPtSi.[26] The structure is an ordered, lattice-equivalent ternary derivative of the α-$ThSi_2$ structure but with the Al atoms substituted for alternate Ge atoms in both chains. Aluminum atoms are all three-bonded to germanium and vice versa (Figure 6), and the phase is a Zintl (valence) compound as well [La^{3+}, $3bAl^{2-}$, $3bGe^{-}$]. This characteristic is fully supported by band calculations.[27]

Since α-$ThSi_2$ and LaGeAl have the same extinctions, their distinction can be achieved only by careful study of the intensities in their powder patterns. Our data follow the observation by Klepp and Parthé[26] on the dependence of the relative intensities on l in such cases: there is no change in $hk6n$ reflections, while all other hkl reflections have increased intensity if the atoms are ordered. Furthermore, independent of the values of the scattering factors for the three atoms, the relative intensity increases must be larger for $hk1$ and $kk4$ than for $kk2$ and $hk5$. This should serve as a guide in searches for ordering in ternary α-$ThSi_2$-like structures.

It has been reported that $LaAl_2$ has the $MgCu_2$ structure and that substitution of Al by Ge leads to an AlB_2 structure.[34] Our results for a broader range of $LaAl_xGe_{2-x}$ phases are summarized Table V. We have confirmed the AlB_2 type of $LaAl_xGe_{2-x}$ for aluminum-rich samples with $1.8 \geq x \geq 1.25$ (±0.05). Tetragonal and substantially stoichiometric $ThSi_2$-like phases were observed for germanium-richer samples, even at $LaAl_{0.2}Ge_{1.8}$, although the presence or absence of ordering could not be established. The La:(Al + Ge) compositions of 1:2 achieved even at these low aluminum contents are in distinct contrast to the $LaGe_{1.67}$ composition limit in its absence. It seems that the orthorhombic $GdSi_2$-type structure is stable only for the $LaGe_{2-x}$ binaries, or nearly so, and the tetragonal structure extends deep into the ternary system with aluminum. A similar result has been reported in the Ti–Al–Si system for the $ZrSi_2$-type ternary phase.[35]

This last result is related to the products of the so-called germaniothermal reactions cited earlier and our repeated note that oxygen perturbs the $LaGe_{2-x}$ system substantially. We conclude that stoichiometric "$LaGe_2$" exists in an α-$ThSi_2$ structure when it is synthesized by reaction 1 only because oxygen is incorporated

$$La_2O_3 + 7Ge \rightarrow 3GeO + 2LaGe_2 \qquad (1)$$

into the structure. We confirmed this by the analogous quantitative reaction (2) in an arc furnace, where x must be small. The

$$La + 2Ge + 0.05La_2O_3 \rightarrow LaGe_{2-x}(O) \text{ (tetragonal)} \qquad (2)$$

tetragonal structure was retained even after annealing at 600 °C for 24 h, and its lattice parameters at room temperature (a = 4.333 (1), c = 14.238 (5) Å) are close to those reported from arcmelting[18] and germaniothermal[20,21] reactions, respectively (a = 4.33, 4.35 (1), c = 14.23, 14.25 (2) Å). Lesser amounts of oxygen

---

(32) Schobinger-Papamantelos, P.; Buschow, K. H. J. *J. Less-Common Met.* **1989**, *146*, 279.

(33) Schobinger-Papamantelos, P.; Janssen, T.; DeMooij, D. B.; Buschow, K. H. J. *J. Less-Common Met.* **1990**, *162*, 197.

(34) Raman, A.; Steinfink, H. *Inorg. Chem.* **1967**, *6*, 1789.

(35) Raman, A.; Schubert, K. *Z. Metallkd.* **1965**, *56*, 44.

presumably serve to lower the tetragonal–orthorhombic transition temperature. We cannot ascertain where the oxygen is in the structure, but the vacancies within the non-metal framework and the spaces between La atoms in the channels seem possible.

Finally, a dimensional analysis of both LaAlGe and $LaGe_{2-x}$ reveals some interesting facts: (a) the lattice parameters of LaAlGe are significantly larger than those of $LaGe_{2-x}$ even if we extrapolate the calculated volumes of $LaGe_{2-x}$ to "$LaGe_2$", and (b) the c/a ratio of ternary LaGeAl (3.42) is larger than that for the binary (3.38). It must be noted that the axial and chain bonds become identical when $c/a = 2 \tan 60° = 3.464$. Tabulations of lattice parameters for a number of rare-earth-metal disilicides and digermanides with aluminum and transition-metal substitutions[34,36] show similar trends, although the assignment of LaAlGe to the $ThSi_2$-type was erroneous.[33]

Band structure calculations to be reported in a future article[27] consider the nature of the transition between $ThSi_2$- and $GdSi_2$-type structures, the possible electronic effects of Al in the $ThSi_2$ bonding, and the effect of Ge vacancies in $LaGe_{2-x}$.

Acknowledgment. We are much indebted to Professor H. F. Franzen for the use of both the arc-melting furnace and the high-temperature powder diffractometer and for valuable discussions regarding Landau theory.

Registry No. La, 7439-91-0; Al, 7429-90-5; Ge, 7440-56-4; $LaGe_{1.60}$, 136952-84-6; LaAlGe, 12279-56-0; $LaGe_{1.63}$, 136952-85-7; $LaGe_{1.66}$, 136952-86-8; $LaGe_{1.67}$, 136952-87-9; $LaAl_2$, 12004-32-9; $LaAl_{1.75}Ge_{0.25}$, 12279-77-5; $LaAl_{1.5}Ge_{0.5}$, 12279-70-8; $LaAl_{1.25}Ge_{0.75}$, 136952-88-0; $LaAl_{0.75}Ge_{1.25}$, 136952-89-1; $LaAl_{0.5}Ge_{1.5}$, 136952-90-4; $LaAl_{0.25}Ge_{1.75}$, 136952-91-5; $LaAl_{0.2}Ge_{1.8}$, 136952-92-6.

Supplementary Material Available: Tables of data collection and anisotropic atom displacement parameters for $LaGe_{1.60}$ and LaAlGe (2 pages); listings of F_o and F_c data for the two structures (3 pages). Ordering information is given on any current masthead page.

---

[36] Hovestreydt, E.; Engel, N.; Klepp, K.; Chabot, B.; Parthé, E. *J. Less-Common Met.* **1982**, *85*, 247.

Contribution from the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Two Novel Titanium Halide Phases: KTi_4Cl_{11} and $CsTi_{4.3}I_{11}$

Jie Zhang, Ru-Yi Qi, and John D. Corbett*

Received April 24, 1991

The title phases were synthesized in high yields from reactions of Ti, $TiCl_3$ or TiI_4, and KCl or CsI, respectively, in sealed tantalum containers at 500–600 °C. Problems associated with the loss of Ti into Ta (or Nb) containers are noted. The structure of each at room temperature was solved and refined by single-crystal X-ray diffraction means. (KTi_4Cl_{11}: *Pnma*, $Z = 4$, $a = 12.534$ (3) Å, $b = 6.897$ (2) Å, $c = 17.134$ (3) Å, $R/R_w = 3.5\%/4.1\%$ for 582 independent reflections with $2\theta \le 55°$. $CsTi_{4.3}I_{11}$: $P6_3/mmc$, $Z = 2$, $a = 8.2058$ (5) Å, $c = 19.723$ (2) Å, $R/R_w = 2.3\%/2.1\%$ for 181 data, $2\theta \le 50°$.) The chloride contains infinite chains of tightly bound $Ti_3Cl^i{}_4Cl^a{}_5Cl^{a-a}{}_{4/2}$ clusters [$\bar{d}$(Ti–Ti) = 2.955 Å]. These are interconnected into puckered sheets by isolated titanium(IV) atoms, leaving titanium(II) in the clusters. The isostructural $CsTi_4Cl_{11}$ also exists. The magnetic susceptibility of KTi_4Cl_{11} and the cluster dimensions are quite similar to those reported for the structurally somewhat more complex Ti_7Cl_{16}. The unusual $CsTi_5I_{11}$ structure type can be viewed as a microscopic intergrowth between Ti_3I_8 (defect CdI_2) slabs and layers containing Ti_2I_9 confacial bioctahedra characteristic of $Cs_3Zr_2I_9$ ($Cs_3Cr_2Cl_9$ type). The structure can be easily derived from the latter type. Metal positions in the former (Ti_3I_8) slabs are only 77% occupied, corresponding to a $CsTi_{4.30(7)}I_{11}$ composition but in an apparent line phase. A binary phase near $TiI_{2.5}$ also exists.

Introduction

Although reduced halides of zirconium as well as of rare-earth metals have been found to encompass a plethora of novel cluster-based phases,[1-4] none has been reported for titanium. Our explorations of the latter for a like chemistry, particularly one in which octahedral metal clusters $M_6X_{12}Z$ are stabilized by any of a variety of an essential interstitial elements Z (H, Be–N, Mn–Ni, etc.), have instead demonstrated that reduced titanium halides have a novel structural chemistry of their own. Even though potential interstitial elements Z (in small proportion) have not contributed to a unique chemistry, the remaining TiX_4, Ti, and alkali-metal halide have afforded new phases with, as often happens, unusual structures. We have already reported the $CsTi_2Cl_7$ example, in which $Ti^{III}Cl_6$ clusters are condensed into layers through sharing of five chlorides, leaving a novel Ti=Cl function projecting into the annular space.[5] The present paper reports on two more of these: KTi_4Cl_{11}, in which triangular rather than octahedral metal clusters are formed, and the $CsTi_5I_{11}$ type, which displays intergrown elements of two common structure types. Problems with tantalum as a container for these studies are also noted.

Experimental Section

The synthetic techniques utilizing welded Ta containers and the Guinier powder pattern procedures have already been described.[2-4] The $TiCl_3$ reactant was prepared as before,[5] while TiI_4 was prepared from the elements and purified by vacuum sublimation. The titanium metal was a crystal bar product and was treated as described.[5]

Syntheses. In order to reduce the loss of Ti into the Ta containers (below), a series of reactions designed to make cluster or condensed cluster chloride analogues of other systems were loaded with Ti chips in place of powder and run at 500–550 °C for 40–55 days. The Ti chips in most of the reactions remained intact, and the resultant changes in stoichiometry in one series designed to make $K_xTi_6Cl_{12+y}Z$ products led to, besides Ti, what turned out to be the black KTi_4Cl_{11} as the major and even single product of several reactions.

Reactions of powdered Ti and TiI_4 with a 3d metal M (Cr, Mn, Fe, etc.) and an alkali-metal iodide (AI) designed to synthesize M-centered cluster phases analogous to zirconium examples gave instead several evidently reduced ternary A_xTiI_y phases, the powder patterns of which did not depend on M. Typical reaction conditions were 550–750 °C for 47–26 days, respectively. One pattern for A = Cs looked like that calculated on the basis of the $Cs_3Zr_2I_9$ structure,[7] but the yield was too high considering the input composition, and there were numerous extra weak lines. Once a structural solution established the composition, a

---

[1] Ziebarth, R. P.; Corbett, J. D. *Acc. Chem. Res.* **1989**, *22*, 256.
[2] Hughbanks, T.; Rosenthal, G.; Corbett, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 1511.
[3] Payne, M. W.; Corbett, J. D. *Inorg. Chem.* **1990**, *29*, 2246.
[4] Zhang, J.; Corbett, J. D. *Inorg. Chem.* **1991**, *30*, 431.
[5] Zhang, J.; Corbett, J. D. *Z. Anorg. Allg. Chem.* **1990**, *580*, 36.
[6] Werner, P. E. TREOR-4: Trial and Error Program for Indexing Unknown Powder Patterns. Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, 106 91 Stockholm, Sweden, 1984.
[7] Guthrie, D. H.; Meyer, G.; Corbett, J. D. *Inorg. Chem.* **1981**, *20*, 1192.