

The Crystal Structure of Two Novel Compounds: CeAlSi₂ and Ce₃Al₄Si₆

Hans Flandorfer and Peter Rogl

Institut für Physikalische Chemie, Universität Wien, Währingerstrasse 42, A-1090 Wien, Austria

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In a reinvestigation of the phase relations within the section CeSi₂–Al at 600 and 500°C, two new compounds were found: CeAlSi₂ and Ce₃Al₄Si₆. The crystal structures were solved from X-ray powder diffraction data employing Patterson and difference Fourier syntheses followed by full-matrix full-profile Rietveld refinement. Both compounds crystallize with new trigonal structure types as follows. CeAlSi₂: *P3m1*, *Z* = 2, *a* = 0.41707(1) nm, *c* = 1.12147(2) nm, *R*₁ = 0.077, *R*_F = 0.050. Ce occupies the 2c site with *z* = 0.1855(1), Si is in the 2d sites with *z*₁ = 0 and *z*₂ = 0.3525(5), and Al is in the 2d site with *z* = 0.5901(6). Ce₃Al₄Si₆: *P3m1*, *Z* = 1, *a* = 0.41887(1) nm, *c* = 1.81202(6) nm, *R*₁ = 0.065, *R*_F = 0.035. Ce occupies the 1b site and the 2c site with *z* = 0.1149(1); Si is in the 2d sites with *z*₁ = 0, *z*₂ = 0.2198(9), and *z*₃ = 0.6096(6); Al is in the 2d sites with *z*₁ = 0.3564(8) and *z*₂ = 0.752(1). Both structures combine structural units of the AlB₂ type, CeSi₂ (*m*), and of the La₂O₃ type, CeAl₂Si₂ (*n*), and form a structural series RE_{*m+n*}Al_{2*n*}Si_{2*m+2n*} with CeAlSi₂ (*m* = 1, *n* = 1) and Ce₃Al₄Si₆ (*m* = 1, *n* = 2) as two early representatives of the series. © 1996 Academic Press

1. INTRODUCTION

In reports of various independent investigations (1–7) concerning the isothermal section of the Al–Ce–Si system at 500°C, a total of four ternary phases, CeAl₂Si₂, CeAl_{1.25–1.75}Si_{2.75–2.25}, CeAl_{1.4–1.9}Si_{0.6–1.1}, and CeAl_{1.64–1.55}Si_{0.36–0.45}, have been mentioned. In particular, the region Ce(Al, Si)₄, assumed to contain the ternary phases CeAl_{1.25–1.75}Si_{2.75–2.25} and CeAl₂Si₂, was rather differently described by (2, 3, 6) [see, e.g., the critical assessment in (8)]. Therefore we have attempted to clarify the hitherto rather incomplete and inconsistent information with the goal of establishing proper phase equilibria and characterizations of crystal structures and physical properties of the ternary compounds. The present work deals with the crystal structures of two novel ternary compounds, CeAlSi₂ and Ce₃Al₄Si₆.

2. EXPERIMENTAL DETAILS

All samples, essentially on the section CeSi₂–Al, each of about 2 g, were synthesized by repeatedly arc-melting the high-purity elements together in a Ti-gettered argon atmosphere. Weight losses due to the arc-melting process were checked to be less than 0.5 mass%. The following starting materials were used: Ce, ingot, m3N, Auer-Remy, Germany; Al, ingots, 99.9%, Johnson & Matthey, Germany; Si, lumps, 99.99%, Johnson & Matthey, Germany. After the melting of the elements, the reguli were packed in molybdenum foil, sealed in evacuated silica tubes, and heat treated for 168 h at 700 and 600°C and for 336 h at 500°C, respectively, in a wire-wound power-controlled tubular furnace calibrated against a Pt/PtRh thermocouple. After the samples were annealed, they were quenched by casting the silica tubes into cold water. Melt spinning under argon was performed on selected samples, starting from the arc-melted master alloy CeAl₂Si₂. The sample was induction-melted in a (*φ* ≈ 10 mm) quartz crucible with a (*φ* ≈ 1 mm) jet nozzle. The liquid was ejected through the quartz jet nozzle by pressurized argon and quenched on a cooled copper wheel rotating at a speed of 10 to 40 m s⁻¹.

Precise lattice parameters and standard deviations were obtained by least-squares refinement of room temperature Guinier–Huber X-ray powder data (CuKα₁) employing an internal standard of 99.9999 mass% pure Ge (*a*_{Ge} = 0.5657906 nm). The program TREOR90 was used for a trial and error indexing of powder patterns (9). For the evaluation of structure factors and quantitative refinement of the atom positions, X-ray intensities were recorded from a flat specimen in a Siemens D5000 automatic powder diffractometer (CuKα). Deconvolution of the intensity profile revealed the integrated Bragg intensities used to generate Patterson functions. Full-matrix full-profile Rietveld refinements were carried out with a PC version of the program by Wiles and Young (10). For Patterson syntheses

TABLE 1
Crystallographic Data on the Alloy CeAl₂Si₂

Heat treatment	Phase analysis	Structure type	Space group	Unit cell dimensions in nm			
				<i>a</i>	<i>c</i>	<i>V</i> (nm ³)	<i>c/a</i>
Arc	CeAl ₂ Si ₂	La ₂ O ₃	$P\bar{3}m1$	0.4217(0)	0.6895(1)	0.1062	1.6350
	Ce(Al _{<i>x</i>} Si _{1-<i>x</i>}) ₂	αThSi ₂	$I4_1/amd$	0.4234(0)	1.4308(1)	0.2565	3.3793
	Al	Cu	$Fm\bar{3}m$	Traces			
Arc, 700°C, 168 h	Ce(Al _{<i>x</i>} Si _{1-<i>x</i>}) ₂	αThSi ₂	$I4_1/amd$	0.4235(0)	1.4237(4)	0.2554	3.3617
	Al	Cu	$Fm\bar{3}m$	0.4052(0)			
	Si	C _{dia}	$Fd\bar{3}m$	0.5434(1)			
Arc, 600°C, 168 h	CeAlSi ₂	CeAlSi ₂	$P\bar{3}m1$	0.4172(0)	1.1216(6)	0.1691	2.6884
	Al	Cu	$Fm\bar{3}m$	0.4049(0)			
	Si	C _{dia}	$Fd\bar{3}m$	0.5429(1)			
Arc, 500°C, 336 h	Ce ₃ Al ₄ Si ₆	Ce ₃ Al ₄ Si ₆	$P\bar{3}m1$	0.4189(0)	1.8111(5)	0.2753	4.3235
	CeAlSi ₂	CeAlSi ₂	$P\bar{3}m1$	0.4175(1)	1.1230(9)	0.1695	2.6898
	Al	Cu	$Fm\bar{3}m$	0.4047(0)			
	Si	C _{dia}	$Fd\bar{3}m$	Traces			
	Melt-spun	Ce(Al _{<i>x</i>} Si _{1-<i>x</i>}) ₂	αThSi ₂	$I4_1/amd$	0.4236(0)	1.4233(4)	0.2554
Melt-spun, 500°C, 336 h	Al	Cu	$Fm\bar{3}m$	0.4056(1)			
	Si	C _{dia}	$Fd\bar{3}m$	0.5438(1)			
	Ce ₃ Al ₄ Si ₆	Ce ₃ Al ₄ Si ₆	$P\bar{3}m1$	0.4189(0)	1.8118(5)	0.2753	4.3251
	Al	Cu	$Fm\bar{3}m$	0.4049(0)			

and difference Fourier syntheses the PC version of the SHELX program was applied (11).

3. RESULTS AND DISCUSSION

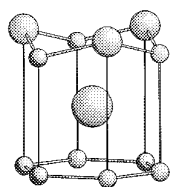
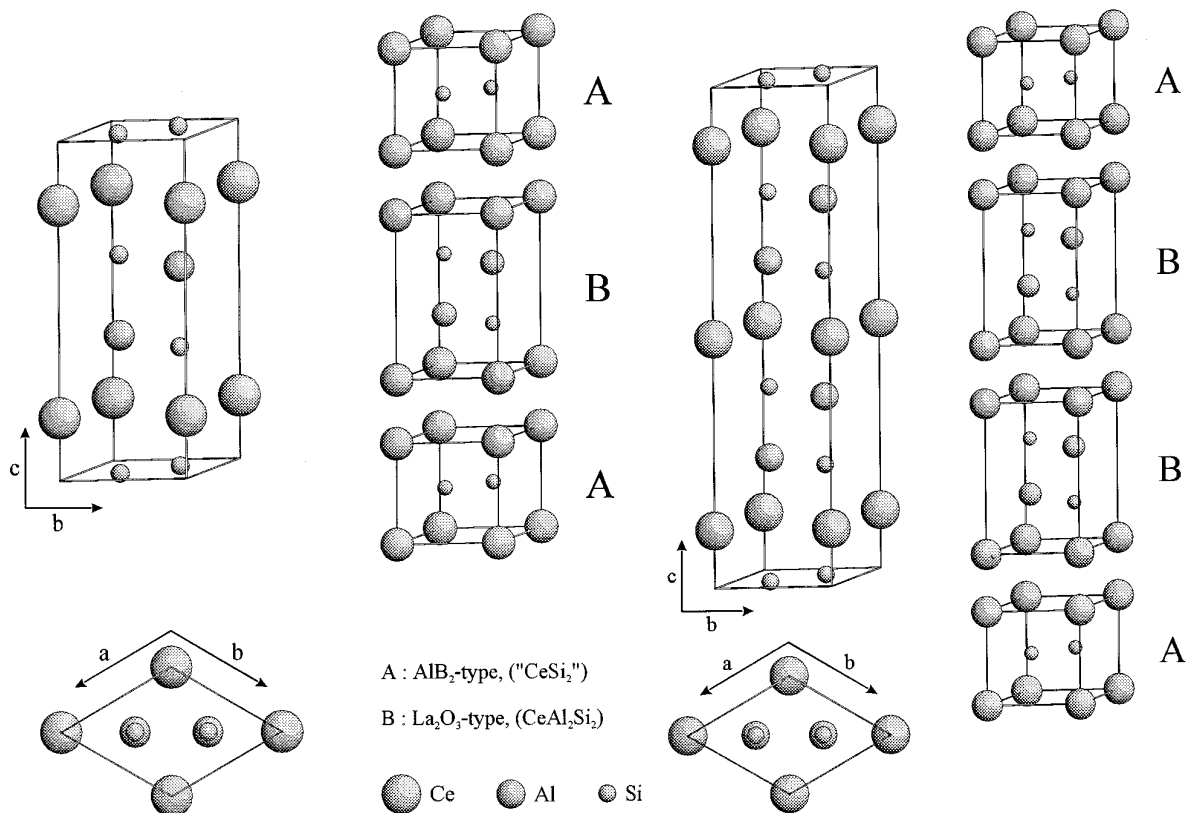
3.1. The Section CeSi₂-Al

In our reinvestigation of the section CeSi₂-Al, the compound CeAl₂Si₂ with the La₂O₃-type structure, reported in (6, 7), could only be obtained in arc melted samples, never in pure form, but usually together with Ce(Al_{*x*}Si_{1-*x*})₂ (αThSi₂ type) and Al. CeAl₂Si₂ disappears after annealing at 700, 600, or 500°C for 168 h (see Table 1). Assuming high temperature behavior we attempted to stabilize CeAl₂Si₂ by melt spinning. Surprisingly, melt spinning of CeAl₂Si₂ yielded a three-phase mixture Ce(Al_{*x*}Si_{1-*x*})₂ (αThSi₂-type) + Al + Si, which also prevailed after annealing at 700°C for 168 h. CeAl₂Si₂ may therefore be considered to be metastable. The only stable compound in this region after annealing between 600 and 650°C is CeAlSi₂. Above 650°C it decomposes into Ce(Al_{*x*}Si_{1-*x*})₂, Al, and Si. Below 600°C, after 336 h of annealing, a further phase with the composition Ce₃Al₄Si₆ appears, with CeAlSi₂ still present. The melt-spun samples of CeAl₂Si₂ show similar behavior; however, after annealing at 500°C (336 h), Ce₃Al₄Si₆ is formed without any impurities of CeAlSi₂. Due to these difficulties in preparing large quantities of a homogeneous powder material, neutron diffraction experiments usually requiring 1 cm³ of material were ruled out

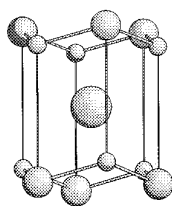
and structure determination by X-ray powder techniques was attempted.

3.2. The Crystal Structure of CeAlSi₂

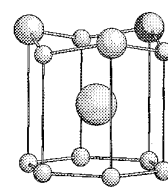
The X-ray powder pattern of the alloy with the nominal composition CeAl₂Si₂ after being annealed for 168 h at 600°C revealed a hitherto unknown structure pattern in addition to the well-known reflections of Al and Si. Employing the program TREOR90 indexation of the Guinier powder data was successful on the basis of a hexagonal lattice $a = 0.4172(0)$ nm and $c = 1.1216(6)$ nm. The absence of any extinctions is consistent with a series of hexagonal and trigonal space groups, $P6/mmm$, $P\bar{6}2m$, $P\bar{6}m2$, $P6mm$, $P622$, $P6/m$, $P\bar{6}$, $P6$, $P3m1$, $P\bar{3}1m$, $P31m$, $P\bar{3}m1$, $P321$, $P312$, $P\bar{3}$, and $P3$, of which $P6/mmm$, $P6/m$, $P\bar{3}m1$, $P\bar{3}1m$, and $P\bar{3}$ were those with a center of symmetry at the origin of the unit cell. Based on the successful indexation, the Rietveld program was used to extract a set of 134 reduced intensities ($|F|^2$) for CeAlSi₂ which in due course were employed to calculate a three-dimensional Patterson map $P(u, v, w)$, which served as the basis for the construction of a suitable structure model. The prominent peaks of the synthesis were easily attributed to two cerium atoms in 2c and the rest of the peaks was then found via a difference Fourier calculation ($F_{\text{obs.}} - F_{\text{Ce}}$) to correspond to the light atoms (silicon and aluminum) in the 2d sites of the space $P\bar{3}m1$ as the one with the highest symmetry. This atom arrangement successfully converged to convincingly low

CeAlSi₂**Ce₃Al₄Si₆**

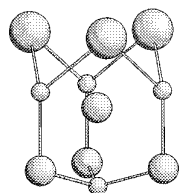
Central Atom: Ce



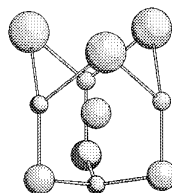
Central Atom: Ce(1)



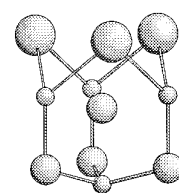
Central Atom: Ce(2)



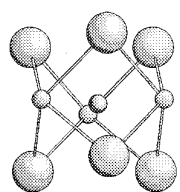
Central Atom: Al



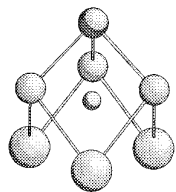
Central Atom: Al(1)



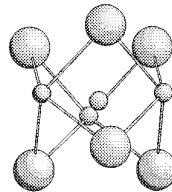
Central Atom: Al(2)



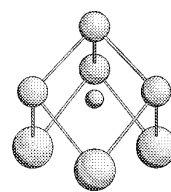
Central Atom: Si(1)



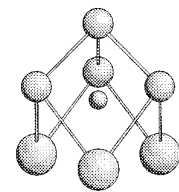
Central Atom: Si(2)



Central Atom: Si(1)



Central Atom: Si(2)



Central Atom: Si(3)

TABLE 2
Rietveld refinement of CeAl₂Si₂ Quenched from 600°C

Method	Full profile refinement of room temperature X-ray powder diffraction data							
Conditions	Number of reflections used in refinement: 154, $14^\circ \leq 2\theta \leq 120^\circ$; number of variables used: 28; 3 phases refined; residual values for the profile: $R_P = 0.102$, $R_{wP} = 0.131$							
Main phase	CeAlSi ₂ , 134 reflections refined							
Lattice param.	$a = 0.41707(1)$ nm, $c = 1.12147(2)$ nm, $V = 0.1689$ nm ³ , $c/a = 2.6889$							
Structure type	CeAlSi ₂							
Space group	$P\bar{3}m1 - D_{3d}^3$, No. 164, origin at $\bar{1}$, $Z = 2$; Wyckoff sequence d ³ c; hP8							
Residual values	$R_I = 0.077$, $R_F = 0.050$							
Atom param.	Atom	Site	x	y	z	B in 10^{-2} nm ²	Occupancy	
	Ce	2c	0	0	0.1855(1)	0.79(2)	1	
	Si(1)	2d	1/3	2/3	0	1.6(1)	1	
	Si(2)	2d	1/3	2/3	0.3525(5)	0.7(1)	1	
	Al	2d	1/3	2/3	0.5901(6)	2.0(1)	1	
Pref. orientation	0.21(1) for [103]							
Interatomic distances <4 nm	Central atom: Ce		Central atom: Si(1)		Central atom: Si(2)		Central atom: Al	
	Ligand atom	Distance	Ligand atom	Distance	Ligand atom	Distance	Ligand atom	Distance
	3 Si(2)	0.3050	3 Si(1)	0.2408	3 Al	0.2497	3 Si(2)	0.2497
	6 Si(1)	0.3178	6 Ce	0.3178	1 Al	0.2658	1 Si(2)	0.2658
	3 Al	0.3496			3 Ce	0.3051	3 Al	0.3128
							3 Ce	0.3496
Second phase	Al, 8 reflections refined							
Lattice param.	$a = 0.4050(0)$ nm, $V = 0.0664$ nm ³ , Cu type, $Fm\bar{3}m$, O_h^5 , No. 225, $Z = 4$							
Residual values	$R_I = 0.155$, $R_F = 0.076$							
Third phase	Si, 12 reflections refined							
Lattice param.	$a = 0.5432(0)$ nm, $V = 0.1603$ nm ³ , C _{dia} type, $Fd\bar{3}m$, O_h^5 , No. 227, $Z = 8$							
Residual values	$R_I = 0.139$, $R_F = 0.066$							

residual values of $R_I = 0.075$ and $R_F = 0.048$. Due to the rather small differences in the X-ray scattering power of Al and Si at that stage, no specific atom site allocation was made for them. Hints for correct Al, Si atom distribution are found from geometrical constraints considering the rather unequal size of the metal atom radii, $R_{Al} = 0.143$ nm, $R_{Si} = 0.134$ nm. Thus the shortest atom–atom distances, $a/\sqrt{3} = 0.2408$ nm, apply rather to contacts among Si atoms, which therefore are then located in the trigonal prismatic coordination of an AlB₂-type slab CeSi₂. No constraints apply to the remaining atoms, which are placed in 2d sites. However, assuming full atom order, an arrangement such as is known for CaAl₂Si₂ (La₂O₃ type) is derived for the remaining structural units. As a confirmation of this structural model the largest distances among the light atoms correctly appear for the Al atoms. Whereas isotropic temperature factors seem to favor this structure model,

practically no differentiation is seen from the R values when various models are refined with (a) Al, Si positions in the CeAl₂Si₂ subunit interchanged or (b) (Al, Si) in random distribution. Conditions of refinement, atom parameters after standardization employing the program STRUCTURE TIDY (12), isotropic temperature factors, and residual values are listed in Table 2. The crystal structure of CeAlSi₂ is composed of alternating layers of CeAl₂Si₂ (La₂O₃ type) and “CeSi₂” (AlB₂ type); see Fig. 1. Both structural units are inherent in the ternary Al–Ce–Si system: CeAl₂Si₂ as a metastable phase ($P\bar{3}m1$) with $a = 0.4217$ nm, $c = 0.6895$ nm and CeAl_{1.64–1.55}Si_{0.36–0.45} as an Al-rich representative of the AlB₂ type ($P6/mmm$) with lattice parameters $a = 0.4315(5)–0.435$ nm, $c = 0.4298–0.430$ nm (4, 5, 6). Considering the smaller Si atoms instead of Al on 2d of the AlB₂ subunit, the c -parameter of 1.1216(6) nm for the new compound is very

FIG. 1. The crystal structures of CeAlSi₂ (left) and Ce₃Al₄Si₆ (right); unit cell and projection along [001], the two structural subunits “CeSi₂” (A) and CeAl₂Si₂ (B), and the coordination figures.

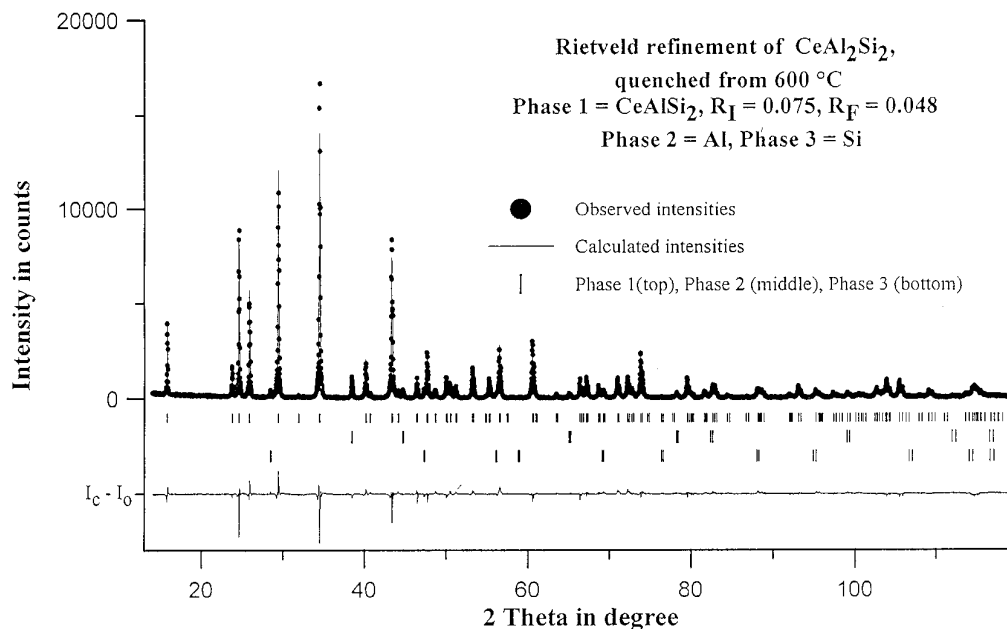


FIG. 2a. Presentation of the full profile Rietveld refinement of CeAlSi_2 .

close to the sum of $c_{(\text{La}_2\text{O}_3\text{-type})}$ and $c_{(\text{AlB}_2\text{-type})}$. The new phase may thus be formally conceived as a topochemical sum $2 \text{CeAlSi}_2 = \text{“CeSi}_2\text{”} + \text{CeAl}_2\text{Si}_2$. Figure 2a shows a graphic presentation of the full profile Rietveld refinement of CeAlSi_2 .

3.3. The Crystal Structure of $\text{Ce}_3\text{Al}_4\text{Si}_6$

As mentioned above, after long annealing of arc-melted CeAl_2Si_2 alloys at 500°C (336 h), another phase appears in addition to CeAlSi_2 . It can be obtained in pure form

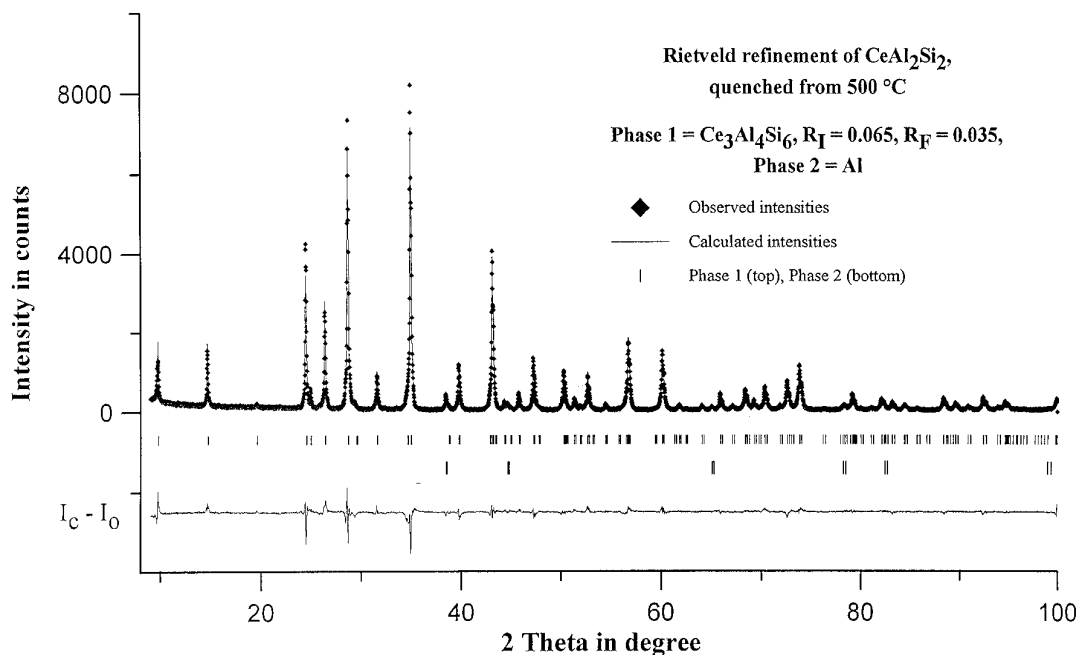


FIG. 2b. Presentation of the full profile Rietveld refinement of $\text{Ce}_3\text{Al}_4\text{Si}_6$.

TABLE 3
Rietveld Refinement of CeAl₂Si₂ Quenched from 500°C

Method	Full profile refinement of room temperature X-ray powder diffraction data							
Conditions	Number of reflections used in refinement: 159, $9^\circ \leq 2\theta \leq 100^\circ$; number of variables used: 28; 2 phases refined; residual values for the profile: $R_P = 0.106$, $R_{wP} = 0.141$							
Main phase	Ce ₃ Al ₄ Si ₆ , 153 reflections refined							
Lattice param.	$a = 0.41887(1)$ nm, $c = 1.81202(6)$ nm, $V = 0.2753$ nm ³ , $c/a = 4.3260$							
Structure type	Ce ₃ Al ₄ Si ₆							
Space group	$P\bar{3}m1 - D_{3d}^3$, No. 164, origin at $\bar{1}$, $Z = 2$; Wyckoff sequence d ⁵ cb; hP13							
Residual values	$R_I = 0.065$, $R_F = 0.035$							
Atom param.	Atom	Site	x	y	z	B in 10^{-2} nm ²	Occupancy	
	Ce(1)	1b	0	0	1/2	1.18(5)	1	
	Ce(2)	2c	0	0	0.1149(1)	0.98(7)	1	
	Si(1)	2d	1/3	2/3	0	2.1(3)	1	
	Si(2)	2d	1/3	2/3	0.2198(9)	3.0(5)	1	
	Si(3)	2d	1/3	2/3	0.6096(6)	0.1(3)	1	
	Al(1)	2d	1/3	2/3	0.3564(8)	2.1(4)	1	
	Al(2)	2d	1/3	2/3	0.752(1)	1.9(4)	1	
Interatomic distances <4 nm	Central atom: Ce(1)		Central atom: Ce(2)		Central atom: Si(1)		Central atom: Si(2)	
	Ligand atom	Distance	Ligand atom	Distance	Ligand atom	Distance	Ligand atom	Distance
	6 Si(3)	0.3129	3 Si(2)	0.3076	3 Si(1)	0.2441	3 Al(2)	0.2472
	6 Al(1)	0.3552	3 Si(1)	0.3088	3 Ce(2)	0.3088	1 Al(1)	0.2475
			3 Si(1)	0.3300	3 Ce(2)	0.3300	3 Ce(2)	0.3076
			3 Al(2)	0.3414				
	Central atom: Si(3)		Central atom: Al(1)		Central atom: Al(2)			
	Ligand atom	Distance	Ligand atom	Distance	Ligand atom	Distance	Ligand atom	Distance
	3 Al(1)	0.2496	1 Si(2)	0.2475	3 Si(2)	0.2471		
	1 Al(2)	0.2582	3 Si(3)	0.2496	1 Si(3)	0.2582		
	3 Ce(1)	0.3129	3 Al(2)	0.3117	3 Al(1)	0.3117		
			3 Ce(1)	0.3552	3 Ce(2)	0.3414		
Second phase	Al, 6 reflections refined							
Lattice param.	$a = 0.4050(0)$ nm, $V = 0.0664$ nm ³ , Cu-type, $Fm\bar{3}m$, O_h^5 , No. 225, $Z = 4$							
Residual values	$R_I = 0.076$, $R_F = 0.037$							

(apart from small amounts of Al) by long annealing of melt-spun CeAl₂Si₂ alloys at 500°C (336 h). Again lattice parameters as determined by TREOR90 are consistent with a hexagonal crystal system, $a = 0.4189(0)$ nm and $c = 1.8118(4)$ nm. No extinctions were observed and the space group $P\bar{3}m1$ was assumed as the one with the highest crystal symmetry. The c parameter strongly indicates a structure model based on the sum of two CeAl₂Si₂ subunits and one “CeSi₂” subunit: $2c_{La_2O_3\text{-type}} + c_{AlB_2\text{-type}}$; see Fig. 1. The composition Ce₃Al₄Si₆ thus simply derives as $2 \text{ CeAl}_2\text{Si}_2 + \text{“CeSi}_2\text{”} = \text{Ce}_3\text{Al}_4\text{Si}_6$. Following a strategy for atom site allocation similar to the one outlined above for the structure of CeAlSi₂, i.e., based on Patterson, difference Fourier syntheses, and Rietveld techniques, the crystal structure of Ce₃Al₄Si₆ was refined successfully to residual values as low as $R_I = 0.065$, $R_F = 0.035$. Conditions of

refinement, free atom parameters, isotropic temperature factors, and residual values are listed in Table 3. Figure 2b shows a graphic presentation of the full profile Rietveld refinement of Ce₃Al₄Si₆.

3.4. Related Structures

With common structural units of CeSi₂ (m) and CeAl₂Si₂ (n), the two new structure types CeAlSi₂ ($m = 1$, $n = 1$) and Ce₃Al₄Si₆ ($m = 1$, $n = 2$) follow the same principle of construction, forming a structural series with the general formula $M_{m+n}M'_{2n}M''_{2m+2n}$, where M , M' , M'' are metal or metmetal atoms. Representatives with higher values of m and n may already exist. Therefore literature data were checked for isotypic and related structures in two manners. At first we looked for already known structure types built

of n La_2O_3 -type units + m AlB_2 -type units, $n, m = 1$ to 5. We came across only two structure types, the Cu_3P type and the Cu_5FeS_6 type, $\{(\text{Cu}, \text{Fe})(\text{Cu}, \text{Fe})\text{S}_2\}$, both hP8 ($n = 1, m = 1$), $P\bar{3}m1$, which show the same space group and Wyckoff sequence d^3c as for CeAlSi_2 . The z values for the 2c and 2d sites, as well as the c/a ratio of these two isopointal structures, are, however, significantly different from those for CeAlSi_2 . Therefore the structures of CeAlSi_2 and $\text{Ce}_3\text{Al}_4\text{Si}_6$ are considered unique structure types. Interatomic distances for both structure types, CeAlSi_2 (Table 2) and $\text{Ce}_3\text{Al}_4\text{Si}_6$ (Table 3), merely reflect the bonding behavior already known from CeAl_2Si_2 and $\text{Ce}(\text{Al}, \text{Si})_2$, characterized by rather short distances between the p -element atoms, Al–Si and Si–Si.

Second, we screened the ternary systems RE –(Al, Ga, In)–(Si, Ge, Sn) for compounds with the composition $RE_{m+n}(\text{Al}, \text{Ga}, \text{In})_{2n}(\text{Si}, \text{Ge}, \text{Sn})_{2m+2n}$. The structures of LaAlSi_2 (6) and GdAlGe_2 (13) are not determined yet. LaAlGe_2 is described as tetragonal with $a = 0.436$ nm and $c = 1.431$ nm in (14). $\text{Ce}_2\text{Al}_3\text{Ge}_4$ ($\text{Ce}_4\text{Al}_6\text{Ge}_8$, $m = 1, n = 3$) crystallizes in the unrelated $\text{Ba}_2\text{Cd}_3\text{Bi}_4$ type (15).

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