Chem. Mater. **2001,** *13,* 4053−4057

Structure Prediction Using Our Semiempirical Structure Map: The Crystal Structure of the New Arsenide ZrTiAs

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Received April 30, 2001. Revised Manuscript Received July 23, 2001

Recently, a novel structure map was presented for metal-rich pnictides and chalcogenides M_2Q (M = valence-electron poor transition metal, Q = pnicogen or chalcogen). Herewith, we introduce ZrTiAs, which crystallizes—in perfect agreement with our structure map—in the La_2Sb type. While Zr_2As apparently forms the Zr_2P type, the (to date) hypothetical "Ti_2As" could not have been prepared yet. ZrTiAs was obtained by arc-melting Zr, Ti, and $TiAs_2$. This arsenide crystallizes in the tetragonal space group $I4/mmm$, with lattice dimensions of $a = 379.28(6)$ pm, $c = 1480.2(3)$ pm, and $V = 212.94(7)\ 10^6$ pm^3 ($Z = 4$). In contrast to (Zr,Ti)Sb, ZrTiAs comprises complete ordering of the Zr and Ti atoms. However, the Zr atom in ZrTiAs may in part be replaced by Ti, i.e., a phase range of $Zr_{1-\delta}Ti_{1+\delta}As$ exists with (at least) $0 \leq \delta \leq 0.42(1)$. The ZrTiAs structure exhibits strong Zr−As, Ti−As, and Ti−Ti bonds, and to a minor extent Zr−Zr and Zr−Ti bonding interactions.

Introduction

Structure maps, having been used to predict crystal structures of hitherto unknown compounds, can provide a guide for the systematic synthesis directed toward new compounds of a known structure type. The structure maps historically used like the Mooser−Pearson,[1] Zunger,[2] and Villars[3] maps, rely solely on physical coordinates, i.e., electronegativity differences, averaged principal quantum numbers, pseudopotential radii, and valence electrons. Pettifor was the first to change this by inventing a structure map using revised atomic numbers.[4] His phenomenological relative order numbers are based on a string running through the periodic table, the path of which he optimized empirically in order to get reasonably good separations of the different structure types in his map for AB compounds.

Last year we published in cooperation with Bernd Harbrecht a novel structure map for M_2Q compounds, wherein M represents a valence-electron poor transition metal atom and Q a pnicogen or chalcogen atom.[5] This includes ternaries $M_{2-\delta}M'_{\delta}Q$ and $M_2Q_{1-\delta}Q'_{\delta}$ like $Zr_{2-\delta}Hf_{\delta}P$.[6] The structures of all of these pnictides and chalcogenides, though quite different, exhibit two common features: (1) In addition to the dominating heteronuclear M−*Q* bonds, bonding M−M interactions occur. (2) Each Q atom is surrounded by M atoms only, which form (fragments of) singly-, bi-, or tri-capped trigonal prisms. Our structure map is based on the facts that the number of M-centered valence electrons (vec_M) and the main quantum number of M (n_M) both favor M−*M* bonding and thus disfavor M−Q bonding and that large Q atoms and small M atoms as well as a high electron deficit of Q favor M−*Q* bonding. It is obvious that all of these effects occur simultaneously, and opposite trends may very well cancel one another; an example is represented in Hf_2P and Zr_2S being isostructural, but different to Zr_2P.

We found particularly good separations of the eleven different structure types of this class by plotting a combination of four different factors in a single coordinate *f* versus the averaged coordination number of the Q atoms $\langle CN(Q)\rangle$. *f* was empirically optimized to correspond to the power product

$$f = vec_M n_M{}^2 (r_M/r_Q)/(8 - e_Q)^2 \qquad (1)$$

with r_M/r_Q = Slater radius of M/Q, e_Q = electrons per Q atom, while $(8 - e_Q)$ was chosen in analogy to the $(8 - N)$ rule. This map was successfully used to predict the Zr_2P type[7] of $Zr_2Sb_{0.5}Se_{0.5} \equiv Zr_4SbSe$,[8] which is particularly interesting because both binaries, Zr_2Sb[9] and Zr_2Se,[10] occur in other structure types, namely, La_2Sb[11] and Ta_2P,[12] respectively.

To further investigate the usability of our structure map, we continue to try to prepare new M_2Q compounds, either by mixing two different M or Q atoms or by looking for the hitherto unknown binaries. Herewith, we report the ZrTiAs structure, which falls into the La_2Sb domain of our structure map and actually does form the La_2Sb type. The correct prediction here is especially fascinating since no transition metal arsenide

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10.1021/cm010433g CCC: $20.00

was known before to form this type; Zr_2As[13] crystallizes in the Zr_2P type, while the hypothetical binary titanium arsenide ("Ti_2As") does not seem to exist.

The multitude of arsenides of divalent metals A_2As earlier reported to crystallize in the La_2Sb type have (in part) been shown to contain oxygen, i.e., to form the electron-precise filled variant of the La_2Sb type $A_2AsO_{0.5} \equiv (A^{2+})_4(As^{3-})_2(O^{2-})$. The discussion of this problem started 25 years ago.[14-16]

Experimental Section

Synthesis. For the synthesis of ZrTiAs, we prepared first the binary arsenide $TiAs_2$[17] by annealing the elements titanium (ALFA: powder, 99.9% purity) and arsenic (Aldrich: powder, 99.5%) in the stoichiometric 1:2 ratio in a fused evacuated silica tube at 600 °C. Subsequently, the main reaction step was performed starting from a mixture of 2 mmol of Zr (Aldrich: powder, 99.5%), 1 mmol of Ti, and 1 mmol of $TiAs_2$ according to

$$2Zr + Ti + TiAs_2 \rightarrow 2ZrTiAs \qquad (2)$$

This mixture was pressed into a pellet and then arc-melted twice after inversion on a water-cooled copper hearth under a flow of argon. The powder diffractogram (BRUKER D500) experimentally obtained from the crushed and ground sample showed no evidence of the formation of any binary arsenides. No ternary zirconium titanium arsenides were known before our investigations. EDS analyses (LEO 1530, with integrated EDAX Pegasus 1200) on five selected crystals revealed the presence of zirconium, titanium, and arsenic in the anticipated ratio of 34(2):30(2):36(2) [in atomic percent], which is very close to the chemical formula ZrTiAs.

Structure Determination. A prismatic shaped single crystal of the dimensions 50 × 40 × 30 [in micrometers] was selected for the data collection using the SMART Apex CCD (BRUKER). A set of 606 frames (exposure time: 60 s) was collected up to $2\theta = 70°$ (Mo radiation). The data were corrected for Lorentz and polarization effects. An analysis of the lattice parameters and, more importantly, of the equivalent reflections indicated a tetragonal crystal system of Laue group $4/mmm$. The systematic absences ($h + k + l = 2n + 1$ for all hkl reflections, typical for body-centered lattices) are in agreement with space group $I4/mmm$, the space group of the predicted La_2Sb type. Thus, the structure model of La_2Sb was used as a starting point, substituting the Sb site by As and the two La sites by Zr (on Wyckoff site 4e) and Ti (on Wyckoff site 4c). The refinement[18] converged smoothly to satisfying residual values of $R(F) = 0.041$ and $R_w(F^2) = 0.098$. Refining the occupancy factors of both metal sites gave full occupancies in both cases (Zr, 1.000(8); Ti, 1.005(10)); therefore mixed occupancies can be excluded. No evidence was found for incorporation with oxygen; the resulting electron density map was featureless. Also, the quantitative yield of ZrTiAs basically rules out the necessity of oxygen to stabilize this compound.

Significant phase widths were proven by single-crystal analyses of Zr-rich and Zr-poor samples. Allowing mixed Zr/Ti occupancies, we found a phase width of $Zr_{1-\delta}Ti_{1+\delta}As$ with $0 \leq \delta \leq 0.42(1)$. Crystallographic details may be found in Table 1; atomic positions and displacement parameters are listed in Table 2.

Table 1. Crystallographic Data for ZrTiAs and $Zr_{0.58(1)}Ti_{1.42}As$

empirical formula	ZrTiAs	$Zr_{0.58(1)}Ti_{1.42}As$
fw (g/mol)	214.04	195.85
T of measurement (K)	295	295
λ (pm)	71.073	71.073
space group	$I4/mmm$	$I4/mmm$
ρ_{calcd} (g/cm^3)	6.68	6.44
a (pm)	379.28(6)	373.25(8)
c (pm)	1480.2(3)	1449.5(5)
V (10^6 pm^3)	212.94(7)	201.94(9)
Z	4	4
μ (cm^{-1})	235.8	243.5
$R(F_o)^a \backslash R_w(F_o^2)^b$	0.041\0.098	0.027\0.070

[a] $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w(F_o^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table 2. Positional and Displacement Parameters of ZrTiAs

atom	site	x	y	z^a	U_{11}/pm^2	U_{22}/pm^2	U_{33}/pm^2	U_{eq}/pm^2
Zr^b	4e	0	0	0.320 97(6)	63(4)	U_{11}	53(5)	59(3)
Ti	4c	0	1/2	0	92(7)	75(7)	51(7)	73(4)
As	4e	0	0	0.130 29(7)	62(4)	U_{11}	60(5)	61(3)

[a] $Zr_{0.58(1)}Ti_{1.42}As$: $z(Zr\backslash Ti) = 0.321\ 21(9)$; $z(As) = 0.132\ 95(8)$. [b] Mixed occupancy in $Zr_{0.6}Ti_{1.4}As$: 58(1)% Zr; 42% Ti.

Band Structure Calculations. We carried out self-consistent tight-binding LMTO calculations (LMTO = linear muffin tin orbitals)[19-21] on ZrTiAs. In this approach, the density functional theory is used with the local density approximation (LDA). The integration in k space was performed by an improved tetrahedron method[22] on a grid of 641 irreducible k points of the first Brillouin zone. Void space was filled with one so-called empty sphere.

Results and Discussion

Crystal Structure. The structure map used to postulate the crystal structure of the hitherto unknown ZrTiAs is shown in Figure 1, emphasizing the structure types with a coordination number of 9 for the main group element Q in M_2Q (coordination spheres: deltahedral tetrakaidecahedra). So far, we found four M_2Q examples with $\langle CN(Q) \rangle = 9$ in the literature, all being pnictides: V_2P (Co_2Si type),[23] La_2Sb, Zr_2Sb (La_2Sb type), and Sc_2Sb (Cu_2Sb type).[24] As anticipated based on the structure map, ZrTiAs forms the La_2Sb type, or, more precisely, an ordered ternary variant thereof, sometimes called the CeScSi type. The values essential for calculating the factor f (see (1)) are summarized in Table 3. The radii were taken from Slater,[25] e_Q is the number of valence electrons of Q, here 5 for As and Sb, n_M is the principal quantum number of M (4 for Sc, Ti, and V; 5 for Zr), and vec$_M$ corresponds to the number of metal-centered valence electrons per M atom, after reduction of the Q atoms, i.e., the number of electrons available for M−M bonding. Thus, vec$_M$ is calculated via $(1/2)[2e_M - (8 - e_Q)]$ with e_M = valence electron of M in the neutral state. E.g., for Zr_2Sb, we get vec$_M = (1/2)[2 \times 4 - (8 - 5)] = 2.5$.

Without knowledge of our structure map, the structure of ZrTiAs would be impossible to predict, for Zr_2As

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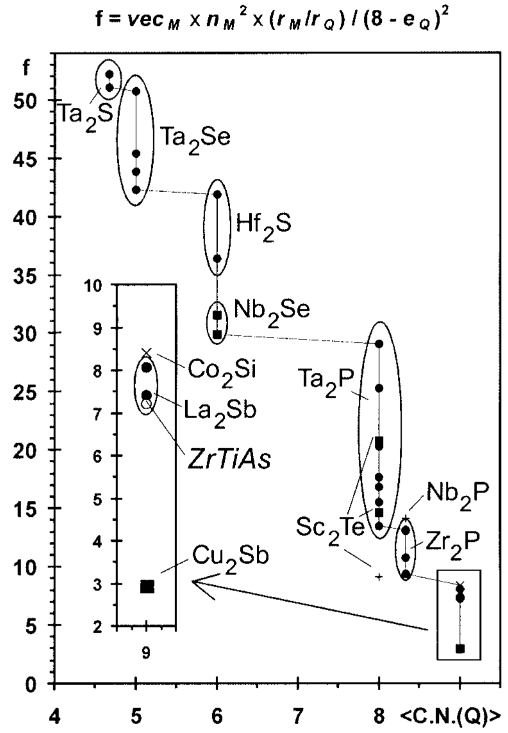

Figure 1. Structure map of M_2Q compounds.

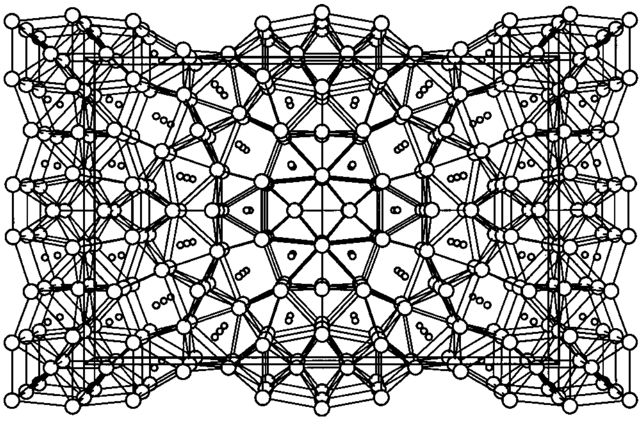

Figure 2. Crystal structure of Zr_2As in a projection along the *c* axis. Horizontal: *a* axis. Large, white circles, Zr; small, gray circles, As. Zr−As bonds are omitted for clarity.

Table 3. Overview of M_2Q Compounds with ⟨CN(Q)⟩ = 9

compd	struct type	vec_M	n_M	r_M/pm	r_Q/pm	e_Q	*f*
V_2P	Co_2Si	3.5	4	135	100	5	8.40
La_2Sb	La_2Sb	1.5	6	195	145	5	8.07
Zr_2Sb	La_2Sb	2.5	5	155	145	5	7.42
“$Zr_{1.5}Ti_{0.5}As$”		2.5	4.75	151.25	115	5	8.24
ZrTiAs	La_2Sb	2.5	4.5	147.5	115	5	7.22
“$Zr_{0.5}Ti_{1.5}As$”		2.5	4.25	143.75	115	5	6.27
Sc_2Sb	Cu_2Sb	1.5	4	160	145	5	2.94

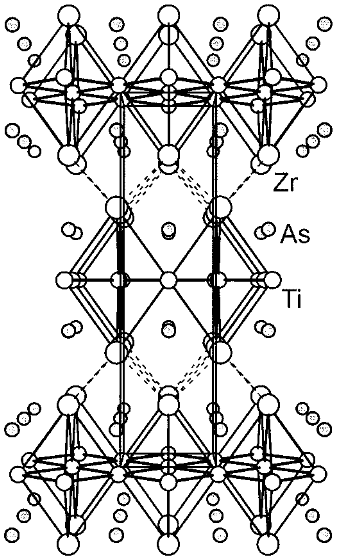

Figure 3. Crystal structure of ZrTiAs in a projection along the *a* axis. Horizontal: *b* axis. Large, white circles, Zr; small, white circles, Ti; small, gray circles, As. M−As bonds are omitted for clarity. Dashed lines: Zr−Zr distances of 341 pm.

forms the Zr_2P type, which has no resemblance to the La_2Sb type (Figure 2), and the corresponding binary titanium arsenide is unknown. For the latter, our function *f* suggests a coordination number of nine for the arsenic atoms, also. That is, if a “Ti_2As” could be realized.

ZrTiAs and Zr_2Sb are examples for compounds where opposite trends equalize one another. The Zr atoms form stronger metal−metal bonds because of the larger extent of the 4d orbitals of the Zr atoms, as expressed via the main quantum number n_M in our formula 1—this favors fewer Zr−Q interactions and thus a smaller ⟨CN(Q)⟩. On the other hand, the radius ratio r_M/r_Q is smaller in the case of the zirconium antimonide because of the large difference between the radii of the Sb and As atoms, which overcomes the difference in the radii of Zr and Ti atoms, according to $r_{Zr}/r_{Sb} = 155/145 = 1.07 < (1/2)(r_{Zr} + r_{Ti})/r_{As} = (1/2)(155 + 140)/115 = 1.28$. The ratio of the radius ratios $1.07/1.28 = 0.83$ is approximately the reciprocal of the ratios of the squared main quantum numbers $n_{Zr}^2/\{(1/2)(n_{Zr} + n_{Ti})\}^2 = 5^2/4.5^2 = 25/16 = 1.23$. Thus, the *f* values of eq 1 are very similar, namely, 7.42 for Zr_2Sb and 7.22 for ZrTiAs. Consequently, both pnictides, Zr_2Sb and ZrTiAs, crystallize in the La_2Sb structure type, the latter shown in Figure 3.

While the Zr and Ti atoms occur well ordered on the two different metal sites in ZrTiAs, we found Zr/Ti mixed occupancies (in different extents) over the whole phase ranges in the antimonides $(Zr,Ti)_5Sb_8$[26] and (Zr,Ti)Sb.[27] Accordingly we investigated the possibilities of mixed occupancies in this case, also. The phase width of $Zr_{1-\delta}Ti_{1+\delta}As$ was determined to be within $0 \leq \delta \leq 0.42(1)$ with Zr/Ti mixed occupancies on one metal site, namely, the Zr site in ZrTiAs. This phase range slightly enlarges the domain of the La_2Sb type in the structure map but does not lead to an overlap with the neighboring types Co_2Si and Cu_2Sb (Table 3).

Main structure motifs of the ZrTiAs structure are As-centered deltahedral Zr_5Ti_4 tetrakaidecahedra (tricapped trigonal prisms) and empty (distorted) Zr_2Ti_4 octahedra. The tetrakaidecahedra are interconnected via common faces to form linear chains parallel to [100] and furthermore via common edges to build the three-dimensional structure, for all atoms of the structure are part of the Zr_5Ti_4As tetrakaidecahedra.

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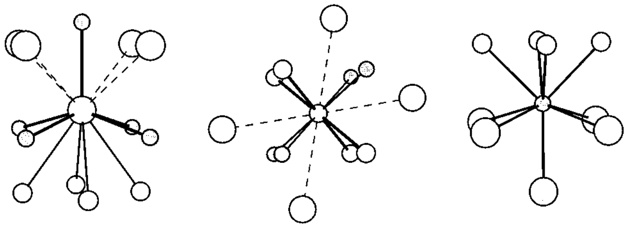

Figure 4. Nearest neighbors of Zr (left), Ti (middle), and As (right) in ZrTiAs.

Table 4. Selected Interatomic Distances (pm) of ZrTiAs and $Zr_{0.6}Ti_{1.4}As$

		d(ZrTiAs)	*d*($Zr_{0.6}Ti_{1.4}As$)
ZrAs	4x	277.73(5)	272.17(7)
ZrAs	1x	282.3(1)	272.9(2)
ZrTi	4x	325.88(9)	319.4(1)
ZrZr	4x	340.7(1)	335.1(2)
TiTi	4x	268.19(4)	263.93(6)
TiAs	4x	270.48(8)	268.3(1)

The local coordination spheres of the three different atoms in ZrTiAs are depicted in Figure 4. The larger, more electropositive Zr atom is coordinated by five As atoms and the Ti atom by four As atoms. The analogous tendency was found in the structure of (Zr,Ti)Sb, namely, that the Zr content per site increases with increasing number of Sb neighbors. Here, both the Zr−As (between 278 and 282 pm) and the Ti−As (270 pm) distances are roughly of the order of the sum of the single bond radii (after Pauling: r_{Zr} = 145 pm, r_{Ti} = 132 pm, r_{As} = 121 pm).[28] All of these bonds are shortened in $Zr_{0.6}Ti_{1.4}As$; the strongest effect occurs in the longer Zr−As bond with a decrease of 9 pm, since the “Zr” site is mixed occupied by 58(1)% Zr and 42% Ti in $Zr_{0.6}Ti_{1.4}As$ (Table 4). The shortness of the M−As bonds is typical for metal-rich arsenides, for the M−As bonds are usually the dominating ones, as confirmed by a comparison with Zr_2As (d_{Zr-As} between 265 and 312 pm) and Ti_5As_3 (d_{Ti-As} between 252 and 282 pm).

The structure of ZrTiAs exhibits short Ti−Ti bonds, namely, four per Ti atom of a length of 268 pm (264 pm in $Zr_{0.6}Ti_{1.4}As$) which correspond to twice the single bond radius of Ti (264 pm). This gives rise to a regular 4^4 layer (Schläfli symbolism) of Ti atoms in the *a*,*b*-plane. An even shorter Ti−Ti bond (258 pm, two bonds per Ti atom, occurring in a linear Ti chain) was found in the structure of $Ti_5(Si,Sb)_3$.[29] On the other hand, the Zr−Ti and Zr−Zr distances are with 326 and 341 pm significantly longer than the sum of the radii (277 and 290 pm). Similar is the situation in Zr_2Sb with short Zr2−Zr2 bonds of 291 pm (with Zr2 on 4c, i.e., the Ti site in ZrTiAs), but longer ones for the Zr1−Zr2 and Zr1−Zr1 distances (350 and 366 pm, respectively). It is concluded that these trends are a consequence of the crystal structure independent of the metal atom kinds. It is instructive, however, to compare these distances with those in the structures of the elements; i.e., d_{Ti-Ti} = 289−295 pm in *hcp* Ti, d_{Zr-Zr} = 318−323 pm in *hcp* Zr, and 309−357 pm in *bcc* Zr. A partial exchange of Ti for Zr on the Ti site in ZrTiAs is inhibited by the short Ti−Ti distances of 268 pm, which are too short for Zr−Ti or—even more so—for Zr−Zr bonds.

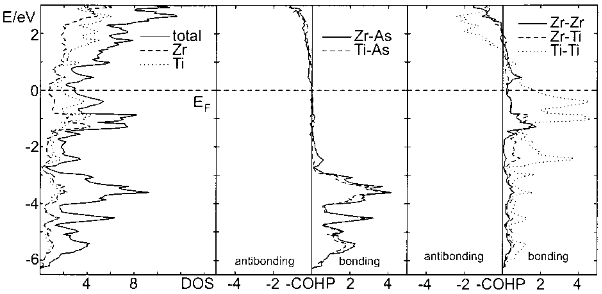

Figure 5. Densities of states (left), M−As (middle) and M−*M* (right) crystal orbital Hamiltonian populations (right) of ZrTiAs.

Electronic Structure. The densities of states (DOS) of ZrTiAs, along with the local densities, are shown in the left part of Figure 5. No band gap occurs in the vicinity of the Fermi level; thus, metallic properties are most likely. The DOS below −3 eV is predominated by arsenic *s* and *p* states; the occurrence of Zr and Ti states at these low energies are indicative of covalent Zr−As and Ti−As mixing. As revealed in the crystal orbital Hamiltonian populations (COHPs,[30] middle part of Figure 4), cumulated for both the Zr−As and Ti−As bonds, only bonding Zr−As and Ti−As states are filled.

Both kinds of metal atoms, Zr and Ti, exhibit some filled states, while the Ti states contribute more to the region below the Fermi level, which was arbitrarily placed at 0 eV. This is in agreement with the more electropositive character of Zr and the occurrence of most significant Ti−Ti contacts. A comparison of the Ti−Ti bonds with the other kinds shows that they may be as significant as the M−As bonds, but that they are much stronger than the Zr−Zr and Zr−Ti bonds (right part of Figure 5).

An increase in the valence-electron concentration would strengthen all M−M interactions, with negligible changes in the M−As bonds. Thus, the electronic structure favors a (partial) substitution of group 4 metals by group 5 metals. We are especially motivated to look for the still hypothetical “$Zr_{1-\delta}V_{1+\delta}As$” and “$Nb_{1-\delta}Ti_{1+\delta}As$” in the La_2Sb type, for these compounds would exhibit *f* values similar to ZrTiAs. On the other hand, since a hypothetical “$Hf_{1-\delta}V_{1+\delta}As$” would exhibit a larger *f* because of n_{Hf} = 6, we expect the formation of the Co_2Si or Zr_2P structure, depending on δ.

Summary

The successful synthesis of ZrTiAs in the predicted La_2Sb type proved the usability of our structure map developed in cooperation with Bernd Harbrecht. Its phase range slightly expands the La_2Sb domain in this structure map.

In contrast to the zirconium titanium antimonides (Zr,Ti)Sb and $(Zr,Ti)_5Sb_8$, no Zr/Ti mixing on any sites takes place in the ZrTiAs structure. However, decreasing the Zr/Ti ratio is possible and occurs with mixed occupancies on the Zr site.

The metallic ZrTiAs is mainly stabilized by strong Zr−As, Ti−As, and Ti−Ti bonds, and to a minor extent by Zr−Zr and Zr−Ti bonding interactions. Increasing the valence-electron concentration, for example by substituting Ti with V, seems to be possible for (i) this

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would lead to stronger metal–metal bonds of all three kinds and (ii) the hypothetical "ZrVAs" of the La_2Sb type would fit into our structure map. Such substitution attempts are underway and will further test the usefulness of our structure map.

Acknowledgment. Financial support from *Materials and Manufacturing Ontario* and *Natural Sciences and Engineering Research Council* is gratefully acknowledged.

Supporting Information Available: Table giving crystallographic data and a figure showing the unit cell of ZrTiAs (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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