

# Impurity Stabilization of Phases with the $Mn_5Si_3$ -Type Structure. Questions Regarding $La_5Sn_3$ and $Zr_5Si_3$

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The hexagonal  $Mn_5Si_3$ -type structure reported several times for  $La_5Sn_3$  is incorrect; the binary compound is a line phase and occurs only in the tetragonal  $W_5Si_3$ -type structure. Phases with a  $Mn_5Si_3$ -type structure and lattice dimensions comparable to the earlier reports for the binary are obtained for the single-phase compositions  $La_5Sn_3C_{0.5}$  ( $La_{15}Ge_4Fe$  structure) or  $La_5Sn_3O_x$ ,  $x = 0.3, 1.0$ . Samples with the  $Mn_5Si_3$  structure cannot be transformed to a  $W_5Si_3$ -type product by annealing. The nonmetals, which occupy interstitial positions, presumably originated with impurities in the lanthanum in earlier studies. The same conditions apply to  $Pr_5Sn_3$  with oxygen impurities. The compound  $Zr_5Si_3$  in the  $Mn_5Si_3$  structure does not require interstitial C, O, etc., for stability, as previously claimed, but is stable only above ca. 1725 °C, as reported by Kocherzhinskii et al. The compound is a line phase near 1750 °C with lattice constants ( $a = 7.958 (1)$ ,  $c = 5.563 (1)$  Å) that are significantly larger than any reported heretofore. Annealed samples containing carbon saturate near  $Zr_5Si_3C_{0.5}$  and show noticeably different lattice constants, while those with added oxygen approach the composition  $Zr_5Si_3O$  and give much smaller parameters than the binary,  $a = 7.9200 (6)$ ,  $c = 5.5502 (7)$  Å. Powder pattern intensity data for the latter support the binding of carbon and oxygen in the usual interstitial position in the  $Mn_5Si_3$  structure.

## Introduction

The large number of metallic  $A_5B_3$  compounds with the  $Mn_5Si_3$ -type structure presents both particular challenges in synthesis and novel opportunities for a new kind of chemistry. The semiinfinite chains of confacial octahedral clusters ( $Mn_{6/2}Si_{6/2}$ ) present in this structure type have in several instances been shown to encapsulate a variety of third elements in the center of the host metal clusters. This capability may serve either to stabilize otherwise unknown binary compounds in this structure, sometimes through the action of unappreciated impurities in the components, or to enable one to systematically alter the stabilities and electronic properties intrinsic to a binary host phase through a selection of interstitials. A wide range of elements has been found to bond in the hosts  $Zr_5Sb_3$ ,<sup>3</sup>  $Zr_5Sn_3$ ,<sup>4</sup>  $La_5Ge_3$ , and  $La_5Pb_3$ ,<sup>5,6</sup> while, on the other hand, groups II-V compounds typified by  $Ca_5Sb_3$  have sufficient valence electrons available to bond only halide.<sup>7</sup>

Our attention was drawn to  $La_5Sn_3$  by reports that this compound is dimorphic, exhibiting both the  $Mn_5Si_3$ - and  $W_5Si_3$ -type structures, in clear contrast to the analogous germanium and lead compounds that occur only in the former arrangement.<sup>5</sup> The first two reports on  $La_5Sn_3$  indicated that the  $Mn_5Si_3$ -type was obtained first by Palenzona and Merlo after melting a pressed pellet at 1200–1500 °C in tantalum<sup>8</sup> and then by Jeitschko and Parthé from arc melting.<sup>9</sup> Both obtained comparable results for many heavier lanthanide stannides (other than

for Eu, Yb), except that only the second investigation produced single-phase  $Ce_5Sn_3$ . A later review by Iandelli and Palenzona<sup>10</sup> listed  $Mn_5Si_3$ -type phases for stannides of all of the lanthanides, although they gave somewhat different lattice constants for  $La_5Sn_3$  without information on the synthesis conditions. This single-structure picture was altered when Franceschi<sup>11</sup> reported a low-temperature  $R_5Sn_3$  phase with the tetragonal  $W_5Si_3$  structure was formed for  $R = La, Ce, Pr$  (but not Nd). This was obtained on slow cooling of the molten alloy in Mo containers or, evidently, after annealing at 400 °C. Alloys for the first three elements also gave products with the  $Mn_5Si_3$  structure on (undefined) rapid cooling, possibly from arc melting, and with lattice constants reported to be in excellent agreement with those in the literature.<sup>8,9</sup> Reversibility of the supposed transition was not demonstrated. The only subsequent information has been the note by Borzone et al.<sup>12</sup> that both forms of  $La_5Sn_3$  had been obtained, although no synthetic details were provided, only lattice constants. In all cases, the  $W_5Si_3$  form exhibited the smaller molar volume.

The fact that only  $R_5Sn_3$  phases for  $R = La, Ce, Pr$  exhibit dimorphism and not the germanium or lead analogues could represent only unappreciated size affects. On the other hand, a need for interstitial impurity atoms Z to stabilize unique pseudobinary  $Mn_5Si_3(Z)$ -type phases has often been invoked,<sup>13,14</sup> although evidently none of these examples has been rigorously established by utilizing modern materials and techniques. In fact, we conclude in the  $La_5Sn_3$  case that the above contradictions did arise because of impurities.

The problem with  $Zr_5Si_3$  is of a different nature. The phase diagram of the Zr–Si system that is still taken as authoritative is the 1958 summary of Hansen and An-

(1) The 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) Kocherzhinskii, Yu. A.; Kulik, O. G.; Shishkin, E. A. *Metallofizika* 1976, 64, 48.

(3) Garcia, E.; Corbett, J. D. *Inorg. Chem.* 1988, 27, 2907; 1990, 29, in press.

(4) Kwon, Y.-U.; Corbett, J. D., unpublished research.

(5) Guloy, A.; Corbett, J. D., unpublished research.

(6) Corbett, J. D.; Garcia, E.; Kwon, Y.-U.; Guloy, A. *Pure Appl. Chem.* 1990, 62, 103.

(7) Hurng, W.-M.; Corbett, J. D. *Chem. Mater.* 1989, 1, 311.

(8) Palenzona, A.; Merlo, F. *Atti Accad. Naz. Lincei., Cl. Sci. Fis. Mat. Nat., Rend.*, 1966, 40, 617.

(9) Jeitschko, W.; Parthé, E. *Acta Crystallogr.* 1967, 22, 551.

(10) Iandelli, A.; Palenzona, A. In *Handbook on Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Eyring, L., Eds.; North-Holland Publishing: Amsterdam, 1979; Vol. 2, p 1.

(11) Franceschi, E. *J. Less-Common Met.* 1979, 66, 175.

(12) Borzone, G.; Borsese, A.; Ferro, R. *Z. Anorg. Allg. Chem.* 1983, 50, 199.

(13) Parthé, E.; Norton, J. T. *Acta Crystallogr.* 1958, 11, 14.

(14) Nowotny, H. In *Electronic Structure and Alloy Chemistry of the Transition Metals*; Beck, P. A., Ed.; Interscience Publishers: New York, 1963; p 179.

derko,<sup>15</sup> which included  $\text{Zr}_5\text{Si}_3$  in the  $\text{Mn}_5\text{Si}_3$  structure. This assessment discounted other studies that concluded certain impurities, B, C, N, O especially, were necessary for the stability of  $\text{Zr}_5\text{Si}_3$  in the  $\text{Mn}_5\text{Si}_3$  structure.<sup>16,17</sup> A level of ~0.3 at. % carbon was cited, although it is not clear that residual impurities could have been controlled at this level with the materials and furnaces available at the time. Boron was later concluded to act similarly,<sup>18</sup> and the same impurity postulate was applied to other pseudobinary phases, e.g.,  $\text{Zr}_5\text{Ge}_3$ .<sup>13</sup> Both boron and oxygen were stated to increase the lattice constants of  $\text{Zr}_5\text{Si}_3$ ,<sup>16,19</sup> while, strangely, dimensional changes with added carbon and nitrogen were said to be unimportant.<sup>16</sup> Greater amounts of these impurities (Z) were found to stabilize the corresponding  $\text{Zr}_5\text{Si}_3\text{Z}$  phases so greatly that two neighboring binary phases,  $\text{Zr}_2\text{Si}$  and  $\text{Zr}_3\text{Si}_2$ , disappeared from the system.<sup>19</sup> As a result of the foregoing findings, ternary diagrams for  $\text{Zr-Si-C}$ ,<sup>16</sup>  $\text{Zr-Si-B}$ ,<sup>13</sup> and  $\text{Zr-Si-Al}$ <sup>14</sup> have omitted the binary component  $\text{Zr}_5\text{Si}_3$  from the description, although it was retained in another instance.<sup>19</sup> Crystallographic compilations are often ambiguous as to whether  $\text{Zr}_5\text{Si}_3$  is actually a ternary phase. However, recent studies of other zirconium systems where impurity stabilization has been claimed or suggested, namely,  $\text{Zr}_5\text{Sb}_3$ ,  $\text{Zr}_5\text{Sn}_3$ , and  $\text{Zr}_5\text{Al}_3$ , have all concluded that the ternary postulate is in these cases incorrect.<sup>20-22</sup>

The above citations on the  $\text{Zr-Si}$  system are all at least 30 years old, and recent phase diagram summaries repeat the 1958 result. However, a 1976 phase study by Kocherzhinskii et al.<sup>2</sup> gives a different picture, with  $\text{Zr}_5\text{Si}_3$  existing only between a peritectic melting point of ~2180 °C and a peritectoid decomposition to  $\text{Zr}_3\text{Si}_2$  and  $\text{Zr}_2\text{Si}$  at  $1745 \pm 15$  °C. On the other hand, it is not clear whether this study used an innocent container in all cases; the niobium involved at least in part of the work could, in our experience, act as a significant sink for zirconium at these temperatures.

In view of these conflicts, we have sought to clarify the status of  $\text{Zr}_5\text{Si}_3$  as well as any ternary phases involving carbon and oxygen. Particular attention has been paid to lattice dimensions as these are probably the best means to distinguish, with hindsight, the effect of interstitials on previously reported materials.<sup>3-7</sup> The investigation also needed to resolve whether misleading changes in lattice dimensions might be induced by silicon acting as a self-interstitial in  $\text{Zr}_5\text{Si}_{3+x}$ , since there are reports of both a clearly recognizable phase breadth for this phase<sup>23</sup> and significantly larger dimensions for  $\text{Zr}_5\text{Si}_3$  crystals isolated from a molten alloy of the composition  $\text{Zr}_5\text{Si}_{3.56}$ .<sup>24</sup> Impurities are again found to have played the major role.

## Experimental Section

**Materials.** The Ames Laboratory lanthanum metal used had been analyzed to be 99.999% metal and to contain 34, 190, 123 wt ppm C, N, O, respectively. It was stored and handled only in a glovebox. The tin and crystal-bar zirconium reagents have

(15) Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, 2nd ed.; McGraw-Hill: New York, 1958; p 1205.

(16) Nowotny, H.; Lux, B.; Kudielka, H. *Monatsh. Chem.* 1956, 87, 447.

(17) Parthé, E. *Powder Met. Bull.* 1957, 8, 23.

(18) Parthé, E.; Norton, J. T. *Monatsh. Chem.* 1960, 91, 1127.

(19) Brewer, L.; Krikorian, O. J. *Electrochem. Soc.* 1956, 103, 38.

(20) Garcia, E.; Corbett, J. D. *Inorg. Chem.* 1988, 27, 2553.

(21) Kwon, Y.-U.; Corbett, J. D. *Chem. Mater.* 1990, 2, 27.

(22) Kim, S.-J.; Kematick, R. J.; Yi, S. S.; Franzen, H. F. J. *Less. Common Met.* 1988, 137, 55.

(23) Schachner, H.; Nowotny, H.; Machenschalk, R. *Monatsh. Chem.* 1953, 84, 677.

(24) Karpinski, O. G.; Evseev, B. A. *Issled. Stalei Splavov* 1964, 54.

been described before,<sup>21</sup> while the silicon was zone-refined (99.999%). Carbon was introduced as spectroscopic grade powder (Union Carbide Corp.) or  $\text{ZrC}$  (CERAC), and oxygen as Ames Lab  $\text{La}_2\text{O}_3$  or  $\text{ZrO}_2$  (Johnson Matthey, Grade 1).

**Reactions.** These were all run with high-quality reagents, inert containers, and glovebox manipulations (where necessary) so that the total content of each reaction product was known and predetermined. Welded containers constructed from tantalum tubing together with melting reactions appear to be completely satisfactory for  $\text{La}_5\text{Sn}_x$  and carbon products. Mixtures of weighed reagents were in these cases cold-pressed into pellets within the glovebox, sealed within  $3/8$ -in.-o.d. Ta containers, and heated in a high-temperature vacuum furnace from room temperature to 1150 °C over 2 days. (The reaction of the elements has been reported to be vigorous.<sup>8,9</sup>) The samples were then melted at 1350 °C, slowly cooled to 1150 °C over 2 days, and then cooled to 300 °C over 4 more days. For some quenching experiments, the welded Ta containers containing similarly pelleted samples were in turn sealed in evacuated and well-baked  $\text{SiO}_2$  jackets. Arc-melting reactions followed by annealing at 1050 °C proved to be more effective for preparing the lanthanum tin oxide phases.

Considerably higher temperatures are necessary to achieve equilibrium with zirconium-silicon samples. Sintering pressed pellets of the elements or of intermediate binary phases is slow, and a more useful procedure is to arc-melt (W electrode) a mixture of the elements, plus  $\text{ZrC}$  when appropriate, and then to anneal the multiphasic, as-cast button in Mo. Oxide samples were prepared by powder sintering a pressed pellet of preformed  $\text{Zr}_3\text{Si}_2$  and  $\text{ZrO}_2$  in Ta. In neither case was any evidence of sample reaction with Mo or Ta seen, and these elements could not be detected in the products by SEM-EDX means. This contrasts with our experiences with the nonstoichiometric  $\text{Zr}_5\text{Sb}_{3+x}$  in Ta.<sup>25</sup>

**Furnaces.** The higher temperature  $\text{Zr-Si}$  reactions were carried out mainly by induction heating as-cast samples in a capped Mo crucible under a vacuum of  $\sim 5 \times 10^{-7}$  Torr, the approximate temperatures being measured by optical pyrometry ( $\pm 25$  °C). The crucible was preheated at 1900–2000 °C for 30 min before each use. A few of the  $\text{Zr-Si}$  studies and most of the  $\text{La-Sn}$  reactions were carried out in a high-temperature high-vacuum furnace, an Astro 1000A graphite resistance furnace that had been modified to avoid carbon contaminants and to maintain a high vacuum in the reaction chamber. The furnace was divided longitudinally into two chambers by a gas-tight alumina muffle tube (with O-rings at the ends), and the outside of this tube near the heaters was also protected by a sheet of Ta wrapped around it. The outside, graphite element chamber was connected to a roughing pump ( $\sim 10^{-3}$  Torr), while the inner chamber was evacuated by a turbo-molecular pump to a working pressure of  $\sim 10^{-6}$ – $10^{-7}$  Torr. To provide further protection, the Ta reaction containers were enclosed in a capped tantalum canister. The Ta sample containers remained ductile under these conditions. Temperatures were measured by a W-Re thermocouple in the inner chamber that was in contact with the bottom of the Ta can. The surfaces of the samples remained completely clean in all of these processes.

The Guinier X-ray powder and lattice constant refinement methods using Si as an internal standard have been described before.<sup>21</sup>

## Results and Discussion

**$\text{La}_5\text{Sn}_3$ .** We postulated that the contradictions regarding the correct structure(s) of  $\text{La}_5\text{Sn}_3$ , namely,  $\text{Mn}_5\text{Si}_3$  or  $\text{W}_5\text{Si}_3$ -type, arose because the relative stabilities of the two were dependent either on stoichiometry or on impurities. Therefore, samples of  $\text{La}_5\text{Sn}_x$  with  $x$  ranging from 2.6 to 3.4 in 0.1 intervals contained in welded Ta tubing were slowly cooled from 1350 °C (see Experimental Section). The Guinier patterns of all these samples could be entirely accounted for with a tetragonal  $\text{W}_5\text{Si}_3$ -type structure ( $I4/mcm$ ) plus, of course, the appropriate  $\text{La}_3\text{Sn}$  and  $\text{La}_5\text{Sn}_4$  patterns on the tin-poor and tin-rich sides of

(25) Kwon, Y.-U.; Sevov, S. C.; Corbett, J. D. *Chem. Mater.*, following article in this issue.

Table I. Lattice Constants (Å) and Cell Volumes (Å<sup>3</sup>) for La<sub>5</sub>Sn<sub>3</sub> Phases

composition	method <sup>a</sup>	type <sup>b</sup>	<i>a</i>	<i>c</i>	X-ray method <sup>c</sup>	<i>V</i>	ref
La <sub>5</sub> Sn <sub>3</sub>	M, S	W <sub>5</sub> Si <sub>3</sub>	12.755 (4)	6.336 (3)	G	1030.8 (7)	this work
La <sub>5</sub> Sn <sub>3</sub>	M, A (An)	W <sub>5</sub> Si <sub>3</sub>	12.749	6.343	D	1031.0	10
La <sub>5</sub> Sn <sub>3</sub>	M	W <sub>5</sub> Si <sub>3</sub>	12.748	6.344	D	1031.0	11
La <sub>5</sub> Sn <sub>3</sub> C <sub>0.5</sub>	S	La <sub>15</sub> Ge <sub>9</sub> Fe	16.357 (4) <sup>d</sup>	6.957 (3)	G	1612.0 (4)	this work
La <sub>5</sub> Sn <sub>3</sub> C <sub>0.75</sub>	S	Mn <sub>5</sub> Si <sub>3</sub>	9.396 (2)	6.934 (1)	G	530.2 (2)	this work
La <sub>5</sub> Sn <sub>3</sub> C	S	Mn <sub>5</sub> Si <sub>3</sub>	9.406 (2)	6.954 (2)	G	532.9 (3)	this work
La <sub>5</sub> Sn <sub>3</sub> C <sub>2</sub>	S	Mn <sub>5</sub> Si <sub>3</sub> <sup>e</sup>	9.403 (4)	6.947 (8)	G	531.9 (8)	this work
La <sub>5</sub> Sn <sub>3</sub> O <sub>0.3</sub>	A, An	Mn <sub>5</sub> Si <sub>3</sub>	9.452 (2)	6.972 (1)	G	539.4 (2)	this work
La <sub>5</sub> Sn <sub>3</sub> O	A, An	Mn <sub>5</sub> Si <sub>3</sub>	9.4316 (3)	6.965 (1)	G	536.6 (3)	this work
La <sub>5</sub> Sn <sub>3</sub>	M	Mn <sub>5</sub> Si <sub>3</sub>	9.416	6.926	D	531.8	8
La <sub>5</sub> Sn <sub>3</sub>	A	Mn <sub>5</sub> Si <sub>3</sub>	9.435 (5)	6.961 (5)	D	536.6	9
La <sub>5</sub> Sn <sub>3</sub>	?	Mn <sub>5</sub> Si <sub>3</sub>	9.425	6.943	?	534.1	10
La <sub>5</sub> Sn <sub>3</sub>	M	Mn <sub>5</sub> Si <sub>3</sub>	9.45	6.975	D	539	12

<sup>a</sup> M, melted in Ta; A, arc melted; S, powder sintered (1050 °C); An, annealed. <sup>b</sup> W<sub>5</sub>Si<sub>3</sub>, tetragonal, D8<sub>m</sub>, I4/mcm; Mn<sub>5</sub>Si<sub>3</sub> (Ti<sub>5</sub>Ge<sub>4</sub>), hexagonal, D8<sub>g</sub>, P6<sub>3</sub>/mcm; La<sub>15</sub>Ge<sub>9</sub>Fe, hexagonal, P6<sub>3</sub>mc with *a*  $\cong \sqrt{3}a$ (Mn<sub>5</sub>Si<sub>3</sub>).<sup>5</sup> <sup>c</sup> G = Guinier (Si standard); D = Debye-Scherrer. <sup>d</sup> *a* =  $\sqrt{3}(9.444)$ . <sup>e</sup> Multiphase product.

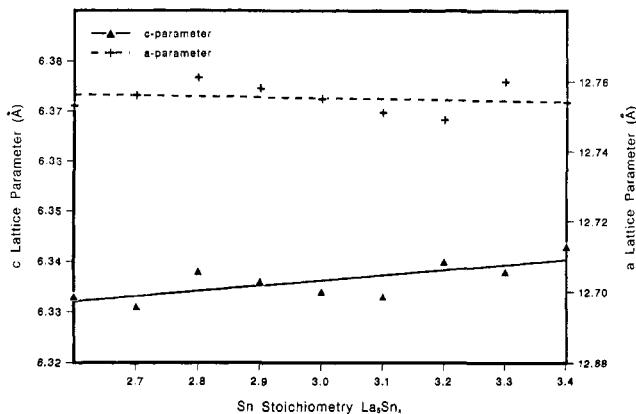


Figure 1. Variation of the lattice parameters (Å) of La<sub>5</sub>Sn<sub>3</sub> (W<sub>5</sub>Si<sub>3</sub>-type, I4/mcm) as a function of *x*: *a*, +; *c*,  $\Delta$  (standard deviations are as follows: *a*, (2–8)  $\times 10^{-3}$ ; *c*, (2–5)  $\times 10^{-3}$  Å).

La<sub>5</sub>Sn<sub>3</sub>, respectively. Refined lattice constants for this phase in the annealed samples are shown in Figure 1. There seems to be very little indication of a significant nonstoichiometry. Average values of the parameters are given in Table I along with our data for other pertinent phases and literature results for La<sub>5</sub>Sn<sub>3</sub>.

Franceschi<sup>11</sup> reported that rapid cooling (at an unspecified rate) was necessary to get the Mn<sub>5</sub>Si<sub>3</sub>-type phase. Therefore, similar SiO<sub>2</sub>-jacketed samples were held for 2 weeks at 1050 °C in a resistance furnace, and the contents quenched by dropping the containers into water. Samples of La<sub>5</sub>Sn<sub>x</sub> with *x* = 2.75, 2.9, 3.0, 3.1, and 3.25 again all gave only the W<sub>5</sub>Si<sub>3</sub> structure for the La<sub>5</sub>Sn<sub>3</sub> component. Moreover, similar samples of La<sub>5</sub>Sn<sub>3</sub> that were induction heated to 1400 °C and cooled by turning the powder off were always W<sub>5</sub>Si<sub>3</sub> type, even when liquid N<sub>2</sub> was sucked into the vacuum system to hasten the cooling. Thus, the earlier observations of the Mn<sub>5</sub>Si<sub>3</sub> structure are not correctly attributed to either a quenchable form, as proposed, or because of a compositional difference between this and the W<sub>5</sub>Si<sub>3</sub>-type material.

Since we have found a significant interstitial (Z) chemistry for the closely related La<sub>5</sub>Ge<sub>3</sub>Z systems,<sup>5</sup> reactions were carried out as before but with a variety of third elements, carbon and oxygen particularly. The oxides could be readily obtained by arc melting La, Sn, and La<sub>2</sub>O<sub>3</sub> followed by annealing, whereas La<sub>5</sub>Sn<sub>3</sub>C<sub>x</sub> samples were obtained by powder sintering of the elements. In these cases, the expected Mn<sub>5</sub>Si<sub>3</sub>-type structure was always found. Lattice dimensions determined for La<sub>5</sub>Sn<sub>3</sub>C<sub>x</sub>, *x* = 0.5, 0.75, 1.0, 2.0, and for La<sub>5</sub>Sn<sub>3</sub>O<sub>x</sub>, *x* = 0.3, 1.0, are included in Table I. It is in fact sufficient to obtain

Mn<sub>5</sub>Si<sub>3</sub>-type samples to simply melt W<sub>5</sub>Si<sub>3</sub>-type La<sub>5</sub>Sn<sub>3</sub> or a mixture of the elements in an arc-melting furnace. The lattice dimensions of these products are close to those of La<sub>5</sub>Sn<sub>3</sub>O<sub>0.3</sub>. Most importantly, no Mn<sub>5</sub>Si<sub>3</sub>-type product would revert to the W<sub>5</sub>Si<sub>3</sub> form when annealed at 1000–1050 °C for 3–7 days, so *the two structures for nominal La<sub>5</sub>Sn<sub>3</sub> are not related by a phase transition*.

The same conditions appear to apply to Pr<sub>5</sub>Sn<sub>3</sub> as well. Samples that have been induction heated and quenched are W<sub>5</sub>Si<sub>3</sub>-type, while arc-melting gives a Mn<sub>5</sub>Si<sub>3</sub>-type product. The intervening Ce<sub>5</sub>Sn<sub>3</sub> is probably similar.

The result with a La<sub>5</sub>Sn<sub>3</sub>C<sub>0.5</sub> composition is noteworthy since it clearly shows just the weak, additional lines expected for the La<sub>15</sub>Ge<sub>9</sub>Fe structure. This is a superstructure ( $\sqrt{3}a$ ) of the Mn<sub>5</sub>Si<sub>3</sub> type in which the confacial metal chains that contain the interstitial atoms are differentiated and partially occupied in an ordered manner.<sup>5</sup> Presumably the carbide has the same stoichiometry (La<sub>5</sub>Sn<sub>3</sub>C<sub>1/3</sub>) and ordering, as has subsequently also been established for the analogous La<sub>15</sub>Ge<sub>9</sub>C.<sup>5</sup> Samples with carbon coefficients of 0.75 and 1.0 show only the patterns of the Mn<sub>5</sub>Si<sub>3</sub> structure, while the La<sub>5</sub>Sn<sub>3</sub>C<sub>2.0</sub> composition contains additional phases, including La<sub>5</sub>Sn<sub>4</sub>. Simple valence rules suggest that the end product would be the Zintl phase La<sub>5</sub>Sn<sub>3</sub>C<sub>0.75</sub>. A unique compound of this composition has not yet been identified in this or any analogous system, but there clearly is a decrease in the equivalent *a* dimension on adding carbon to La<sub>5</sub>Ge<sub>3</sub>C<sub>0.5</sub>. We conclude that a second carbide phase evidently exists as well.

Possible reasons for the four earlier and evidently erroneous reports of La<sub>5</sub>Sn<sub>3</sub> with the Mn<sub>5</sub>Si<sub>3</sub> structure can be based only on speculation regarding common impurities and the reported lattice constants. The latter were evidently all determined by Debye-Scherrer methods, which are less precise in general use. Furthermore, our data indicate that La<sub>15</sub>Sn<sub>9</sub>C and La<sub>5</sub>Sn<sub>3</sub>O are virtually indistinguishable by this means. The dimensional data of Jentschko and Parthé<sup>9</sup> and Iandelli and Palenzona<sup>10</sup> are all consistent with such an assignment, while those by Borsone et al.<sup>12</sup> come closer to La<sub>5</sub>Sn<sub>3</sub>O<sub>0.3</sub>. (Franceschi<sup>11</sup> did not report dimensional data.) The extra lines unique to the superstructure would not likely be either seen by Debye-Scherrer methods or, as in our case, appreciated without a prior structure determination.

The very pervasive oxygen would be sufficient to account for most observations as glovebox protection for the lanthanum reagent was generally not provided. However, a sufficient carbon impurity level also seems quite possible; Gschneidner reported that commercial samples available in the 1970s from several sources contained up to 0.3 wt % C<sup>26</sup> (La<sub>15</sub>Sn<sub>9</sub>C requires 0.4 wt %). Of course, mixed

**Table II.** Lattice Constants ( $\text{\AA}$ ) and Cell Volumes ( $\text{\AA}^3$ ) for  $Zr_5Si_3$  and Related Products with the  $Mn_5Si_3$ -Type Structure ( $P6_3/mcm$ )

prep method; conditions <sup>a</sup>	<i>a</i>	<i>c</i>	<i>V</i>	ref
A; 1575, 5 <sup>b</sup>	7.9582 (9)	5.5638 (8)	305.16 (8)	this work
A; ~1775, 10; $Zr_5Si_{2.8}^b$	7.9563 (5)	5.5645 (7)	305.06 (6)	this work
A; ~1725, 24; $Zr_5Si_{3.1}^b$	7.9582 (6)	5.5613 (8)	305.03 (6)	this work
A; ~1875, 24; $Zr_5Si_3C_{0.5}^b$	7.9409 (5)	5.6016 (6)	305.90 (5)	this work
A; ~1825, 9; $Zr_5Si_3C^b$	7.9400 (6)	5.6116 (8)	306.38 (7)	this work
S; ~1725, 24; $Zr_5Si_3O^b$	7.9200 (6)	5.5502 (7)	301.50 (6)	this work
S; 1600, 20; 1700, 7; $Zr_5Si_3O^b$	7.9147 (8)	5.5572 (9)	301.48 (8)	this work
S; 1000–1400	7.88	5.55 <sub>8</sub>	299. <sub>3</sub>	23
S; 1600 ( $H_2$ ); C-free <sup>b,c</sup>	7.91 <sub>4</sub>	5.55 <sub>9</sub>	301. <sub>5</sub>	16
S; 1600 ( $H_2$ ); 0.3 at. % C	7.90 <sub>9</sub>	5.57 <sub>9</sub>	302. <sub>2</sub>	16
M; ~2200; 0.2 at. % C	7.85 <sub>4</sub>	5.53 <sub>5</sub>	295. <sub>7</sub>	17
M; ~2200; $Zr_5Si_{3.56}$	7.945 (1)	5.559 (1)	303.9 (2)	24
A; >1745 <sup>c</sup>	7.908	5.531	299.6	2
M; ~2200	7.880 (2)	5.553 (5)	298.6	31

<sup>a</sup>S, reactive sintering; M, melting in Mo; A, arc-melting and annealing; <sup>b</sup>°C, hours; compositions other than stoichiometric  $Zr_5Si_3$ . <sup>c</sup>Other phases were also present—see text or reference. <sup>c</sup>Iodide-zirconium.

interstitial phases originating from adventitious impurities have been seen in centered cluster halides<sup>27,28</sup> and could certainly occur here. There is not much reason to doubt that  $La_5Sn_3N$  will exist. The neighboring  $La_5Ge_3$  takes up stoichiometric amounts of B, C, O, P, and many others, while the previously reported  $La_5Ge_3$  was doubtlessly the oxide as well.<sup>5</sup>

In contrast, we are in agreement that  $La_5Pb_3$  and  $Pr_5Pb_3$  do occur in the  $Mn_5Si_3$  structure, as reported by some of the same authors.<sup>8,29</sup> The stannides appear to be consistently only  $Mn_5Si_3$ -type from neodymium on without (and presumably with) suitable impurities. The factors that make only the  $W_5Si_3$  form more stable for the larger  $La_5Sn_3$  and  $Pr_5Sn_3$  are probably rather subtle.

**$Zr_5Si_3$ .** Investigation of the true character of this phase—binary or impurity-stabilized ternary—had to do with methods suitable for synthesis, the temperatures utilized, the structural effects of controlled impurity additions to high purity samples, and the purities that can be maintained experimentally. Three phases in this composition region,  $Zr_2Si$ ,  $Zr_5Si_3$ , and  $Zr_3Si_2$ , evidently melt with decreasing incongruency at temperatures between 1925 and 2210 °C according to the most recent study.<sup>2</sup> This is in qualitative agreement with the original assessment<sup>30</sup> save for corrections in the compositions of some phases. Such melting relationships can create serious problems in attempts to synthesize single-phase samples solely by arc-melting,<sup>3,21</sup> and three-phase samples containing  $Zr_3Si_2$ ,  $Zr_5Si_3$ , and  $Zr_2Si$  in approximately equal proportions are so obtained for a  $Zr_5Si_{3.0}$  composition. Single-phase products are not achieved therefrom in 10 days at 1000 °C or after one day at 1575–1675 °C even when the button is ground and pelletized, which lessens inhomogeneities,<sup>21</sup> or when the sample is quenched from 1600 °C. In fact, the proportions of  $Zr_5Si_3$  decreased at the temperatures just cited, although it did not disappear. On the other hand, annealing the as-cast pellet about 1 day at ~1725–1775 °C does produce single-phase  $Zr_5Si_3$  in the  $Mn_5Si_3$  structure. Therefore, the conclusion of Kocherzhinskii et al.<sup>2</sup> that  $Zr_5Si_3$  decomposes peritectoidly at ~1745 °C is essentially correct, although we did not at-

tempt to measure the transition temperature accurately. The question of a phase breadth was also settled by analogous equilibrations of compositions  $Zr_5Si_{2.8}$  and  $Zr_5Si_{3.1}$  at ~1750 and 1775 °C, respectively. These gave  $Zr_5Si_3$  (plus  $Zr_2Si$  and  $Zr_3Si_2$ , respectively) with lattice constants that were very close to each other and to that in a three-phase mixture annealed at 1575 °C. The lattice constants of all of these  $Zr_5Si_3$  products are significantly greater than anything reported before (Table II). The existence of  $Zr_5Si_3$  as a binary phase seems clear, in agreement with the conclusions of others.<sup>2,19</sup>

To assess possible reasons for the diverse lattice dimensions reported by others, we investigated a portion of the ternary systems involving carbon or oxygen. Samples of  $Zr_5Si_3C_x$ ,  $x = 1/3, 1/2, 1$ , prepared by arc melting typically showed  $ZrC$ ,  $ZrSi$ , and  $Zr_3Si_2$  impurities, especially the last. Annealing  $Zr_5Si_3C_{0.5}$  gave a phase with  $Mn_5Si_3$  structure plus ~15%  $ZrSi$  (FeB structure) and a few extra lines, the first phase having  $a \sim 0.017 \text{ \AA}$  smaller and  $c \sim 0.04 \text{ \AA}$  larger than for  $Zr_5Si_3$  (Table II). The composition  $Zr_5Si_3C$  gave the phase of interest with the same  $a$  dimension and a  $c$  that was 0.01  $\text{\AA}$  greater still, together with ~20%  $ZrC$  and 10%  $ZrSi$ . Carbon solubility at this temperature appears to be limited, and the lattice shifts are distinctive.

Contamination of  $Zr_5Si_3$  from oxygen sources is probably a more general problem, and the reaction is much more extensive. Pressed pellets of  $Zr_3Si_2$  and  $ZrO_2$  with the composition  $Zr_5Si_3O$  that were sintered either inductively at ~1725 °C and quenched or in the vacuum furnace at 1600–1700 °C and cooled slowly gave only a phase with a  $Mn_5Si_3$  structure and  $\lesssim 5\%$   $ZrO_2$  (one weak line in the Guinier pattern). The lattice constant contractions from the binary are both sizable, ~0.040 and 0.025  $\text{\AA}$ , respectively, and distinctive from the carbide, which exhibits an increased volume. Arc melted samples of the same stoichiometry showed only  $Zr_3O$  as an extra phase and gave dimensional contractions that were not quite as large as for annealed products. The latter circumstance likewise pertains to as-cast carbon and binary samples; atom distributions achieved at such high temperatures generally result in lattice constants that underestimate the effect of an impurity or ordering.<sup>3,21</sup>

Changes in the intensity of particularly the (100) line on forming  $Zr_5Si_3O$  support the presence of oxygen in the expected interstitial position. The calculated intensity is 2.2% of  $I_{\text{max}}$  for binary  $Zr_5Si_3$ , and this falls to 0.0% with full oxygen occupation. The (100) line was observed in the

(26) Gschneidner, K. A., Jr. In *Science and Technology of Rare Earth Materials*; Subbarao, E. C., Wallace, W. E., Eds.; Academic Press: New York, 1980; p 25.

(27) Smith, J. D.; Corbett, J. D. *J. Am. Chem. Soc.* 1985, 107, 5704.

(28) Hwu, S.-J.; Corbett, J. D. *J. Solid State Chem.* 1986, 64, 331.

(29) Palenzona, A.; Fornasini, M. L. *Atti Acad. Naz. Lincei, Cl. Sci. Fis. Mat. Nat., Rend.*, 1966, 40, 1040.

(30) Lundin, C. E.; McPherson, D. J.; Hansen, M. *Trans. Met. Soc. AIME* 1953, 45, 901.

(31) Seropgin, Yu. D.; Panteleimonov, L. A.; Guseva, I. A.; Osipova, L. V. *Vestn. Mosk. Univ., Ser. 2, Khim.* 1980, 21, 400.

Guinier pattern of the binary phase but not for  $Zr_5Si_3O$ , either for the arc melted or the better sintered sample. Obviously, the same general condition applies to carbon; a faint (100) reflection was seen for  $Zr_5Si_3C_{0.33}$  but not for the carbon-richer samples.

Although not tested, we presume that at least boron and nitrogen can be bound in  $Zr_5Si_3$  and will produce similar dimensional effects, boron the most positive. The analogous  $Zr_5Sn_3$  and  $Zr_5Sb_3$  form stoichiometric ternary phases with C, N, O, Al, Si, etc., and in these only second-period elements cause marked contractions of the cells. Fractional occupancy in ordered superstructures as found for  $La_{15}Ge_9C$  has not been observed in zirconium systems.

Comparison of our lattice constant data with earlier reports for supposed  $Zr_5Si_3$  (Table II) suggests that most were seriously contaminated, probably by the more pervasive nonmetals. Some dimensions and volumes fall well below what we have been able to achieve with oxygen alone, even in earlier studies that utilized iodide-zirconium. The only exception is a 1964 study of a single crystal isolated at  $\sim 2200$  °C from molten alloy  $Zr_5Si_3$ <sup>56</sup> that had been prepared from 99.6% Zr and 99.7% Si.<sup>24</sup> A simple-minded interpretation of the dimensions suggests 30–50% of the oxygen limit  $Zr_5Si_3O$ . Of course, the sample may have been nonstoichiometric at that temperature or contaminated by third-period and heavier elements that would

mask a dimensional view of the true situation.

These investigations of  $La_5Sn_3$  and  $Zr_5Si_3$  highlight the problems that impurities can have on stability of supposed binary phases. Our studies have focused particularly on those examples in the rather common  $Mn_5Si_3$  structure where an avidity for binding impurity atoms interstitially within confacial manganese octahedra seems particularly strong. Phases of this general character have been designated "Nowotny phases" after the early investigator of many examples in this and other structure types.<sup>14</sup> Many other unrecognized examples of such effects or errors are presumably present in the literature. Oxygen is a particularly common and troublesome example with lanthanum, zirconium, and related metals.

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**Registry No.**  $La_5Sn_3$ , 12209-13-1;  $La_5Sn_3C_{0.5}$ , 129124-12-5;  $La_5Sn_3C_{0.75}$ , 129124-13-6;  $La_5Sn_3C$ , 129124-14-7;  $La_5Sn_3C_2$ , 129124-15-8;  $La_5Sn_3O_{0.3}$ , 129124-16-9;  $La_5Sn_3O$ , 129124-17-0;  $Zr_5Si_3$ , 12039-97-3;  $Zr_5Si_{2.8}$ , 129124-18-1;  $Zr_5Si_{3.1}$ , 129124-19-2;  $Zr_5Si_3C_{0.5}$ , 129124-20-5;  $Zr_5Si_3C$ , 129124-21-6;  $Zr_5Si_3O$ , 129124-22-7;  $Zr_5Si_{3.56}$ , 129124-23-8.

## Substituted $W_5Si_3$ - and $Zr_6Al_2Co$ -Type Phases Formed in the Zirconium-Antimony and Zirconium-Tin Systems with Iron Group Metals

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Arc-melting and annealing reactions near the composition  $Zr_5Sb_3Fe$  yield  $ZrFe_2$  plus an  $Mn_5Si_3$ -type phase with a composition near  $Zr_5Sb_{3.3}Fe_{0.3}$ . A lower antimony content and a variety of iron group metals produce tetragonal  $W_5Si_3$ -type phases with a narrow compositional range,  $\sim Zr_5Sb_{2.5}T_{0.5}$ , T = Fe, Co, Ni, Ru, Rh. A single-crystal study of the  $W_5Si_3$ -type  $Zr_5Sb_{2.55(1)}Fe_{0.45(1)}$  established a mixed Sb-Fe population on the Sb1 site centering the Zr2 antiprisms ( $I4/mcm$ ,  $Z = 4$ ,  $a = 11.066$  (1) Å,  $c = 5.535$  (1) Å,  $R/R_w = 1.9/2.8\%$ ). The analogous Zr-Sn-Fe system contains a  $W_5Si_3$ -like phase  $Zr_5Sn_{2+x}Fe_{1-x}$ ,  $0 \leq x \leq 0.28$ , but in this case with a lower symmetry tetragonal cell that has distinctly different mixed Fe-Sn populations centering adjacent Zr2 antiprisms (91 (2) and 52 (2)% Fe for  $x = 0.28$ ) ( $I422$ ,  $Z = 4$ ,  $a = 11.1763$  (7) Å,  $c = 5.4794$  (6) Å,  $R/R_w = 1.7/2.2\%$ ). The lower symmetry cannot be deduced from powder pattern data. The hexagonal line phase  $Zr_6Sn_2Fe$ , previously known as the  $\theta$  phase, is obtained when still more zirconium is present ( $Zr_6Al_2Co$  structure,  $P62m$ ,  $Z = 1$ ,  $a = 7.9675$  (6) Å,  $c = 3.4863$  (5) Å,  $R/R_w = 2.6/2.9\%$ ). Antimony systems provide analogous substitutional products  $\sim Zr_5Sb_{2.3}T_{0.7}$ , T = Fe, Co, Ni. Some regularities associated with the three structure types are discussed.

### Introduction

Our intensive studies of  $Zr_5Sb_3$ - $Zr_5Sb_3Z$  and  $Zr_5Sn_3$ - $Zr_5Sn_3Z$  systems have shown that phases with the parent  $Mn_5Si_3$ -type structure exist for a wide range of Z as an interstitial component.<sup>2-4</sup> However, attempts to introduce

iron in this position in either system have been troublesome. These have always led to  $ZrFe_2$  precipitation and to a phase with the  $Mn_5Si_3$  structure but with evidently mixed Sb-Fe or Sn-Fe interstitials judging from SEM analyses.<sup>2,4,5</sup> Attempts to avoid the mixed products by decreasing the amount of antimony or tin produced new tetragonal phases. We herein report the identification of these as  $W_5Si_3$ -type structures or a lower symmetry version of the same in which iron has been systematically substituted for some of the Sb or Sn atoms. The stabilization

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(2) Garcia, E.; Corbett, J. D. *Inorg. Chem.* 1988, 27, 2907; 1990, 29, 3274.

(3) Corbett, J. D.; Garcia, E.; Kwon, Y.-U.; Guloy, A. *Pure Appl. Chem.* 1990, 62, 103.

(4) Kwon, Y.-U.; Corbett, J. D., unpublished research.

(5) Sevov, S. C.; Corbett, J. D., unpublished research.