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Exploration of the Interstitial Derivatives of La_5Pb_3 (Mn_3Si_3-Type)

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Powder sintering reactions of the elements or of appropriate binary phases in welded Ta containers have resulted in the single phase syntheses of 17 La_5Pb_3Z derivatives of La_5Pb_3 with stuffed Mn_5Si_3-type structures ($P6_3/mcm$), namely, $Z = B_x, C_x$, P, S, Cl, As, Se, Sb, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ru, and Ag. (Z = N, O form a Cr_5B_3-type derivative.) Possible x values for B and C are consistent with, but not proof of, Zintl phase characteristics. La_5Pb_3 was shown to be a line phase, while the reported binary La_4P_3 (anti-Th_3P_4) was not found. The volume changes observed on incorporation of Z into La_5Pb_3 are the smallest found in this sort of system except for chloride in the even more weakly bound alkaline-earth-metal–pnictide analogues.

INTRODUCTION

Compounds with Mn_5Si_3-type structure ($P6_3/mcm$) are proving to be rich in interstitial chemistry. The center of interest in this structure (Fig. 1) is quasi-infinite chains composed of confacial trigonal antiprisms of metal on which the shared triangular faces are all bridged with isolated silicon atoms, viz., $Mn_{6/2}Si_3$. Another parallel linear chain of well-bound metals, reminiscent of an A15 component, shares the same silicon atoms in a distorted trigonal prismatic coordination. On the order of 170 examples of the structure have been reported (1). An interesting and novel chemistry results because a wide variety of third elements (Z) may be bound in the centers of the metal antiprisms without a change in structure type; this feature also affords a novel means of altering properties of a given host.

Our earliest efforts on these systems dealt with the means for preparing well-ordered, single-phase samples of both the binary hosts and their interstitial derivatives, together with some studies of their structures, bonding, and properties. The first were Zr_5X_3 substrates for X = Sb (2, 3), Sn (4), and Pb (5), for which ~15–20 Zr_5X_3Z compounds of each were established with, for example, Z = B–O, Al–S, Cu–Se, Ag, and Sn in Zr_5Sn_3. Observed Zr–Z distances are relatively short. The related Zr_5Pb_3Z compounds were novel in that the larger host also accommodated additional heavier main-group interstitials (Ag–Tc), as well as late transition elements (Mn–Ni). In all cases, the existence of any particular compound is naturally limited by the stability of alternate phases formed with Z. Unit cell expansions that accompany bonding of all Z but N, O, and some C reflect mainly variations in d(Zr–Z), which follow metallic/covalent radii of Z fairly well. Particular increases in c or c/a often observed for the pnictogen and chalogen members appear to be associated with repulsions between polar Z that are separated by only $c/2 \sim 3.0$ Å along the chain (3–5).

All of the foregoing examples are metallic, since a relatively large number of conduction electrons presumably remain after the valence orbitals on the isolated main group elements are filled, e.g., $5 \cdot 4 - 3 \cdot 4 = 8$ in $Zr_5(Sn, Pb)_3$. Examples of this structure type for earlier transition metals give interesting opportunities to use Z to tune the conduction electron count to zero and to gain a semiconducting (Zintl) phase, presuming, of course, that a conduction/valence band gap exists in these relatively polar examples. For instance, the alkaline-earth-metal (Ae) members $Ae_5(Sb, Bi)_3$ afford this end point in Z = Cl, Br, H (6, 7). Recently, the host La_5Ge_3, with $5 \cdot 3 - 3 \cdot 4 = 3$ extra electrons, has also been found to behave as expected, namely, to give isostructural semiconductors with Z = P, As, and phases that are substoichiometric in Z with the electron-poorer B, C, and Si (specifically $La_5Ge_3Si_{0.75}$ with the last) (8). Introduction of larger amounts of these or related electron-poorer elements (Ge, Sn, Al, Ga) always cause a change to other structures in which some or all of the main-group elements are dimerized (Sm_5Ge_4, Zr_5Si_4, etc., types) rather than having holes in the valence band (9).

The present study of La_5Pb_3 was prompted by the above considerations as well as the contrast in lattice constants that has been reported for this phase. Although Jeitschko and Parthé (10), Palenzona and co-workers (11), and McMasters, *et al.* (12) found similar lattice dimensions

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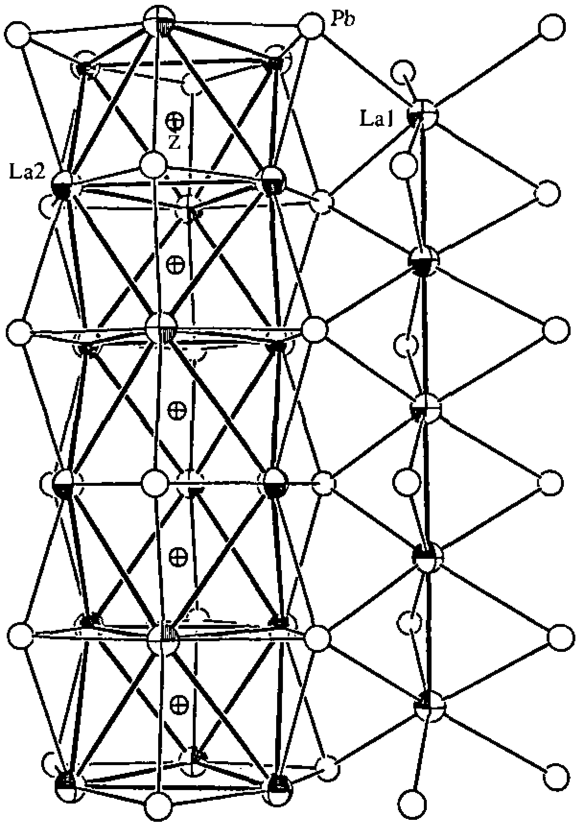

FIG. 1. A partial [110] section of a stuffed Mn_5Si_3-type structure for La_5Pb_3Z. La, shaded circles with La1 in lineark chain (right) and La2 defining confacial antiprismatic chain (left); Pb, open circles; Z, crossed circles centered in La2 antiprisms.

for La_5Pb_3, a distinctly smaller c axis (by 0.02 Å, 5σ) was obtained by Demel (13) for samples prepared by induction heating of the high purity elements in tantalum. Our experience has been that such a feature is often symptomatic of impurity (interstitial) effects; for example, clear La_5Tt_3O examples, Tt = Si, Ge, Sn, have been reported in the literature as supposed binaries (8, 14). In addition, an La_5Ge_3C composition prepared by Demel had a c lattice dimension 0.023 (5) Å larger than La_5Pb_3 and was close to the earlier values for the supposed binary phase. According to Demel, the La_5Ge_3C sample was single phase metallographically, melted 60°C higher than La_5Pb_3, and showed metallic conductivity, as does La_5Pb_3 but with a smaller temperature coefficient. We have recently found that the analogous La_5Pb_3O and La_5Pb_3N phases occur only as interstitial derivatives of a Cr_5B_3-type structure (without clear Pb–Pb dimers), not as stuffed Mn_5Si_3 examples, evidently because this result affords better tetrahedral bonding sites for these small interstitials (15). All of these earlier reports indicated that La_5Pb_3 and its derivatives are very air and moisture sensitive.

The stoichiometry of the above La_5Pb_3C was not studied, although it should be noted that the interstitial monocarbide should have one hole per formula unit $[(5 \cdot 3) - (3 \cdot 4) - 4]$ in the valence band. The assignment of a -4 oxidation state (not charge) to isolated carbon atoms bonded to elements with higher energy valence orbitals like lanthanum is intuitively clear. Covalence does not alter the state. Extended Hückel calculations on Zr_5Sb_3S and La_5Ge_3P and the two empty hosts support these ideas (3, 8).

EXPERIMENTAL SECTION

Because of the reactivity of lanthanum and some of the products with oxygen and moisture, all reactants and products were either handled and stored only in a glovebox (Vacuum Atmospheres) or sealed in ampoules. The moisture in the box was regularly <1 ppm vol and, although the oxygen level was not measured, bare 60-W light bulb filaments would burn for 12 hr or more therein.

Materials

Lanthanum in the form of rod or turnings was an Ames Laboratory product (5–9's) with principal impurities in ppm atomic of O, 190; N, 128; C, 34; F, 80; Fe, 7.6. The metal was scraped free of any dark surface in the box before pieces were cut and weighed. Electropolishing was not carried out in order to minimize adventitious C, F, O values. Electroytic lead (Ames Lab, 5–9's) was cold-rolled to a 3-mm sheet, and any dark, oxidized surface scraped off before use. The other reactants utilized were: B (amorphous 99.5%) and Co (3–9's), Aesar; C (spec-grade), Union Carbide; La_2O_3 (5–9's) and Ti (crystal bar), Ames Lab; P (5–9's) and As (6–9's), Aldrich; Sb (reagent), Allied Chemical; S (5–9's), Alfa; Se (5–9's), American Smelting & Refining; Bi (reactor grade), Oak Ridge National Lab; Zn and V (4–9's), Fisher Scientific; Mn (3–9's), Cr (3–9's 5), A. D. Mackay; Fe (3–9's), Plastic Metals; Ni (reagent), Matheson, Colman & Bell; Cu (4–9's), J. T. Baker; Ru (3–9's 5), Ag (reagent), G. F. Smith Chem. Co. In house preparation of sublimed $LaCl_3$ was the source of that nonmetal.

Syntheses

Tantalum proved to be a satisfactory container for all of the systems described here. It was cleaned and welded as before (2, 3). Postreaction ductility of these containers is a good indication of the absence of attack since such side reactions usually result in precipitation of tantalum compounds at the grain boundaries. Guinier powder pattern techniques and lattice constant determinations therefrom via Si as an internal standard have been described before (3).

Reactions were usually run within sealed but bare Ta containers in the high temperature vacuum furnace described earlier (3, 16). Mixtures of weighted elements were cold-pressed into pellets within a glovebox, sealed in Ta containers, and heated to 1150°C over 2 days. The samples were then melted at 1300°C, slowly cooled to 1150°C over 7 days, and then cooled to room temperature over 4 more days. Binary intermediates were used for sintering reactions when reaction of Z with the container might present a problem. These LaZ_x phases were selected for their brittleness (LaAs, LaS, etc.).

Attempts to synthesize La_5Pb_3 as well as La_5Pb_3Z interstitial compounds through arc-melting were not successful because of both the high volatility and low melting point of Pb, and the sensitivity of the La reagent and the products to contamination. This technique was used in the earliest study (10) despite the limited control of stoichiometry. We have already noted the major role that oxide contamination during arc-melting can play in the instability of compounds like Zr_4Sn (17).

RESULTS AND DISCUSSION

The means by which we have deduced the formation of ternary La_5Pb_3Z phases are based on our prior experiences with related systems (see Introduction). Overall, ~90 A_5B_3Z phases with a stuffed Mn_5Si_3 structure (2–8, 14, 18) have been identified. Our general conclusions are, most of all, based on the consistent production of substantially *single phase* products from quantitative syntheses (in Ta) in closed systems with A_5B_3Z compositions. Phase identification has been based largely on Guinier powder diffraction where detection limits are ~2–5 mol%. Generally well-formed products allow refinement of lattice constants to 1–2 parts in 10^4. SEM/EDX studies have also been used in difficult cases (8, 14), none of which was encountered here. Our general conclusions apply to equilibrium systems at ~900–1300°C, depending on what is necessary for diffusional mobility, and in these cases complete structural discrimination between atoms on B and Z sites has been found. The sizable problems encountered with arc-melting without subsequent annealing have been discussed before (3, 4). The foregoing structural conclusions are based on ~25 single crystal studies. Mixed B–Z and fractional Z atom distributions were almost always found in products quenched from arc-melting reactions and in one case, in Zr_5Sn_{3+x}, near 1800°C as well. The only cases of unintentionally mixed atoms on the Z site from A_5B_3Z compositions have occurred in equilibrium Zr_5B_3Z, B = Sb, Sn, Sb, Z = Fe and some Mn, Co, Ni systems (4, 5, 14) in which other phases, $ZrFe_2$ especially, alter the composition (20). Interchange of Z and B is probably most possible when these are chemically most similar, but none has been established in the equilibrium systems examined. In fact, exchange is *not* the case for Zr_5Sn_3Z, Z = Ga, Ge, even though the corresponding Zr_5Z_3 compounds in the same structure are also known. Size differences appear to be important in the hexagonal ($P6_3/mcm$) matrix. We have avoided those few cases where such problems seem most possible, e.g., with La_5Pb_3Sn.

The usual means of establishing the existence of an A_5B_3Z product (above) do not themselves determine whether Z may also be nonstoichiometric and fractional. The number that are substoichiometric when tested (for instance, with $A_5B_3Z_{0.5}$ compositions) are surprisingly few, as discussed before (3, 8). Zr_5Sb_{3+x}, $Zr_5Sn_3S_{1-x}$ and perhaps $Zr_5Sn_3O_{1-x}$, $Zr_5Pb_3Cu_{1-x}$, and Zr_5Pb_{4-x} (limited stability), La_5Ge_3B, and perhaps La_5Ge_3C, and some $Ae_5Pn_3H_x$ examples are the most certain. On the other hand, an ordered superstructure for the fractional composition $La_{15}Ge_9Z$ ($La_5Ge_3Z_{1/3}$) is known for Z = C, O, P, Mn, Fe, Ru, Co, Ni, Cu and for $La_{15}Sn_9C$. A broad region between the two line phases exists in the cases studied (C, P, Mn, Co, Ni) (19). This superstructure was not seen in the present study.

Unsuccessful reactions of La_5Pb_3 with Ti, V, Tl, Te, etc. usually resulted in multiphase products containing La_5Pb_4 (Sm_5Ge_4 type) (19), sometimes unknown phases plus, often, an LaZ_x binary. The last is common with excess Z. All of the interstitial compounds are less air and moisture sensitive than La_5Pb_3 but more reactive than the corresponding La_5Ge_3Z phases. Particular details associated with obtaining a pure sample of each of the La_5Pb_3Z phases are outlined below.

The Binary Phase

A possible composition range in La_5Pb_3 was surveyed first. Samples of La_5Pb_x with x ranging from 2.5 to 3.3 in 0.1 intervals were melted (>1450°C (12)), annealed, and slowly cooled from 1250°C. The Guinier powder patterns could be entirely accounted for with a hexagonal Mn_5Si_3-type structure plus the proper La_5Pb_4 and La patterns on the lead-rich and lead-poor sides of La_5Pb_3, respectively. (We did not see the anti-Th_3P_4-type La_4Pb_3 reported once before (12).) This procedure gave a barely perceptible increase in dimensions across the composition range, but the maximum variation in each was only 0.003 Å, well within the margins of error. Hence, there is little evidence of appreciable nonstoichiometry in La_5Pb_3. Average values for the refined cell parameters are given in Table 1 along with values pertinent to the ternary carbide (below) and some literature data. Our La_5Pb_3 dimensions agree well with those of Demel (13) but the c values in particular are consistently less than reported by others, although the ~0.016 Å differences are only in the range of 4–12σ.

Samples of La_5Pb_x with x = 2.75, 3.0, and 3.25 were also quenched from high temperatures to test whether this would produce dimensions that were similar to those

TABLE 1

Lattice Constants (Å) and Cell Volumes (Å^3) for La_5Pb_3 and $La_5Pb_3C_x$ Products[a]

Composition	Method[b]	*a*	*c*	Volume	*c*/*a*	Powder diffraction method[c]	Reference
La_5Pb_3	M, S	9.534 (1)	6.977 (1)	549.2 (2)	0.732	G	This work
La_5Pb_3	M, Q	9.538 (2)	6.981 (2)	550.0 (4)	0.732	G	This work
La_5Pb_3	M(An)	9.532 (2)	6.974 (3)	548.8 (5)	0.732	D	(13)
La_5Pb_3	A	9.528 (5)	6.993 (3)	549.8 (8)	0.734	D	(10)
La_5Pb_3	M	9.528	6.993	549.6	0.734	D	(11)
La_5Pb_3	M, S	9.525 (2)	6.994 (1)	549.5 (3)	0.734	D	(12)
La_5Pb_3C	M, S'	9.531 (3)	6.997 (2)	550.5 (5)	0.734	D	(13)
La_5Pb_3C	M, S	9.535 (1)	6.995 (1)	550.8 (2)	0.734	G	This work
$La_5Pb_3C_{0.75}$	M, S	9.529 (1)	6.992 (1)	549.8 (2)	0.734	G	This work

[a] All single phase, Mn_5Si_3-type powder patterns.

[b] M, melted in Ta; S, slowly cooled from 1250°C; Q, quenched from 1050 or 1400°C; A, arc-melted; An, annealed below 775°C; S', slow cooling to 1200°C.

[c] Guinier (Si standard); D, Debye–Scherrer.

obtained earlier following arc-melting. Samples in welded Ta tubes that were in turn enclosed in silica jackets were equilibrated at 1050°C for 3 weeks and then water-quenched. Identical samples were also inductively heated to 1400°C and cooled either by turning the power off or, more rapidly, by sucking the off-gas from liquid nitrogen into the vacuum system. The refined parameters of all of these quenched hexagonal phases were on average only 0.004 Å larger than for slowly cooled samples, suggesting only that some small disorder or defect concentration had been quenched in these processes.

Carbon

Sintering of cold-pressed pellets of the three elements produced single phase samples (to Guinier powder diffraction) with larger cell constants and volume, strong support for the production of a ternary carbide (Table 1). A collection of sintered samples of $La_5Pb_3C_x$ with x ranging from 0.250 to 1.25 in 0.125 intervals was also slowly cooled from 1300°C. The Guinier diffraction patterns of products with nominal stoichiometries $0 \leq x \leq 1.0$ could entirely be accounted forwith a hexagonal Mn_5Si_3-type structure. Greater carbon contents ($1.1 \leq x \leq 2.5$) produced mostly multiphase products that, in different regions, included Mn_5Si_3- and Sm_5Ge_4-type phases and lesser amounts of LaC_2. (A new phase $La_5Ge_3C_2$ was recovered and characterized from a reaction with $x = 2$ (9).) The lattice constants for the single phase samples with $x \leq 1.0$ shown in Fig. 2 exhibit a sharp break in the c dimension somewhere between $x = 0.62$ and $x = 0.75$. The behavior does not appear to be that of a solid solution, but splitting of lines suggestive of a mixture for $x < 0.625$ was not observed either, probably because of their small dimensional differences. Apparently only the dominant phase is resolved. The composition of the new, larger product appears to lie in the range $x = 0.7 \pm 0.2$, similar to that deduced for $La_5Ge_3C_x$ (8). The composition of a valence (Zintl) phase with filled valence levels for carbon and lead would be $La_5Pb_3C_{0.75}$.

Interestingly, the average lattice constants found for $La_5Pb_3C_x$ are close to those reported for La_5Pb_3C by Demel (13) and for La_5Pb_3 in three earlier instances (10–12), suggesting that the latter may have been contaminated, a particularly easy event with a Mn_5Si_3-type structure. How they were contaminated is not easy to establish. Of course, mixed impurities C, N, O, etc., at low levels could have been responsible, but we note again that pure La_5Pb_3N and La_5Pb_3O have a different, Cr_5B_3-like structure (15). The three earlier studies used commercial lead products of 4 to 5–9's purity in *metal* content as received. Though it may not "explain" these differences, we have

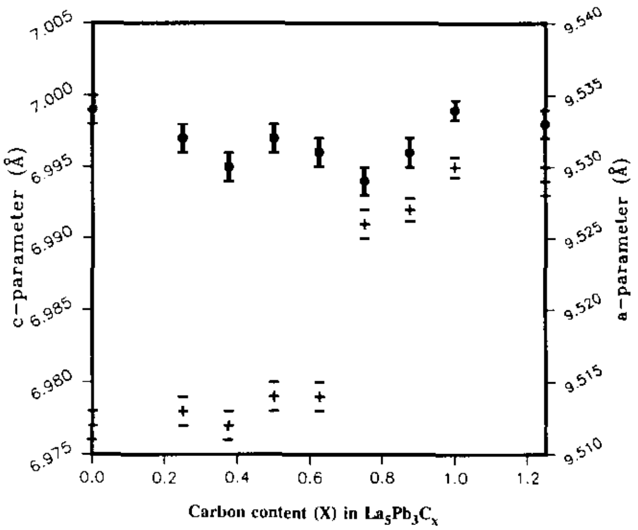

FIG. 2. Variation of the cell parameters of $La_5Pb_3C_x$ samples as a function of x: (●) a; (+) c. The error bars are single standard deviations.

repeatedly observed that fusion of granular "reagent grade" commercial lead products (Fisher, Baker, etc.) under an inert atmosphere leaves significant amounts of solids on the surface, evidently carbon, oxide, etc., remaining from their production.

Boron

The powder diffraction pattern for the composition La_5Pb_3B revealed Mn_5Si_3-type (major) and Th_3P_4-type (minor) structures. The indicated composition shift suggests that poorly crystalline LaB_x may have formed but was not seen. This is the only time we saw a Th_3P_4-type phase with or without a nonmetal Z. (Such a possibility was, of course, not tested in most systems in which other La_5Pb_3Z compounds are stable.) The corresponding binary La_4Pb_3 has been reported only once and could not be obtained as a pure phase (12). The absence of any other R_4Pb_3 example (R = rare-earth element), and of R_4Sn_3 as well except for Sm_4Sn_3 (which also could not be obtained pure) (21), suggests these supposed binary phases may have resulted from unknown contamination.

Reactions with lower boron contents in $La_5Pb_3B_x$, x = 0.25, 0.5, 0.75, all gave single-phase Mn_5Si_3-type products with lattice parameters that increased slightly in this order. The average value is listed in Table 2. This range includes the ideal Zintl phase composition $La_5Pb_3B_{0.6}$, but the small parameter changes do not give a clear definition of stoichiometry. Attempts to grow suitable single crystals were unsuccessful, as these yielded mostly multiple crystals, judging from oscillation photographs.

Pnictogens, Chalcogens, and Halogens

In order to avoid container problems that could derive from the volatility of elemental phosphorus, arsenic, etc., powdered LaP, LaAs, LaS, LaSe, or $LaCl_3$ was mixed with a prereacted La_4Pb_3 composition, pressed into pellets, and then sealed in Ta tubes. The components were slowly heated over 2 days to 1000°C, up to 1200°C (1000°C for Cl) after 2 more days, then equilibrated for 1 week and slowly cooled. The reactions with antimony started with the elements. All products were single phase according to the Guinier patterns, but exchange between Pb and Sb sites cannot be excluded. The two chalcogen products were marked by larger c lattice constants, as first observed more markedly for Zr_5Sb_3S where the expansion was attributed to the large repulsion between the relatively negative S (Se) interstitials separated by $c/2 \simeq 3.0$ Å along the chains (3). Single crystals of the chloride were obtained but not investigated further.

Iron

Past experience has shown that Fe at these temperatures diffuses into Ta significantly, particularly when present at higher activities, but that a lining of 6-mil Mo sheet prevents this very well (4). The absence of any $LaFe_x$ or $FePb_x$ binary compounds limited the starting materials to

TABLE 2

La_5Pb_3Z Phases with Mn_5Si_3-Like Structures

Composition	Synthetic conditions[a]	Lattice parameters (Å)		Cell volume (Å^3)	c/a Ratio
		a	c		
La_5Pb_3	S	9.534 (1)	6.977 (1)	549.2 (2)	0.732
$La_5Pb_3B_x$	S	9.537 (1)	6.997 (2)	551.1 (3)	0.734
$La_5Pb_3C_x$	S	9.535 (1)	6.995 (1)	550.8 (2)	0.733
La_5Pb_3P	B	9.545 (1)	7.009 (2)	553.0 (3)	0.734
La_5Pb_3As	B	9.553 (1)	7.024 (2)	555.1 (3)	0.735
La_5Pb_3Sb	S	9.558 (1)	7.035 (1)	556.6 (2)	0.736
La_5Pb_3S	B	9.547 (1)	7.022 (1)	554.0 (2)	0.736
La_5Pb_3Se	B	9.553 (1)	7.035 (1)	556.0 (2)	0.736
La_5Pb_3Cl	B	9.549 (1)	7.020 (2)	554.3 (3)	0.735
La_5Pb_3Cr	B	9.547 (1)	7.012 (2)	553.5 (3)	0.734
La_5Pb_3Mn	B	9.543 (1)	7.010 (1)	552.9 (2)	0.734
La_5Pb_3Fe	S	9.543 (1)	7.008 (2)	552.7 (3)	0.734
La_5Pb_3Co	S	9.542 (1)	7.009 (1)	552.7 (2)	0.734
La_5Pb_3Ni	S	9.545 (1)	7.011 (2)	553.2 (3)	0.734
La_5Pb_3Cu	B	9.550 (1)	7.026 (2)	554.9 (3)	0.736
La_5Pb_3Zn	S[b]	9.551 (1)	7.028 (2)	555.2 (3)	0.736
La_5Pb_3Ru	S	9.558 (1)	7.035 (1)	556.6 (2)	0.736
La_5Pb_3Ag	S	9.560 (1)	7.037 (2)	557.0 (3)	0.736

[a] S, sintered pellet of elements at 1150–1350°C for 10–14 days; B, pellets of preacted binaries slowly heated to 1100–1250°C and annealed at 1000°C for 10 days.

[b] See text regarding conditions.

Fe plus either La_5Pb_3 or the corresponding elements. Cold-pressed pellets of the latter were heated to 1000°C over 4 days, then to 1350°C over 2 days, kept there for another 4 days, then slowly cooled to 1050°C over 20 hr and to room temperature over 12 hr. In spite of the potential difficulties, this procedure resulted in a clean synthesis. The compound is distinguished by a significant increase of the cell parameters and a dull appearance relative to La_5Pb_3. The product is strongly attracted by a magnet and is ferromagnetic (saturation moment = 1.8 μ_B) with a Curie temperature above room temperature. Although the possibility that this arises from some metallic iron dispersed in the sample cannot be completely discounted, the lattice dimensions observed suggest the quantity of free iron would be small. Furthermore, the analogous La_5Ge_3Fe has been found to be a bona-fide soft ferromagnet with a saturation moment of 1.93 μ_B per iron (8, 9).

Cr, Mn, Co, and Ni

The preparation of these ternary phases took into account some of the problems encountered with iron as well as the higher volatilities of Cr and Mn. Thus, whenever possible, the interstitial components were introduced as their binary compounds with lanthanum. Elemental reagents also provided positive results but required higher annealing temperatures (>1200°C) and longer reaction times (14–21 days at 1250°C). Oxygen in the manganese once used also led to the discovery of La_5Pb_3O (15).

Copper

The reactions of La_5Pb_3 and Cu gave clear, sharp lines of only the new product. Powder sintering of a La_4Pb_3 composition and LaCu at 950°C provided a lower temperature route to the same compound.

Zinc

The synthesis of La_5Pb_3Zn was a result of attempts to use a zinc flux in the synthesis of other La_5Pb_3Z compounds. Quantitative results were also obtained from stoichiometric amounts of Zn and La_5Pb_3 at 1000°C, but the Guinier powder patterns were marked by diffuse lines.

Ruthenium

A contrasting result to the difficulty of synthesizing La_5Pb_3Fe was the single phase sample of La_5Pb_3Ru ob-

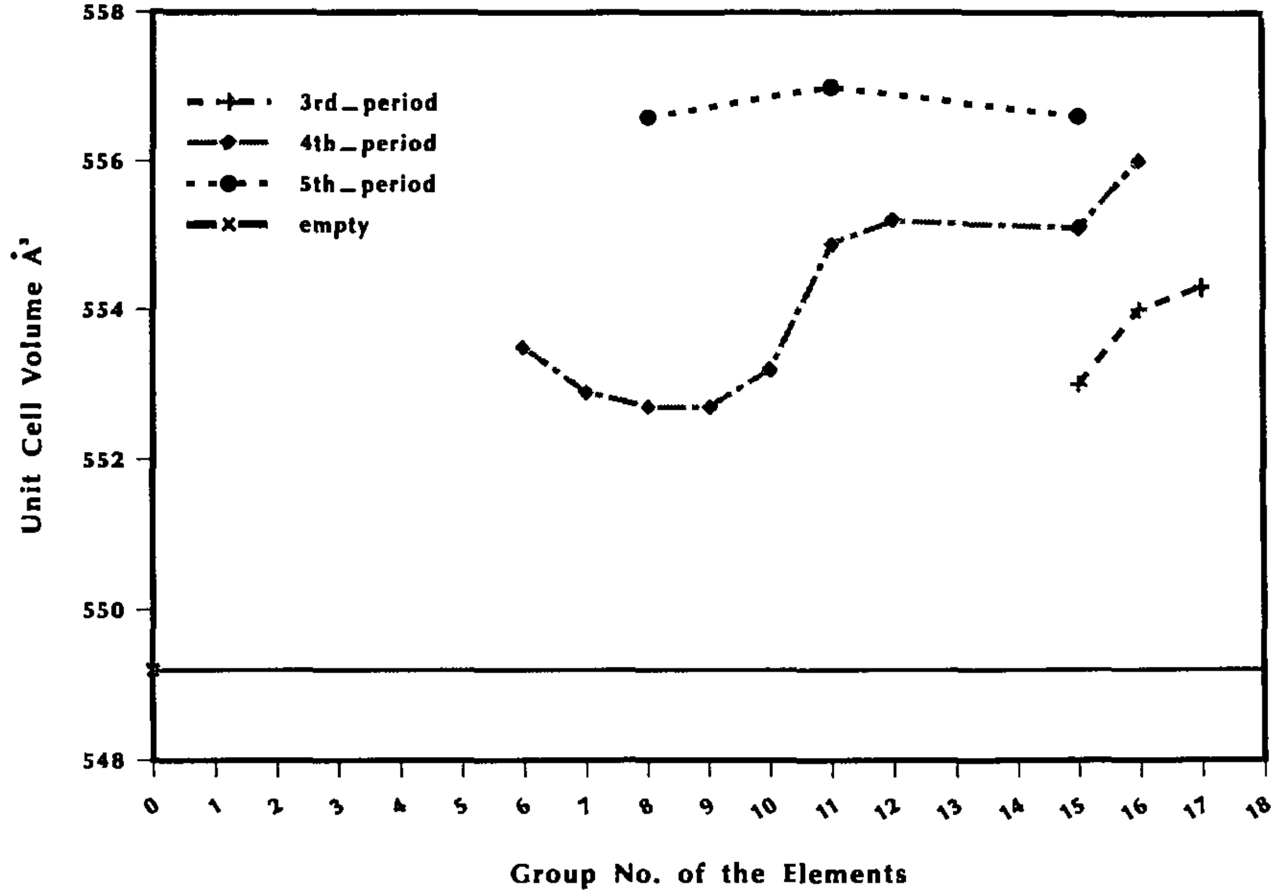

FIG. 3. Cell volumes for La_5Pb_3Z phases by group and period of Z. The solid line marks the empty host. Data for the probably fractional B and C products (V_{cell} ~ 551 Å^3) are not shown (see text).

tained after powder sintering of La_5Pb_3 and Ru. The compound was very hard, brittle, and dull in appearance.

Silver

The compound was prepared from the elements at 1350°C. Lower temperatures were insufficient. The phase had the largest cell of any La_5Pb_3Z product obtained.

Other Reactions

Attempts to synthesize other interstitial compounds with V or Ti proved to be unsuccessful. Reactions involving vanadium resulted in multi-phasic products that included V_3Pb (Cr_3Si-type). The titanium reaction also yielded a mixed product that included Ti_4Pb (Ni_3Sn-type) (1). Other phases common to the two powder patterns were La and La_5Pb_3. Powder sintering of La_5Pb_3 and equal molar quantities of Si, Ge, or Sn gave essentially single phase products, the patterns of which could be completely indexed as a Sm_5Ge_4 structure type (9). Success with aluminum family interstitials was not expected based on our results with La_5Ge_3 (8).

Volumes

Some generalities and trends can be deduced from the cell parameter data. The unit cell volumes are illustrated in Fig. 3 as a function of period and group. The relatively small but still distinctive expansions of the more weakly bound La_5Pb_3 are noticeable relative to those observed for Zr_5Pb_3 (5). Indeed, these are the smallest volume increases we have encountered in any of the systems where an appreciable range of Z can be studied. Comparisons with the standard volumes derived by Biltz (22) naturally show significantly lower partial molar volumes for Z in these systems, meaning that a good fraction of the volume is already present in the empty cavity. The alternate Cr_5B_3-derivative structure provides better bonding for the small Z = N, O, and the phase has an equivalent volume that is within 0.2% of that of La_5Pb_3.

The La_5Pb_3Z phases containing $3d$ metals exhibit volume trends that follow the atomic volumes of the interstitials. Variations in c/a with the more electronegative Z and indeed through the entire array are minimal, reflecting the larger c dimensions that go with weaker binding in La_5Pb_3 (and Ae_5Pn_3) as the free electron count approaches zero. This effect was also evident in extended-Hückel calculations on La_5Ge_3Z examples (8). The effect of this electron count can also be seen in the expansions obtained on insertion of the fixed Z chloride into La_5Pb_3 vs $Ae_5(Sb,Bi)_3$ binaries (6) once the volumes of the latter are corrected for the formerly unrecognized effects of bound hydrogen (7). The 0.9% volume increase for chloride in La_5Pb_3 is very logically related to a 0.37% increase on formation of the comparably sized Ba_5Bi_3Cl, these changes smoothly increasing to 2.0% with Ca_5Sb_3Cl. In general, the combined effects of relative cation sizes and varying (vanishing) metal–metal contributions to the bonding appear to be dominant.

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