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New Ternary Rare-Earth Transition-Metal Antimonides $RE_3M\mathrm{Sb}_5$ (RE = La, Ce, Pr, Nd, Sm; M = Ti, Zr, Hf, Nb)

Gwénaël Bolloré, Michael J. Ferguson,
Ryan W. Hushagen, and Arthur Mar*

Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada T6G 2G2

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Investigations into ternary rare-earth transition-metal antimonide systems $RE_xM_y\mathrm{Sb}_z$ have been going on for at least two decades. These studies have been carried out variously to search for new magnetic materials,[1-3] to test the validity of bonding models,[4,5] and perhaps most importantly, to systematize an interesting structural chemistry that is not as well understood as that of the corresponding phosphides or arsenides.[2-16] Some of these antimonides have counterparts in phosphides or arsenides, such as $REM\mathrm{Sb}_2$ (M = Mn–Zn, Pd, Ag, Au)[2-6] with the $\mathrm{HfCuSi_2}$ structure, $REM_2\mathrm{Sb}_2$ (M = Mn, Ni, Pd)[1,7-10] with the $\mathrm{CaBe_2Ge_2}$ and $\mathrm{ThCr_2Si_2}$ structures, and $REM_4\mathrm{Sb}_{12}$ (M = Fe, Ru, Os)[11,12] with the filled skutterudite $\mathrm{LaFe_4P_{12}}$ structure. Others, such as $RE_3M_3\mathrm{Sb}_4$ (M = Pt, Cu, Au)[13-15] and $REM\mathrm{Sb}_3$ (M = Cr, V),[16] are unique to antimonides so far. We report here the synthesis of a new series of ternary antimonides $RE_3M\mathrm{Sb}_5$ containing an early transition metal M = Ti, Zr, Hf, Nb.

The title compounds were prepared by reactions of powders of the rare-earth metals (RE = La, Ce, Pr, Nd, Sm; all 99.9%), transition metals (M = Ti, 99.98%; Zr, 99.7%; Hf, 99.8%; Nb, 99.8%), and antimony (99.999%), all obtained from Cerac. Initial investigations were carried out in the La/Ti/Sb phase system by analyzing arc-melted samples with diverse starting compositions. In general, 0.25-g samples were prepared in a drybox in the form of pressed pellets, which were then melted in a Centorr 5TA tri-arc furnace under argon (gettered by melting a titanium pellet) at slightly greater than atmospheric pressure. The cooled buttons were flipped over and remelted. Since some vapourization occurs during the arc-melting, the weight loss is assumed to be attributable entirely to Sb and was compensated for by adding a 10% weight excess of Sb prior to melting. Aggregates of thin, shiny silver, needle-shaped crystals were first observed in the sample prepared from the ratio La:Ti:Sb = 2:3:6. EDX analysis (energy-dispersive X-ray analysis) on numerous crystals with a JEOL JSM-6301FXV field-emission scanning electron microscope revealed that all three elements were present in atomic percentages of 31(1)% La, 11(1)% Ti, and 58(2)% Sb, in good agreement with the expected values 33% La, 11% Ti, and 56% Sb from the formula $\mathrm{La_3TiSb_5}$ determined from the crystal structure. Subsequently, the isotypic compounds $RE_3M\mathrm{Sb}_5$ with RE = La, Ce, Pr, Nd, Sm, and M = Ti, Zr, Hf, Nb were prepared by arc-melting pellets containing the stoichiometric ratio of the elements. The phase $\mathrm{Sm_3NbSb_5}$ could not be prepared, and attempts at substituting M with V or Ta were not successful. Although $RE_3M\mathrm{Sb}_5$ is the major phase formed in these reactions, minor amounts of binary antimonides could not be completely eliminated. The compounds are slightly sensitive in air; they begin to degrade over 1 day and completely decompose within 1 week.

Table 1. Lattice Parameters[a] for Compounds $RE_3M\mathrm{Sb}_5$ (RE = La, Ce, Pr, Nd, Sm; M = Ti, Zr, Hf, Nb) with the $\mathrm{La_3TiSb_5}$ Structure

compound	a (Å)	c (Å)	c/a	V (Å^3)
$\mathrm{La_3TiSb_5}$	9.526(1)	6.278(2)	0.6590	493.3(2)
$\mathrm{Ce_3TiSb_5}$	9.439(2)	6.235(2)	0.6606	481.1(2)
$\mathrm{Pr_3TiSb_5}$	9.401(3)	6.224(2)	0.6621	476.4(3)
$\mathrm{Nd_3TiSb_5}$	9.353(1)	6.196(1)	0.6625	469.4(1)
$\mathrm{Sm_3TiSb_5}$	9.275(1)	6.162(1)	0.6643	459.1(2)
$\mathrm{La_3ZrSb_5}$	9.587(1)	6.358(1)	0.6632	506.1(1)
$\mathrm{Ce_3ZrSb_5}$	9.506(1)	6.318(2)	0.6646	494.4(1)
$\mathrm{Pr_3ZrSb_5}$	9.450(1)	6.293(1)	0.6659	486.7(1)
$\mathrm{Nd_3ZrSb_5}$	9.413(1)	6.275(1)	0.6666	481.6(2)
$\mathrm{Sm_3ZrSb_5}$	9.344(1)	6.234(2)	0.6672	471.4(2)
$\mathrm{La_3HfSb_5}$	9.582(1)	6.356(1)	0.6633	505.3(1)
$\mathrm{Ce_3HfSb_5}$	9.483(2)	6.298(2)	0.6641	490.4(2)
$\mathrm{Pr_3HfSb_5}$	9.419(2)	6.271(3)	0.6658	481.8(2)
$\mathrm{Nd_3HfSb_5}$	9.390(2)	6.261(2)	0.6668	478.1(2)
$\mathrm{Sm_3HfSb_5}$	9.340(2)	6.230(2)	0.6670	470.6(2)
$\mathrm{La_3NbSb_5}$	9.534(2)	6.264(2)	0.6570	493.1(2)
$\mathrm{Ce_3NbSb_5}$	9.438(2)	6.219(2)	0.6589	479.7(2)
$\mathrm{Pr_3NbSb_5}$	9.396(1)	6.201(2)	0.6600	474.1(2)
$\mathrm{Nd_3NbSb_5}$	9.360(2)	6.186(2)	0.6609	469.4(2)

[a] Obtained on arc-melted samples.

The cell parameters were refined by least-squares fits of 20–30 reflections in the X-ray powder diffraction patterns obtained on an Enraf-Nonius FR552 Guinier camera (Cu Kα_1 radiation; Si standard), and these are listed in Table 1. Small variations in the cell parameters are observed, depending on the initial pellet composition (e.g., "$\mathrm{La_3TiSb_5}$" led to a = 9.526(1), c = 6.278(2) Å, V = 493.3(2) Å^3, while "$\mathrm{La_2Ti_3Sb_6}$" led to a = 9.520(3), c = 6.267(3) Å, V = 491.9(3) Å^3); this may suggest the existence of a narrow homogeneity range.

After preliminary photographic work on a single crystal of $\mathrm{La_3TiSb_5}$, the crystal structure was determined.[17,18] Final values of the atomic and equivalent isotropic displacement parameters are given in Table 2. Refinements in which the occupancies of successive atoms were allowed to vary (while fixing the displacement parameters) resulted in values of 100(1)% for La, 96(3)% for Ti, 98(1)% for Sb(1), and 103(1)% for Sb(2). Moreover, the displacement parameters are unexcep-

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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for La_3TiSb_5

atom	Wyckoff position	x	y	z	U_{eq}[a]
La	6g	0.6176(1)	0	$^1/_4$	0.0054(3)
Ti	2b	0	0	0	0.0066(9)
Sb(1)	6g	0.2507(1)	0	$^1/_4$	0.0057(3)
Sb(2)	4d	$^1/_3$	$^2/_3$	0	0.0057(4)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

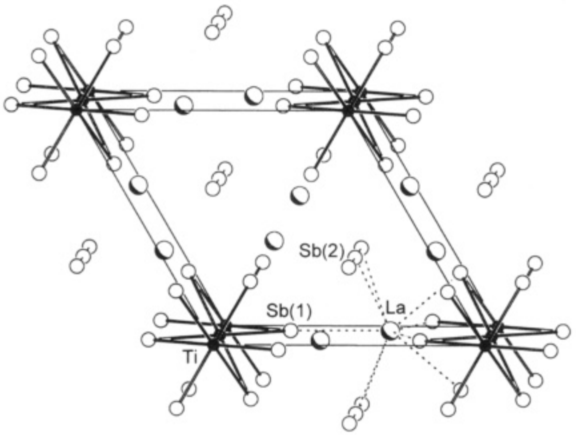

Figure 1. View down the c axis of La_3TiSb_5 with the unit cell outlined. The partly shaded circles are La atoms, the solid circles are Ti atoms, and the open circles are Sb atoms.

tional. Thus, we can assume the ideal stoichiometry La_3TiSb_5.

A view of the structure of La_3TiSb_5 down the c axis is given in Figure 1, which also shows the labeling scheme. It is isostructural to the recently discovered compounds U_3MSb_5 (M = Ti, V, Cr, Mn).[19] As in U_3TiSb_5, the RE_3MSb_5 structure may be regarded as an antitype of the Hf_5Sn_3Cu structure,[20] which in turn is derived by filling the interstitial sites[21] of the Mn_5Si_3 structure.[22] For those compounds in which all the atoms participate considerably in covalent bonding, this is a valid and useful way of building up the structure. But the rare-earth element La is significantly more electropositive than U (Pauling electronegativities 1.10 vs 1.38, respectively),[23] and if we regard the bonding component from the La atoms to be entirely ionic, then the structure possesses a strongly one-dimensional character that can be emphasized in the crystal chemical formulation:[24] $(La^{3+})_3\,{}^1_\infty[TiSb_{6/2}]^{5-}\,{}^1_\infty[SbSb_{2/2}]^{4-}$. That is, the structure consists of anionic chains aligned parallel to the c axis that are held together by intervening La^{3+} cations.

Table 3. Selected Interatomic Distances (Å) for La_3TiSb_5

La–Sb(1)	3.2064(8) (2×)	Ti–Sb(1)	2.859(1) (6×)
La–Sb(2)	3.3598(4) (4×)	Ti–Ti	3.1400(5) (2×)
La–Sb(1)	3.3815(8) (2×)	Sb(2)–Sb(2)	3.1400(5) (2×)
La–Sb(1)	3.496(1)	Sb(1)–Sb(1)[a]	3.9456(8) (4×)
La–La	3.858(1) (2×)	Sb(1)–Sb(1)[b]	4.138(2) (2×)

[a] Between shared faces of $TiSb_6$ octahedra. [b] Within shared faces of $TiSb_6$ octahedra.

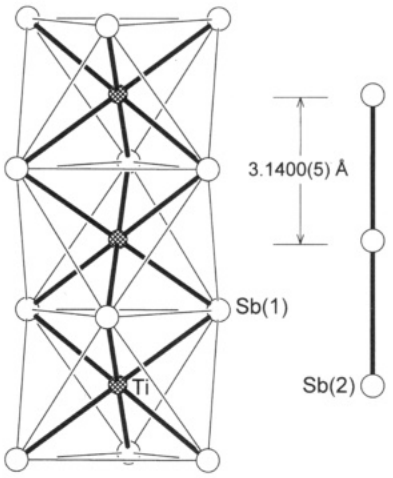

Figure 2. View projected approximately on (110) showing a column of face-sharing $TiSb_6$ octahedra (outlined by light lines) and a chain of Sb(2) atoms, both running along the c direction.

Some important interatomic distances are listed in Table 3. The Ti atoms are coordinated by six Sb(1) atoms at 2.859(1) Å in an octahedral fashion. These octahedra share their faces along the c direction to form infinite columns, as shown in Figure 2. The Sb(2) atoms are surrounded above and below by symmetry equivalent Sb(2) atoms at 3.1400(5) Å (half the c-parameter), forming a skewer aligned along $^1/_3$, $^2/_3$, z. The La atoms are coordinated by five Sb(1) and four Sb(2) atoms at distances of 3.2064(8)–3.496(1) Å, forming a roughly tricapped trigonal prism. Each La atom is 3.858(1) Å distant from two other La atoms in a zigzag arrangement running along the c direction.

The key feature in RE_3MSb_5 is the flexibility that is conferred by introducing the electropositive rare-earth atoms, allowing the ionic and covalent components of the bonding to be clearly separated in a Zintl-type approximation.[25] Thus, the significance of the RE_3MSb_5 series rests on its particular suitability as a model system for probing some important properties of low-dimensional systems, since we can now separate steric effects (RE substitution) from largely electronic effects (M substitution). The Sb(2)–Sb(2) interactions of ~3.14 Å fall in an intermediate regime between a full single Sb–Sb bond and the van der Waals distance between nonbonding Sb atoms (e.g., 2.908 vs ~3.36 Å, respectively, in elemental antimony).[26] These Sb–Sb interactions appear to be prevalent in many antimonides and can be manifested as chains in RE_3MSb_5 or as sheets in $RECrSb_3$,[16] for instance. Indeed, since Sb–Sb distances as long as ~3.15 Å have been implicated as noninnocent,[27] weak homoatomic bonding may turn out to be as important a feature of the solid state chemistry

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(17) La_3TiSb_5: fw 1073.38, space group $D^3_{6h} - P6_3/mcm$, a = 9.5294(8), c = 6.2801(11) Å, V = 493.9(1) Å^3 at −60 °C, Z = 2, ϱ_{calc} = 7.218 g cm^{-3}. Crystal size 0.033 × 0.039 × 0.335 mm. Diffractometer Siemens P4RA, radiation graphite-monochromated Mo Kα, μ = 267.9 cm^{-1}, transmission factors 0.21–0.44. Scan type ω, 2θ range 5°–60°, data collected 3063, octants $+h$, $\pm k$, $\pm l$, unique data (incl $F_o^2 < 0$; R_{int} = 0.142) 290, unique data (with $F_o^2 > 2\sigma(F_o^2)$) 280, variables 13, $R(F)$ (for $F_o^2 > 2\sigma(F_o^2)$) = 0.041, $R_w(F_o^2)$ (all data) = 0.102, GOF = 1.41.

(18) (a) Structure solution (direct methods): Sheldrick, G. M. *SHELXTL* Version 5.0, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1994. (b) Least-squares refinement on F_o^2 (SHELXL-93): Sheldrick, G. M. *J. Appl. Crystallogr.*, in press.

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of antimony as it is for its neighbor tellurium.[28] In attempting to formulate a first approximation of an oxidation state assignment for La_3TiSb_5, it is reasonable to assume 3+ for La, 4+ for Ti, and 3− for Sb(1). A two-bonded antimony atom would normally be assigned Sb^-, but the Sb(2)−Sb(2) distances here are too long for a single bond. We thus arrive at the tentative formulation of $(La^{3+})_3Ti^{4+}(Sb(1)^{3-})_3(Sb(2)^{2-})_2$, where the Sb(2)−Sb(2) interactions are assigned a *half* bond order, similar to the case proposed for U_3TiSb_5.[19] The situation may be different for the other transition-metal analogues, however. The $MSb_{6/2}$ columns and Sb chains both run parallel to the *c* direction, and the *M*−*M* and Sb(2)−Sb(2) distances are both equal to half the *c* parameter, so that we can examine Table 1 for any trends in these interactions. While a ~3.14 Å distance precludes any Ti−Ti bonding in La_3TiSb_5, a ~3.18 Å distance may possibly portend some weak Zr−Zr bonding in La_3ZrSb_5 and the oxidation state assignment must be modified. The Sb(2)−Sb(2) distance is thus also determined by the *M*−*M* distance, since they must necessarily be equal.

Some of these compounds are expected to display interesting magnetic properties that reflect the low-dimensional nature of the isolated $^{1}_{\infty}[MSb_{6/2}]$ columns and the arrangement of *RE* atoms between them. In particular, if the proposed oxidation state assignment is generalized to the niobium analogue La_3NbSb_5, there would be isolated chains of Nb^{4+} (d^1) atoms separated ~3.13 Å from each other. We are currently checking for the presence of superstructure, if any. A range of magnetic interactions is expected from the *RE* atoms, which appear to be 3+ for all these compounds, as there are no anomalies in the trend of decreasing cell volume as a function of *RE* size. We are thus planning to measure the physical properties and to develop a coherent band structure model for these compounds.

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Supporting Information Available: Tables of crystallographic data, anisotropic displacement parameters, and selected interatomic distances and angles (3 pages); observed and calculated structure amplitudes for La_3TiSb_5 (2 pages). Ordering information is given on any current masthead page.

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