



The hunt for LaFeSbO: Synthesis of La₂SbO₂ and a case of mistaken identity

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ABSTRACT

The phase La₂SbO₂ has been identified and characterized in the course of our efforts to realize LaFeSbO, a composition of great interest to the superconductor community. The compound La₂SbO₂ is a tetragonal layered oxypnictide containing La₂O₂ layers similar to LaMPnO compositions (where *M*=transition metal, *Pn*=pnictide) separated by pnictide anion layers. In order to better understand why LaFeSbO has remained elusive, density functional theory calculations have been used to determine the ground state heats of formation for LaFeSbO, La₂SbO₂, and other competing phases within the La–Fe–Sb–O system, as well as the phonon spectrum for LaFeSbO. These efforts suggest that LaFeSbO is a potentially metastable composition.

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1. Introduction

Following the discoveries of superconductivity for LaFePnO (*Pn*=P, As) systems it seems quite natural to ask whether the oxyantimonide and oxybismuthide analogs can be stabilized [1,2]. Our investigation of other possible LaMSbO compositions (*M*=Fe–Ni) led us to identify and characterize the compound La₂SbO₂, a layered oxyantimonide without a transition metal. This layered oxypnictide is somewhat peculiar in that the pnictide anion has an average charge state of *Pn*^{2−} if all atomic positions are fully occupied.

La₂SbO₂ crystallizes in a tetragonal ThCr₂Si₂ type structure (*I4/mmm* #139) with O coordinated to La in a fluorite like arrangement. These layers are stacked alternatively along the *c*-axis with a square mesh sub-lattice of Sb anions. Each Sb atom is in square prismatic coordination with La atoms from the fluorite layers, see Fig. 1. The Sb–Sb distance is equal to the *a*-parameter and for La₂SbO₂ materials is about 4 Å; too far for any significant Sb–Sb bonding interaction. Cerium based compositions were originally reported by Benz, however Nuss and Jansen have recently reinvestigated Ce₂SbO₂ as well as Pr₂SbO₂ single crystals and found evidence of antimony displacement within the *a*–*b* plane, resulting in both short (3.2 Å) and long (4.8 Å) antimony distances within the plane [3,4]. The related Ln₂BiO₂ (*Ln*=Y,La–Er) compositional series was very recently reported on by other researchers [5]. We will

therefore limit our discussion to Sb compositions except for highlighting a likely case of mistaken identity in the literature regarding LaNiBiO and LaFeBiO.

The composition LaNiBiO was reported to be superconducting (*T*_c~4.4 K) [6] and has been cited in the literature as one example of a ZrCuSiAs type layered oxybismuthide [7,8]. However, the PXRD pattern reported for LaNiBiO (*P4/nmm* #129) is missing a strong (1 1 2) reflection at approximately 36° 2θ if it was in fact *P4/nmm* [6]. The powder pattern instead matches completely with that of the nickel free compound La₂BiO₂ as reported in Ref. [5]. The compound LaFeBiO was simultaneously reported; however lattice parameters for LaFeBiO are nearly identical to those found for LaNiBiO, which is taken as further evidence that in fact La₂BiO₂ was the major phase in both cases. Our own studies have not found evidence of LaNiBiO or superconductivity for La₂BiO₂ compositions; however, NiBi₃ and NiBi are known to superconduct at approximately 4.0 K and 4.2 K, respectively [9]. We therefore conclude that there have been no experimental reports to date of LaMPnO (where *M*=3*d*, 4*d*, 5*d* and *Pn*=Sb, Bi) aside from LnMnSbO and LnZnSbO compositions [10].

Thus the question begs to be asked, why won't these heavier analogs form? As others have pointed out, it may simply be the high stability of iron antimonide impurity phases and the desire of Sb to form Sb–Sb bonds which prevents the formation of LaFeSbO [11]. Nevertheless, reports of compositions such as CsFe₂Sb₂ give hope to the search for an energetically stable iron antimonide composition with the same tetrahedral metal–pnictide coordination environment observed for LnFeAsO and AeFe₂As₂ superconducting materials [12]. To gain further insight into the still elusive LaFeSbO, we used density functional theory to calculate formation energies for phases within the La–Fe–Sb–O system.

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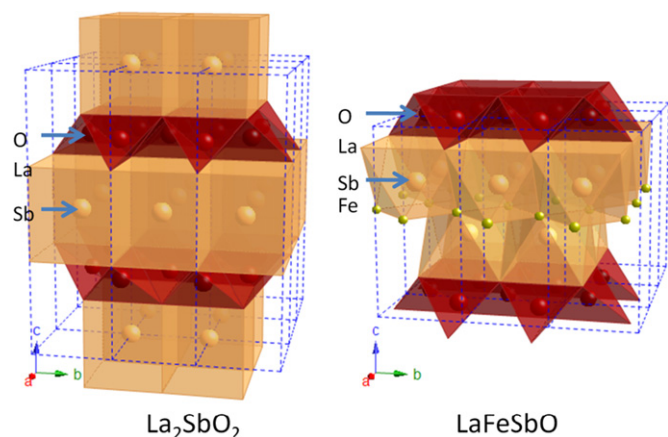


Fig. 1. Crystal structures for La_2SbO_2 and the hypothetical compound LaFeSbO . Unit cells are drawn to scale using experimentally determined parameters for La_2SbO_2 and DFT calculated parameters for LaFeSbO .

2. Experimental

Reagents used throughout this study include La_2O_3 (99.9 at%), La (99.9 at%), and Sb (99.5 at%). The composition $\text{La}_{1.9}\text{Sr}_{0.1}\text{SbO}_2$ was investigated by substitution of La_2O_3 by SrO (99 at%). All starting materials were weighed, ground, and pressed into pellets inside of an Ar filled glove box before sealing in fused silica ampoules, evacuated to approximately 1×10^{-4} Torr. La_2O_3 was heated overnight at 1023 K while SrO was heated at 1473 K before transferring to the glove box. First efforts to synthesize a pure phase sample of La_2SbO_2 for characterization always showed La_2O_3 products despite careful dehydration of all reagents and ampoules as well as the use of a Zr foil oxygen getter and alumina reaction crucible inside the ampoule. High quality samples were only obtained when the nominal oxygen content was reduced to approximately $\text{La}_2\text{SbO}_{1.5-1.6}$. The oxygen content was controlled by limiting the amount of La_2O_3 and therefore compensating with La metal to maintain a 2:1 ratio of $\text{La}:\text{Bi}$. Similar to La_2SbO_2 , high quality samples of the bismuth analog could only be produced for nominal compositions around $\text{La}_2\text{BiO}_{1.5}$. The sealed ampoules were typically heated at 1223 K for 12–18 h. in a programmable box furnace. To achieve a pellet suitable for property measurement it was necessary to regrind, press, and heat again at 1173–1223 K for 24 h. All La_2SbO_2 compositions examined are air sensitive and therefore stored in an Argon glove box or under vacuum. Resistivity was determined using a Quantum Design Physical Properties Measurement System (PPMS) using a four probe method with copper wires and silver paint to make electrode contact. Samples were prepared in air immediately before measuring to minimize exposure and sample decomposition is practically unnoticeable by XRD before and after the measurement. La_2SbO_2 appears black with a slightly reddish hue. Crystal structures at room temperature were characterized by powder X-ray diffraction (PXRD) using a Rigaku MiniFlex2 scanned from $2\theta = 20\text{--}68^\circ$ with a step size of 0.02° and a graphite monochromator on the diffracted beam ($\text{CuK}\alpha$). Rietveld refinement of PXRD patterns was carried out using GSAS [13] via the ExpGUI software [14]. The PXRD peaks corresponding to La_2SbO_2 were originally identified and indexed using the program DICVOL [15] via CMPR [16] from multi-phase products obtained while attempting to synthesize LaFeSbO .

3. Calculations

Lattice parameters and heat of formation energies at zero temperature were calculated using ab-initio density functional theory (DFT). The projector augmented plane wave method as

implemented in the Vienna ab-initio simulation package (VASP) [17,18] was used together with the generalized gradient approximation (GGA) for the exchange correlation functional in the Perdew–Burke–Ernzerhof (PBE) parameterization [19]. Total energies were converged to less than 1 meV/atom by controlling all calculation parameters (plane wave cutoff, Fermi broadening and k-point mesh density).

4. Results and discussion

In the course of our efforts to realize LaMSbO ($M = \text{Fe–Cu}$) compositions, using standard solid state methods, we have consistently identified the phases La_2SbO_2 and $M_{1+x}\text{Sb}$ as being the products of formation. The need to reduce oxygen content in order to produce high quality samples implies that oxygen vacancies may be possible in the La_2SbO_2 structure. In fact the formulas $\text{La}_2\text{SbO}_{2-x}$ ($x \geq 0.5$) can be charge balanced assuming an average pnicide charge greater than Pn^{2-} . The perovskite intergrowth composition $\text{Y}_2\text{SrFeCuO}_{6.5}$ is known to contain 25% oxygen vacancies within a yttrium and oxygen fluorite type layer [20]. The compensating yttrium and surrounding oxygen atomic displacements cause the symmetry to shift from tetragonal to orthorhombic. As shown in Fig. 2 we have not observed any visible splitting of the (1 1 0) or (2 1 3) peaks as would be expected if oxygen vacancies were ordered and the surrounding atoms displaced. It has been reported, using x-ray diffraction that the Sb atoms in Pr_2SbO_2 displace from their ideal positions and form an ordered $(4 \times 4 \times 1)$ supercell. Further neutron studies should therefore address the possibility that oxygen vacancies are present within the general Ln_2PnO_2 family and may in fact be the driving force for Sb displacement. Any deviation from full oxygen occupancy would indicate a deviation from the unusual Sb^{2-} ($5s^25p^5$) charge state towards a more typical Sb^{3-} ($5s^25p^6$) state, as found for LaMnSbO via Mössbauer studies [21]. Attempts to resolve the oxygen content using standard x-ray diffraction techniques and thermogravimetric analysis have thus far been inconclusive due to the air sensitivity of these compositions. Until further direct evidence of oxygen deficiencies is observed the compositions will simply be referred to as La_2SbO_2 and $\text{La}_{1.9}\text{Sr}_{0.1}\text{SbO}_2$.

Lattice parameters and cell volume determined for La_2SbO_2 are $a = 4.05653(32) \text{ \AA}$ and $c = 13.8559(13) \text{ \AA}$, $\text{Vol.} = 228.0(1) \text{ \AA}^3$.

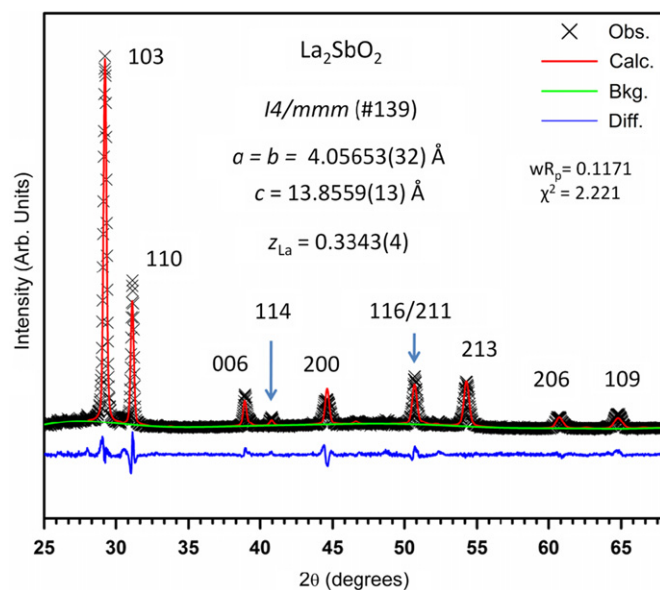


Fig. 2. Powder x-ray diffraction pattern and LeBail profile fitting along with $(h k l)$ labels for the composition La_2SbO_2 .

Comparing these parameters to those found for LaFeSbO via DFT (discussed below) it is readily observed that the Sb coordination environment in LaFeSbO is truncated compared to that of La₂SbO₂, see Fig. 1, because of Fe–Sb bonding. As expected from ionic radii considerations, there is an increase in the unit cell lattice parameters of La₂SbO₂ upon Sr substitution for La. For La_{1.9}Sr_{0.1}SbO₂ the lattice parameters are found to be, $a=4.06079(34)$ Å, $c=13.9773(15)$ Å, with Vol.=230.0(1) Å³. Both La₂SbO₂ and La_{1.9}Sr_{0.1}SbO₂ display semiconducting behavior with respect to temperature, shown plotted in Fig. 3. An inset detailing the natural log of resistivity on a reciprocal temperature scale is also shown in Fig. 3 and from this plot the activation energy of La₂SbO₂ is calculated to be 0.29 eV. The plot for La_{1.9}Sr_{0.1}SbO₂ remains nonlinear even when a temperature scale of $1/T^{(1/3)}$ or $1/T^{(1/4)}$ is used. Previously Nuss and Jansen [4] explained the semiconducting behavior of Ce₂SbO₂ and Pr₂SbO₂ by giving evidence of Sb shifting within the a – b plane and concluding that covalently bonded Sb₂⁴⁻ dimers were forming.

Calculated zero temperature structural parameters based on DFT/GGA for stoichiometric La₂SbO₂ are $a=4.06$ Å, $c=13.97$ Å, and $z_{La}=0.3392$, which agree well with the experimental numbers. Similarly, the calculated tetragonal lattice parameters for LaFeAsO, $a=4.02$ Å, $c=8.64$ Å, and LaFePO, $a=3.93$ Å, $c=8.50$ Å, agree well with reported room temperature lattice parameters [1,2]. The energy minimized structural parameters found for LaFeSbO are $a=4.168$ Å, $c=9.214$ Å, $z_{La}=0.1283$, $z_{Sb}=0.6595$, which are in good agreement with those found by Moon et al. [22]. The heat of formation at zero temperature of LaFePnO ($Pn=P, As, Sb$) relative to the standard state of the constituent elements (solid P, As, Sb, La, ferromagnetic Fe, and gaseous molecular oxygen) are summarized in Table 1. We find a negative heat of formation for LaFeSbO but its magnitude is smaller than the heat of formations of LaFePO and LaFeAsO. In a search for competing phases in the space of the constituent elements La, Fe, O, and (P, As, Sb) we have calculated total energies for 68 compounds. In Table 2 the formation energies per formula unit of LaFePnO versus its nearest competing phases are summarized. We find LaFePO and LaFeAsO to be thermodynamically stable relative to their nearest competing phases, as they must, but LaFeSbO is thermodynamically unstable relative to the formation of La₂SbO₂ by $\Delta H \sim 0.1$ eV per formula unit of LaFeSbO. Two questions remain: is LaFeSbO a potentially metastable compound and if so, can it be made? To answer the first question, we have calculated the phonon spectrum of LaFeSbO, shown Fig. 4, and found no imaginary phonon frequencies.

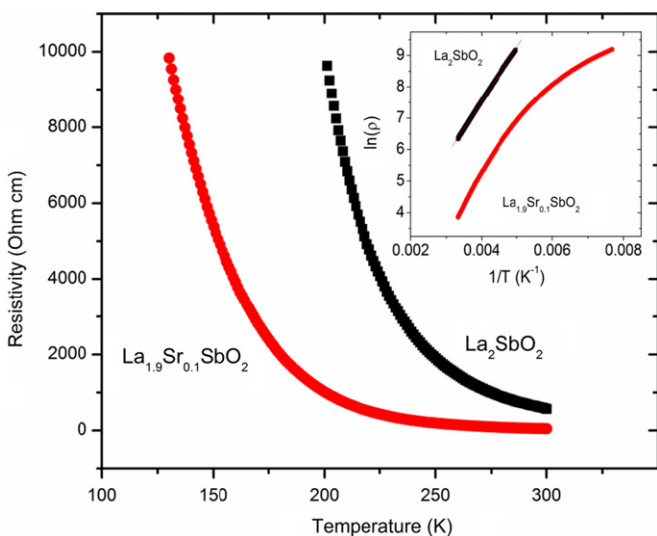


Fig. 3. Temperature dependence of resistivity for La₂SbO₂ and La_{1.9}Sr_{0.1}SbO₂ compositions. Inset shows natural log of resistivity versus reciprocal temperature.

Table 1

Zero temperature heat of formation energy per formula unit of LaFePnO relative to the standard state of the constituent elements and relative to more common starting reagents.

Stability equations for LaFePO, LaFeAsO, and LaFeSbO	ΔH_{0K} (eV)
$La_{(s)} + Fe_{(s)} + P_{(s)} + 1/2O_{2(g)} \rightarrow LaFePO$	-8.3
$La_{(s)} + Fe_{(s)} + As_{(s)} + 1/2O_{2(g)} \rightarrow LaFeAsO$	-7.7
$La_{(s)} + Fe_{(s)} + Sb_{(s)} + 1/2O_{2(g)} \rightarrow LaFeSbO$	-6.7
$1/3La_{(s)} + 1/3La_2O_{3(s)} + Fe_{(s)} + P_{(s)} \rightarrow LaFePO$	-2.4
$1/3La_{(s)} + 1/3La_2O_{3(s)} + Fe_{(s)} + As_{(s)} \rightarrow LaFeAsO$	-1.8
$1/3La_{(s)} + 1/3La_2O_{3(s)} + Fe_{(s)} + Sb_{(s)} \rightarrow LaFeSbO$	-0.9

Table 2

Zero temperature heat of formation energy per formula unit of LaFePnO relative to the most stable competing phases.

Stability equations for nearest competing phases to LaFePO, LaFeAsO, and LaFeSbO	ΔH_{0K} (eV)
$La_2O_{3(s)} + LaAs_{(s)} + FeAs_{2(s)} + 2Fe_{(s)} = 3LaFeAsO$	-0.31
$La_2O_{3(s)} + LaFe_2P_{2(s)} + FeP_{(s)} = 3LaFePO_{(s)}$	-0.13
$La_2SbO_{2(s)} + FeSb_{(s)} + Fe_{(s)} = 2LaFeSbO_{(s)}$	0.27

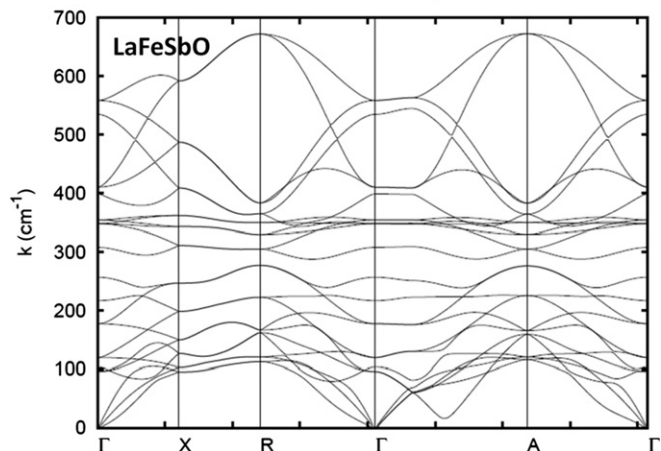


Fig. 4. Phonon spectrum for LaFeSbO as found using the DFT energy minimized structural parameters, $a=4.168$ Å, $c=9.214$ Å, $z_{La}=0.1283$ and $z_{Sb}=0.6595$.

Hence there are no lattice instabilities and the formation energy of LaFeSbO is indeed a local minimum. To answer the second question would require as a first step the determination of the depth of the energy well around the local minimum for the LaFeSbO compound. This is a formidable task, which would require the determination of an unknown number of transition states and we must leave our second question unanswered. We conclude that LaFeSbO is thermodynamically unstable relative to the formation of La₂SbO₂, but can potentially exist in a metastable state. Our calculations allow no prediction of the stability range of this metastable state. A detailed theoretical study of the electronic structure of La₂SbO₂ and possible Sb₂⁴⁻ dimer formation will be published elsewhere.

5. Conclusions

The compound La₂SbO₂ has been isolated and investigated in the course of searching for LaFeSbO. This phase is isostructural to Ce₂SbO₂ as well as La₂BiO₂. La₂SbO₂ is found to be semiconducting

similar to the previously reported compositions Ce_2SbO_2 and Pr_2SbO_2 . Indirect evidence of oxygen vacancies is observed for La_2SbO_2 and La_2BiO_2 compositions. A wider reinvestigation of these materials using neutron diffraction is warranted in order to examine oxygen content and possible ordering. It may turn out that the average Pn charge states in these and other Ln_2PnO_2 compositions are closer to the more usual Pn^{3-} .

A case of mistaken identity within the literature on layered oxyphnictides has been addressed and based on the reported XRD pattern for LaNiBiO it is concluded that in fact La_2BiO_2 has been observed not LaNiBiO .

Density functional theory has been used to calculate the ground state heats of formation for LaFePnO compositions ($Pn = \text{P}, \text{As}, \text{Sb}$) and competing phases within the La-Fe-Pn-O systems. The phosphorus and arsenic analogs are found to be stable with respect to their elemental constituents as well as nearest competing phases, while LaFeSbO is found to be stable only with respect to the elemental constituents. The ground state phonon spectrum of LaFeSbO reveals no lattice instabilities and suggests that LaFeSbO is possibly metastable.

While many researchers have attempted the synthesis of LaFeSbO , some even utilizing high pressure, thus far there have still been no reports of LaFeSbO . Our work suggests that using standard high temperature synthesis methods will not yield LaFeSbO due to the high stability of competing phases such as La_2SbO_2 and FeSb . Whether or not LaFeSbO (or similar compositions containing Fe_2Sb_2 layers separated by a $2+$ charge donor layer) can be formed remains an open question but sequential

layering of Fe, Sb , and charge donor constituents may still allow these thermodynamically favored phases to be sidestepped and for LaFeSbO to be experimentally characterized.

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