Structural studies of two novel La-Sn compounds: $\text{La}_{30}\text{Sn}_{30}$ and $\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$

by

Amie S. Yang

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

Major: Inorganic Chemistry

Program of Study Committee:
John D. Corbett, Major Professor
Gordon Miller
Vitalij Pecharsky

Iowa State University

Ames, Iowa

2005

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Chapter 1: INTRODUCTION

In scientific research, exploring the basic concepts of structure and bonding is essential to understand complex systems. For example, finding the right material for hydrogen storage systems depends on the site of the hydride atoms which can be located by using expensive neutron diffraction techniques. Much research has been done to theoretically derive possible sites of hydrides based on thermodynamics and geometrical theoretical calculations. However, locating hydride sites can be achieved by using single crystal diffraction if the sites that hydrides occupy contain more electron density.¹ This can be done if anions are small enough to occupy the hydride interstitial sites. Considering that the crystal radius for H^- is $1.10 \text{ \AA}$, the most similar anion in size is the fluoride anion with a crystal radius of $1.17 \text{ \AA}$.² If successful, single crystal x-ray diffraction studies can eliminate cost and time spent on neutron diffraction.

X-ray diffraction allows us to determine unit cell parameters and atom sites by studying how atoms in a crystalline material interact with x-rays. When a monochromated x-ray beam hits the sample, the x-rays are scattered by the electrons surrounding the atoms. The sum of the scattered intensities is known as the structure factor, or form factor, f , and it is directly proportional to the electrons of Z , the atomic number. Form factors of atoms are tabulated in the *International Tables of Crystallography*, Vol 3 (1952) against $\sin\theta/\lambda$. Because the form factor is dependent on electron density, powder patterns at high 2θ angles

¹*Basic Solid State Chemistry* 2nd Ed. West, A. R; John Wiley & Sons. LTD Chichester, England, 1999.

²R.D. Shannon, *Acta Cryst.*, 1976, **A32**, 751.

are weak, and light atom (H, Li) sites are hidden when surrounded by heavier atoms.

Because of these effects, high electron density surrounding small atoms poses as a problem when trying to determine the sites of hydride interstitials in hydrogen storage alloys.

Considering that the sites that the hydride anions occupy are unknown in many intermetallic hydrogen storage materials, an approach to solve this mystery is to increase the amount of electron density by substituting hydrogen with a more electron rich element F. Hydride ions have a small crystal radius of 1.10Å and fluoride ions are the closest in comparison ($r(\text{IV}) = 1.17\text{\AA}$).³ Fluorides and hydrides also occupy tetrahedral sites in some systems similar to the Mn_5Si_3 -type or Cr_5B_3 -type structures i.e., $\text{Ca}_5\text{Sb}_3\text{F}$, $\text{Ca}_5\text{Ge}_3\text{H}$ and $\text{Ca}_5\text{Bi}_3\text{F}$.^{4,5} Therefore, it was suggested to substitute hydrides with fluorides in prospective hydrogen storage alloys.

Many intermetallic compounds with the compositions of AB_2 , AB_3 , AB_5 , and A_2B_{17} (A= rare earth metals and B= transition metals) are capable of absorbing hydrogen.^{6,7} Most hydrogen storage materials consist of a hydride forming metal A and a non-hydride forming metal B.⁸ The systems that have been considered are mostly intermetallic Laves phases composed of rare-earth metals and late transition metals AB_2 (A=Y, La, Ce, Dy, and Er;

³Corbett, J. D. and Marek, H. S. *Inorg. Chem.* **1983**, 22 (22), 3194.

⁴Leon-Escamilla, E. A; Corbett, J. D. *J. Solid State Chem.* **2001**, 159(1), 149-162.

⁵Hung, W.-M; Corbett, J. D. *Chem. Mater.* **1989**, 1, 311.

⁶Gualtieri, D. M; Narasimhan, K. S. V. L; Takeshita, T. *J. Applied Phys.* **1976**, 487(8), 3432.

⁷Yvon, K. *J. Less-Common Met.* **1984**, 103, 53-70.

⁸Morinaga, M; Yukawa, H; Nakatsuka, K; Takagi, M. *J. Alloys Comp.* **2002**, 330-332, 20.

B=Mn, Fe, and Ni). The Laves phases formed by these metals are cubic MgCu_2 -type structures. Experimentally, hydrogen gas enters the alloy where it undergoes absorption via $\text{H}_2 \rightarrow 2\text{H}$ at the surface of the alloy⁹ at pressures ranging from 1- 70 atm and at temperatures ranging from room temperature to 700°C.¹⁰ In many Laves phases, hydrogen absorption results in a crystalline binary metal hydride or an amorphous material. However, in crystalline phases, hydrides occupy approximately one third of the available tetrahedral sites experimentally.

Many research groups have tried to approach this problem via geometrical or thermodynamic computations, however there has been no model that can predict hydride interstitial sites. According to Westlake, metals absorb hydrogen into tetrahedral holes when $0.33 \text{ \AA} < r_h < 0.43 \text{ \AA}$.¹¹ For MgCu_2 -type Laves phases, the hole size is 0.335 Å according to Goldschmidt radii for A_2B_2 tetrahedral holes, and fluorides can indeed occupy these sites. However it is not merely the size of the tetrahedral site that determines the occupancy by hydride but the relative affinity of the four metal atom neighbors (A_2B_2 , AB_3 , and B_4).¹²

Many systems were examined for ternary fluoride Laves phases; however, none was formed, much to my disappointment. Table 1 shows the different systems and temperature ranges that I have used in trying to form the desired ternary fluoride compounds. All of the

⁹Gualtieri, D. M; Narasimhan, K. S. V. L; Takeshita, T. *J. Applied Phys.* **1976**, 487(8), 3432

¹⁰Shaltiel, D. *J. Less-Common Met.* **1978**, 62, 407.

¹¹Westlake, D. G. *J. Less-Common Met.* **1983**, 90, 251.

¹²Raj, P; Shashikala, K; Sathyamoorthy, A. *Phil. Mag. B* **1999**, 79(8), 1185.

Laves phases listed did not form any interstitial fluoride. Although the reasons for poor substitution of hydrides are unknown, we can speculate that although hydrides and fluorides have some similar characteristics, they differ in other ways-

- 1) Hydride anions participate in significant covalency while fluoride anions behaves ionically.¹³
- 2) The known ternary hydride-fluoride equivalent phases are more ionic rather than intermetallic compounds

Also, the elements in Zintl phase compounds have a larger electronegativity difference than Laves phase compounds which may attribute to the lack of formation of fluoride compounds; Zintl phase compounds allow the formation of a more ionic compound with fluorides.

Table 1. Attempted Laves phase reactions using A-type atom fluorides and B-type non-hydride forming metals

Laves Phase	Temperature range	Products
$1-x \text{ La} + 2 \text{ Ni} + x \text{ LaF}_3$	800-1250°C,	La-Ni binaries, LaF_3
$1-x \text{ La} + 2 \text{ Mg} + x \text{ LaF}_3$	800-1050°C	La-Mg binaries, LaF_3
$1-x \text{ Ce} + 2 \text{ Ni} + x \text{ CeF}_3$	800-1250°C	Ce-Ni binaries, CeF_3
$1-x \text{ Ce} + 2 \text{ Mg} + x \text{ CeF}_3$	800-1050°C	Ce-Mg binaries, CeF_3
$1-x \text{ Er} + 2 \text{ Mn} + x \text{ ErF}_3$	800-1250°C	Er-Mn binaries, ErF_3
$\text{Er} + 2-x \text{ Mn} + x \text{ MnF}_2$	800-1250°C	Er-Mn binaries, ErF_3
$1-x \text{ Er} + 2 \text{ Fe} + x \text{ ErF}_3$	800-1250°C	Er-Fe binaries, ErF_3
$1-x \text{ Dy} + 2 \text{ Mn} + x \text{ DyF}_3$	800-1250°C	Dy-Mn binaries, DyF_3
$1-x \text{ Dy} + 2 \text{ Fe} + x \text{ DyF}_3$	800-1250°C	Dy-Fe binaries, DyF_3
$1-x \text{ Ca} + 2 \text{ Ni} + x \text{ CaF}_2$	800-1250°C	Ca-Ni binaries, CaF_2
$1-x \text{ Ca} + 2 \text{ Mg} + x \text{ CaF}_2$	800-1050°C	Ca-Mg binaries, CaF_2
$1-x \text{ Ca} + 2 \text{ Al} + x \text{ CaF}_2$	800-1050°C	Ca-Al binaries, CaF_2
$1-x \text{ Y} + 2 \text{ Mn} + \text{YF}_3$	800-1250°C	Y-Mn binaries, YF_3

Clearly, although the sizes of the hydride and fluoride are similar, other chemical factors

¹³Kowalczyk, S. P; Ley, L; McFeely, F. R; Shirley, D. A. *Phys. Rev. B* **1977**, 15(10), 4997.

make it difficult to produce fluoride-substituted Laves phases. Instead at high temperatures, 1250°C, two new crystalline compounds were formed in small yields in the Y-Mn and Er-Fe system and can be seen by powder patterns,

Another system that was looked at briefly was the LaNiSn system. LaNiSn has an orthorhombic TiNiSi-type structure¹⁴. This system differs from the previously noted intermetallic alloys in that it contains a main group element, Sn, and shows sign of deuterium absorption, LaNiSnD₂.¹⁴ Very little research has been done on the absorption capabilities of LaNiSn therefore making it a good candidate to study. The desired fluoride-substituted compound did not form in this system as well, however, new binary and ternaries did. In these systems, single crystals of La₂₅Sn₂₈Ni_{4.9}, La₁₃Sn₁₇, La₃₂Ni₂Sn₃₅ and La₃₀Sn₃₀ were found and refined; those for La₃₂Ni₂Sn₃₅ and La₃₀Sn₃₀ will be discussed in detail.

¹⁴Yartys, V. A; Olavesen, T; Hauback, B. C; Fjellvag, H; Brinks, H. W *J. Alloys Comp.* **2002**, 330-332, 141.

Chapter II. EXPERIMENTAL

Materials

Source

High purity elements and fluoride salts were used as reagents in the reactions. Most of the rare earth elements and their fluorides were purchased from Ames Laboratory and had purities of 99.99%. These compounds include Y, La, Ce, Dy, LaF_3 , CeF_3 , DyF_3 , and ErF_3 . Er metal was purchased from Research Chemicals and had purity of 99.9%. Sn, Fe, Ni, and MnF_2 were purchased from Alfa Aesar and had purities of 99.99%, 99.5%, 99.99%, and 99% respectively. Mn was purchased from Fisher Scientific with a 99.95% purity.

Most of the synthetic methods and techniques that were developed in the Corbett lab group were used in the synthetic work up.¹⁵

Handling

Owing to air and moisture sensitivity of the reagents, most of the elements and fluorides were handled in an inert atmosphere. A dry box filled with Ar gas was used to handle La and Ce as thin sheets where it was then scraped to remove any tarnish and cut into small pieces before loading all reactions.

¹⁵Corbett, J. D. *Inorg. Synth* **1983**, 22, 15.

General Synthetic Techniques

Prior to loading reactions, Ta tubes (3/8" o.d.) were cut into lengths of ~4 cm. The tubes were cleaned in a solution of 55% conc. H_2SO_4 , 25% conc. HNO_3 , and 20% conc. HF (by volume) for 30 seconds in a fume hood. The tubes were thoroughly rinsed with $\text{NaHCO}_3(\text{aq})$ and then in distilled water. The tubes were dried in air, crimped at one end and arc welded.

All reagents were weighed in an Ar- filled dry box on an analytical balance with ± 0.0005 g precision. The total mass of the reactants was ~ 0.25 g, and this was pelletized using a 5 mm die from Specac under two tons of pressure from a pneumatic pellet press. The pellets were placed in Ta tubes, and the latter were crimped, and transported to the arc welder in a tightly shut jar, and were welded shut to prevent leakage of gases and/or liquids of loaded elements at high temperatures.

Because Ta reacts with air at elevated temperatures, the reaction vessels were placed in fused silica tubes. Then one end of the tube was carefully sealed using a hydrogen/oxygen torch, and on the other end a ball joint with a long neck (~ 30 cm) was carefully attached to the body of the jacket. The ball joint was attached to a dynamic vacuum line. After thirty minutes of rough pumping by a rotary pump, the line was open to a diffusion mercury pump through a trap filled with acetone and dry ice for thirty more minutes. The silica jacket was heated with a natural gas/oxygen torch three times to evaporate any sign of moisture; this allowed the atmosphere in the silica jacket to reach $\sim 10^{-6}$ atm. The jacket was then carefully sealed and tested via a tesla coil for any leaks. The reactions were then placed in the center of a Thermcraft Marshall furnace controlled by a Eurotherm controller model 2416.

Chromel-alumel thermocouples were placed adjacent to the jacket to monitor the temperature and programmed cycles. Ceramic wool was placed at both ends of the furnace to minimize heat loss to the outside environment.

The reactions were opened in a N₂-filled Blickman glovebox equipped with a Vacuum Atmospheres model HE-493 regeneration system. The moisture level was monitored with a Panametrics model 700 hygrometer and stayed constant at ~1-3 ppm. The Ta tubes were opened by working the crimped ends of the tubes. The contents were placed on a glass Petri dish and particles that appeared to be single crystals were picked using a pyrex crystal picker made by heating a 2 mm pyrex rod and pulling it until it reaches a thickness of ~0.4- 0.2 mm. The crystals were placed in a capillary tube with an inner diameter range of 0.5-0.3 mm that were lined with Apiezon L grease, 1.5cm apart from other crystals, and sealed. Remaining products were either kept in a vial in the dry box or used as a sample for x-ray powder diffraction studies.

Non- air- sensitive products were carefully examined outside of the glove box through a STEMI SV8 optical microscope ($f=100$). Crystals were mounted on pyrex fibers using Permabond glue.

Synthesis via Arc Melting

Because many of the reagents that were used have high melting points, arc melting was used to melt and blend the metals for maximum surface contact and to bring the system into chemical equilibrium. Prior to arc melting, the reactants were weighed and pelletized as stated above. The pellets were then placed on a copper hearth with a water cooling system,

vacuum line, and an Ar gas line. The chamber was evacuated using a Duo Seal Vacuum Pump and refilled with argon gas three times. After the third backfill, an overflow of Ar was allowed to release any excess gas that form during melting from the chamber. Using a Miller Maxstar 91 CC•DC Inverter Welding Power Source, 11- 20 amps of current was sent through the sample for 30 seconds. The pellet was flipped over and melted again for another thirty seconds. This process continued four more times or until the sample appeared to be homogeneous. After melting, the sample was sealed in a Ta tube and annealed at varying temperatures.

Synthesis via High Temperature Vacuum Furnace

After the weighed material was pelletized, the sample was placed in a Ta tube which was crimped and welded shut. The tubes were then placed in a Ta jacket (1.5" i.d) which acted as a secondary container, and placed in the middle of the HTVac chamber from Thermal Technology High Temperature Experts. Using a rough pump, the chamber was evacuated to $\sim 10^{-4}$ atm for thirty minutes. After the initial pump- down, the Alcatel cff 450 turbo molecular pump (tmp) was turned on and allowed to pump the system down until a vacuum of $\sim 10^{-6}$ torr was reached. The quality of the vacuum was monitored using an IG 4400 Ionization gauge. The HTVac system was equipped with graphite heaters and a Eurotherm controller. At low temperatures, < 700 °C, there was little control over the ramp rate. Therefore, the initial command was a step program that allowed the temperature to reach 700 °C in ~ 25 minutes. As the temperature stepped to 700°C, the amount of current fed to the system was manually raised 1 amp per 5 minutes from 25 amps to 30 amps. At 30

amps, the program continued with the heating cycle. After the completion of the heating cycle, the furnace cooled to room temperature and the Ta tubes were removed and opened in a dry box.

Characterization

X-ray Diffraction

All reactions were characterized and analyzed by x-ray diffraction. Crystalline materials have characteristic fingerprints and therefore it is easy to recognize known compounds by comparison. Fingerprinting powder patterns allow us to identify known phases in multi-phased samples and to identify new phases as they appear in greater concentrations.

The sample holder is a ring with a round 1" window covered with a smooth mylar film. A saturated solution of petroleum jelly in toluene was applied on the mylar film and dried in air; this provides a smooth and consistent surface for the sample. The contents were ground in a mortar with pestle until a uniform powder. The sample was spread thinly and evenly across the template block and another piece of mylar film was used to cover the sample to protect it from air. The sample ring holder was placed on the diffractometer where it oscillated across the x-ray beam to allow sampling across the full span of the sample.

All x-ray powder diffraction was done on a Huber Imaging Plate Guinier Camera G670. Exposure time was dependent on the sample, however each sample was exposed for at least 30 minutes. The monochromated Cu K α_1 radiation ($\lambda = 1.50598 \text{ \AA}$) was produced by

a sealed tube x-ray generator operating at 45 kV and 20 mA. The x-ray beam strikes an oscillating sample while data points were taken at a step value of 0.005° with the option to multiscan the image plate ten times. All experimental powder patterns were viewed in a program called WinPLOTTR alongside calculated powder diffraction patterns produced by Powdercell v 2.4. All unidentified peaks were compared to other experimental or calculated powder patterns to determine the identity of unknown phases and to note the 2θ -values and intensities of the unknown peaks.

Single Crystal X-ray Diffraction

Crystallographic data were collected with the aid of a monochromated Mo K_α radiation ($\lambda = 0.70173 \text{ \AA}$) on a Smart Apex CCD detector system operated at 50kV and 30mA. The crystal was centered on diffractometer using Smart and Video. Prior to data collection, a full rotation diffraction pattern of the crystal was taken with a 60 second exposure time to determine the quality of the crystal. Afterwards, matrix data collection was taken to determine the unit cell of the single crystal. Each frame had an exposure time of 10-15 seconds depending on the size and x-ray absorptivity of the crystal. The Smart program searched for good quality reflections and calculated the unit cell and hkl values. A full collection of data took place if the unit cell parameters of the single crystal did not correlate with those of a known structure. A full sphere data collection (multi run) with 15 seconds per frame was taken for small crystals ($<15 \text{ \AA}^3$) and for crystals originally indexed in low symmetry; this allowed data collection at varying 2θ , ω , ϕ , and χ values. The reflections that were considered had a low I/σ threshold value of 15 and an high I/σ limit of 9999. All

frames were processed by indexing and least squares refinement using a program, Smart 32, to determine the correct unit cell and Bravais lattice. Stray reflections were removed from the reflection list prior to integration and site refinement.

The program, SaintPlus, was used to integrate reflections and to make absorption corrections. It eliminates reflections with shapes that correlate poorly with model profile shapes relative to other spots of similar I/σ . The Laue class designated constrains the integration, global refinement constraints and sorting. The program sorts the reflections into point-group-equivalent order to create specified output reflection files and refines the unit cell parameters from a large number of intense peaks. SADABS was used for absorption corrections. The program is primarily used to exploit data redundancy and to correct 3D-integrated data from Bruker CCD detectors.¹⁶ SADABS was also used for correcting systematic errors including variation in the volume of the irradiated crystal, incident beam inhomogeneity, absorption by the atoms in the crystal, and crystal decay.

After integration, XPREP was used to determine the correct cell and space group for the provided data. XPREP can also display reciprocal lattice, empirical and face-indexed absorption corrections, intensity statistics, scaling and merging of different data sets, and preparation of the input files for structure solution with the SHELXTL program XS etc.¹⁶

After space group determination, SHELXTL was used for structure refinement. In this program, a full- matrix least squares calculation of F^2 and Fourier synthesis were used to

¹⁶ <http://shelx.uni-ac.gwdg.de/SHELX>

refine atomic positions and thermal displacement parameters. The structure factors were calculated using neutral atom scattering factors with corrections in real and imaginary parts of anomalous dispersion for heavier elements with $Z > 10$.¹⁷ All structures have undergone extinction coefficient refinements, and mixed and partial occupancy refinements. The quality of the structure was measured by residual electron density from the final difference Fourier map, reasonable isotropic and anisotropic parameters, and R1 and wR2 values. Definitions of some important structure refinement parameters are given below:

Linear Absorption Correction:

$$\mu = \frac{n}{V} \sum_i n_i (\mu_a)_i$$

in which n_i is the number of atoms of elements i , in the unit cell volume, V . μ_a is the atomic absorption coefficient found in the International Tables of Crystallography.

*Extinction Parameters, x .*¹⁸

The extinction coefficient x is refined in which F_c is multiplied by

$$k [1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$$

¹⁷ *International Tables for X-Ray Crystallography*, 2nd ed; Lonsdale, K; Macgillavry, C. H; Rieck, G. D; Eds. Kynock Press: Brimingham, England. 1968, Vol. III.

¹⁸ <http://shelx.uni-ac.gwdg.de/SHELX>

and k is the overall scale factor. For the analysis of variance, the F_o^2 values (the experimental measurements) are brought onto the absolute scale of F_c^2 by dividing them by the scale factor(s) and the extinction factor. This expression is empirical and represents a compromise to cover both primary and secondary extinctions.

R int

The R factor represents the quality of the structure refinement and averaged experimental data:

$$R(int) = \Sigma | F_o^2 - F_o^2(\text{mean}) | / \Sigma [F_o^2]$$

in which F_o^2 is the experimental measurement; this includes all input reflections for which more than one symmetry equivalent is averaged.

Crystallographic R indices

$wR2$ depends on F_o^2 :

$$wR2 = \{ \Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2] \}^{1/2}$$

in which w is based on the weighting scheme. $R1$ is more conventional and is independent of the weighting scheme. $R1$ is often based on observed F values larger than $4\sigma(F_o)$:

$$R1 = \Sigma || F_o | - | F_c || / \Sigma | F_o |$$

Goodness of Fit (GooF)

GooF is calculated from F^2 according to:

$$GooF = \{ \Sigma [w (F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$$

in which n is the number of reflections and p is the total number of parameters refined. A

Goof close to unity is ideal.

Anisotropic Displacement Factor (U_{ij}) in units of $\text{\AA}^2$

$$\exp(-8\pi^2 U_{eq} [\sin(\theta) / \lambda]^2)$$

Site Occupation Factor

$$\text{s.o.f.} = (PS)/G$$

P is the refined site occupancy, S is the site multiplicity per unit cell from the International Tables,¹⁹ and G is the multiplicity of the general position for the specific space group.

Drawings of all structures were produced using the computer program Diamond (v.

2.1, Crystal Impact © 1996-1998, Klaus Brandenburg).

¹⁹International Tables for Crystallography, 2nd rev. ed. Hahn, T; Ed. Luwer Academic Publishers: Dordrecht, Germany, 1989, Volume A.

Chapter III: La-Sn AND La-Sn-Ni SYSTEMS

Introduction

In previous research, it has been shown that LaNi_5 is a good hydride former. Its ternary derivative, $\text{LaNi}_{5-x}\text{Sn}_x$, has also shown promise as a hydriding material.¹ During the process of producing $\text{LaNi}_{5-x}\text{Sn}_x$, its constituent LaNiSn was found which in turn can absorb deuterium to give its saturated form, LaNiSnD_2 . LaNiSn has the orthorhombic TiNiSn -type structure and upon deuteration, it transforms into the hexagonal ZrBeSi -type structure. This structure transformation allows easy detection of hydride absorption as well as fluoride detection if fluoride is able to enter the system. In this system, a main group element, Sn, is present that may facilitate the addition of the fluoride atom; Zintl compounds containing a tetrel group element tend to form ternary fluoride compounds. Unfortunately, not much research has been done on this system however, during the process of synthesizing LaNiSnF_2 , several single crystals were discovered (table 1).

Table 1. Loaded compositions and new compounds via single crystal studies

Loaded composition	Refined Structures	Structure type
LaSnNiF_3	$\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$ (I4/mmm)	USi
$\text{La}_{68}\text{Sn}_{70}$	$\text{La}_{30}\text{Sn}_{30}$ (Cmmm) ~15% yield	New
$\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$	$\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$ ~65% + unknown phase	Usi

¹Yartys, V. A; Olavesen, T; Hauback, B. C; Fjellvag, H; Brinks, H. W. J. *Alloys and Comp.* **2002**, 330-332, 141.

La₃₂Ni₂Sn₃₅

A reaction with a LaNiSnF₃ stoichiometry heated at 1200°C for four days in a high temperature vacuum furnace resulted in LaF₃ and several unknowns. Among these unknown compounds, a single crystal of La₃₂Ni₂Sn₃₅ was found. La₃₂Ni₂Sn₃₅ is body-centered tetragonal belonging to the space group I4/mmm with refined unit cell parameters of $a = 12.181(2) \text{ \AA}$, $c = 28.405(8) \text{ \AA}$ ($R = 0.0330$, $wR = 0.0700$, table 2). This compound was made in moderate yield (~65%) when loaded stoichiometrically and heated at 1250°C for four days (figure 1). It is air stable. LaSn was also present however, there were no visible single crystals of La₃₂Ni₂Sn₃₅ is similar in structure to USi which is body-centered tetragonal I4/mmm with unit cell parameters of $a = 10.587(3) \text{ \AA}$, $c = 24.310(5)$ (figure3). Another compound with similar crystal structure to USi is NpGe. The exact formula unit of uranium silicide is USi_{1.03} when all sites are fully occupied; however the refined composition is USi_{1.012} and La₃₂Ni₂Sn₃₅ compositionally agrees. La₃₂Ni₂Sn₃₅, the 64 La and 4 Ni atoms fully occupy the uranium atom sites (4e, 8f, 8j, 16n, 16m) and 70 Sn atoms occupy the Si atom sites (2a, 4c, 4e, 8h, 16n, 16m), analogous to the composition USi_{1.03}. The Si1 2a site is half occupied when USi_{1.01} is the product and not USi_{1.03}. As seen in table 3, each atom in the La₃₂Ni₂Sn₃₅ occupies uranium and silicon sites. La atoms occupy most U atom sites and Sn atoms occupy the majority of Si atom sites. The Ni1 atoms occupy Si1 atom sites and Sn3 atoms occupy U1 atoms sites. This “switching” of atom sites is probably due to atomic radii differences. Ni atoms are closer in atomic size to Si atoms than U atoms therefore, preferring

²Boulet, P; Bouëxière, D; Rebizant, J; Wastin, F. *J. Solid State Chem.* **2001**, *156*, 313.

to occupy a Si site rather than a U site.

Because the U atom sites are fully occupied by La and Ni atoms it would suggest that the LaSn structure would be similar to the USi structure. However, the LaSn structure has a orthorhombic CrB-structure type and belongs to the space group Cmc₂m with unit cell parameters $a = 4.782(3) \text{ \AA}$, $b = 11.94(1) \text{ \AA}$, and $c = 4.422 \text{ \AA}$.³ A reaction was run with a loaded composition of LaSn_{1.03}. X-ray powder diffraction patterns and several refined single crystal data sets verified that LaSn does not form in the USi structure. It appears that in order to form the USi structure, Ni must be present in the system.

³*Pearson's Handbook of Crystallographic Data for Intermetallic Phases* 2nd Ed. Vol. 2 and 4; Villars, P. and Calvert, L. D; ASM International, Materials Park, OH, USA 1991.

Figure 1. Comparison of calculated pattern from single crystal refinement and experimental powder pattern for $\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$

Table 2. Crystal data and structure refinement for $\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$.

Identification code	I4/mmm
Empirical formula	$\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$
Formula weight	455.84
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal system	tetragonal
Space group	I4/mmm
Unit cell dimensions	$a = 12.181(2)$ Å $b = 12.181(2)$ Å $c = 28.405(8)$ Å
Volume	$4214.5(17)$ Å ³
Z	2
Density (calculated)	6.825 Mg/m ³
Absorption coefficient	25.527 mm ⁻¹
F(000)	7229
Theta range for data collection	1.43 to 28.26°.
Index ranges	$-16 \leq h \leq 15$, $-15 \leq k \leq 9$, $-37 \leq l \leq 37$
Reflections collected	13286
Independent reflections	1522 [R(int) = 0.0442]
Completeness to theta = 28.26°	98.3 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1522 / 0 / 70
Goodness-of-fit on F ²	1.080
Final R indices [I > 2sigma(I)]	R1 = 0.0330, wR2 = 0.0700
R indices (all data)	R1 = 0.0378, wR2 = 0.0716
Extinction coefficient	0.000001(3)
Largest diff. peak and hole	7.024 and -5.119 e.Å

Table 3. Comparison of USi to La₃₂Ni₂Sn₃₅^a

La ₃₂ Ni ₂ Sn ₃₅	Wyckoff site	x ^b	y ^b	z ^b	U(eq) ^b	USi	x ^c	y ^c	z ^c
Ni	4e	0	0	0.0960	23(1)	Si3	0	0	0.098
La1	8f	¼	¼	¼	13(1)	U2	¼	¼	¼
La2	8j	0.2538(1)	0.5	0	9(1)	U3	0.2652	0.5	0
La3	16n	0	0.2569	0.0619	11(1)	U4	0	0.2594	0.0617
La4	16n	0	0.3530	0.1919	11(1)	U5	0	0.3567	0.1924
La5	16m	0.1826(1)	0.1826(1)	0.3846(1)	10(1)	U6	0.3132	0.3132	0.1156
Sn1	2a	0	0	0	24(1)	Si1 ^d	0	0	0
Sn2	4c	0	½	0	10(1)	Si2	0	½	0
Sn3	4e	0	0	0.2516(1)	11(1)	U1	0	0	0.2579
Sn4	4e	0	0	0.4352(1)	17(1)	Si4	0	0	0.430
Sn5	8h	0.2345(1)	0.2345(1)	0	11(1)	Si5	0.234	0.234	0
Sn6	16n	0	0.2597(1)	0.3009(1)	11(1)	Si6	0	0.259	0.3037
Sn7	16n	0	0.3792(1)	0.3987(1)	10(1)	Si7	0	0.385	0.3990
Sn8	16m	0.1319(1)	0.1319(1)	0.1524(1)	13(1)	Si8	0.125	0.125	0.1552

^a atom sites standardized by Structure TIDY program⁴^b coordinates belong to La₆₄Sn₇₀Ni₄^c coordinates belong to USi^d site is ½ occupied in USi⁴Gelato, A. and Parthe, E. *J. Appl. Crystallogr.* 1987, 20, 139.

Table 4. Anisotropic displacement parameters $\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$ ($\text{\AA}^2 \times 10^3$) for I4/mmm. The anisotropic displacement factor exponent takes the form: $2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
La1	14(1)	14(1)	12(1)	-2(1)	-2(1)	4(1)
La2	9(1)	9(1)	9(1)	0	0	0
La3	12(1)	10(1)	10(1)	0	-1(1)	0
La4	13(1)	11(1)	11(1)	0	0(1)	0
La5	11(1)	11(1)	9(1)	1(1)	1(1)	3(1)
Sn3	7(1)	7(1)	20(1)	0	0	0
Sn1	15(1)	15(1)	41(2)	0	0	0
Sn2	12(1)	9(1)	10(1)	0	0	0
Ni	11(1)	11(1)	46(2)	0	0	0
Sn4	10(1)	10(1)	33(1)	0	0	0
Sn5	10(1)	10(1)	12(1)	0	0	1(1)
Sn6	10(1)	13(1)	10(1)	0(1)	0	0
Sn7	11(1)	8(1)	11(1)	1(1)	0	0
Sn8	12(1)	12(1)	15(1)	-1(1)	-1(1)	1(1)

Comparatively, the thermal parameters on Ni1 and Sn1 (table 4) are relatively large in the U^{33} anisotropic component, implying that the anisotropic ellipsoid for Ni1 and Sn1 are large along the c-axis. The environment around Ni1 and Sn1 (table 5 and figure 2) are as follows:

1) Both atoms, Ni1 and Sn8, occupy the same type of Wyckoff site at (0, 0, z), and the centers lie close to each other at 2.82Å along the c-axis.

2) Sn3 occupies the site directly opposite in direction to Sn8 along the c-axis at 4.318Å so that the Ni1 atom are “sandwiched” between the two Sn atoms.

3) Ni1 atoms are surrounded outward from the c-axis by four Sn8 atoms forming a square pyramid with the base along the ab-plane.

4) Sn1 atoms are coplanar with four Sn5 atoms forming a square plane along the ab-plane at a distance of ~4.0Å

Apart from the short distance between Ni1 and Sn1, all other atoms along the

c-axis are farther from Ni1. Unfortunately, since Sn1 and Ni1 distances are short, the large thermal parameter along the c-direction cannot be explained by its environment. Fourier plots show no evidence of disordered bonding; the electron density surrounding Ni, Sn1, and Sn3 were spherical. CCD images show no evidence of superstructures and removing the mirror operation normal to the c-axis and refining the crystal data in a lower symmetry space group I4mm (#107) worsened thermal parameters and overall refinement.

All considering, large U^{33} anisotropic thermal parameters are intrinsic to what is in this system. Models used in refining requires centric thermal ellipsoids; however, realistically thermal ellipsoids are more likely to be acentric.

Table 5. Ni1 and Sn1 neighbor distances

Atoms	Distance
Ni1-Sn8	2.730Å
Sn1-Sn5	4.040Å
Ni1-Sn3	4.318Å
Sn1-Ni1	2.828Å

Figure 2. Thermal ellipsoid representation of Ni1 and Sn1 and their neighbors

Discussion

Structural Description

This structure is very difficult to explain because there is no simple structural correlation with existing structure types and because a large number of atoms present per unit cell. However the description for USi can be used as a very basic model to describe the structure of $\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$; a more precise description will be given in this section.

A perspective along the b-axis of the unit cell is shown in figure 3 and a table of nearest neighbors is provided in table 6. Four Sn6 atoms and four Sn8 atoms form a square antiprism (figure 4) though in the USi literature, the atoms at these positions form a distorted-square antiprism. Two Sn8 atoms and four Sn6 atoms form an octahedron as shown figure 5. These four octahedra are corner sharing through the equatorial Sn6 atoms therefore forming the buckled sheet of octahedra shown in figures 6. Four La4 and two La5 atoms are found outside of each face of these octahedra forming a large rhombohedron. Figure 7 shows the connectivity between Sn8 and Sn1 atoms to Ni1 atoms forming a trimer which extends into the octahedra sheets. The Sn8 atoms on the octahedra are bonded to Ni1 atoms at a reasonable distance of 2.73Å. Ni1 is also connected to Sn1 atoms at a slightly longer bond distance of 2.82Å. Eight La2-centered, 1-face, 1-corner sharing pentagonal prisms form a ring made from two Sn4, two Sn5, two Sn6 and one Sn2 atoms. A ring of dodecahedra are formed from Sn6 and Sn8 atoms. This cluster shares a Sn8 atom with an adjacent octahedron (figure 8).

Figure 9 is the quarter-unit cell view of $\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$. This shows the tilt of the La1-centered octahedra and their connectivity to Sn and Ni atoms.

Effects of Ni

$\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$ has a USi structure and was refined under the space group $I4/mmm$. Because Ni and La occupies uranium atom sites, one would think that the LaSn structure would be similar to that of USi. However, LaSn has an orthorhombic CrB- structure type in the space group $Cmcm$; 6% Ni alters the LaSn structure drastically. The presence of Ni may also contribute to the air stability of the compound compared to its LaSn counterpart.

Figure 3. Structure of $\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$ along the b-axis

Table 6. Distances of nearest neighbors in $\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$

<i>Atom-Atom</i>	<i>Distance Å</i>	<i>Atom-Atom</i>	<i>Distance Å</i>
La1-La4	3.683	Sn5-La2	3.246
La1-La5	3.996	Sn5-La3	3.366
La2-La2	4.163	Sn5-La5	3.575
La2-La5	4.026	Sn5-Sn8	4.675
La3-La3	4.42	Sn6-La1	3.373
La3-La4	3.876	Sn6-La4	3.297
La3-La5	4.219	Sn6-La4	3.437
La3-Ni1	3.303	Sn6-La5	3.389
La4-La4	3.580	Sn6-Sn4	4.955
La4-La4	4.157	Sn6-Sn6	4.474
La4-La5	4.457	Sn6-Sn7	3.135
La5-La5	4.449	Sn7-La2	3.331
Sn1-La3	3.586	Sn7-La3	3.494
Sn1-Sn5	4.040	Sn7-La4	3.463
Sn1-Ni	2.828	Sn7-La5	3.293
Sn2-La2	3.147	Sn7-Sn4	4.734
Sn2-La3	3.447	Sn7-Sn7	2.943
Sn2-Sn5	4.315	Sn7-Sn8	4.714
Sn3-La1	4.307	Sn8-La1	3.439
Sn3-Sn6	3.46	Sn8-La3	3.390
Sn3-Sn8	3.620	Sn8-La4	3.332
Sn4-La2	3.472	Sn8-La5	3.363
Sn4-La5	3.458	Sn8-Sn8	4.545
		Sn8-Sn8	3.213
		Sn8-Ni	2.723

Figure 4. Sn6-Sn8 square anti-prism in $\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$

Figure 5. Sn6 atoms forming the equator of the octahedron in $\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$

Figure 6. View along the b and c-axis of buckled octahedra of $\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$

Figure 7. Connectivity of Sn and Ni atoms to octahedra sheets without La atoms in $\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$

Figure 8. 8-member ring of pentagonal prism and dodecahedra (light clusters) found in between buckled octahedra sheets (dark clusters) of $\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$.

Figure 9. View of one fourth of the unit cell of $\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$.

La₃₀Sn₃₀

While trying to synthesize La₆₈Sn₇₀, La₃₀Sn₃₀ was found and the structure refined in the space group Cmmm (table 7 and figure 10). The unit cell parameters are $a = 17.667(4)$ Å, $b = 17.734(4)$ Å, and $c = 11.947(2)$ Å ($R = 0.0245$, $wR = 0.0439$). The presence of this phase can be seen in x-ray powder powder patterns as a minor phase (yield ~15%) as seen in figure 11. The major phase found in the powder patterns is LaSn as reported in the Pearson's Handbook of Crystallography by Eremenko et al.¹ The reported lattice parameters of LaSn are $a = 4.782(3)$ Å, $b = 11.94(1)$ Å, and $c = 4.422(3)$ Å and it belongs to the space group Cmc m .² It appears that the new Cmmm phase does not form at low temperatures and must be brought up to high temperatures (~1250°C) for 4 or more days and quickly cooled (~200°C/hr). The major known Cmc m phase undergoes incongruent melting at 1297°C.

In the Cmc m phase, La and Sn atoms occupy 4c Wyckoff sites with coordinates at (0, 0.4360, 1/4) and (0, 0.14525, 1/4), while La and Sn atoms in the Cmmm occupy several different sites other than the (0, y, z) sites therefore resulting in a complex structure. The x-ray powder diffraction patterns of the Cmmm phase show a few low intensity peaks at ~33° and at ~42° in 2 θ and broadening of peaks in the Cmc m phase where peaks in both phases tend to overlap.

The La atoms fully occupy the 4h, 4j, 4l, 8p, and 16r Wyckoff sites and the Sn atoms fully

¹Eremenko, V. N, Bulanova, M.V., Martsenyuk, P. S, Listovnichii, V. E; *Soviet Powder Metallurgy and metal Ceramics*, Translates from *Poroshkovaya Metallurgiya*, Kiev, 1989, 28(2) 145.

²*Pearson's Handbook of Crystallographic Data for Intermetallic Phases* 2nd Ed. Vol. 4; Villars, P. and Calvert, L. D; ASM International, Materials Park, OH, USA 1991.

occupy 2a, 2b, 4h, 4i, 4j, 4k, 8m, 8n, 8o, and 8q sites as seen in table 8. The thermal ellipsoid for Sn10 atoms is relatively larger than the those of other atoms (table 9). This site is fully occupied and therefore partial occupancy does not explain the large U^{33} value. Studying the environment and the nearest neighbors surrounding Sn10 may clarify the large U^{33} value. Two Sn3 atoms lie along the b-axis at a distance of 3.072 Å from Sn10 which is a slightly long Sn-Sn bond distance. Four La3 atoms lie along the ab-plane to form a square at a distance of 3.879 Å from Sn10, and there are Sn9 atoms along the c-axis at a distance of 3.704 Å from Sn10. All La-Sn and Sn-Sn distances are fairly large, however the largest distance is the Sn-Sn distance between Sn10 and Sn 9 atoms. Because of the large Sn-Sn distances, Sn 10 evidently has a rattling motion along the c-direction as suggested in the thermal parameters. However, heavier atoms tend not to rattle, but instead have an intrinsic (static) disorder. Removing the mirror plane normal to the c-axis and refining the crystal system in a lower symmetry space group, Cmm2, did not affect the quality of the refinement. There is also no evidence of a superstructure from the x-ray data.

Table 7. Crystal data and structure refinement for La₃₀Sn₃₀

Identification code	cmmm
Empirical formula	La ₃₀ Sn ₃₀
Formula weight	286.22
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Cmmm
Unit cell dimensions	a = 17.667(3) Å b = 17.734(2) Å c = 11.9467(17) Å
Volume	3743.0(9) Å ³
Z	2
Density (calculated)	6.857 Mg/m ³
Absorption coefficient	26.465 mm ⁻¹
F(000)	6420
Theta range for data collection	1.63 to 28.25°
Index ranges	-20 ≤ h ≤ 23, -23 ≤ k ≤ 20, -15 ≤ l ≤ 15
Reflections collected	11809
Independent reflections	2478 [R(int) = 0.0321]
Completeness to theta = 28.25°	96.1 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2478 / 0 / 95
Goodness-of-fit on F ²	1.164
Final R indices [I > 2σ(I)]	R1 = 0.0245, wR2 = 0.0439
R indices (all data)	R1 = 0.0304, wR2 = 0.0451
Extinction coefficient	0.000033(2)
Largest diff. peak and hole	5.475 and -1.590 e.Å ⁻³

Figure 10. $\text{La}_{30}\text{Sn}_{30}$ along the a , b , and c -axis; light grey- Sn, dark grey- La.

Figure 11(a). X-ray powder pattern in the low angle range of $\text{La}_{30}\text{Sn}_{30}$ (circle); * show the peaks and broadening of LaSn peaks in the Cmcm phase (square)

Figure 11(b). X-ray powder diffraction pattern in the 2θ range of 28-33°

Figure 11 (c). X-ray powder diffraction pattern in the 2θ range of 33-45°

Table 8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{La}_{30}\text{Sn}_{30}$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	Wyckoff site	x	y	z	$U(\text{eq})$
La(1)	4l	0	5000	2691(1)	10(1)
La(2)	8p	1009(1)	3373(1)	0	10(1)
La(3)	8p	1938(1)	1028(1)	0	12(1)
La(4)	4j	0	3154(1)	5000	13(1)
La(5)	4h	1611(1)	0	5000	12(1)
La(6)	16r	3120(1)	1320(1)	3233(1)	10(1)
La(7)	16r	939(1)	1646(1)	2561(1)	13(1)
Sn(1)	8n	0	3233(1)	2369(1)	11(1)
Sn(2)	8o	1795(1)	0	2289(1)	13(1)
Sn(3)	4i	0	1732(1)	0	14(1)
Sn(4)	8m	2500	2500	1365(1)	11(1)
Sn(5)	8q	1748(1)	2080(1)	5000	13(1)
Sn(6)	8o	3378(1)	0	1244(1)	10(1)
Sn(7)	4j	0	1250(1)	5000	19(1)
Sn(8)	4h	3720(1)	0	5000	12(1)
Sn(9)	4k	0	0	3101(1)	23(1)
Sn(10)	2a	0	0	0	39(1)
Sn(11)	2b	5000	0	0	10(1)

Table 9. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{La}_{30}\text{Sn}_{30}$. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
La(1)	10(1)	9(1)	10(1)	0	0	0
La(2)	10(1)	10(1)	9(1)	0	0	0(1)
La(3)	16(1)	11(1)	9(1)	0	0	-1(1)
La(4)	13(1)	18(1)	7(1)	0	0	0
La(5)	14(1)	14(1)	7(1)	0	0	0
La(6)	11(1)	11(1)	9(1)	0(1)	0(1)	-1(1)
La(7)	13(1)	13(1)	14(1)	2(1)	1(1)	-1(1)
Sn(1)	13(1)	10(1)	9(1)	0(1)	0	0
Sn(2)	18(1)	10(1)	11(1)	0	3(1)	0
Sn(3)	17(1)	11(1)	15(1)	0	0	0
Sn(4)	12(1)	10(1)	12(1)	0	0	0(1)
Sn(5)	13(1)	14(1)	11(1)	0	0	-1(1)
Sn(6)	11(1)	11(1)	8(1)	0	0(1)	0
Sn(7)	26(1)	18(1)	14(1)	0	0	0
Sn(8)	17(1)	12(1)	8(1)	0	0	0
Sn(9)	18(1)	14(1)	38(1)	0	0	0
Sn(10)	21(1)	2(1)	74(2)	0	0	0
Sn(11)	12(1)	10(1)	8(1)	0	0	0

Structural Description

The $\text{La}_{30}\text{Sn}_{30}$ structure is difficult to describe because it contains many atoms to the unit cell. Although there are many atoms, few are within bonding distances as seen in table 10. There are several Sn-Sn bonds in the structure; this can be seen in figure 12. These bonds are slightly long; bond distances range between 3.0- 3.25 Å. La atoms form bonds with Sn atoms with the exception of Sn3 and Sn10 (figure 13). The bond distances range from 3.1 -3.4 Å.

A type of cluster that is apparent in this structure is a Sn-centered biaugmented triangular prism (figure 14 a). Biaugmented triangular prisms, in general, have 8 vertices, 17 edges, 8 triangular faces, and 1 square face. This cluster can be described by two square pyramids fused to two square faces of a trigonal prism. There are two such biaugmented prisms. One set of these prism is made from La2, La3, La6, and La7 atoms with a Sn4 atom at the center of the cluster, and another prism is made from La4, La5, La6, and La 7 atoms with Sn5 atoms in the center. These two clusters share triangular faces through La6 and La7 atoms (figure 14b).

LaSn single crystals crystallizing in the Cmcm space group could not be obtained. Hence, only x-ray powder diffraction patterns were studied and compared to the CrB - structure. It was found that the $\text{La}_{30}\text{Sn}_{30}$ form good single crystals and that the structure can be easily refined.

Table 10. Bonding distances between La and Sn atoms in La₃₀Sn₃₀

Atoms	Distance Å	Atoms	Distance Å	Atoms	Distance Å
La1-Sn1	3.157	La5-Sn2	3.255	Sn2-Sn6	3.062
La1-Sn6	3.347	La6-Sn2	3.498	Sn2-Sn9	3.317
La1-Sn8	3.487	La6-Sn4	3.249	Sn3-Sn10	3.072
La1-Sn11	3.215	La6-Sn5	3.486	Sn5-Sn5	3.047
La2-Sn1	3.354	La6-Sn6	3.366	Sn6-Sn11	3.228
La2-Sn3	3.412	La6-Sn8	3.369	Sn7-Sn9	3.172
La2-Sn4	3.464	La7-Sn1	3.275		
La2-Sn6	3.422	La7-Sn2	3.303		
La2-Sn11	3.392	La7-Sn3	3.483		
La3-Sn2	3.296	La7-Sn4	3.456		
La3-Sn3	3.645	La7-Sn5	3.336		
La3-Sn4	3.235	La7-Sn7	3.426		
La3-Sn6	3.464	La7-Sn9	3.418		
La4-Sn1	3.146				
La4-Sn7	3.376

Figure 12. Sn-Sn bonds; light grey- Sn atoms, dark grey- La atoms.

Figure 13: La-Sn distances ranging from 3.1 -3.4Å (black); Sn-Sn bonds (grey)

Figure 14. a) The biaugmented triangular prism in $\text{La}_{30}\text{Sn}_{30}$

Figure 14. b) Face sharing biaugmented triangular prism clusters in $\text{La}_{30}\text{Sn}_{30}$

CONCLUSIONS

Two novel intermetallic compounds containing lanthanum and tin have been obtained for the first time. Single crystal structures of these two phases, $\text{La}_{30}\text{Sn}_{30}$ and $\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$ have been studied by X-ray crystallography. $\text{La}_{30}\text{Sn}_{30}$ is a new 1 : 1 binary containing La and Sn and has been refined in the Cmmm space group. This phase was made at high temperatures ($>1200^\circ\text{C}$) from a loaded composition of $\text{La}_{68}\text{Sn}_{70}$. Unlike the reported 1:1 binary, LaSn which crystallizes in the Cmcn space group (only powder X-ray diffraction studies reported), $\text{La}_{30}\text{Sn}_{30}$ forms good crystals for structural determination. The crystal structure of $\text{La}_{30}\text{Sn}_{30}$ show Sn-Sn dimers and Sn-centered, face-sharing biaugmented triangular prisms composed of La atoms. $\text{La}_{30}\text{Sn}_{30}$ does not belong to any known structure -type.

$\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$ was obtained in high yields at high temperatures ($>1200^\circ\text{C}$) and refined in the $I4/mmm$ space group. It belongs to the USi structure type in which the Ni / Sn atoms occupy the Si sites, and La / Sn atoms occupy the U sites. The crystal structure of $\text{La}_{32}\text{Ni}_2\text{Sn}_{35}$ consists of buckled sheets made from La-centered, corner-shared octahedra of Sn. These sheets are intraconnected through Ni-Sn-Ni bonds along the c-axis. The crystals are not air sensitive, unlike $\text{La}_{30}\text{Sn}_{30}$, which can be attributed to the presence of Ni in the crystal structure.

ACKNOWLEDGEMENTS

I would like to thank my major Professor John D. Corbett for all his guidance and patience during my research term in the Chemistry Department.

I would also like to thank:

- My mom who urged me to do my best
- Dr. Ashok Ganguli who has helped me during his visit from India
- Michael Vasbinder who amused me and comforted me during difficult times; He also tried very hard to keep up with chores
- The Corbett lab group
- Last but not least, my friends here in Ames