Powder X-Ray Diffraction and Electron Microscopy Studies of Polycrystalline Au_2PrIn

Robin T. Macaluso,^{1*} Brian Wells,² Chad Wangeline,² Kenneth Cochran,² Benjamin K. Greve²

¹Department of Chemistry and Biochemistry, University of Texas at Arlington, Arlington, TX 76019

²Department of Chemistry and Biochemistry, University of Northern Colorado, Greeley, CO 80639

*Corresponding Author: robin.macaluso@uta.edu

Abstract

Heusler intermetallic compounds, with a general formula of X_2YZ encompass over 1500 known compounds and are considered strong candidates in thermoelectrics and solar cell applications as well as their more fundamental phenomena such as topological insulators. It is important therefore, to investigate the synthesis and treatment conditions. Polycrystalline samples of Au_2PrIn were synthesized and characterized by powder X-ray diffraction. Selective etching of impurity phases was followed and studied using secondary and backscatter electron microscopy and powder X-ray diffraction.

Keywords: Au_2PrIn , Heusler, scanning electron microscopy

Graphical Abstract

Synopsis

Polycrystalline samples of the Heusler compound, Au_2PrIn , were synthesized using arc-melting techniques. Powder X-ray diffraction and scanning electron microscopy methods were used to optimize synthesis of polycrystalline Au_2PrIn . Secondary and backscatter electron images showed that nitric acid could be used to remove small amounts of gold-rich impurities.

1. Introduction

Heusler phases are a large class of intermetallic compounds (over 1500) with a 2:1:1 stoichiometry. The crystal structure of Heusler compounds, with a general chemical formula of X_2YZ , is shown in Figure 1. The X, Y, and Z atoms occupy the $8c$, $4a$ and $4b$ Wyckoff sites, respectively. The compounds crystallize in the $Fm\bar{3}m$ space group (No. 225) and are described and possess four interpenetrating face-centered cubic sublattices, two of which are occupied by the X metal.

Unlike most intermetallic compounds, Heusler compounds uniquely follow valence electron counts. This has led to an abundance of investigations of Heusler compounds as candidates in thermoelectrics, solar cell, and for their more fundamental phenomena such as topological insulators. Magnetic X_2YZ compounds show various magnetic behavior and properties, such as magneto-optical [1], magnetocaloric [2] and magneto-structural phase transitions [3]. Such phase transitions lead to Heusler compounds as shape-memory alloys. One well-known example is demonstrated in Ni_2MnGa , which undergoes a martensitic transition at 210 and 370 K [4, 5]. Shape-memory alloys undergo stress-driven (typically with temperature) martensitic transitions where the low-temperature phase is crystallographically unique from the high-temperature phase and results from a homogeneous lattice deformation. An excellent review of Heusler compounds will provide the reader with further insight into the rich history of Heusler phases [6].

Ag_2PrIn is a Heusler compound that has been shown to exhibit a rarely observed quadrupolar Kondo effect. The quadrupolar Kondo effect originates from the combination of the f^2 electron configuration and the cubic symmetry of the Pr^{3+} ion. Under these conditions, the quadrupolar moments of the Pr^{3+} hybridize with conduction electrons to produce unusual magnetic and thermodynamic behavior [7-10].

Because the bonding between Pr and Ag play an important role in its physical behavior, we investigated the synthesis and characterization of Au_2PrIn . Because Ag and Au both belong to Group 11 of the periodic table, we expected that Au_2PrIn would also form a Heusler phase and that we should be able to make direct comparisons between Au_2PrIn and Ag_2PrIn . In this paper, we report the synthesis of polycrystalline Au_2PrIn and characterization of these samples by scanning electron microscopy.

2. Materials and Methods

2. 1. Synthesis

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4 Pr, Au, and In were weighed stoichiometrically and placed on a copper hearth of an arc-melter.
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6 The chamber of the arc-melter was then evacuated and back-filled with ultra-pure argon gas three
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8 times. With Ar gas flowing through the chamber, the metal pieces were melted into a button and
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10 allowed to cool on a water-cooled copper hearth. The button was flipped and melted three times to
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12 ensure homogeneity. The resulting button was metallic in luster. No weight loss occurred during the
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14 synthesis. A small portion of the button was separated and finely ground in an agate mortar and pestle
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16 for powder diffraction experiments. The sample is stable in air.

17 The pellet was mounted into an epoxy stub. The surface of the pellet was subsequently polished
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19 in order of 15, 6, and 3 and 1 micron diamond polishing disks. An optical microscope was used to visually
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21 inspect the surface for smoothness before applying the next polishing disk.

22 A plastic pipette was used to place 1-2 drops of acid onto the polished surface of the Au₂PrIn to
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24 etch. Glacial acetic acid and various concentrations of HNO₃ were tested. Once the acid was placed onto
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26 the surface of the pellet, a timer was started for various durations to determine the optimal time for
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28 etching the sample surface. Once the timed etch was complete, the sample surface was immediately
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30 rinsed with copious amounts of distilled water and dried in air. The sample was then placed into the
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32 vacuum chamber of an SEM for elemental analysis.

33 *2.2 Powder X-ray Diffraction*

34 Powder X-ray diffraction (XRD) data were collected on ground samples of Au₂PrIn using a GBC
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36 powder X-ray diffractometer equipped with a Cu K α_1 radiation source ($\lambda = 1.54184 \text{ \AA}$). A range of 2θ
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38 values from 10° to 110° , with a scan rate of $0.1^\circ/\text{min}$ and a step size of 0.01° were used. High
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40 resolution XRD data were collected through the mail-in service at the 11-BM beamline at the Advanced
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42 Photon Source (APS) at Argonne National Laboratory. Discrete detectors covering an angular range from
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44 -6 to $16^\circ 2\theta$ were scanned over a $34^\circ 2\theta$ range, with data points collected every $0.001^\circ 2\theta$ and scan
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46 speed of $0.01^\circ/\text{s}$.

47 Refinements of synchrotron data were carried out using GSAS software package to determine
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49 lattice parameters [11, 12]. All data were collected at room temperature.

50 *2.3 Scanning Electron Microscopy*

51 Surfaces of Au₂PrIn were characterized by electron dispersive spectroscopy (EDS) using a JEOL
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53 6610LV Scanning Electron Microscope (SEM), equipped with an Oxford XMax EDS detector with a
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55 20mm^2 window, operated with an accelerating voltage of 20 kV and a working distance of 10 mm. The
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57 arc-melted button was cut into four fragments. Several spots on each fragment were analyzed for 45 s,
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and the results from at least five measurements were averaged, and atomic ratios were normalized to Pr.

ImageJ is an open source software program developed by the National Institutes of Health that can evaluate area and pixel statistics of images [13]. ImageJ was applied to SEM images to quantify compositions of the samples.

3. Results and Discussion

3.1. X-ray Diffraction

LeBail fits were performed on the diffraction data collected at APS (provided in Supplementary Material) to determine the unit cell dimension $a = 7.0507(2)$ Å, which is similar to previously reported value of 7.055 Å [14]. It is well-known that diffraction patterns can be used to investigate order or disorder in Heusler compounds. Disorder within the YZ sublattice extinguishes odd superlattice diffraction peaks, e.g., $h + k + l = 2n + 1$, while disorder between the X and YZ sublattice extinguishes $(h + k + l)/2 = 2n + 1$, e.g., (200) peaks. Figure 2 shows an X-ray diffraction pattern of the sample as synthesized. The absence of $(h + k + l) = 2n + 1$ peaks, e.g., (111) and (331) calculated to be at $2\theta \sim 5.8^\circ$ and 14.7° , respectively, suggests disorder between Pr and In. Rietveld refinements were not performed because the severe overlap of peaks from the impurity and desired Au_2PrIn phases led to inconclusive results. The major portion of the sample can be identified as Au_2PrIn , but some peaks, i.e., $2\theta \sim 34^\circ$, could not be matched to Au_2PrIn and indicate the presence of an impurity. The impurity peaks can be more easily seen in the Figure 2 inset. Based on the relative peak intensity, it is estimated that this impurity is approximately 10% of the entire sample volume. We compared the powder patterns of binary compounds to the collected powder pattern, but were unable to successfully identify the composition of the impurity through diffraction.

3.2. Sample Composition

In SEM, inelastic scattering of secondary electrons from the incident electron beam varies exponentially with sample depth. Hence, images with high spatial resolution can be obtained. Elastic scattering of backscattered electrons, on the other hand, are responsive to composition contrast. Generally, brighter areas in backscattered images correspond to compositions of higher electron density, and darker areas correspond to compositions of lower electron density. Quantification can be performed with backscattered electron images [15]. Therefore, secondary and backscattered electron images can provide complimentary information about a material.

Figure 3a shows a typical secondary electron image of the sample surface. The surface is relatively smooth; however, small pits and valleys are distributed over the entire surface. These features are less than $1\mu\text{m}$ and may have resulted from surface polishing or they could have been artifacts of the sample.

Figure 3b shows a typical backscattered electron image of the same sample surface as that observed in Figure 3a. Three distinct regions can be observed: bright (light grey), intermediate (grey), and dark (black). The bright, intermediate and dark areas accounted for approximately 9.36, 83.0 and 7.44% of the surface area, respectively. This sample composition agrees with our estimate of impurity volume based on X-ray diffraction.

Energy-dispersive spectra (EDS) were collected for at least three spots on each area to semi-quantitatively determine the composition of each area. The bright and intermediate areas correspond to $\text{Au}_{3.7(2)}\text{Pr}_{1.2(2)}\text{In}_{1.0(1)}$ and $\text{Au}_{2.6(2)}\text{Pr}_{1.2(1)}\text{In}_{1.0(1)}$, respectively. These compositions are statistically different from each other. Upon comparing the backscattered and secondary electron images of the same surface, we conclude that the black areas observed in the backscattered image correspond to the void spaces observed in the secondary electron images. Renormalizing the $\text{Au}_{2.6(2)}\text{Pr}_{1.2(1)}\text{In}_{1.0(1)}$ formula to Indium results in $\text{Au}_{2.2(1)}\text{Pr}_{1.0(1)}\text{In}_{0.8(1)}$, where the sample can be viewed as deficient in Indium. The deficiency may have been due to the low vapor pressure of In (10^{-8} mmHg at 800 K) compared to Au and Pr (which do not vaporize until 1400 and 1000 K, respectively)[16, 17].

3.3. Etching

In our first attempt at etching the pellet, glacial acetic acid was applied to the sample surface. After 5 h and 45 min of exposure to acetic acid, no changes were observed. In fact, the epoxy mount degraded after some exposure to acetic acid, and the Au_2PrIn sample was remounted into fresh epoxy and re-polished.

A 1M hydrochloric (HCl) acid solution was then applied to the sample surface. After 2 h, no etching of the sample surface was observed. The sample surface was cleaned with deionized (DI) water and acetone before applying a 1M nitric acid (HNO_3) solution.

After 3.5 h of exposure to 0.10M and 1M HNO_3 solutions, there were not any observable changes on the sample surface. Applying a 5M HNO_3 solution to the sample, however, resulted in more drastic changes to the surface, which can be seen in Figure 4. Figures 4a and 4b show the sample surface before and after application of 5M HNO_3 for 3 hours. Backscatter images show valleys in bright regions, while the rest of the surface remains unchanged. EDS spectra were collected to determine that bright

and intermediate regions correspond to $\text{Au}_{3.9(5)}\text{Pr}_{1.2(3)}\text{In}_{1.0(3)}$ and $\text{Au}_{2.7(5)}\text{Pr}_{1.3(3)}\text{In}_{1.0(3)}$, respectively. These compositions match the compositions of the sample before etching. Hence application of HNO_3 is simply resulting in etching away the Au-rich phase; the sample had not undergone chemical changes.

After an additional hour (for a total of 4 h) of exposure to 5M HNO_3 , another backscatter image (shown in Figure 4c) was collected. This image was collected from another location on the sample surface (different than the location shown in Figures 4a and 4b), so we cannot firmly conclude that etching had progressed with time; however, the presence of valleys in the bright regions indicates that etching was not isolated to one small spot on the sample surface. Figure 4d shows the same location as Figure 4c after 5.5 h of exposure to 5 M HNO_3 . The valleys in Figure 4d are located in the same spots, but are considerably larger than those in Figure 4c. This observation leads us to conclude that etching of the $\text{Au}_{3.9(5)}\text{Pr}_{1.2(3)}\text{In}_{1.0(3)}$ phase was still proceeding.

Conclusion

Arc-melting synthesis methods yielded two phases detectable by backscattered electron microscopy: $\text{Au}_{3.9(5)}\text{Pr}_{1.2(3)}\text{In}_{1.0(3)}$ and $\text{Au}_{2.7(5)}\text{Pr}_{1.3(3)}\text{In}_{1.0(3)}$. We demonstrated the ability to selectively etch the Au-rich phase, $\text{Au}_{3.9(5)}\text{Pr}_{1.2(3)}\text{In}_{1.0(3)}$, when both $\text{Au}_{3.9(5)}\text{Pr}_{1.2(3)}\text{In}_{1.0(3)}$ and $\text{Au}_{2.7(5)}\text{Pr}_{1.3(3)}\text{In}_{1.0(3)}$ are present in a matrix.

Gold is generally considered to be insoluble in acid. It has been previously shown that small quantitative amounts of gold can be recovered from filtrates of nitric acid that was boiled with solid gold or gold-containing alloys [18]. The ability to dissolve only small amounts of Au allowed us to selectively etch the Au-rich phase of the $\text{Au}_{3.9(5)}\text{Pr}_{1.2(3)}\text{In}_{1.0(3)}$ / $\text{Au}_{2.7(5)}\text{Pr}_{1.3(3)}\text{In}_{1.0(3)}$ mixture. We determined that a minimum concentration of 5M HNO_3 was needed to successfully etch, and that the etching process requires at least 5 h. The etching process was visually followed by secondary and backscatter SEM images. Stronger concentrations of HNO_3 and longer exposure times (greater than 5 h) could be used to determine optimal etching conditions.

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Figure Captions

Figure 1. The crystal structure of X_2YZ Heusler compounds highlighting two interpenetrating *fcc* sublattices (marked as dashed lines). Blue, green and red represent X, Y, and Z atoms, respectively.

Figure 2. Laboratory powder XRD pattern with most intense peaks of the Au_2PrIn phase indexed. Peaks of the Au_2PrIn phase, shown as black crosses, match the calculated pattern, shown as red tick marks. Green line represents the background fit. *Inset*: A zoomed-in portion of XRD pattern. Peaks in the XRD pattern match the calculated pattern, shown as red tick marks. Asterisks mark unidentified impurity phases.

Figure 3. a) Secondary and b) backscatter images taken of the same spot on Au_2PrIn surface. The dark grey “valleys” in a) are observed as black features in b).

Figure 4. Backscatter images of Au_2PrIn surface after exposure to 5 M HNO_3 a) with no exposure to HNO_3 and after b) 3 h, c) 4 h, and d) 5.5 h of exposure to 5 M HNO_3 .

Figure 1.

Figure 2.

Figure 3.

Figure 4.