Chem. Mater. **2000,** *12,* 697−700

High-Pressure Stability, Pressure−Volume Equation of State, and Crystal Structure under Pressure of the Thermoelectric Material $IrSb_3$

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Received July 15, 1999. Revised Manuscript Received December 23, 1999

There is considerable current interest in filled and unfilled skutterudites because of their potential applications as thermoelectric materials. We have compressed the unfilled skutterudite $IrSb_3$ to pressures of 42 GPa and find that it is surprisingly stable in view of the presence of large cavities in the structure. This has implications for the both the implantation of atomic or molecular species within the cavities by means of pressure and the stability of $IrSb_3$ under hot isostatic pressing conditions. From a fit to the pressure−volume equation of state, values were obtained for the bulk modulus and pressure derivative of the bulk modulus of 136 ± 5 GPa and 4.8 ± 0.5, respectively. Rietveld refinement of the crystal structure at high-pressure further demonstrates the stability of the cavities under compression.

Introduction

There is considerable interest in the thermoelectric properties of filled and unfilled skutterudites because they can exhibit substantial thermoelectric figures of merit. The crystal structure of a skutterudite is body centered cubic with $Im3$ symmetry. An unfilled skutterudite, such as $IrSb_3$, has an open crystal structure (Figure 1) which contains cavities. A filled skutterudite, such as $CeFe_4Sb_{12}$,[1] has electropositive atoms filling the cavities of the skutterudite structure. Here we report the stability, pressure−volume relation to 42 GPa, and crystal structure to 4.7 GPa, as determined by Rietveld refinement, for the unfilled skutterudite $IrSb_3$.[2] We find that the structure is surprisingly stable to compression in view of the presence of the relatively large cavities. This suggests that compression of $IrSb_3$ together with noble gases or molecules such as diatomic gases may permit the filling of the cavities with these species. Filling of the cavities in this manner has been a long sought after goal because according to the "electron crystal/phonon glass" model[3] for thermoelectric materials it should reduce the thermal conductivity of unfilled skutterudites, while having little effect on their electronic properties. A reduction in thermal conductivity would result in a substantial increase in the product of the thermoelectric figure of merit Z and the temperature T. ZT, which is defined as

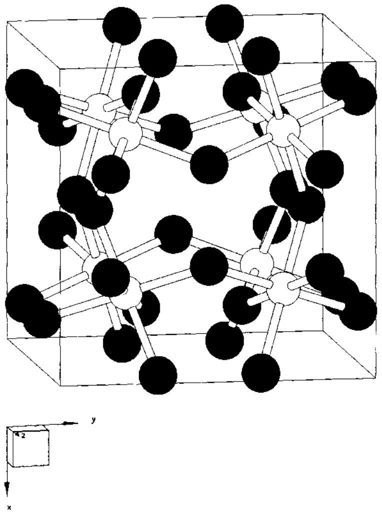

Figure 1. Crystal structure of the unfilled skutterudite $IrSb_3$ (space group $Im3$). Ir atoms are unshaded, while Sb atoms are black. One cavity surrounded by 12 Sb atoms can be seen in the center of the unit cell. Other cavities are located at the vertexes of the cubic unit cell. The coordination of the Sb atoms around the Ir atoms is slightly distorted from octahedral.

$$ZT = \frac{S^2\sigma}{\kappa} T \tag{1}$$

where S is the thermoelectric power (V/K), σ is the electrical conductivity (S/cm), and κ is the thermal conductivity (W·cm/K), determines the fraction of Car-

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10.1021/cm990446i CCC: $19.00

not efficiency attainable in a solid-state thermoelectric cooling device. Successful incorporation of atomic or molecular species into the cavities would provide a valuable test of the electron crystal/phonon glass model.[3]

The stability of $IrSb_3$ under extreme compression at room temperature suggests that it is possible that this material may be stable under compression at higher temperatures. Hot pressing techniques are typically used to prepare $IrSb_3$ for use as a thermoelectric material and it is critically important to know if there is any decomposition at the pressure and temperature typically used for pressing. It has been questioned whether incipient decomposition to small amounts of impurity phases, which would have a substantial impact on the thermoelectric transport properties, may be a problem. Using the Clapeyron equation, we estimate the stability of $IrSb_3$ under hot pressing conditions.

Experimental Section

Stoichiometric quantities of iridium (99.99%) and antimony (99.9999%) were placed in a chemical vapor deposited boron nitride crucible covered with a lid. The crucible was enclosed in a quartz ampule and sealed under 0.25 atm of argon. The system was kept at a temperature of 1013 °C for 81 h. The resulting product was cooled, ground, and mixed, then resealed in the BN crucible and a new quartz ampule under a partial argon atmosphere, and annealed for another 76 h at 1013 °C. The dark gray, homogeneous product obtained did not show any adherence to the BN crucible.

The product was ground with a mortar and pestle and then in a tungsten carbide ball mill with ethylene glycol. The ethylene glycol was subsequently evaporated in a vacuum oven at 170 °C under Ar and the powder was sieved through a 400-mesh (38 μm) stainless steel sieve. BET surface area measurements and SEM observations gave grain sizes between 3 and 10 μm. EDS analysis showed no elements other than Ir and Sb. Powder X-ray diffraction data exhibited only those peaks corresponding to the skutterudite phase and to the Si powder used as an internal standard. A lattice parameter of $a = 9.2512 \pm 0.0011$ Å was determined.

Before high-pressure experiments were performed, the $IrSb_3$ powder was further ground using a McCrone micronizing mill. The $IrSb_3$ powder was mixed with an Ag powder internal standard in a 9:1 ratio by mass and loaded into a Mao-Bell diamond anvil cell (DAC).[4] Several drops of a 4:1 ratio by volume methanol:ethanol solution were added to the powder mixture to ensure hydrostatic pressure conditions. A very small amount of powdered ruby (Cr^{3+} doped Al_2O_3) was placed on top of the $IrSb_3$–Ag powder mixture in the sample chamber and used for pressure determination. T301 stainless steel gaskets were indented to a depth of ~50 μm and drilled to a diameter of ~150 μm. Pressure was measured using both ruby fluorescence and the pressure dependence of the Ag diffraction peaks.

Powder diffraction patterns were obtained within the DAC using a diffraction system consisting of a Guiner–Johansson monochromator that allows for the focusing of a nearly monochromatic X-ray beam ($I_{K\alpha2} \cong 0.12 I_{K\alpha1}$) on the sample. A Rigaku RU-200H rotating anode generator with a 0.1 × 1 mm molybdenum fine focus target is used as the X-ray source in this arrangement, and diffracted X-rays are collected in a 50 mm radius film cassette on Kodak DEF-392 X-ray film. Diffraction patterns were then digitized through scanning into a Macintosh computer, where they were collapsed into diffraction profiles using the program of Nguyen and Jeanloz.[5]

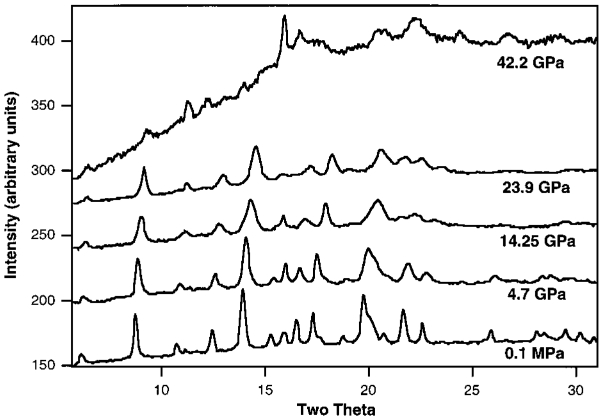

Figure 2. Diffraction profiles of $IrSb_3$ obtained at several pressures within the DAC.

Table 1. Pressure–Volume Relation for $IrSb_3$

P (GPa)	a (Å)	V (Å^3)	V/V_o	M_{20}[a]
1.9	9.2111	781.52	0.98706	29
4.2	9.1867	775.31	0.97922	27
4.7	9.1491	765.84	0.96726	28
6.3	9.1350	762.31	0.96280	37
9.5	9.0706	746.29	0.94257	19
14.3	8.9956	727.93	0.91939	16
15.3	8.9771	723.44	0.91371	33
20.8	8.8887	702.29	0.88700	28
23.9	8.8649	696.65	0.87988	23
26.0	8.8261	687.55	0.86839	39
33.8	8.7391	667.43	0.84297	27
42.2	8.6731	652.40	0.82399	22

[a] M is the figure of merit obtained from AIDS.

Refinement of the lattice parameter of $IrSb_3$ at various pressures was done using the program NBS*AIDS.[6] Rietveld analysis was performed using the program GSAS.[7] Background, lattice, peak profile, phase fraction, atomic position, preferred orientation, and isotropic thermal parameters were refined. The psuedo-Voigt profile function of Thompson, Cox, and Hastings was used to model peak shapes,[8] while the Dollase–March model was used for preferred orientation.[9]

Results and Discussion

Diffraction profiles of $IrSb_3$ obtained at pressures to 42 GPa indicate that there is no change in crystal structure type (Figure 2). All diffraction peaks not associated with $IrSb_3$ can be attributed to either the Ag powder used as an internal standard or the ruby powder included for pressure measurement. The pressure and relative volume data for $IrSb_3$ (Table 1, Figure 3) were fit to the universal equation of state (EOS):[10]

$$P = \frac{3(1-x)}{x^2} B_o[\exp \eta(1 - x)] \qquad (2)$$

where $x = (V/V_o)^{1/3}$, $\eta = 3/2(B_o' - 1)$, B_o is the bulk

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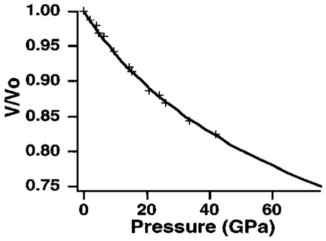

Figure 3. Plot of the $IrSb_3$ P−V EOS determined from the relative volume vs pressure data shown in Table 2. The solid line shows the fit of the experimental points (crosses) to the universal equation of state.

modulus, which gives fundamental information about the bonding and stability of a structure, and B_o' is the first derivative of the bulk modulus. B_o and B_o' were determined to be 136 ± 5. GPa and 4.7 ± 0.5, respectively. The value of 136 GPa for the isothermal bulk modulus of $IrSb_3$ is ~20% larger than the value of 112.1 GPa determined by means of ultrasonic measurements.[2] Such differences in bulk moduli obtained with the two techniques are typical; however, as ultrasonic techniques are affected by the presence of grain boundaries and thus give lower values for B_o. The profile obtained at 42.2 GPa (Figure 2) is characteristic of $IrSb_3$ with a lattice parameter a = 8.6731 Å (Table 1). There is considerable diffuse scattering present in this profile, suggesting that the sample may have begun to amorphize at this extreme pressure. Further investigation by means of X-ray diffraction and Raman spectroscopy at higher pressures could determine if amorphization is actually occurring.

The relatively large value of 136 GPa determined for the bulk modulus of $IrSb_3$ is somewhat surprising in view of the open structure of this unfilled skutterudite. Such a system might be expected to collapse readily or undergo a phase transformation when compressed. Upon quenching the sample from 42 to 6 GPa, the diffraction pattern was still indicative of $IrSb_3$ with lattice parameter $a = 9.1166$ Å, in good agreement with the pressure−volume relation previously determined.

To determine the changes in crystal structure and cavity shape under pressure, a Rietveld analysis using the program GSAS was performed.[7] At ambient pressure the agreement factors between calculated and experimental diffraction profiles were $R_{wp} = 0.0172$, $R_p = 0.0122$, $\chi^2 = 0.0529$, and $R_F{}^2 = 0.1100$. For the diffraction profile collected at a pressure of 4.7 GPa (Figure 4) the agreement factors were $R_{wp} = 0.0124$, $R_p = 0.0095$, $\chi^2 = 0.02845$, and $R_F{}^2 = 0.0594$. At 4.7 GPa, the Sb atomic coordinates, which determine the size and shape of the cavities, refined to $y = 0.33920$ and $z = 0.15365$. The Ir coordinates and Sb x coordinate are constrained by symmetry to $^1/_4$, $^1/_4$, $^1/_4$, and 0, respectively. At ambient pressure, the Sb atomic coordinates refined to $y = 0.3376$ and $z = 0.15365$, in good agreement with previous determinations. Thus, there is little change in the shape of the cavities at pressures of at least 4.7 GPa. The shrinkage of the $IrSb_3$ unit cell at 4.7 GPa (Table 1) has the effect of very slightly decreasing the size of the cavity in the $IrSb_3$ structure, from dimensions of 2.844 Å × 6.246 Å at ambient pressure to 2.812 Å × 6.207 Å at 4.7 GPa. Additionally, the refined isotropic thermal parameters for the Ir and Sb atoms also decrease slightly with pressure, from 0.03200 and 0.02779 at ambient pressure to 0.03084 and 0.01630 at 4.7 GPa. The relatively small change in the $IrSb_3$ cavity dimensions and stability of the crystal structure under compression are encouraging for experiments designed to implant atomic or molecular species in the cavities at pressures of several GPa or more.

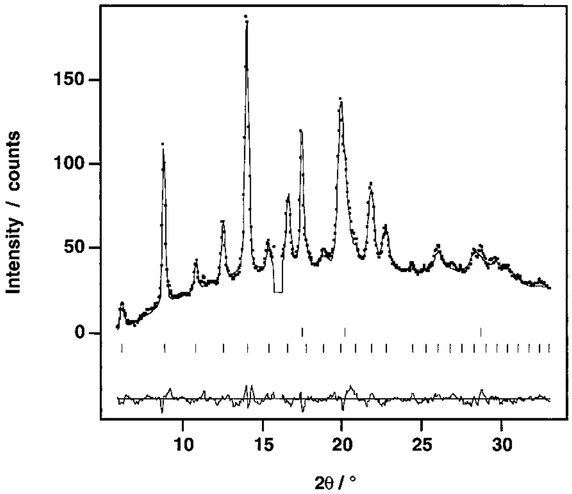

Figure 4. Diffraction profile of the 9:1 $IrSb_3$:Ag powder mixture at a pressure of 4.7 GPa.

Finally, the stability of the $IrSb_3$ structure under extreme compression suggests that it may be stable under compression at high temperatures. Higher temperatures may be necessary to increase the kinetics of the incorporation of atoms or molecules into the skutterudite cavities. Although this study did not include experiments performed at both high temperature and high pressure, the relationship between pressure and temperature can be determined thermodynamically from the Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \tag{3}$$

The most likely phase transformation for $IrSb_3$ at extreme conditions is decomposition into $IrSb_2$ and Sb. According to the Ir−Sb phase diagram this transformation occurs at ~1150 °C at atmospheric pressure. The change in volume is −0.867 cm^3 per mole of $IrSb_3$ at atmospheric pressure.

Entropic information was obtained using the estimation techniques of Latimer (we could not find thermodynamic data for $IrSb_3$),[11,12] which is based on the assertion that the standard molar enthalpy of a solid can be estimated by taking the sum of the entropy contributions of the constituent elements. The entropic contribution of a given element is given by[11,12]

$$S = 1.5R \ln A_r - 3.9 \tag{4}$$

where A_r is the relative atomic mass of the element of interest and R is the gas constant. The accuracy of the estimation is improved to within ~5% when using a

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similar compound with a known entropy as a starting point. Estimation of $S°$ for $IrSb_2$ and $IrSb_3$ was done using the entropy of InSb (86.2 J mol^{-1} K^{-1})[13] and adding the difference between the Ir and In contributions and the contribution of additional Sb atoms determined using eq 4. We thus can estimate the entropy of $IrSb_2$ as 141.2 J mol^{-1} K^{-1} and that of $IrSb_3$ as 196.2 J mol^{-1} K^{-1}. Using this and the entropy of Sb (45.7 J mol^{-1} K^{-1}),[13] a value of $\Delta S° = -9$ J mol^{-1} K^{-1} was calculated for the reaction $IrSb_3 \rightarrow IrSb_2 + Sb$. However, given the uncertainties in Latimer's method, $\Delta S°$ could also be slightly positive or slightly more negative, possibly ranging from 10 to -20 J mol^{-1} K^{-1}.

Using the value of ΔV and the range of $\Delta S°$ values estimated above, the initial slope, dT/dP, for the phase boundary ranges from -87 to 43 K/GPa. During hot isostatic pressing (HIP) processing, pressures ranging from 0.05 to 0.20 GPa and temperatures near 1000 °C are used to consolidate the desired skutterudite phase. If the least favorable value for the slope is chosen, by 0.2 GPa the phase boundary will drop by about 18 K. Thus, decomposition during hot pressing does not appear to be a significant problem.

Acknowledgment. This work has been funded by DARPA/ONR grant N00014-97-1-0565 to J.V.B. and ONR grant 00014-91-1-0341 to G.A.S.

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