Existence and Some Properties of New Ternary Skutterudite Phases

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Abstract: Skutteruditerelated phases can be derived from binary skutterudite compounds (prototype CoAs) by substituting the anion or the cation atom with neighboring atoms, in these phases, the valence-electron count remains constant. Several of these ternary related phases were already reported in the literature. We have synthesized a new skutterudite related phase. The substitution of ruthenium in the binary compound RhSb5 resulted in an isoelectronic and isostuctural phase Ru0.5Pd0.5Sb3. X-ray investigations showed that this compound has a cubic lattice and belongs to the space group Im3 (Ia3). The lattice constant is 9.294 Å and the X-ray density is 7.75 g cm−3. Single phase, polycrystallinesamples were prepared by direct reaction of elemental powders of ruthenium, palladium and antimony in a stoichiometric ratio and subsequent cold-pressing and sintering. A decomposition temperature of 647 °C was determined from differential thermal analysis measurements for the skutterudite phase Ru0.5Pd0.5Sb3. Seebeck coefficient, electrical resistivity, thermal conductivity and Hall effect measurements were performed between room temperature and 500 °C. The results of these measurements are presented and discussed. Preliminary results show that Ru0.5Pd0.5Sb3 behaves like a heavily doped semiconductor. A band gap of about 0.56 eV was estimated from high temperature Hall effect measurements.

INTRODUCTION

The thermoelectric properties of InSb and CoSb3 have been recently investigated at JPL, and these binary compounds have shown a good potential for thermoelectric and other applications [1, 2]. In particular, p-type samples have shown exceptionally high carrier mobilities. However, the room temperature thermal conductivity of these compounds is about 12 W m−1 K−1 which is substantially higher than that of the highest performance thermoelectric materials. High ZT values might be possible for some skutterudite materials if lower lattice thermal conductivities can be achieved. Different approaches can be considered to attempt finding skutterudite materials with lower lattice thermal conductivity than InSb and CoSb3. The first one is to form solid solutions between isostuctural compounds and reduce the lattice thermal conductivity by increasing point defect scattering. Investigations of the properties of InSb-CoSb3 solid solutions are now in progress at JPL [3]. Ternary skutterudite-type phases can be obtained by substitution of the transition-metal or pnictogen atom in a binary skutterudite by elements on the left and on the right of this atom similarly to diamond-like semiconductors [4]. The resulting phases are isoelectronic to the binary compounds. A number of ternary skutterudite related phases are listed in Table 1.

All these phases are derived from binary skutterudite compounds, the condition being that the valence-electron count remains constant. The substitution can occur on the anion site (CoAs) or on the cation site (CoSb3). Structurally related skutterudite phases can also be formed by partial substitution of the cation or the anion (InSb3→Rsh5,5In9,5Sb8). Very little is known in the literature about the electrical properties of these phases listed in Table 2. Such ternary phases might have lower thermal conductivity than the binary compounds InSb3 and CoSb3 and hence interesting thermoelectric properties. We attempted to synthesize new skutterudite-related phases and successfully prepared a new phase: Ru0.5Pd0.5Sb3. Some properties of this new phase are presented and discussed.

EXPERIMENTAL DETAILS

We prepared a new skutterudite phase resulting from the substitution of ruthenium and palladium for the rhodium atom in the binary skutterudite RhSb5. The resulting isoelectronic phase is Ru0.5Pd0.5Sb3. Single phase, polycrystalline samples of Ru0.5Pd0.5Sb3 were prepared by direct synthesis of the elements, Ruthenium (99.997%), palladium (99.9%) and antimony (99.999%) were mixed in stoichiometric ratio in a plastic vial before being loaded and sealed in a quartz ampoule under vacuum. The ampoule was then heated for 8 days at 600°C (lower than any of the melting points of the elements). The product was removed from the ampoule, crushed and ground in an agate mortar and the mixture was then reloaded in a second quartz ampoule, heated for 4 days at 550°C. The preparation of several other ternary skutterudite phases was also attempted using a similar preparation technique. Products of the annealing were removed from the ampoules and analyzed by X-ray diffraction (XRD). XRD analysis was conducted using a Siemens D-500 diffractometer with the CuKα radiation. Powder X-ray patterns were taken using platinum as a reference with scan steps of 0.05° and counting time of 3 s.

Samples of Ru0.5Pd0.5Sb3 were prepared for thermoelectric...
RESULTS AND DISCUSSION

The X-ray spectrum of the reacted powders could be indexed on the basis of a primitive cubic unit cell with the reflections corresponding to the skutterudite structure, space group Im3(Tl3). Some properties of the phase $R_u_0.5Pd_0.5Sb_3$ are summarized in Table 2.

Table 2. Some properties of the base $R_u_0.5Pd_0.5Sb_3$

<table>
<thead>
<tr>
<th>Property</th>
<th>$R_u_0.5Pd_0.5Sb_3$</th>
</tr>
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<tbody>
<tr>
<td>Lattice constant (Å)</td>
<td>9.2944</td>
</tr>
<tr>
<td>X-ray density (g cm$^{-3}$)</td>
<td>7.75</td>
</tr>
<tr>
<td>Experimental density (g cm$^{-3}$)</td>
<td>7.49</td>
</tr>
<tr>
<td>Decomposition temperature ii vacuum (°C)</td>
<td>647</td>
</tr>
<tr>
<td>Conductivity type</td>
<td>p</td>
</tr>
<tr>
<td>Electrical resistivity (mΩ cm)</td>
<td>1.45</td>
</tr>
<tr>
<td>Hall mobility (cm$^{-2}$ V$^{-1}$ s$^{-1}$)</td>
<td>35</td>
</tr>
<tr>
<td>1 Ian carrier concentration (cm$^{-3}$)</td>
<td>1.2 x 10$^{20}$</td>
</tr>
<tr>
<td>Seebeck coefficient (μV K$^{-1}$)</td>
<td>18</td>
</tr>
</tbody>
</table>

The calculated lattice constant is 9.2944 Å, which is larger than the binary compound RhSb$_3$ (9.2222 Å). The experimental density measured of the sintered sample is about 96.6% of the calculated density. The room temperature electrical properties show that this phase behaves like a heavily doped p-type-sclilicon. The Hall mobility is reasonably large despite the high carrier concentration measured this sample.

Figures 1 and 2 show the electrical resistivity and Hall coefficient values as a function of inverse temperature, respectively. The electrical resistivity increases with increasing temperature and reaches a maximum value of 2.87 mΩ cm at 520°C. The variations of the Hall coefficient are different. Up to a temperature of about 220°C, the Hall coefficient is nearly constant corresponding to the extrinsic temperature range. Above 200°C, the Hall coefficient decreases with increasing temperature corresponding to an intrinsic behavior. A bandgap of 0.56 eV was estimated for $R_u_0.5Pd_0.5Sb_3$ from the quasi-linear variations of the Hall coefficient at high temperature. We estimated a bandgap of 0.8 eV for the binary compound RhSb$_3$ which is larger than for the ternary-derived phase. Hence, it seems that substitution in the skutterudite phases can be used to tailor bandgaps and select materials for applications in a specific range of temperature.

The variations of the Hall mobility and the Seebeck coefficient are shown in Figures 3 and 4, respectively. The Hall mobility decreases with increasing temperature and a minimum value of about 10 cm$^2$ V$^{-1}$ s$^{-1}$. The Hall mobility decreases with increasing temperature and a minimum value of about 10 cm$^2$.
thermal conductivity values of p-type Bi$_2$Te$_3$-based alloys (state-of-the-art thermoelectric material in the low temperature range) are also shown in Figure 5 [7]. Low thermal conductivity values are observed for the phase Ru$_{0.5}$Pd$_{0.5}$Sb$_3$ over the entire range of temperature. As the temperature decreases, the thermal conductivity of p-type Bi$_2$Te$_3$-based alloys increases and varies as 1/T. For Ru$_{0.5}$Pd$_{0.5}$Sb$_3$, the thermal conductivity decreases as for a glassy material [8]. Most of the crystalline materials where low thermal conductivity was observed do not have good electrical conductivity. Ru$_{0.5}$Pd$_{0.5}$Sb$_3$ is a unique material where low thermal conductivity and good electrical resistivity are combined and this makes this material an excellent candidate for low temperature thermoelectric applications. Provided lower carrier concentrations are obtained, good thermoelectric performance might be achieved in the low temperature range for Ru$_{0.5}$Pd$_{0.5}$Sb$_3$.

CONCLUSION

The discovery of a new skutterudite phase Ru$_{0.5}$Pd$_{0.5}$Sb$_3$ was made in the course of a broad search for new thermoelectric materials. This phase is an interesting candidate as low temperature thermoelectric materials due to the combination of very low thermal conductivity with good electrical properties. Its properties will be investigated further in the future and efforts will focus on preparing samples with lower doping level by controlling the stoichiometry of the samples or doping with impurities. Skutterudite phases can also be formed by a variety of substitution of either the transition-metal or the pnictogen in binary compounds, Ru$_{0.5}$Pd$_{0.5}$Sb$_3$ being an example of this formation. It is likely that many of these skutterudite compounds will show interesting properties for thermoelectric and other applications. Some of these phases are currently prepared and studied.

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REFERENCES