Existence and *Some* Properties of *Ncw* Ternary Skutterudite Phases

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Abstract. Skutterudite related phases can bc. derived from binary skutterudite compounds (prototype $CoAs_3$) 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 ncw skutterudite related phase. The substitution of ruthenium rind palladium in the binary compound $RhSb_3$ resulted in the isostructural and isoelectronic phase $Ru_{0.5}Pd_{0.5}Sb_3$. X-ray investigations showed that this compound has a cubic lattice and belongs to the space group $Im3$ (T_h^5), The lattice constant is 9.2944 Å and the X-ray density is 7.75 $g.cm^{-3}$. Single phase, polycrystalline samples were prepared by direct reaction of elemental powders of ruthenium, palladium and antimony in the 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 $Ru_{0.5}Pd_{0.5}Sb_3$. 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 $Ru_{0.5}Pd_{0.5}Sb_3$ behaves like a heavily doped semiconductor. A bandgap of about 0.56 eV was estimated from high temperature hall effect measurements.

IN'1'ROI)UCTION

The the.rlncrclcc[ric properties of $IrSb_3$ and $CoSb_3$ 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 [ban for sta[c-of-the-art thermoelectric cooling materials. High ZT values might be possible for some skutterudite materials if lower thermal conductivities can be achieved. Different approaches can be considered to attempt finding skutterudite materials with lower lattice thermal conductivity than $IrSb_3$ and $CoSb_3$. The first onc is to form solid solutions between isostructural compounds and reduce the lattice thermal conductivity by increasing point defect scattering. investigations of the properties of $IrSb_3$-$CoSb_3$ solid solutions arc now in progress at JPL [3]. Ternary skutterudite-type phases can be obtained by substitution of the transition-metal or pnicogen 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 relate.d phases arc listed in Table 1.

Allthese phases arc derived from binary skutterudite compounds, the condition being that the valence-electron count remains constant, The substitution can occur on the anion site ($CoAs_3$->$CoGe_{1.5}Se_{1.5}$) or *on the* cation site ($CoSb_3$->$Fe_{0.5}Ni_{0.5}Sb_3$). Structurally related skutterudite phases can also be formed by partial substitution of the cation or the anion ($IrSb_3$->$PtSn_{1.2}Sb_{1.8}$). Very little is known in the literature about (he electrical properties of the phases listed in Table 1. Such ternary phases might have lower thermal conductivity than the binary compounds $IrSb_3$ and $CoSb_3$ anti have interesting thermoelectric proper ties. W c attempted to synthesize new skutlc.ruditc-related phases and successfully prepared a ncw phase: $Ru_{0.5}Pd_{0.5}Sb_3$. Some properties of this ncw phase are presented and discussed.

Table 1. Skutterudite related phases

Material	a (Å)	Decomposition temperature (C)	Ref.
$CoGe_{1.5}S_{1.5}$	8.017	1000	5
$CoGe_{1.5}Se_{1.5}$	8.299	800	5
$RhGe_{1.5}S_{1.5}$	8.2746	> 800	9
$IrGe_{1.5}S_{1.5}$	8.297	> 800	9
$IrGe_{1.5}Se_{1.5}$	8.5591	> 800	9
$IrSn_{1.5}S_{1.5}$	8.7059	> 800	9
$Fe_{0.5}Ni_{0.5}Sb_3$	9.0904	729	6
$Fe_{0.5}Ni_{0.5}As_3$	8.256	?	10
$PtSn_{1.2}Sb_{1.8}$	9.39	?	11

EXPERIM ENTAL DETAILS

W c prepared a ncw skutterudite phase resulting from the substitution of ruthenium and palladium for the rhodium atom in the binary skutterudite $RhSb_3$. The resulting isoelectronic phase is $Ru_{0.5}Pd_{0.5}Sb_3$. Single phase, polycrystalline samples of $Ru_{0.5}Pd_{0.5}Sb_3$ were prepared by direct synthesis of the elements, Ruthenium (99.997%), palladium (99.9%) and antimony (99.9999%) powders were mixed in stoic. hiometric ratio in a plastic vial before being loaded and scaled in a quartz ampoule under vacuum. The ampoule was then heated for 8 days at 600°C (lower than any of the melting point 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 diffractometry (XRD). XRD analysis was conducted using a Siemens D-500 diffractometer with the CuK_α radiation. Powder X-ray patterns were taken using platinum as a reference with scan steps of 2θ=0.05° and counting time of 3s.

Samples of $Ru_{0.5}Pd_{0.5}Sb_3$ were prepared for thermoelectric

'properties measurements by col(l-pressing of the prereacted powders and subsequent sinte ring at 600° C for a week in scaled quartz ampoules. Microprobe analysis were performed on these samples to check their composition. The density of all samples was measured by the immersion technique using toluene as liquid. Samples were also prepared for differential thermal analysis (DTA) in order to determine [heir decomposition temperature. l'hc samples were scaled under 10^{-5} Torr vacuum in quartz capsules and a Dupont 1600°C DTA apparatus was used for the measurements. The decomposition/melting temperature was recorded from the heating curves. Samples were characterized at room temperature by van dcr Paw, Hall effect and Seebeck coefficient measurements. I ligh temperature Seebeck coefficient, electrical resistivity, thermal conductivity and Hall effect measurements were also performed on selected samples.

RESULTS ANI) DISCUSSION

The X-ray spectrum of the reacted powder could be indexed on the basis of a primitive cubic unit ccl] with the reflections corresponding to the skutterudite structure, space group $Im3 (T_h^5)$. Some properties of the phase $Ru_{0.5}Pd_{0.5}Sb_3$ are summarized in Table 2.

Table 2. Some properties of th base $Ru_{0.5}Pd_{0.5}St$

	$Ru_{0.5}Pd_{0.5}Sb_3$
Lattice constant (Å)	9.2944
X-ray density ($g.cm^{-3}$)	7.75
Experimental density ($g.cm^{-3}$)	7.49
Decomposition temperature in vacuum (“C)	647
Conductivity type	p
Electrical resistivity (mΩ.cm)	1.45
Hall mobility ($cm^2.V^{-1}.s^{-1}$)	35
1 Ian carrier concentration (cm^{-3}	1.2×10^{20}
Seebeck coefficient ($\mu V.K^{-1}$)	18

The calculated lattice constant is 9.2944 Å which is larger than the binary compound $RhSb_3$ (9.2322 Å). The experimental density measure.d 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-scliliconductor. The Hall mobility is reasonably large despite the high carrier concentration measure.dcm 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 I Ian coefficient decreases with increasing temperature corresponding to an intrinsic behavior. A bandgap of 0.56 CV was estimated for $Ru_{0.5}Pd_{0.5}Sb_3$ from the quasi-linear variations of the Hall coefficient at high temperature. We estimate.d a bandgap of **0.8** eV for the binary compound $RhSb_3$ which is larger than for the ternary-derived phase. Hence, it secms that substitution in the skutterudite phases can be used to tailor bandgaps and select materials for applications in a specific range of temperat ure.

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.

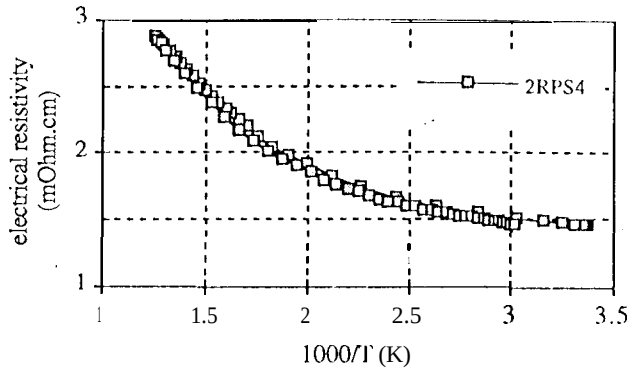

Figure 1: Electrical resistivity as a function of inverse temperature for sample 2RPS4 ($Ru_{0.5}Pd_{0.5}Sb_3$).

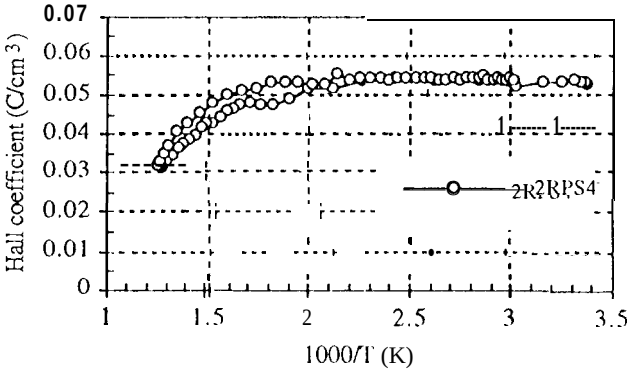

Figure 2: Hall coefficient as a function of inverse temperature for sample 2RPS4 ($Ru_{0.5}Pd_{0.5}Sb_3$).

$V\text{-}^{1}.s^{-1}$ was measured at a temperature of about 520°C. The room temperature Seebeck coefficient is about 20 $\mu V.K^{-1}$. It increases with temperature up to a maximum of about 38 $\mu V.K^{-1}$ at a temperature of about 400°C and then decreases for higher temperatures. The Seebeck coefficient values are relatively low but the sample was heavily doped. Reducing the doping level by addition of dopants or control of the stoichiometry should increase the Seebeck coefficient.

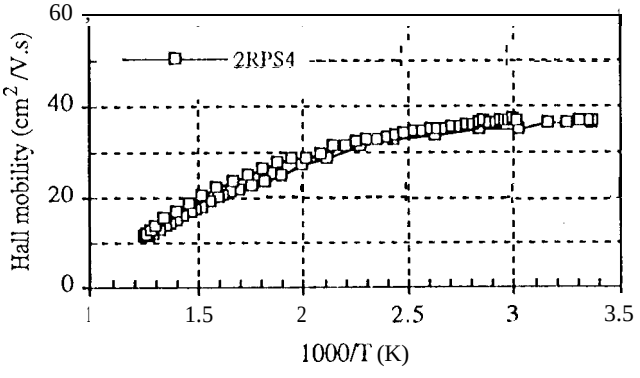

Figure 3: 1 Ian mobility as a function of inverse temperature for sample 2RPS4 ($Ru_{0.5}Pd_{0.5}Sb_3$).

The low temperature thermal conductivity values of sample 2RPS4 ($Ru_{0.5}Pd_{0.5}Sb_3$) are shown in figure 5. A room temperature value of 8×10^{-3} W .$cm^{-1}.K^{-1}$ was measured at room temperature, ten times lower than typical p-type $IrSb_3$ which has the same crystal structure but higher melting point and bandgap. For comparison, typical

thermal conductivity values of p-type Bi_2Te_3-based alloys (state-of-the-art thermoelectric material in the low temperature range) are also shown in figure 5 [7]. Lowe thermal conductivity values are

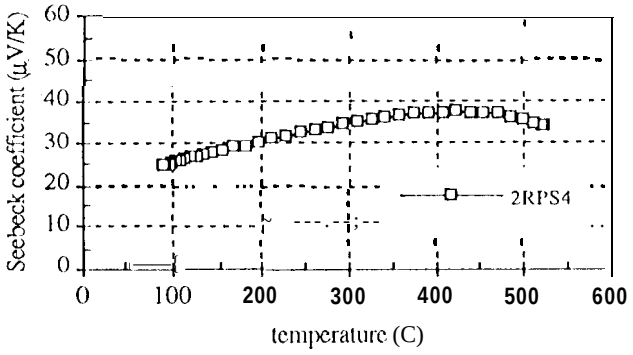

Figure 4: Seebeck coefficient as a function of temperature for sample 21<1's4 ($Ru_{0.5}Pd_{0.5}Sb_3$).

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_2Te_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 $Ru_{0.5}Pd_{0.5}Sb_3$.

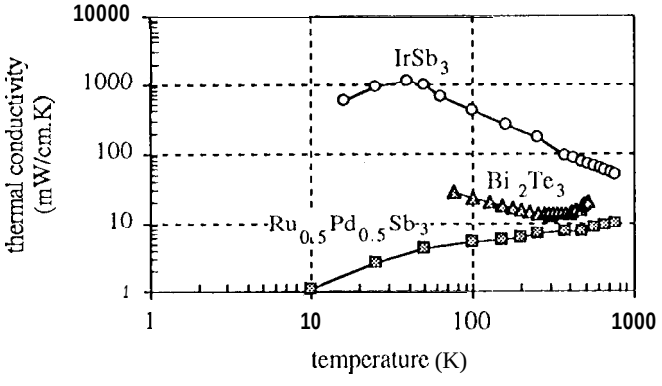

Figure 5: Thermal conductivity as a function of temperature for $Ru_{0.5}Pd_{0.5}Sb_3$ (sample 2RPS4). Typical values for p-type $IrSb_3$ and Ili_2Te_3-based alloys are also plotted for comparison.

CONCLUSION

I'hc discovery of a ncw 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 duc 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 bc formed by a variety of substitution of either the transition-metal or the pnicogen 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 arc currently prepared and studied.

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