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Beneficial influence of Ru on the thermoelectric properties of Mo_3Sb_7 Christophe Candolfi,^{1,a)} Bertrand Lenoir,¹ Juliusz Leszczynski,¹ Anne Dauscher,¹ and Emmanuel Guilmeau²¹Laboratoire de Physique des Matériaux, Nancy Université, CNRS, Ecole Nationale Supérieure des Mines de Nancy, Parc de Saurupt, 54042 Nancy Cedex, France²CRISMAT-ENSICAEN, CNRS/UMR 6508, 6 Bd Maréchal Juin, 14050, Caen Cedex, France

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Zintl phases have recently been identified as potential thermoelectric materials typified by the discovery of a high thermoelectric figure of merit in the $\text{Yb}_{14}\text{MnSb}_{11}$ compound above 1000 K. We report on the synthesis and the thermoelectric properties measurements over a wide temperature range (300–1000 K) of other Zintl phases exhibiting a complex crystalline structure, namely, Mo_3Sb_7 and its related compounds $\text{Mo}_{3-x}\text{Ru}_x\text{Sb}_7$. While the binary compound displays low figure of merit values due to its metallic nature, we show that the partial substitution of Mo by Ru significantly improves its value to reach 0.45 at 1000 K in $\text{Mo}_{2.2}\text{Ru}_{0.8}\text{Sb}_7$. © 2009 American Institute of Physics. [DOI: 10.1063/1.3097384]

I. INTRODUCTION

Extensive effort has been devoted for more than 50 years for optimizing materials to achieve outstanding thermoelectric properties.^{1,2} The effectiveness of a material to make direct conversion between thermal and electrical energies is captured in the dimensionless figure of merit at a given temperature T , ZT , expressed as $ZT = \alpha^2 T / \rho \lambda_T$ where α , ρ , and λ_T are the Seebeck coefficient or thermopower, the electrical resistivity, and the total thermal conductivity, respectively.³

In the last decade, intermetallic Zintl phases have been proposed as a prospective class of compounds for thermoelectric power generation. Even though few studies have dealt with their thermoelectric properties up-to-now, high ZT values have been reported in $\text{Yb}_{14}\text{MnSb}_{11}$ and its related compounds.^{4–7} These materials possess the requirements involved to attain superior thermoelectric performance: a complex crystalline structure to get low thermal conductivity together with the possibility to tune their electrical properties by appropriate substitutions.

Recently, other Zintl phases of the Ir_3Ge_7 structure type (space group $Im\bar{3}m$) have been considered for high temperature thermoelectric applications.^{8–10} Among this family, the Mo_3Sb_7 compound has attracted attention due to the coexistence of superconductivity below 2.3 K and a spin gap in the magnetic excitations spectrum, which opens at $T^* = 53$ K.^{11–13} The presence of such a gap arising from antiferromagnetically coupled molybdenum dimers yields to exotic temperature dependences of the magnetic and transport properties. However, its metallic nature does not favor the obtention of high ZT values in both the low and high temperature limits,¹⁴ and therefore, further optimization must be achieved. To improve the thermoelectric properties, one can take part of the particular band structure of this metal since the Fermi level is located in the valence band just below a gap arising from strong d - p interactions.¹⁵ Thus, add-

ing electrons to the structure could result in a progressive transition from a metalliclike to a semiconducting state. Band structure calculations showed that two more electrons per formula unit are required to position the Fermi level into the gap.¹⁵ The only attempt to add electrons to the structure was made by replacing some Sb atoms by Te atoms.^{8,9} This partial substitution was found to markedly affect all the relevant properties involved in thermoelectricity resulting in higher ZT values compared to those of the parent compound.^{9,14}

Additional electrons can also be provided by judicious substitutions on the molybdenum site. Preliminary band structure calculations suggest that a semiconducting state could be attained by replacing one Mo atom by one Ru atom per formula unit.¹⁶ In this article, we not only demonstrate that Mo can be successfully substituted by Ru but we also show that this partial substitution significantly improves the thermoelectric properties of Mo_3Sb_7 in the 300–1000 K temperature range.

II. EXPERIMENT

Polycrystalline $\text{Mo}_{3-x}\text{Ru}_x\text{Sb}_7$ compounds with nominal composition of $x = 0, 0.25, 0.5$, and 1 were synthesized using the same powder metallurgical route described in detail previously.¹¹ The consolidation of the powdered materials was performed by using uniaxial hot press in an argon atmosphere at 600 °C for 2 h under 51 MPa. Structural and chemical characterizations were performed through x-ray diffraction (XRD), neutron diffraction, as well as electron probe microanalysis (EPMA).

High temperature transport measurements including electrical resistivity, thermopower, and thermal conductivity were carried out on samples cut with a diamond wire saw. Four probe electrical resistivity measurements based on the Van der Pauw method have been performed in the 300–800 K temperature range. The thermopower has been measured on a commercial system (ZEM 3, Ulvac) using a standard method over the 300–900 K temperature range. Thermal

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TABLE I. Nominal and actual chemical compositions determined by EPMA, lattice parameters deduced from XRD data, relative densities, Hall carrier concentrations (p) and Hall mobilities (μ_H) at 300 K of the $\text{Mo}_{3-x}\text{Ru}_x\text{Sb}_7$ samples.

Nominal composition	Actual composition	Relative density (%)	Lattice parameter (\AA)	μ_H ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	p
Mo_3Sb_7	$\text{Mo}_3\text{Sb}_{6.95}$	93	9.568(8)	4.0	8.5×10^{21}
$\text{Mo}_{2.75}\text{Ru}_{0.25}\text{Sb}_7$	$\text{Mo}_{2.75}\text{Ru}_{0.25}\text{Sb}_7$	98	9.550(4)	5.0	6.0×10^{21}
$\text{Mo}_{2.5}\text{Ru}_{0.5}\text{Sb}_7$	$\text{Mo}_{2.5}\text{Ru}_{0.5}\text{Sb}_7$	99	9.524(9)	10.0	2.4×10^{21}
Mo_2RuSb_7	$\text{Mo}_{2.2}\text{Ru}_{0.8}\text{Sb}_7$	88	9.500(8)	5.0	1.2×10^{21}

conductivity has been obtained via thermal diffusivity measurements using a laser flash technique in the 300–1000 K temperature range. Hall measurements were also performed at room temperature.

Both XRD and neutron diffraction experiments unequivocally show that Ru atoms can be successfully inserted on the Mo site of the Mo_3Sb_7 crystalline structure. If the $x=0.25$ and 0.5 samples do not exhibit any secondary phases, the situation is different in the case of the $x=1$ compound where a small amount of RuSb_2 (<4 vol %) is present. This last result seems to underline the existence of a solubility limit of ruthenium in this structure. All these conclusions are corroborated by EPMA that revealed the good chemical homogeneity of the $x=0.25$ and 0.5 samples. Thus, the actual compositions are close to the nominal compositions except for the $x=1$ compound whose real composition is close to $x=0.8$. This result demonstrates that semiconducting properties cannot be attained in $\text{Mo}_{3-x}\text{Ru}_x\text{Sb}_7$. This impossibility was also claimed in $\text{Mo}_3\text{Sb}_{7-x}\text{Te}_x$ where a solubility limit of Te ($x \sim 1.6$), lower than the theoretical required value ($x=2$), has been determined.⁹ It is worth mentioning that the real compositions were obtained by normalizing to full occupancy of the metalloid site and will always be used in the present article. Table I summarizes the nominal and actual compositions of the prepared samples as well as their lattice parameters and relative densities.

III. RESULTS AND DISCUSSION

The Hall coefficient at room temperature was found to be positive whatever x , indicating hole conduction. As Ru should supply more electrons than Mo, it is expected that the hole concentration should decrease with increasing x . This picture is well respected if one refers to the measured Hall carrier concentration (see Table I), which decreases linearly with increasing x suggesting a “rigidlike” behavior of the electronic structure. The rather low hole mobilities observed are coherent with the high carrier concentrations displayed by $\text{Mo}_{3-x}\text{Ru}_x\text{Sb}_7$ (between 4 and $10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$). Figures 1(a) and 1(b) show the temperature dependence of the thermopower and the electrical resistivity for the different $\text{Mo}_{3-x}\text{Ru}_x\text{Sb}_7$ compounds, respectively. Both α and ρ values of the substituted compounds increase nearly linearly in magnitude with temperature and with Ru concentration. The Seebeck coefficient is positive whatever the sample is, indicative of hole conduction. At 330 K, the measured values are 21, 27, 35, and $63 \mu\text{V K}^{-1}$ for $x=0, 0.25, 0.5,$ and 0.8 , respectively. This increase confirms the hypothesis of a pro-

gressive transition to a semiconducting state as the Ru content increases.¹⁶ For $x=0.8$, both the thermopower and the electrical resistivity display a temperature dependence reminiscent to those reported for the $\text{Mo}_3\text{Sb}_{7-x}\text{Te}_x$ compounds with $x=1.5$ and $x=1.6$.⁴ As a result of the decrease in the hole concentration with increasing Ru content, the electrical resistivity rises with x .

The temperature dependence of the total thermal conductivity is shown in Fig. 2. It must be noted that these data have been corrected to take into account the different densities of our samples.¹⁷ These compounds display thermal con-

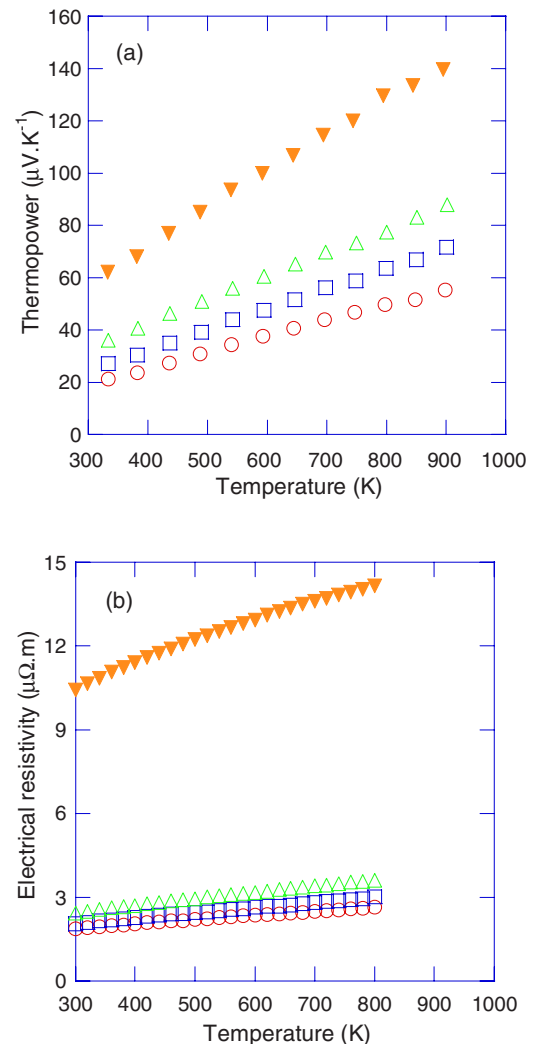


FIG. 1. (Color online) Temperature dependence of the thermopower (a) and electrical resistivity (b) for the Mo_3Sb_7 (○), $\text{Mo}_{2.75}\text{Ru}_{0.25}\text{Sb}_7$ (□), $\text{Mo}_{2.5}\text{Ru}_{0.5}\text{Sb}_7$ (△), and $\text{Mo}_{2.2}\text{Ru}_{0.8}\text{Sb}_7$ (▼) compounds.

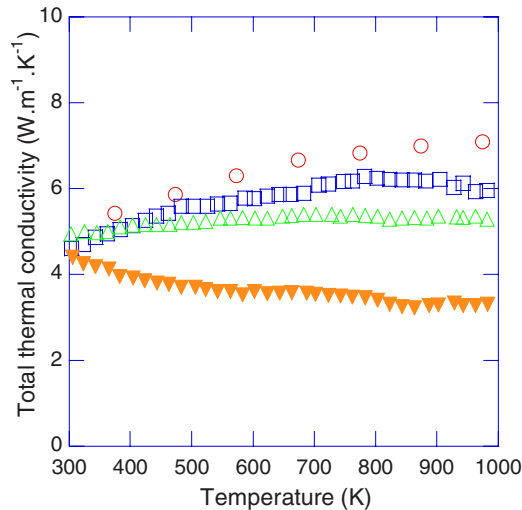


FIG. 2. (Color online) Total thermal conductivity as a function of the temperature for the Mo_3Sb_7 (\circ), $\text{Mo}_{2.75}\text{Ru}_{0.25}\text{Sb}_7$ (\square), $\text{Mo}_{2.5}\text{Ru}_{0.5}\text{Sb}_7$ (\triangle), and $\text{Mo}_{2.2}\text{Ru}_{0.8}\text{Sb}_7$ (\blacktriangledown) compounds.

ductivities ranging between $3.8\text{--}5.5\text{ W m}^{-1}\text{ K}^{-1}$ at 1000 K. The thermal conductivity of the $x=0$ and 0.25 samples increases with temperature up to 1000 K, while the $x=0.5$ compound shows a nearly temperature independent behavior. For the highest Ru concentration ($x=0.8$), the thermal conductivity decreases to attain $3.2\text{ W m}^{-1}\text{ K}^{-1}$ at 1000 K. If these values are low due to the complex crystalline structure of these materials, the observed temperature dependences for $x=0, 0.25$, and 0.5 constitute the most striking features. In the case of the Mo_3Sb_7 parent compound, such an unusual behavior has been tentatively ascribed to a complex interplay between antiferromagnetically coupled molybdenum dimers and phonons.¹⁴ The partial substitution of Mo by Ru drastically affects this dependence and seems to reinforce the scenario proposed for the Mo_3Sb_7 compound. Actually, this exotic behavior could be then related to the disappearance of the magnetic interactions when the Ru content increases and as a result, of the dimer-phonon interactions. Low temperature transport properties measurements, which will be described in detail in a forthcoming article, give further experimental support for this hypothesis.

From these different measured transport properties, the dimensionless figures of merit ZT have been calculated for all compounds and are depicted in Fig. 3. To further determine the thermoelectric potential of these materials, we have linearly extrapolated the electrical resistivity and thermopower dependences up to 1000 K. Such dependences are highly likely in these compounds because of both the absence of minority carriers effect and strong similarities of experimental results obtained in $\text{Mo}_3\text{Sb}_{7-x}\text{Te}_x$ (for $x=1.5$ and 1.6).⁴ For all samples, the ZT increases monotonically with temperature up to 1000 K. The best ZT of 0.45 at 1000 K is achieved with $\text{Mo}_{2.2}\text{Ru}_{0.8}\text{Sb}_7$.

IV. CONCLUSION

Polycrystalline $\text{Mo}_{3-x}\text{Ru}_x\text{Sb}_7$ samples with $x=0, 0.25, 0.5$, and 1 have been successfully synthesized. Structural and chemical investigations have clearly shown the existence of

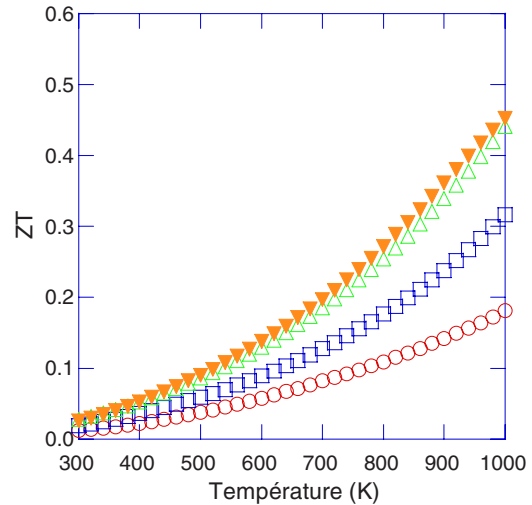


FIG. 3. (Color online) Temperature dependence of the dimensionless figure of merit ZT for Mo_3Sb_7 (\circ), $\text{Mo}_{2.75}\text{Ru}_{0.25}\text{Sb}_7$ (\square), $\text{Mo}_{2.5}\text{Ru}_{0.5}\text{Sb}_7$ (\triangle), and $\text{Mo}_{2.2}\text{Ru}_{0.8}\text{Sb}_7$ (\blacktriangledown).

a solubility limit of Ru close to 0.8. Transport properties measurements have demonstrated the beneficial effects of a partial substitution of Mo by Ru since an increase in the thermopower together with a decrease in the total thermal conductivity occur. In addition, these results support the idea that the variation in the electronic structure can be understood within a rigid band model. This partial substitution leads to an enhancement of the ZT values up to 0.45 at 1000 K. Despite this value is lower than those observed in the case of Te substituted compounds, this work opens new route for further optimization. It could be worthwhile to explore for instance substitutions on both the Mo and Sb sites.

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