



**HAL**  
open science

## Beneficial influence of Ru on the thermoelectric properties of Mo<sub>3</sub>Sb<sub>7</sub>

Christophe Candolfi, Bertrand Lenoir, Juliusz Leszczynski, Anne Dauscher,  
Emmanuel Guilmeau

► **To cite this version:**

Christophe Candolfi, Bertrand Lenoir, Juliusz Leszczynski, Anne Dauscher, Emmanuel Guilmeau. Beneficial influence of Ru on the thermoelectric properties of Mo<sub>3</sub>Sb<sub>7</sub>. *Journal of Applied Physics*, 2009, 105 (8), pp.083701. 10.1063/1.3097384 . hal-03996157

**HAL Id: hal-03996157**

**<https://hal.science/hal-03996157>**

Submitted on 19 Feb 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Beneficial influence of Ru on the thermoelectric properties of $\text{Mo}_3\text{Sb}_7$

Cite as: J. Appl. Phys. **105**, 083701 (2009); <https://doi.org/10.1063/1.3097384>

Submitted: 13 November 2008 • Accepted: 07 February 2009 • Published Online: 16 April 2009

Christophe Candolfi, Bertrand Lenoir, Juliusz Leszczynski, et al.



View Online



Export Citation

## ARTICLES YOU MAY BE INTERESTED IN

[Transport and magnetic properties of  \$\text{Mo}\_{2.5}\text{Ru}\_{0.5}\text{Sb}\_{7-x}\text{Te}\_x\$](#)

Journal of Applied Physics **107**, 093709 (2010); <https://doi.org/10.1063/1.3388056>

[Transverse thermoelectric generation using magnetic materials](#)

Applied Physics Letters **118**, 140504 (2021); <https://doi.org/10.1063/5.0046877>

[Layered thermoelectric materials: Structure, bonding, and performance mechanisms](#)

Applied Physics Reviews **9**, 011303 (2022); <https://doi.org/10.1063/5.0074489>

Journal of Applied Physics **Special Topics** Open for Submissions

Learn More

**Beneficial influence of Ru on the thermoelectric properties of Mo<sub>3</sub>Sb<sub>7</sub>**

Christophe Candolfi,<sup>1,a)</sup> Bertrand Lenoir,<sup>1</sup> Juliusz Leszczynski,<sup>1</sup> Anne Dauscher,<sup>1</sup> and Emmanuel Guilmeau<sup>2</sup>

<sup>1</sup>Laboratoire de Physique des Matériaux, Nancy Université, CNRS, Ecole Nationale Supérieure des Mines de Nancy, Parc de Saurupt, 54042 Nancy Cedex, France

<sup>2</sup>CRISMAT-ENSICAEN, CNRS/UMR 6508, 6 Bd Maréchal Juin, 14050, Caen Cedex, France

(Received 13 November 2008; accepted 7 February 2009; published online 16 April 2009)

Zintl phases have recently been identified as potential thermoelectric materials typified by the discovery of a high thermoelectric figure of merit in the Yb<sub>14</sub>MnSb<sub>11</sub> 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<sub>3</sub>Sb<sub>7</sub> and its related compounds Mo<sub>3-x</sub>Ru<sub>x</sub>Sb<sub>7</sub>. 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 Mo<sub>2.2</sub>Ru<sub>0.8</sub>Sb<sub>7</sub>. © 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.<sup>1,2</sup> 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  $\alpha$ ,  $\rho$ , and  $\lambda_T$  are the Seebeck coefficient or thermopower, the electrical resistivity, and the total thermal conductivity, respectively.<sup>3</sup>

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 Yb<sub>14</sub>MnSb<sub>11</sub> and its related compounds.<sup>4-7</sup> 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<sub>3</sub>Ge<sub>7</sub> structure type (space group  $Im\bar{3}m$ ) have been considered for high temperature thermoelectric applications.<sup>8-10</sup> Among this family, the Mo<sub>3</sub>Sb<sub>7</sub> 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.<sup>11-13</sup> 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,<sup>14</sup> 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.<sup>15</sup> 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.<sup>15</sup> The only attempt to add electrons to the structure was made by replacing some Sb atoms by Te atoms.<sup>8,9</sup> 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.<sup>9,14</sup>

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.<sup>16</sup> 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<sub>3</sub>Sb<sub>7</sub> in the 300–1000 K temperature range.

**II. EXPERIMENT**

Polycrystalline Mo<sub>3-x</sub>Ru<sub>x</sub>Sb<sub>7</sub> compounds with nominal composition of  $x = 0, 0.25, 0.5, \text{ and } 1$  were synthesized using the same powder metallurgical route described in detail previously.<sup>11</sup> 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

<sup>a)</sup> Author to whom correspondence should be addressed. Tel.: (33) 3 83 58 41 63. FAX: (33) 3 83 58 43 44. Electronic mail: candolfi@mines.inpl-nancy.fr.

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 ( $\mu_H$ ) at 300 K of the  $\text{Mo}_{3-x}\text{Ru}_x\text{Sb}_7$  samples.

Nominal composition	Actual composition	Relative density (%)	Lattice parameter ( $\text{\AA}$ )	$\mu_H$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )	$p$
$\text{Mo}_3\text{Sb}_7$	$\text{Mo}_3\text{Sb}_{6.95}$	93	9.568(8)	4.0	$8.5 \times 10^{21}$
$\text{Mo}_{2.75}\text{Ru}_{0.25}\text{Sb}_7$	$\text{Mo}_{2.75}\text{Ru}_{0.25}\text{Sb}_7$	98	9.550(4)	5.0	$6.0 \times 10^{21}$
$\text{Mo}_{2.5}\text{Ru}_{0.5}\text{Sb}_7$	$\text{Mo}_{2.5}\text{Ru}_{0.5}\text{Sb}_7$	99	9.524(9)	10.0	$2.4 \times 10^{21}$
$\text{Mo}_2\text{RuSb}_7$	$\text{Mo}_{2.2}\text{Ru}_{0.8}\text{Sb}_7$	88	9.500(8)	5.0	$1.2 \times 10^{21}$

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  $\text{Mo}_3\text{Sb}_7$  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  $\text{RuSb}_2$  (<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.<sup>9</sup> 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  $\alpha$  and  $\rho$  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.<sup>16</sup> 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  $x=1.6$ .<sup>4</sup> 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.<sup>17</sup> These compounds display thermal con-

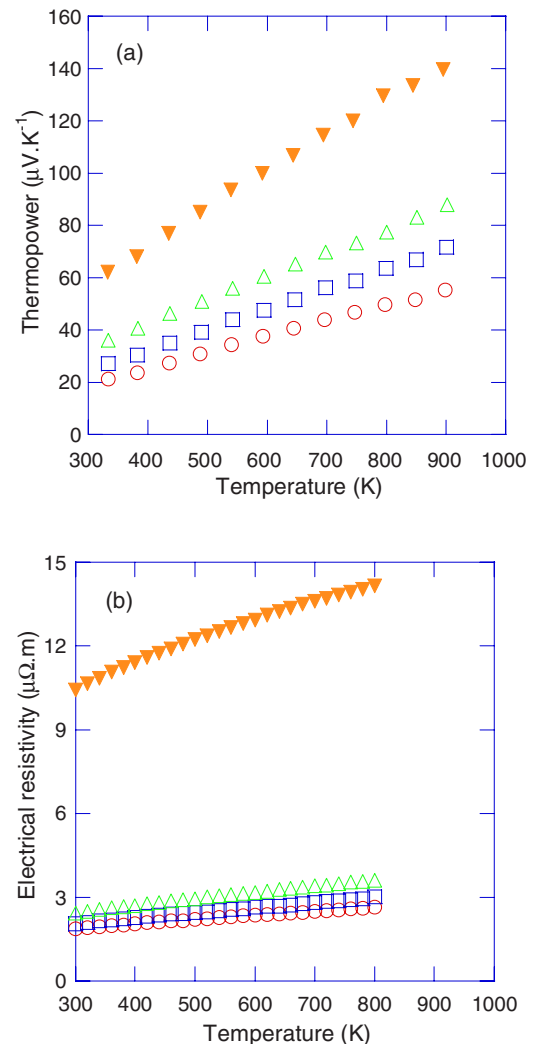


FIG. 1. (Color online) Temperature dependence of the thermopower (a) and electrical resistivity (b) for the  $\text{Mo}_3\text{Sb}_7$  (○),  $\text{Mo}_{2.75}\text{Ru}_{0.25}\text{Sb}_7$  (□),  $\text{Mo}_{2.5}\text{Ru}_{0.5}\text{Sb}_7$  (△), and  $\text{Mo}_{2.2}\text{Ru}_{0.8}\text{Sb}_7$  (▼) compounds.

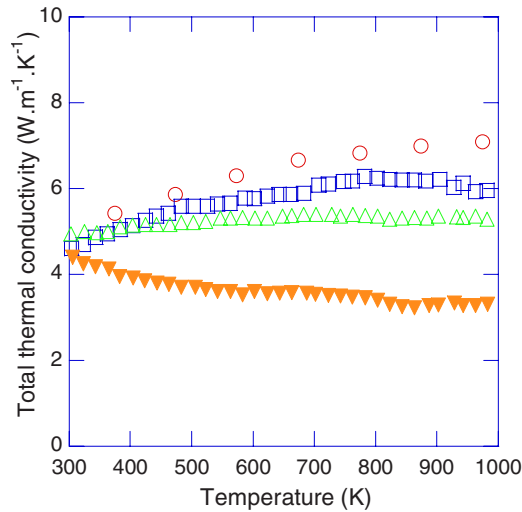


FIG. 2. (Color online) Total thermal conductivity as a function of the temperature for the  $\text{Mo}_3\text{Sb}_7$  ( $\circ$ ),  $\text{Mo}_{2.75}\text{Ru}_{0.25}\text{Sb}_7$  ( $\square$ ),  $\text{Mo}_{2.5}\text{Ru}_{0.5}\text{Sb}_7$  ( $\triangle$ ), and  $\text{Mo}_{2.2}\text{Ru}_{0.8}\text{Sb}_7$  ( $\blacktriangledown$ ) 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  $\text{Mo}_3\text{Sb}_7$  parent compound, such an unusual behavior has been tentatively ascribed to a complex interplay between antiferromagnetically coupled molybdenum dimers and phonons.<sup>14</sup> The partial substitution of Mo by Ru drastically affects this dependence and seems to reinforce the scenario proposed for the  $\text{Mo}_3\text{Sb}_7$  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  $1.6$ ).<sup>4</sup> 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

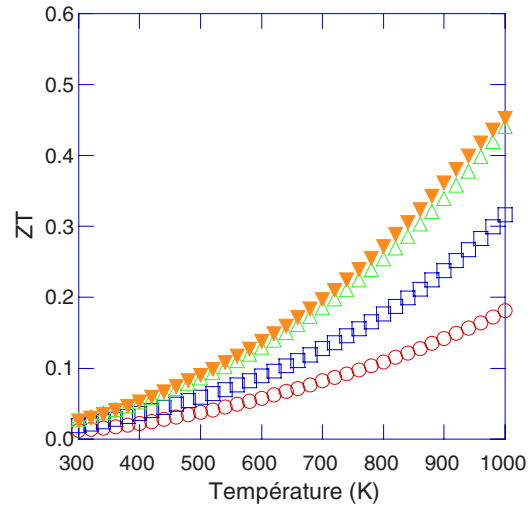


FIG. 3. (Color online) Temperature dependence of the dimensionless figure of merit  $ZT$  for  $\text{Mo}_3\text{Sb}_7$  ( $\circ$ ),  $\text{Mo}_{2.75}\text{Ru}_{0.25}\text{Sb}_7$  ( $\square$ ),  $\text{Mo}_{2.5}\text{Ru}_{0.5}\text{Sb}_7$  ( $\triangle$ ), and  $\text{Mo}_{2.2}\text{Ru}_{0.8}\text{Sb}_7$  ( $\blacktriangledown$ ).

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.

#### ACKNOWLEDGMENTS

C.C. greatly thanks M. Amiet and P. Maigné, and acknowledges DGA (Délégation Générale pour l'Armement, Ministry of Defense, France) and the Network of Excellence CMA (Complex Metallic Alloys) for financial support.

- <sup>1</sup>D. M. Rowe, *CRC Handbook of Thermoelectrics* (CRC Press, Boca Raton, FL, 1995).
- <sup>2</sup>A. Dauscher, B. Lenoir, H. Scherrer, and T. Caillat, *Recent Res. Dev. Mater. Sci.* **3**, 180 (2002).
- <sup>3</sup>A. F. Ioffe, *Physics of Semiconductors* (Academic Press, New York, 1960).
- <sup>4</sup>S. R. Brown, S. M. Kauzlarich, F. Gascoin, and G. J. Snyder, *Chem. Mater.* **18**, 1873 (2006).
- <sup>5</sup>S. R. Brown, E. S. Toberer, T. Ikeda, C. A. Cox, F. Gascoin, S. M. Kauzlarich, and G. J. Snyder, *Chem. Mater.* **20**, 3412 (2008).
- <sup>6</sup>E. S. Toberer, S. R. Brown, T. Ikeda, S. M. Kauzlarich, and G. J. Snyder, *Appl. Phys. Lett.* **93**, 062110 (2008).
- <sup>7</sup>E. S. Toberer, C. A. Cox, S. R. Brown, T. Ikeda, A. F. May, S. M. Kauzlarich, and G. J. Snyder, *Adv. Funct. Mater.* **18**, 2795 (2008).
- <sup>8</sup>E. Dashjav, A. Szczepienowska, and H. Kleinke, *J. Mater. Chem.* **12**, 345 (2002).
- <sup>9</sup>F. Gascoin, J. Rasmussen, and G. J. Snyder, *J. Alloys Compd.* **427**, 324 (2007).
- <sup>10</sup>N. Soheilnia, H. Xu, H. Zhang, T. M. Tritt, I. Swainson, and H. Kleinke, *Chem. Mater.* **19**, 4063 (2007).
- <sup>11</sup>C. Candolfi, B. Lenoir, A. Dauscher, C. Bellouard, J. Hejtmanek, E. Santava, and J. Tobola, *Phys. Rev. Lett.* **99**, 037006 (2007).
- <sup>12</sup>V. H. Tran, W. Miiller, and Z. Bukowski, *Phys. Rev. Lett.* **100**, 137004 (2008).

<sup>13</sup>C. Candolfi, B. Lenoir, A. Dauscher, J. Hejtmanek, E. Santava, and J. Tobola, *Phys. Rev. B* **77**, 092509 (2008).

<sup>14</sup>C. Candolfi, B. Lenoir, A. Dauscher, J. Hejtmanek, E. Guilmeau, J. Tobola, B. Wiendlocha and S. Kaprzyk *Phys. Rev. B* **70**, 035114 (2009).

<sup>15</sup>U. Häussermann, M. Elding-Ponten, C. Svensson, and S. Lidin, *Chem.-Eur. J.* **4**, 1007 (1998).

<sup>16</sup>J. Tobola, personal communication.

<sup>17</sup>R. Landauer, *J. Appl. Phys.* **23**, 779 (1952).