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# Crystal structure and high temperature thermoelectric properties of the $\text{Mo}_{3-x}\text{Ru}_x\text{Sb}_7$ compounds

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## Abstract

Zintl phases are currently focusing great attention for their thermoelectric potential typified by the discovery of a high  $ZT$  value in  $\text{Yb}_{14}\text{MnSb}_{11}$  based compounds. Here, we report on the crystallographic characterization via neutron and X-ray diffraction experiments and on the thermoelectric properties measured in the 300 – 1000 K temperature range of  $\text{Mo}_3\text{Sb}_7$  and its isostructural compounds  $\text{Mo}_{3-x}\text{Ru}_x\text{Sb}_7$ . Even though  $\text{Mo}_3\text{Sb}_7$  displays rather high  $ZT$  values given its metallic character, the partial substitution of Mo by Ru improves substantially its thermoelectric properties resulting in a  $ZT$  value of  $\sim 0.45$  at 1000 K for  $x = 0.8$ .

An interesting field of investigation to discover high-efficiency thermoelectric materials is linked to the research of complex crystalline structure displaying a large number of atoms per unit cell. Among the different classes of compounds investigated up-to-now, Zintl phases have attracted great attention in the last five years from a thermoelectric point of view.<sup>1</sup>  $ZT$  values greater than unity have been obtained in the  $\text{Yb}_{14}\text{MnSb}_{11}$  and  $\text{Yb}_{14}\text{Mn}_{1-x}\text{Zn}_x\text{Sb}_{11}$  compounds at high temperature, near 1200 K, demonstrating their potential for high temperature power generation.<sup>2,3</sup>

Recently, other Zintl phases of the  $\text{Ir}_3\text{Ge}_7$  structure type (space group  $Im\bar{3}m$ ) have been considered for high temperature thermoelectric applications.<sup>4-6</sup> Among this family, the  $\text{Mo}_3\text{Sb}_7$  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.<sup>7-9</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>10</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>11</sup> Thus, adding electrons to the structure could result in a progressive transition from a metallic-like 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>11</sup> The only attempt to add electrons to the structure was made by replacing some Sb atoms by Te atoms.<sup>4,5</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>5,10</sup>

Additional electrons can also be provided by judicious substitutions on the

molybdenum site. Band structure calculations have shown that a semiconducting state could be attained by replacing one Mo atom by one Ru atom per formula unit.<sup>12,13</sup> In the present paper, we report on the variations of the  $\text{Mo}_3\text{Sb}_7$  crystal structure when Mo is substituted by Ru and on the thermoelectric properties of these ternary compounds in the 300-1000 K temperature range.

Polycrystalline  $\text{Mo}_{3-x}\text{Ru}_x\text{Sb}_7$  compounds with nominal composition of  $x = 0, 0.25, 0.50$  and  $1$  were synthesized using the same powder metallurgical route described in detail elsewhere.<sup>7</sup> The consolidation of the powdered materials was performed by using uniaxial hot press in an argon atmosphere at  $600^\circ\text{C}$  for 2h under 51 MPa. Structural and chemical characterizations were performed through x-ray diffraction (XRD), neutron diffraction as well as electron probe micro analysis (EPMA). Neutron diffraction experiments were performed over the 4-300 K temperature range on the time-of-flight diffractometer POLARIS at the ISIS facility, Rutherford Appleton Laboratory, U.K.

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 conductivity has been obtained via thermal diffusivity measurements using a laser flash technique in the 300 – 1000 K temperature range.

Both x-ray and neutron diffraction experiments unequivocally show that Ru atoms can be successfully inserted into the  $\text{Mo}_3\text{Sb}_7$  crystalline structure. If the  $x = 0.25$  and  $0.50$  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 analysis revealing the good homogeneity of the  $x = 0.25$  and  $0.50$  samples. The real composition are close to the nominal ones except for the  $x = 1$  compound whose real composition is  $x = 0.80$ . Thus the real compositions are  $\text{Mo}_{2.75}\text{Ru}_{0.25}\text{Sb}_7$ ,  $\text{Mo}_{2.5}\text{Ru}_{0.5}\text{Sb}_7$  and  $\text{Mo}_{2.2}\text{Ru}_{0.8}\text{Sb}_7$ . 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 report. The relative densities of these samples, defined as the ratio of the measured density to the theoretical density, are 93, 98, 99 and 88 % for  $\text{Mo}_3\text{Sb}_7$ ,  $\text{Mo}_{2.75}\text{Ru}_{0.25}\text{Sb}_7$ ,  $\text{Mo}_{2.5}\text{Ru}_{0.5}\text{Sb}_7$  and  $\text{Mo}_{2.2}\text{Ru}_{0.8}\text{Sb}_7$  respectively.

The partial substitution of Mo by Ru leads to a strong decrease of the unit cell volume. This trend can be easily appreciated through the variation of the lattice parameters together with the different bond lengths as shown in Table I. The lattice parameter linearly decreases with  $x$ . Similarly, all the bond lengths decrease with  $x$ . The only exception lies in the Mo-Mo distances which increase with the Ru content.

Figures 1a and 1b 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. This increase confirms the hypothesis of a progressive transition to a semiconducting state as the Ru content increases as suggested by band structure calculations.<sup>12</sup> For  $x = 0.8$ , both the thermopower and the electrical resistivity display both a temperature dependence and values reminiscent to those reported for the  $\text{Mo}_3\text{Sb}_{7-x}\text{Te}_x$  compounds for  $x = 1.5$  and  $x = 1.6$ .<sup>5</sup> As a result of the decrease of the hole concentration with increasing Ru content, the electrical resistivity rises with  $x$ .

The temperature dependence of the total thermal conductivity is shown in Figure 2. It must be noted that these data have been corrected to take into account the different densities

of these samples.<sup>14</sup> These compounds display thermal conductivities ranging between 3.8 – 5.5 W.m<sup>-1</sup>.K<sup>-1</sup> 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 behaviour. For the highest Ru concentration ( $x = 0.8$ ), the thermal conductivity decreases to attain 3.2 W.m<sup>-1</sup>.K<sup>-1</sup> at 1000 K. In the case of the Mo<sub>3</sub>Sb<sub>7</sub> parent compound, such an unusual behaviour has been tentatively ascribed to a complex interplay between antiferromagnetically coupled molybdenum dimers and phonons.<sup>10</sup> Low temperature magnetic susceptibility data together with transport properties measurements on the Mo<sub>3</sub>Sb<sub>7-x</sub>Te<sub>x</sub> compounds have brought further experimental evidence in favour of this picture. Likewise, a similar picture may be at play in the isostructural Mo<sub>3-x</sub>Ru<sub>x</sub>Sb<sub>7</sub> compounds.

From the measured transport properties, the dimensionless figures of merit  $ZT$  have been calculated for all compounds and are depicted in Fig. 3. To determine the  $ZT$  values up to 1000 K, we have linearly extrapolated the electrical resistivity and thermopower dependences above 800 and 900 K, respectively. 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 the Mo<sub>3</sub>Sb<sub>7-x</sub>Te<sub>x</sub> compounds.<sup>5</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 Mo<sub>2.2</sub>Ru<sub>0.8</sub>Sb<sub>7</sub>, a value slightly lower than those reported in the isostructural Mo<sub>3</sub>Sb<sub>5.4</sub>Te<sub>1.6</sub> compound.

In conclusion, we have reported on the crystal structure and the high temperature thermoelectric properties of the Mo<sub>3-x</sub>Ru<sub>x</sub>Sb<sub>7</sub> system for  $x = 0.25, 0.50$  and 0.80. The partial substitution of Mo by Ru leads to a strong decrease of the unit cell volume reflected through both the lattice parameters and the interatomic distances. The presence of Ru significantly improves the Seebeck coefficient leading to higher dimensionless figures of merit compared to that of the parent compound.

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## Table

Table I. Lattice parameter ( $a$  in Å) and selected interatomic distances (Å) of  $\text{Mo}_3\text{Sb}_7$ ,  $\text{Mo}_{2.75}\text{Ru}_{0.25}\text{Sb}_7$  and  $\text{Mo}_{2.2}\text{Ru}_{0.8}\text{Sb}_7$  as determined from neutron diffraction at 300 K.

	$\text{Mo}_3\text{Sb}_7$	$\text{Mo}_{2.75}\text{Ru}_{0.25}\text{Sb}_7$	$\text{Mo}_{2.2}\text{Ru}_{0.8}\text{Sb}_7$
$a$	9.5715	9.5483	9.5073
Mo-Mo	2.995(1) x1	2.991(4) x1	2.998(2) x1
Mo-Sb1	2.822(9) x4	2.816(9) x4	2.810(1) x4
Mo-Sb2	2.799(7) x4	2.792(1) x4	2.775(8) x4
Sb2-Sb2	2.907(5) x1	2.895(5) x1	2.871(2) x1
Sb2-Sb2	3.107(1) x3	3.102(4) x3	3.096(1) x3
Sb1-Sb1	3.384(0) x4	3.375(8) x4	3.361(3) x4
Sb1-Sb2	3.683(1) x8	3.673(2) x8	3.655(1) x8

## Captions

Figure 1: Temperature dependence of the thermopower (a) and electrical resistivity (b) for the  $\text{Mo}_3\text{Sb}_7$  ( $\circ$ ),  $\text{Mo}_{2.78}\text{Ru}_{0.22}\text{Sb}_7$  ( $\square$ ),  $\text{Mo}_{2.5}\text{Ru}_{0.5}\text{Sb}_7$  ( $\triangle$ ) and  $\text{Mo}_{2.2}\text{Ru}_{0.8}\text{Sb}_7$  ( $\blacktriangledown$ ) compounds.

Figure 2: Temperature dependence of the total thermal conductivity for the  $\text{Mo}_3\text{Sb}_7$  ( $\circ$ ),  $\text{Mo}_{2.78}\text{Ru}_{0.22}\text{Sb}_7$  ( $\square$ ),  $\text{Mo}_{2.5}\text{Ru}_{0.5}\text{Sb}_7$  ( $\triangle$ ) and  $\text{Mo}_{2.2}\text{Ru}_{0.8}\text{Sb}_7$  ( $\blacktriangledown$ ) compounds. These data have been corrected to take into account the different densities of these samples.

Figure 3: Temperature dependence of the dimensionless figure of merit  $ZT$  for the  $\text{Mo}_3\text{Sb}_7$  ( $\circ$ ),  $\text{Mo}_{2.78}\text{Ru}_{0.22}\text{Sb}_7$  ( $\square$ ),  $\text{Mo}_{2.5}\text{Ru}_{0.5}\text{Sb}_7$  ( $\triangle$ ) and  $\text{Mo}_{2.2}\text{Ru}_{0.8}\text{Sb}_7$  ( $\blacktriangledown$ ) compounds.

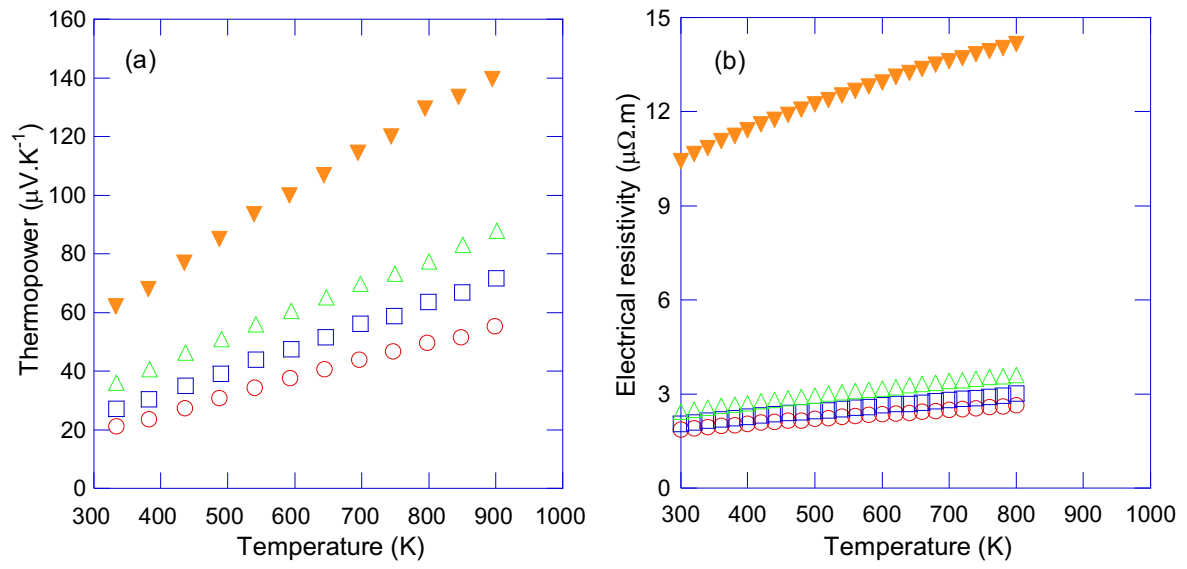


Figure 1

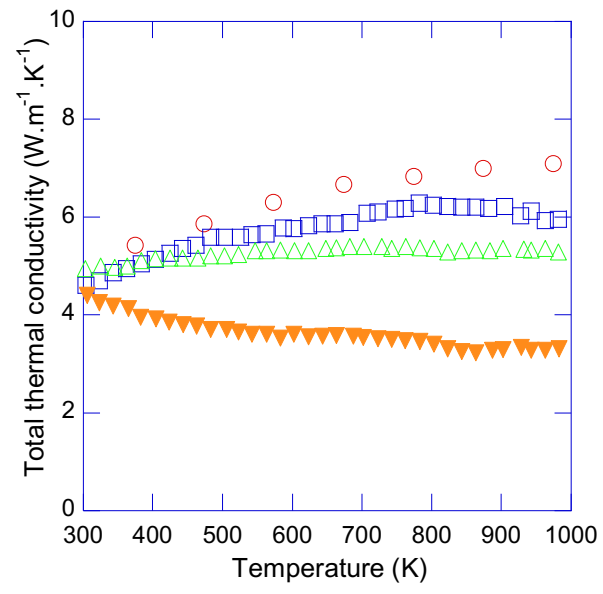


Figure 2

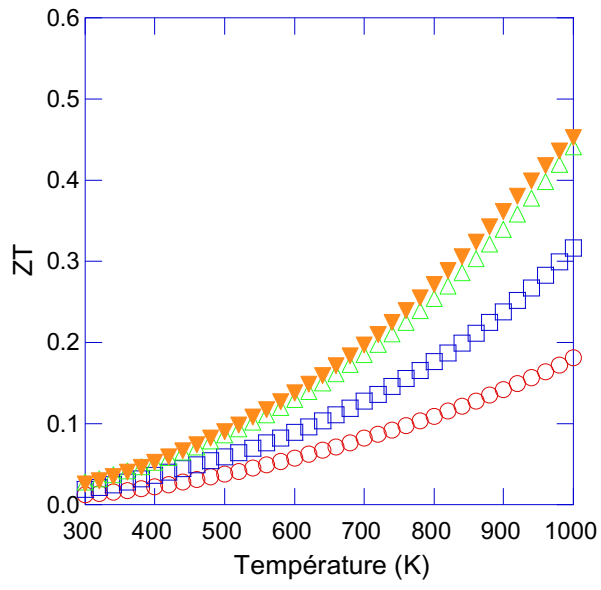


Figure 3