Thermoelectric properties of the $Mo_{3-x}Ru_xSb_7$ compounds

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Abstract

Zintl phases recently received a great attention for their thermoelectric potential typified by the discovery of a high ZT value in the $Yb_{14}MnSb_{11}$ compound. Here, we report on the synthesis and the transport properties measurements over a wide temperature range from 2 to 350 K of other materials having a complex crystalline structure, namely Mo_3Sb_7 and its related compounds $Mo_{3-x}Ru_xSb_7$. While the binary compound displays low ZT values due to its metallic behavior, the partial substitution of Mo by Ru significantly improves the thermoelectric properties.

Extensive efforts have been devoted for more than 50 years to optimize materials to achieve outstanding thermoelectric properties. The effectiveness of this kind of compounds is captured in the dimensionless figure of merit given at a temperature T, *ZT*, expressed as $ZT = \alpha^2 T / \rho\lambda_T$ where α, ρ, λ_T are the Seebeck coefficient or thermopower, the electrical resistivity and the total thermal conductivity respectively.

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, high *ZT* values have been reported in $Yb_{14}MnSb_{11}$ and $Yb_{14}Mn_{1-x}Zn_xSb_{11}$.[1,2] These materials achieve the requirements involved in the ZT formula: a complex crystalline structure to lower the thermal conductivity as well as a high number of possible substitutions to precisely tune the electrical properties.

Recently, other Zintl phases of the Ir_3Ge_7 structure type (space group *Im3m*) have been considered for high temperature thermoelectric applications.[3-5] Among this family, the Mo_3Sb_7 compound has focused great attention due to the coexistence of superconductivity below 2.3 K and a spin gap in the magnetic excitations spectrum.[6-8] 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 results in low *ZT* value and therefore, further optimization must be achieved.[9] To improve the thermoelectric properties, one can take part of the band structure of this material. Actually, strong *d-p* interactions

give rise to a gap near the Fermi level.[10] Thus, adding electrons to the structure could result in a progressive transition from a metalliclike to a semiconducting state. Band structure calculations show that two more electrons per formula unit are required to position the Fermi level into the gap. This approach has been successfully applied by considering a partial substitution of antimony by tellurium.[3,4] This substitution was found to markedly affect all the relevant properties involved in thermoelectricity resulting in a high *ZT* value of 0.8 at 1050 K in $Mo_3Sb_{5.4}Te_{1.6}$.[4]

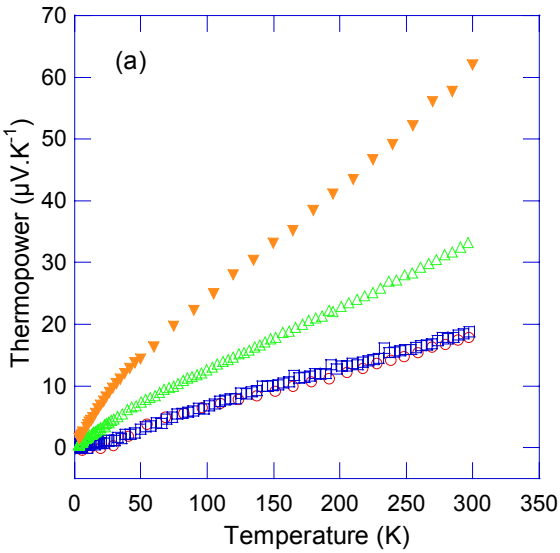
In the present paper, we show that a similar approach can be envisaged on the molybdenum site by substituting with ruthenium. We report on the transport properties measurements needed to calculate *ZT* to shed some light on the potential of these compounds for thermoelectric devices.

Low temperature transport measurements were carried out on parallelepipedic shaped samples cut with a diamond wire saw to typical dimensions of 2x2x10 mm^3. Electrical resistivity, thermopower and thermal conductivity, were measured from 5 to 300 K using an automated closed-cycle refrigerator system.

Synthesis of $Mo_{3-x}Ru_xSb_7$ compounds with nominal composition of x = 0.25, 0.5 and 1 was described in details previously. Powdered materials were hot pressed using graphite dies in an argon atmosphere at 600 °C for 2h under 51 MPa. Structural and chemical characterization were performed through x-ray diffraction, neutron diffraction as well as electron probe micro analysis (EPMA).

Both x-ray and neutron diffraction experiments unequivocally show that Ru atoms can be successfully inserted into 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 analysis revealing the good homogeneity of the x = 0.25 and 0.5 samples. The real composition are close to the nominal ones except for the x = 1 compound whose real composition is x = 0.8. Thus the real compositions are $Mo_{2.78}Ru_{0.22}Sb_7$, $Mo_{2.5}Ru_{0.5}Sb_7$ and $Mo_{2.2}Ru_{0.8}Sb_7$. 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 Mo_3Sb_7, $Mo_{2.78}Ru_{0.22}Sb_7$, $Mo_{2.5}Ru_{0.5}Sb_7$ and $Mo_{2.2}Ru_{0.8}Sb_7$ respectively.

Figure 1a and 1b shows the measured thermopower and electrical resistivity from 2 up to 350 K for the different compounds. The Mo_3Sb_7 data were taken from Ref. 6 for a more convenient comparison with those of substituted samples.



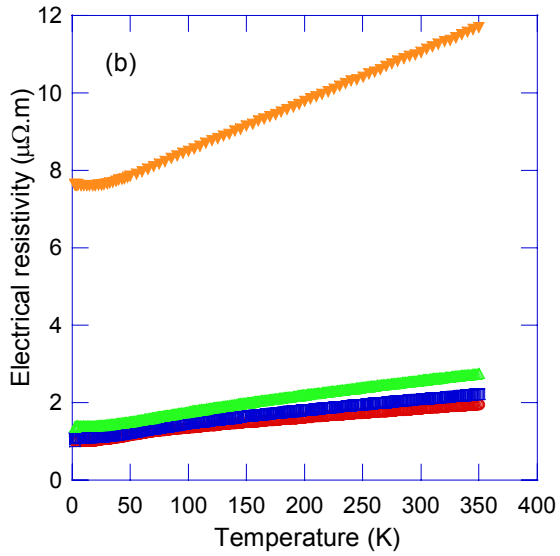


Figure 1: Temperature dependence of the thermopower (a) and electrical resistivity (b) for the Mo_3Sb_7 (○), $Mo_{2.78}Ru_{0.22}Sb_7$ (□), $Mo_{2.5}Ru_{0.5}Sb_7$ (Δ) and $Mo_{2.2}Ru_{0.8}Sb_7$ (▼) compounds.

Both α and ρ values of the substituted compounds increase linearly with temperature and with Ru concentration. The thermopower is positive whatever the sample is indicative of hole conduction. At room temperature, the measured values are 18, 19, 33 and 62 $\mu V.K^{-1}$ for x = 0, 0.22, 0.5 and 0.8 respectively. These evolutions corroborate the hypothesis of a progressive transition to a semi-conducting state as the Ru content increases. The x = 0.8 compound dispalys a thermopower temperature dependence typical of heavily doped semi-conductors and is reminiscent to those reported for the $Mo_3Sb_{7-x}Te_x$ compounds for x = 1.5 and x = 1.6.[4]

This conclusion remains unchanged if we analyze the electrical resistivity. Actually, KKR-CPA calculations reveal a displacement of the Fermi level to the edge of the valence bands by increasing the Ru content. Thus, this evolution is related to a decrease of both the density of states and the carrier concentration. Therefore, the higher the Ru content is, the higher should be the electrical resistivity. This is exactly what we can observe in figure 1b. It must be mentioned that the huge difference between the x = 0.5 and 0.8 data is linked to the lower density of the latter compound. All these tendencies are strongly supported by magnetotransport measurements as well as by the results reported on the $Mo_3Sb_{7-x}Te_x$ compounds.

The temperature dependence of the thermal conductivity is shown in Fig. 2. At room temperature, the total thermal conductivity attains 5,5, 4,8, 5,2 and 3,8 $W.m^{-1}.K^{-1}$ for Mo_3Sb_7, $Mo_{2.78}Ru_{0.22}Sb_7$, $Mo_{2.5}Ru_{0.5}Sb_7$ and $Mo_{2.2}Ru_{0.8}Sb_7$ respectively.

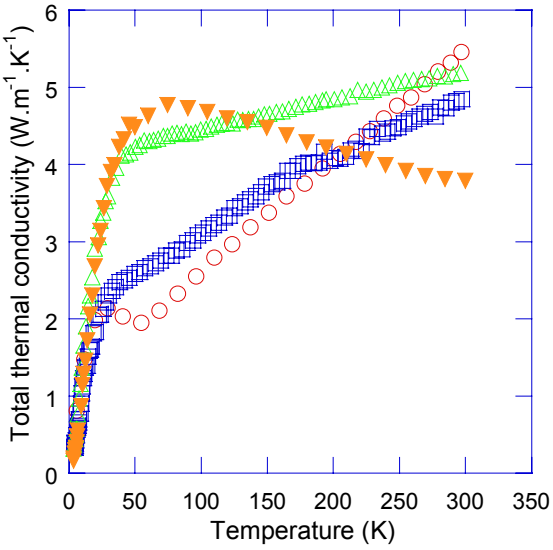


Figure 2: Temperature dependence of the total thermal conductivity for the Mo_3Sb_7 (○), $Mo_{2.78}Ru_{0.22}Sb_7$ (□), $Mo_{2.5}Ru_{0.5}Sb_7$ (Δ) and $Mo_{2.2}Ru_{0.8}Sb_7$ (▼) compounds.

It is worth mentioning that these data have been corrected to take into account the different densities of our samples. If these values are low due to the complex crystalline structure of these materials, the observed temperature dependences as well as the evolution with the Ru content constitute the most striking features. In the case of the Mo_3Sb_7 parent compound, this unusual behaviour could be tentatively ascribed to a complex interplay between antiferromagnetically coupled dimers and phonons as well as to the spin gap opening.[9] The partial substitution of Mo by Ru drastically affects this dependence since the

total thermal conductivity increases with the Ru fraction. Thus, this evolution seems to reinforce the scenario proposed for the Mo_3Sb_7 compound since this exotic behaviour 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.

Based on these different measured transport properties, the dimensionless figures of merit *ZT* can be calculated for these three compounds and are depicted in Fig. 3.

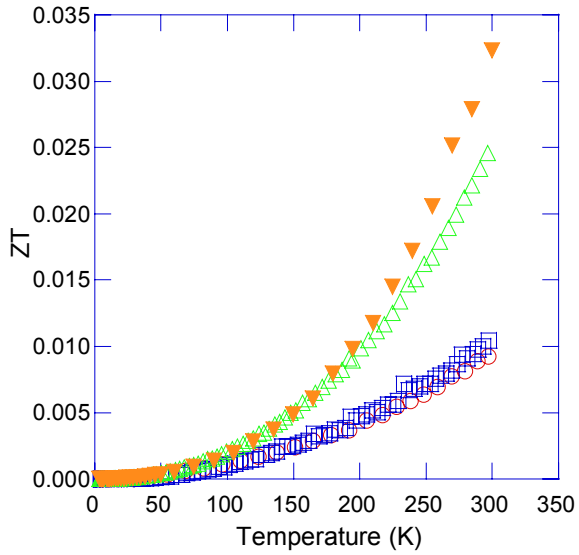


Figure 2: Temperature dependence of the dimensionless figure of merit ZT for the Mo_3Sb_7 (○), $Mo_{2.78}Ru_{0.22}Sb_7$ (□), $Mo_{2.5}Ru_{0.5}Sb_7$ (Δ) and $Mo_{2.2}Ru_{0.8}Sb_7$ (▼) compounds.

For all the samples, the *ZT* increases monotonically with temperature up to 300 K. The best *ZT* of 0.033 at 300 K is obtained for $Mo_{2.2}Ru_{0.8}Sb_7$. This result makes this material a possible candidate for thermoelectric applications at high temperature.

In conclusion, we have reported on the thermoelectric properties of the $Mo_{3-x}Ru_xSb_7$ system for x = 0.22, 0.5 and 0.8. 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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