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Promising thermoelectric properties in $Ag_xMo_9Se_{11}$ compounds ($3.4 \leq x \leq 3.9$)

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Polycrystalline Mo_9 cluster chalcogenides $Ag_xMo_9Se_{11}$ ($3.4 \leq x \leq 3.9$) have been prepared by powder metallurgy techniques, sintered by spark plasma sintering and characterized by x-ray diffraction. Their thermoelectric properties (electrical resistivity, thermopower, thermal conductivity) have been determined in the 300–800 K temperature range. The $Ag_xMo_9Se_{11}$ compounds show p-type conduction characteristics. The outstanding low lattice thermal conductivities give rise to a rather high value of the dimensionless thermoelectric figure of merit *ZT* of ~0.65 at 800 K for $x=3.8-3.9$, making this family of materials particularly promising for thermoelectric power generation applications. © *2011 American Institute of Physics*. [doi:10.1063/1.3579261]

Currently, there is a resurgence of interest in thermoelectric materials with enhanced efficiency. These materials can convert directly heat (solar heat, geothermal heat, and waste heat from cars or industrial processes, etc.) to electricity, and also can act as solid state heat pumps when supplied with electrical current. The conversion efficiency is determined by the dimensionless figure of merit *ZT*, given by $ZT=(S^2/\rho\lambda)T$, where *S* is the thermopower, ρ the electrical resistivity, λ the thermal conductivity, and *T* the absolute temperature at which the properties are measured.[1] For many years, the best thermoelectric materials, mainly heavily doped semiconductor compounds and alloys such as Bi_2Te_3, PbTe, and Si–Ge, possessed *ZT* values not exceeding unity.[1–3] Recent approaches using the "phonon glass electron crystal (PGEC)" concept and more recently the introduction of nanometer-size grains or other nanostructures in a matrix phase have demonstrated the possibility to obtain more performant thermoelectric materials.[1–4] Several classes of materials have been proofed to epitomize the PGEC concept, specifically partially filled-skutterudites,[1–3,5,6] Zn_4Sb_3-based materials,[1–3,7] clathrates,[1–3,8] and semiconducting Chevrel phases.[2,9,10]

Most Chevrel compounds can be described by the chemical formula MMo_6X_8, where M stands for alkaline, alkaline earth, rare earth, actinide elements, or transition metals, and X is usually a chalcogen (S, Se, Te).[11] The fundamental structural unit Mo_6X_8 is the octahedral cluster Mo_6 surrounded by eight chalcogens forming a distorted cube. Mo_6X_8 units build up a progression of channels, where a variety of M atoms can be accommodated. The best Chevrel phase thermoelectric material discovered to date is $Cu/FeMo_6Se_8$.[9] This compound has a *ZT* value near 0.6 at 1150 K.[9] Molybdenum clusters with a nuclearity higher than six can also be obtained and derive from the one-dimensional transface sharing of Mo_6 octahedra.[12–14] Among them the ternary $Ag_xMo_9Se_{11}$ (with $x \sim 3.6-3.8$) compounds discovered by Gougeon *et al.*[12] could be also interesting thermoelectric candidates. Actually, their Fermi level is close to a band edge and their crystal structure is complex (high molecular weight, nondirectional bonding, large number of atoms per molecule). All these conditions are beneficial to achieve a low thermal conductivity at high temperature. So far, the electrical resistivity at low temperature has only been investigated.[12] In this letter we report on the high temperature thermoelectric properties of $Ag_xMo_9Se_{11}$ ($3.4 \leq x \leq 3.9$) ternary compounds and show that the *ZT* values surpass those of the best Chevrel phase.

Stoichiometric amounts of highly pure Ag, Mo, and $MoSe_2$ powders were used for the preparation of the materials by solid state reaction, already described.[13] The obtained samples were ground and subsequently densified by spark plasma sintering (SPS) at 1050 °C with a holding time of 10 min under 80 MPa in an argon atmosphere. X-ray diffraction (XRD) analyses were performed on a monochromatized Cu $K\alpha 1$ Bruker D8 Advance diffractometer. Rietveld refinement was realized using FULLPROF software.[15] The temperature dependences of the thermopower and electrical resistivity were measured simultaneously in the 300–800 K temperature range by a standard four-probe method using a ULVAC-ZEM3 device on bar-shaped samples, which were cut perpendicularly to the press direction. The thermal diffusivity α was measured in the same temperature range by the laser flash method (NETZSCH, LFA 427) on disk-shaped samples, which were cut perpendicularly to the press direction. The specific heat C_p was determined using a differential scanning calorimetry (DSC) apparatus (NETZSCH, DSC 403 F3). The thermal conductivity λ was evaluated through the standard equation $\lambda=\alpha \cdot C_p \cdot d$, where *d* is the density. The measured density of all samples was above 95% of the theoretical density. Hall coefficient measurements were con-

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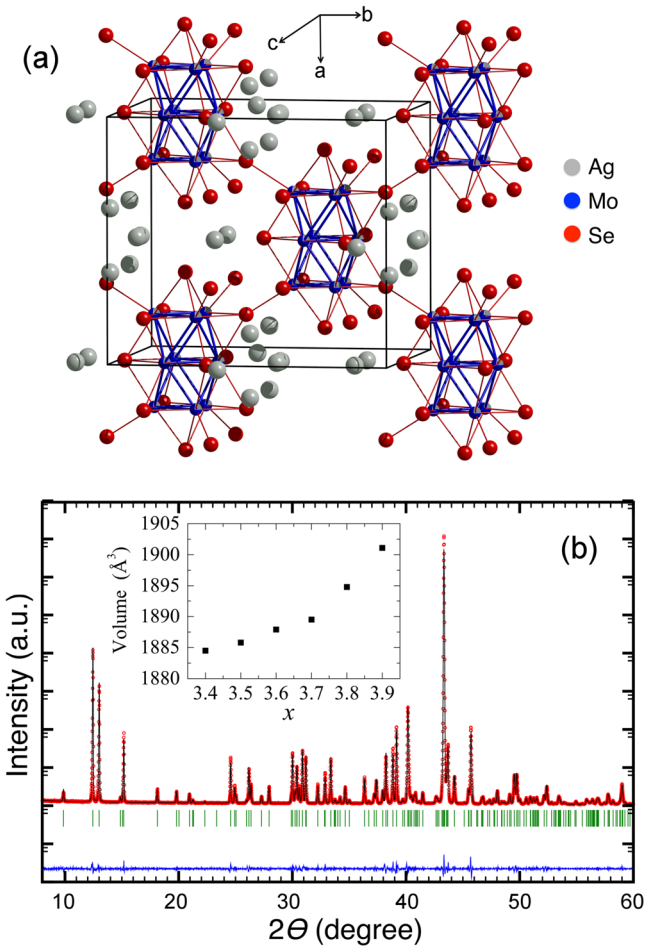

FIG. 1. (Color online) (a) Crystalline structure highlighting the $Mo_9Se_{11}Se_6$ cluster unit. (b) XRD pattern for $Ag_{3.7}Mo_9Se_{11}$ before SPS sintering (similar pattern after SPS sintering). The unit cell volume as a function of Ag content x in $Ag_xMo_9Se_{11}$ is shown in the inset.

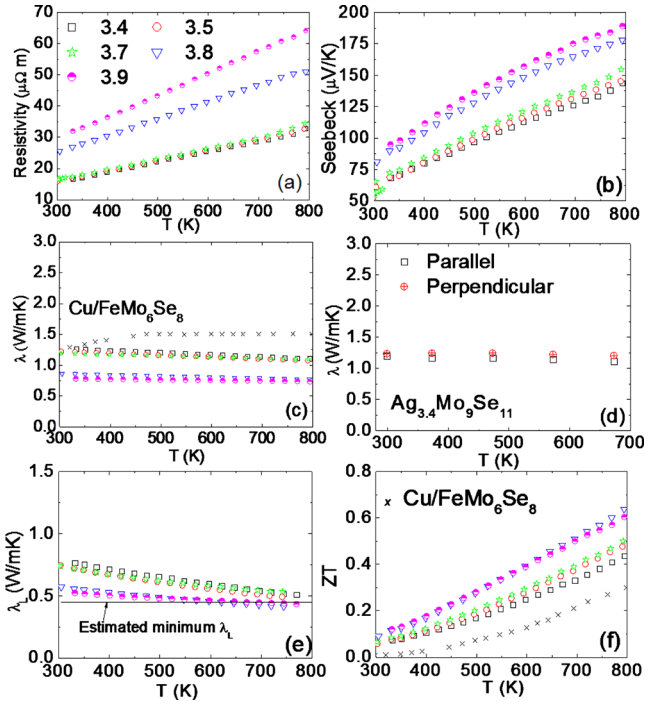

FIG. 2. (Color online) Temperature dependence of (a) the electrical resistivity, (b) the thermopower, (c) the total thermal conductivity λ, and (f) *ZT* of the $Ag_xMo_9Se_{11}$ compounds. The thermal conductivity measured along and perpendicular to the press direction for sample $Ag_{3.4}Mo_9Se_{11}$ is shown in (d). The lattice thermal conductivity λ_L of $Ag_xMo_9Se_{11}$ is represented in (e) together with the minimum lattice thermal conductivity depicted by the solid line. The behaviors of the Cu/Fe filled Chevrel phase is shown for comparison (after Ref. 9).

ducted at room temperature using a five probes method on a Quantum Design model physical property measurement system. Sound velocity measurements were made at a frequency of 10 MHz using the ultrasonic pulse-echo method. The mean sound velocity v was determined from $v=[1/(3v_l^3)+2/(3v_s^3)]^{-1/3}$, where v_l and v_s are the longitudinal and the shear wave velocities, respectively.

The $Ag_xMo_9Se_{11}$ compounds crystallize in the orthorhombic space group *Cmcm*. The building block is the $Mo_9Se_{11}Se_6$ cluster unit, as shown in Fig. 1(a). The bioctahedral Mo_9 cluster results from the uniaxial face-sharing condensation of two Mo_6Se_8 units with loss of Se atoms belonging to the shared face. This cagelike structure can accommodate Ag atoms, which are delocalized over four crystallographically independent sites. Pioneer works on $Ag_xMo_9Se_{11}$ single crystals prepared by chemical transport in a vapor phase led to x values limited to 3.6–3.76.[11] In this letter, single phase polycrystalline samples have been obtained for $3.4 \leq x \leq 3.9$. The presence of secondary phases, mainly $MoSe_2$ and the Chevrel phase $Ag_yMo_6Se_8$ or Ag metal, has been detected outside this range of content. A typical XRD pattern is displayed in Fig. 1(b) for $Ag_{3.7}Mo_9Se_{11}$. The enhancement of the unit cell volume with the Ag filling level is also shown in the inset.

The electrical resistivity and thermopower of $Ag_xMo_9Se_{11}$ are displayed as a function of temperature in Fig. 2. The resistivity shows a linear increase in all the temperature range studied, whatever the sample is, characteristic of a metal-like behavior. For a given temperature, ρ increases with x, e.g., from around 32 $\mu\Omega$ m for $x=3.4$ to 64 $\mu\Omega$ m for $x=3.9$ at 800 K. The positive sign of S indicates that holes are the majority carriers in the system. The S values increase with both temperature and Ag concentration, ranging from 140 μV/K for $x=3.4$ to 188 μV/K for $x=3.9$ at 800 K. For the analogous Chevrel phases, one of the most important electronic parameter is the metallic electron count (MEC), also termed as valence electron count (VEC), i.e., the total number of valence electrons per Mo_6 cluster. MEC is a convenient measure for determining the degree of filling of the valence band near the Fermi level.[16] Chevrel phases are reported with MEC values between 20 and 24, this last value turning the material to a semiconducting state. The compositions with a MEC lower than 24 are metallic and this has been experimentally confirmed in binary Chevrel compounds inserted with Cu, Cu/Fe, or Ag atoms.[9,17] High MEC values can be obtained either by increasing the concentration of filler atoms or by substitutions in the framework of Mo_6Se_8. For example, mixed clusters such as $Mo_4Ru_2Se_8$ or $Mo_2Re_4Se_8$ and the Ti filled Mo_6Se_8 are found to be semiconductors.[9,18–20] A previous theoretical study on the Mo_9 clusters has shown that the MEC in the metastable binary Mo_9Se_{11} is 32 and that the semiconducting state can be reached for 36.[21,22] Supposing Ag to be formally +1, increasing x in $Ag_xMo_9Se_{11}$ should then result in a decrease in the hole concentration and hence in an increase in both the resistivity and the thermopower. Our results support well this picture. However, the galvanomagnetic study indicates that

the electronic properties of these interesting compounds cannot be classified as usual. Actually, Hall coefficients of $Ag_xMo_9Se_{11}$ ($3.4 \leq x \leq 3.9$) at 300 K are negative and field independent from 10 to 50 kOe. This field independence suggests that the weak field limit always remains. This is expected if the states near the Fermi energy have significant *d* character, leading to high effective masses and correspondingly low mobilities. Given that *S* is positive at 300 K, it is clear that both holes and electrons are contributing to the conduction.

The temperature dependence of the thermal conductivity of the $Ag_xMo_9Se_{11}$ compounds is plotted in Fig. 2(c), and compared to that of $Cu/FeMo_6Se_8$.[9] One can see that whatever *x* is, λ in $Ag_xMo_9Se_{11}$ compounds is lower than in the Chevrel phase. At 300 K, the values range from 0.8 to 1.2 W/mK for $x=3.9$ and $x=3.4$, respectively. The λ value remains nearly constant with temperature, indicating that the thermal conductivity approaches a glasslike limit. It is worthy to point out here that λ was not measured along the same direction as ρ and *S*. However, by measuring the thermal conductivity along and perpendicular to the press direction for a given composition, no appreciable texture influence could be detected [Fig. 2(d)]. Using the measured values of ρ and supposing that the Wiedemann–Franz law is valid, the lattice thermal conductivity, λ_L, was evaluated. The values, displayed in Fig. 2(e), are in the range 0.4–0.7 W/mK over the entire range studied. These values are lower than those reported for the best thermoelectric materials such as partially filled skutterudites.[23] Figure 2(e) also shows an estimate of the "minimum" lattice thermal conductivity of $Ag_xMo_9Se_{11}$, when the mean free path *l* reaches the interatomic distance. We used, for this estimate, the kinetic formula $\lambda_L = 1/3 C_v v l$, where the specific heat C_v was taken equal to C_p, the determined sound velocity *v* is 2110 m/s and the interatomic distance *l* is 0.3 nm. We can note that λ_L of the studied compounds approaches the minimum value possible. The origin of the very low lattice thermal conductivity in these compounds is not yet fully addressed. We rule out any influence of the microstructure because scanning electron microscopy images indicate an average grain size of about some micrometers. Rather, we speculate that the crystal complexity as well as a static and/or dynamic disorder coming from the Ag atoms should play an important role.

The dimensionless figure of merit *ZT* as a function of temperature for all the compounds is displayed in Fig. 2(f) for all the compounds together with the $Cu/FeMo_6Se_8$.[9] The $Ag_xMo_9Se_{11}$ ternary compounds possess *ZT* values greater than the best Chevrel phase over the temperature range investigated. *ZT* reaches the value of 0.65 at 800 K in compounds having the highest Ag nominal content ($x=3.8-3.9$). These encouraging results show the interest for further investigating this family of Mo_9 chalcogenide compounds as potential thermoelectric materials. It is of particular importance to determine the origin behind such surprisingly low lattice thermal conductivity. The relevant study is currently underway.

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