Order−Disorder Transition in AgCrSe$_2$: a New Route to Efficient Thermoelectrics

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Ⓢ *Supporting Information*

On the basis of the conversion of waste heat into electricity, thermoelectric generators are today well recognized as viable renewable energy sources. Good thermoelectric materials are up to now heavily doped (extrinsic) small band gap semiconductors with low thermal conductivity. Such materials represent a good balance between the high Seebeck semiconductors and the low resistivity metals. In contradiction with all the known state-of-the-art materials, here we show that while its electrical resistivity is about 1 order of magnitude larger than in known efficient thermoelectric materials, the layered compound AgCrSe$_2$ possesses an unprecedented glass like thermal conductivity due to disordered silver atoms over two tetrahedral sites and a large Seebeck coefficient. The discovery of such remarkable combination of properties together with the wide chemical variability of this kind of structure type suggests that this type of material can be easily optimized and is worthy of further investigations.

The quality of a thermoelectric material is evaluated by its figure of merit zT, where $z = \alpha^2/\rho\kappa$ with α the Seebeck coefficient, ρ the electrical resistivity, κ the thermal conductivity, and T the absolute temperature. Furthermore, κ is the sum of two independent components, a lattice contribution κ_l and an electronic contribution κ_e equal to LT/ρ according to the Wiedemann−Franz law (L is the Lorenz constant and equal to $2.45 \times 10^{-8}\,\mathrm{W \cdot \Omega \cdot K^{-2}}$). Moreover, α and ρ vary inversely with the carrier concentration so that the power factor α^2/ρ is difficult to improve. Consequently, the optimization of zT remains problematic and the number of materials with zT reaching values above the unity remains scarce. Nearly all efficient thermoelectric materials are heavily doped small band gap semiconductors with carrier concentration spanning from 10^{19} to $10^{21}\,\mathrm{cm^{-3}}$, ideally placed between the metals (with high conductivity but low Seebeck and high thermal conductivity) and insulators (with large Seebeck and low thermal conductivity but high resistivity). If α, ρ, and κ_e are all dependent on the carrier concentration, κ_l is the sole term only governed by structural features. Thus, good thermoelectric materials are usually associated with complex structures, large unit cell, presence of defects, interstitial atoms, and mixed occupancy and heavy elements, all of these being responsible for increasing the phonon scattering, hence decreasing the lattice thermal conductivity. Obviously, glasses have lower thermal conductivity than crystalline materials as their amorphous nature scatters phonons to mean free path of atomic dimension, however an amorphous structure also scatters charge carriers resulting in an increased electrical resistivity through decreased carrier mobility.[1]

The layered compound AgCrSe$_2$ is a known Ag-ion conductor whose structure can be described as CdI$_2$-type layers of CrSe$_2^-$ in which the Cr^{3+} cations are in a distorted octahedral coordination by Se^{2-} anions, the interlayer spaces being filled by the silver ions occupying tetrahedral sites (Figure 1).[2] The title compound was synthesized directly from the pure elements in sealed fused silica tube. This container was heated at 900 °C in 12 h and stayed at that temperature for 24 h before being cooled back to room temperature in 12 h. The resulting powder was then compacted by spark plasma sintering using a maximum temperature of 750 °C. The density of the pressed puck was higher than 95% of the theoretical density. All the property measurements were performed on the same puck, which was also analyzed by scanning electron microscopy coupled with energy dispersive spectroscopy and X-ray diffraction. Seebeck coefficient and electrical resistivity were measured on an Ulvac Riko ZEM3 measuring system, a Netzsch 457 microflash laser flash system was used to assess the thermal conductivity. The heat capacity, the differential scanning calorimetry and thermogravimetric analysis were measured on a Netzsch DCS 404 Pegasus system (DSC curves can be found as Supporting Information). All measurements were performed under inert atmosphere, i.e. dynamic vacuum or partial pressure of helium.

There are two different tetrahedral sites in the structure of AgCrSe$_2$ situated between the CrSe$_2^-$ sandwiches that form a slightly puckered honeycomb lattice.[3] At low temperature, only one site is 100% occupied by silver, but with rising temperature, the silver ions gradually migrate to the other site and a complete disorder is reached at a transition temperature of 475K. This disorder consequently generates a change of space group from the low temperature non centrosymmetric $R3m$ to the high temperature centrosymmetric $R\bar{3}m$. In the latter, the Cr^{3+} ions adopt a perfect octahedral symmetry. Furthermore, as the two tetrahedral sites have a slightly different z coordinate, the distribution of the silver atoms is called quasi-two-dimensional.[3]

Thus, above the structural transition the structure can be divided in two distinct parts, the covalently bonded slabs CrSe$_2^-$ and disordered silver cations. This description resembles that of
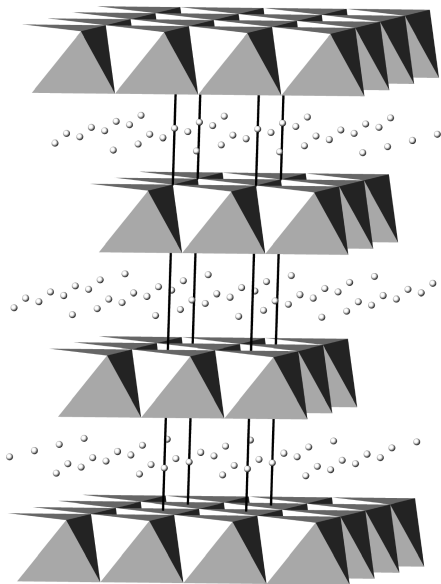
Figure 1. the structure of AgCrSe$_2$ with CdI$_2$-type layers of CrSe$_2$ (represented as CrSe$_6$ edge-shared octahedra) and disordered Ag$^+$ cations over two sites (high temperature case with 50% occupancy of the silver atoms on each tetrahedral site).

many good thermoelectric materials that show a clear separation between the region of electronic conduction and the zone of phonon scattering. This is the case for instance in Zn$_4$Sb$_3$,[4] or Ca$_x$Yb$_{1-x}$Zn$_2$Sb$_2$.[5] In the latter compound, anionic slabs of Zn$_2$Sb$_2^{2-}$ are separated by the divalent cations Ca^{2+} and Yb^{2+}. The disorder created by the mixed occupation of the cationic site by the calcium and the ytterbium deteriorates the thermal conduction that becomes temperature independent just like in amorphous (disordered) materials.[5] In the state-of-the-art compound Zn$_4$Sb$_3$, there are again two different substructures, the anionic antimony atoms that are either isolated (Sb^{3-}) or that form dumbbells of Sb$_2^{4-}$ that provide a suitable crystalline structure for the electronic conduction, and diffuse, disordered channels of zinc that reduce the phonon mean free path substantially. For these two reasons, Zn$_4$Sb$_3$ is often referred to as an ideal phonon glass electron crystal thermoelectric material.[6] The case of AgCrSe$_2$ is somewhat similar as the disordered layer of silver atoms clearly provides a great way to scatter phonons efficiently as it acts like an amorphous region within a crystalline solid. The effect of the disorder on the diffusivity is clearly seen in Figure 2. Below 200 °C, the diffusivity decreases sharply with increasing temperature whereas it plateaus at about 0.25 mm^2/s after the phase transition and remains nearly temperature independent as expected in the case of amorphous materials.

On the same figure is plotted the evolution of the specific heat with temperature that also evidence the structural phase transition. Moreover, it reaches a value of 0.12 J/g·K above 300 °C comparable to the specific heat of heavy metals such as lead (0.129 J/g·K) and mercury (0.139 J/g·K),[7] whereas its room temperature value compares well with the calculated Dulong−Petit value (0.314 J/g·K).[8] This is actually a really surprising not to say unrealistic result to find such a low heat capacity at high temperature. It has thus been decided to use the Dulong−Petit calculated value of the C_p to estimate the thermal conductivity. However, measurements have repeatedly given the same value and our measuring system has been tested on other materials
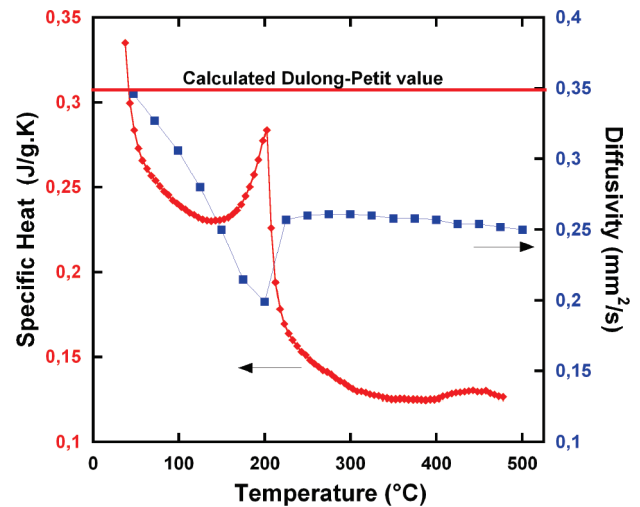

Figure 2. Evolution of the specific heat (red) and of the thermal diffusivity (blue) of AgCrSe$_2$ as a function of temperature.
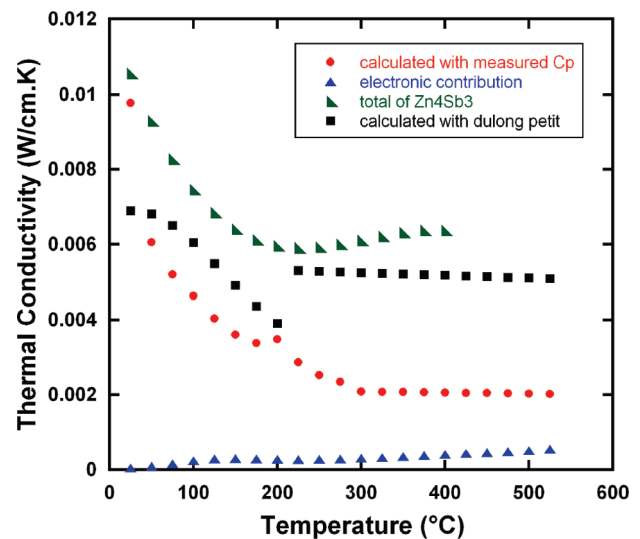
Figure 3. Thermal conductivity of Zn$_4$Sb$_3$ (from ref 4) and of AgCrSe$_2$ as a function of temperature. The data are calculated from either the experimental C_p values or the Dulong−Petit calculated value.

(AgCrS$_2$ and TiS$_2$), and the measured values were in accordance with the published data and with the Dulong−Petit value. For these reasons, the thermal conductivity and the zT plots (Figures 3 and 5) also include the value obtained with the measured C_p even if these are to be taken with much precaution.

The thermal conductivity can be calculated from these two measurements as it is equal to the product $C_p \times$ diffusivity $\times$ density. Thus, as shown in Figure 3, the thermal conductivity is extremely low independently of the utilized C_p value. With the Dulong−Petit C_p, it decreases from about 7 mW/cm·K at room temperature to 5 mW/cm·K above 300 °C. At such temperatures, it is simply outstanding that AgCrSe$_2$ has a thermal conductivity lower than that of Zn$_4$Sb$_3$, a compound considered as having a glass-like thermal conductivity.[6] It is also noticeable that the thermal conductivity is proportional to T^{-x} below the
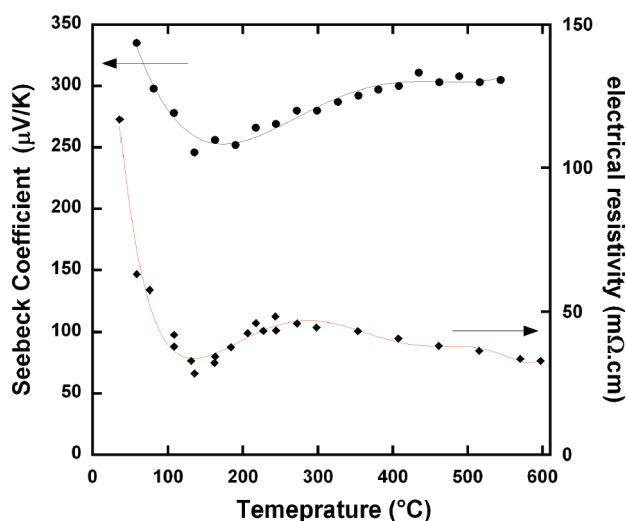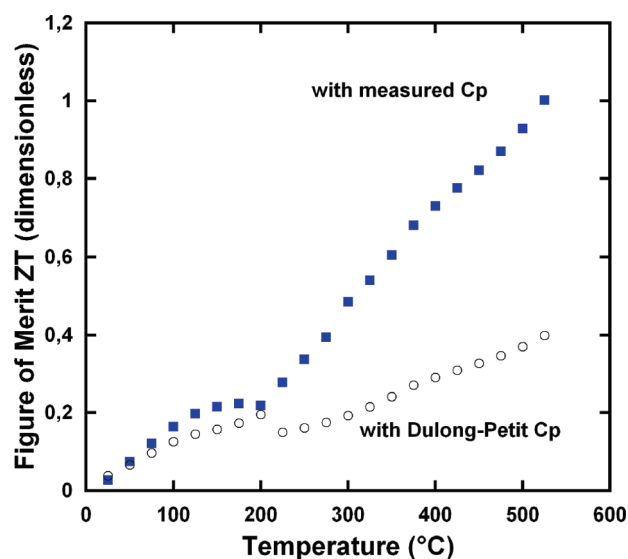
Figure 4. Electrical resistivity (in red) and Seebeck coefficient (in blue) of $AgCrSe_2$ as a function of temperature.

Figure 5. Dimensionless thermoelectric figure of merit zT of $AgCrSe_2$ as a function of temperature.

transition temperature whereas it is nearly temperature independent after the transition. This behavior is in good agreement with a transition from a crystalline material to a disordered material.

The variation of the electrical resistivity with temperature is shown on Figure 4. It appears that $AgCrSe_2$ resembles an intrinsic semiconductor with moderate electrical resistivity ranging from more than 100 m$\Omega \cdot$cm at room temperature to around 35 m$\Omega \cdot$cm at 575 °C. These values are in agreement with the previously reported values,[9] these values are also considered very high for any thermoelectric material and usually result in a very low figure of merit. However, high resistivity values generate a very low (if not negligible) κ_e as evidenced here in Figure 3 (blue triangles). The electronic contribution of the thermal conductivity does not reach values higher than 0.5 mW/cm·K. The effect of the gradually disordered silver atoms on the electronic transport is also noticeable as the resistivity reaches a minimum at around 150 °C before being nearly temperature independent (even if the slope is slightly negative and thus reminiscent of a semiconductor behavior). The same "bump" is visible on the evolution of the Seebeck coefficient, with temperature as a minimum value of 250 μV/K obtained at around 150 °C before increasing again (Figure 4). The positive value of the Seebeck coefficient is consistent with dominant carriers in the sample being holes indicating p-type behavior. Moreover, and just like the electrical resistivity, the Seebeck coefficient is nearly temperature independent above the phase transition and reaches a value of 300 μV/K above 400 °C. Because of the relatively high electrical resistivity, the power factor of $AgCrSe_2$ is actually very low compared with the known state of the art thermoelectric materials as it bearly reaches 2.5 μW/(cm·K^2) at 525 °C. However, what makes $AgCrSe_2$ truly remarkable is the fact that even with such a low power factor, its thermoelectric figure of merit zT is reasonably high (Figure 5).

We have shown here a new type of potentially efficient thermoelectric material, namely a compound that exhibits high Seebeck coefficient, relatively high electrical resistivity, but ultralow thermal conductivity comparable to that of a glass. However, because $AgCrSe_2$ is an ionic conductor, its use in a thermoelectric device is precluded because the material would quickly

deteriorate (the silver atoms diffusing out of the structure) if placed in a electric circuit. Nonetheless, $AgCrSe_2$ can be looked as a remarkable exception within the thermoelectric materials with an electrical resistivity ranging in the tenths of milli$\Omega \cdot$cm. This unique case might lead to the discovery of other efficient thermoelectric materials. Up to now, to realize the ideal thermoelectric material, the concept of phonon glass electron crystal has been extensively used. In particular, the layered A_nMX and A_nMX_2 compounds, where n is for the number of insulating layers, made of elements A separating MX or MX_2 conducting layers and where M is for a metal and X for an anion (O, S, Se, As, Sb), respectively forming NiAs (MX) or CdI_2 (MX_2) layers, have been the focus of much interest.[10] In principle, their separating layers provide an ideal playground to make the phonons scatter as in misfit structures, oxides or sulfides. In the present study, it is found that the $AgCrSe_2$ thermoelectric figure of merit is above all values reported for A_nMX and A_nMX_2 compounds. This major achievement results from the existence of an order−disorder structural transition at the level of the separating sublattice which allows a thermal conductivity similar to that of a glass to be reached.

This ultra low value of κ, achieved by taking advantage of the cationic disorder in the layered compounds, opens the route to the discovery of other efficient thermoelectric materials. Even band insulators, with relatively high electrical resistivity, deserve to be revisited, providing that their structures offer a sublattice with structural disorder.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. DSC and TGA data about the thermal stability of the title compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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dx.doi.org/10.1021/cm200581k |*Chem. Mater.* 2011, 23, 2510–2513

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