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Semiconducting glasses: A new class of thermoelectric materials?

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ABSTRACT

The deeper understanding of the factors that affect the dimensionless figure of merit, ZT, and the use of new synthetic methods has recently led to the development of novel systems with improved thermoelectric performances. Albeit up to now with ZT values lower than the conventional bulk materials, semiconducting glasses have also emerged as a new family of potential thermoelectric materials. This paper reviews the latest advances on semiconducting glasses for thermoelectric applications. Key examples of tellurium-based glasses, with high Seebeck coefficients, very low thermal conductivities and tunable electrical conductivities, are presented. ZT values as high as 0.2 were obtained at room temperature for several tellurium-based glasses with high copper concentrations, confirming chalcogenide semiconducting glasses as good candidates for high-performance thermoelectric materials. However, the temperature stability and electrical conductivity of the reported glasses are still not good enough for practical applications and further studies are still needed to enhance them.

1. Introduction

The development of the "phonon glass and electron crystal" (PGEC) idea by Slack [1] led to a better understanding of the mechanisms affecting the phonon propagation, without interfering too much with the electrical charge propagation. Several general rules to increase the thermoelectric efficiency by decreasing the lattice contribution to the thermal conductivity were launched (or recovered from ideas earlier developed on the 1950s), the most important ones being (i) the use of compounds with complex crystal structures, (ii) the presence of heavy atoms weakly bounded to the structures, (iii) the existence of inclusions and/or impurities, (iv) the formation of solid solutions and (v) the existence of a large number of grain boundaries [2].

Glasses can have most of these characteristics, and in fact they show some of the lowest thermal conductivities observed in solids. However, the high degree of disorder usually produces large electron scatterings that imply a low mobility and, consequently, a low electrical conductivity. Moreover, it also normally generates broad electronic bands, which led to low Seebeck coefficients. Therefore, low power factors are expected for normal glasses. Nevertheless, the huge amount of different types of already identified glasses raises the question if there is any with high Seebeck coefficients and electrical conductivities, being, consequently, suitable for thermoelectric applications.

It is known that the maximum of the power factor in crystalline materials is observed for low gap and/or heavily doped semiconductors, with carrier concentrations between 10^{19} and 10^{21} carriers per cm^3 [3]. Therefore, it should be also expected that the best potential glasses for thermoelectric applications must have a semiconducting behavior.

Semiconducting glasses and amorphous systems differ from the crystalline counterparts by their structural disorder. While in the crystalline state there is a regular repetition in the three-dimensional space of a unit cell, semiconducting glasses and amorphous systems have a very high degree of structural disorder and no long range order in the arrangement of atoms exists. Three main types of disorder can be classified in these systems: (i) different bond lengths, (ii) different bond angles and (iii) under- and over-coordinate sites. All this affects their electronic structure when compared with the crystalline materials. In a crystalline semiconductor the energy of the bands can be described as a function of the wavevector, *k*, but, due to the lack of long range structural periodicity, in a highly disordered systems all states must be considered localized, as their eigenfunctions cannot be written using a periodic probability amplitude [4]. However, (and similarly to the crystalline systems), a discontinuity in the density of

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states, separating valence and conduction bands (or quasi-continuous states), can be observed, although (i) and (ii) types of disorder give rise to band tail localized states, which are located above and below the valence and conduction bands, respectively. The border between band and tail states is called the mobility edge, as in these tails the carrier mobility decreases to very low values, and therefore a mobility gap can be considered [5]. Disorder of type (iii) promotes the formation of dangling bonds (filled non-bonding orbitals), which lie in the middle of the bonding and anti-bonding energy states [4]. The electrical conductivity at high temperatures usually occurs in bands, but at low temperatures the conduction in the localized tail states normally dominates the electrical transport and a considerable hopping energy, E_{Hopp},is required. As thermoelectric power is independent from this hopping energy in semiconducting glasses and amorphous systems, the possibility of an independent tuning of electrical conductivity and thermoelectric power in these materials at medium and low temperatures exists.

A large number of semiconducting glasses and amorphous systems were studied in the last decades [6]. From these, two distinct semiconducting disordered families were predominantly analyzed, the tetrahedrally bonded amorphous semiconductors, like Si and GaAs, and the chalcogenide semiconducting glasses, as Se and As_2S_3. In the tetrahedrally bonded amorphous semiconductors sp^3 hybridization occurs and normally four covalent bonds are formed, while in chalcogenide semiconducting glasses a chalcogen (two-fold) atom can coexist with a three-fold and four-fold coordinated elements, the first two types having filled (or lone pair) p orbitals. As a result, the origin of the valence band is different in both families: in the tetrahedrally bonded amorphous semiconductors the valence band arises from the sp^3 bonding combinations, whereas in the chalcogenide semiconducting glasses it is produced by non-bonding (electron-filled or lone-pair) p electron states of the chalcogen atoms [4–7]. This difference leads to distinct physical properties, in the tetrahedrally bonded amorphous semiconductors only localized states near the middle of the gap appear (originated from type (iii) defects [5]), while an intrinsic narrow electronic band in the density of states close to the Fermi level can exist in chalcogenide glasses [7], as the valence bandwidth is governed by the interaction between lone-pair electrons. Therefore, chalcogenide semiconducting glasses seem to be the best highly disordered candidates for thermoelectrical applications.

In this contribution a review on chalcogenide semiconducting glasses for thermoelectric applications is made, being presented several examples of this type of glasses showing high Seebeck coefficients, very low thermal conductivities and tunable electrical conductivities. In particular, the cases of $Cu_xA_yTe_z$ (A=Ge, As, Ga and Si) general composition tellurium-based glasses will be stressed, demonstrating that this family of glasses is currently one of the most attractive for high-performance thermoelectric materials.

2. The tellurium-based semiconducting glasses

Chalcogenide semiconducting glasses normally have small electrical conductivity values and high Seebeck coefficients [8]. However, similarly to the chalcogenide elements (S, Se, Te), an increase of the metallic character of chalcogenide semiconducting glasses along the periodic table column is observed [8]. Therefore, tellurium glasses show the smaller gaps, pointing *a priori* these materials as the best candidates for thermoelectric applications. On the other hand (and contrary to the tetrahedrally bonded amorphous semiconductors), the activation energy for the electronic conduction of chalcogenide semiconducting glasses changes smoothly with composition, which can be due not only to the pinning of the Fermi level midway between the positive and negative charged defect states, but also to an intrinsic character of the electrical conductivity for these materials [4,8,9]. Consequently, the possibility of a considerable increase of the electrical conductivity of chalcogenide semiconducting glasses by changing composition must be considered.

$Ge_{20}Te_{80}$ is a tellurium-based semiconducting glass having a small electrical conductivity value but presenting a high Seebeck coefficient [10]. This glass was reported as being composed by $GeTe_4$ tetrahedral units bridged by Te–Te bonds or shared tellurium atoms connected to two germanium atoms, with both germanium and tellurium obeying the 8-N rule [11–14]. A recent study on Cu–Ge–Te chalcogenide glasses based on $Ge_{20}Te_{80}$ shows that glassy materials with copper concentrations as high as 27.5% at. can be obtained by melt spinning [15,16]. Structural studies indicate that at low concentrations ($<5\%$ at.) copper has a coordination of ~ 2, with only tellurium as next neighbor atoms, and germanium and tellurium continue obeying the 8-N rule [14]. However, at higher concentrations ($\geq 8\%$ at.) Cu–Cu bonds are also formed, the coordination number of copper increases to $N_{Cu} > 3$ and the coordination number of tellurium is higher than 2, pointing that a significant percentage of tellurium atoms have three neighbors [14]. These studies also indicate that copper mainly occupies the free space of the host matrix, without strongly affecting the network of germanium and tellurium atoms [14]. On the other hand, adding copper and decreasing the germanium concentrations result in a dramatically reduction (five orders of magnitude) of the electrical resistivity of the chalcogenide glass (Fig. 1(a)). Moreover, the Seebeck coefficients

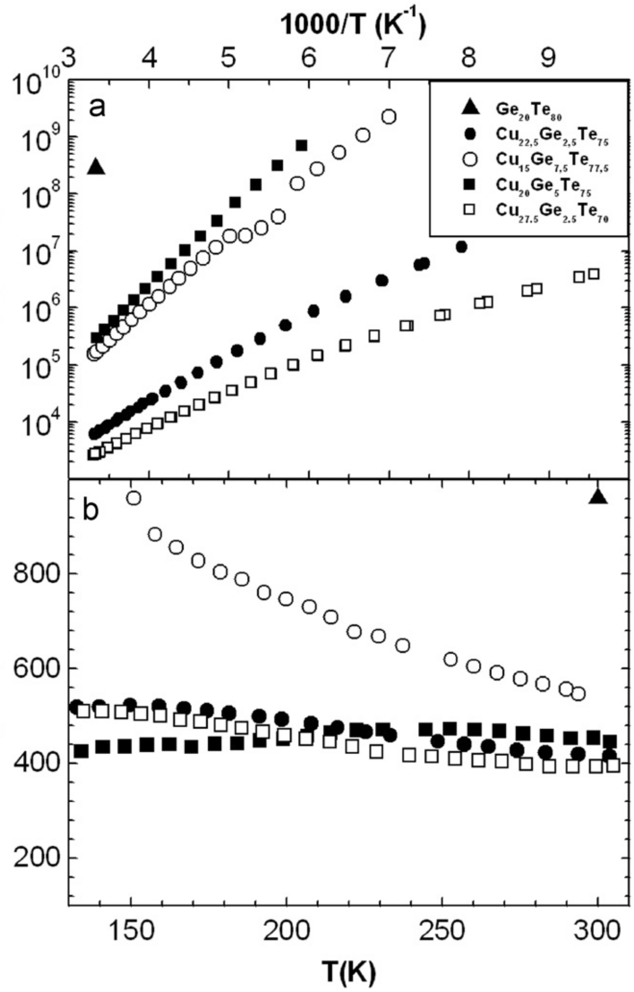

Fig. 1. Temperature dependence of (a) the electrical resistivity and (b) Seebeck coefficient for $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses.

are kept at larger values (Fig. 1(b)) and, as a consequence, a huge increase in the power factor is observed. The combination of a large power factor with an extremely small thermal conductivity ($\sim$0.1 W K^{-1} m^{-1} at 300 K) lead to a maximum ZT of $\sim$0.2 at 300 K in the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glassy system [15,16]. A deeper analysis of these glasses shows that the activation energy for the electronic conduction, E_ρ, (half of the mobility gap) strongly decreases with the increase of copper content, while the activation energy for the thermoelectric power, E_S, is not so drastically affected (Fig. 2(a) and (b)). Therefore, a considerable decrease of the hopping energy, E_{Hopp}, with the rise of copper concentration is observed (Fig. 2(c)) and the intrinsic semiconducting nature of the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses can be concluded, opening the possibility for further improvements.

Experiments made on other tellurium-based semiconducting glasses prepared by melt spinning and containing high concentrations of copper and tellurium show that they can also have interesting thermoelectric properties. Fig. 3 presents the temperature dependence of the electrical transport properties (electrical resistivity and Seebeck coefficient) of $Cu_{x+y}A_{20-x}Te_{80-y}$ (A=Ga and Si) glasses, together with the best $Cu_{x+y}Ge_{20-x}Te_{80-y}$ composition ($Cu_{27.5}A_{2.5}Te_{70}$). It can be seen that alloying with other elements does not significantly change their electrical transport properties. Nevertheless, some general trends can be taken. In particular, it seems that for $Cu_{x+y}A_{20-x}Te_{80-y}$ (A=Ge, Ga and Si) glasses the increase of copper concentration decreases the electrical resistivity, while the increase of tellurium increases the Seebeck coefficient. However, the practical use of these glasses at temperatures higher than 100 °C collides with their relatively small glass transition temperatures ($T_g\sim$120 °C) and low stabilities (T_C–$T_g<$20 °C, where T_C is the crystallization temperature). DSC results indicate that alloying with extra elements, albeit not appreciably changing the glass transition temperature, stabilizes the glass (Fig. 4).

The very low thermal conductivity of $Ge_{20}Te_{80}$-based glasses has been recently confirmed from studies on the bulk amorphous chalcogenides $Ge_{20}Te_{80-x}Se_x$ (x=0. 1, 2, 8) [17]. Moreover, they point to thermal conductivities close to the minimum limit for $Ge_{20}Te_{80-x}Se_x$ glasses. The phonon mean free path of these glasses was found to saturate at temperatures above their

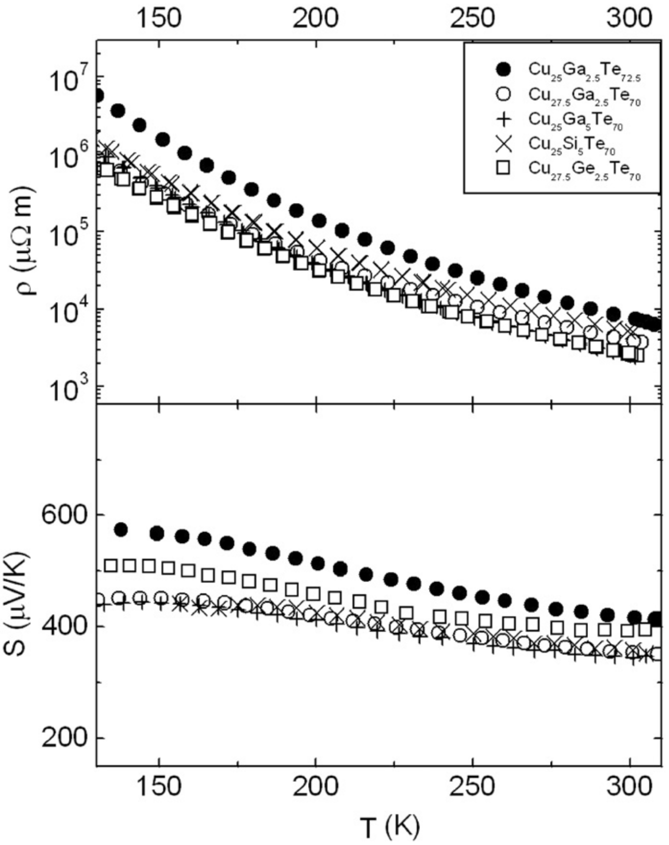

Fig. 3. Temperature dependence of the electrical resistivity and Seebeck coefficient for $Cu_{x+y}A_{20-x}Te_{80-y}$ (A=Ga and Si) glasses.

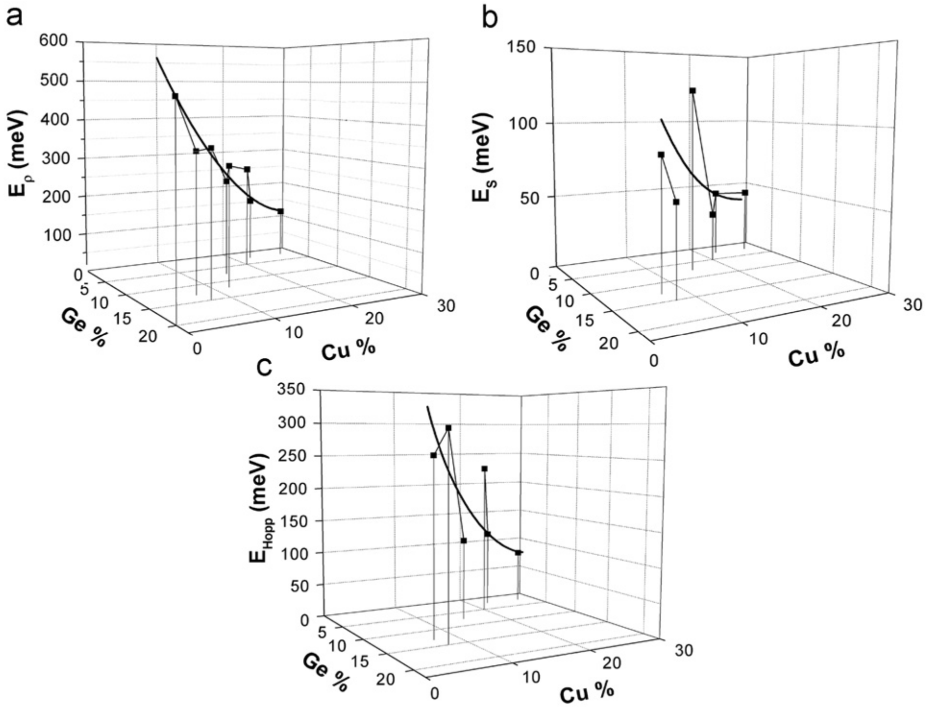

Fig. 2. Variation of the (a) activation energy for the electronic conduction, E_ρ, (b) activation energy for the thermoelectric power, E_S, and (c) hopping energy, E_{Hopp}, of the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses as function of composition.

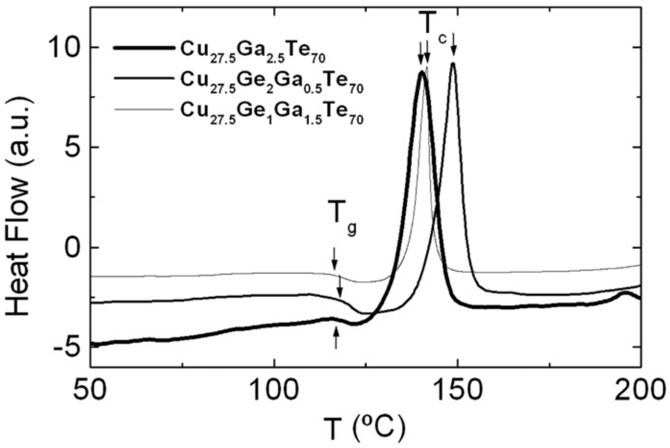

Fig. 4. DSC measurements versus temperature showing glass transition (T_g) and crystallization temperatures (T_c) in $Cu_{27.5}Ga_{2.5}Te_{70}$, $Cu_{27.5}Ge_{2}Ga_{0.5}Te_{70}$ and $Cu_{27.5}Ge_{1}Ga_{1.5}Te_{70}$.

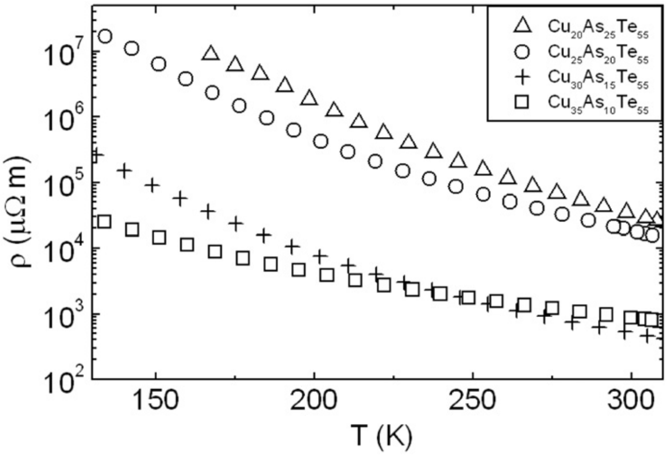

Fig. 5. Temperature dependence of the electrical resistivity for $Cu_xAs_{45-x}Te_{55}$ ($20 < x < 35$) glasses.

Debye temperatures ($\theta_D \sim 110$ K), reaching 3–4 Å. This value is close to the dimensions of the smallest coherent scattering region (2.5–3 Å) [17], which justifies the very low thermal conductivities observed on the $Ge_{20}Te_{80}$-based glasses [18].

Albeit the encouraging results of thermoelectric properties obtained on $Cu_{x+y}A_{20-x}Te_{80-y}$ (A=Ge, Ga and Si) glasses, high temperatures cannot be attained by these materials due to their relatively low glass transition temperatures and stability. However, better glass-forming ability and thermal stability exist in other tellurium-based semiconducting glasses. In particular, As–Te glasses with low tellurium content (when compared with $Ge_{20}Te_{80}$) show an increase of the glass stability and T_g (as an example, $As_{50}Te_{50}$ has $T_g \sim 152$ °C and $T_C - T_g \sim 51$ °C [19]). The inclusion of copper in the As–Te system has been reported to enhance the glassy domain (prepared by conventional melt quenching) [20] and the electrical conductivity of the chalcogenide glasses [21]. Moreover, recent studies on $Cu_xAs_{45-x}Te_{55}$ ($20 < x < 35$) glasses prepared by melt spinning show a significant increasing of the vitreous domain when compared with the conventional melt quenching technique, which allowed higher copper concentrations in the glassy materials [22]. Besides, $Cu_xAs_{45-x}Te_{55}$ glasses have $T_g \sim 135$ °C and $T_C - T_g \sim 35$–40 °C that permits working temperatures higher than those of the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses [22]. Similarly to the Cu–Ge–Te glasses, the increase of copper concentration leads to an increase of the electrical conductivity, while the Seebeck coefficients remain at high values [22]. An almost doubling of the power factor at 300 K for the best composition ($Cu_{30}As_{15}Te_{55}$) is observed, when compared with $Cu_{27.5}A_{2.5}Te_{70}$, reflecting the significantly decrease of the electrical resistivity (Fig. 5). By combining this promising power factor value to the thermal conductivity found in [23] for the $As_{50}Te_{50}$ parent glass would lead to a ZT ~ 0.2 at 300 K suggesting chalcogenide semiconducting glasses as good candidates for high-performance thermoelectric materials.

If a direct comparison between the thermal conductivities of $Ge_{20}Te_{80}$-based and $Cu_{30}As_{15}Te_{55}$ glasses is made, it can be concluded that the arsenic glasses have higher values than the germanium ones. This is not unexpected, as the thermal conductivity of a non-metallic glass is inversely proportional to the molecular weight [24], which is higher for the $Ge_{20}Te_{80}$-based glasses than for the $Cu_{30}As_{15}Te_{55}$ ones.

3. The processing of tellurium-based semiconducting glasses

The practical use of materials for thermoelectric applications needs a proper shaping and setup. Glasses are usually obtained by the conventional melt quenching technique or by melt spinning. The melt spinning technique, which allows very fast quenching rates, is particularly interesting for tellurium-based composition glasses where the stability criterion $T_C - T_g$ is very small and leads to partially crystallized glasses by the conventional melt-quenching technique. However, this technique usually gives only amorphous ribbons and/or flakes that are not directly suitable for most of the thermoelectric applications.

The Spark Plasma Sintering (SPS) technique is a technique of fast sintering under pressure that mainly avoids the grain growth observed in the conventional hot press methods. It is mostly used with powder (or powdered) samples, but other type of materials, as ribbons or flakes, can be easily sintered by SPS. Glassy tellurium-based composition ribbons and/or flakes were sintered by SPS to get amorphous bulks with different shapes and dimensions (Fig. 6). The SPS technique allows fast heating rates and is suitable for the sintering of glasses by avoiding uncontrollable crystallization phenomenon (depending on the difference between the glass transition temperature, T_g, and the crystallization temperature, T_C) with an appropriate thermo-mechanical treatment. Moreover, different types of dies can be used, depending on the

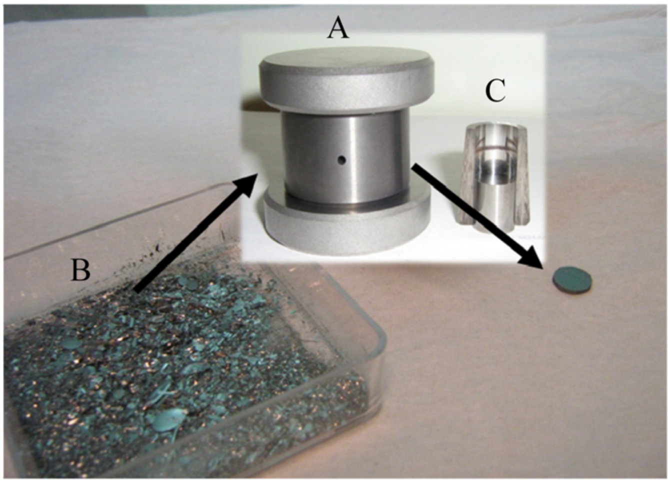

Fig. 6. Scheme of the preparation of thermoelectric glass bulk cylinder: Spark Plasma Sintering (A) of amorphous chalcogenide flakes obtained from Melt Spinning technique (B) using WC die (C).

specific application. In particular, the use of tungsten carbide (WC) die is of practical use for tellurium-based glasses, since it supports pressures up to 1 GPa and the pressure helps the sintering process. Therefore, the same porosity can be obtained at lower temperatures if very high pressures are applied, with the additional advantage to avoid crystallization in the case of tellurium-based glasses.

Preliminary results on the SPS bulk sintered from the $Cu_{15}As_{30}Te_{55}$ initial composition show a lower ZT value at 300 K ($\sim$0.04), when compared with the ZT value expected on ribbons. The lower power factor in mainly due to a higher electrical resistivity (3000 $\mu\Omega$ m) observed on the bulk in comparison with the initial ribbon [22]. EDS analysis of the bulk material showed a different chemical composition ($Cu_{32}As_8Te_{60}$) that was most probably due to the use of another melt-spinning equipment (suitable for handling the large quantities needed for the SPS sintering tests but with no precise temperature control under 800 °C) and the evaporation of arsenium and tellurium. Moreover, only a high load applied using a WC die (400 MPa) and lower sintering temperature (<100 °C) leads to amorphous bulk samples, with a compactness of only 90%. Other sintering parameters (lower applied pressure, higher sintering temperature) lead to very low compactness or crystallized samples. Sintering of proper composition ribbons under higher load is now under study to get higher compactness and optimum ZT value.

4. Conclusions

Recent results on $Cu_xA_yTe_z$ (A=Ge, As, Ga and Si) general composition glasses point to chalcogenide semiconducting glasses as a new family of potential high-performance thermoelectric materials. The studies made on tellurium-based semiconducting glasses containing high concentrations of copper have shown interesting ZT values, up to $\sim$0.2 at 300 K. However, the glass transition temperatures and thermal stabilities of these glasses are still low when compared with the optimized bulk materials and further efforts must be made in order to stabilize them or identify new families of thermoelectric glasses. Moreover, the electrical conductivity is still too low for applications and additional work must be done to increase it without affecting the other properties.

Semiconducting chalcogenide glasses can also be used as raw materials. The possibility of a controllable partial crystallization of the glass, and especially the presence of nano-crystals in situ generated from the glassy matrix by an appropriate thermal treatment, could lead to an improvement of the thermoelectric properties. This possibility is now starting to be explored in our group.

Acknowledgments

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