Conducting glasses as new potential thermoelectric materials: the Cu–Ge–Te case

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Recent approaches to improve performance of bulk thermoelectric (TE) materials show that they should have complex structures, include inclusions and impurities, possess mass fluctuations, disorder and be based on heavy elements. Glasses can possess these properties. In order to identify glasses with interesting TE potential, attention should be focused on small gap semiconducting or semimetallic glasses. Chalcogenide glasses with $Cu_{x+y}Ge_{20-x}Te_{80-y}$ ($0 \leq x \leq 20$; $0 \leq y \leq 10$) compositions were prepared by melt spinning. Their powder X-ray diffraction analyses point to a short-range order analogous to $Ge_{20}Te_{80}$, with Cu atoms most likely replacing Ge atoms in the $GeTe_4$ structural unit. It also indicates, together with the differential scanning calorimetry results, a reduction in the glass stability with the increase in Cu concentration. The enhancement of Cu content dramatically reduces (five orders of magnitude) the electrical resistivity, while keeping the Seebeck coefficients at large values (~400 μV K^{-1}). As a consequence, a huge increase in the power factor is observed, up to a maximum value of 60 μW K^{-2} m^{-1} for the $Cu_{27.5}Ge_{2.5}Te_{70}$ glass at $T = 300$ K. $Ge_{20}Te_{80}$ has extremely low lattice thermal conductivity values (~0.1 W K^{-1} m^{-1} at 300 K), which points to relatively high values for the figure of merit ZT for this family of glasses, and indicates $Cu_{x+y}Ge_{20-x}Te_{80-y}$ based glasses as good candidates for obtaining high performance thermoelectric materials.

Introduction

Thermoelectric materials, which are able to directly convert thermal into electrical energy (by the Seebeck effect) and, reversibly, electrical into thermal energy (by the Peltier effect), have seen renewed interest due to their potential to provide a sustainable energy solution and optimization. Moreover, the absence of greenhouse effect substances, such as CO_2, and the lack of moving parts make thermoelectric devices highly attractive and reliable (NASA Voyager spacecrafts have used SiGe-based thermoelectric generators working uninterruptedly for more than 30 years).

The actual commercial thermoelectric devices are mostly based on Bi_2Te_3. However, their efficiencies are low (<10%). The thermoelectric efficiency of a device is mainly controlled by: (i) the adimensional figure of merit, ZT, which is given by $ZT = \alpha^2 T\sigma/\lambda$ (T, absolute temperature; α, Seebeck coefficient; σ and λ, electrical and thermal conductivities, respectively) and only depends on the material; (ii) the temperature difference, ΔT, between the hot and cold junctions. The maximum value of ΔT depends on the characteristics of the constituent materials (their thermal and chemical stability) and on the available heat and cooler sources. ZT maximization can be done by maximizing the numerator, $\alpha^2\sigma$ (power factor), and/or minimizing the denominator, λ. α and σ depend on the charge carriers concentration, a $\alpha^2\sigma$ maximum being observed for ~10^{18}–10^{21} carriers cm^{-3} that corresponds to low gap semiconductors or semimetals. Depending on the working temperature of the thermoelectric material, a value of the gap around 10 kT would be ideal.[1,2] λ can be considered as a sum of two different contributions, $\lambda = \lambda_e + \lambda_L$, ($\lambda_e$, electronic contribution; λ_L, phonons contribution). As λ_e is related to σ *via* the Wiedemann–Franz law, $\lambda_e = LT\sigma$ (L, Lorentz factor), ZT maximization implies the minimization of λ_L. To summarize, a good thermoelectric material has to be a good electrical conductor and a bad thermal conductor.

In the early 90's Slack presented the concept of "Phonon Glass Electron Crystal" (PGEC)[3] that proposes the study of materials that conduct electricity as a crystalline material and heat as a glass. This has led to a better understanding of the mechanisms that affect the phonons propagation without altering the electrical charge propagation, and to the development of general rules to increase the thermoelectric systems efficiency, the most important ones being:[4] (i) use of compounds with complex crystal structures; (ii) presence of heavy atoms weakly bound to the structures; (iii) existence of inclusions and/or impurities; (iv) formation of solid solutions; (v) existence of a large number of grain boundaries; these rules are not exclusive and several can exist simultaneously in the same material. The PGEC concept, together with the use of modern synthesis techniques, has led to the discovery of new improved thermoelectric materials, as skutterudites, clathrates, half-Heusler phases or low dimensional systems.[5] However, the efficiency increase in the new bulk materials is still limited to ~50%[5] and the cost of low dimensional systems is high. Therefore, it is highly desirable to identify new thermoelectric materials. A brief review of new materials, bulk and nano, and their shaping prior to use can be found in ref. 6.

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The careful analysis of the main general rules to increase the thermoelectric systems performance points to conducting glasses as one of the best potential materials. Indeed, this type of materials follows almost all the main rules: they have extremely complex structures, with a certain degree of order only at small distances, can have heavy atoms weakly bound to the structure and present mass fluctuations, easily allowing high concentrations of inclusions and impurities. To identify glasses with improved thermoelectric performances it is necessary to center the studies on the low gap semiconducting and semimetallic ones. Several glasses with semiconducting properties and containing heavy elements are reported in the literature, most of them based on pnictides and chalcogenides.[7,8] The semiconducting $Ge_{20}Te_{80}$ glass was reported as having a high Seebeck coefficient;[9] moreover, it is mainly formed by heavy atoms, is easy to prepare[10] and, albeit being described as having small electrical conductivity values,[9] doping it with Ag or Cu dramatically increases its electrical conductivity.[11,12]

In the present work the first study on the possibility of using conducting glasses for thermoelectric applications is described, by testing $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses. Preliminary results have already resulted in a national patent[13] and were partially presented in international conferences and workshops.[14–16] Before this work only a theoretical paper was dedicated to semiconducting amorphous materials, in a general approach.[17] Recently, a publication reported results on the structural and thermal properties of amorphous $Ge_{20}Te_{80-x}Se_x$ ($x = 0,1,2,8$).[18] Here, the synthesis of $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses and their study by differential thermal analysis and X-ray diffraction, thermal conductivity and electrical transport (electrical resistivity and Seebeck coefficient) measurements are presented.

Experimental

Samples with $(x+y)$Cu:$(20-x)$Ge:$(80-y)$Te general nominal composition (Fig. 1) were prepared from the proper amounts of the elements (Cu, Goodfellow, >99.99%; Ge, Johnson Matthey, 99.999%; Te, Alfa Aesar, >99.999%). The elemental mixtures were sealed into quartz ampoules under vacuum (10^{-5} mbar) and heated at 850 °C for 5 periods of 10 min each. In between these periods, the ampoules were removed from the furnace, shaken and turned upside down (with the products still melted) in order to achieve a good homogeneity. After the last period, the 20Ge:80Te composition sample was quenched into ice water, the other samples just being removed from the furnace with no extra procedure. Pieces of all samples were used as starting materials to prepare the ribbons. The pieces were put into a quartz tube with a 0.5 mm diameter nozzle, which was inserted in the stainless steel chamber containing the melt spinning system. The pieces were then melted under the protection of an Ar atmosphere and injected with a pressure of 1 bar of Ar onto a copper roller rotating with a linear speed of 1.6 m s^{-1}.

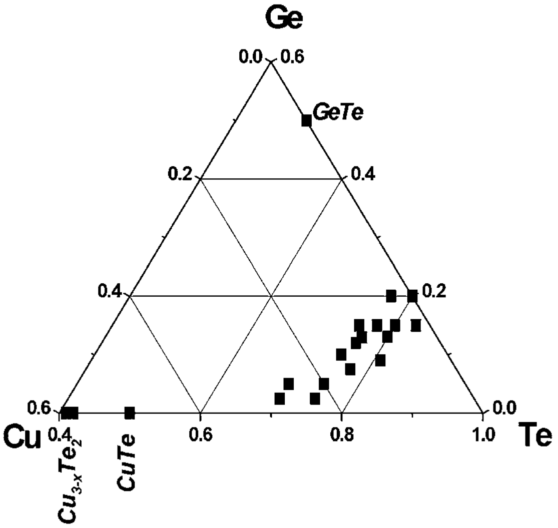

Fig. 1 Ternary diagram Cu–Ge–Te showing the prepared compositions.

The quality of the samples was checked *via* X-ray diffraction and differential thermal analysis measurements, together with optical microscope observations. The X-ray powder diffraction measurements were made on powders representative of the totality of the sample, at room temperature and under a dehumidified air atmosphere. The scans were performed using a Philips X'Pert diffractometer (Bragg–Brentano assembly) with a monochromatized Cu-Kα radiation, a 2θ-range of 10°–70°, a step width of 0.03° and 30 s of counting time per 2θ step. The glass transition (T_g), crystallization (T_c) and melting (T_m) temperatures of the materials were measured by differential scanning calorimetry (DSC), by using a DuPont 910 system, under an argon flux atmosphere, from 25 °C to 360 °C and with a constant heating rate of 10 °C min^{-1}. The measurements were made using 30–40 mg of material, which was put inside an aluminium sample container; an empty aluminium container was used as reference.

Electrical resistivity and Seebeck coefficient measurements were performed in the ~60–300 K temperature range on purely glassy pieces, with a needle-like shape of ~2 mm × 0.25 mm^2, removed from each sample. A previously described cell,[19] attached to the cold stage of a closed cycle cryostat, was used. The resistivity was measured by a four-probe method using the DC technique with a Keithley 220 current source and a Keithley 619 electrometer. The Seebeck coefficient was measured by a slow ac technique (*ca.* 10^{-2} Hz), the voltage across the sample and gold leads being measured with a Keithley 181 nanovoltmeter. The oscillating thermal gradient was kept below 1 K and was measured by a Au-0.005 at % Fe *versus* chromel thermocouple. The absolute Seebeck coefficient of the sample was obtained after correction for the absolute Seebeck coefficient of the gold leads (99.99% pure gold) by using the data of Huebener.[20]

The thermal conductivity of the $Cu_{20}Te_{80}$ glass was measured by a standard four-contact slow ac method, relative to a constantan wire. The method used was very similar to that previously described,[21] only this time the sample and the constantan wire were thermally connected to the copper cell with the help of screws and copper plates, and glued together with silver paste. The two constantan-chromel 12 μm diameter thermocouples were glued with GE varnish, one to the sample and the other to the constantan, and the voltages measured with two Keithley 181 nanovoltmeters. The temperature gradients used were as small as possible (typically <5 K) and the results were calculated using the data reported by Powers and co-workers.[22]

Results and discussion

Fig. 2 shows the X-ray diffraction patterns of selected $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses. All glasses display X-ray diffraction patterns comparable to $Ge_{20}Te_{80}$, pointing to an analogous short-range order in this type of material. The structure of Ge_xTe_{100-x} ($10 \le x \le 25$) glasses has been extensively investigated due to their possible technological applications in optical data storage devices. Published synchrotron radiation X-ray diffraction studies[23,24] agree with neutron diffraction works[25] and describe $Ge_{20}Te_{80}$ as composed by $GeTe_4$ tetrahedral structural units, which are bridged by Te–Te bonds. $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses have been much less studied, but the reported X-ray diffraction investigations made on $Cu_{0.08}Ge_{0.18}Te_{0.74}$ also indicate the existence of the $GeTe_4$ units, together with other tetrahedral units centered on the Cu atoms, such as $CuGeTe_3$ and $CuTe_4$[26] ($CuTe_4$ tetrahedral units also exist in the CuTe compound[27] that crystallizes in the orthorhombic CuTe-type structure, space group *Pmmm*, supporting the possibility of having this type of unit in the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses). Therefore, in $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses, the increase in Cu content, simultaneously with a larger Ge and a smaller Te decrease (87.5% and 12.5%, respectively, for the case of higher Cu concentration glass, $Cu_{27.5}Ge_{2.5}Te_{70}$), can be mainly seen as Cu replacing Ge atoms in the $GeTe_4$ structural unit, together with the formation of some $CuTe_4$ structural units.

Optical microscope observations of the samples show that they generally have a glassy aspect. However, those with higher Cu concentrations frequently present regions where crystallization already appears. This is most probably due to: (i) a decrease in the glass stabilization with the increase in Cu content; (ii) the existence of inhomogeneities in the cooling rate during the melt spinning process. These facts are also evidenced in the X-ray diffraction measurements, where many of the higher Cu concentration samples already show small crystallization peaks, which can be indexed as Te and $Cu_{1.33}Ge_{0.67}Te_2$ (Fig. 2). The extreme composition 30Cu:70Te, albeit still presenting some disorder, is formed by Te and CuTe, and therefore its physical properties have not been studied.

DSC measurements show a single glass transition for all compositions, albeit samples containing Cu present more than one exothermal peak, pointing to a sequential crystallization of more than one phase (Fig. 3). This can be due to different atomic-scale structures of the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses, with Te segregation followed by $Cu_{1.33}Ge_{0.54}Te_2$ crystallization, similarly to what was reported for $Ge_{20-x}Te_{80-x}$ (x = 5, 10) glasses (Te segregation followed by GeTe crystallization),[28] pointing to the existence of Te atoms not directly bonded to Ge or Cu (Te atoms connecting ATe_4, A = Ge, Cu, tetrahedra). A significant decrease in the glass transition (T_g), crystallization (T_C) and melting (T_m) temperatures with the increase in Cu concentration is observed, confirming the reduction of the glass stability, already indicated by the observation of crystalline regions. A maximum decrease of ~50 °C is observed for the higher Cu concentration glass, $Cu_{27.5}Ge_{2.5}Te_{70}$, when compared with $Ge_{20}Te_{80}$, indicating a limited temperature range of applicability for $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses as thermoelectric materials.

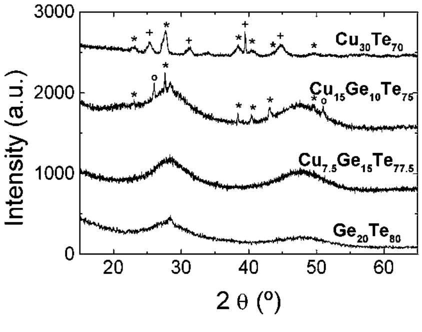

Fig. 2 X-Ray diffraction patterns of the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses (asterisks: Te; crosses: CuTe; circles: $Cu_{1.33}Ge_{0.67}Te_2$).

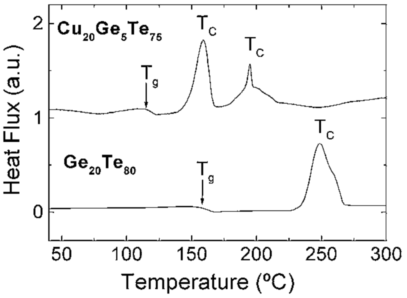

Fig. 3 DSC measurements *versus* temperature showing glass transition (T_g) and crystallization temperatures (T_C) in $Ge_{20}Te_{80}$ and $Cu_{20}Ge_5Te_{75}$.

The variation of the room temperature resistivity of the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses as a function of composition is plotted in Fig. 4. A large drop of five orders of magnitude, from $\sim 3 \times 10^8$ to 2.6×10^3 μΩ m, is observed, the lower values corresponding to glasses with higher Cu and lower Ge concentrations. This drop is much higher than those previously reported for the $Ag_xGeTe_{4.7}$ ($0 \le x \le 1.4$) and $Cu_xGe_{15}Te_{85-x}$ ($0 \le x \le 9$) glasses,[11,12] probably due to the successful increase in the Cu concentration in the present work. The electrical conductivity of chalcogenide glasses has been ascribed to depend on three major factors: (i) the bond strengths, (ii) the network connectivity and (iii) the density.[29] In the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses the main factor should be the first one (change in the bond strengths). Indeed, in the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses it is expected that Cu mainly replaces Ge in the $GeTe_4$ structural unit, which neither changes the network connectivity nor appreciably decreases the glass density (the change produced by the lower atomic mass of Cu should be compensated by its lower atomic volume, when

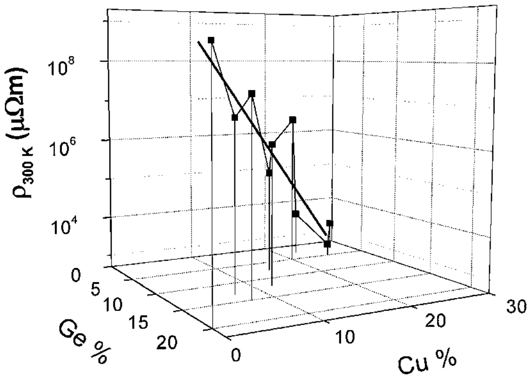

Fig. 4 Variation of the room temperature resistivity of the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses as function of composition.

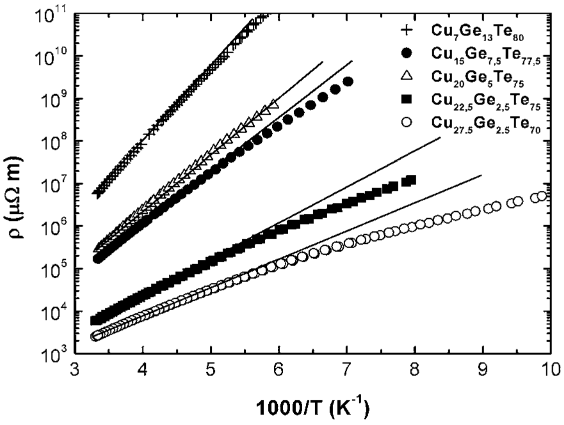

Fig. 5 Electrical resistivity *versus* temperature in the Cu–Ge–Te glass system.

compared with Ge). The formation of new $CuTe_4$ structural units could significantly change the network connectivity, but its increase is expected to cause a larger splitting between σ (bonding) and σ* (antibonding) orbitals, and, consequently, should increase the electrical resistivity,[29] which is not observed. On the other hand, the Cu–Te bond dissociation energy (230.5 ± 14.6 kJ mol^{-1})[30] is significantly smaller than the Ge–Te one (396.7 ± 3.3 kJ mol^{-1}),[30] and therefore a smaller splitting between σ and σ* orbitals is expected and thus a decreasing of the gap, with the consequent increase in the electrical conductivity.[29]

All the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses show semiconducting behavior, with the electrical resistivity increasing with the decreasing temperature (Fig. 5). The temperature dependence of the electrical resistivity, $\rho(T)$, obeys the $\rho(T) = \rho(0)\ \exp(E_a/kT)$ relation (E_a: activation energy for the electronic conduction (half of the energy gap); k: Boltzmann constant). A significant variation in the high temperature E_a can be observed with the change in composition (Table 1), the highest and the lowest values (470 meV and 126 meV) being observed for the un-substituted $Ge_{20}Te_{80}$ and the highest Cu concentration glass, $Cu_{27.5}Ge_{2.5}Te_{70}$, respectively. When it was possible to measure a large enough temperature range, it was observed that E_a starts to slightly decrease below a certain temperature. The magnitude of the high temperature E_a confirms the narrow-gap semiconducting character of the studied glasses, being similar to those observed on the best classical thermoelectric materials, PbTe (~100–250 meV), Si–Ge (~350–550 meV) and Bi_2Te_3 (~75–140 meV).[31] Albeit room temperature resistivity values of the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses are consistent with narrow-band-gap semiconductors, the best ones are still one order of magnitude higher than those of the new materials with good thermoelectric properties, such as the skutterudites or half-Heusler phases.[32,33]

The variation in the room temperature Seebeck coefficient of the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses as a function of composition is shown in Fig. 6. Despite the huge resistivity drop, increasing the Cu concentration has only a small effect on Seebeck coefficients. After a small Cu introduction in the composition, a decrease of ~40% from the original $Ge_{20}Te_{80}$ value (980 μV K^{-1}) is observed, but further increase in the Cu concentration just slightly decreases this value, which stabilizes at ~400 μV K^{-1}. The Seebeck coefficient variation as a function of temperature of the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses is plotted in Fig. 7. Seebeck coefficients are always positive, indicating dominant p-type conduction. For higher Cu concentration glasses, the Seebeck coefficient is only slightly dependent on the temperature, increasing with the

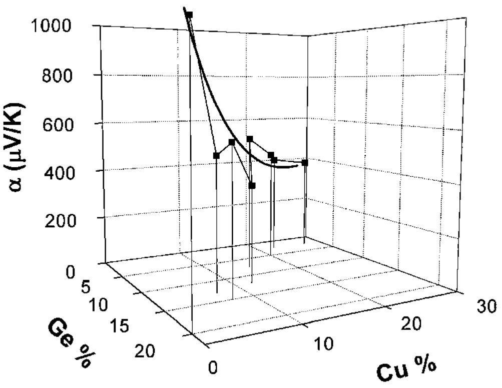

Fig. 6 Variation in the room temperature Seebeck coefficient of the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses as a function of composition.

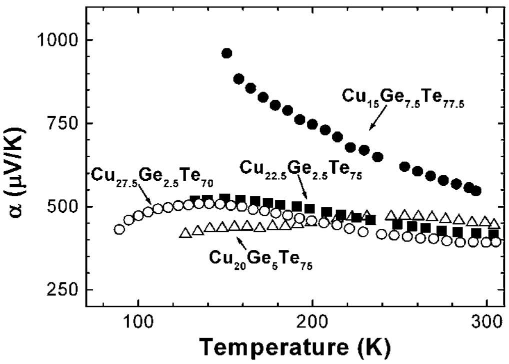

Fig. 7 Variation in the Seebeck coefficient of the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses *versus* temperature.

Table 1 Electrical transport properties ($\rho_{300\ K}$, E_ρ, $\alpha_{300\ K}$, E_α, E_{Hopp} and power factor parameters) of the $Ge_{20}Te_{80}$-based glasses

Glass Composition	$\rho_{300\ K}$ (μΩ m)	$E_{\rho(High\ T)}$ (meV)	$\alpha_{300\ K}$ (μV K^{-1})	$E_{\alpha(High\ T)}$ (meV)	E_{Hopp} (meV)	α^2/ρ (μW K^{-2} m^{-1})	Reference
$Ge_{20}Te_{80}$	2.8×10^8	470	960	—	—	3.3×10^{-3}	9
$Cu_7Ge_{13}Te_{80}$	$5.\ 8 \times 10^6$	340	505	84	256	4.4×10^{-2}	This work
$Cu_{7.5}Ge_{15}Te_{77.5}$	2.1×10^7	351	562	58	293	1.5×10^{-2}	This work
$Cu_{12}Ge_{12}Te_{76}$	1.2×10^6	298	361	—	—	1.1×10^{-1}	This work
$Cu_{15}Ge_{7.5}Te_{77.5}$	1.6×10^5	244	540	122	122	1.8	This work
$Cu_{20}Ge_5Te_{75}$	2.9×10^5	263	453	34	229	0.7	This work
$Cu_{22.5}Ge_{2.5}Te_{75}$	6×10^3	164	415	46	117	29	This work
$Cu_{27.5}Ge_{2.5}Te_{70}$	2.6×10^3	126	394	45	81	60	This work

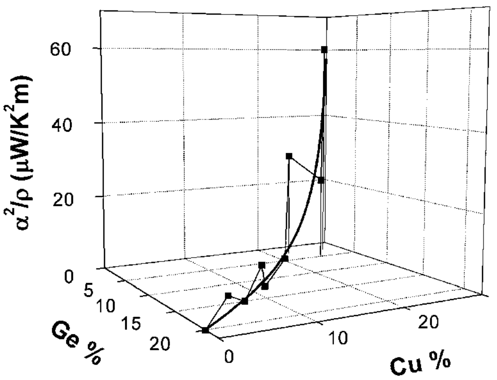

Fig. 8 Variation in the room temperature power factor of the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses as a function of composition.

decreasing temperature, their values ranging from 400 to 500 μV K^{-1}; the low Cu concentration glasses show a higher increase in the Seebeck coefficient with the decreasing temperature.

The combination of the very large electrical resistivity decrease, together with the stabilization of the Seebeck coefficients at high values, consequently induces a dramatic increase (of five orders of magnitude) in the power factor with the increasing Cu concentration (Fig. 8). The power factor increases exponentially with temperature, the maximum value of 60 μW K^{-2} m^{-1} being obtained in the $Cu_{27.5}Ge_{2.5}Te_{70}$ material at $T = 300$ K, the highest temperature measured. In order to discard the possibility of extra contributions from crystalline phases, some crystallized counterparts of the conducting glasses were prepared and studied. However, the crystallization of the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses leads to materials with metallic character (very small values of resistivity and Seebeck coefficients) and with low power factors.

X-Ray diffraction patterns and DSC curves cannot attest to a completely amorphous state of the measured samples, without any kind of nano-precipitates. However, the previous structural studies on Cu–Ge–Te glasses[26] clearly indicate them as having a glassy state. Moreover, the continuity in the change in the properties (electrical and thermal) observed in the present study strongly suggests that the good thermoelectric properties observed are not due to a structural discontinuity, like the formation of nanoparticles, but are in fact intrinsic to the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses.

Due to the difficulty in obtaining $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses with an appropriate shape, it was decided to measure the thermal conductivity only on $Ge_{20}Te_{80}$ and to use the obtained values for the other compositions, after correcting them with the help of the Wiedemann–Franz law (albeit the Wiedemann–Franz law was empirically deduced for metallic systems, it can be considered for semiconducting systems, with the expenses of a non-constancy of the Lorentz number). Due to their resemblance, as a first approximation the thermal conductivity of a non-metallic glass can be described like a non-metallic liquid with very high viscosity, which has only the phonons contribution given by[34]

$$\lambda_L = v\rho^{2/3}C_V/3M^{2/3}N_A^{1/3}$$

where v is the velocity of sound, ρ is the density, C_V is the specific heat capacity per mole at constant volume, M is the molecular weight and N_A is Avogadro's number. The numerator mainly depends on the bond strengths and atomic volumes and weights, whereas the denominator only depends on the atomic weights. In our case ρ should remain constant, as the decrease in volume (with the increase in Cu content) is compensated for by a decrease in the atomic weight. The lower Cu–Te bond strength increases the rattling, decreasing v and C_V, which is compensated for by the lower M. Therefore, Ge replacement by Cu is not expected to greatly change the lattice thermal conductivity of the glass.

The measured thermal conductivity of $Ge_{20}Te_{80}$ is extremely low, ~0.1 W K^{-1} m^{-1} at 300 K, lower than that obtained by Zhang *et al.*[18] The heat radiation losses are not negligible, especially at high temperatures, due to the high difference between the thermal conductivities of the sample and the constantan wire used as the reference (but unfortunately not easy to estimate), so the true value of $Ge_{20}Te_{80}$ thermal conductivity at 300 K is certainly smaller than 0.1 W K^{-1} m^{-1}. This value is in agreement with measurements made on other chalcogenide glasses, where very low thermal conductivities were observed.[35] These values are most probably a mutual consequence of the high disorder and of the high atomic weights of the constituents. The relatively high electrical resistivities of $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses (Table 1) result in a low electronic contribution to their thermal conductivity: in $Cu_{27.5}Ge_{2.5}Te_{70}$ (glass with the lowest resistivity value) this contribution is only ~3 × 10^{-4} W K^{-1} m^{-1} and therefore can be neglected. Even if the Lorentz number increases one order of magnitude, which can be considered as a maximization of it, the electronic contribution to the thermal conductivity remains negligible. For the $Cu_{27.5}Ge_{2.5}Te_{70}$ glass, which has the highest power factor at 300 K, and considering a 0.1 W K^{-1} m^{-1} value of the thermal conductivity at room temperature, a figure of merit value of $ZT = 0.19$ is obtained. Albeit not reaching the values of the best actual thermoelectric materials at 300 K, it is a relatively high ZT and definitely puts conducting glasses as a new class of materials candidate for obtaining high performance thermoelectric materials.

A deeper understanding of the nature of $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses can give some hints on how to optimize their properties. The Seebeck coefficient of a semiconducting chalcogenide glass can be expressed as[36]

$$\alpha = \pm k/e\ (E_\alpha/kT + A)$$

where e is the electronic charge, E_α is the activation energy for the thermoelectric power, A is a constant that depends on the mechanism of the electrical transport, and the positive and negative signs represent the p- and n-type conduction mechanism, respectively. The observed positive Seebeck coefficient at high temperatures is common in chalcogenide glasses, being consistent with an intrinsic conduction: if an intrinsic semiconductor is considered, the positive Seebeck coefficient is a consequence of the hole mobility being much higher than the electron mobility in that temperature region. The activation energies obtained by fitting the data using this expression at high temperatures, E_α, are considerably smaller than the activation energies obtained from the resistivity data, E_a (Table 1). This difference between E_a and E_α points to conduction occurring predominantly in band tails, with more density of states in the valence band, when compared to the conduction band. The $E_{\mathrm{Hopp}} = E_a - E_\alpha$ difference is the hopping energy for holes or small polarons, also shown in Table 1, which is not very surprising since these materials are amorphous semiconductors, with no long range order. The values obtained for hopping energies, between 0.08 V and 0.25 V, are typical for chalcogenide glasses.[36] In some samples it is very clear that the Seebeck coefficient presents a smooth maximum at ~155 K, which is probably due to the transition to a further localized variable range hopping conduction regime at lower temperatures.[36] The predicted temperature dependence, $\rho = \rho_o \exp(A/T^{1/4})$, for the variable range hopping regime is not clearly observed at low temperatures, most probably because the change in regime occurs very smoothly and the temperature range of measurements was not wide and low enough.

The likely intrinsic semiconducting nature of the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ glasses opens the possibility of further changes in their composition to optimize the electrical properties. Moreover, it should also allow the addition of glass chalcogenide stabilizing agents, such as small quantities of praseodymium, arsenic or lanthanum oxide, without degrading their electrical properties, in order to increase the glass transition temperatures and, consequently, their maximum temperature of application as thermoelectric materials and ZT values.

Conclusion

New chalcogenide glasses, with $Cu_{x+y}Ge_{20-x}Te_{80-y}$ ($0 \le x \le 20$; $0 \le y \le 10$) compositions, have been prepared by melt spinning and used to test the possibility of obtaining conducting glasses for thermoelectric applications. Their short-range order is most likely analogous to $Ge_{20}Te_{80}$ glasses, being based on $GeTe_4$ and $CuTe_4$ structural units (which corresponds to a Cu replacement of Ge atoms in $GeTe_4$). The addition of Cu reduces the glass stability, but increases their thermoelectric properties, with a consequent huge increase in the power factor at $T = 300$ K, from 3.3×10^{-3} μW K^{-2} m^{-1} up to 60 μW K^{-2} m^{-1} for the glasses with the extreme $Ge_{20}Te_{80}$ and $Cu_{27.5}Ge_{2.5}Te_{70}$ compositions, respectively. The exceptionally low thermal conductivity measured on the $Ge_{20}Te_{80}$ glass, together with the type of structural replacement and the low electrical contribution for the thermal conductivity, point to a similar behavior on all series, definitely indicating the $Cu_{x+y}Ge_{20-x}Te_{80-y}$-based glasses as having good potential for high performance thermoelectric materials. Their probable intrinsic semiconducting nature opens the possibility of further improvements, and clearly indicates conducting glasses as very promising thermoelectric materials.

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