Chalcogenide Glasses as Prospective Thermoelectric Materials

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Despite the fact that glasses have interesting characteristics for thermoelectric (TE) applications, their potential as TE materials has only recently been tested. In a recent article, we focused on glasses based on the $Ge_{20}Te_{80}$ composition, which has a high Seebeck coefficient, S, showing that in $Cu_{x+y}Ge_{20-x}Te_{80-y}$ the power factor, S^2/ρ (where ρ is the resistivity), strongly improves with increasing Cu concentration. Herein we report on the preparation of glasses in the Cu-Te-As system and their characterization by x-ray diffraction (XRD), differential scanning calorimetry (DSC), and measurements of ρ and S. Our preliminary results show that the melt-spinning technique allows us to extend the Cu-Te-As glassy domain and leads to T_g values that permit use of these glasses in applications up to 100°C. A maximum S^2/ρ value of ~ 100 μW K^{-2} m^{-1} was obtained for the $Cu_{30}As_{15}Te_{55}$ composition, confirming the potential of these glasses for TE applications.

Key words: Glass, chalcogenides, synthesis, thermoelectric
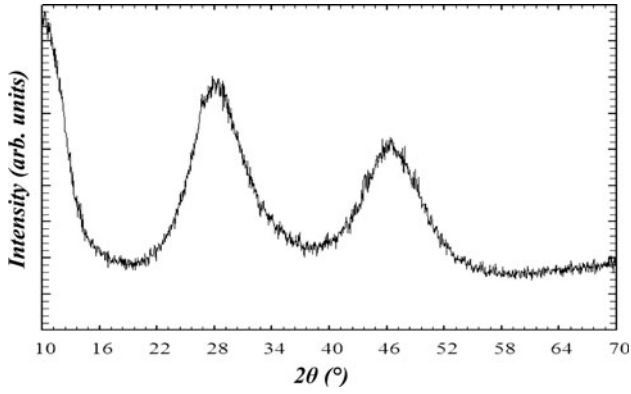
INTRODUCTION

Recent approaches to improve the performance of bulk TE materials have shown that they should have complex structures and disorder, include inclusions and impurities, possess mass fluctuations, and be based on heavy elements. Glasses can possess these properties. Moreover, they should be semiconductors with a small gap or semimetallic.[1] Bulk chalcogenides, especially with Te, are known to form different series of good TE materials [Bi_2Te_3/Sb_2Te_3, PbTe, $AgSbTe_2$, the so-called TAGS (Te-Ag-Ge-Sb) and LAST ($AgPb_mSbTe_{2+m}$)[2] materials]. The origin of the good TE properties in TAGS and LAST materials has been attributed to particular microstructures. In fact, nanodomains naturally formed during synthesis (by cooling the liquid phase) are intrinsic to these materials. This has led to the discovery of new families with much higher TE figure of merit, ZT ($ZT = S^2T/\rho K$; S and ρ as in Abstract; K, thermal conductivity), than the classical value of 1, such as $Na_{0.95}Pb_{19}SbTe_{22}$,[3] $AgPb_{12}Sn_4Sb_{0.4}Te_{20}$,[4] and $K_{0.95}Pb_{20}Sb_{1.2}Te_{22}$.[5] Among Te-based glasses, $Ge_{20}Te_{80}$ is of special interest since it is easy to obtain in amorphous form, is close to a metal–semiconductor transition (under pressure),[6] has a very high Seebeck coefficient[7] that depends on the annealing conditions,[8] accepts many doping elements (Bi, Pb, Se, Sb, As, Al, Ga, I, etc.), and consequently exists as *n*- or *p*-type. Nanocrystals which appear by phase separation during annealing seem to improve the TE properties.[8] In $Cu_{x+y}Ge_{20-x}Te_{80-y}$ chalcogenide glasses, we recently reported that an increase of the Cu content dramatically increases the power factor and, together with their extremely low thermal conductivity values, points to relatively high ZT values.[9] Moreover, better glass-forming ability and thermal stability have very recently been observed in the presence of As.[10] In this paper, we report new preliminary results on the preparation of glasses in the Cu-Te-As system and their characterization by XRD, as well as their thermal and TE properties studied by DSC, resistivity, and Seebeck coefficient measurements.

EXPERIMENTAL PROCEDURES

The structure and electrical properties have been reported for $Cu_yAs_{55-y}Te_{45}$ semiconducting glasses;[11] we have prepared and studied samples with
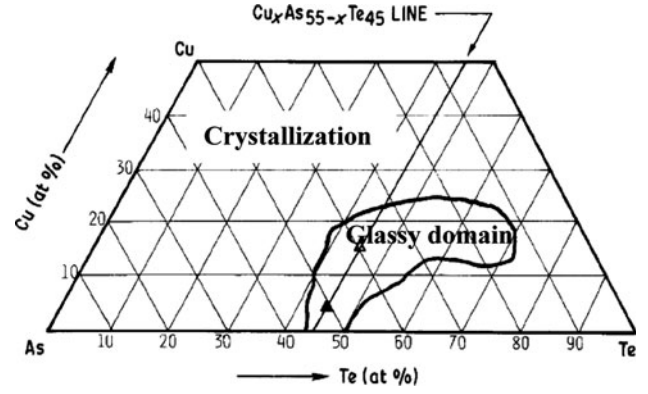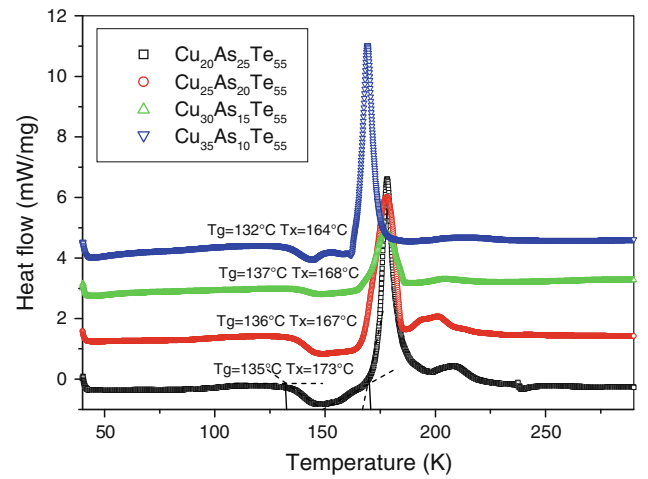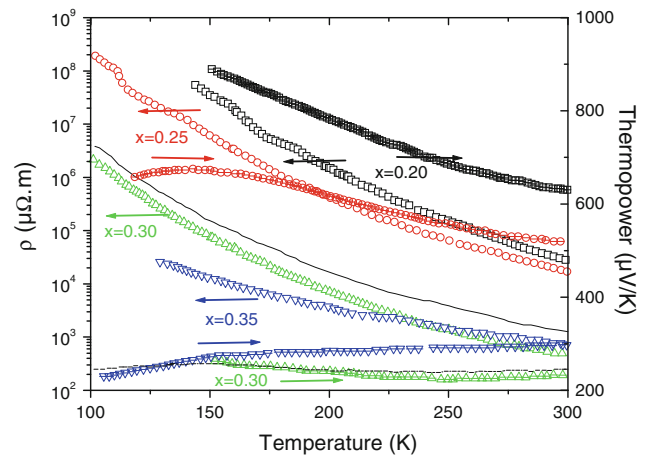
Fig. 1. XRD pattern of the $Cu_{35}As_{19}Te_{55}$ glass.

Fig. 2. Glass-formation region in the Cu-As-Te system according to Ref. 11.

Fig. 3. DSC curves versus temperature for $Cu_xAs_{45-x}Te_{55}$ ($20 \leq x \leq 35$) glass.

Fig. 4. Resistivity (open symbols) and Seebeck coefficient (centered symbols) versus temperature for $Cu_xAs_{45-x}Te_{55}$ (x = 0.20, 0.25, 0.30, and 0.35). Lines are for the $Cu_{26}Ga_2Ge_2Te_{70}$ composition.

$Cu_xAs_{45-x}Te_{55}$ ($20 \leq x \leq 35$) general composition. The elemental mixtures (Cu, Te, and As, all 4 N) were sealed into quartz ampoules under vacuum (10^{-5} mbar) and heated at 850°C for five periods of 10 min each. Ribbons were produced by melt spinning on a copper roller (300 K, linear speed ~6 m s^{-1}). DSC and powder XRD measurements were performed, respectively, on a TA Q100 instrument, with a heating rate of 10°C min^{-1}, and a D8 Bruker, in the 2θ range of 10° to 70° with a step size of 0.02° and a counting time per step of 2 s. T_g and T_c were obtained from DSC curves using the intersection of tangents (Fig. 3). The resistivity and Seebeck coefficient were determined using the same procedure as described in Ref. 9.

RESULTS

After melt spinning, the amorphous state of the $Cu_xAs_{45-x}Te_{55}$ ($20 \leq x \leq 35$) ribbons was confirmed by XRD (Fig. 1).

In comparison with Fig. 2,[11] where the glassy domain was obtained by conventional melt quenching, the melt-spinning technique significantly enlarges the vitreous domain, due to the faster quenching rate. This allows us to introduce larger amounts of Cu into the glass, which is an important parameter to tune the electronic properties of the material.

DSC measurements (Fig. 3) confirmed the vitreous nature of all the ribbons, since glass-transition temperatures, T_g, were observed. These temperatures lay in the range from 132°C to 137°C, which is slightly higher than reported for the Cu-Ge-Te system.[9]

Figure 3 also shows crystallization temperatures, T_c, the parameter $T_c - T_g$ being less than 40°C, which indicates the limited stability of the glass. However, both temperature domains allow the glass to be used in devices based on temperature differences of 100°C from room temperature.

Figure 4 shows ρ as well as S versus temperature for different compositions $Cu_xAs_{45-x}Te_{55}$ ($20 \leq x \leq 35$). The figure also shows preliminary results for a quaternary composition Ge-Te-Cu-Ga, although no further preparations have been attempted in this system. The highest Seebeck coefficient was obtained for the lowest Cu concentration,
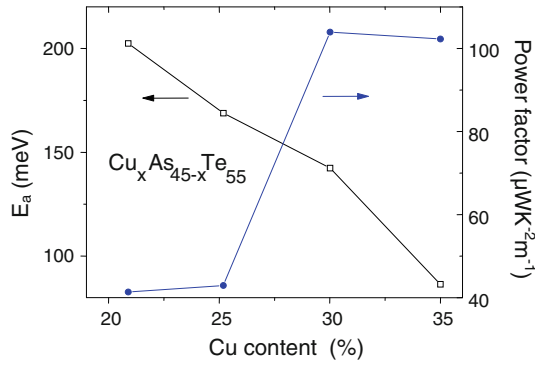
Fig. 5. Activation energy (E_a) and power factor versus Cu content in $Cu_xAs_{45-x}Te_{55}$.

which unfortunately had the higher resistivity. It is possible to fit the resistivity to $\rho(T) = \rho(0)\exp(E_a/kT)$ (E_a, activation energy; k, Boltzmann constant) and derive an activation energy for the electronic conduction (half of the energy gap), which decreases with increasing Cu content (Fig. 5). The same figure also shows the power factor (S^2/ρ) versus Cu content, the highest value of ~100 μW K^{-2} m^{-1} being obtained for the $Cu_{30}As_{15}Te_{55}$ composition. This value is twice what we reported in the Ge-Te-Cu glass system.[9]

DISCUSSION

In comparison with crystalline TE materials, glass is easier and faster to prepare and its composition can be easily tuned over a wide range of compositions. Our preliminary results on Cu-As-Te show that the melt-spinning technique allows us to extend the glassy domain and leads to values of T_g that can be used in applications up to 100°C, with a power factor twice that of the Cu-Ge-Te system and at a much lower cost of As compared with Ge,

without increasing toxicity when inserted in the glass.[12] Further work will include thermal conductivity measurements, thermoelectric power measurements at higher temperature, namely up to the glass-temperature transition, as well as a better understanding of the glassy structure and attempts to make bulk glass for practical applications.

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