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Thermal stability and thermoelectric properties of $\text{Cu}_x\text{As}_{40-x}\text{Te}_{60-y}\text{Se}_y$ semiconducting glasses

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Abstract

We report on the thermal behavior and thermoelectric properties of bulk chalcogenide glasses in the systems $\text{Cu}_x\text{As}_{40-x}\text{Te}_{60}$ ($20 \leq x \leq 32.5$) and $\text{Cu}_x\text{As}_{40-x}\text{Te}_{60-y}\text{Se}_y$, ($0 \leq y \leq 9$) synthesized by conventional melt-quenching techniques. The thermal stability of these glasses was probed by differential scanning calorimetry to determine the characteristic T_g and ΔT temperatures, both of which increasing noticeably with y . Thermoelectric properties were found to be mainly influenced by the Cu concentration with respect to the Se content. The thermal conductivity is practically composition-independent throughout the compositional

range covered. A maximum ZT value of 0.02 at 300 K increasing to 0.06 at 375 K was achieved for the composition $\text{Cu}_{30}\text{As}_{10}\text{Te}_{54}\text{Se}_6$.

1.Introduction

The efficiency of thermoelectric materials, which enable to convert a temperature gradient into electrical energy through Seebeck effect, and conversely electrical energy into thermal energy by the Peltier effect, is governed by the dimensionless thermoelectric figure of merit ZT defined as $ZT = S^2T / \rho\lambda$. This formula relates three physical properties intrinsic to the material: the electrical resistivity ρ , the thermopower or Seebeck coefficient S , and the thermal conductivity λ , all given at the absolute temperature T . The conventional strategy to enhance the ZT values consists in modifying the crystalline structure of materials that possess inherently good electrical properties by alloying and/or inserting foreign species to decrease the thermal conductivity. Alternatively, designing novel materials with inherently low thermal conductivity values would leave the power factor S^2/ρ the only relevant parameter to be optimized. Glasses naturally belong to this class of materials since they show extremely low thermal conductivities due to strong phonon scattering induced by their non-periodic structure. Yet, their high electrical resistivity remains an obstacle to push their ZT values closer to those observed in crystalline semiconductors and semimetals.

Te-containing chalcogenide glasses [1] were recently studied to determine their thermoelectric properties near room temperature. Studies focusing on the influence of a partial substitution by transition metals demonstrated that introducing Cu in glassy matrix, such as Ge-Te or As-Te, leads to a sharp drop in electrical resistivity by several orders of magnitude. The concomitant less-pronounced decrease in the thermopower values then

resulted in a drastic increase in the power factor up to up to $0.1 \text{ mW.K}^{-2}.\text{m}^{-1}$ at 300K (measured on $\text{Cu}_x\text{As}_{45-x}\text{Te}_{55}$ ribbons), bringing ZT values to encouraging levels [2,3]. However, the amorphous state of these glasses should be thermodynamically stable *i.e.* the glass-transition temperature T_g should be high enough to prevent crystallization to occur. Investigations on the thermal behavior of Cu-As-Te glasses have shown that transition-metal doping noticeably modifies both T_g and the glass-stability criterion ΔT [1,4] (defined as the difference between the onset temperature of the crystallization T_x and T_g). This last parameter, that embodies the crystallization ability of the material, was found to be substantially affected by the Cu concentration.

Glasses in the Cu-As-Te system show a rather low T_g (slightly above 130°C) and ΔT parameters [3,5], both of which limiting their potential use as thermoelectric materials. Their poor thermal stability may be also a major hurdle to the glass-ceramization process that constitutes an alternative way to enhance the thermoelectric properties.

In this study, efforts were devoted to enlarge the stability domain of Cu-As-Te glasses by systematically varying the Cu and Se contents in $\text{Cu}_x\text{As}_{40-x}\text{Te}_{60-y}\text{Se}_y$, while trying to maintain or enhance the thermoelectric properties of the system. The influence of this substitution on the thermoelectric properties was investigated by means of electrical resistivity, thermopower and thermal conductivity measurements between 300 and 375 K.

2. Experimental

2.1 Samples preparation and characterization

$\text{Cu}_x\text{As}_{40-x}\text{Te}_{60-y}\text{Se}_y$ samples with $x = 20, 22.5, 25, 27.5, 30$ and 32.5 at% and $y = 0, 3, 6$ and 9 at% were prepared from high-purity copper pellets (99.9995%, Sigma-Aldrich), tellurium (99.995%, 5NPlus), arsenic (99.99%, Goodfellow) and selenium powders (99.99%, Sigma-Aldrich). Regardless of the starting composition, a total stoichiometric weight of 4 g was placed into a quartz ampoule (6mm inner diameter) and sealed under secondary vacuum (10^{-5} mbar). The ampoules were then heated at 850°C with a $9^\circ\text{C}\cdot\text{h}^{-1}$ heating rate and kept at this temperature for one hour. The tubes were regularly rocked in the furnace to ensure a better chemical homogenization. The ampoules were then cooled down to 600°C and further quenched in a “salt + ice + water” bath. To improve the mechanical properties of the glasses by releasing stresses, the obtained ingot was further annealed at $T_g - 10^\circ\text{C}$ for 20 minutes. Powder x-ray diffraction (PXRD) was carried out using a Philips X-PERT PRO II to confirm the amorphous state of the samples (see Figure 1 for a typical XRPD pattern). The thermal behavior of the bulk glasses was investigated on powdered samples (about 7mg) by differential scanning calorimetry (DSC) using a DSC1 (Mettler Toledo) at a rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ in sealed Al crucibles.

2.2 Thermoelectric properties measurements

To determine the thermoelectric potential of these materials, the three relevant transport properties were measured separately for each composition. The thermal conductivity λ was obtained by measuring the thermal diffusivity a and specific heat C_p of the samples. The thermal conductivity was then calculated following the formula $\lambda = aC_p\rho_V$, where ρ_V is the density calculated from the weight and geometrical dimensions of the samples. Thermal diffusivity was determined using the laser flash technique with a LFA 427 (Netzsch) on $6\times 6\times 1$ mm³ square-shaped samples. C_p was measured using a DSC 404 F3 Pegasus (Netzsch).

Electrical resistivity measurements were performed on disk-shaped samples ($\varnothing \approx 8$ mm) using the Van der Pauw method. The disks were further cut into bar-shaped samples ($\approx 1\times 1\times 8$ mm³) for thermopower measurements carried out between 300K and 375K at fixed temperature using a homemade apparatus based on the differential method. Stabilized positive and negative thermal gradients ($\Delta T \approx 2$ K) were obtained by heating alternatively each end of the sample: the thermopower values then stands for an average of the forward and reverse values. The temperature gradient and thermoelectric voltage were measured by two N-type thermocouples pressed by mulite rods against one side of the sample. A test of the accuracy of this system was obtained by measuring elemental Ni and comparing it to a standard measurement performed in the temperature range 300 – 400 K by Laubitz et al. [6]. The absolute average difference between this test and literature is $0.4 \mu\text{V.K}^{-1}$ *i.e.* 1.6% as a relative average difference.

3. Thermal Stability properties

The glass transition temperature T_g and the glass stability ΔT of $\text{Cu}_x\text{As}_{40-x}\text{Te}_{60-y}\text{Se}_y$ samples were determined from DSC measurements and are shown in Figure 2. It is worth noticing that the Se substitution enlarges the vitreous domain relatively to Cu, *i.e.* the higher the concentration of Se, the higher the concentration of Cu in the vitreous state (Fig. 2). These results evidence two main trends of these thermal parameters with the Cu and Se concentrations. First, increasing the Se content results in a higher T_g . Secondly, at a given Cu content, Se substitution increases ΔT . Further, samples of composition nearer to the vitreous domain limit tend to exhibit lower stability towards crystallization regardless of Se ratio.

The fact that crystallization occurs in several steps – each leading to visible peaks on DSC scans as shown in Figure 3 – suggests that their evolution with Se or Cu concentration plays a major role in determining glass stability. A main characteristic is that, depending on the proximity to the amorphous border, additional peaks associated to crystallization of phases drastically lower ΔT . To confirm this feature, additional data were collected for glasses of compositions $\text{Cu}_x\text{As}_{40-x}\text{Te}_{60}$ with $x > 25$ at%. Because these compositions cannot be obtained by conventional melt-quenching technique, they were synthesized by twin-roll melt-spinning as described in detail by Piarristeguy et al. [7]. The results show that an additional crystallization peak shows up for compositions with $x > 30$ at % (see Figure 3).

The effect of Se and Cu on the thermal properties of Cu-As-Te glasses may be a direct consequence of modifications of the local environment of the As and Te atoms *i.e.* of their coordination number. The Cu-As-Te glasses are believed to be structured with Cu located at the center of tetrahedral units linked together by As atoms or Te chains [8,9]. We surmise that, at low substitution levels, Se atoms directly replaces Te atoms in the matrix thereby diminishing the number of Te-Te bonds in favor of Te-Se and, to a lesser extent, Se-Se bonds.

Since both types of bonds exhibit higher binding energies with respect to Te-Te bonds ($184.2 \text{ kJ}\cdot\text{mol}^{-1}$ for Se-Se compared to $138.2 \text{ kJ}\cdot\text{mol}^{-1}$ for Te-Te [10]), the resulting network should be then more tightly bound and thus, less susceptible to crystallization.

In addition, the introduction of Cu in quantities over 3 at% strongly affects the glass structure [11]. Glassy As_2Te_3 , similarly to As_2Se_3 glasses, is supposed to be structurally made of distorted layers bound together by van der Waals interactions [4], though the more metallic nature of Te compared to Se may lead to a higher degree of interactions between the different layers. The substitution of trigonally-coordinated As atoms by tetrahedrally-coordinated Cu atoms develops stronger binding between the layers, resulting in a more rigid network *i.e.* in a higher average coordination number [12]. In principle, an increase in T_g should be then observed with increasing the Cu content [13]. Our data, however, follows this trend only up to 27.5 at%. Above this concentration, T_g decreases suggesting that the structural assumptions described above are no longer valid. Xin et al. [14] have shown that homopolar Cu-Cu bonds dominate in Cu-As-Se glasses at large Cu concentrations ($> 20\%$) while the coordination of Cu and As (respectively tetrahedral and trigonal) remains unaffected. Given the lower energy of Cu-Cu bonds ($488.7 \text{ kJ}\cdot\text{mol}^{-1}$, calculated from [15]) compared to Cu-Te, Cu-Se and Cu-As bonds ($536.8, 666.9$ and $533.5 \text{ kJ}\cdot\text{mol}^{-1}$, respectively, calculated from Pauling's relation [16]), the presence of homopolar bonds might give rise to a balance between the rigidity of the network and the bonding energies. Yet, because of the different nature of the Te and Se bonds, the possibility that Cu could be trigonally-coordinated at high Cu concentrations cannot be strictly excluded in the present case. Another possible origin of the observed dependence could be related to the presence of nano-sized crystals undetectable by PXRD that might grow due to the proximity of the glass-domain border in the Cu-As-Te phase diagram. Further work is in progress to better understand the overall dependence of T_g with the Cu and Se contents.

4. Thermoelectric properties at 300K

Figure 4 shows the electrical resistivity and thermopower measured at 300 K on the different $\text{Cu}_x\text{As}_{40-x}\text{Te}_{60-y}\text{Se}_y$ samples. Increasing the Cu concentration leads to a decrease in ρ (Figure 4a) while substituting Se for Te has the opposite effect. Assuming that the network structure remains unchanged upon alloying with Se, this last feature may be related to the less metallic character of Se compared to Te [1,4]. For compositions falling near the glass-domain limit (*i.e.* at the lowest Se content for a given Cu concentration), the beneficial influence of Cu on ρ overwhelms the detrimental effect of Se. This property enables to substantially lower ρ by one order of magnitude while maintaining the glass stability in this system. Noteworthy, ionic conductivity associated with mobile Cu atoms seems unlikely to play a significant role on the decrease in the ρ values observed in the present case. A decrease in the band gap width, as demonstrated by Goncalves et al. in Cu-Ge-Te glasses [2], appears more reasonable due to the less ionic nature of Te compared to Se. This conclusion seems further corroborated by the results obtained by Bychov et al. [17,18] in the Cu-As-Se system indicating a negligible ionic contribution to the electrical conductivity.

Figure 4b depicts the evolution of the thermopower values with the Cu content. A clear trend towards a decrease in S with x can be easily noticed. The influence of Se is more pronounced on S since the measured values range between 400 and 700 $\mu\text{V}\cdot\text{K}^{-1}$ as typically observed in Se-containing glasses. Such high values originate from a large density of states at the Fermi level due to charged and neutral coordination defects (dangling bonds) [4,19]. The composition $\text{Cu}_{25}\text{As}_{15}\text{Te}_{51}\text{Se}_9$ does not seem to follow the trend observed *i.e.* a decrease in the thermopower values with y . This behavior might be related to the proximity of this composition to the crystalline border, possibly leading to differences in the glass structure and/or to the presence of nano-sized crystals in the glassy matrix that might affect S .

The power factor at 300K for each composition is shown in Figure 4c. These results show that the power factor faithfully reflect the trend observed for the electrical resistivity, whose evolution is mainly driven by the Cu content. A maximum value of $22 \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ was measured, showing that a sensible increase can be achieved near the vitreous domain limit as in $\text{Cu}_{30}\text{As}_{10}\text{Te}_{54}\text{Se}_6$ for instance. These power factors are of the same order of magnitude as those obtained by Goncalves et al. [3], yet, with a high concentration of Se.

The thermal conductivity values measured at 300 K are shown in Figure 5. Because of the experimental inaccuracy that inevitably accompanies the measurement of λ via the density, specific heat and thermal diffusivity, no clear trend with the Cu and/or Se concentration is observed. The λ values only slightly vary with the composition since no drastic structural changes were unveiled. All the samples are amorphous, synonymous to intrinsically low λ values that amount to $0.3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. The calculated ZT values are displayed in Figure 6. Due to the apparent lack of influence of Cu and Se contents on thermal conductivity, the ZT values follow the variations in the power factor. The maximum ZT value obtained in the present series of samples reaches 0.02 in the $\text{Cu}_{30}\text{As}_{10}\text{Te}_{51}\text{Se}_6$ glass.

5. Thermoelectric properties up to 375 K for the compositional line $\text{Cu}_x\text{As}_{40-x}\text{Te}_{54}\text{Se}_6$

The temperature dependence of the thermoelectric properties for the glasses lying on the compositional line $\text{Cu}_x\text{As}_{40-x}\text{Te}_{54}\text{Se}_6$ ($x = 25, 27.5$ and 30) is depicted in Figure 7. Due to the low T_g (around 400 K) and the narrow domain of stability of these glasses, these measurements were limited to 375 K. The $\rho(T)$ data decreases with increasing temperature indicating that charge carriers are thermally excited across the band gap (Figure 7a). This semiconducting behavior can be modeled by an Arrhenius law $\rho(T) = \rho_0 e^{\frac{E_a}{k_B T}}$ where E_a is the activation energy and k_B is the Boltzmann constant. Fitting the $\rho(T)$ data with E_a and ρ_0 as

free parameters (Figure 8) led to activation energies of 455 meV, 444 meV and 348 meV for the $x = 25, 27.5$ and 30 samples, respectively. According to Mott and Davis [19], when the conduction occurs through extended states rather than through hopping between localized states, the activation energy equals to the width of the band gap $E_a = (E_c - E_v) / 2$. The values inferred decreases with the Cu content and are therefore consistent with the idea that the decrease in ρ is mainly due to gap narrowing.

The thermal conductivity data (Figure 7b) show only weak temperature dependence as expected from the amorphous nature of these materials. The slight decrease observed is likely due to increasing phonon-phonon scattering events as the temperature increases. As a consequence, the evolution of ZT (Figure 7c) is mainly driven by electrical properties, especially by the decrease in resistivity that overwhelms the decrease in thermopower. We finally obtain a noticeable threefold increase in ZT on going from 300K to 375K for each composition of the system $\text{Cu}_x\text{As}_{40-x}\text{Te}_{54}\text{Se}_6$, reaching a peak ZT of 0.06 at 375K for $x = 30$.

6. Conclusion

The thermal behavior together with the thermoelectric properties of $\text{Cu}_x\text{As}_{40-x}\text{Te}_{60-y}\text{Se}_y$ chalcogenide glasses was investigated by means of DSC, electrical resistivity, thermopower and thermal conductivity measurements. Our results show that substituting Se for Te in small quantities help to broaden the stability domain by increasing both T_g and ΔT . The electrical resistivity values decrease with increasing the Cu content and shows a metallic-like behavior. The introduction of Se in these glasses drives the system towards a semiconducting regime of conduction. These trends are reflected by the composition and temperature dependences of the thermopower. The thermal conductivity is practically unperturbed by the chemical substitutions and remains typical of chalcogenide-based amorphous compounds. Taken as a

whole, these measurements highlighted the opposite effect of Cu and Se on the ZT values: an increase in the Cu content results in an increase in ZT , while an increase in the Se content is detrimental to the thermoelectric properties. Nevertheless, the beneficial influence of Cu overweighs that of Se, leading to an overall increase in ZT that reaches 0.02 at 300K and increases to 0.06 at 375K in $\text{Cu}_{30}\text{As}_{10}\text{Te}_{54}\text{Se}_6$. In addition, the thermal stability of glassy samples can be of significant importance in the case of glass-ceramization process that requires large ΔT in order to control precisely the crystalline fraction in the glassy matrix. This technique may possibly give rise to enhanced thermoelectric performance in chalcogenide glasses and will be the subject of forthcoming studies dedicated to Cu-As-Te-Se glasses.

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Figure captions

Figure 1: PXRD pattern of $\text{Cu}_{25}\text{As}_{15}\text{Te}_{60}$.

Figure 2: Thermal parameters of the $\text{Cu}_x\text{As}_{40-x}\text{Te}_{60-y}\text{Se}_y$ glasses within the vitreous domain for $x = 20, 22.5, 25, 27.5, 30, 32.5$ and $y = 0, 3, 6, 9$.

Figure 3: DSC patterns measured in the system $\text{Cu}_x\text{As}_{40-x}\text{Te}_{51}\text{Se}_9$ for $x = 25, 27.5, 30$ and 32.5 .

Figure 4: Room temperature electrical resistivity (a), thermopower (b) and power factor (c) of the $\text{Cu}_x\text{As}_{40-x}\text{Te}_{60-y}\text{Se}_y$ glasses.

Figure 5: Room temperature thermal conductivity values for $\text{Cu}_x\text{As}_{40-x}\text{Te}_{60-y}\text{Se}_y$.

Figure 6: ZT values at room temperature for the system $\text{Cu}_x\text{As}_{40-x}\text{Te}_{60-y}\text{Se}_y$.

Figure 7: Temperature dependence of the electrical resistivity (a, dashed lines), thermopower (b, solid lines), thermal conductivity (c) and ZT (d) of the $\text{Cu}_x\text{As}_{40-x}\text{Te}_{54}\text{Se}_6$ glasses between 300 and 375 K.

Figure 8: Arrhenius fitting of resistivity data between 300 and 375 K for the compositional line $\text{Cu}_x\text{As}_{40-x}\text{Te}_{54}\text{Se}_6$.

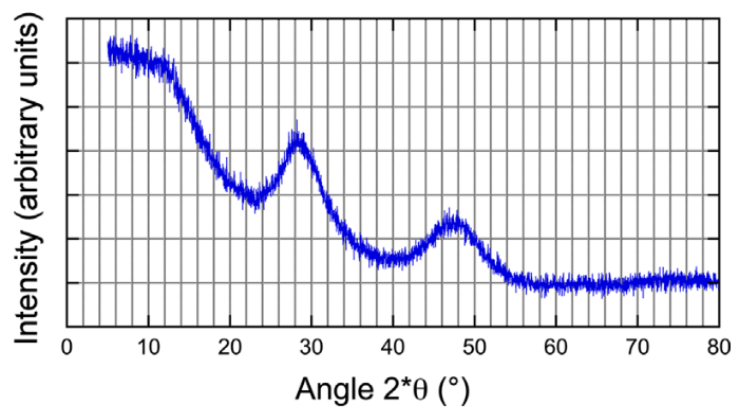


Figure 1

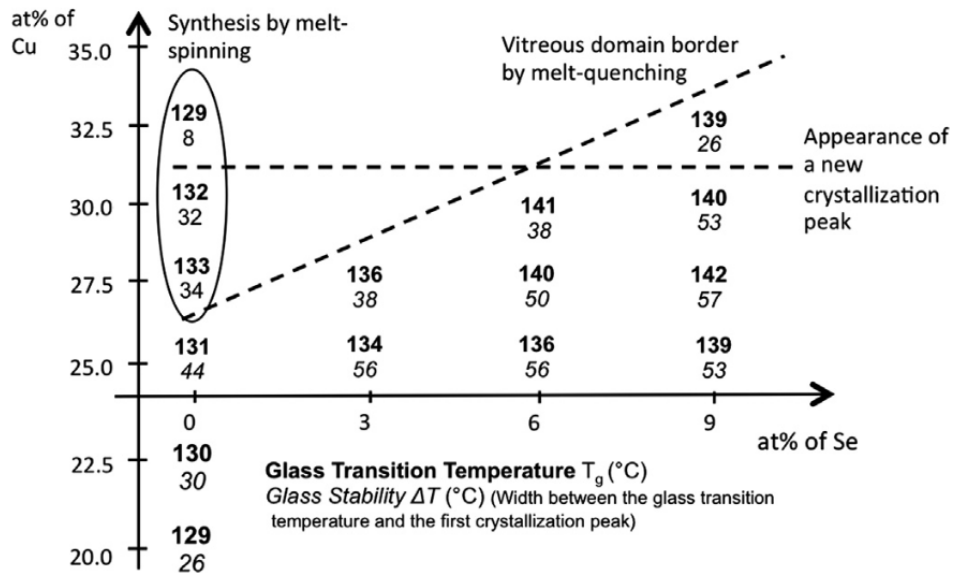


Figure 2

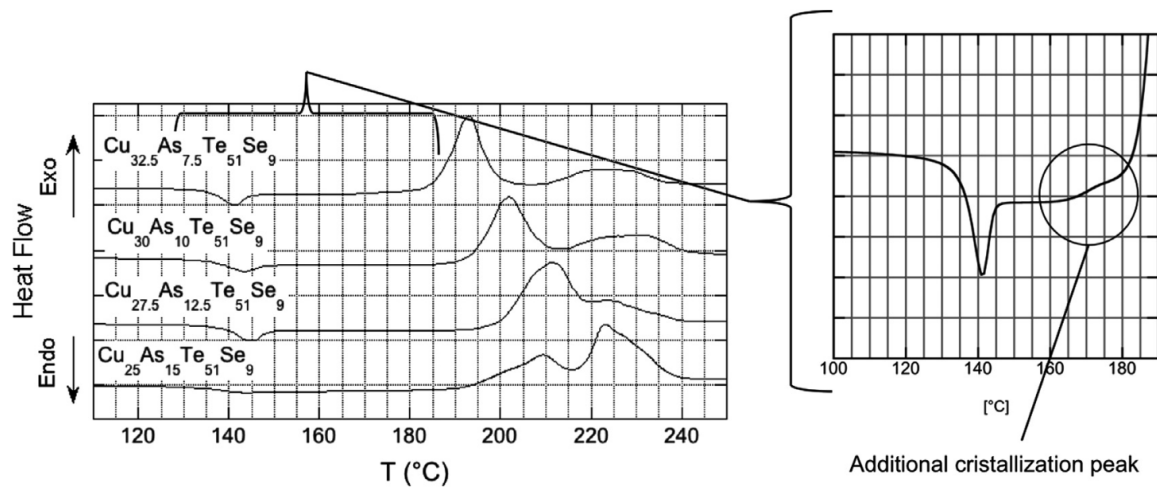


Figure 3

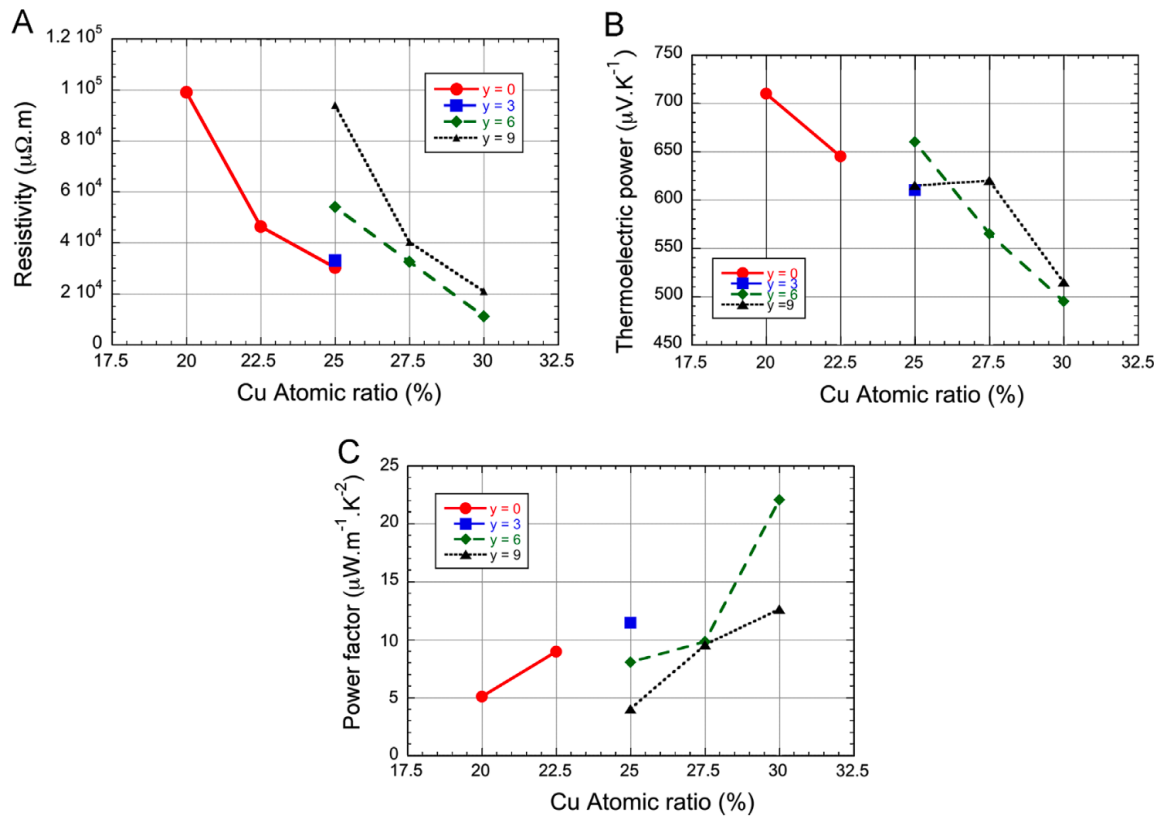


Figure 4

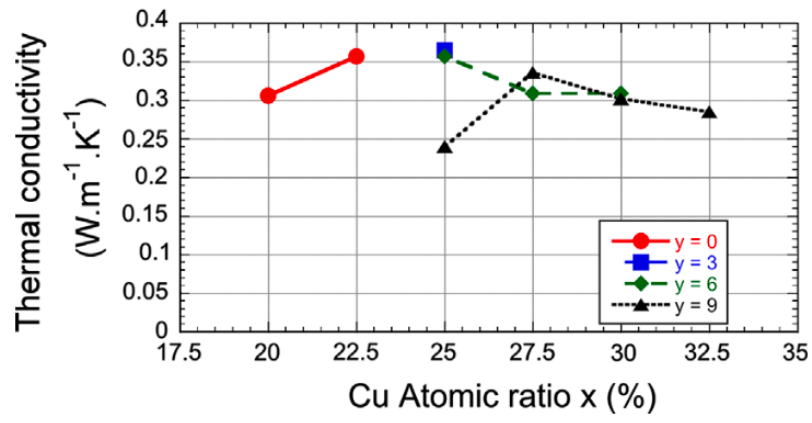


Figure 5

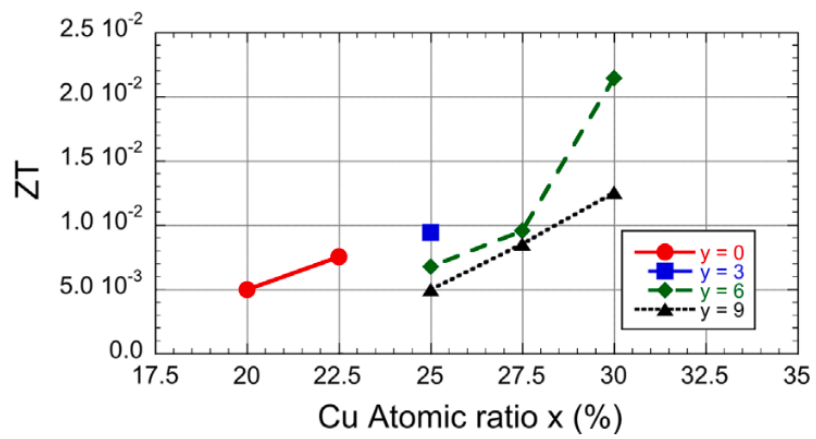


Figure 6

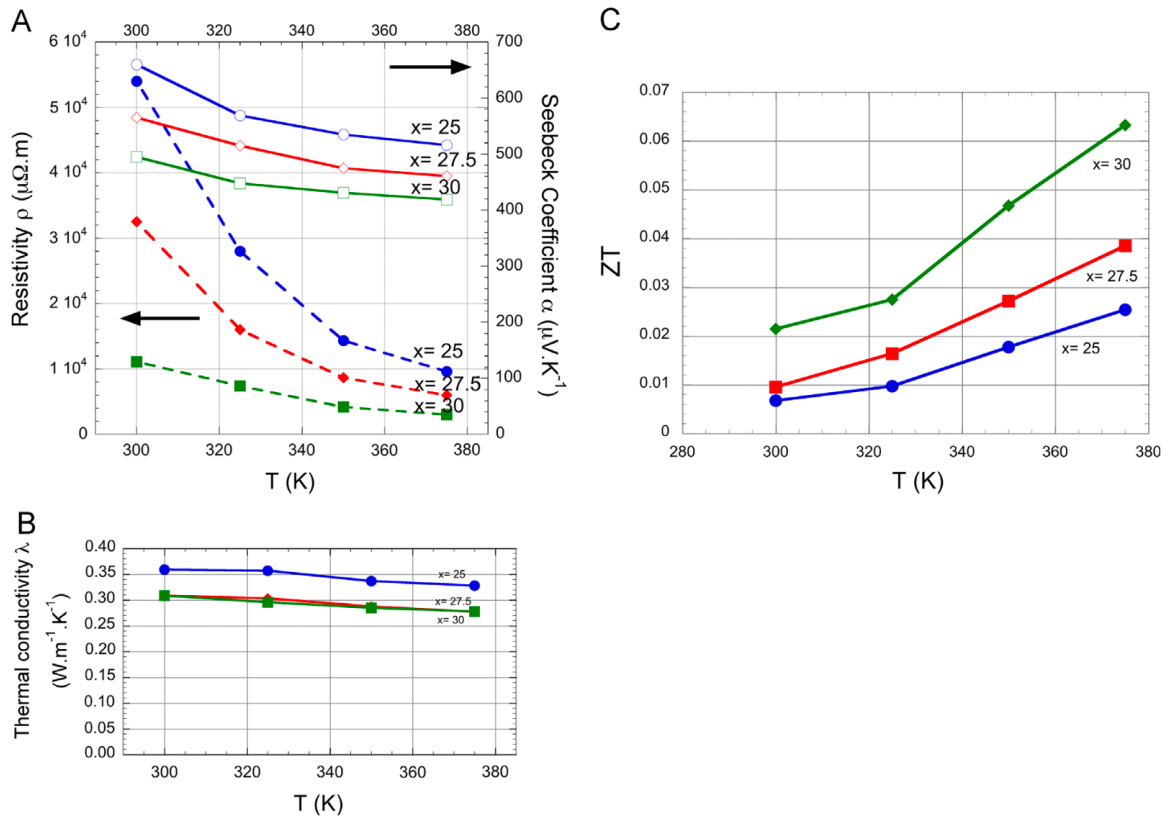


Figure 7

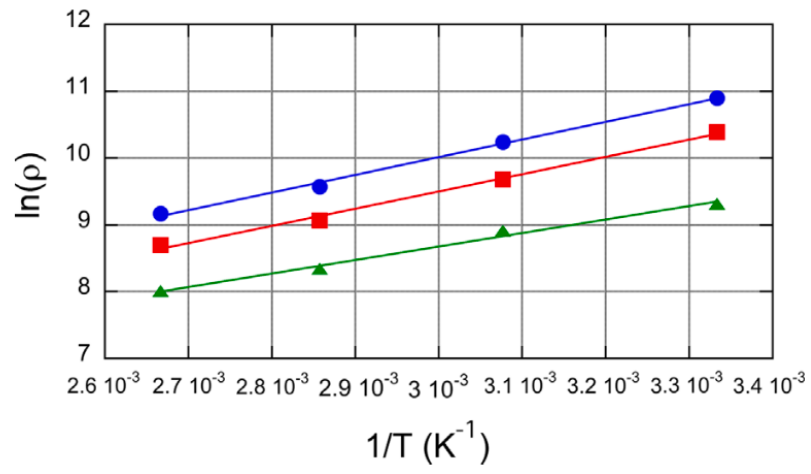


Figure 8