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Thermoelectric Power Measurements of xSb-(60-x)V_2O_5-40TeO_2 Glasses

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Bulk xSb-(60-x)V_2O_5-40TeO_2 glass systems (with $0 \le x \le 15$ in mol.%) were prepared by using the standard melt quenching procedure, and their Seebeck coefficients, S, were measured within the temperature range of 250–470 K. For the understudied samples, the thermoelectric powers at typical temperatures of 296 K, 370 K and 407 K were measured, and were in the ranges (−405) to (−698) μVK^{-1}, (−394) to (−685) μVK^{-1} and (−392) to (−691) μVK^{-1}, respectively. The selection of typical temperatures aims at the evaluation of the trend of figure of merit in these glasses. Based on the negative sign of S, the present glasses were found to be n-type semiconductors; also, the experimental relationship between S and C_V ($C_V = [V^{4+}]/V_{tot}$ is the ratio of the content of reduced vanadium ions) satisfied the theoretical Heikes formula, relating S to $\ln(C_V/1 - C_V)$, and also the Mackenzie formula, relating S to $\ln([V^{5+}]/[V^{4+}])$. The parameter α' in Heikes formula was determined to be $\ll 1$ and so the small polaron hopping conduction mechanism was certified to occur in these glasses; this result confirms the previously reported results of direct current (DC) electrical conduction experiments on the same samples. Results of thermoelectric measurements show the compositional dependence of S on Sb content and C_V, indicating that S increases with the increase in Sb content; these results show that the dominant factor determining S is C_V. Also, figure of merit was determined for these glasses, which show the highest value for $60V_2O_5$-$40TeO_2$ glass system, as a good candidate in thermoelectric applications.

Key words: Amorphous materials, glasses, thermoelectric effects, electrical conductivity

INTRODUCTION

Thermoelectric materials show the thermoelectric effect in a convenient form. The thermoelectric effect refers to phenomena by which either a temperature difference creates an electric potential (Seebeck effect), or an electric potential creates a temperature difference (Peltier effect). However, low-cost materials that have a sufficiently strong thermoelectric effect (and other required properties) could be used in applications including power generation and refrigeration. On the other hand, in the equation of figure of merit (as is presented in the "Figure of Merit" section), thermal conductivity and electrical conductivity compete. In order to optimize and so maximize the figure of merit, phonons, which are major contributors for thermal conductivity, must experience the material as they would in a glass (experiencing a high degree of phonon scattering-lowering thermal conductivity).[1] Furthermore, semiconducting glasses, which show increase of conductivity with increase in temperature, are more suitable candidates for thermoelectric materials. Specifically, maximizing electrical conductivity at high temperatures and minimizing thermal conductivity optimizes the figure of merit.

Several papers have been published on the electrical properties, the electrical conduction mechanism and optical properties,[2–11] and also the

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thermoelectric power[9,12,13] of oxide glasses containing transition metal (TM) ions. Among the multicomponent oxide glasses, vanadium-tellurite glasses have attracted a great deal of attention, because of some aspects such as: (i) lack of hygroscopy in glasses containing TeO_2, and also their low melting temperature, good optical transparency and very high glass forming ability; and (ii) good semiconductivity nature of TM containing glasses.[2,3,14,15] Besides, the thermoelectric properties such as Seebeck measurements are of great importance and are useful for some characterization of amorphous semiconductors; the negative/positive sign of the Seebeck coefficient determines the negative/positive feature of the charge carrier. Furthermore, our knowledge on the electrical conductivity (σ) and Seebeck coefficient (S) can help us to interpret the mechanism of electrical conduction and charge carrier transport, and also to introduce the materials with a higher figure of merit.

There are few reports[9,12,13,16–20] on the Seebeck coefficient of oxide glasses. In our recent works, the electrical conductivity[2] and optical properties[6] of Sb-V_2O_5-TeO_2 glasses have been reported; so, for the mentioned glasses, the objectives of this work are (a) to present and discuss the data of Seebeck coefficients, (b) to attempt to identify/clarify the electrical conduction mechanism and compare the results with the previously reported electrical data,[2] (c) to search for samples with higher figure of merit for thermoelectric applications, such as power generation and thermoelectric coolers.

EXPERIMENTAL DETAILS

Glassy samples of the form xSb-(60-x)V_2O_5-40TeO_2 with $0 \le x \le 15$ in mol.% are hereafter termed as TVSbx. Details of the glass preparation process, structural characterization and some physical properties have been precisely described in our recently published works.[2,6] Also, the results of the direct current (DC) electrical conductivity of hopping transport mechanism are presented in Ref. 2. The Seebeck coefficient of the under studied samples was measured within the temperature range of 250–470 K; details of this experiment are the same as presented elsewhere.[13] The total V ion concentration and V ion reduction ratio ($C_V = [V^{4+}]/V_{tot}$), in as-quenched glasses used in this study, were determined by titration using $KMnO_4$ and $FeSO_4$ $(NH_4)_2SO_4$ solutions. The determined ratio of high valence to low valence vanadium ions, $[V^{5+}]/[V^{4+}]$, and the ratio of reduced vanadium ions, $C_V = [V^{4+}]/V_{tot}$, are given in Table I.

RESULTS AND DISCUSSION

Thermoelectric Considerations

As mentioned in the "Introduction" section, the Seebeck measurements are of great importance and are useful for some characterization of amorphous semiconductors; also, the sign of the Seebeck coefficient determines the sign of majority charge carrier in semiconductors. In addition, our knowledge on the electrical conductivity (σ) and Seebeck coefficient (S) can help us to interpret the mechanism of electrical conduction and the mechanism of charge carrier transport, and also to introduce materials with suitable figure of merit. However, it is very important to clarify the relation between the DC electrical conduction and the results of thermoelectric measurements, with a great deal of attention to C_V. Generally, for thermoelectric power of oxide glasses, two formulas have been proposed:

(a) One is Heikes formula[21,22] given as:

$$S = (K_B/e)\left[\ln\left(\frac{C_V}{1 - C_V}\right) + \alpha'\right] \tag{1}$$

where C_V, K_B, e and α' are the reduced ratio of transition metal ions, Boltzmann's constant, electronic charge and a constant of the proportionality between the heat transfer and the kinetic energy of an electron, respectively.

(b) Another formula, known as the Mackenzie formula,[16] is a slightly modified formula written in the form:

$$S = -(K_B/e)\ln\left(\frac{\text{high valence ions}}{\text{low valence ions}}\right) = -(K_B/e)\ln\left(\frac{[V^{5+}]}{[V^{4+}]}\right) \tag{2}$$

By using Heikes formula, one can discuss the electrical conduction mechanism in samples with the charge carrier mobility $\mu \langle\langle 10^{-2}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$.[9,12,13]

Table I. The data of charge carrier mobility (μ), the ratio of reduced vanadium ions to total vanadium ions (C_V), Seebeck coefficient (S), electrical conductivity (σ) and $[V^{5+}]/[V^{4+}]$ for TVSbx glasses

Glass	C_V	$[V^{5+}]/[V^{4+}]$	μ ($cm^2\ V^{-1}\ s^{-1}$) (at 296 K)[1]	σ_{296K} ($S\ cm^{-1}$)[1]	$S_{296\ K}$ (μVK^{-1})	σ_{370K} ($S\ cm^{-1}$)[1]	$S_{370\ K}$ (μVK^{-1})	σ_{407K} ($S\ cm^{-1}$)[1]	S_{407K} (μVK^{-1})
TVSb0	0.010	96.65	3.19×10^{-5}	1.11×10^{-5}	−698	1.08×10^{-4}	−685	2.44×10^{-4}	−691.13
TVSb5	0.098	9.19	9.09×10^{-6}	6.02×10^{-6}	−530	6.11×10^{-5}	−530	1.46×10^{-4}	−522.80
TVSb8	0.163	5.15	4.29×10^{-7}	1.50×10^{-6}	−471	2.14×10^{-5}	−458	5.96×10^{-5}	−459.18
TVSb10	0.179	4.60	7.97×10^{-8}	5.51×10^{-7}	−460	9.37×10^{-6}	−460.83	2.58×10^{-5}	−462.27
TVSb12	0.188	4.32	4.78×10^{-9}	3.34×10^{-7}	−441	6.22×10^{-6}	−446.74	1.77×10^{-5}	−447.06
TVSb15	0.204	3.90	3.95×10^{-10}	2.26×10^{-7}	−405	4.80×10^{-6}	−394.68	1.32×10^{-5}	−392.99

Within this carrier mobility limit (resulted from the strong localization of electrons), the heat transfer will be small compared to that of K_BT. Also, it has been reported that small polaron hopping (SPH) will occur if $\alpha' \langle\langle 1$, while large polarons are responsible for electrical conduction if $\alpha' \rangle\rangle 2$.[9,12,13] On the other hand, the compatibility between the experimental results and the mentioned formulas can be verified by plotting the S-ln(C_V/1 − C_V) curves (for Heikes) and S-ln([V^{5+}]/[V^{4+}]) curves(for Mackenzie). The slope of the mentioned plots should be near to the theoretical value of $(K_B/e) = 86.18\ \mu VK^{-1}$.

In the present work, ternary TVSbx glasses are investigated and discussed to verify the temperature dependence of Seebeck coefficient, and hence the applicability of the Heikes and Mackenzie formulas. For these samples, the Seebeck coefficient (S) is shown in Fig. 1, within the temperature range of 250–470 K. The negative sign of S indicates the n-type nature for the present semiconductors; their semiconductivity feature has been certified in our recent works.[2,6] Also, Fig. 1 shows no temperature dependence of S for the entire temperature range under investigation, which justifies the applicability of the temperature-independent Heikes formula (see Eq. 1); the temperature-independent Seebeck coefficients are usually observed in solids when high-temperature electrical conduction is governed by the hopping of a nearly constant density of small polarons. Standard treatment of small polaron Seebeck effect yields at independent Seebeck coefficients for a constant carrier density. Specially, remember that the Seebeck coefficients are a measure of the entropy transported with a charge carrier divided by the carrier's charge. The standard treatment of the Seebeck coefficient considers only the change in the entropy of mixing produced by adding a charge carrier. At sufficiently high temperatures, the ratio of the density of polarons to the density of available sites is constant; thus, glasses that possess localized states and obey the SPH mechanism, demonstrate good agreement with the Heikes formula.[23] To investigate the complete compatibility of Eq. 1, Fig. 2 shows the linear plots of S versus ln(C_V/1 − C_V) at typical temperatures 296 K, 370 K and 407 K, by using the least squared method. The linear correlation coefficient R^2 was in the range of0.951–0.966. The slopes of these curves were 84.08 μVK^{-1}, 81.28 μVK^{-1} and 83.05 μVK^{-1} at 296 K, 370 K and 407 K, respectively, and are in good agreement with the theoretical value of $(K_B/e) = 86.18\ \mu VK^{-1}$. These results certify the applicability of Heikes formula; also, the value of α' can be obtained from the intercept of S-ln(C_V/1 − C_V) plots as: intercept = $(K_B/e)\ \alpha'$. The obtained values for α' are in the range of (−3.70) to (−3.75), which are $\ll 1$. These results justify the SPH mechanism for electrical conduction, and confirm the direct electrical conduction results of our previous work[2] on the same samples (resulting from (i) the applicability of SPH relation, (ii) very low charge carrier mobility), see Table I and other criteria presented in Refs. 2, 3, and 8. Such values of α' have been reported previously for TeO_2-MoO_3,[9] TeO_2-V_2O_5-MoO_3,[13] TeO_2-V_2O_5-Sb_2O_3[12] and TeO_2-V_2O_5-Bi_2O_3.[12] In brief, results of electrical conductivity,[2] optical band gap and band tailings,[6] as well as the thermoelectric data presented in this study, reveal the SPH mechanism for the electrical conductivity. The data of charge carrier mobility, C_V, S, σ and [V^{5+}]/[V^{4+}], are listed in Table I.

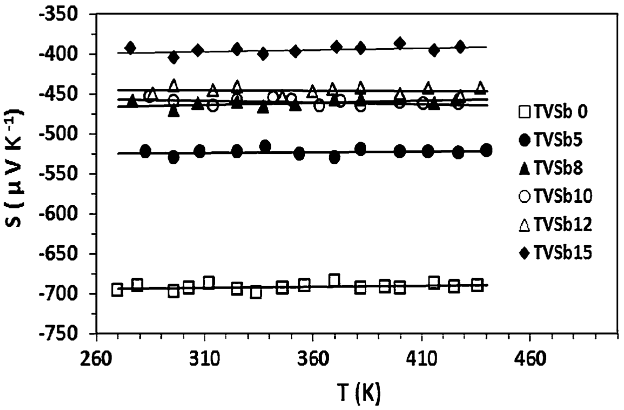

Fig. 1. Plots of Seebeck coefficients (S) versus temperature (T) for TVSbx glasses.

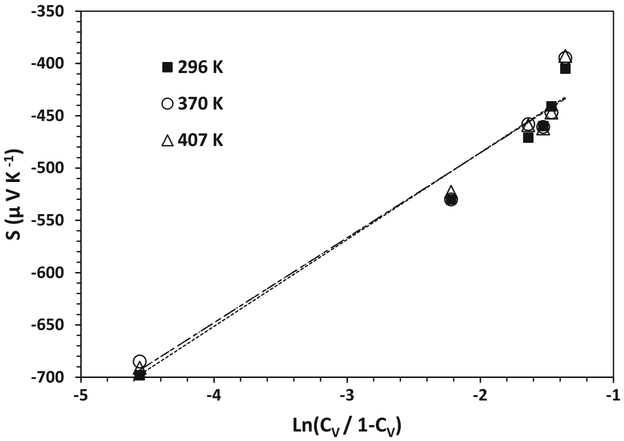

Fig. 2. Relationship between S and Ln (C_V/1 − C_V) for TVSbx glasses at 296 K, 370 K and 407 K.

From Fig. 1, it is obvious that Seebeck coefficient has a compositional dependence, which indicates an increase in S with an increase in Sb content. From the insensitivity of S to temperature (Fig. 1), results shown in Fig. 2 and the compositional dependence of C_V and S (evident from Table I), we can conclude that the dominant factor determining S is the ratio of reduced vanadium ions C_V.

As mentioned before, a slightly modified Mackenzie formula can be used for oxide glasses. In other word, in glasses containing TM ions (such as V ions), only a small fraction of the high valence ions (i.e., V^{5+}) is reduced to low valence ions (i.e. V^{4+}).

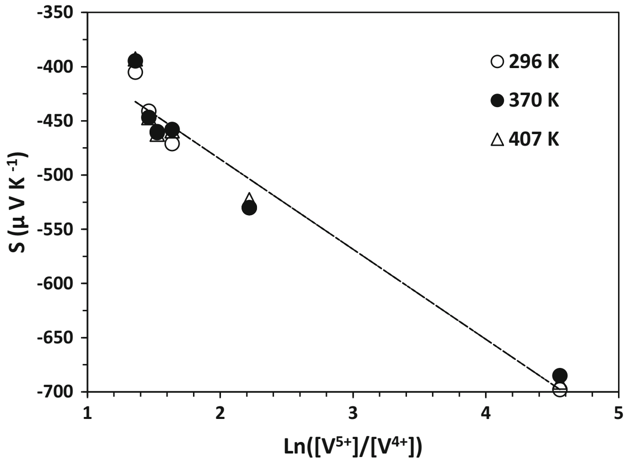

Fig. 3. Plots of S versus ln([V^{5+}]/[V^{4+}]) for TVSbx glasses at 296 K, 370 K and 407 K.

Thus, it may be proposed that the addition of charge carriers (i.e. electrons) remains and they later act as charge carriers, and the electrical conduction takes place by electron hopping between V^{4+} and V^{5+} ions. Then the Makenzie formula can be used. So, to certify the validity of this formula (Eq. 2) for the present samples, one can plot the curves of S versus ln([V^{5+}]/[V^{4+}]) by using the data listed in Table I. Another result of Eq. 2 is the prediction of n- or p-type nature of semiconductor directly from C_V. However, if for [V^{5+}]/[V^{4+}]> 1 the sample is n-type, in a highly reduced glass with [V^{5+}]/[V^{4+}]< 1, S will be positive and the sample is p-type. Based on this criterion, the present glasses are n- type, which justifies the negative sign of experimentally obtained data for S. Figure 3 shows the S-ln([V^{5+}]/[V^{4+}]) plots for TVSbx glasses. The slopes of these lines (with the linear correlation coefficient R^2 in the range of 0.9518–0.9685) are 84.08 μVK^{-1}, 81.28 μVK^{-1} and 83.05 μVK^{-1} at 296 K, 370 K and 407 K, respectively, and are in approximately good agreement with the theoretical value of (K_B/e) = 86.18 μVK^{-1}; these results certify the applicability of the Mackenzie formula.

Figure of Merit

It is evidently pleasant to select or find materials with the highest possibility of application in the desirable temperature range. So, finding a material to be used in thermoelectric applications is to a large degree dependent on the figure of merit (F). This parameter is defined as[13,18]:

$$F = S^2 \sigma / k_t \qquad (3)$$

where σ and k_t and S are electrical conductivity, thermal conductivity and Seebeck coefficient of the sample, correspondingly. Selection of desirable materials, involves simultaneously controlling the S, σ and k_t. Generally, oxide glasses have small k_t, and so further measurements such as thermal conductivity are necessary to make more precise conclusions, which will be presented in future works.

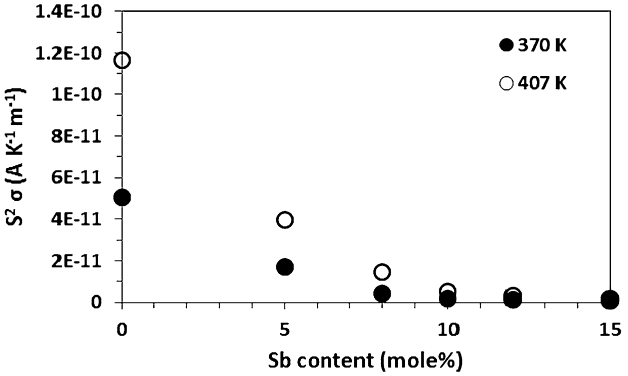

Fig. 4. The compositional dependence of power factor (S^2 σ) dependence in TVSbx glasses at 370 K and 407 K.

Figure 4 shows the experimental power factor $S^2\sigma$ at different temperatures, which shows that TVSb0 has the highest figure of merit as a suitable candidate for in thermoelectric applications.

CONCLUSIONS

1. The Seebeck coefficients (S) of xSb-(60-x)V_2O_5-40TeO_2 glasses were measured within the temperature range of 250−470 K. The values of S temperatures 296 K, 370 K and 407 K were in the ranges (−405) to (−698) μVK^{-1}, (−394) to (−685) μVK^{-1} and (−392) to (−691) μVK^{-1}, respectively.
2. The studied glasses were found to be n-type semiconductors. The experimental relationship between S and C_V (C_V = [V^{4+}]/V_{tot}) satisfied the theoretical Heikes and Mackenzie formulas.
3. The parameter α' in Heikes formula was determined to be $\ll 1$. Thus, the SPH conduction mechanism was certified to occur in these glasses; this result confirms the previously reported results of DC electrical conduction experiments on the same samples.
4. Results of thermoelectric measurements show the compositional dependence of S on Sb content and C_V, indicating that S increases with an increase in Sb content; these results show that the dominant factor determining S is C_V.
5. 60V_2O_5-40TeO_2 glass system has the highest value for being a good candidate in thermoelectric applications.

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