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# Thermoelectric power (TEP) and structural properties of ternary semiconducting $V_2O_5$–NiO–$TeO_2$ glasses

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**Highlights**

- **Thermoelectric power (TEP), density and molar volume of two glass systems: (90–x)$V_2O_5$–10NiO–x$TeO_2$ (30≤x≤60 mol%) and (80–x)$V_2O_5$–20NiO–x$TeO_2$ (20≤x≤50 mol%) were studied.**
- **The TEP above 303K of the two glass systems does not depend on temperature and the glasses were n-type semiconducting.**
- **The high-temperature TEP provides evidence for small polaron formation but the condition of the TEP of two glass systems must be explained adequately by Heikes' relation.**
- **TEP increases with the increase of NiO compositions from 10 mole% to 20 mole%.**
- **The geometry and topology of the structure do not change with glass compositions.**
- **The glasses appear to be in a single phase.**

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ABSTRACT

A press-quenching method from glass melt was used to prepare two series of ternary semiconducting $V_2O_5$–10NiO–$TeO_2$ and $V_2O_5$–20NiO–$TeO_2$ glasses. TEP, density ($\rho$) and molar volume of oxygen ($V_m$) of these glasses were studied. Measurement of TEP at the temperature range 302 – 512K for the above glass samples has been made. Details on the formation of the polarons as well as the disorder energy resulting from randomized fields were obtained. Heikes' equation and small polaron model theory relating to TEP managed to account sufficiently for the results from the experimental data. Results showed that as the content of $V_2O_5$ in glass increase there will be a fall in density in addition to a monotonical increase in molar volume. All the glasses appear to be in a single-phase structure.

## 1. Introduction

Mixing oxides known as glass formers such as $P_2O_5$, $TeO_2$, $GeO_2$ (Denton *et al.*, 1945; Mackenzie, 1964; Murawski *et al.*, 2005) with Transition metal oxides (TMO) can produce homogeneous glasses. Impending applications of TMO glasses, their semiconducting characteristics, and switching behavior render them an interesting topic of research (Mackenzie, 1964; Hansen, 1965; Murawski *et al.*, 1979; Hirashima *et al.*, 1987). The semiconducting behavior of TMO glasses is dependent on the condition that transition metal ion (TMI) should be present in multi oxidation states so that electrons will be transferred from low valence state to a higher one and the conductivity process will then occur (Mott, 1968; Austin *et al.*, 1969). Accordingly, within glass containing TMI the electron transfer could be ascribed to be as the process of a small polaron hopping which relates the self-induced distortions that extend over their nearest surroundings to the trapping of charge carries (Mogus-Milankovic *et al.*, 2001). There are many reports have been done previously by different researchers on the structural and thermoelectric power of semiconducting TMO glasses of different materials (El-Desoky *et al.*, 2007; Ghosh, 1989; Sakata *et al.*, 1999; Tawati *et al.*, 2003; Tawati *et al.*, 2004; Tawati *et al.*, 2010; Tawati *et al.*, 2019; Souri, 2008; Souri, 2016; Souri *et al.*, 2016). These reports showed that some TMO glasses have large Seebeck coefficients and their structure is dependent on the nature of network formers and network modifiers. In addition, measurements of the TEP of these materials are important, because they provide details on the formation of the polarons as well as the disorder energy resulting from randomized fields (Mott, 1968; Austin et al., 1969; Mansingh et al., 1978; Heikes et al., 1961). In our previous works (Tawati *et al.*, 2003; Tawati *et al.*, 2004; Tawati *et al.*, 2010), we have investigated the TEP of binary CoO–$P_2O_5$, NiO–$P_2O_5$ and ternary CoO–NiO–$P_2O_5$ glasses. These investigations showed that the TEP is not related to temperature whatever the composition of glass is, and the glasses have low Seebeck coefficients. In addition, Heikes' relation managed to account sufficiently for the results from the experimental data (Heikes *et al.*, 1961). This paper reports the structural and the TEP of ternary semiconducting $V_2O_5$–NiO–$TeO_2$ glasses in an assortment of compositions with temperature extending from the 302 K to 512 K.

## 2. Experimental Procedure

Two series compositions of glass samples in (mol%) of the systems (90–x)$V_2O_5$–10NiO–x$TeO_2$ with 30≤x≤ 60 and (80–x)$V_2O_5$–

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20NiO–xTeO2 with 20≤x≤ 50 were prepared by reagent grade melting of the following oxide$V_2O_5$ (99.9%), NiO (99.9%) and $TeO_2$ (99.9%) in a platinum crucible at 1025 K and left for about 1 h in an electric furnace with frequent stirring. The homogenized melts were then quickly casted onto a mold made of steel mold, which has been pre-heated to a temperature of 480 K. This procedure assists in reducing any thermal stress cracks that might occur in the glass. The formed glasses were then annealed in an annealing furnace at 500 K for one hour and subsequently allowed to slowly cool down. Following this procedure, disk-shaped samples of diameter about 2.5 cm and a thickness of about 2.0 mm were obtained. These samples were then cut and polished with very fine quality lapping papers. The amorphous structure of all glass samples was first checked visually and ascertained from X-ray diffraction (XRD) analysis. The density of glasses was determined by the simple displacement method by immersion in toluene, and employing the relation:

$$\rho_s = \frac{w_a \rho_t}{w_a - w_t} \tag{1}$$

Where, $\rho_s$ is the sample density, $w_a$ is the glass sample weighed in air, $w_t$ is the glass sample weighed in toluene and $\rho_t$ is the density of the toluene. A specially designed sample holder was constructed to measure TEP at the temperature extending from 302 K to 512 K. The details of TEP measurements have been reported elsewhere (Tawati *et al*., 2003). A difference in temperature of about 5–10 K was achieved for two glass parallel surfaces. The TEP was determined by measuring EMF created between the surfaces using Keithley's 2400 Series Source meter. All the above measurements were achieved in air.

## 3. Results and Discussion

The TEP–Temperature relation of ternary (90–x)$V_2O_5$– %10 NiO–x$TeO_2$ with 30≤x≤ 60 and ternary (80–x)$V_2O_5$–%20 NiO–x$TeO_2$ with 20 ≤x≤ 50 glasses in the temperature 302–512 K are shown in Fig. 1 and Fig. 2. The results clearly indicate that the TEP is independent of temperature for all glass compositions. This means that our results are in good agreement with the reported results by other workers for different materials (Ghosh, 1989; Mansingh *et al*., 1978; Mandal *et al*., 1996; Allersma *et al*., 1967). All TEP values have a negative sign for every glass compositions, suggesting that either an electronic charge carrier or a polaronic one to be found in those ternary glass systems.

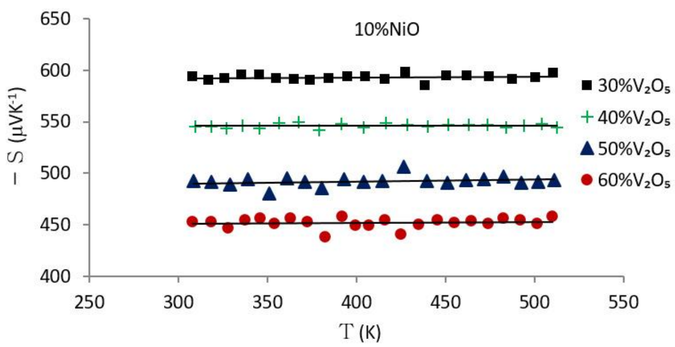


**Fig.1.** TEP plotted against temperatures for ternary ($V_2O_5$–10%NiO–$TeO_2$) glass system.

The composition dependence of TEP of $V_2O_5$–10NiO–$TeO_2$ and $V_2O_5$–20NiO–$TeO_2$ in the range 302 – 512 K is given in Fig. 3. It can be seen that TEP increases with the decrease of $V_2O_5$ glass content for both $V_2O_5$–10NiO–$TeO_2$ and $V_2O_5$–20NiO–$TeO_2$ glasses. The effect of NiO composition in TEP of both glass systems is clearly observed. It is seen that the increase of NiO composition from 10% to 20% into all glass components leads to an increase in TEP of these glasses. This means the compositions of the NiO play the dominant role in increasing the TEP measured, and this attributed to the increase of charge carrier due increase of NiO content in the glass matrix.

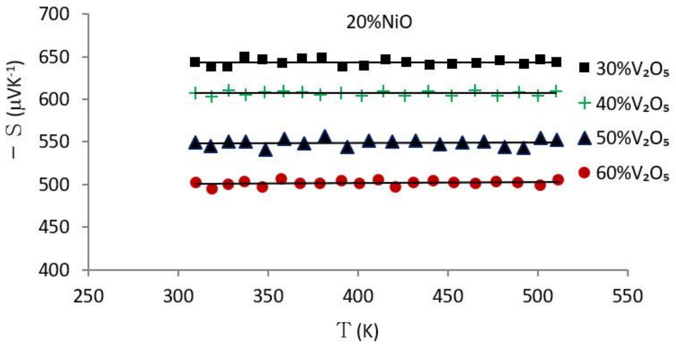


**Fig. 2.** TEP plotted against temperatures for ternary ($V_2O_5$–20%NiO–$TeO_2$) glass system.

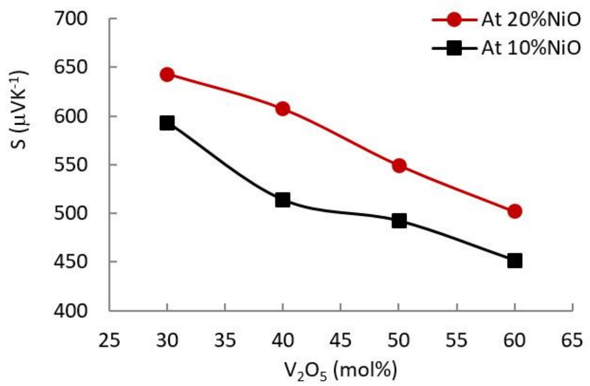


**Fig. 3.** Variation of TEP above 302 K with glass compositions in ($V_2O_5$–10%NiO–$TeO_2$) and ($V_2O_5$–20%NiO–$TeO_2$) glasses.

The measured TEP values of different compositions of $V_2O_5$–10%NiO–$TeO_2$ and$V_2O_5$–20%NiO–$TeO_2$ glasses above 302 K with other related parameters are reported in Table 1 and Table 2.

**Table 1**

Chemical composition and measured TEP of $V_2O_5$–10%NiO–$TeO_2$

| Glass composition (molv%) | | | Melting Temperature (K) | $-S_{exp.}$(μV/K) above 302 K | ρ (gm/cm³) | $V_m$ (cm³/mol%) |
|---|---|---|---|---|---|---|
| $V_2O_5$ | NiO | $TeO_2$ | | | | |
| 60 | 10 | 30 | 1025 | 451.77 | 3.597 | 45.73 |
| 50 | 10 | 40 | 1025 | 492.26 | 3.768 | 43.06 |
| 40 | 10 | 50 | 1025 | 513.72 | 4.079 | 39.23 |
| 30 | 10 | 60 | 1025 | 593.02 | 4.242 | 37.20 |

**Table 2**

Chemical composition and measured TEP of $V_2O_5$–20% NiO–$TeO_2$

| Glass composition (mol %) | | | Melting Temperature (K) | $-S_{exp.}$(μV/K) Above 302 K | ρ (gm/cm³) | $V_m$ (cm³/mol%) |
|---|---|---|---|---|---|---|
| $V_2O_5$ | NiO | $TeO_2$ | | | | |
| 60 | 20 | 20 | 1025 | 501.61 | 3.664 | 42.57 |
| 50 | 20 | 30 | 1025 | 549.17 | 3.846 | 39.98 |
| 40 | 20 | 40 | 1025 | 607.11 | 4.170 | 36.34 |
| 30 | 20 | 50 | 1025 | 643.10 | 4.322 | 34.54 |

Materials of mixed valence states have their TEP investigated theoretically by Heikes' relation (Heikes *et al*., 1961):

$$S = \frac{k_B}{e}\left[ln\frac{C}{1-C} + \alpha\right] \tag{2}$$

Where, $e$ is the charge of the electron, $k_B$ is Boltzmann constant, $c$ is the ratio of the concentration of reduced TMI to the concentration of total TMI and $\alpha$ is a proportionality constant links the heat transfer and the kinetic energy of the electron. TEP which has been predicted by Eq. (2) is not related to temperature. The magnitude of $\alpha$ determines the existence of polaron formation in the materials. Mott (Mott, 1968) proposed that α value less than one for small polarons, while, a value of α≥2 is suggested by (Austin *et al.*, 1969), for large polarons. Another suggestion (Sewell, 1963) used a value of constant α=0 in the case of band polaron, indicating that S should depend only on $c$ and should be independent of the nature of the TMI. If $c$ is not a temperature dependent as in TMO glasses (Lynch *et al.*, 1971), then S is expected to be temperature independent. The $\alpha$ term can be zero only if the disorder energy in the system is zero (Austin *et al.*, 1969). If there is disorder energy, then the $\alpha$ term should be finite and given by:

$$\alpha = \frac{(1-\theta)W_H}{(1+\theta)k_B T} \tag{3}$$

Where $W_H$ is the energy of polaron hopping and $\theta$ is a constant that is related to the system disorder. If $\theta$=1 means a zero disorder energy. If $\theta$ deviates from unity imply the existence of disorder within the system. The parameter $c$ which appears in Eq. (2) plays an essential role in the description of the Seebeck coefficient. The c parameter was not measured in this work, but the present results used c values obtained from previous research (Mansingh *et al.*, 1978; Allersma *et al.*, 1967; Sayer *et al.*, 1972; Murawski *et al.*, 1973; Mansingh *et al.*, 1977; Mansingh, 1978; Hogarth *et al.*, 1983; Santic *et al.*, 2001). The above researchers proposed the formation of small polarons in most of the TMO glasses. According to these suggestions, we can assume that the condition for small polaron formation in these glasses is satisfied, which means that α is less than one. The results presented in Fig. 1 and Fig. 2 show good agreement with the results reported by different researchers (Tawati *et al.*, 2003; Tawati *et al.*, 2004; Tawati *et al.*, 2010; Souri, 2008; Flynn, 1977; Mori *et al.*, 1996). However, if the TEP for $V_2O_5$–10NiO–$TeO_2$ and $V_2O_5$–20%NiO–$TeO_2$ glasses which has been determined at a high temperature can be explained by Heikes formula, then it can be assumed that the disorder energy increases with the increase of $V_2O_5$ content in the glass. In order to achieve a complete agreement between the theoretical and experimental values for TEP, the value of $\alpha$ parameter in Eq. (2) is needed but $c$ parameter values are unknown. Therefore, for a better understanding of the physical properties of these glassy materials, the values of $c$ need to be known.

Fig. 4 and Fig. 5 show that the density ($\rho$) and oxygen molar volume ($V_m$) of the $V_2O_5$–10%NiO and $V_2O_5$–20%NiO glasses are related to the glass composition. It may be observed that density decreases gradually with the increase of the $V_2O_5$ content in the various glass compositions. The relationship between the composition and the density of an oxide glass system can be expressed in terms of an apparent volume $V_m$ occupied by 1 g atom of oxygen.

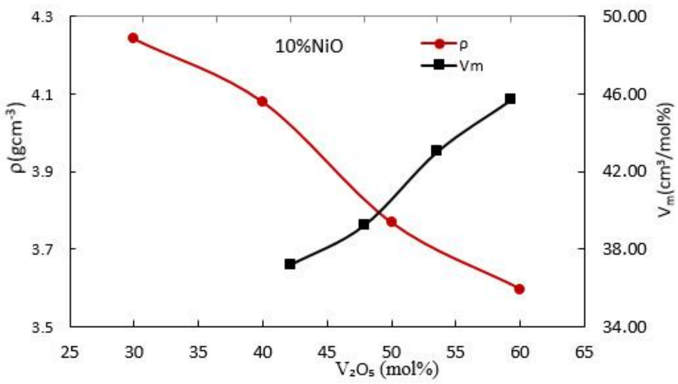


**Fig. 4**. Composition dependence of density ($\rho$) and molar volume ($V_m$) for $V_2O_5$–10%NiO–$TeO_2$ glasses.

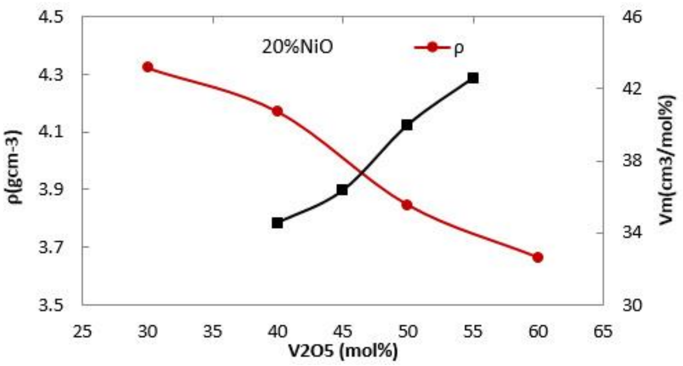


**Fig. 5.** Composition dependence of density ($\rho$) and molar volume ($V_m$) for $V_2O_5$–20%NiO–$TeO_2$ glasses.

$V_m$ is calculated from the density and composition of glass using the relation:

$$V_m = \frac{M}{\rho} \tag{4}$$

Where $V_m$ is the molar volume of Oxygen, $\rho$ is the density of the glasses and M is the molecular weight of the glass compositions expressed in$\left[\frac{g}{mol\%}\right]$. Fig. 4 and Fig. 5 show that $V_m$ increases monotonically with an increase of $V_2O_5$ content in the composition. Therefore, network topology does not considerably change with composition and the glass composition appear to be in single phase with random network structure. Table 1 and Table 2 give the density ($\rho$) and molar volume ($V_m$) for $V_2O_5$–10%NiO and $V_2O_5$–20%NiO glasses.

## 4. Conclusions

Semiconducting $V_2O_5$–10%Ni–$TeO_2$ and $V_2O_5$–20%NiO–$TeO_2$ glasses of various compositions were prepared by the press–quenching technique from the melts. TEP, density and molar volume results were reported. The TEP of all glasses at the temperature range of 302–512 K was investigated. The glass samples were found to be n-type semiconducting material and the TEP above 303 K is not related to temperature. The TEP investigations provide evidence of the existence of small polaron formation and give information that the disorder energy increases with the increase of $V_2O_5$ content in the glass samples but with the condition of the Heikes' relation should explain the results. The increase of NiO composition from 10% to 20% in the glass system leads to an increase in TEP. The density was found to fall with an increase in $V_2O_5$ content. The glasses appear to be in a single phase, and the geometry and topology of the structure do not change with glass compositions.

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