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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: $(90-x)V_2O_5$ – $10NiO$ – $xTeO_2$ ($30 \leq x \leq 60$ mol%) and $(80-x)V_2O_5$ – $20NiO$ – $xTeO_2$ ($20 \leq x \leq 50$ 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 (ρ) 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 carriers (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 $(90-x)V_2O_5$ – $10NiO$ – $xTeO_2$ with $30 \leq x \leq 60$ and $(80-x)V_2O_5$ –

20NiO- x TeO₂ with $20 \leq x \leq 50$ were prepared by reagent grade melting of the following oxide V₂O₅ (99.9%), NiO (99.9%) and TeO₂ (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:

$$\rho_s = \frac{w_a \rho_t}{w_a - w_t} \quad (1)$$

Where, ρ_s is the sample density, w_a is the glass sample weighed in air, w_t is the glass sample weighed in toluene and ρ_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)V₂O₅- %10 NiO- x TeO₂ with $30 \leq x \leq 60$ and ternary (80- x)V₂O₅-%20 NiO- x TeO₂ with $20 \leq x \leq 50$ 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.

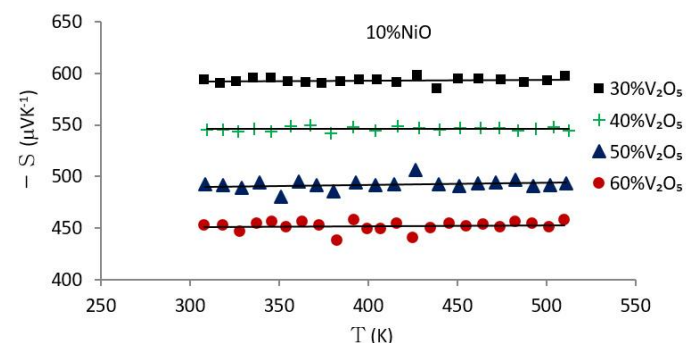


Fig.1. TEP plotted against temperatures for ternary (V₂O₅-10%NiO-TeO₂) glass system.

The composition dependence of TEP of V₂O₅-10NiO-TeO₂ and V₂O₅-20NiO-TeO₂ in the range 302 – 512 K is given in Fig. 3. It can be seen that TEP increases with the decrease of V₂O₅ glass content for both V₂O₅-10NiO-TeO₂ and V₂O₅-20NiO-TeO₂ 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.

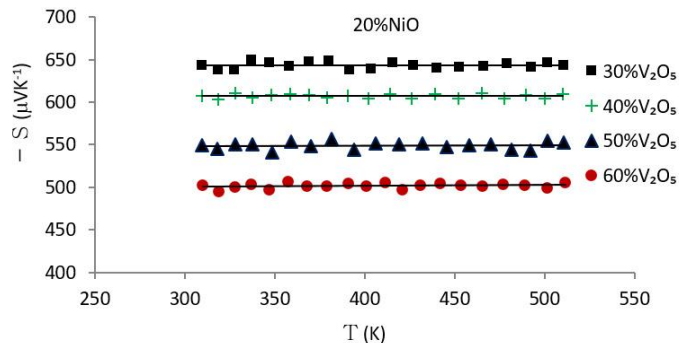


Fig. 2. TEP plotted against temperatures for ternary (V₂O₅-20%NiO-TeO₂) glass system.

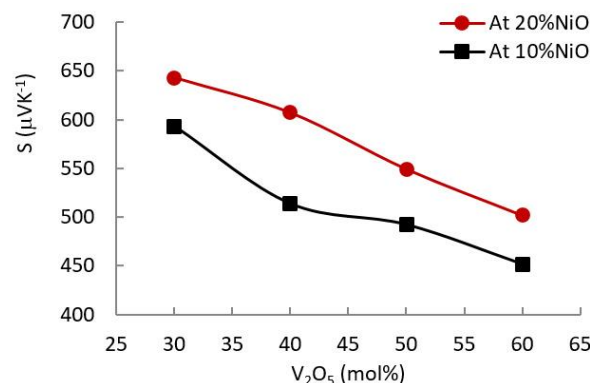


Fig. 3. Variation of TEP above 302 K with glass compositions in (V₂O₅-10%NiO-TeO₂) and (V₂O₅-20%NiO-TeO₂) glasses.

The measured TEP values of different compositions of V₂O₅-10%NiO-TeO₂ and V₂O₅-20%NiO-TeO₂ glasses above 302 K with other related parameters are reported in Table 1 and Table 2.

Table 1

Chemical composition and measured TEP of V₂O₅-10%NiO-TeO₂

Glass composition (mol%)			Melting Temperature (K)	$-S_{exp.}$ (μV/K) above 302 K	ρ (gm/cm ³)	V_m (cm ³ /mol%)
V ₂ O 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 V₂O₅-20% NiO-TeO₂

Glass composition (mol %)			Melting Temperature (K)	$-S_{exp.}$ (μV/K) Above 302 K	ρ (gm/cm ³)	V_m (cm ³ /mol%)
V ₂ O 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):

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

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 α 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 α 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 $\alpha \geq 2$ is suggested by (Austin et al., 1969), for large polarons. Another suggestion (Sewell, 1963) used a value of constant $\alpha=0$ 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 α 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 α term should be finite and given by:

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

Where W_H is the energy of polaron hopping and θ is a constant that is related to the system disorder. If $\theta=1$ means a zero disorder energy. If θ 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; Sourti, 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 α 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 (ρ) 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.

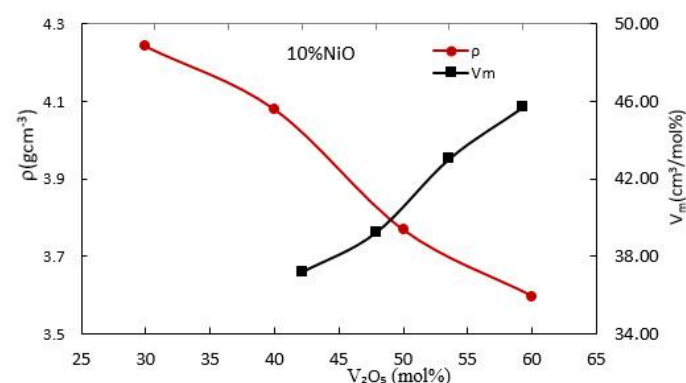


Fig. 4. Composition dependence of density (ρ) and molar volume (V_m) for V_2O_5 -10%NiO- TeO_2 glasses.

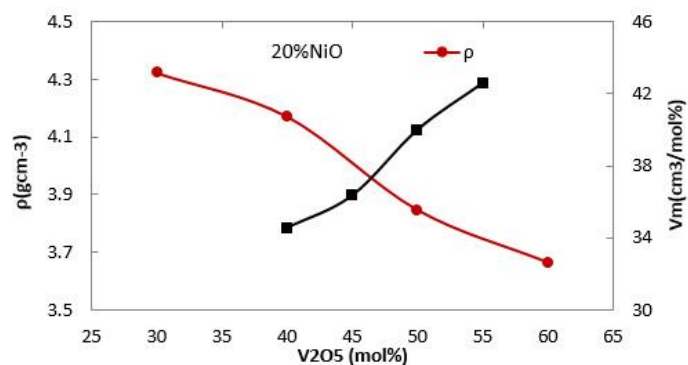


Fig. 5. Composition dependence of density (ρ) and molar volume (V_m) for V_2O_5 -20%NiO- TeO_2 glasses.

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

$$V_m = \frac{M}{\rho} \quad (4)$$

Where V_m is the molar volume of Oxygen, ρ 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 (ρ) 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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References

- Allersma, T., and Mackenzie, J. D. (1967) 'Seebeck coefficient of semiconducting oxide glasses', *J. Chem. Phys.*, 47(4), pp. 1406–1409.
- Austin, I. G., and Mott, N. F. (1969) 'Polarons in crystalline and non-crystalline materials', *Adv. Phys.*, 18, pp. 41–102.
- Denton, E. P., Rawson, H. and Stanworth, J. E. (1954) 'Vanadate glasses', *Nature*, 173, pp. 1030–1032.
- El-Desoky, M. M., and Al-Assiri, M. S. (2007) 'Structural and polaronic transport properties of semiconducting CuO- V_2O_5 - TeO_2 glasses', *Mater. Sci. Eng. B*, 137(1-3), pp. 237–246
- Flynn, B. W., (1977) PhD Thesis University of Edinburgh, Scotland.

- Ghosh, A., (1989) 'Temperature-dependent thermoelectric power of semiconducting bismuth-vanadate glass', *J. App. Phys.*, 65(1), pp. 227–230.
- Hansen, K.W. (1965) 'Semiconducting in iron phosphate glasses', *J. Electrochem. Soc.*, 112(10), pp. 994–996
- Heikes, R. R., and Ure R. W., (1961) Thermoelectricity. *Sci. Eng. New York: Interscience Publishers*: 81.
- Hirashima, H., Watanabe, Y., and Yoshida, T. (1987) 'Switching of $\text{TiO}_2\text{-V}_2\text{O}_5\text{-P}_2\text{O}_5$ glasses', *J. Non-Cryst. Solids*, 95-96, pp. 825–832.
- Hogarth, C. A., and Basha, M. J., (1983) 'Electrical conduction in cobalt-phosphate glasses', *J. Phys. D Appl. Phys.*, 16, pp. 869–878.
- Lynch, G. F., Sayer, M., Segel, S. L., and Rosenblatt, G. (1971) 'Electron and nuclear magnetic resonance in semiconducting phosphate glasses', *J. Appl. Phys.*, 42(7), pp. 2587–2591.
- Mackenzie, J.D., (1964) Modern Aspects of the vitreous state. *Butterworth, Washington* (Vol.3): 126.
- Mandal, S., Banerjee, D., Bhattacharya, R. N., and Ghosh A. (1996) 'Thermoelectric power of unconventional lead vanadate glass', *J. Phys. Condens. Matter*, 8, pp. 2865–2868.
- Mansingh, A., and Dhawan, A. (1978) 'Thermoelectric Power in transition metal oxide glasses', *J. Phys. C. Sol. St. Phys.*, 11, pp. 3439–3445.
- Mansingh, A., Dhawan, A., Tandon, R. P., and Vaid, J. K. (1978) 'Dc electrical conduction in tungsten phosphate glasses', *J. Non-Cryst. Solids*, 27, pp. 309–318.
- Mansingh, A., Vaid, J. K., and Tandon, R. P., (1977) 'Dc conductivity of molybdenum phosphate glasses', *J. Phys. C solid state phys.*, 10, pp. 4061–4066.
- Mogus-Milankovic, A., Santic, B., Day, D. E., and Ray, C. S. (2001) 'Electrical conductivity in mixed-alkali iron phosphate glasses', *J. Non-Cryst. Solids*, 283, pp. 119–128.
- Mori, H., and Sakata, H. (1996) 'Seebeck coefficient of $\text{V}_2\text{O}_5\text{-R}_2\text{O}_3\text{-TeO}_2$ (R = Sb or Bi) glasses', *J. Mater. Sci.*, 31, pp. 1621–1624.
- Mott, N. F. (1968) 'Conduction in glasses containing transition metal ions', *J. Non-Cryst. Solids*, 1, pp. 1–17.
- Murawski, L., and Gzowski, O. (1973) 'Dc conductivity of semiconducting iron phosphate glasses', *Phys. Stat. Sol. (a)*, 19, pp. K125–K128.
- Murawski, L., Chung, C.H., and Mackenzie, J.D. (1979) 'Electrical properties of semiconducting oxide glasses', *J. Non-Cryst. Solids*, 32, pp. 91–104.
- Murawski, L., Barczynski, R. J., (2005) 'Electronic and ionic relaxation in oxide glasses', *Solid State Ionics*, 176, pp. 2145–2151.
- Sakata, H., and Segal, K. (1999) 'Multiphonon tunneling conduction in vanadium-cobalt-tellurite glasses', *Phys. Rev. B*, 60(5), pp. 3230–3236.
- Santic, B., Mogus-Milankovic, A., and Day, D. E. (2001) 'The dc electrical conductivity of iron-phosphate glasses', *J. Non-Cryst. Solids*, 296, pp. 65–73.
- Sayer, M., and Mansingh, A. (1972) 'Transport properties of semiconducting phosphate glasses', *Phys. Rev. B*, 6(12), pp. 4629–4643.
- Sewell, G. L. (1963) 'Model of thermally activated hopping motion in solids', *Phys. Rev.*, 129(2), pp. 597–608.
- Souri, D., (2008). Seebeck coefficient of tellurite-vanadate glasses containing molybdenum. *J. Phys. D: App. Phys.* 41: 1–3.
- Souri, D. (2016) 'Suggestion for using the thermal stable thermoelectric glasses as a strategy for improvement of photovoltaic system efficiency: Seebeck coefficient of tellurite-vanadate glasses containing antimony oxide', *Solar Energy*, 139, pp. 19–22.
- Souri, D., Siahkali, Z., and Moradi, M. (2016) 'Thermoelectric power measurements of $\text{xSb-(60-x)V}_2\text{O}_5\text{-40TeO}_2$ glasses', *J. Elect. Mater.*, 45(1), pp. 307–311.
- Tawati, D. M., and Basha, M. J. (2003) 'Thermoelectric power of semiconducting cobalt-phosphate glasses', *J. Solid St. and Technol. Letters*, 10(2), pp. 165–170.
- Tawati, D. M., and Basha, M. J. (2004) 'Thermoelectric power (TEP) of semiconducting $\text{CoO-NiO-P}_2\text{O}_5$ glasses', *Ceram. Int.*, 30, pp. 1737 –1739.
- Tawati, D. M., Basha, M. J., and Arof A. K. (2010) Thermoelectric Power (TEP) of semiconducting Nickel-Phosphate Glasses. *AIP Conf. Proceeding*, 1250, PERFIK2009: pp. 93–96.
- Tawati, D. M., Mohamed, A. B., Hussein, N. A., Saltani, H. A., and Arof, A. K. (2019) 'Seebeck coefficient of ternary semiconducting vanadium-cobalt-tellurite glasses', *Inter. J. App. Sci. Special Conf. Issue*, 1(1), pp. 169–175.