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Physical and Thermoelectric Properties of Ternary Semiconducting $NiO–V_2O_5–TeO_2$ Glasses

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الخصائص الفيزيائية والكهرو حرارية للزجاج الثلاثي شبه الموصل $V_2O_5–NiO–TeO_2$

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Abstract

Five samples of ternary semiconducting $65V_2O_5$ –xNiO–(35–x) TeO_2 glasses, with $5 \leq x \leq 25$ (x in mol%), were prepared using a press-quenching method from a glass melt. The thermoelectric Power (TEP), density (ρ), oxygen molar volume (V_m) and x-ray diffraction (XRD) were analyzed. TEP measurements were conducted within the temperature range of 300 – 506 K for the mentioned glass compositions. Information on the creation of polarons and the disorder energy arising from random fields was gathered. By applying Heikes' equation and the small polaron model theory to the TEP, the results obtained from experimental data were effectively explained. The study revealed that an increase in the NiO content in the glass led to a rise in density and a consistent decrease in molar volume. All glasses exhibited a singular phase structure.

Keywords:

TEP of semiconducting oxide glasses; tellurite glasses; structure of oxide glasses; glass density; Heikes formula

الملخص

تم تحضير خمس عينات من الزجاج ذو التركيب شبه الموصل الثلاثي V_2O_5 –xNiO–(35– TeO_2(65x حيث $5 \leq x \leq 25$ (مول%) باستخدام طريقة الإخماد والضغط مع التبريد السريع للمصهور الزجاجي. تم تحليل كل من الطاقة الحرارية(TEP) ، الكثافة (ρ)، الحجم المولي للأكسجين (V_m) وحيود الأشعة السينية (XRD). تم إجراء قياس القدرة الكهروحرارية (TEP) ضمن نطاق درجة حرارة 300 – 506 كلفن للتركيبات الزجاجية المذكورة. تم جمع معلومات عن تكون البولارونات (Polarons) وطاقة الاضطراب الناشئة عن المجالات العشوائية. من خلال تطبيق معادلة هيكس (Heikes) ونظرية نموذج قفز البولارون الصغير "small polaron hoping model" على TEP، تم شرح النتائج التي تم الحصول عليها من البيانات التجريبية بشكل فعال. وكشفت الدراسة أن الزيادة في محتوى NiO في الزجاج أدت إلى ارتفاع الكثافة وانخفاض ثابت في الحجم المولي.

أظهرت النتائج أنّ جميع العينات الزجاجية بنيتها ذات الطور المفرد.

الكلمات المفتاحية:

القدرة الكهروحرارية لأكاسيد الزجاج الشبه موصلة، زجاج التيلورايت، بنية أكسيد الزجاج، كثافة الزجاج، قانون هيكس.

1. Introduction

Nowadays, there is an urgent need for **utilizing alternative sources of energy**, because of the depletion of the energy resources on our planet. Hence, humans are facing the challenge of the century to solve this problem. People **around the** world are running the risk of exhausting fossil fuel reserves. Scientists all over the world are working hard to solve this problem. Researchers at many Universities are banking heavily on properties of thermoelectric materials, which is of great importance for their practical applications (Quinn & Bos, 2023; Feng **et al.,** 2018; Zhang **et al.,** 2022; Yang **et al.,** 2023; Liu **et al.,** 2023; **and** Tao; 2023). This material **converts waste** heat into useful electricity more efficiently than anything available today. Hence development of materials which convert thermal energy to electrical energy with high efficiency (Thermoelectric conversion materials) is being promoted using technologies that can be applied realistically. In order to produce useable power, researchers are looking for ways to increase the thermoelectric conversion efficiency by employing charge carriers (Dadhich **et al.**, 2023). The focus on producing thermoelectric power from waste heat is in line with the global trend toward environmentally friendly energy sources and a reduction in environmental impact (Dadhich etal,2023; Saqlik,2023).

A good thermoelectric material should have three important qualities: large Seebeck coefficients, high electrical conductivity and low thermal conductivity (Beeforth & Goldsmith, 1970). The thermoelectric effect, which involves the conversion of thermal energy into electrical current, is observed in various materials, including semiconductors with small band gaps. Semiconductors with small or no band gaps, but high asymmetry between their conduction and valence bands, can exhibit large Seebeck coefficient values, making them attractive for thermoelectric applications (Song, 2023). Additionally, by tuning the band gap of semiconducting materials to an optimum value and breaking band symmetry, a high figure of merit (ZT) can be achieved, especially when combining different polynomial powers in the energy dispersion relations of the material (Adhidewata & Nugraha, 2022; **and** Alashkar & Alami, 2021). This research highlights the potential of semiconductors with specific band characteristics to enhance thermoelectric performance, **displaying** the importance of material properties in optimizing thermoelectric efficiency. Despite many researches that were carried out on thermoelectric power (TEP) properties for different materials especially on semiconducting chalcogenide glasses (EL-Sayed, 2009; **and** Goncalves, et al. 2010), the energy conversion efficiency of these materials was not enough to create more electricity.

Glassy materials with strong thermal stability, low susceptibility to air, and non-toxicity make transition metal oxide (TMO) glasses promising prospects for commercial thermoelectric applications (Jianxiao, 2008). Examples of some publications that have been done previously by different researchers on the thermoelectric power of semiconducting transition metal oxide (TMO) glasses of different materialsare by (Ghosh, 1989; Sakata, 1999; Tawati & Basha, 2003; Tawati & Adlan, 2004; Souri, 2008; Tawati **et al.**, 2019; Tawati **et al.**, 2020; **and** Tawati **et al.**, 2023). These reports came to the conclusion that there are significant Seebeck coefficients in various TMO glasses. As a result, researchers are now focused on studying the TEP of TMO glasses in order to produce better thermoelectric materials. This finding makes the topic of study much more fascinating. The current work aims to determine the TEP of ternary V2O5–NiO–P2O5 glasses across a temperature range of 300–506 K and a variety of compositions.

2. Experimental Procedures

The pure powder raw materials utilized were V2O5 (99.99%), CoO (99.99%), NiO (99.99%), CuO (99.99%), ZnO (99.99%), TeO2 (99.99%), and oxide powder in the appropriate weights. Research grade chemicals were also utilized. The appropriate mixes were combined in a platinum crucible and put in a furnace that was kept at 300 °C for an hour. **Afterwards**, the mixtures were transferred to a melting furnace that was kept at **a temperature between** 900 ˚**C and** 1150 ˚C and agitated periodically for about two hours. After dumping the melt onto a copper block, another copper block was utilized to press it down quickly. The resulting glasses were placed in an annealing furnace and heated to 400 ˚C for an hour before being allowed to cool gradually. The glass sample blocks that are produced from this process are roughly 2 cm in diameter and 2.5 mm in thickness, and they are black and opaque. The samples are then prepared for analysis by being ground with extremely fine lapping paper. The samples' amorphous nature was verified using **the** X-ray diffraction (XRD) examination. The densities of the glass samples were measured at room temperature using Archimedes' principle. The glass sample densities were determined by employing equation (1):

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

In the equation, ρ_g **is** the glass density, w_a is the glass sample weighed in air, $w_t$is the glass sample weight in the toluene and ρ_t the density of toluene.

To evaluate thermoelectric power, disk-shaped samples having a diameter of around 2.5 cm and a thickness of approximately 2.3 mm were polished and sliced using extremely fine lapping paper. In Fig. 1, a schematic diagram of the custom-made sample container utilized for the TEP measurements is displayed. The sample was positioned between two electrodes: an aluminum hollow rod holding a copper probe on the positive electrode, which is isolated from the sample holder's base by a mica sheet. To guarantee correct electrical contact between two sample surfaces, there are springs at the bottom of the block. The TEP was ascertained by measuring the thermo-EMF that generated between the two parallel surfaces of the samples, which had a temperature differential of 5–10K.

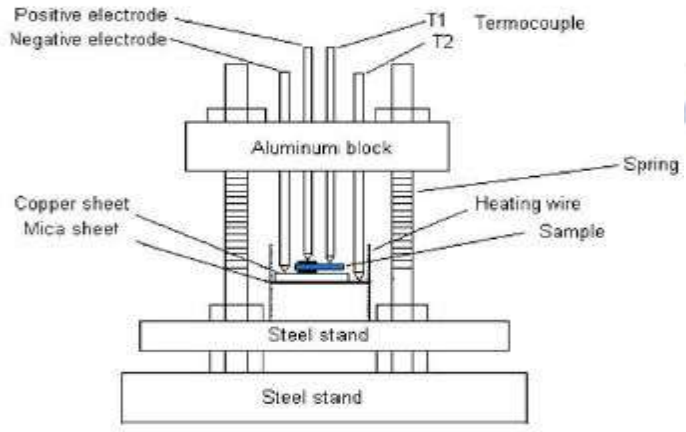

Fig. 1: shows the sample holder's schematic diagram for thermoelectric power measurements.

3. Results and discussion

3.1Structural Characterization of TMO Glasses

3.1.1 XRD Analysis

The amorphous nature of V_2O_5–NiO–TeO_2 glasses has been checked by XRD analysis. The XRD patterns shown in Fig.2 of all quenched samples indicate a homogeneous glassy character without showing any trace of crystallization. This confirms that all samples are non-crystalline with a short-range order.

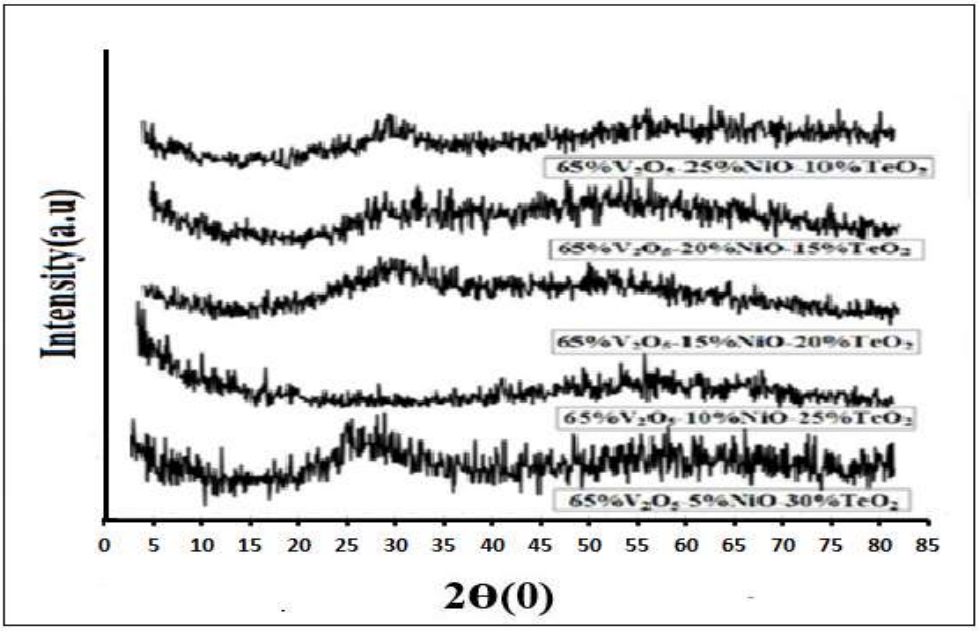

Fig.2: XRD patterns for V_2O_5-NiO-TeO_2glass of different compositions.

3.1.2: Density and Molar Volume

The density ρ and molar volume V_m dependency on the concentrations of the four glass systems are displayed in Figure 3. The link between an oxide glass system's composition and density can be stated in terms of the apparent volume Vm occupied by a single gram of oxygen. V_m is calculated from the density and composition of glass using equation (2):

$$V_m = \frac{M}{\rho} \qquad (2)$$

In the above equation, M is the molecular weight of the glass compositions given in [g/mol%], V_M is the molar volume of oxygen, and ρ is the density of the glasses.

It can be seen that while V_m decreases monotonically as the TM oxide content in the composition increases, ρ increases gradually as the TM oxide content increases in the glass compositions. This suggests that the network's topology is not greatly affected by composition.

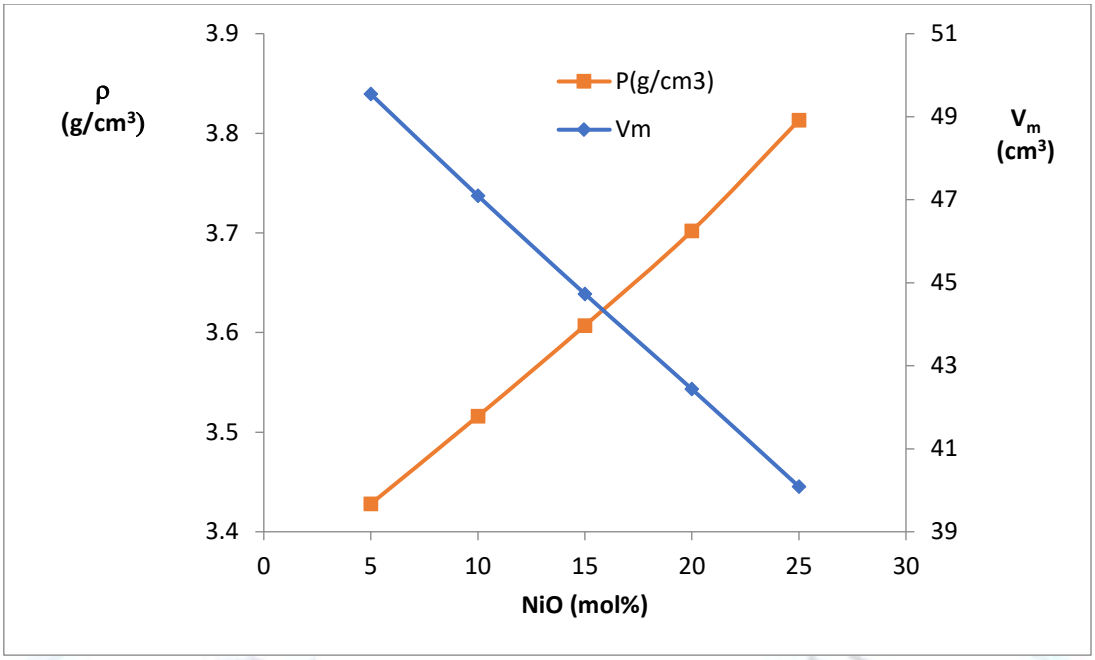

Fig. 3: Composition dependence of density (ρ) and molar volume (Vm) on NiO (mol%) contents.

3.2 Thermoelectric Power (TEP)

TEP as a function of temperature for ternary V_2O_5-NiO-TeO_2 glasses in the temperature range 300 –506 K is shown in Fig. 4. The results clearly indicate that the Seebeck coefficient (S) is independent of temperature for all these glass compositions. The sign of the TEP is negative for all **glass** compositions, showing that all glasses in present systems are n-type semiconductors and also suggesting an electron or polaronic nature of the charge carrier. The results of this work are in good agreement with the results reported for the same glass system but with different compositions (Mansingh & Dhawan, 1978; Mori & Sakata, 1996; Tawati **et al.**, 2019) **This suggests that Heikes's formula expressed in equation**:

(The above sentence is incomplete.)

$$S = \frac{K_B}{e}\left[In\left(\frac{c}{1-c} + \alpha\right)\right] \qquad (3)$$

In the equation above, c is the fraction of concentration of reduced Transition Metal Ions (TMIs) to the total TMIs, K_B is the Boltzmann constant, e is the electron charge and α is a constant of proportionality between the heat transfer and the kinetic energy of the electron.

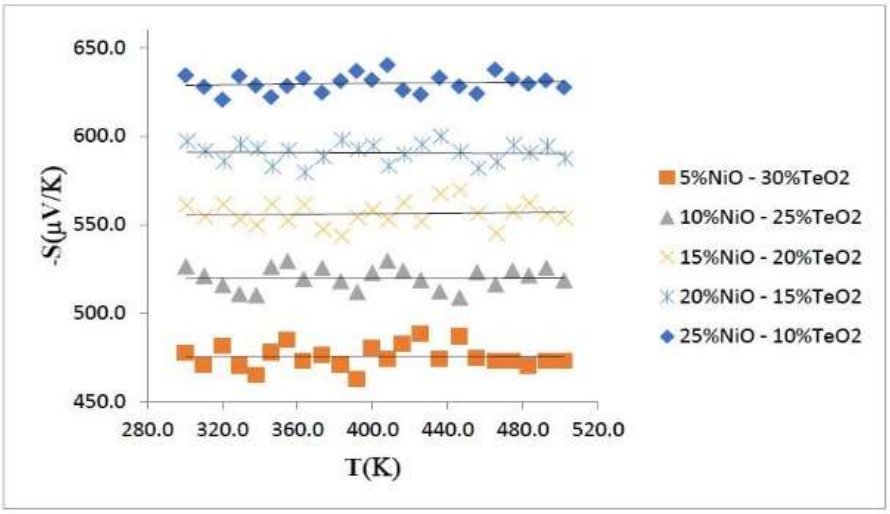

Fig. 4: Seebeck Coefficient(S) vs temperature T for five NiO glass composition.

The TEP dependence on the composition in the temperature range 300–506 K for all studied glasses is shown in Fig.5. It is clearly seen that for the glass systems V_2O_5-NiO-TeO_2 the magnitude of S increases with **the increase** of NiO content in the glass. This means that the compositions of the TMO glasses play the dominant role in the increase of the measured TEP. These results are in good agreement with results reported by different authors using various materials (Tawati & Adlan, 2004; Souri, 2008; Tawati **et al.**, 2019; Tawati **et al.**, 2020; **and** Tawati **et al.**, 2023)

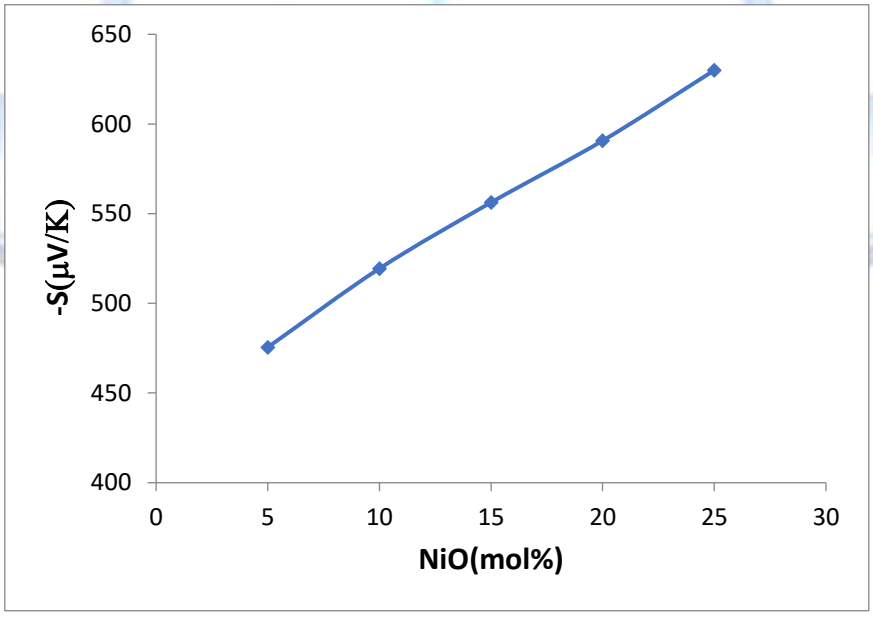

Fig. 5: Variation of the Seebeck coefficient with V2O5-NiO-TeO2 glass.

The Seebeck coefficient can be estimated theoretically for all glass systems using equation (3) with α=0 (Ghosh, 1989) and C values from Table 1. Although the estimated S values with $\alpha = 0$ are close to the measured S values, there appears to be a consistent difference between the calculated and measured values for all glass compositions. This supports Austin and

Mott's **(1969)** hypothesis that α makes a significant impact ~~**(Austin & Mott, 1969)**~~. They proposed **that** α ≥ 2 for large polaron creation**s** and α < 1 for small polaron formation**s**, following Mott's (1968) suggestion. The parameter α indicates whether small or large polarons are formed in the glasses. Other researchers (Sewell, 1963; Appe, 1968; **and** Klinger, 1968) have proposed that in the case of band polarons, the value of constant α is zero, indicating that the Seebeck coefficient should solely rely on C and be independent of the nature of TMI. If C is temperature independent, as in TMO glasses (Lynch eta, 1971), the Seebeck coefficient should also be temperature independent. According to Austin and Mott (1969), the term of α can only have a zero value if the system's disorder energy is also zero. If there is a disorder energy between the occupied and vacant sites, then the term α in equation (4) should be finite, as indicated by (Masingh & Dhawan, 1978):

$$\alpha = \frac{(1-\theta)W_H}{(1+\theta)k_B T} \qquad (4)$$

The constant θ correlates with the amount of disorder in the system, while W_H represents the polaron hopping energy. The unity value for θ implies zero disorder energy, while departure from unity measures the system's disorder. The parameter C plays an essential role in explaining the Seebeck coefficient. The results demonstrate good agreement between the measured values of S and those derived from equation (3). Table 1 shows that α has negative values, hence α<<1.

TeO_2-MoO_3 and TeO_2-V_2O_5-MoO glasses had comparable negative α values (Souri, 2008; Pal et al., 2001). The α results support the formation of small polarons in all glass systems. This result also confirms that the constant α in Equation (4) deviates from unity, showing that the system's disorder energy increases as the TMO composition increases in glass systems. Figure 6 illustrates how equation (3) relates to the measured S as a function of the current glass percent C. The theoretical equation (3) determines the slope of S as a function of [ln(C/(1-C)] K_B/e, resulting in 86.18 μV/K

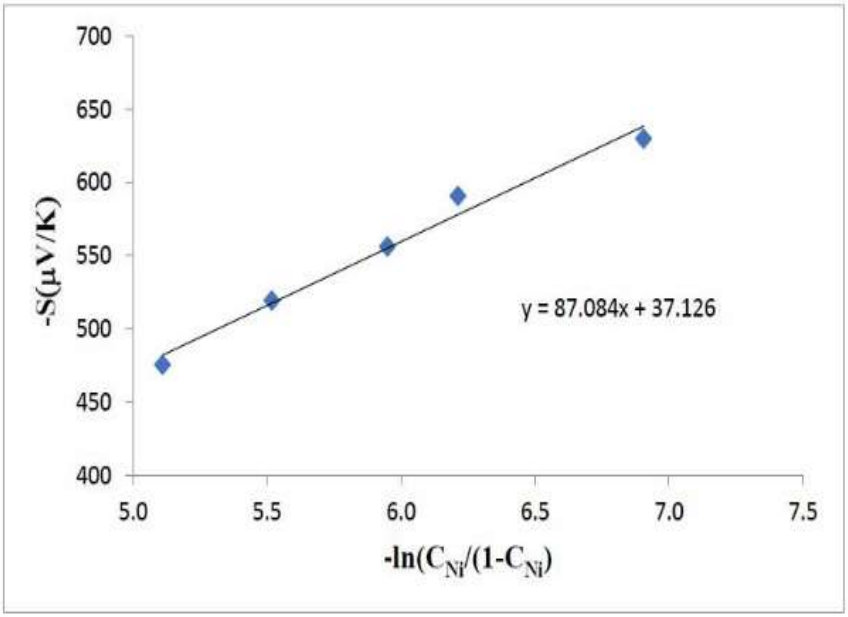

Fig. 6: Relationship between –S (μV/K) and [ln(C/(1-C)] for the five $65V_2O_5$-NiO-TeO_2 glass compositions.

Regarding Fig. 6, The slope for each glass system obtained from the experimental relationship between S and [ln(C/(1-C))] is equal to 87.084 µV/K. The outcomes nearly match the theoretical value (K_B/e = 86.18 µV/K) adequately. This demonstrates that the experimental data for the current glasses can be satisfactorily explained by the Hekikes Equation (3).

Table1: Seebeck coefficient and other related parameters of five V_2O_5–NiO–TeO_2 glasses.

Glass composition (mol%)			Density (g/cm^3)	C $\left[\frac{Ni^{2+}}{Ni_{Tot.}}\right]$	$-S_{exp.}$ (µV/K) Above 300 K	$-S_{cal.}$(µV/K) from eq.1 with α = 0	α
V_2O_5	NiO	TeO_2					
65	05	30	3.428	0.006	475	441	-0.402
65	10	25	3.516	0.004	519	476	-0.504
65	15	20	3.607	0.0026	556	513	-0.499
65	20	15	3.702	0.002	591	536	-0.636
65	25	10	3.813	0.001	630	596	-0.398

4. CONCLUSIONS

The Seebeck coefficient of ternary semiconducting V_2O_5 –CoO-TeO_2 glasses for different compositions at the temperature range 300-506 K was reported. The glasses were found to be n-type semiconductor with the Seebeck coefficient ranging from –475 to –630 μVK^{-1}. The TEP above 300 K does not vary strongly with temperature and can be adequately explained by Heikes' formal. The analysis of the seebeck coefficient data provides evidence for the polaron formation and confirms that small polaron hopping conduction occurs between 300 and 506 K for these glasses. The disorder energy was found to be increasing with NiO content in the glass.

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