

SEEBECK COEFFICIENT OF TERNARY SEMICONDUCTING VANADIUM–COBALT–TELLURITE GLASSES

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Abstract:-

The Seebeck coefficient, S , of semiconducting V_2O_5 – CoO – TeO_2 bulk glasses have been measured in the temperature range 300 – 506 K. The glass samples were prepared by the press–quenching method from glass melt. The thermoelectric power, TEP, data revealed that all glasses were n–type semiconductors with Seebeck coefficient in the range from –602 to –790 $\mu V/k$. The investigations provide information on the polaron formation and the disorder energy due to random fields. The Seebeck coefficient was found to be dependent on the CoO content and the temperature independent of TEP for all glass compositions. TEP experimental results were adequately explained by Heikes' formula.

Keywords:- Seebeck coefficient, Heikes formula, TEP

INTRODUCTION

Thermoelectric power, TEP, measurements of semiconducting oxide glasses containing transition metal ions, TMIs, are of considerable importance, as they provide information on the polaron formation, the nature of charge carriers and the disorder energy due to random fields [1, 2]. Although quite a few researches on the TEP of binary and ternary semiconducting transition metal oxide, TMO, glasses were conducted [3–15], more research work is still needed to cover this type of glass. The published research works of TEP were explained in relation to temperature dependence of Seebeck coefficient (S) using Heikes' formula [16] which is given by:

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

Where c is the fraction of concentration of reduced 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. In addition, the conduction mechanism of these glasses on the basis of equation (1) was confirmed to be due to a small polaron hopping because of the very low mobility ($\mu \ll 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [17]) and the EPH - International Journal of Applied Science | ISSN: 2208-2182 parameter $\alpha < 1$ [1]. On the other hand, a relationship between S and C for some Vanadate–Tellurite glasses was also investigated [4, 8, 13], and it was confirmed that C is the dominant factor for determining S.

The main purpose of the present work is to determine the Seebeck coefficient, S, of ternary semiconducting V_2O_5 –CoO– TeO_2 glasses at various CoO compositions and over the temperature range 300 – 506 K. The conduction mechanism of the present glass compositions were based on equation (1) and S – C relationship were also discussed.

Experimental Procedure

The glass samples of the system $65\text{V}_2\text{O}_5$ – $x\text{CoO}$ – $(35-x)\text{TeO}_2$; $x = 5, 10, 15, 20$ and 25 mol % were obtained by melting the reagent grade V_2O_5 (99.9 %), CoO (99.9 %) and TeO_2 (99.9 %) in a platinum crucible at 1025 K and left for about one hour in an electric furnace with frequent stirring. The homogenized melts were quickly casted on to a steel–plate mold (pre-heated to 400 K). This procedure serves to minimize cracking of the glass due to thermal stress. The glasses formed were transferred to an annealing furnace at 400 K for one hour and then allowed to cool slowly. Following this procedure disk-shaped samples of diameter ~ 2.0 cm and thickness ~ 2.5 mm were obtained after cutting and polishing using very fine quality lapping papers. The amorphous nature of the glass samples was checked visually and ascertained from X–ray diffraction (XRD) analysis; results of such analysis are shown in figure 1. The concentrations of Co^{+2} and total cobalt ions (Co_{Tot}) in the glass samples were determined from the redox titration method and using atomic absorption spectrometer (AAS) respectively [18]. For TEP measurements, a specially designed sample holder was employed in the temperature range 300 – 506 K. The details of the TEP measurements were reported elsewhere [11, 12]. A temperature difference of about 5 – 10 K between two parallel surfaces of the glass was achieved. TEP was determined by measuring EMF created between the surfaces using Keithley's 2400 Series measurements were being carried

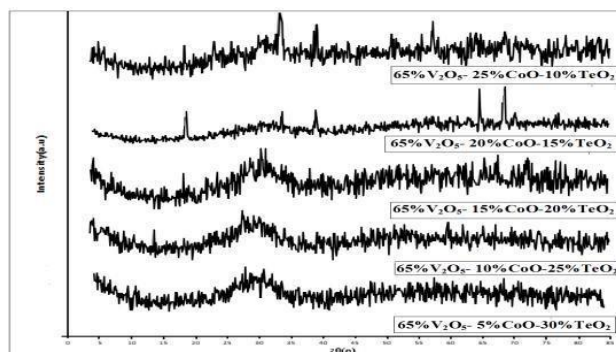


Figure 1. XRD patterns for various glass compositions.

RESULTS AND DISCUSSION

The relationship between S and CoO concentration above 300 K is shown in figure 2. It is observed that the magnitude of S increases with increasing of CoO content in the glass. This means that the compositions of the CoO play the dominant role in the increasing measured TEP. This result is in good agreement with the previously documented papers reported by other authors using various materials [5, 7, 8, 12, and 15]. The sign of TEP was found to be negative for all glass compositions, indicating that the glass in the present system was n-type semiconductor. The Seebeck coefficient as a function of temperature above 300 K for five glass compositions of the system V_2O_5 –CoO– TeO_2 is shown in figure 3. It can be seen that the TEP is independent of temperature for all glass compositions. The results of this work are in good agreement with the results reported for the same glass system but with different compositions [10] and also in good agreement with other Vanadate–Tellurite glasses [4, 8, and 13]. This suggests that Heikes's formula expressed in equation (1) is appropriate for explaining these experimental results.

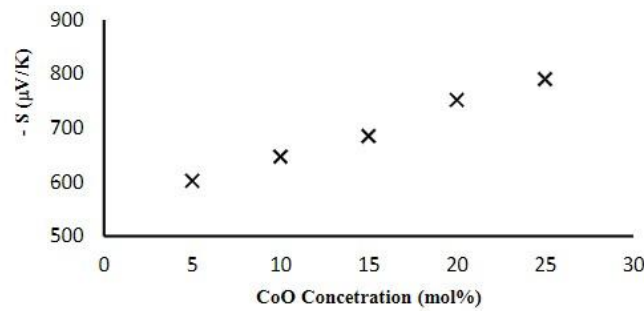


Figure 2. Variation of the Seebeck coefficient with glass composition above 300 K.

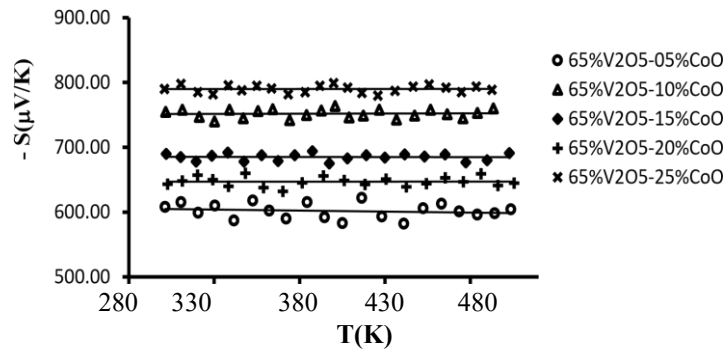


Figure 3. Seebeck Coefficient, S versus temperature, T for five compositions of V₂O₅–CoO–TeO₂ glasses.

The negative sign of TEP shows that the nature of charge carrier in the present glass can be either electronic or polaronic. The experimental Seebeck coefficient values above 300 K and other related parameters of V₂O₅–CoO–TeO₂ glasses are given in table 1.

Table 1. Seebeck coefficient and other related parameters of five V₂O₅–CoO–TeO₂ glasses.

Glass composition (mol%)			Melting Temperature (K)	C $\left[\frac{Co^{2+}}{Co_{Tot.}}\right]$	$-S_{exp.} (\mu V/K)$	$-S_{cal.} (\mu V/K)$	α
V ₂ O ₅	CoO	TeO ₂			Above 300 K	from eq.1 with $\alpha = 0$	
65	05	30	1025	0.0014	602	567	-0.41
65	10	25	1025	0.0010	647	596	-0.59
65	15	20	1025	0.0008	685	615	-0.81
65	20	15	1025	0.0003	752	700	-0.61
65	25	10	1025	0.00018	790	744	-0.54

The Seebeck coefficient can be calculated theoretically from equation (1) assuming $\alpha = 0$ [7] and using the C values from table 1. It may be noted that, although the calculated S values with $\alpha = 0$ are close to the measured S values, there appears a systematic deviation of the calculated values from the measured values for all glass compositions. This suggests that the contribution of α is not negligible and in accordance with the prediction of Austin and Mott [2]. They suggested that $\alpha \geq 2$ for large polaron formation, while, as suggested by Mott [1], $\alpha < 1$ for small polaron formation. Therefore, the parameter α can be used to confirm whether there is small polaron or large polaron formation taking place in the studied glasses. Other workers [19–21], have proposed in the case of band polarons, the value of constant α is zero, indicating that Seebeck coefficient should depend only on C and independent of the nature of TMI. If C is independent of temperature as in TMO glasses [22], then Seebeck coefficient is expected to be independent of temperature. Austin and Mott [2] suggested that α term can be zero value only if the disorder energy in the system is zero. If there is a disorder energy between the occupied and unoccupied sites, then the term α in equation (1) should be finite and is given by [5]

$$\alpha = \frac{(1-\theta)W_H}{(1+\theta)k_B T} \quad (2)$$

Where the constant θ is correlated to the amount of disorder in the system and W_H is the polaron hopping energy. The unity value for θ indicates zero disorder energy and deviation from unity is a measure of disorder in the system. The

parameter C is an important factor in explaining the Seebeck coefficient. Our results show good agreement between the Measured values of S and those calculated from equation (1) with the values of α included in table 1. The table shows that $\alpha \ll 1$ and in the range from -0.41 to -0.81 . Similar negative values of α were reported for $\text{TeO}_2\text{--MoO}_3$ and $\text{TeO}_2\text{--V}_2\text{O}_5\text{--MoO}_3$ glasses [13, 23]. This result of α confirms the condition for small polaron formation in the ternary system of semiconducting $\text{V}_2\text{O}_5\text{--CoO--TeO}_2$ glasses. Also this result confirms that the constant θ in equation (2) deviates from unity and then it can be assumed that the disorder energy increases in the system as CoO composition increases in the glass. The applicability of equation (1) to the measured S as a function of the fraction C of the present glasses is explained in figure 4. The theoretical equation (1) gives that the slope of S versus $\ln \left[\frac{C_{\text{CoO}}}{1-C_{\text{CoO}}} \right]$ which is equal to the value of 86.18

μVK^{-1} the slope obtained from the experimental relationship between S and $\ln \left[\frac{C_{\text{CoO}}}{1-C_{\text{CoO}}} \right]$ using the least squares methods

is equal to $88.722 \mu\text{VK}^{-1}$ ($R^2 = 0.9843$), which agrees satisfactorily with the theoretical value ($k_B = 86.18 \mu\text{VK}^{-1}$). This confirms that the equation (1) (Heikes' formula) can give adequate explanation for the experimental data of the present glasses.

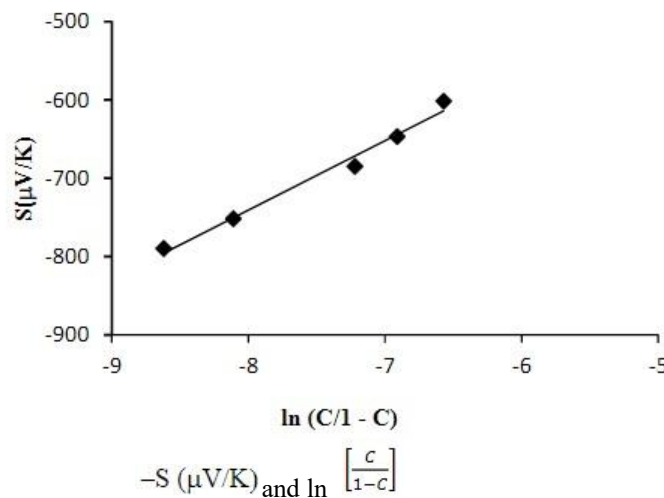


Figure 4. Relationship between $-S$ ($\mu\text{V/K}$) and $\ln \left[\frac{C}{1-C} \right]$ for five CoO and TeO_2 composition glasses.

CONCLUSIONS

The Seebeck coefficient of ternary semiconducting $\text{V}_2\text{O}_5\text{--CoO--TeO}_2$ glasses for different compositions at the temperature range $300 - 506 \text{ K}$ was reported. The glasses were found to be n -type semiconductor with the Seebeck coefficient ranging from -790 to $-602 \mu\text{VK}^{-1}$. The TEP above 300 K does not vary strongly with temperature and can be adequately explained by Heikes' formula. 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 CoO content in the glass.

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