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

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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 – 512 K 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 of the experimental data. Results showed that 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 semi-conducting 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 thermolectric 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 $(80-x)V_2O_5$–$10$...
The composition dependence of TEP of V\textsubscript{2}O\textsubscript{5}–10\%NiO–TeO\textsubscript{2} glasses in the range 302 – 512 K is given in Fig. 3. It can be seen that TEP increases with the decrease of V\textsubscript{2}O\textsubscript{5} glass content for both V\textsubscript{2}O\textsubscript{5}–10\%NiO–TeO\textsubscript{2} and V\textsubscript{2}O\textsubscript{5}–20\%NiO–TeO\textsubscript{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 50\% 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.

Materials of mixed valence states have their TEP investigated theoretically by Heikes’ relation (Heikes \textit{et al.}, 1961):

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

(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 \( \text{Eq. (2)} \) is not related to temperature. The magnitude

Fig. 2. TEP plotted against temperatures for ternary (V\textsubscript{2}O\textsubscript{5}–20\%NiO–TeO\textsubscript{2}) glass system.

Fig. 3. Variation of TEP above 302 K with glass compositions in (V\textsubscript{2}O\textsubscript{5}–10\%NiO–TeO\textsubscript{2}) and (V\textsubscript{2}O\textsubscript{5}–20\%NiO–TeO\textsubscript{2}) glasses.

Table 1

| Glass composition (mol %) | Melting Temperature (K) | \( -S_{\text{rep}} \) (μV/K) above 302 K | \( \rho \) (gm/cm\textsuperscript{3}) | \( V_m \) (cm/mol%)
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Table 2

| Glass composition (mol %) | Melting Temperature (K) | \( -S_{\text{rep}} \) (μV/K) above 302 K | \( \rho \) (gm/cm\textsuperscript{3}) | \( V_m \) (cm/mol%)
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of $\alpha$ determines the existence of polaron formation in the materials. Mott (Mott, 1968) proposed that $\alpha$ 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 $\alpha$ and should be independent of the nature of the TML 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:

$$\alpha = \frac{(1 - \theta)W_B}{(1 + \theta)k_BT}$$

(3)

Where $W_B$ 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 $\alpha$ 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 $V_{2}O_{5}$-10NiO-TeO$_2$ and $V_{2}O_{5}$-20NiO-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 $V_{2}O_{5}$ 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 $V_{2}O_{5}$-10NiO and $V_{2}O_{5}$-20NiO glasses are related to the glass composition. It may be observed that density decreases gradually with the increase of the $V_{2}O_{5}$ 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.

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

(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 $g$ (moles$^{-1}$). Fig. 4 and Fig. 5 show that $V_m$ increases monotonically with an increase of $V_{2}O_{5}$ content in the composition. Therefore, network topology does not consider change with composition and the glass composition appears to be in single phase with random network structure. Table 1 and Table 2 give the density ($\rho$) and molar volume ($V_m$) for $V_{2}O_{5}$-10NiO and $V_{2}O_{5}$-20NiO glasses.

4. Conclusions

Semiconducting $V_{2}O_{5}$-10NiO-TeO$_2$ and $V_{2}O_{5}$-20NiO-TeO$_2$ glasses of various compositions were prepared by the pressure 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 $V_{2}O_{5}$ content in the glassy glasses 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 $V_{2}O_{5}$ 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


