Thermoelectric Power (TEP) of Semiconducting Cobalt–Tellurite Glasses

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Abstract

The TEP, or Seebeck coefficient (S), for five bulk glasses in different compositions of binary semiconducting CoO–TeO2 glasses has been measured in the temperature range 304–490K. The glasses were prepared by melting dry mixtures of analytical reagent grades of CoO and TeO2 at a temperature of 1000 °C for 1h using quenching form the melt technique. TEP measurements have been performed utilizing specifically designed sample holders on annealed samples. The glasses were found to be n-type semiconductors with S in the range from −293 to −460 μV/K. S was found to be independent of temperature for all glass compositions, and Heikes’ formula adequately satisfied the TEP experimental results. The analyses provide evidence on the polaron formation and the disorder energy due to random fields.

Introduction

The development of materials that convert thermal energy to electrical energy with high efficiency (Thermoelectric conversion materials) is being promoted using technologies that can realistically be applied. A good thermoelectric material should have three important qualities: large Seebeck coefficients, high electrical conductivity, and low thermal conductivity [1]. The process of the thermoelectric effect works with a variety of materials and especially well with semiconductors with small band gaps [2]. Despite a lot of research being carried out on TEP properties for different materials, especially semiconducting chalcogenide glasses [3–5], the energy conversion efficiency of these materials was not enough to create more electricity. To date, the highest efficiency of thermoelectric materials is about 10%. Because of their good thermal stability, lack of sensitivity to the air, and non-toxicity, transition metal oxides are potential candidates for commercial thermoelectric applications [6]. There have been few reports done previously by different researchers on the TEP of semiconducting transition metal oxide (TMO) glasses of different materials [7–17]. These reports showed that some TMO glasses have a large Seebeck coefficient. Also, measurements of the TEP of these materials are important because they provide information on the nature of charge carriers, the formation of polarons, and the extent of disorder due to random fields [18–21]. In our previous works [10–14], the TEP of CoO–P2O5, NiO–P2O5, CoO–NiO–P2O5, V2O5–CoO–TeO2, and V2O5–NiOTeO2 glasses were investigated. These investigations

الملخص

تم في هذه البحث قياس القدرة الكهروحرارية (TEP) لزجاج الكوبالت-تيلورايت شبه الموصل (CoO–TeO2) لخمس عينات مختلفة التراكيز من الزجاج النانسي CoO–TeO2 الثنائي. تم تحضير العينات بإضافة مضافات عديدة متبوعة بتسخينها إلى درجة حرارة 1000 °C وقياس القدرة الكهروحرارية باستخدام حامل عينات مطريح للكهرباء. وجد بأن القيمة النهائية لمعامل سيبك (S) لجميع العينات كانت من النوع n والطريقة معامل سيبك في المدى 293–460 μV/K. المقال يشير إلى تأثيرات عناصر طيفية على تأسيس القوة الكهروحرارية وتوصيفات نتائج تأسيس القوة الكهروحرارية. يتم كذلك وجود نتائج على تأسيس البولارون وطاقة الاضطراب نتيجة عن المجالات العشوائية.
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showed that the TEP is independent of temperature for all glass compositions, and the glasses have low Seebeck coefficients. Also, Heikes’ relation gave an adequate explanation for the experimental data [21]. Several studies have shown that many thermoelectric transition metal oxides, including cobalt oxide when mixed with tellurite glass, exhibit a high Seebeck coefficient [8, 9, 13–16]. For this reason, CoO is now drawing increased attention, especially when added to TeO₂ glasses [22]. This paper reports the TEP of binary CoO–TeO₂ glasses in a variety of compositions and over the temperature range of 304 K–490 K since there is no prior investigation of these glasses available.

**Experimental**

Five glass samples with the chemical compositions 2xCoO–(100 - x)TeO₂, where x = 30, 40, 45, 50, and 60 mol%, were prepared. The CoO and TeO₂ powders were placed in a platinum crucible and melted in an electric furnace for about an hour. To ensure a bubble-free and homogenous melt, the chemicals in the crucible were periodically agitated. The melt was promptly poured into a steel-plate mold that had been preheated to 350 °C, moved to an annealing furnace for an hour at 350 °C, and then left to cool gradually. Final samples were in the form of a disc-shape of diameter 2 cm and thickness 2.5 mm obtained after cutting and polishing using very fine quality lapping paper. The amorphous nature of the glass was checked visually and by X-ray analysis. The density of the samples was measured by Archimedes’ principle using toluene as a buoyant liquid, employing the relation:

\[ \rho_s = \frac{w_{al}}{w_{lu}} \]  

Where \( \rho_s \) is the density of the sample, \( w_{al} \) is the sample weighed in air, and \( w_{lu} \) is the sample weighed in toluene liquid, and \( \rho_t \) is the density of toluene.

For thermoelectric power measurements, a specially designed sample holder was used in the temperature range 304 – 490 K [10, 11]. A temperature difference of about 5 – 10 K between two parallel surfaces of the glasses was achieved. The TEP was determined by measuring the EMF created between the surfaces using Keithley’s 2400 Series Sourcecemeter. All measurements were carried out in air.

**Results and discussion**

Fig. 1 shows the temperature dependence of the TEP for five glasses of different compositions in the temperature range 304 – 490 K. It is seen that the TEP is independent of temperature for all glass compositions. The sign of the TEP power is negative for all glasses, indicating an electron or polaronic nature of the charge carrier. Table 1 gives the values of TEP above room temperature of CoO–TeO₂ glasses, along with other parameters. The composition dependence of the TEP in the temperature range 304 – 490 K is shown in Fig. 2. It is observed that the magnitude of the TEP increases with increasing CoO content in the glass. The results also revealed that the TEP values are high in comparison to those of our previous study and other research that used cobalt oxide or any transition metal oxide glasses with a different glass former, such as phosphate glass [8 – 17]. This may be due to the high electrical conductivity and low thermal conductivity of TeO₂, and these are the most important requirements for obtaining the best thermoelectric materials [1].

**Table 1 Composition, measured TEP (S) and melting temperature of a range of CoO–TeO₂.**

<table>
<thead>
<tr>
<th>Composition (mol%)</th>
<th>MELTING TEMP (°C)</th>
<th>DENSITY (g/cm³)</th>
<th>S exp above 303 K (µV/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO</td>
<td>TeO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>1000</td>
<td>3.302</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>1000</td>
<td>3.514</td>
</tr>
<tr>
<td>45</td>
<td>55</td>
<td>1000</td>
<td>3.789</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>1000</td>
<td>4.019</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>1000</td>
<td>4.234</td>
</tr>
</tbody>
</table>

**Fig.2 Variation of TEP above 304 K with glass composition.**

The expression that explains the temperature independent TEP of transition metal oxides, is given by Heikes’ formula [18]:

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

Where \( k_B \) is the Boltzmann constant, \( e \) is the electron charge, \( C \) is the ratio of the concentration of reduced TMI to the concentration of total TMI, and \( \alpha \) is a constant of proportionality between the heat transfer and the kinetic energy of the electron. It has been suggested that \( \alpha < 1 \) for small polaron [18], and \( \alpha = \frac{B}{C} \) for large polaron [19, 23]. Therefore, the magnitude of \( \alpha \) can be used to confirm whether there is small polaron or large polaron formation taking place in the materials. Another suggestion [23–25] made a value of \( \alpha = 0 \) if there is no band polarons, indicating that \( S \) should be independent on C and should be independent of the nature of the TMI. If the ratio \( C \) is independent of temperature as in TMO glasses [26], then \( S \) is expected to be independent of temperature. Austin and Mott [19] have suggested that \( \alpha \) term can be zero only if the disorder energy in the system is zero. If there is a disorder energy between the occupied and unoccupied sites, then the \( \alpha \) term should be finite and given by [20]

\[ \alpha = \frac{(1-\theta)W_H}{(1+\theta)k_B} \]  

Where \( W_H \) is the polaron hopping energy and \( \theta \) is a constant correlated to the amount of disorder in the system. \( \theta = 1 \) corresponds to zero disorder energy and any deviation from unity is a measure of disorder in the system. Our results are based mainly on the suggestions of earlier different researchers [15, 20, 27, 28], because the \( C \) values were not measured, they suggested that small polarons formed in the majority of TMO glasses. Previous research [29 – 33] suggested that the theory of small polaron hopping in the non-adiabatic approximation might be the most appropriate for tellurite glasses. Based on these suggestions, we can assume that the condition for small polaron formation in the CoO–TeO₂ glasses is satisfied, which means that \( \alpha < 1 \). Our results as in Figs. 1 and 2 show conformity with the previous results reported by different researchers [8, 9, 13, 15, 16, 26 – 33]. Interestingly, if the Heikes’ formula can explain TEP of CoO–TeO₂ glasses at high temperature, we can assume that the disorder energy increases with the increase of CoO content. To have a better understanding of the physical properties of these materials, the value of \( C \) needs to be found.

**Fig.1 TEP for five compositions of CoO – TeO₂ glasses plotted against temperature.**

**Conclusion**

The TEP above room temperature of CoO–TeO₂ glasses for different materials [1].
compositions was reported. The investigations showed that the TEP does not depend on temperature and that the glasses were n-type semiconducting. The TEP also provides evidence for small polaron formation and gives information that the disorder energy increases with the increase of CoO content in the glass, but with the condition of the TEP of these glasses must be adequately described by Heikes’ formula.

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References