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Thermoelectric Power (TEP) of Semiconducting Cobalt–Tellurite Glasses

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A B S T R A C T

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 grads 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.

القدرة الكهروحرارية (TEP) لزجاج الكوبالت-تيلورايت شبه الموصل

ضيف الله محمد التواتي[1] و هند أبوبكر السلطني[1] و فاطمة ميلاد الشريف[1]و إبراهيم محمد حممو[1] و سامح أحمد نجم[1] و عبد الكريم عروف[2]

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الملخص

تم في هذه البحث قياس القدرة الكهروحرارية أو معامل سيبك (S) لخمس عينات مختلفة التراكيز من الزجاج الثنائي CoO–TeO2 شبه الموصل في درجات حرارة من K490-304. تم تحضير العينات باذابة مخاليط جافة من المساحيق الكيميائية CoO و TeO2 عند درجة حرارة 1000 oC لمدة ساعة متبوعا بتبريد مفاجئ للمصهور. و تم قياس القدرة الكهروحرارية باستخدام حامل عينات خاص صمم لهذا الغرض. وجد بأن العينات شبه موصلة من نوع n و معامل سيبك في المدى 293– to 460– μV/K. بينت الدراسة أن معامل سيبك لايعتمد على درجة الحرارة لكل تراكيب العينات كما أن معادلة هيك حققت نتائج القدرة الكهروحرارية. تبين كذلك وجود دلائل على تكوين البولارون و طاقة الاضطراب ناتجة عن المجالات العشوائية.

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

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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 TeO_2 glasses [22]. This paper reports the TEP of binary $CoO–TeO_2$ 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 $xCoO-(100 - x)TeO_2$, where x = 30, 40, 45, 50, and 60 mol%, were prepared. The CoO and TeO_2 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:

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

Where ρ_s is the density of the sample, w_a is the sample weighed in air, w_t is the sample weighed in toluene liquid, and ρ_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 Sourcemeter. 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 shows the values of the TEP above 304 K for CoO – TeO_2 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 TeO_2, and these are the most important requirements for obtaining the best thermoelectric materials [1].
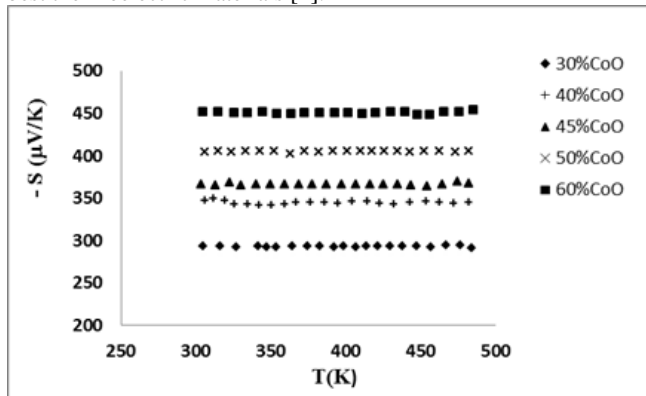

Fig.1 TEP for five compositions of CoO – TeO2 glasses plotted against temperature.

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

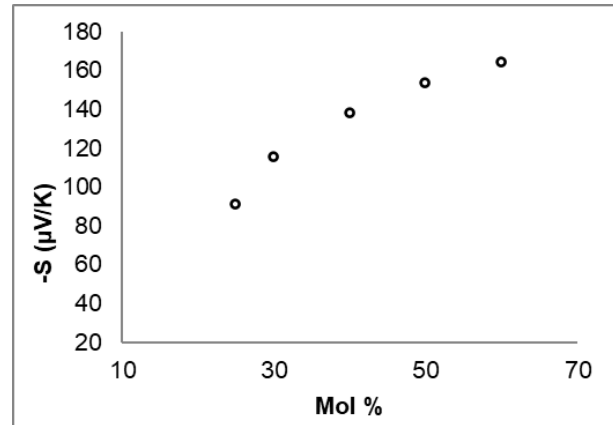| Composition (mol%)		Melting Temp (°C)	Density (g/cm³)	S_{exp} above 303 K (µV/K)
CoO	TeO₂			
30	70	1000	3.302	293
40	60	1000	3.514	345
45	55	1000	3.789	369
50	50	1000	4.019	402
60	40	1000	4.234	460

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]:

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

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 α is a constant of proportionality between the heat of transfer and the kinetic energy of the electron. It has been suggested that ▯<1 for small polaron [18], and ▯▯≥▯▯ for large polaron [19, 23]. Therefore, the magnitude of α 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 $\alpha = 0$ in case of band polarons, indicating that S should depends only 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 α 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 α term should be finite and given by [20]

$$\alpha = \frac{(1-\theta)W_H}{(1+\theta)kT} \qquad (2)$$

Where W_H is the polaron hopping energy and θ 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–TeO_2 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–TeO_2 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.

Conclusion

The TEP above room temperature of CoO–TeO_2 glasses for different

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.

References
[1]- T. H. Beeforth and H. J. Goldsmith, Physics of Solid State Devices, London: Pion Limited, 1970.

[2]- D. M. Rowe, Handbook of Thermoelectrics, CRC Press: FL. Boca Roton , 1995

[3]- EL-Sayed, S., (2009), Electrical and Thermoelectric Power Properties of $Cd_{23}Se_{43}S_{34}$. Chalcogenide Lett., **6**, 241 - 249.

[4]- Goncalves, A. P., Lopes, E. B., Rouleau, O., Godart, C., (2010), Conducting Glasses as New Potential Thermoelectric Materials: The Cu–Ge–Te Case. , J. Mater. Chem., **20**, 1516 – 1521. doi.org/10.1039/B908579C

[5]- Goncalves, A. P., Delaizir, G., Lopes, E. B., Ferreira, L. M., Rouleau, O., Godart, C., (2011), Chalcogenide Glasses as Prospective Thermoelectric Materials., J. Elect. Mater., **40**, 5, 11015 - 11017. DOI: 10.1007/s11664-010-1486-8

[6]- Xu. Jianxiao, Thermoelectric Properties of Transition Metal Oxides and Thallium Main, PhD Thesis, University of Waterloo, Ontario, Canada, (2008).

[7]- Ghosh, A., (1989), Temperature Bependent Thermoelectric Power of Semiconducting Bismuth–Vanadate Glass., J. Appl. Phys., **65,** 227-230. https://doi.org/10.1063/1.342575.

[8]- Mori, H., Sakata, H., (1996), Seebeck Coefficient of V_2O_5 – R_2O_3 – TeO2 (R = Sb or Bi) glasses, J. Mter. Sci., 31, 1621–1624.

[9]- Sakata, H., Sega, K., (1999), Multiphonon Tunneling Conduction in Vanadium-Cobalt-Tellurite glasses., Phys. Rev. B, **60**, 5, 3230 – 3236. https://doi.org 4

[10]-Tawati, D. M., Basha, M. J., (2003), Thermoelectric Power of Semiconducting Cobalt – Phosphate Glasses., J. Solid St. & Technol. Lett. **10**, 165 -170.

[11]-Tawati, D. M., Basha, M. J., (2004), Thermoelectric Power (TEP) of Semiconducting CoO – NiO – P_2O_5 Glasses., Ceram. Int., **30,**1737 - 1739. DOI: 10.1016/j.ceramint.2003.12.138

[12]-D. M. Tawati, M. J. Basha, and A. K. Arof, (2010), Thermoelectric Power (TEP) of Semiconducting Nickel–Phosphate Glasses, AIP Conf. Proc., **1250** PERFIK2009, p. 93.

[13]- Tawati, D. M., Mohamed, A. B., Hussein, N. A., Saltani, H. A., Arof, A. K. , (2019), Seebeck Coefficient of Ternary Semiconducting Vanadium–Cobalt–Tellurite Glasses, Inter. J. App. Sci. Special Conf. Issue, **1**. 169–175.

[14]- Tawati, D. M., Hussein, N. A., Ayad, A. A., Mohammed H. M., Saltani, H. A., Arof, A. K. ,(2020), Thermoelectric Power (TEP) and Structural Properties of Ternary Semiconducting V_2O_5–NiO–TeO_2 Glasses. , Lib. J. Sci. & Tech., **11,** 39 – 42.

[15]- Souri, D., (2008), Seebeck coefficient of tellurite–vanadate glasses containing molybdenum, J. Phys. D: App. Phys., 41, 105102.

[16]- Souri, D., Siahkali, K., Moradi, M., (2016), Thermoelectric Power Measurements of xSb–(60–x)V2O5–40TeO2 Glasses., J. Electron Mater., 45, 307–311.

[17]- Sharma, B. I., Srinivasan, A., (2005), Electrical Properties of V2O5 – CaO – P2O5 glasses exhibiting majority charge carrier reversal, J. Mater. Sci., 40, 5125 – 5131.

[18]- Mott, N.F., (1968), Conduction in Glasses Containing Transition Metal Ions, J. Non-Cryst. Sol., **1**, 11-17.

[19]- Austin, I.G., and Mott, N.F., (1969), Polarons in Crystalline and Non-Crystalline Materials. Adv. Phys., **18**, 41–102.

[20]- Mansingh, A. and Dhawan, A. (1978), Thermoelectric Power in Transition Metal Oxide Glasses. J. Phy. C: Sol. Stat. Phy., **11**, 16 3439.

[21]- R.R. Heikes, and R.W. Ure, Thermoelectricity: Science and Engineering: Interscience Publishers, New York 1961.

[22]- Walia, S., Balendhran, S., Nili, H., Zhuiykov, S., Rosengarten, G., Wang, Q., H., Bhaskaran, M., Sriam, S., Strano, M., S., Kalantar-zadeh, K., (2013), Transition Metal Oxides – Thermoelectric Properties, Prog. Mater. Sci., 58, 8, 1443–1489. doi.org/10.1016/j.pmatsci.2013.06.003.

[23]- M. I. Klinger, Problems of Linear Electron (Polaron). Transport Theory in Semiconductors. International series in natural philosophy, 1st edition, 1, 1979.

[24]- Sewell, G.L., Model of Thermally Activated Hopping Motion in Solids, Phys. Rev.**129**, 2 (1963), 597–608.

[25]- Lynch, G. F., Sayer, M., Segel, S. L., Rosenblatt, G., (1971), Electron and Nuclear Magnetic Resonance in semiconducting phosphate glasses, J. Appl. Phys., **42**, 2587–2591. doi: 10.1063/1.1660593.

[26]- El-Desoky, M. M., Al-Assiri, M. S., (2007), Structural and Polaronic Transport Properties of Semiconducting CuO-V_2O_5-TeO_2 Glasses, Mater. Sci. and Eng.: **B**, **137**, 237–246. DOI: 10.1016/j.mseb.2006.11.032

[27]- Mori, H., and Sakata, H., (1996), Seebeck Coefficient of V_2O_5 – R_2O_3–TeO2 (R=Sb or Bi) glasses, J. Mat. Sci. **31**,1621–1624.

[28]- Mandal, S., Banerjee, D., Bhattacharya, R. N., and Ghosh, A., (1996), Thermoelectric Power of Unconventional Lead Vanadate Glass, J. Phys. Cond. Matt., **8**, 2865.

[29]- El-Mallawany, R., (1994, Theoretical Analysis of the Electrical Properties of Tellurite Glasses, Mater. Chem. Phys., 37, 376 – 381. doi.org/10.1016/0254-0584(94)90178-3

[30]- Mori, H., Matsuno, H., Sakata, H., (2000), Small Polaron Conduction in V2O5–Sb–TeO2 Glasses, J. Non-cryst. Solids, 276, 78 – 94. doi.org/10.1016/S0022-3093(00)00280-5.

[31]- El – Desoky, M. M., (2003), Small Polaron Transport in V2O5 – NiO – TeO2 Glasses, J. Mater. Sci.: Meterials in Electronics, 14, 215 – 221. doi.org/10.1023/A:1022981929472

[32]- Souri, D., (2010), Small Polaron Hopping Conduction in Tellurium Based glasses Containing Vanadium and Antimony, J. Non – Cryst. Solids, 356, 2181 – 2184. doi.org/10.1016/j.jnoncrysol.2010.08.020.

[33]- Amarkumar, M., Sankarappa, T., Ashwajeet, J., Sujatha, T., (2019), Polaron Conduction Mechanisms in (B2O3) – (TeO2) – (MoO3) – (Er2O3) Glasses, J. Phys.: Conf. Series, 1172, 012012. DOI: 10.1088/1742-6596/1172/1/012012