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Ceramics International 30 (2004) 1737–1739

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Thermoelectric power (TEP) of semiconducting $CoO–NiO–P_2O_5$ glasses

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Received 19 November 2003; received in revised form 17 December 2003; accepted 22 December 2003

Available online 6 May 2004

Abstract

Five bulk samples of ternary $CoO–NiO–P_2O_5$ glasses were prepared by a press-quenching method from glass melt. TEP measurements have been made on annealed samples using a specially design sample holder in the temperature range 303–530 K. The temperature difference between upper and lower surfaces was maintained between 5 and 10 K. The investigations provide information on the polaron formation and the disorder energy due to random fields. TEP was found to be independent of temperature.

Keywords: TEP of oxide glasses; Semiconducting glasses; Transition metal oxide glasses; Phosphate glasses

1. Introduction

Oxide glasses containing transition-metal ions (TMI's) are of continuous interest because of their semiconducting properties, switching behavior and potential applications [1–4]. The general condition for this semiconducting behavior is that the TMI should be capable of existing in more than one valency state, so that conduction occurs by the hopping of small polarons from the lower valency state to the higher valency state [5,6]. Small polarons are defined as charge carriers trapped by self-induced lattice distortions which extend over-their nearest surroundings [7].

Although extensive studies were carried out on the electrical properties of the semiconducting transition metal oxide (TMO) glasses [8–14], there are few reports for the TEP of these glasses [15–18]. The quantitative agreement in the results reported by different workers is also poor [15–17,19]. Measurements of the TEP of TMO glasses are also of interest because they provide information on the nature of charge carriers, the formation of polarons, the extent of disorder due to random fields, etc. [5,6,16,20]. dc conductivity of different composition of binary $CoO–P_2O_5$ and $CoO–NiO–P_2O_5$ glasses were reported previously [13]. However, the incorporation of NiO into the glass system lowers the conductivity in comparison with binary glass with similar CoO content. TEP of binary cobalt–phosphate glasses of different compositions at temperatures from 300 to 530 K was also reported [18]. This binary composition glass has shown that the TEP is independent of temperature for all glass composition. Also the TEP increases with increasing CoO content in the glass.

The purpose of the present work is to study the TEP of ternary $CoO–NiO–P_2O_5$ glasses in a range of compositions and over the temperature range 303–530 K.

2. Experimental

The appropriate weights of analytical reagent grads of CoO (99.99%), NiO (99.99%) and P_2O_5 (99.99%) were carefully mixed in an alumina crucible and placed in a furnace maintained at 300 °C for 1 h. This initial heating served to minimize material volatilization. The crucible was then transferred to melting furnace maintained at 1250 °C and left for about 2 h with frequent stirring. The homogenized melts were quickly cast on to a steel-plate mold (pre-heated to 400 °C). This procedure served to minimize cracking of the glass due to thermal stress. The glasses formed were transferred to an annealing furnace at 400 °C for 1 h and were then allowed to cool slowly. The glasses obtained were dark and opaque in appearance. The amorphous nature of the glass was checked visually and by X-ray analysis. For

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0272-8842/$30.00
doi:10.1016/j.ceramint.2003.12.138

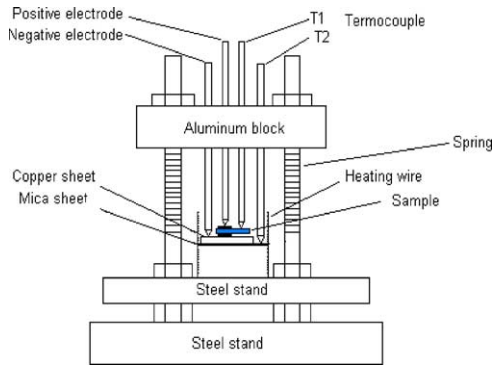

Fig. 1. Schematic diagram of the sample holder for thermoelectric power measurements.

thermoelectric power measurements, disk-shaped samples of diameter ~2.5 cm and thickness ~2.3 mm were cut and polished with very fine quality lapping papers.

A schematic diagram of especially designed sample holder used for the TEP measurements is shown in Fig. 1. The sample was placed between two electrodes, the negative electrode is a copper sheet insulated from the base of the sample holder by a mica sheet and the positive electrode is a copper probe inserted in aluminum hollow rod. Springs at the bottom of the block used to ensure proper electrical contact between two of the sample surfaces. A temperature difference of 5–10 K between two parallel surfaces of the samples was established and the TEP was determined by measuring the thermo-EMF developed between these surfaces in MV-852A dc Micro-Volt-Ammeter using silver as an electrode material. The temperature difference (ΔT), between two surfaces of the sample was measured by Keithley 165 Auto ranging Multimeter, using calibrated copper-constantan thermocouples T1 and T2 (Fig. 1). All measurements were made with the samples under a vacuum in the order 10^{-5} Torr.

3. Results and discussion

The temperature dependences of the TEP for five compositions of CoO–NiO–P_2O_5 glasses in the temperature range 303–530 K are shown in Fig. 2, which clearly indicates that

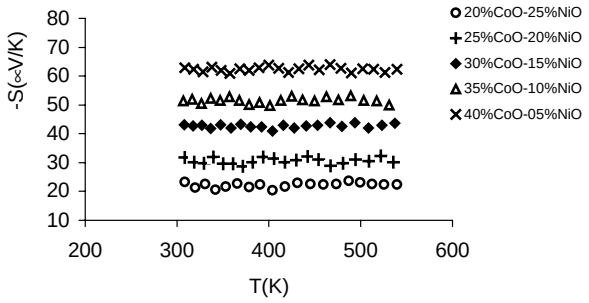

Fig. 2. TEP for four compositions of CoO–NiO–P_2O_5 glasses Plotted against temperature.

Table 1
Composition, measured TEP S and melting temperature of a range of CoO–NiO–P_2O_5

Composition (mol%)			$-S_{exp}$ above 303 K (μV/K)	Melting temperature (°C)	Density (g/cm^3)
CoO	NiO	P_2O_5			
20	25	55	22.29	1250	3.190
25	20	55	30.61	1250	3.158
30	15	55	42.73	1250	3.137
35	10	55	51.54	1250	3.080
40	05	55	62.41	1250	3.041

the TEP is independent of temperature for all glass compositions. The signs of the TEP for all glass compositions are negative, suggesting an electronic or polaronic nature of charge carriers. Table 1 shows the values of the TEP above 303 K for CoO–NiO–P_2O_5 glasses along with other parameters. The composition dependence of TEP in the temperature range 303–530 K is shown in Fig. 3. It is seen that the magnitude of the TEP increases with increasing CoO content in the glass and decreases with increasing NiO content in the glass. The addition of NiO into CoO–P_2O_5 increase the TEP in comparison with cobalt–phosphate glass with similar CoO content as shown in Table 1.

The TEP of materials with mixed valence states has been investigated theoretically by Heikes [20] and Austin and Mott [6]. The expression for the TEP derived by Heikes is given by:

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

where e is the electron charge, k_B is the Boltzmann constant, C is the fraction of ions in the reduced valence states and α is a constant of proportionality between the heat of transfer and the kinetic energy of the electron. It may be noted that the TEP predicted by Eq. (1) is independent of temperature. The magnitude of α can be used to ascertain whether there is polaron formation in the materials. It has been suggested that $\alpha < 1$ for small polarons [5], while for large-polaron formation $\alpha \geq 2$ [6]. Another suggestion [21] made a value of constant $\alpha = 0$ in case of band polarons. This indicating that S should depend only on C and should be independent of the nature of the TMI. If C is independent of temperature as in TMO glasses [22], then S is expected to be independent

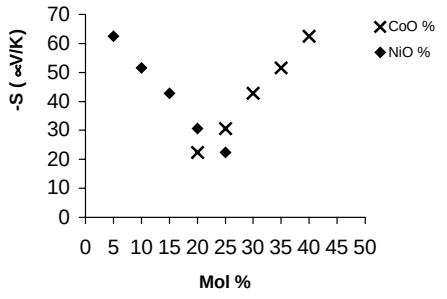

Fig. 3. Variation of TEP above 303 K with glass composition.

of temperature. A suggestion [21] is made 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 α in Eq. (1) is given by [16].

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

where W_H is the polaron hopping energy and θ is a constant correlated to the extent 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. Then C is an important parameter in describing the Seebeck coefficient.

Our results are based mainly on the suggestions of earlier different workers [9,16], because the C values were not measured. They suggested in most of the TMO glasses small polarons are formed. Other workers [9,13] suggested that the theory of small polaron hopping in the adiabatic approximation might be the most appropriate for phosphate glass. Depending on these suggestions, we can assume that the condition for small polaron formation in the CoO–NiO–P_2O_5 glasses is satisfied, means that $\alpha < 1$.

Our results as shown in Figs. 2 and 3 show good agreement with the results reported by different workers [15–18]. However, if the TEP of CoO–NiO–P_2O_5 glasses at high temperature can be explained by Heikes' formula, then we can assume that the disorder energy increases with the increase of CoO content and decrease NiO content in the glass.

The value of α needed in Eq. (1) for complete agreement between the theoretical and experimental values of the TEP but C values unknown. To have a better understanding of the physical properties of these materials, the values of C need to be known.

4. Conclusions

The TEP of CoO–NiO–P_2O_5 glasses for different compositions at the temperature range 303–530 K was investigated. The glasses were n-type semiconducting and the TEP above 303 K does not depend on temperature. The high-temperature TEP provides evidence for small polaron formation and gives information that the disorder energy increases with the increase of CoO content in the glass and decreases with increase NiO content in the glass but with the condition of the TEP of CoO–NiO–P_2O_5 glasses must be explained adequately by Heikes' relation.

Acknowledgements

The authors would like to thank the School of Physics, University of Science Malaysia, Penang, and would like to give special acknowledgment to the lab assistances Ee Bee Choo and Azmi Omar for their help. Mr. D.M. Tawati also wishes to thank the University of Garyounis. Benghazi, Libya for their financial support.

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