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# Thermoelectric power of unconventional lead vanadate glass

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**Abstract.** The thermoelectric power above room temperature of the unconventional lead vanadate glass is reported. It has been observed that the thermoelectric power shows weak variation with temperature and its magnitude decreases with increase in  $V_2O_5$  content in the glass compositions. Heikes' formula for the thermoelectric power can give an adequate explanation for the experimental data. Thermoelectric power data also give information for the formation of small polarons in these glasses.

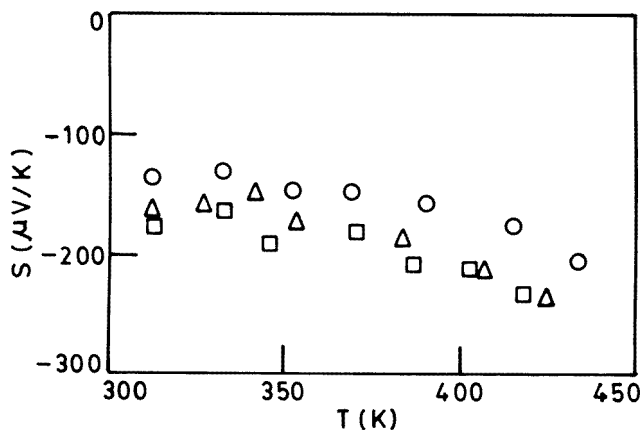
## 1. Introduction

Measurements of the thermoelectric power of semiconducting oxide glasses containing transition-metal ions are interesting, because they provide information on the nature of charge carriers, the formation of polarons, the extent of disorder due to random fields, etc [1–3]. However, the thermoelectric power of these glasses has not been studied so extensively as the electrical conductivity [4–13]. The quantitative agreement in the results reported by different workers is also poor [4–10]. Nester and Kingery [5] have reported an almost linear decrease in the thermoelectric power with decrease in temperature for the vanadium phosphate glasses, while Brown [4] has reported a very rapid increase in thermoelectric power with decrease in temperature for the same glasses. Mansingh and Dhawan [9] have observed a slight increase in thermoelectric power below 200 K for vanadium and tungsten phosphate glasses and a temperature-independent thermoelectric power above 300 K for vanadium, tungsten and molybdenum phosphate glasses. For vanadium tellurite and bismuthate glasses [8, 10], a rapid decrease in thermoelectric power at low temperatures and a temperature-independent thermoelectric power at high temperatures have been observed. The objective of the present work is to study the thermoelectric power of the unconventional lead vanadate glasses. It is worth mentioning that the structure of the lead vanadate glasses is different from conventional vanadium phosphate glasses [14] and the electrical conduction in the lead vanadate glasses occurs by the non-adiabatic hopping of polarons between two different valence states ( $V^{4+}$  and  $V^{5+}$ ) of the vanadium ions [15] in contrast with the adiabatic hopping observed in vanadium and other transition metal phosphate glasses [12].

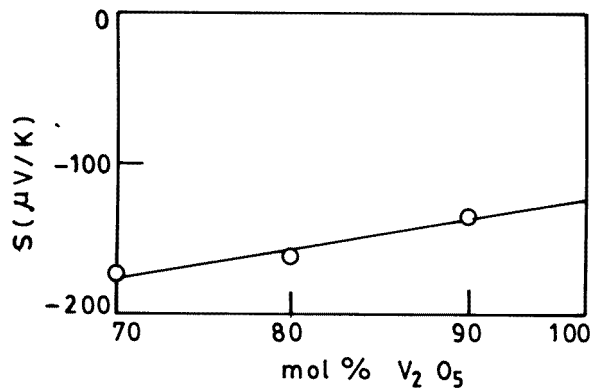
## 2. Experimental procedure

The details of preparation of the lead vanadate glasses of compositions  $(V_2O_5)_x(PbO)_{100-x}$  where  $x = 50$ – $90$  mol% have been reported elsewhere [14]. In brief, glass compositions

were obtained by melting the reagent grade  $V_2O_5$  and  $PbO$  in an alumina crucible at  $1000^\circ C$  for 1 h in an electric furnace and subsequently quenching the melts by pressing between two brass plates. The amorphous nature of the samples was confirmed by x-ray diffraction [14]. Chemical analysis and ESR spectra of the glasses [14] show that the vanadium exists as  $V^{5+}$  and  $V^{4+}$  ions in all glass compositions. For thermoelectric power measurements, samples of dimension  $10\text{ mm} \times 5\text{ mm} \times 1\text{ mm}$  were cut and polished. A temperature difference of 3–10 K between two parallel surfaces of the samples was established and the thermoelectric power was determined by measuring the thermo-EMF developed between these surfaces in a Keithley microvoltmeter (model 177) using gold as an electrode material. Attempts were made to measure the thermoelectric power of all glass compositions in a wide temperature range. However, reliable data were obtained only for the three glass compositions with 90, 80 and 70 mol%  $V_2O_5$  above room temperature and are reported here.



**Figure 1.** Temperature dependence of the thermoelectric power of the different lead vanadate glass compositions: ○, 90 mol%  $V_2O_5$ –10 mol%  $PbO$ ; Δ, 80 mol%  $V_2O_5$ –20 mol%  $PbO$ ; □, 70 mol%  $V_2O_5$ –30 mol%  $PbO$ .



**Figure 2.** Composition dependence of the thermoelectric power at 310 K. The solid line is the theoretical fit to equation (1).

### 3. Results and discussion

The temperature dependences of the thermoelectric power above room temperature for three glass compositions are shown in figure 1, which clearly indicates that the thermoelectric power does not vary strongly with temperature. The signs of the thermoelectric power for all glass compositions are negative, suggesting an electronic or polaronic nature of charge carriers. The composition dependence of thermoelectric power at 310 K is shown in figure 2. The magnitude of the thermoelectric power decreases with increase in  $V_2O_5$  content in glass composition similar to vanadium phosphate glasses reported by Mansingh and Dhawan [9].

The thermoelectric power of materials with mixed valence states has been investigated theoretically by Heikes [3] and Austin and Mott [2]. The expression for the thermoelectric power derived by Heikes is given by

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

where  $e$  is the electronic charge,  $k_B$  is the Boltzmann constant,  $C$  is the fraction of ions in the reduced valence states and  $\alpha$  is such that  $\alpha(k_B T)$  is the kinetic energy of a carrier. It may be noted that the thermoelectric power predicted by equation (1) is independent of temperature. According to Heikes [3],  $\alpha = \Delta s'/k_B$ , where  $\Delta s'$  is the change in entropy of an ion due to the presence of a charge carrier. On the other hand, Austin and Mott [2] have shown that  $\alpha = \sum \Delta\omega_0/\omega_0$ , where  $\Delta\omega_0$  is the change in the characteristic phonon frequency  $\omega_0$  of the ion due to the presence of the charge carrier and the summation extends over all neighbouring ions. The magnitude of  $\alpha$  can be used to ascertain whether there is polaron formation in the materials. It has been suggested that  $\alpha < 1$  for small polarons, while for large-polaron formation  $\alpha > 2$  [1, 2].

**Table 1.** Parameters  $\alpha$  and  $\theta$  obtained from the analysis of thermoelectric power.

Glass composition (mol%)		$\alpha$	$W_H^a$ (eV)	$\theta$
$V_2O_5$	PbO			
90	10	0.20	0.29	0.95
80	20	0.21	0.33	0.95
70	30	0.29	0.35	0.94

<sup>a</sup> From [15].

Our data for thermoelectric power presented in figure 1 do not show a strong temperature dependence. Values of  $\alpha$  needed in equation (1) for complete agreement between the theoretical and experimental values of the thermoelectric power were calculated using values of  $C$  from our earlier report [14] and are shown in table 1. The theoretical fit of the thermoelectric power is shown in figure 2. It is observed that the values of  $\alpha$  are less than unity and thus satisfy the condition for the formation of small polarons in these glasses. Values of  $\alpha$  can also be used to ascertain the extent of disorder in the materials [2]. Austin and Mott [2] have shown that

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

where  $W_H$  is the polaron hopping energy and  $\theta$  is a constant correlated to the extent of disorder in the systems.  $\theta = 1$  corresponds to zero disorder energy and any deviation from unity is a measure of disorder in the system. Values of  $\theta$  were calculated from equation (2)

using values of  $W_H$  at 350 K taken from our earlier report [15] and are shown in table 1. It is noted that values of  $\theta$  are less than unity but do not vary significantly with glass composition. Thus, for the glass compositions reported in table 1, the extent of disorder is almost the same. This conclusion is also supported by the magnitude of the disorder energy calculated from the DC conductivity results of these glasses [15].

#### 4. Conclusions

The thermoelectric power above room temperature of the lead vanadate glasses does not vary strongly with temperature and can be adequately explained by Heikes' formula. The analysis of the thermoelectric power data provides evidence for the formation of small polarons and almost constancy of the disorder energy in these glasses.

#### Acknowledgments

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