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Helium gas-sensing behaviour of iron-tellurite glasses

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Semiconducting iron-tellurite and iron-aluminium-tellurite glasses were prepared by a press-quenching technique of the melt, and the helium gas-sensing behaviour of these was investigated. The glasses were *n*-type semiconductors. For powder-sintered pellet glass samples, the d.c. conductivity was larger in helium than in air and oxygen for the temperature range 463–598 K, and the conduction was confirmed to be due to small polaron hopping of electrons. In periodic switching of helium and air at 598 K, dynamic changes in conductivity were observed for both glasses, and the variations in conductivity were found to be reproducible. A helium gas sensitivity of 10.6 and 9.3 was obtained for both glasses, respectively. The dynamic changes in conductivity could be explained by a helium diffusion model. © *2001 Kluwer Academic Publishers*

1. Introduction

Since the discovery of semiconducting oxide glasses [1] with transition metal ions, there have been considerable interests in the fabrication of semiconducting oxide glasses with different compositions [2–5] and in understanding the conduction mechanism. Recently, vanadium tellurite [5–8] or iron tellurite [9, 10] glasses have been targeted in electrical conductivity studies. The conduction of these glasses was understood as involving small polaron hopping of electrons in the glass network [11–13], accompanying a valence exchange between the transition metal ions. Little work, however, has been performed to develop applied devices [14]. Recent works on V_2O_5-SrO-Sb_2O_3 [15] and V_2O_5-Sb_2O_3-TeO_2 [16] *n*-type semiconducting glasses reported on O_2 gas-sensing behaviour in Ar atmosphere at high temperatures. The gas-sensing mechanism was understood as conductivity change due to O_2 gas diffusion into the glass network. An *n*-type semiconducting Fe_2O_3-Sb-TeO_2 glass [17] also exhibited oxygen gas-sensing properties with a sensitivity of 8.1 at 598 K. We expected such highly conductive iron-tellurite glasses to have helium gas-sensing properties in air, because oxide glasses have shown helium gas permeation characteristics [18]. We report here some positive results on He gas-sensing in some iron-tellurite semiconductive glasses. The results can be extended to studies on other semiconducting oxide glasses with different compositions applicable to helium and other rare-gases.

2. Experimental

Reagent grade (99.99% purity) Fe_2O_3, TeO_2, and Al (99.5%) were used as raw materials. Aluminium was added to obtain higher conductivity glass using the reducing effect of Al during melting. The required components to prepare $20Fe_2O_3{\cdot}80TeO_2$ (mol%) and $20Fe_2O_3{\cdot}5Al{\cdot}75TeO_2$ (mol%) glasses were well mixed in an mortar in argon atmosphere for 20 min. A batch of 5 g was melted for 30 min in an electric furnace at 1073 K in a flowing argon atmosphere. The melt was then quickly quenched between two copper blocks kept at room temperature. Thus we obtained bulk glasses of about 1 mm in thickness. The amorphous nature of these as-quenched glasses was confirmed by the X-ray diffraction pattern (Philips, X'pert system PW3020).

The density measurement of the glass samples at 293 K was due to the Gay–Lussac method using toluene. The thermoelectric powers of the glasses were measured in air at 598 K keeping a temperature difference of 5–10 K between the two electrodes by blowing argon gas on one electrode. Negative signs of the Seebeck coefficient for the samples confirmed the glasses to be *n*-type semiconductors. From the earlier results [15–17, 19] it was necessary to increase the surface area of the samples to observe clearly the gas-sensing properties of these glasses. Hence we prepared porous glass samples [15–17, 19] as follows: the glass sample was powdered in air in an agate mortar for 30 min. A pellet (1.5 cm in diameter and 0.1 mm in thickness) was prepared from 0.8 g of the powdered glass sample by pressing at 490MPa in air, followed by sintering in an electric furnace in air for 3 h at 633 K which was lower than the glass transition temperature ($T_g = 663$ K) of the $20Fe_2O_3{\cdot}5Al{\cdot}75TeO_2$ (mol%) glass. The lower sintering temperature was used to avoid crystallization of glass during sintering. The apparent density of the

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pellet was obtained by measuring its size and weight. Thus we obtained the porosity (p) of these two glass samples: $p = 31.0\%$ (for the $20Fe_2O_3{\cdot}80TeO_2$ (mol%) glass (A)) and 26.9% (for the $20Fe_2O_3{\cdot}5Al{\cdot}75TeO_2$ (mol%) glass (B)).

Measurements of the d.c. conductivity σ for the pelleted glass samples were made using the two-point probe technique. Silver paste electrodes with a spacing of 5 mm were made on one surface of the pellet sample, the ohmic contact being checked at 603 K. The d.c. current for a constant applied d.c. voltage (2.5 V–3.0 V) was measured with a digital electrometer (Advantest, TR8652). The conductivity was measured for temperatures in the range 463 K–598 K. No polarization due to ionic current was found, indicating the conduction to be solely electronic.

3. Results and discussion

Fig. 1a and b show the Arrhenius plots of log (σT) for the $20Fe_2O_3{\cdot}80TeO_2$ (mol%) (A) and $20Fe_2O_3{\cdot}5Al{\cdot}75TeO_2$ (mol%) (B) pelleted glasses, where σ was measured, after the samples had been kept for 60 min at 603 K in He or O_2, or air, decreasing the temperature in He, O_2, or air. The linear relationships were confirmed by the best fitting of the Arrhenius plots (Fig. 1a and b), indicating that the plots can be expressed by $\sigma T = \sigma_0 \exp(-W/\mathrm{kT})$, where W is the activation energy for conduction. For small polaron hopping conduction of electrons in the glasses with transition metal ions, the conductivity σ is given by [12],

$$\begin{aligned}\sigma &= \nu_0 e^2 C(1-\mathrm{C})R^2 N\beta \exp(-2\alpha R)\exp(-W/\mathrm{kT})\\ &= (\sigma_0' T)\exp(-W/\mathrm{kT}),\end{aligned} \qquad (1)$$

where ν_0 is the optical phonon frequency, α, the inverse of the wave function decay, C, the ratio of concentration of the ions in the lower valance state to the total concentration of the transition metal ions (here $Fe^{2+}/Fe_{\mathrm{total}}$), N is the number of transition metal ion (Fe) sites per unit volume and is R^{-3}, where R is the mean spacing between transition metal ions obtainable from the density of glass, e, the electron charge, and k, the Boltzmann constant and $\beta = (\mathrm{kT})^{-1}$. In Equation 1 the activation energy for conduction W, assuming a strong electron-phonon interaction, is given by [12],

$$W = W_{\mathrm{H}} + W_{\mathrm{D}}/2 \quad (\text{for } T > \Theta_{\mathrm{D}}/2) \qquad (2)$$

$$W = W_{\mathrm{D}} \quad (\text{for } T < \Theta_{\mathrm{D}}/2), \qquad (3)$$

where W_{H} is the hopping energy, W_{D}, the disorder energy, and Θ_{D} is the Debye temperature.

Fig. 1a and b show the conductivity σ of the glasses A and B to be higher in He than in air and in an O_2 atmosphere in the measured temperature range. The conductivity in air, which is higher than that in an O_2 atmosphere, may be due to the difference in O_2 concentration in both atmospheres, i.e., the effect of N_2 in air diffused in the glass. σ in air for the glass A is slightly higher than that in the glass B at fixed temperatures. So the effect of Al on Fe ion was observed.

Since no change in the slope of the Arrhenius plots of log (σT) yields single-valued activation energies (W), we obtained W with the best fit technique as $W = 0.716$ eV (in He), 0.908 eV (in air) and 0.953 eV (in O_2) for the glass A, and 0.719 eV (in He), 0.899 eV (in air) 0.934 eV (in O_2) for the glass B. The pre-exponential factor σ_0 extrapolated from Fig. 1a and b gave log σ_0 (S cm^{-1} K) $= 3.53$ and 3.91 in He for the glasses A and B, respectively, which agreed fairly well with log σ_0 (S cm^{-1} K) $= 3.54$ and 3.63 for the glasses A and B calculated from Equation 1 with $R = 0.49$ nm and 0.54 nm for the glasses A and B , and assuming $C = 0.1$ [20] for the glass A and 0.4 [17] for the glass B from the iron tellurite glasses with similar composition, $\alpha^{-1} = 0.02$ nm and $\nu_0 = 10^{12}$ Hz. Thus we confirmed small polaron hopping transport in the glasses in a He atmosphere.

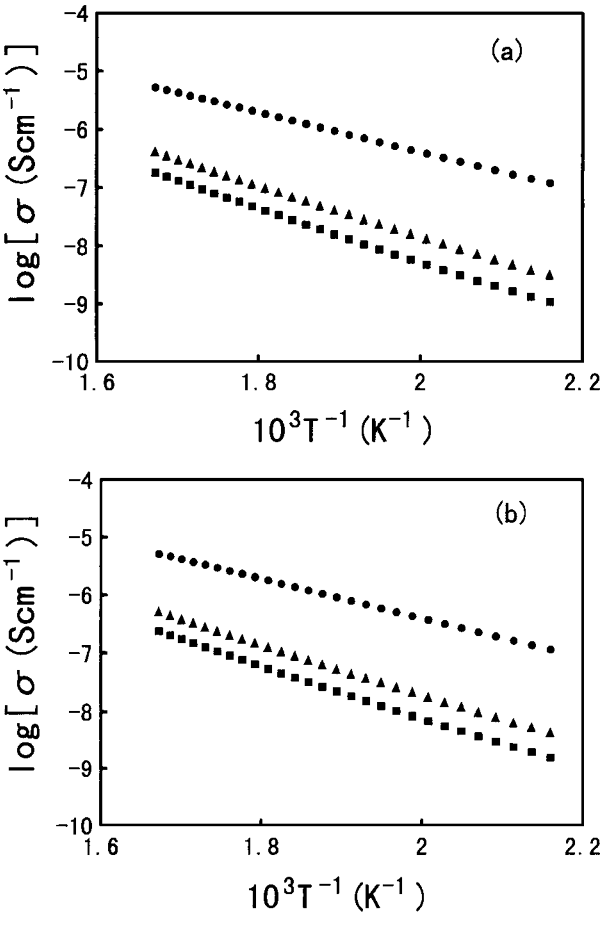

Figure 1 Temperature dependence of d.c. conductivity for $20Fe_2O_3{\cdot}80TeO_2$ (mol%) (a) and $20Fe_2O_3{\cdot}5Al{\cdot}75TeO_2$ (mol%) (b) pelleted glasses in different gas atmospheres: ● in He, ▲ in air, ■ in O_2.

The surface texture of the powder-sintered pellet glass (A) is shown in Fig. 2, indicating grains 0.5 μm–2 μm in size and a porous structure. Since the porosity of the samples A and B are 31.0% (A) and 26.9% (B) as described earlier, we expect from the results that He diffusion into the samples at elevated temperature is highly possible.

Fig. 3a and b show the variations of the conductivity of the glasses (A and B) with time (t) in alternate switching of helium and dry air every 1 h at 598 K. In

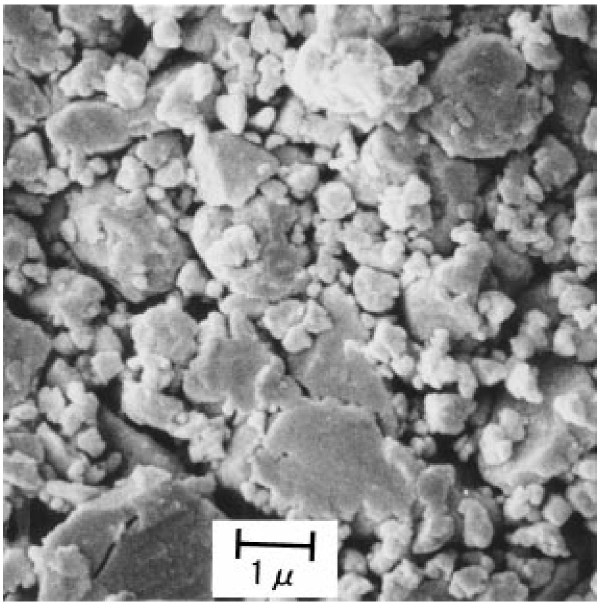

Figure 2 Scanning electron micrograph of the surface of the pellet of $20Fe_2O_3{\cdot}80TeO_2$ (mol%) glass.

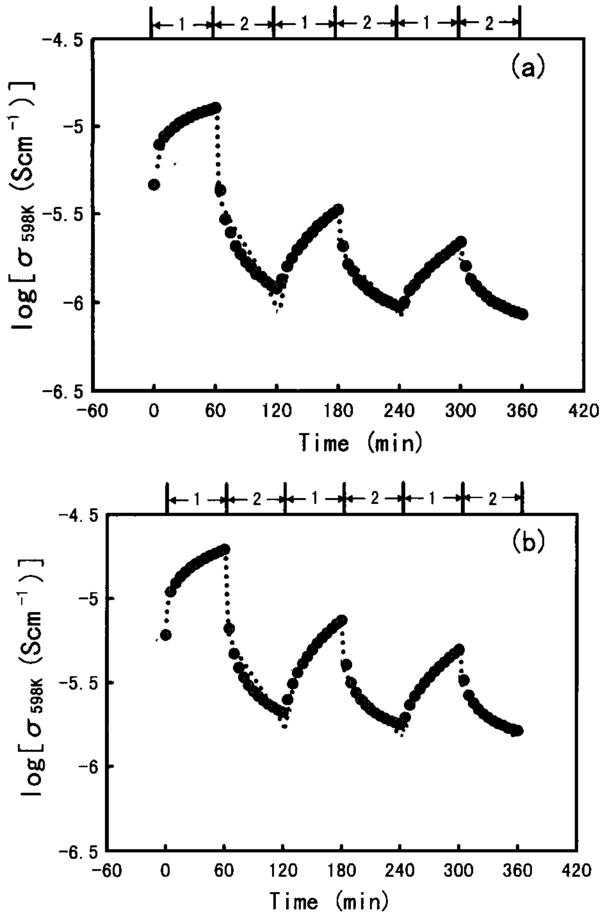

Figure 3 Variations in d.c. conductivity of $20Fe_2O_3{\cdot}80TeO_2$ (mol%) (a) and $20Fe_2O_3{\cdot}5Al{\cdot}75TeO_2$ (mol%) (b) pelleted glasses with time at 598 K on alternate switching to He and air. For (a) and (b), 1 : He; 2 : air.

these experiments, we started the measurements with the samples which had been preserved in air (in a desiccator) at room temperature. The changes in conductivity were similar and reproducible for both glass samples as well as in O_2 gas-sensing in Ar atmosphere [15–17, 19]. When He was introduced into the systems, σ increased first for $t = 0$ h–1 h then, after exchange for air, it decreased for $t = 1$ h–2 h and became lower than the initial values of σ. The reintroduction of He caused an increase in σ for $t = 2$ h–3 h. When air was exchanged again for He, σ decreased for $t = 3$ h–4 h to almost the same values as at the end of the first introduction of air. Since the conductivity change in oxide ceramics due to gas adsorption (NO_2) normally occurs very rapidly, from less than 1 min [21] to several min [22] after the gas introduction, we could not understand the above slow changes in terms of a gas adsorption model.

Hence these changes in conductivity were interpreted as follows. The conduction is based on the valence change of Fe ion in the glasses, $Fe^{2+} \rightarrow Fe^{3+} + e$, leading to the small polaron hopping of electrons along the Fe-O-Fe chains in the glass network. The O_2 in air diffused into the glasses traps hopping electrons ($O_2 + e \rightarrow O_2^-$), causing a decrease in the concentration of hopping electron in the glasses. When the glasses are exposed to He, it easily diffuses into the glasses after physisorption on the surface of the porous sample (Fig. 2). Conversely, the O_2 molecules previously diffused and stored in the glasses [15–17] rediffuse out from the sample surfaces, where electrons are liberated as hopping electrons in the glass network. Thus the concentration of hopping electrons, (i.e, the conductivity) again increases, assuming that the electron mobility is unchanged during this gas exchange process.

Next on exposing the glass samples to air, O_2 molecules diffuse into the glass and He dissolved in the glass diffuses out from the glass, thus O_2 again traps hopping electrons. The effects of O_2 diffusion and rediffusion on conductivity were formulated earlier, which explained adequately the O_2 gas-sensing behavior for iron-antimony-tellurite [17] and vanadium–tellurite [15–17, 19] glasses. When He diffuses in and O_2 diffuses out from the glass, we can apply the O_2 diffusion model [15–17, 19] to the present case in terms of mutual diffusion of He and O_2,

$$\sigma = \sigma_b + a_1 t^{1/2}, \qquad (4)$$

where t is time, σ_b is the bulk glass conductivity at $t = 0$, and

$$a_1 = (\sigma_b - \sigma_s)(2CDV_0)^{1/2}/d, \qquad (5)$$

here σ_s is conductivity of He-diffused layer, d the mean thickness of He-diffused layer, D the diffusion constant of He, V_0, the volume of a He atom and C is a constant. Conversely, when O_2 in air diffuses in the glass and He previously diffused in the glass diffuses out in exchange for oxygen,

$$\sigma = \sigma(t_0) - a_2(t - t_0)^{1/2}, \qquad (6)$$

where t_0 is the time at switching He to air, and

$$a_2 = (\sigma_b - \sigma_s)(2C'D'V_0)^{1/2}/d, \qquad (7)$$

here D' is the diffusion constant of the case where the He atoms occluded in the glass are rediffused by the inflow of air thus D and D' are likely to differ, and C' is a constant. $a_1 = a_2$, providing both diffusion processes are the same. It is noted that an estimation of D and D' from the experimental data is difficult because of many undetermined parameters in a_1 and a_2.

In Fig. 3a and b we see the dotted lines calculated with this model with a_1 and a_2 chosen suitably. The rapid decreases in σ on exposure to air may be due to O_2 adsorption on the outermost glass surfaces [17], which causes trapping of electrons involved in hopping conduction. In the first cycle of exposure of He and air, the difference between the theoretical and experimental curves in exchange of He for air is probably due to the effect of air involved in the glasses prior to the contact with He gas. In the second and third cycles of switching between He and air, agreements between the theoretical and experimental curves are satisfactory. We obtained the He gas sensitivity (S) defined as $S = \sigma(\text{He})/\sigma$ (air) $S = 10.6$ and 9.3 for the glasses A and B at $T = 598$ K, respectively. These are larger than those for O_2 sensing in vanadate [15, 16, 19] ($S = \sigma(\text{Ar})/\sigma$ $(O_2) = 1.2$–4.5) and iron-antimony tellurite glasses [17] ($S = 8.1$).

Finally we mention that in the above analysis the effect of N_2 gas in air was neglected, because N_2 molecules in air diffused in the glass may have almost no effects on the conductivity. Thus these iron-tellurite semiconducting glasses in hopping conduction showed clearly He-sensing properties. Providing the glass is adequately improved in structure so as to increase the mutual diffusion of He and O_2, the present results may be useful in developing semiconducting amorphous materials applicable to He gas sensing. These large values of He gas sensitivity (10.6 and 9.3) are important for full development of such a gas sensor applied in space and environmental science.

4. Conclusions

Fe_2O_3-TeO_2 and Fe_2O_3-Al-TeO_2 semiconducting glasses were prepared by a press-quenching technique, and the helium gas-sensing properties were investigated for the powder-pelleted glass samples. The d.c conductivity for both glass samples was larger in helium than in air and oxygen. The conduction for the pellets was confirmed as small polaron hopping of electrons.

For the periodic switching of helium and air, variations in the conductivity were observed with reproducibility at 598 K for both samples. The dynamic changes in conductivity were attributed to helium diffusion in and rediffusion from the glasses. A sensitivity for helium in air at 598 K was obtained as 10.6 and 9.3 for both samples, respectively. Thus these glasses demonstrated potential applicability to use as a helium gas sensor. Such a solid state helium gas sensor using these glasses may be useful in space and environmental science.

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