JOURNAL OF MATERIALS SCIENCE 31 (1996) 6339–6343

Dielectric properties and polarizability of molybdenum tellurite glasses

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The dielectric behaviour of the $[TeO_2]_{1-x}[MoO_3]_x$, $x = 0.2$, 0.3 and 0.45 mol %, glassy system is reported for the temperature range 300–573 K and the frequency range of 0.1–10 kHz. Both the static and high frequency dielectric constants for these binary tellurite glasses decrease with increasing MoO_3 content. The temperature dependence of the dielectric constants of these glasses are positive. The frequency dependence of the dielectric constant identifies a frequency dependence which does not show a flattening at low frequency. The room temperature static dielectric polarizability is discussed in terms of the MoO_3 concentration. The temperature dependence of the dielectric constant has been analysed in terms of the temperature changes of both volume and polarizability and also a volume change of the polarizability.

1. Introduction

Our interest in the electrical properties of transition metal (TM) tellurite glasses is due to the reports of TeO_2–WO_3 glasses behaving as n-type semiconductors [1–3]. The semiconducting behaviour arises from electron transfer of an unpaired d-electron of the transition metal ion (TMI) in a low oxidation state [1]. The measurements of the low (static) and high frequency dielectric constants of pure TeO_2 [2] and TeO_2–WO_3 glasses in the temperature range of 77–300 K were discussed in terms of the molar polarizabilities of the glasses. The most important parameters of the charge transfer process in these glasses were calculated [3] as being:

(i) In the high temperature region: hopping, disorder energies, the number of ions per unit volume, the polaron radius and the polaron separation distance.

(ii) In the intermediate temperature region: the electron coupling coefficient, the number of polarizable atoms per unit volume and the polarizability of these atoms.

(iii) In the low temperature region: wave function decay of the electron and density of states near the Fermi energy level.

A study of the dc conductivity of a range of TeO_2–MoO_3 glasses has been reported [4]. In addition we have reported an analysis of the ac conductivity of the present glass system [5].

The aim of the present study is to measure and analyse both the frequency and temperature dependencies of the dielectric constant and polarizability of $[TeO_2]_{1-x}[MoO_3]_x$ and the effect of MoO_3 additions on these parameters.

2. Experimental

In this investigation glass samples of $[TeO_2]_{1-x}[MoO_3]_x$ were prepared for x values of 0.2, 0.3, and 0.45 mol %. The glasses were prepared by mixing TeO_2 and MoO_3 in an alumina crucible. In order to reduce volatization the mixtures were calcined at 400 °C for 1 h. The crucible was then transferred to the melting furnace at a temperature determined by the composition of the sample. The melt was cast at room temperature into a steel split mold and annealed at 300 °C for 1 h. The amorphous nature of the samples was confirmed from X-ray diffraction (Shemadzu X-ray diffractometer model XD-3). The densities of the prepared samples were measured using the Archemides principle. The dielectric measurements were performed on disk shaped samples of diameter $\cong 0.1$ cm and thickness $\cong 0.4$ cm that were cut and polished using a fine Al_2O_3 lapping powder, (0.1 μm particle size). Silver electrodes were coated on both faces of the samples. The dielectric constant was measured using the method discussed elsewhere [6].

3. Results and discussion

The experimental results on the temperature and frequency dependence of the measured dielectric constant, ε, for the prepared samples over the temperature range (300–573 K) and the frequency range (0.1–10 kHz) are presented in Fig. 1(a–c). These measurements showed that while ε was almost frequency and temperature dependent, it was noticeably affected by the molybdenum concentration, as is shown in Figs 1(a–c) and 2(a–c). The low frequency region can be used to obtain the value of the static dielectric constant ε_s (zero frequency). The experimental results will be discussed in terms of, frequency, temperature and composition. Firstly, the dielectric constant of these transition metal tellurite glasses decreases with increasing the percentage of MoO_3 in the glass. For example, ε_s decrease at room temperature from 9.8 to

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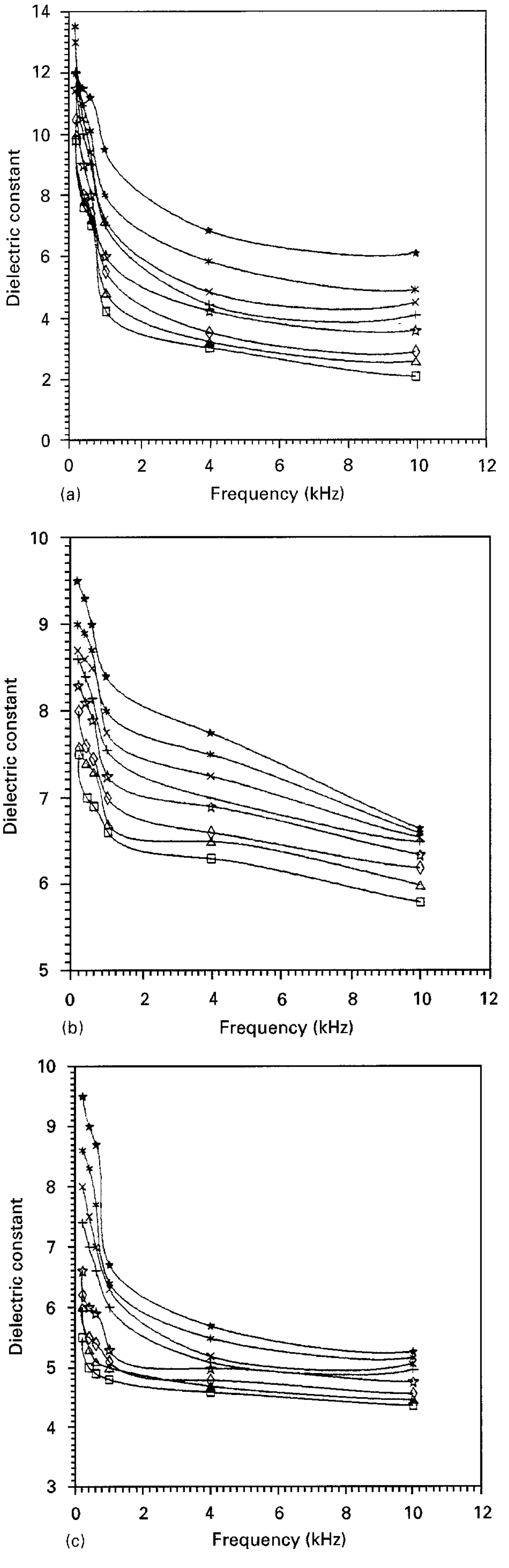

Figure 1 The dielectric constant as a function of frequency at the temperature; (□) 15 °C, (△) 30 °C, (◇) 50 °C, (☆) 70 °C, (+) 100 °C, (×) 130 °C, (∗) 160 °C and (★) 190 °C for the glasses (a) 80% TeO_2–20% MoO_3, (b) 70% TeO_2–30% MoO_3 and (c) 55% TeO_2–45% TeO_2.

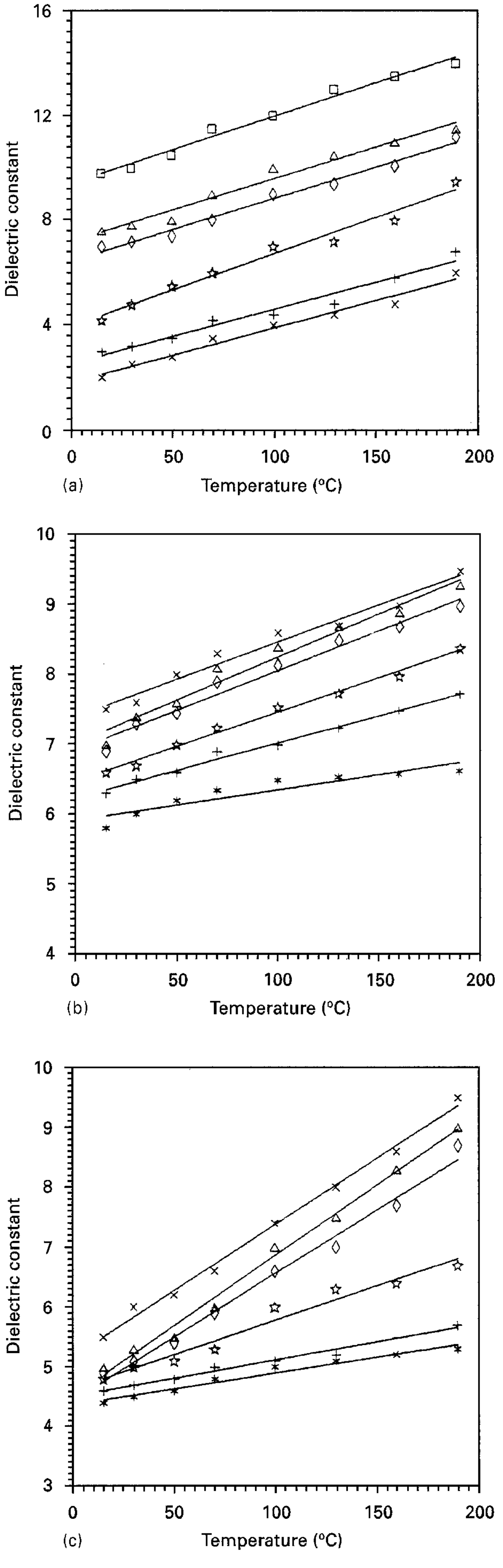

Figure 2 The temperature dependence of the dielectric constant measured at frequencies of: (□) 0.2 kHz, (△) 0.4 kHz, (◇) 0.6 kHz, (☆) 1.0 kHz, (+) 4.0 kHz and (×) 10 kHz on samples of (a) 80% TeO_2–20% MoO_3, (b) 70% TeO_2–30% MoO_3 and (c) 55% TeO_2–45% MoO_3.

7.5 to 5.5 for MoO_3 = 20, 30, and 45 mol % respectively. The dielectric constant has a negative $d\varepsilon/df$, and a positive $d\varepsilon/dT$ depending upon the percentage of MoO_3.

Whilst the data clearly shows that the dielectric constant decreases with increasing molybdenum content, it is not clear what causes this decrease. Two potential reasons can be identified by making use of the macroscopic Clausius–Mosotti equation

$$\frac{\varepsilon_s - 1}{\varepsilon_s + 2} = \frac{4\pi\alpha N_A \rho}{3M_g} \quad (1)$$

where, α, ρ, M_g, and N_A are the static polarizability, the density, the molar weight, and Avogadro's number, respectively. An increasing concentration of MoO_3 can affect either α or ρ/M. A plot of $(\varepsilon_s - 1)M_g/(\varepsilon_s + 2)$ against ρ (Fig. 3) should give a straight line of gradient $4\pi\alpha/3$, if the effect of molybdenum is to alter ρ/M_g. Unfortunately in the present studies we observe a nonlinear relationship in Fig. 3 which means that α has a real effect which produces these nonlinear results. This suggests that the MoO_3 does not alter the polarizability of TeO_2. A useful check for this would be to examine the position of pure TeO_2 [2]. The reduction of the dielectric constant for higher MoO_3 contents is due to a hopping process between TM atoms [5] rather than polarizing. Table I summarizes the static dielectric constants at room temperature for the tellurite glasses containing different MoO_3 contents and for comparison purposes data for the TeO_2–WO_3 glasses is also listed. The conclusion of a hopping process operating in these systems can be confirmed from Fig. 4, which shows the variation of static dielectric constant and dc electrical conductivity at room temperature for different TeO_2–MoO_3 glasses [4]. It is clear that a high MoO_3 content increases the electrical conductivity due to the higher number of TM ions in the glass which produces easier conditions for electron hopping and decreases the electrical polarizability. Fig. 5 shows a comparison between the static dielectric constant of pure TeO_2 glass [2] and the binary tellurite glasses TeO_2–WO_3 [2] and TeO_2–MoO_3. The WO_3 slightly decreases ε_s from 20.1 to 17.8, while MoO_3 decreases ε_s to approximately half of the value for the pure TeO_2 glass for the same mol % of modifier. This reduction in ε_s closely agrees with the values of the dc electrical conductivity of both glass systems σ_{dc} (TeO_2–MoO_3) = $9.9 \times 10^{-2}\ \Omega^{-1}\,cm^{-1}$ [4], σ_{dc} (TeO_2–WO_3) = $7.2 \times 10^{-4}\ \Omega^{-1}\,cm^{-1}$ [1]. Both the TM ions

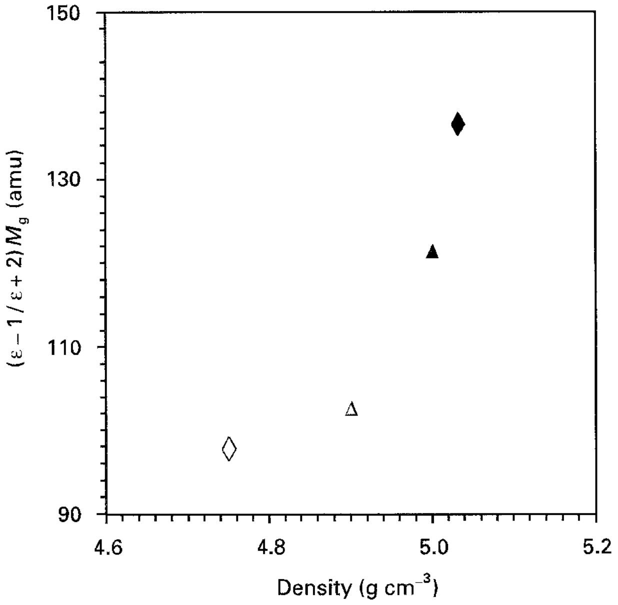

Figure 3 Plot of $[(\varepsilon - 1)/(\varepsilon + 2)]\ M_g$ against density for a series of TeO_2–MoO_3 glasses. The glasses shown are: (◆) pure TeO_2 [2], (▲) TeO_2 80% TeO_2–20% MoO_3, (△) 70% TeO_2–30% MoO_3 and (◇) 55% TeO_2–45% MoO_3.

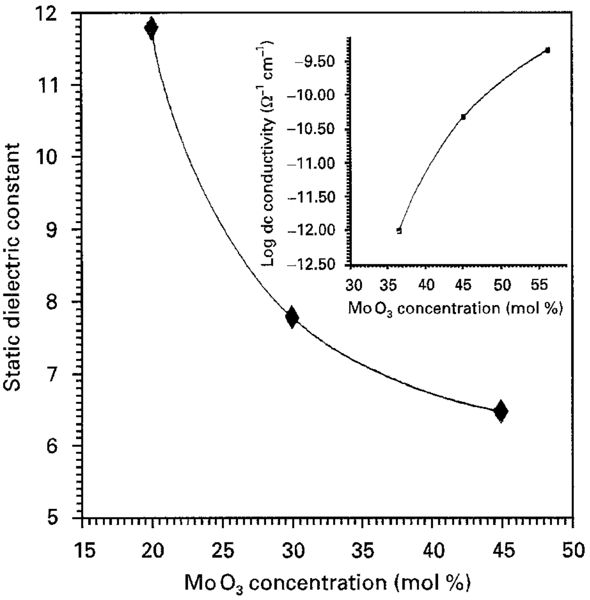

Figure 4 The static dielectric constant (290 K) as a function of molybdenum content and the static electrical conductivity of TeO_2–MoO_3 glass system.

TABLE I The composition, frequency and temperature dependence of the static dielectric constant of TeO_2–MoO_3 glasses and other selected vitreous tellurite glasses

Glass	Density (gm cm^{-3})	ε_s at 290 K	$d\varepsilon/df$ (Hz^{-1})	$d\varepsilon/dT$ ($\times 10^{-3}$ K^{-1}	$\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)M_g$	$\frac{10^{-5}\ d\varepsilon/dT}{(\varepsilon - 1)(\varepsilon + 2)}$
TeO_2 [2]	5.101	20.1	-6.2×10^{-7}	8.2	137.9	1.90
$(TeO_2)_{0.8}$–$(MoO_3)_{0.2}$	5.0 [5]	12.0	-41.2×10^{-5}	25	122.9	17.0
$(TeO_2)_{0.7}$–$(MoO_3)_{0.3}$	4.9 [5]	7.8	-16.6×10^{-5}	7.0	107.4	11.3
$(TeO_2)_{0.55}$–$(MoO_3)_{0.45}$	4.8 [5]	6.5	-3.3×10^{-5}	23	99.2	57.5
$(TeO_2)_{0.67}$–$(WO_3)_{0.33}$	5.7	17.8	-5.7×10^{-7}	6.3	156.1	2.10

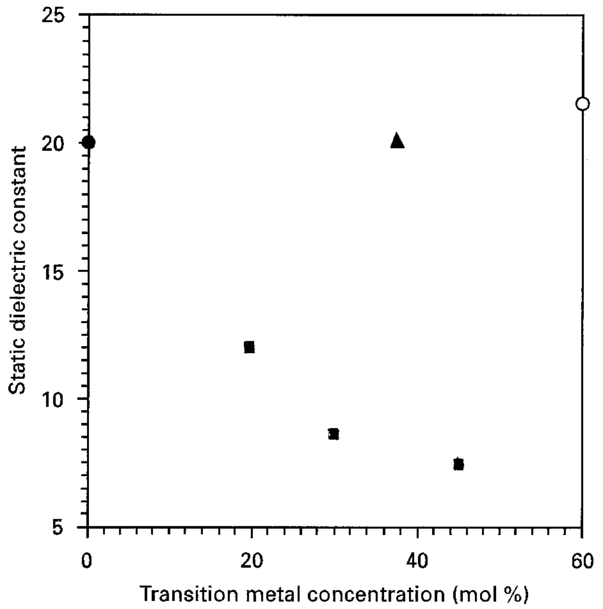

Figure 5 The static dielectric constant of; (■) TeO_2–MoO_3 glasses, and (●) pure TeO_2 and [2] (▲) TeO_2–WO_3 glasses.

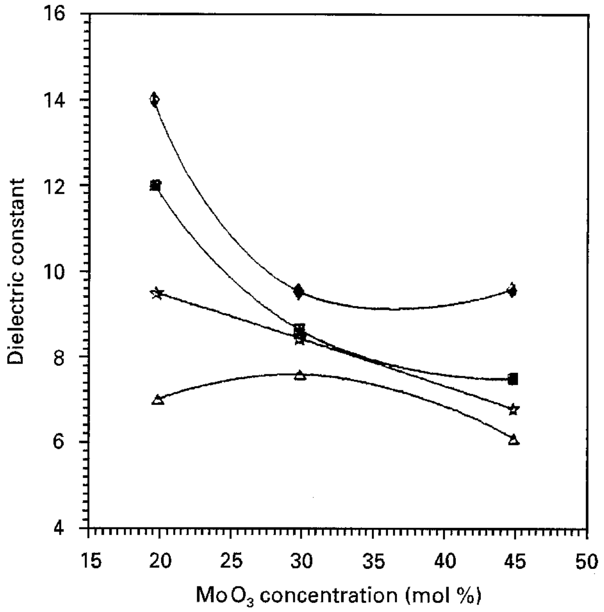

Figure 6 Static and high frequency dielectric constant of binary TeO_2–MoO_3 glasses, measured at; (□) f = 0.2 kHz, T = 100 °C, (△) f = 0.2 kHz, T = 190 °C, (◇) f = 1.0 kHz, T = 100 °C and (☆) f = 1.0 kHz, T = 190 °C.

prefer to be octahedrally co-ordinated however the TeO_2 network only contains tetrahedral sites. The presence of the octahedral ions inside the TeO_2 tetrahedral network creates non bridging oxygen ions (NBOI). As the NBOI replace bridging oxygen ions in the glass structure, the glass network is weakened, making ion displacement easier. The weakening of the glass structure with MoO_3 substitution is clear from the observed decrease in the Young's modulus [7]. We have quantitatively analysed in a previous publication [8] the high values of the elastic moduli [9] of TeO_2–WO_3 glasses in terms of high values of the stretching force constant of the W–O bond.

The temperature dependence of the dielectric constant at different frequencies for the TeO_2–MoO_3 glasses is shown in Fig. 2(a–c). This figure shows two features of interest; namely that the variations are linear with temperature, and also an increasing rate of change as the frequency decreases, that is especially true for higher MoO_3 content samples. This behaviour in the TeO_2–MoO_3 glasses has been previously reported for binary TeO_2–WO_3 glasses [2]. The present analysis will be based on Equation 2 [10] for an isotropic material at constant pressure.

$$\left[\frac{1}{(\varepsilon-1)(\varepsilon+2)}\left(\frac{d\varepsilon}{dT}\right)_p = \left[\frac{-1}{3v}\left(\frac{dv}{dT}\right)\right]_p + \left[\frac{v}{\alpha}\left(\frac{d\alpha}{3v_T}\right)\cdot\frac{1}{3v}\left(\frac{dv}{dT}\right)\right]_p + \left[\frac{1}{3\alpha}\left(\frac{d\alpha}{dT}\right)\right] = A + B + C \right. \tag{2}$$

where, v is the volume and the rest of notation is as before. The three constants A, B, and C have the following significance. A represents the decrease in the number of polarizable particles per unit volume as the temperature increase and it has a direct effect on the volume expansion; B relates to the increase in the polarizability of a constant number of particles as the available volume increases and C reflects the change in polarizability due to temperature changes at constant volume. It may be noted that the term A is inversely related to ε but both B and C are directly related to ε. It has been found that the sum $(A + B)$ is always positive [9] and hence it contributes to an increase of ε with increasing temperature. However, the factor C is negative for solids with $\varepsilon > 10$ whilst being positive for those with $\varepsilon < 10$. The experimental values of $[(\varepsilon - 1)\ (\varepsilon + 2)]^{-1}\ (d\varepsilon/dT)$ obtained for molybdenum tellurite glasses are given in Table I, together with data for other selected vitreous materials selected for comparison purposes. This positive behaviour can be attributed to the higher values of thermal expansion of TeO_2–MoO_3 glasses as compared to TeO_2 glass due to the presence of NBO atoms in the network. In addition, the increase in polarizability with the increase in available volume as the temperature raised is greater for these binary glasses than for pure tellurite glasses. The change in polarizability with temperature for a constant volume corresponding to process C appears to be small. Fig. 6 summarizes the behaviour of the dielectric constant for these binary TM tellurite glasses. It is clear that the dielectric constant for all compositions between frequencies of 0.2–1.0 kHz at a temperature of 190 °C are higher than those of 100 °C.

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Received 1 December 1994
and accepted 13 February 1996