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Frequency and temperature dependent conductivity spectra of mixed transition metal oxide doped semiconducting glassy system

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ABSTRACT

Frequency and temperature dependent conductivity of mixed transition metal oxide (TMO) doped semiconducting glassy system, xV_2O_5–(1 − x) ($0.05MoO_3$–0.95ZnO) have been investigated in the wide range of frequency and temperature. The dc conductivity (σ_{dc}), crossover frequency (ω_H), frequency exponent (n) and power law exponent (s) have been computed from the best fitted plots of experimental data. We have estimated the values of activation energy of ac conduction (E_{ac}) and free energy of polaron migration (E_H). Dc conductivity of the as-prepared samples shows thermally activated non–linear nature, which has been interpreted with Vogel–Tammann–Fulcher (VTF) model. From the fitting, pseudo activation energy (E_a) and thermodynamic ideal glass transition temperature (T_0) have been estimated. Nature of variation of conductivity and the power law exponent (s) data exhibit that non–overlapping small polaron tunnelling (NSPT) model is suitable to interpret these data for compositions x = 0.3, 0.5 and 0.7. On the other hand, correlated barrier hopping (CBH) model is most applicable mechanism for ac conduction for compositions x = 0.9 and 0.93. Formation of some complex Mo-O-V structures may be possible reason for applicability of CBH model for composition x = 0.9, 0.93. It is also observed that conductivity relaxation process of charge carriers (polarons) is independent of temperature, but depends upon composition.

1. Introduction

Transition metal oxide (TMO) doped glassy materials generally exhibit semiconducting properties [1–4]. These glassy materials are particularly important due to their engrossing applications such as switching, electro–chromatic devices, optical and memory switching devices, etc. [5–9] In glasses containing vanadium, the electrical conduction takes place by hopping of unpaired 3d [1] electron between V^{4+} and V^{5+} states [1,2]. Hopping of electron between Mo^{5+} and Mo^{6+} states in molybdate glasses [10,11] is responsible for electrical conduction. These unpaired electrons induce polarization around vanadium or molybdenum ions to form polarons [1,2,10,11] (quasi-particle). The transparent conducting oxide (TCO), ZnO has been widely used as window electrodes for flat panel displays, touch panels and solar cells because they exhibit good optical and electrical properties [12–14]. Additionally, it has also been widely used in piezoelectric transducers, varistors, gas sensor and optical waveguides [14,15]. Ac conductivity measurement [16–24] of semiconducting glassy system is a powerful tool to retrieve information of defect states present in the system and can also be used to understand the conduction process. Ac conductivity measurement usually uses to differentiate between free band conduction (dc conduction) and localized conduction. In most studies [16–24] it has been observed that the frequency dependent conductivity in amorphous glassy semiconductor exhibit sub-linear frequency dependence at low frequencies and temperatures. In localized conduction, the ac conductivity is frequency dependent, while in the free band conduction the conductivity is almost frequency independent. To explain the ac conduction mechanism, various models such as quantum-mechanical tunnelling model (QMT), [25,26] non–-overlapping small polaron tunnelling model (NSPT), [26] over lapping large polaron tunnelling model (OLPT), [27] atomic hopping model (AH), [26,27] and correlated barrier hopping (CBH) model [28,29] and also some other models [1,3,30,31] have been proposed by many scientists to interpret relaxation dynamics due to hopping or tunnelling of electrons or polarons.

In this paper, the ac conductivity of a glassy system, xV_2O_5–(1 − x) ($0.05MoO_3$–0.95ZnO) with x = 0.3, 0.5, 0.7, 0.9 and 0.93 has been investigated in the frequency range from 42 Hz–5 MHz and over a wide

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temperature range. Experimental findings regarding ac conduction have been analysed in terms of the existing theoretical models. It has been observed that non–overlapping small polaron tunnelling (NSPT) for glassy samples x = 0.3, 0.5, 0.7 and correlated barrier hopping (CBH) models for glassy samples x = 0.9 and 0.93 can be employed respectively to explain most dominant conduction mechanism.

2. Experimental procedure

TMO doped semiconducting glassy samples, xV_2O_5–(1 − x) ($0.05MoO_3$–0.95ZnO) for x = 0.30, 0.50, 0.70, 0.90 and 0.93 have been prepared using conventional melt quenching method [14] from reagent grade chemicals. The appropriate amounts of precursors vanadium pentoxide (V_2O_5) (purity 99.5%), molybdenum trioxide (purity 99.5%) and zinc oxide (ZnO) (purity 99.9%) have been thoroughly mixed and preheated in an alumina crucible and the mixtures are then melted in an electric muffle furnace in the temperature range from 820 °C to 970 °C depending upon composition. It is observed that as the content of V_2O_5 increases the melting temperature of as-prepared samples decreases. The melts have been equilibrated for 30 min and quenched between two aluminium plates. Non–transparent glassy flakes of thickness ~ 1 mm have been obtained. For electrical measurements, both sides of the samples are coated with silver paste to provide the electrodes. The parallel capacitance (C_P), conductance (G) and dielectric loss tangent (tan δ) of the as-prepared samples have been measured using HIOKI made programmable high precision LCR meter (model no: 3532–50) at various temperatures in the frequency range 42 Hz–5 MHz.

3. Results and discussion

The present glassy system is amorphous semiconductor [1–4], whose band gap energy has been estimated using UV–vis absorption spectra [32]. Here, the onset point of $(\alpha h\nu)^{1/2}$ versus hν curve (known as Tauc's plot) suggests that the present glassy system is indirect band gap semiconductor [32].

Fig. 1(a) shows typical conductivity spectra for composition x = 0.9 at various temperatures. Similar frequency (ω) and temperature (T) dependence conductivity have been observed for all as-prepared samples. The contour of frequency dependent conductivity reveals two distinct regions: (i) almost flat or plateau region and (ii) dispersion region. Plateau region is identified at lower frequencies, where conductivity σ (ω) is almost independent of frequency and the width of plateau region (low frequency range) goes on increasing as temperature increases. However, dispersion region is detected at higher frequencies, where conductivity (σ (ω)) shows highly dependence on frequency, which is the characteristic feature of power law [33–35]. The width of dispersion region (high frequency range) is observed to decrease with increase in temperature. In general, the ac conductivity of many materials shows following power law, proposed by Almond–West [33–35]

$$\sigma(\omega) = \sigma_{dc}\left[1 + \left(\frac{\omega}{\omega_H}\right)^n\right] \quad (1)$$

where, σ_{dc} is dc conductivity, ω_H is hopping or crossover frequency separating dc regime (plateau region) from the dispersive conduction regime and n is the frequency exponent. The values of σ_{dc}, ω_H and n are obtained from the non–linear curve fitting (best fitting) of conductivity spectra using Eq. (1) as shown in Fig. 1(a). The values of σ_{dc} and ω_H at temperature 543 K and average value of ‘n’ are presented in Table 1 for all compositions. In Fig. 1(a), solid lines represent are the non–linear best fitted curves of experimental data using Almond–West power law as indicated in Eq. (1). In view of this discussion, ac conduction in the present glassy system may be achieved due to hopping mechanism [36]. In Almond–West formalism, ‘n’ is the dimensionality parameter [24], which is also associated with charge carrier conduction. The frequency

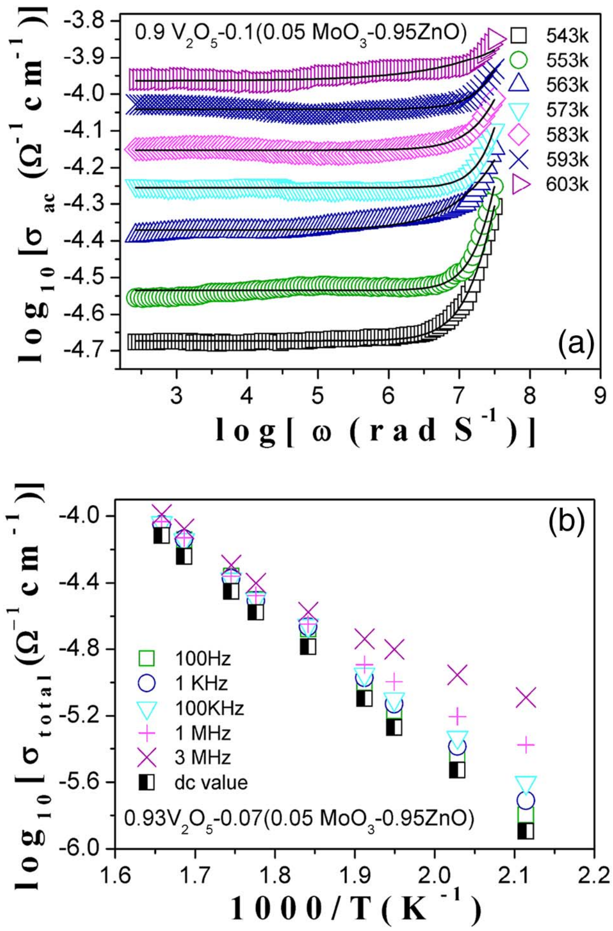

Fig. 1. (a) Measured ac conductivity (log σ_{ac}) for xV_2O_5–(1 − x) ($0.05MoO_3$–0.95ZnO), x = 0.90 glass composition, shown as function of frequency (log ω) at different temperatures. The solid lines in the figure are the best fits obtained from fitting of experimental data with Almond–West power law (Eq. (1)); (b) measured total conductivity (σ_{total}) for xV_2O_5–(1 − x) ($0.05MoO_3$–0.95ZnO), x = 0.93 glass composition, shown as a function of inverse of temperature at five different frequencies. Dc conductivity data are also included for comparison.

exponent (n) value usually suggests diffusion [24] of charge carriers in random charge conducting paths. It may be stated that the dispersion in the ac conductivity is influenced by the dimensionality of the charge carrier [24], which is manifested by the frequency exponent (n). The frequency dependence of ac conductivity corresponds to the hopping of charge carriers (polarons) in short range order between neighbouring sites separated by energy barriers of different heights. If hopping takes place between random distributions of localized charge states, “n” value lies between 0.5 and 1 (Ref. [24]). The lower value of n generally occurs for multiple hops [24] while the higher value of n occurs for single hops [24] and it indicates a strong drift [24] of charge carriers (polarons). It may be concluded from above facts that due to this morphological dispersion, intersite potential energy barriers may change considerably, which may result to thoroughly rise in hopping rates of charge carriers (polarons).

The measured total conductivity (σ_{total}) at five different frequencies is presented in Fig. 1(b) as a function of reciprocal temperature for composition x = 0.93. The dc conductivity (σ_{dc}) is also included in the Fig. 1(b) for comparison. It is observed in Fig. 1(b) that at low temperatures, σ_{total} is thermally activated in nature. It is also noted in Fig. 1(b) that at the low temperature, frequency dependency of σ_{total} plays dominant role, but at high temperature, frequency dependency of σ_{total} becomes insignificant. Total conductivity (σ_{total}) for all the composition has been plotted with reciprocal temperature at a fixed frequency 100 KHz in Fig. 2(a). The activation energy for ac conduction