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THE AC CONDUCTIVITY OF SAMARIUM PHOSPHATE GLASSES

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Abstract:

The ac conductivity of σ_{ac} samarium phosphate glasses with different Sm_2O_3 content is measured in frequency range of 10^3 to 10^7 Hz over the temperature range of 300 to 553 K. The observed frequency dependence can be expressed as $\sigma_{ac} = A \omega^s$, where $0.6 < s < 1$ which confirms the electron hopping phenomena. The bulk conductivity increases with increasing temperature and decreases with the increasing neodymium content.

1. Introduction

Phosphate glasses have been developed for a variety of applications. Rare-earth containing metaphosphate glasses possess high stimulated emission cross-section and low thermo-optical coefficients and are primary host materials for high power laser applications [1]. There are numerous publications on the electrical properties of phosphate glasses especially those containing rare-earth oxide [2-4]. In this paper, we report on the synthesis and ac conductivity measurement of 5 samples of binary samarium phosphate glasses $(x)\text{Sm}_2\text{O}_3$ $(1-x)\text{P}_2\text{O}_5$ with x varying from 0.05 to 0.25 in steps of 0.05. Phosphorous pentoxide P_2O_5 with low melting point was chosen as the glass former and Sm_2O_3 was introduced as network modifier. The presence of Sm_2O_3 would induce changes in network structure and bonding by reacting with the glass former [5].

2. Experimental Procedure

2.1. Glass preparation

Neodymium copper phosphate glasses of general formula Sm_2O_3 - P_2O_5 can be prepared by melting mixtures of high-purity dry samarium oxide with phosphorus pentoxide P_2O_5 in preweighed proportions in a closed platinum crucible of 80 cm^3 capacity. The batch was heated first at 500 $^\circ\text{C}$ for 1 h in order to reduce any tendency toward volatilization and then in an electrical furnace and held at 1450 $^\circ\text{C}$ for 2 h. The glass melts were stirred occasionally using an alumina rod to ensure homogeneous melts. The highly viscous melt was cast into a hot steel split mold. The glass produced was annealed at 500 $^\circ\text{C}$ in a second furnace for 3 h. The density of the glass samples was measured by a simple Archimedes process using toluene as an immersion liquid. The amorphous nature of the samples was checked by X-ray diffractometer which revealed no discrete lines, indicating a high degree of amorphous glassy state.

2.2. Electrical conductivity measurements

For the measurements of the a.c. conductivity, the sample with 1-2 cm in diameter and 0.3-0.4 cm thick was polished with two parallel faces. The cell constructed for the electrical measurements consists of silica tube surrounded by nickel chrome wire as a heater. A Chromel-Alumel thermocouple (type K) was surrounded by metallic shielding to remove noise.

Silver electrodes were painted on both side of the samples to give good ohmic contacts. The A.C. conductivity was measured using a Agilent impedance analyzer type 3192 A. LF which gave a digital read-out of capacitance of the sample for an a.c. input signal of 500 mV, r.m.s applied across it. The frequency could be varied over the range of 5 Hz to 13 MHz. All measurements were measured over a temperature range of 303 – 573 K. The Arrhenius plot was later done for each sample. The electrical conductivity was calculated using the following formula [6-7].

$$\sigma = d / AR = Gd / A$$

where d is the thickness of the glass sample, A is the cross section area and R is the resistance and G

the reciprocal of resistance.

3. Results and Discussion

3.1. The a.c. conductivity as a function of frequency

Table 1 shows a typical glass composition that has been made. The value of s are also inserted.

The frequency dependence $\sigma(\omega)$ at various temperatures is shown in Fig. 1 for all compositions results were similar. As can be seen, the dependence satisfies the following universal empirical relation of: $\sigma_{ac}(\omega) = A\omega^s$, where A is the temperature dependent constant and the frequency exponent s is less than or equal to 1 [8]. From this figure, it is seen that, the a.c. conductivity increases linearly with the increasing frequency for all compositions on different temperature.

From the measurements of the variation of the a.c. conductivity with frequency at different temperatures, the value of s which can be taken as, the slope of the linear dependence of $\log \sigma$ versus $\log \omega$, can be obtained. The estimated frequency exponent s is tabulated in Table 1 and shown in Fig. 2 as a function of temperature. The exponent s decreases with increasing temperature. The numerical values of s are found to be in the range $0.6 < s < 1$, which are closely associated with hopping mechanism [9]. Mansingh and Dahwan [10] analyzed the σ_{AC} in light of different theoretical model based on QMT and HOB models explain the data quantitatively.. A linear dependence of the σ and temperature dependence s at low temperatures with a nonlinear increase of σ at the higher temperatures for higher frequencies agrees respectively with QMT and HOB models.

3.2. The a.c. conductivity as function of temperature

Experimental results of the temperature dependence of the a.c. conductivity as a function of temperature in the range 423 K to 553 K for various compositions are measured and the results are shown in Figure 3 for $(x)\text{Sm}_2\text{O}_3$ $(1-x)\text{P}_2\text{O}_5$ glass. It is shown at higher frequency (> 60 kHz) the conductivity of the glass changes with frequency. This may be due to the hopping of electrons controlled by the electric field, in addition to the thermal excitation energy in the low-temperature range and was attributed to band-to band transitions or hopping over a barrier in the higher temperature range. Many different models have been proposed to clarify the mechanism of the a.c. conductivity in many disordered materials. The quantum mechanical tunneling (QMT) model was first proposed by Pollack and Geballe [10] to interpret impurity conduction in n-type silicon. In this model, the exponent s is temperature and frequency dependent. This in contrast with the present result. The correlated barrier hopping (CBH) model proposed by Elliot [11] has been applied to the glassy semiconductors. In this model, electrons in the charged defect state hop over the Coulombic barrier, and the exponent s is predicted to be frequency and temperature dependent, with s increasing towards unity. Therefore the CBH model might be an appropriate theory for the a.c. conduction in $(x)\text{Sm}_2\text{O}_3$ $(1-x)\text{P}_2\text{O}_5$ and the conduction σ would operate by an interstitial pair mechanism between nonbridging oxygens.

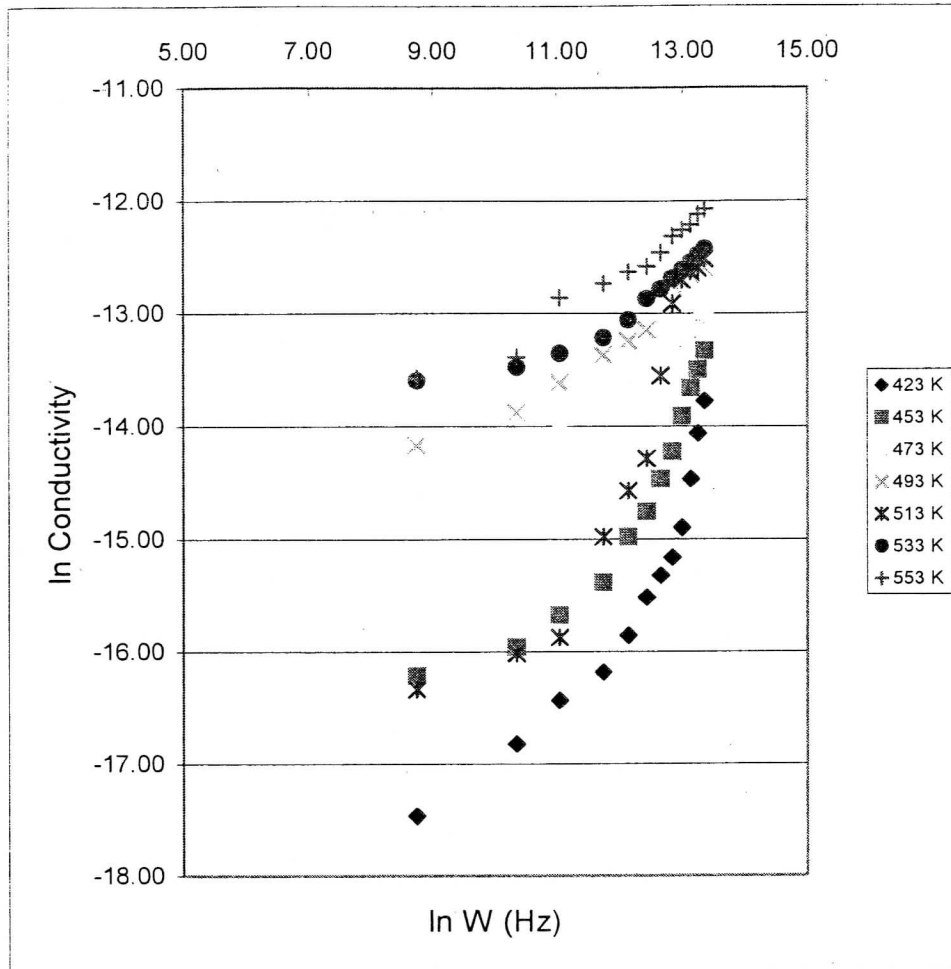


Figure 1. \ln Conductivity, σ versus \ln frequency, ω for 10 Sm_2O_3 -90 P_2O_5

Table 1. Typical glass composition and the value of s for binary samarium phosphate glasses

Glass Composition	S
5 Sm_2O_3 -95 P_2O_5	0.654-0.97
10 Sm_2O_3 -90 P_2O_5	0.648-0.943
15 Sm_2O_3 -85 P_2O_5	0.64-0.84
20 Sm_2O_3 -80 P_2O_5	0.628-0.987
25 Sm_2O_3 -75 P_2O_5	0.626-0.933

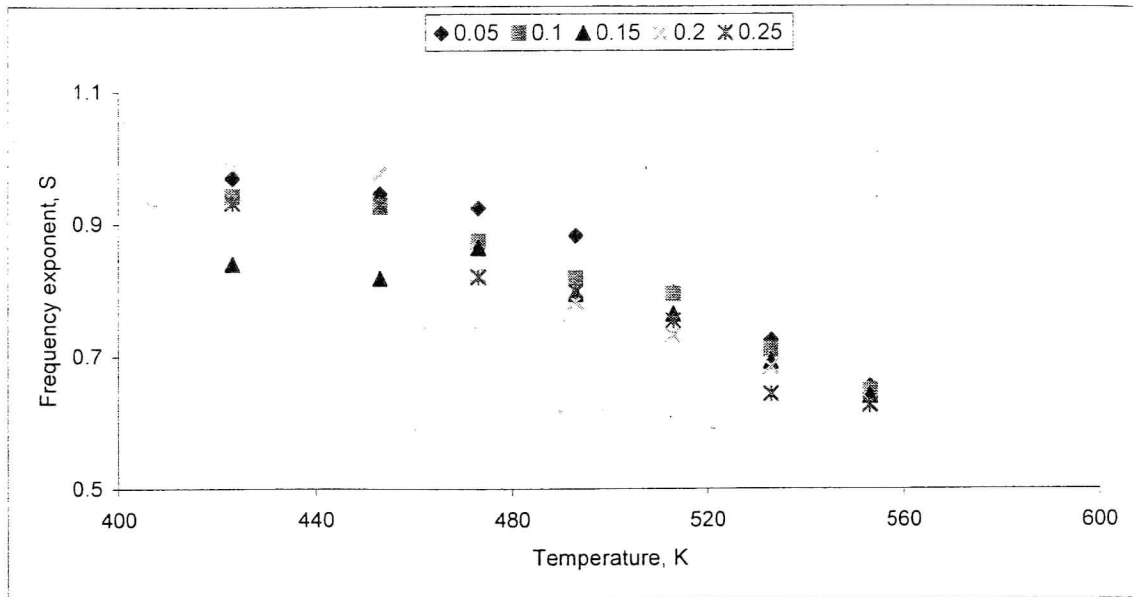


Fig. 2. Variation of the frequency exponent s with temperature for $(x)\text{Sm}_2\text{O}_3 (1-x)\text{P}_2\text{O}_5$ glass system

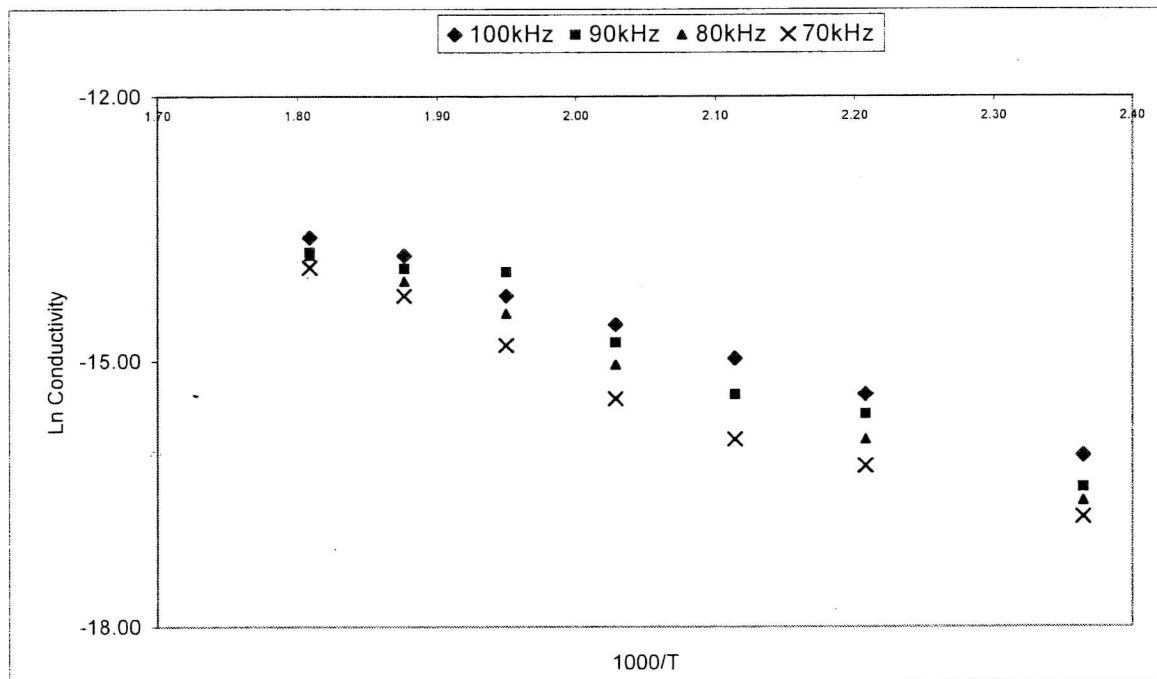


Figure 3. \ln Conductivity, σ versus inverse temperature for 10 Sm_2O_3 -90 P_2O_5

Conclusion

The measurements of a.c. conductivity of the semiconducting samarium phosphate glasses in the temperature range 423 – 553 K have been reported. The power law $\sigma_{ac}(\omega) = A\omega^s$ represents the experimental data rather well over a wide frequency range. By applying various conduction models to describe the a.c. conductivity in amorphous semiconductors in the present glass system, it is found that the correlated barrier hopping model is the most appropriate one

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