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NOTE

Electrical Conduction in Solution Grown Thin Films of the Complex of Fe(II) with Cyclodichlorophosphazene Trimer

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Current transport mechanism in thin films of the complex of Fe(II) with cyclodichloro phosphazene trimer (PNCl₂)₃ have been studied under normal and different illuminating conditions. It is found that at low fields film exhibit an ohmic behaviour and high field region is dominated by Poole-Frenkel (PF) type mechanism.

Key Words: Cyclodichlorophosphazene trimer, Thin films, Electrical conduction.

Recently conduction in thin films of inorganic heterocyclics like cyclohexathiazenium chloride $(S_6N_4)^{2+}$ Cl^{2–} and cyclodichlorophosphazene trimer (PNCl₂)₃ have been studied^{1,2}. In view of this a new complex of (PNCl₂)₃ with FeSO₄ has been prepared and investigated for its electrical conduction under normal and illuminating conditions with sodium and mercury light.

The complex of Fe(II) with $(PNCl_2)_3$ was prepared³ by refluxing an equimolar solution of $(PNCl_2)_3$ and FeSO₄ in ethanol for about 24 h. Light brown coloured precipitate formed was separated and washed with ethanol for removal of unreacted reactants. The complex has the composition⁴ $[P_3N_3Cl_3FeCl_3]SO_4$. The films of the complex of FeSO₄ with $(PNCl_2)_3$ were deposited on to a ultrasonically cleaned glass slides in a benzene solution, maintained at 305 K using isothermal immersion technique⁵. The film was vacuum dried for about 8.64×10^4 s to remove any residual solvent. The thickness of the film was measured by means of mechanical stylus arrangement. A bare copper wire was placed across the film of the complex on the glass slide prior to vacuum deposition of copper electrode. After deposition the copper wire was removed and a width of 0.15 cm between the two electrodes was obtained.

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Illumination of the film were done with the help of 60 watt sodium lamp and 80 watt mercury lamp. The sodium light intensity was 44.17 w/cm² and mercury light intensity 58.89 W/cm². I-V characteristics of thin film have been measured as described elsewhere⁶.

Fig. 1 shows I-V characteristics of $[P_3N_3Cl_3FeCl_3^-]SO_4$ film under normal and different conditions of illumination. Films were illuminated with sodium and mercury light of intensity 44.19 W/cm² and 58.89 w/cm², respectively. It is seen from these curves that magnitude of current depends upon the type of illumination. The log I-log V plots are mostly linear in nature in low fields for all the 3 films. Normal, sodium and mercury light illuminated films show two types of conduction. The calculated value of slope in the low field region is *ca*. 1 for all the 3 curves. This shows that Ohm's law holds good in low field region. Thin films illuminated under normal, sodium and mercury light have slope *ca*. 0.71, *ca*.1.29 and *ca*. 0.94, respectively in the high field region. Plots of thin films illuminated under normal conditions, sodium light and mercury light are the same (Fig. 1) in the lower voltage region due to independence of velocity of charge carriers on applied field.

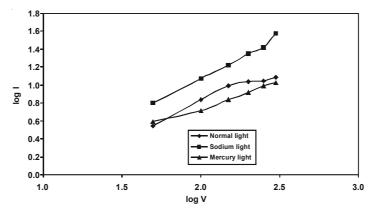


Fig. 1. Plot of log I (μA) vs. log V of [P₃N₃Cl₃FeCl₃⁻]SO₄⁻ thin film illuminated under different conditions

The data of Fig. 1 were replotted on semi log plot as log I vs. $v^{1/2}$ for all three films (Fig. 2). The log I vs. $V^{1/2}$ plots show linearity in high field region. This observation shows that current in this region obeys I $\propto \exp(\beta v^{1/2})$ where β is a constant. Such a dependence of current on voltage will only be observed⁷ if the high field conduction is being governed either by Richardson Schottky (RS) or Poole-Frenkel (PF) effect, the only point of distinction between the two being the values of β *i.e.* $\beta_{PF} = 2\beta_{RS}$. The theoretical value of β have been calculated by Schottky relation.

$$\beta_{\rm RS} = (e^3/4\pi\epsilon_0\epsilon_r)^{4}$$

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where e is the electronic charge, ε_r is the dielectric constant of the complex and ε_0 is the permittivity of free space. We have used: $e = 1.6 \times 10^{-19}$ coulomb, $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m, $\varepsilon_r = 3.63$, calculated value of $\beta_{RS} = 3.18 \times 10^{-24}$.

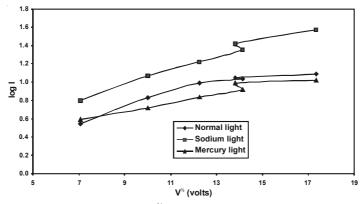


Fig. 2. Plot of log I (μ A) vs. V^{1/2} of [P₃N₃Cl₃FeCl₃⁻]SO₄⁻ thin film illuminated under different conditions

The experimental value of β obtained from slopes of log I vs. v^{1/2} plots by using the relation $\beta = kTx$ slope are less than the calculated value of β *i.e.* $\beta = 2\beta_{RS}$ for the dielectric constant 3.63 of [P₃N₃Cl₃-FeCl₃⁻]SO₄ films suggest that PF mechanism of conduction at high field for all the three films (Table-1).

TABLE-1 VALUE FOR β FROM THE SLOPES OF log I vs. v^{1/2} PLOTS Film illumination Film under normal Film illuminated Temp. condition with sodium light with mercury light (K) Slope β Slope β Slope β 305 0.00037 $1.5 imes 10^{-24}$ 0.00069 2.90×10^{-24} 0.00050 2.1×10^{-24}

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