



RAST - 17

ENHANCEMENT OF ELECTRICAL CONDUCTIVITY IN POLYVINYL ALCOHOL FILMS BY DOPING WITH Nd³⁺ IONS

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Abstract

The electrical properties of polyvinyl alcohol (PVA) films have been improved pronouncedly by doping with Neodymium (III) nitrate hexahydrate. Pure PVA and PVA: Nd³⁺ films have been prepared by solution casting method. Both type of films were characterized by X-ray diffraction technique for structural studies. XRD pattern shows the appreciable shift of 2 θ towards higher value with increase in Nd³⁺ concentration. This signifies the presence Nd³⁺ dopant in polymer matrix. Further direct current electrical conductivity (σ) of Nd³⁺ doped PVA films in the temperature range 50⁰C-160⁰C has been studied using four probe techniques. For a given concentration σ increases with increase in temperature and with dopant concentration. At 120⁰C, conductivity of PVA: Nd³⁺ (10 mol %) film is 7.116 $\mu\Omega^{-1}\text{cm}^{-1}$, PVA: Nd³⁺ (15 mol %) film is 11.176 $\mu\Omega^{-1}\text{cm}^{-1}$, PVA: Nd³⁺ (20 mol %) film is 17.418 $\mu\Omega^{-1}\text{cm}^{-1}$ and PVA: Nd³⁺ (25 mol %) film is 23.740 $\mu\Omega^{-1}\text{cm}^{-1}$. This result indicated the enhancement of the electrical conductivity of PVA films with Nd³⁺ concentration.

Keywords: Polyvinyl Alcohol; Nd³⁺ Ions; DC Electrical Conductivity.

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1. Introduction

Ion conduction in polymers was reported for the first time in 1973. Ion doped polymers finds applications in Solid polymer electrolytes. These electrolytes have tremendous technological promise to develop all-solid state electrochemical power sources, due to their flexible, compact, light-weight, good mechanical strength and optical properties [1].

Polyvinyl alcohol (PVA) is semicrystalline, water soluble, with low electrical conductivity polymer [2]. PVA has certain physical properties resulting from crystal-amorphous interfacial effects. Its electrical properties can be tailored to a specific requirement by the addition of suitable dopant material. Depending on the chemical nature of the doping substances and the

way in which they interact with the host matrix, the dopant alters the properties to different degrees.

2. Materials and Method

Polyvinyl alcohol and Neodymium (III) nitrate hexahydrate used in this work have been taken from Sigma-Aldrich Company. Pure polyvinyl alcohol and PVA: Nd³⁺ (10, 15, 20 and 25 mol %) films were prepared by the solution casting method. Required quantity of PVA was dissolved in double distilled water and then heated gently, using water bath. Also required quantity Neodymium (III) nitrate hexahydrate was dissolved in doubly distilled water to get the 10, 15, 20 and 25 mol% concentration of Nd³⁺. Both the solutions were mixed with each other and stirred thoroughly with a magnetic stirrer. This solution was kept aside to get a suitable viscosity. Known quantity of obtained solution was poured on to a leveled clean glass plate and left to dry at room temperature. After 24hrs, the films were peeled off from the glass plate and kept in vacuum desiccator [3].

3. Results and Discussions

3.1. XRD Analysis

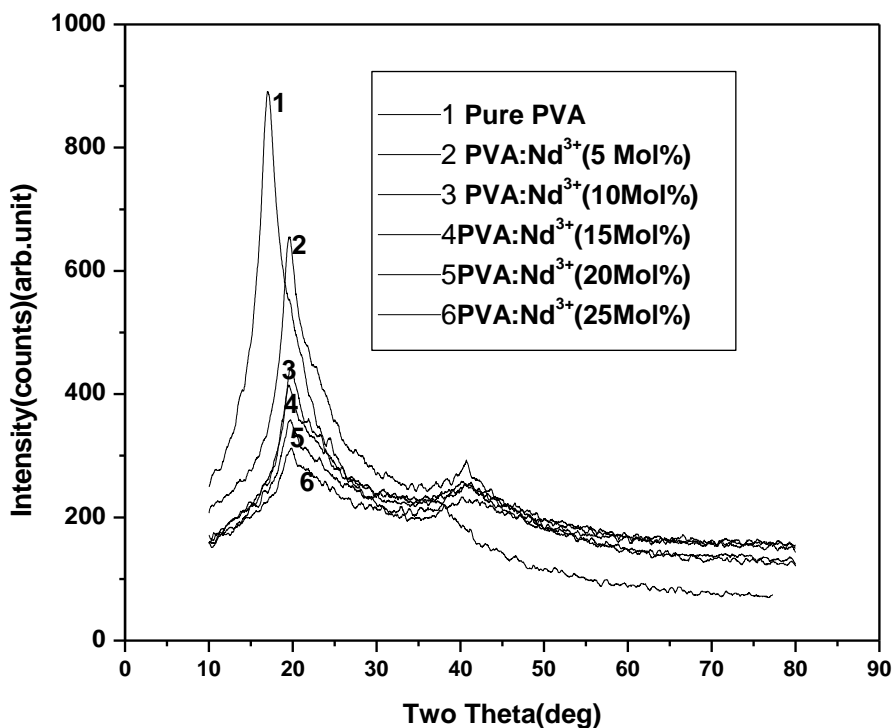


Figure 1: X- ray diffractograms of Pure PVA and PVA: Nd³⁺ (10, 15, 20 and 25 mol %) films

Fig.1. shows the XRD pattern of the pure PVA and PVA:Nd³⁺ (10,15,20 and 25 mol%) films. XRD pattern of Pure PVA displays two sharp reflections at $d=5.2097 \text{ \AA}$ and 2.4051 \AA [4]. The diffraction spacing for PVA: Nd³⁺ films are similar to PVA but the peaks are less in intensity level. The obtained peaks are sharp enough and appears at $d=4.5016 \text{ \AA}$ and 2.219 \AA (for 10 mol %), $d=4.5481 \text{ \AA}$ and 2.241 \AA (for 15 mol %), $d= 4.5240 \text{ \AA}$ and 2.209 \AA (for 20 mol %), $d=$

4.4676 \AA^0 and 2.2403 \AA^0 (for 25 mol %) respectively. The drop in the intensity of XRD pattern indicated an increase in the amorphosity of PVA. Hence it is evident that interaction of Nd^{3+} ions occurs in the PVA matrix which brings about the disorderliness in the polymer chain molecular arrangement.

3.2. DC Electrical Conductivity

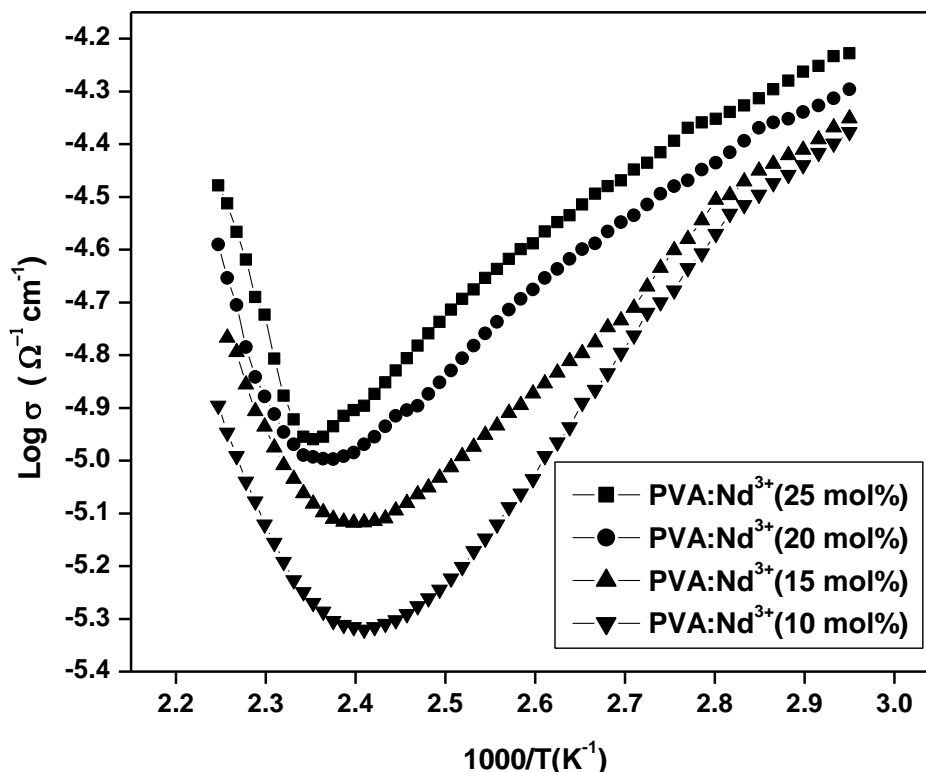


Figure 2: Variation of electrical conductivity of PVA: Nd^{3+} (10, 15, 20, 25 mol %) with temperature

Fig.2. shows the dc conductivity of PVA: Nd^{3+} films versus temperature with various mole percentages such as (10, 15, 20, and 25 mol %). It is observed that the conductivity (σ) decreases with increase temperature as well as the dopant concentration after which the conductivity increases. This can be observed in the figs .2. Addition of Nd^{3+} ions in PVA matrix generally increases the electrical conductivity [5]. This is due to the Nd^{3+} ions coordinated through ionic bonds with hydroxyl group belonging to the different chains in PVA. This reduces the intermolecular interaction between the PVA molecules and increases the required volume for ionic carriers to drift in the polymer matrix. This enhances the ionic mobility and hence increases in conductivity. At high temperature, Conductivity (σ) may be due to the liberation of electrons or ions through the amorphous region of PVA and also probably the internal stress in the doped PVA. At low temperature, Conductivity (σ) is due to semicrystalline nature of PVA. For each dopant the minimum conductivity is due to the phase transition of PVA from semicrystalline to amorphous.

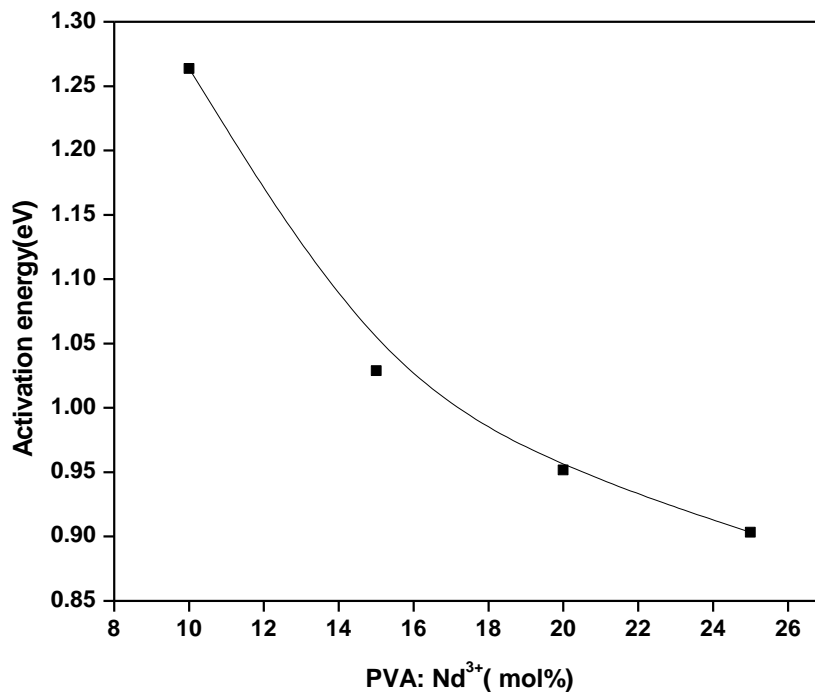


Figure 3: Variation of activation energy of PVA: Nd³⁺ (10, 15, 20, 25 mol %) films.

The thermal activation energy E_a can be estimated from the slope of $\log \sigma$ versus $1/T$ plot using $\sigma = \sigma_o \exp (-E_a / kT)$ relation [5], Where σ_o is a constant, E_a is the activation energy of electrical conduction, k is the Boltzmann's constant and T is the temperature. Fig.3. shows the variation of activation energy of PVA: Nd³⁺ and it is obvious that the values of the activation energy decreases with increase in dopant concentration. The decrease in activation energy upon doping with Nd³⁺ can be explained as being due to the formation of molecular aggregates. The charge carriers become more localized, which gives the increase in the trapped carrier density. These molecular aggregates results to the inhomogeneous distribution of the dopant as well as the nonbonding part of the dopant.

4. Conclusions

XRD pattern indicated the presence of Nd³⁺ dopant in polymer matrix. Dopant reduces the intermolecular interaction between the PVA molecules and increases the required volume for ionic carriers to drift in the polymer matrix hence increase in conductivity. At high temperature conductivity may be due to the liberation of electrons or ions through the amorphous region of PVA and at low temperature conductivity is due to semi crystalline nature of PVA.

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