



Optical and electrical properties of cobalt chloride doped polyvinylalcohol polyvinylpyrrolidone blend

R. V. Patil, M. R. Ranganath, and Blaise Lobo

Citation: [AIP Conference Proceedings](#) **1591**, 183 (2014); doi: 10.1063/1.4872537

View online: <http://dx.doi.org/10.1063/1.4872537>

View Table of Contents: <http://scitation.aip.org/content/aip/proceeding/aipcp/1591?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Optical, electrical, thermal properties of cadmium chloride doped PVA – PVP blend](#)

AIP Conf. Proc. **1665**, 070037 (2015); 10.1063/1.4917901

[Structural and optical properties of Ag and Co doped ZnO nanoparticles](#)

AIP Conf. Proc. **1447**, 431 (2012); 10.1063/1.4710064

[Correlation between electrical transport, optical, and magnetic properties of transition metal ion doped ZnO](#)

J. Appl. Phys. **103**, 07D108 (2008); 10.1063/1.2834443

[Structural, magnetic, and magneto-optical properties of Co-doped Ce O 2 – \$\delta\$ films](#)

J. Appl. Phys. **103**, 07D138 (2008); 10.1063/1.2833839

[Electrical properties of Co-doped \$\beta\$ - FeSi 2 crystals](#)

J. Appl. Phys. **89**, 3798 (2001); 10.1063/1.1350996

Optical and Electrical Properties of Cobalt Chloride Doped Polyvinylalcohol Polyvinylpyrrolidone Blend

R V Patil¹, M R Ranganath² and Blaise Lobo^{2,*}

¹Department of Physics, Bangalore University, J.B Campus, -Bangalore 560056, India

²Department of Physics, Karnatak Science College, Karnatak University, Dharwad 580001, India

*E-mail:blaise.loblo@gmail.com

Abstract. Films of Cobalt Chloride Doped Polyvinylalcohol – Polyvinylpyrrolidone blend were prepared by solution casting method, in the doping range 0 wt% up to 42 wt%. These films were characterized by XRD, UV-Visible spectrometry, FTIR, thermal analysis and electrical measurements. The films were semi-crystalline, with an average crystallite size of few nanometers. The optical band gap due to indirect allowed transitions (in k-space) decreases from 4.6 eV for 1.5 wt% doping level to 4.0 eV at 35 wt% doping level. In addition, absorption peaks were observed at 2.3 eV, 3.0 eV and 1.7 eV, which indicate that doping results in formation of allowed energy bands within the forbidden gap. The Urbach energy, which measures the width of band tails within the forbidden gap, is found to significantly decrease with increase in doping level. DC electrical measurements show a good fit for 3-D Variable Range Hopping model of conductivity. The temperature variation of electrical resistivity obeys the Arrhenius relation, from which the activation energy obtained is found to decrease from 4.1 eV for 1.5 wt% doping level to 3.1 eV for 19 wt% doping level.

Keywords: Doping, polymer blend, Cobalt chloride, Activation Energy, Optical Band gap

PACS: 61.25.hk, 78.40.-q, 61.43.-j, 72.80.Ng, 78.20.Ci

INTRODUCTION

Polyvinylalcohol (PVA) is a polymeric material which is of significant interest due to its ease of processability and potential applications. PVA doped with different redox agents like iodine, ferric chloride have been studied, and these samples show significant modification of structural, optical and electrical properties [1-5]. The miscible blend of PVA with polyvinylpyrrolidone (PVP) has also been studied by researchers [6]. Cobalt chloride (CoCl_2) has a potential to significantly modify the dielectric and optical properties of a material [7]. The structural properties of the PVA-PVP blend are expected to change on incorporation of CoCl_2 . Usually, at low concentrations of CoCl_2 , it is expected that there is molecular level distribution of dopant in the host polymeric matrix (PVA-PVP blend). The increase in CoCl_2 concentration to moderate levels is expected to result in cluster formation and molecular aggregation of the dopant. At higher levels of doping, the material is expected to undergo a phase separation into a polymer rich region and a cobalt chloride rich region.

This paper presents the details of preparation, characterization, electrical and optical investigations

on cobalt chloride doped polyvinylalcohol (PVA) – polyvinylpyrrolidone (PVP) blend. It is found that cobalt chloride (CoCl_2) is a promising dopant material for modifying the optical properties, causing major modifications in the band structure of the polymeric blend. After preparation of cobalt chloride doped blend of polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP) and its characterization, the quantitative analysis of the optical spectra revealed significant changes like energy levels incorporated into the band gap of PVA-PVP blend. Electrical properties revealed interesting variation of the activation energy with dopant level. The Mott's Variable Hopping model in three dimensions was able to fit with the data on the temperature variation of electrical conductivity in this sample.

EXPERIMENTAL

The films of PVA-PVP- CoCl_2 blend were prepared by solution casting method. Films having different concentrations (doping levels) of CoCl_2 were prepared. A standard 1M doping solution of cobalt chloride in distilled water was prepared, and different volumes of this solution were added to two grams

Solid State Physics

AIP Conf. Proc. 1591, 183-185 (2014); doi: 10.1063/1.4872537

© 2014 AIP Publishing LLC 978-0-7354-1225-5/\$30.00

each, of an aqueous solution of PVA and PVP which was prepared earlier, and the same was stirred magnetically, and later placed in an air cooled temperature controlled oven, maintained at 40 degree Celsius. The films were slowly dried on flat glass petri-dishes, and were later peeled off. Since the films were highly hygroscopic, they were stored in a dessicator. The powder XRD spectra were recorded using Rigaku X-ray Spectrometer. The samples prepared were semi-crystalline in nature, with an average crystallite size of a few nanometers.

A Hitachi U 3310 UV-Visible spectrometer was used in the wavelength range 200-1000 nm for obtaining the Optical absorption (UV-Visible) spectra. The spectra were recorded at room temperature, using dry films, removed from the dessicator just before exposure to light in the spectro-photometer. The spectra were analyzed to extract optical parameters like activation energy, optical band gap and Urbach energy. The energy width of tails of localized states in the forbidden band gap (E_u) was evaluated using the Urbach edges method and the activation energy (E_a) was calculated from the wavelength (λ_g) corresponding to the absorption band edge. It was observed that the absorption coefficient is a function of photon energy, and obeys Mott-Davis model [8].

An arrangement for temperature variation (PID Controlled oven/ furnace) of polymer samples has been used with a temperature controller accurate to one degree celsius for the study of temperature variation of electrical conductivity, using two-probe method.

RESULTS AND DISCUSSION

It was observed (from UV-Visible spectra) that the absorption edge gives a good fit for both indirect allowed transitions and direct allowed transitions in k-space. According to Mott and Davis [8], one can obtain the optical band gap E_g of materials from the application of equation (1).

$$\alpha(\nu) h\nu = B(h\nu - E_g)^m \quad (1)$$

In equation (1), B is the disorder parameter, and E_g is the optical energy band gap. The value of m is $1/2$, $3/2$, 2 and $1/3$ for direct allowed transition, direct forbidden transition, indirect allowed transition and indirect forbidden transition, respectively.

The activation energy for optical transitions reduced from 4.6 eV at 1.5 wt% doping level (DL) to 4.0 eV at 42 wt% doping level. The absorption intensity at these intermediate energies also increases with concentration of CoCl_2 in PVA-PVP blend. The

optical band gap for indirect allowed transitions in k-space, decreases from 4.6 eV for 1.5 wt% doping level to 4.0 eV at 35 wt% doping level. In addition, absorption peaks were observed at 2.3 eV, 3.0 eV and 1.7 eV, which indicate that doping results in formation of allowed energy bands within the forbidden gap. The optical band gap due to direct allowed transitions reduces from 4.8 eV at 1.5 wt% doping level to 4.4 eV at 42 wt% doping level. The optical band gap at 42 wt% doping concentration for indirect and direct allowed transitions due to the absorption band created in the forbidden gap by the doping process is 1.64 eV and 1.68 eV respectively. The Urbach energy which is the width of band tails in the forbidden gap, is found to decrease significantly with increase in doping level of cobalt chloride in PVA-PVP blend films. It is 0.87 eV at 1.5 wt% doping level, 0.12 eV at 4.3 wt% doping level and becomes negligible at 42 wt% doping level, suggesting an increase in degree of structural order in the CoCl_2 doped PVA-PVP blend, when the concentration of CoCl_2 is increased.

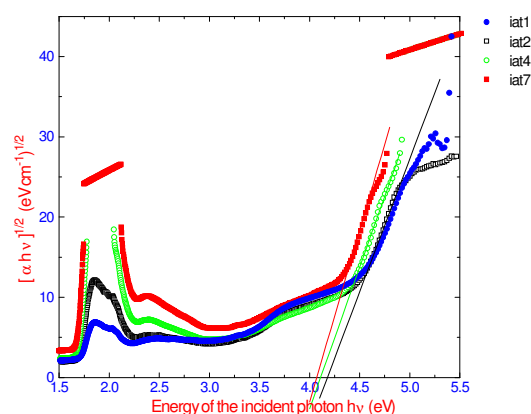


FIGURE 1. Determination of the optical band gap due to indirect allowed transitions, for PVA-PVP- CoCl_2 blend films. Note the absorbance bands at lower energies also (between 1.7 and 2.6 eV). Legend: iat1 = 5.6 wt%, iat2 = 10.6 wt%, iat4 = 19 wt% and iat7 = 29 wt%.

In CoCl_2 doped PVA-PVP polymeric blend sample, there was found to be a negative temperature coefficient of electrical resistivity (ρ). In fact, there is an exponential drop in electrical resistivity with absolute temperature (T), which can be explained with the help of the Arrhenius relation (equation (2)). In equation (2), k_B is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$).

$$\rho = \rho_0 \exp\left(\frac{E_a}{2k_B T}\right) \quad (2)$$

From the data of variation of electrical resistivity with temperature, using equation (2), the energy gap for charge mobility (Activation energy E_a) can be determined. The results are presented in table (1). Note that this activation energy decreases from a high of 4.1 eV for 1.5 wt% doping level to a low value of 3.1eV for 19 wt% of CoCl_2 in PVA-PVP blend.

TABLE 1. The variation of activation energy with respect to CoCl_2 doping level in PVA-PVP blend. This information is extracted from temperature variation of electrical resistivity using Arrhenius equation.

Doping Level (wt%)	Activation Energy (eV)
1.5	4.1
3	3.8
8	3.6
15	3.4
19	3.1
23	3.4
35	3.2

It is also observed that, in these polymeric samples, the Variable Range Hopping model is valid to explain the temperature variation of electrical conductivity. When the graph of when $\ln(\sigma T^2)$ is plotted versus $(1/T)^{1/4}$ is plotted for different doping levels of CoCl_2 in PVA-PVP blend films [where σ is the electrical conductivity ($\sigma = \rho^{-1}$)], a good straight line fit is observed, implying that the Variable Range Hopping (VRH) model in three dimensions is valid model for the mechanism of electrical conduction in these films.

CONCLUSIONS

Cobalt Chloride doped PVA-PVP blend films were prepared by solution casting technique and characterized. They showed semi-crystalline nature, with an average crystallite size of a few nanometers. The UV-Visible spectra of these PVA-PVP- CoCl_2 films were recorded in the wave length range from 200 nm up to 1000 nm. The nature of optical transitions were found to be of indirect allowed type (best fit), although the fit of the absorption edge data for direct allowed transitions was also good. The optical spectra obtained were analyzed quantitatively. The optical band gap reduces from 4.6 eV for 1.5 wt% doping level to 4.0 eV at 42 wt% doping level. Addition absorption peaks were also observed at lower activation energies 2.3 eV, 3.0 eV and 1.7 eV, which indicate the formation of allowed energy bands within the forbidden gap, due to doping. The Urbach energy, which measures the width of band tails within the forbidden gap, is found to significantly decrease with increase in doping level, from 0.87 eV at 1.5 wt%

doping level to 0.12 eV at 4.3 wt% doping level. This indicates an increased degree of order in the sample, on increase in concentration of cobalt chloride. The temperature variation of electrical resistivity obeys the Arrhenius relation, from which the activation energy obtained is found to decrease from 4.1 eV for 1.5 wt% doping level to 3.1eV for 19 wt% doping level.

ACKNOWLEDGMENTS

The authors acknowledge the use of facilities in the University Science Instruments Centre (USIC), Karnatak University, Dharwad (KUD) for UV-Visible spectra. X-ray diffraction data was recorded using the facility at the Department of Physics, Gulbarga University, Gulbarga. The funding for this work is in terms of a Major Research Project from the University Grants Commission (UGC), Government of India; Sanction Number F.38-103/2009(SR) dated 19th December 2009. RVP acknowledges financial assistance in terms of a Project Fellowship from the UGC, Government of India.

REFERENCES

1. Blaise Lobo, M R Ranganath, T S G Ravi chandran, G V Rao, V Ravindrachary and S Gopal, *Phys. Rev B* **59**, 13693-13698 (1999).
2. M R Ranganath and Blaise Lobo "Analysis of the Optical Spectra of UV irradiated Fe:PVA" in *Proceedings of the 53rd DAE Solid State Physics Symposium*, edited by Meenakshi Sunder, A.K.Rajaraman, G.P. Kothiyal, Mumbai: BARC & TIFR, 2008, pp 589-590.
3. A Tawansi, A El-Khodary, M M Abdelnaby, *Current Applied Physics* **5**, 572-578 (2005).
4. R F Bhajantri, V Ravindrachary, A Harisha, V Crasta, S P Nayak and B Poojary, *Polymer* **47**, 3591-3598 (2006).
5. Blaise Lobo and M R Ranganath "Changes in the optical properties caused by doping ferric ions in PVA" *Proceedings of the 54th DAE Solid State Physics Symposium*, 2009 edited by A.K.Rajaraman, Alka B Garg, G.P. Kothiyal. Mumbai: BARC, pp 479-480.
6. Vladimir Sedlank, Nabanita Saha, Ivo Kuritka, Petr Saha, *Polymer Composites* **27**, 147-152 (2006).
7. M.A. El-Shahawy, M.M. Elkholy, *European Polymer Journal* **30**, 259-263 (1994).
8. N. F. Mott and E. Davis, *Electronic processes in Non Crystalline materials* 2nd Edn; Oxford: Clarendon, 1979.