



DC conductivity and spectroscopic properties of cobalt nitrate doped polyaniline

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Abstract:

The Conducting polymeric materials have many physical properties which enable them to use invarious field like bioengineering, electronic, optical, chromic, electrical and medical engineering etc. Such one of promising candidate, polyaniline was synthesized via chemical oxidative polymerization process in acidic hydrochloric acid, taking potassium dichromate as an oxidant with doping of cobalt nitrate in different concentrations. The prepared doped polymeric composites were characterized by UV-visible spectroscopy, X-ray diffraction and dc conductivity measurement techniques. The UV-visible spectra of prepared composites revealed that the band gap decreases continuously with increases in dopant cobalt nitrate concentration and the peaks exhibiting the presence of charged particles. X-ray diffraction patterns of powdered composites showed amorphous nature as most conducting polymers exhibit. The DC conductivity of polymer composites has been measured in a specially designed measurement holder by two probe method in temperature range of 300-400 K and significant enhancement in dc conductivity has been observed with dopant and increase in temperature, proving the semiconductor nature of synthesized polymer composites.

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1.Introduction:

Conducting polymeric materials find applications in a number of scientific and technological fields and we can say that these synthetic polymers are important pillars of our civilization. In the pristine form polymers are generally found to be insulators but these are various polymerization techniques to make them conductive. Conductive polymers are special synthetic polymers having distinctive electrochemical properties involving conjugated chains with alternating single and double bonds [1]. Among conducting polymers, Polyaniline has outstanding potential applications in nearly all traditionally dominated semiconducting material scientific fields due to less toxicity, good environmental stability, high electrical conductivity and nanostructured morphology. The understanding of the relations between structural hierarchy and macroscopic behaviour, brought about by polymer physics, led to important modifications of existing polymers and the development of new polymeric materials with added value. When such polymers are chemically treated with oxidizing/reducing agents, some of them behave as conductors with considerable electrical conductivity. So, being a novel candidate, polyaniline with backbone modifications have applications in electric, electronic, chromic, optical, drug delivery, tissue engineering, biosensors, nerve regeneration, batteries, EMI shielding and other



countless techno-scientific applications [2-4]. Chemical oxidation polymerization route is generally used to make polyaniline in bulk quantities and it can be doped by several methods/charge transfer techniques for backbone modification to acquire better electrical/electronic properties. Both doping methods yield doped polyaniline composites with an increase in electrical conductivity by several orders of magnitude [5]. Various dopants and solvents for control of physical and chemical properties of polyaniline have been examined. The emeraldine form of polyaniline can be converted to the conductive form via oxidation doping at the amine nitrogen atoms.

From last decades, conductive polymers, specially polyaniline appeared as a novel candidate in medical science, especially in neuroscience to stimulate the growth of cells, coating of dry electrodes used for monitoring biopotential, repairing sciatic nerve injuries [6-8]. As polyaniline is simultaneously biodegradable and conductive so it is an ideal candidate to repair electrically excitable tissues such as tissues in heart, bone, nerve, skin etc. [9] In the present work host novel polyaniline was synthesized by chemical oxidation polymerization and polyaniline cobalt nitrate polymeric composites were prepared by chemical doping of the host polymer with different concentrations of cobalt nitrate to get a noted electrical conductivity value. To find out the influence of the cobalt nitrate on the polyaniline, the prepared doped polymeric composites were characterized by UV-visible spectroscopy, X-Ray diffraction and dc conductivity measurements.

2. Experimental methods: The polyaniline (99.9 %, Merck, India), Potassium dichromate (99 %, S.D. Fine Chemicals, India), hydrochloric acid (99 %, Qualigens Chemicals, India), tetrahydrofuran (99.9 % Merck, India), 28 % ammonia solution in water (S.D. Fine Chemicals, India) and cobalt nitrate (Hi-Media Chemicals, India) all these chemicals were of analytical grade and twice purified distilled water were used for polymerization process. The distilled polyaniline (0.1 M) was cooled up to 280 K and stirred throughly by adding drop wise potassium dichromate (0.1 M) as an oxidant in hydrochloric acid medium (1 N) as suggested by MacDiarmid [10]. The prepared mixture was again cooled down to 280 K for 24 h to get pristine form of polyaniline with completion of the polymerization process. The obtained precipitates were filtered, washed with distilled water thoroughly, treated with aqueous ammonia solution and again washed with distilled water until the filtrate become colorless and neutral as measured by both pH paper and pH electronic meter. The dark colored polyaniline powder was dried in oven by increasing temperature at regular intervals up to 350 K for 48 h to acquire moisture free host polymer. The dried powder of polyaniline was grinded to very fine. Now 2 gram grinded powder of polyaniline and cobalt nitrate with different concentrations (3, 6, and 10 % (w/w)) were added in 15 ml tetrahydrofuran plus 5 ml distilled water solution with mechanical stirring for one hour and again kept the solutions in an oven at 300 K for 24 h to complete the chemical doping process. To get moisture free composites for characterization, the doped composites were placed in oven at 380 K for 4 h. Samples for UV-visible spectra were prepared by dissolving a small amount of composites in tetrahydrofuran in quartz cuvettes. Hitachi 330, UV-visible spectrometer was used to record the absorption spectra in wavelength range of 200-800 nm. The pellets containing homogeneous mixture of potassium bromide and composites were used to take



the FTIR spectra in wavenumber range of $400\text{-}4000\text{ cm}^{-1}$ by FTIR spectrophotometer (Perkin Elmer) having resolution of 1 cm^{-1} . X-ray diffractometer (X'Pert Pro PANalytical's) having wavelength 1.5406 \AA ($\text{CuK}\alpha_1$) was employed for structural analysis of composites. For analyzing dc conductivity, the pellets with dimensions of 10 mm diameter and 1 mm thickness of pristine polyaniline and doped composites were made by applying 3 ton/cm^2 pressure using hydraulic pellet press (Kimaya, WT-324). The dc conductivity was measured by specially designed sample holder (potential difference $0\text{-}15\text{ V}$) using two probe method in the temperature range $300\text{-}400\text{ K}$ using Pico-ammeter (Keithley, 617).

3.UV-Visible spectra:The UV-Visible spectra of pristine polyaniline and doped polymer composites with dopant concentrations of 3, 6 and 10 % (w/w) are shown in Fig.1 (a-d) below

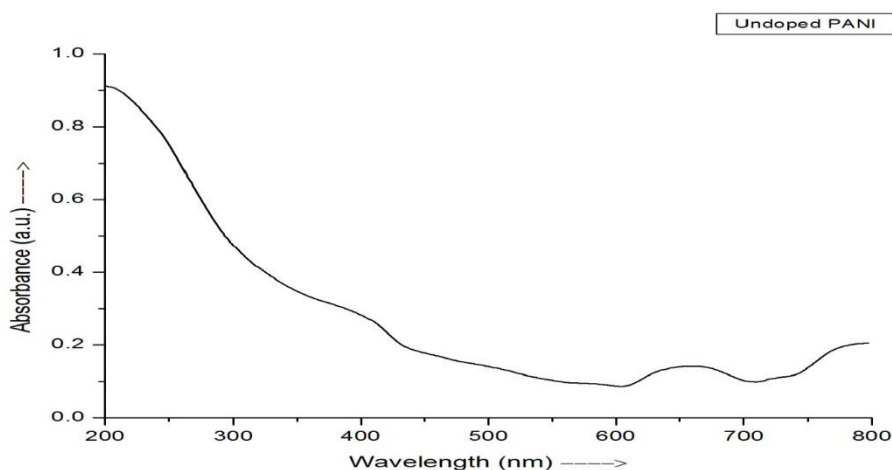


Fig.1(a)

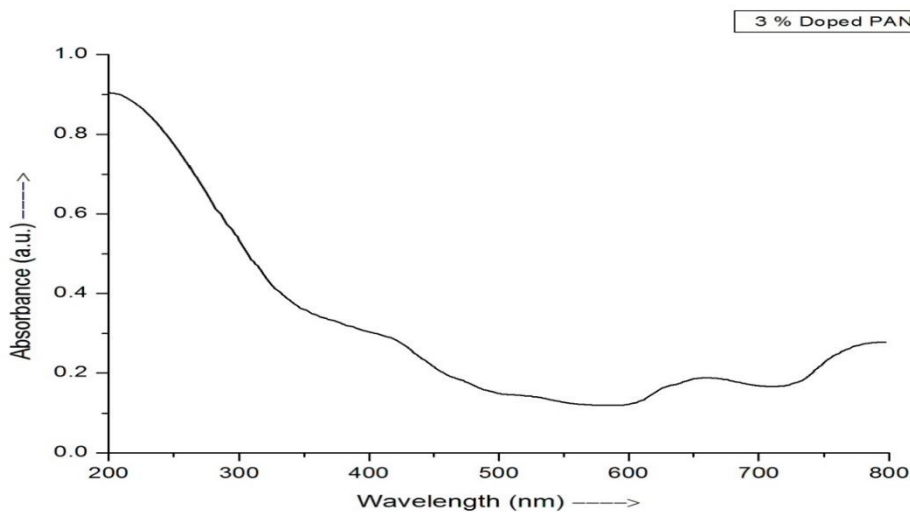


Fig.1(b)



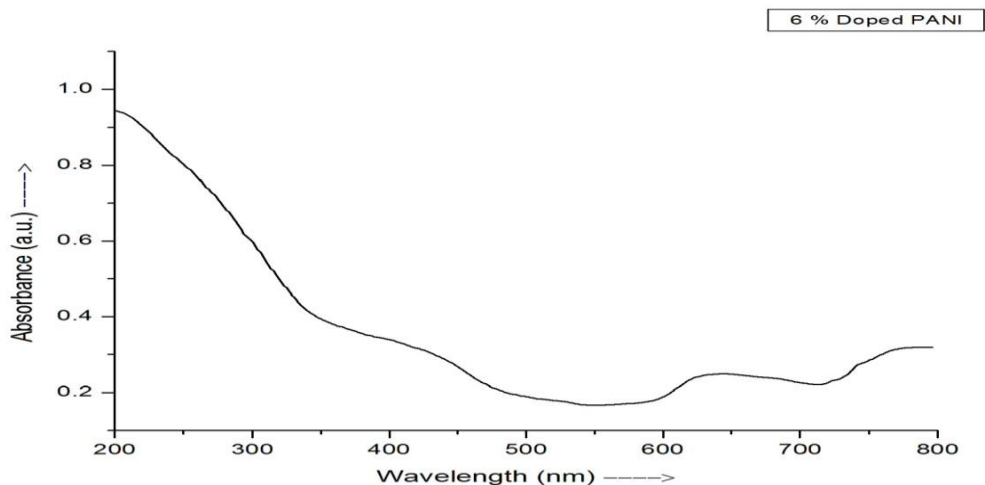


Fig 1(c)

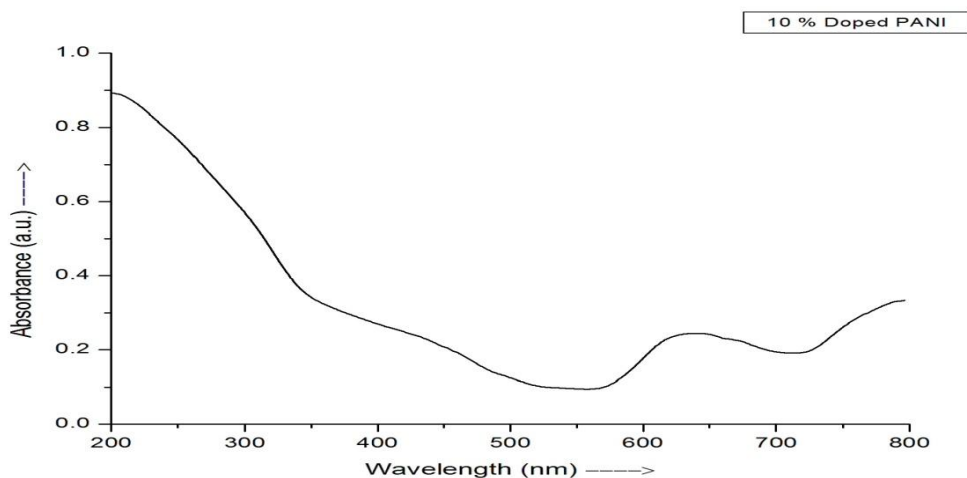


Fig 1(d)

The UV electronic spectra showed mainly absorption bands appeared at ~ 340, 430, 680 and 790 nm. As per spectroscopic data, we know that band at about 340 nm attributed to the $\pi - \pi^*$ exciton transition [11]. The polaron absorption band at ~ 430 nm depicts the $\pi - \pi^*$ electronic transitions of benzene rings [12-13]. The absorption band at ~ 680 nm is attributed to excitonic transitions and it is very sensitive to the overall oxidation of the polymerization [14]. The polaron absorption bands, visible at 430 and 790 nm, are due to the π -polaron and polaron- π^* band transitions respectively and are conformation of the conductive form of the polyaniline [15].

The optical band gap (E_g) of the polymer composites was determined using the famous Tauc's relation [16]

$$\alpha h\nu = A(h\nu - E_g)^n \quad (1)$$



where α is the absorption coefficient, $h\nu$ is the energy of the incident photon and A is a proportionality constant. The band gaps for the 3, 6 and 10 % (w/w) cobalt nitrate doped polyaniline composites are found to be 3.8, 3.2 and 2.8 eV respectively, and for the undoped polyaniline it is 4.6 eV. The band gap decreased continuously with increase in dopant concentration. It is fact that the values of energy band gap are also influenced by various factors like experimental conditions during the synthesis, degree of polymerization, monomer-oxidant ratio, temperature, etc. [18-19].

4.XRD studies: The XRD patterns of polyaniline-cobalt nitrate composites are shown in Fig.2 (a-c). The X-ray diffraction patterns provide significant information in relation to the nature and structure of the prepared samples. The figures do not show any sharp peaks in undoped, 3% and 6 % doped polymer composites and suggest a purely amorphous nature of all the polymer samples. However in 10 % doped sample we found some semicrystalline behavior in structure [3]. The XRD pattern of polymer generally differs due to uncertainty in polymeric chains and it also depends on the synthesis route, solvent and ionized state [19-20]. Researchers tried different methods to align the chain more perfectly in conducting polymer [21].

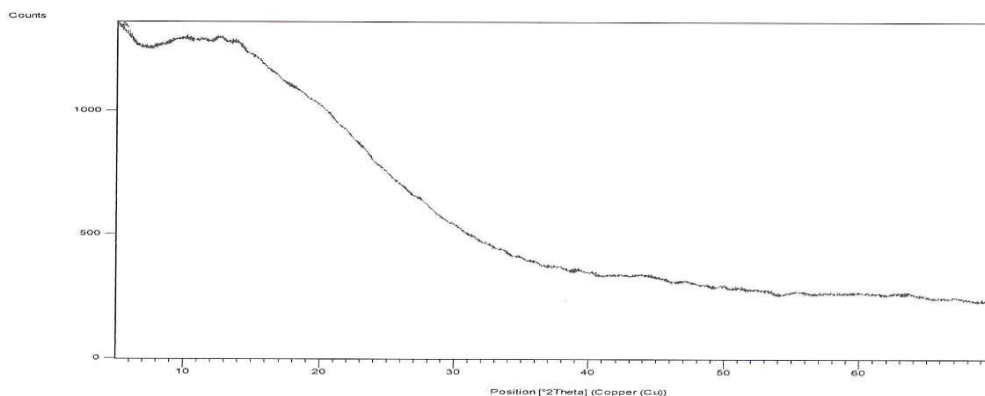


Fig 2 (a)

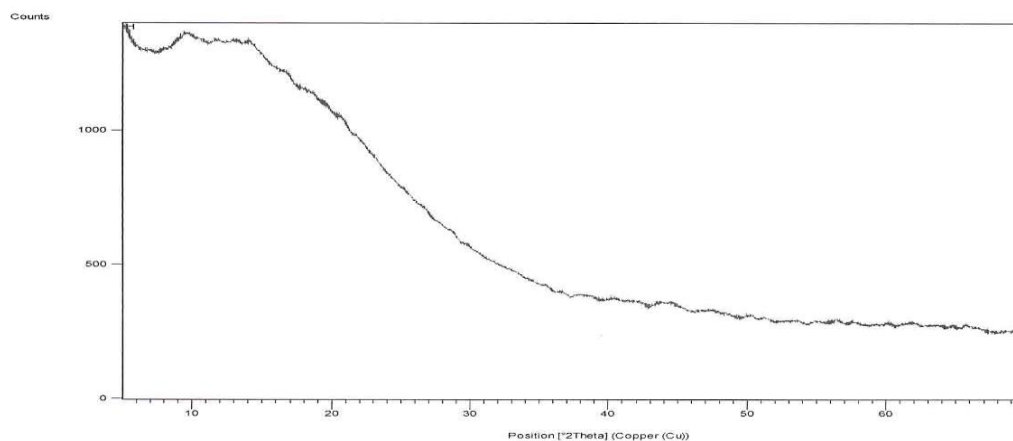


Fig 2 (b)



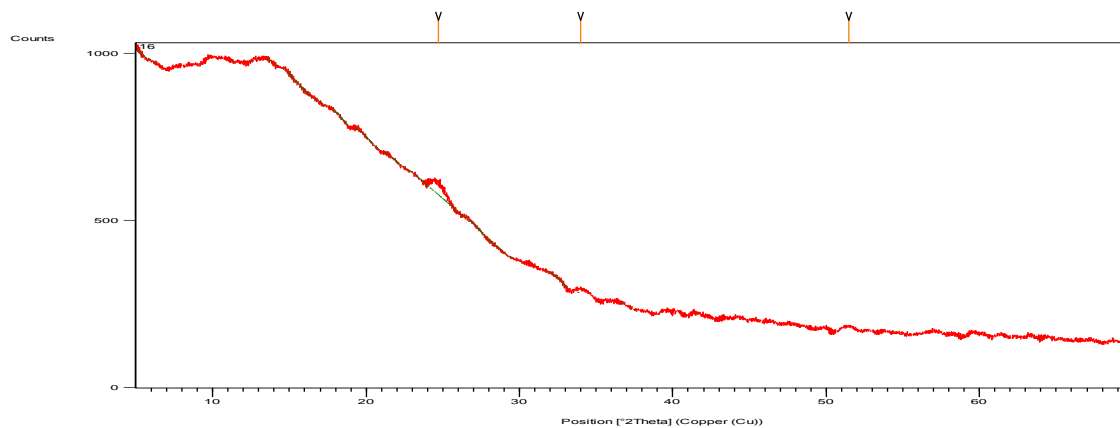


Fig 2 (c)

Generally assumed that a well crystallized polymer always possesses higher conductivity due to streamline polymer chain and charged particle mobility [22]. However, chemical doping to increase the charge carriers may distort the order of material, hence no surety to get desired high value of electrical conductivity, so it is challenge to keep good charge transport pathways in doped polymers [23].

4.DC Conductivity: In case of polymers doping process, there is insertion of metal ions into the whole polymer backbone rather than just at the surface and as a result, we get a sufficient amount of charge carriers per unit volume. The conduction mechanism in conducting polymers is much different as to semiconductors. Due to applied voltage, there is appearance of strong coupling between electrons and phonons which causes lattice distortions leads to formation of new quasi-particles; solitons, polarons and bipolarons, so the charge transport is through these polarons and bipolarons. As the applied field increases the formation of polarons and bipolarons increases which contributes to the increase in current with applied voltage [24-25]. The dc conductivity of polyaniline cobalt nitrate polymeric composites was measured by a two-probe method using a specially designed sample holder in the temperature range 300-400K. For the pristine polyaniline sample, the conductivity was 6.93×10^{-8} S/cm, while in the case of the 3, 6 and 10 % (w/w) doped polymer composites, the values of conductivity at room temperature (300 K) were 6.34×10^{-6} , 2.82×10^{-4} and 1.77×10^{-3} S/cm. It was also observed that at 400 K, conductivity increased significantly with temperature, exhibiting the semiconductor behaviour of prepared doped polymer samples.

References:

1. N.Yi, Abidian M R; *Biosynthetic Polymers for Medical Applications*, Woodhead Publishing Series in Biomaterials, P 243-276 (2016).



2. Marder, S. R.; Sohn, J. E.; Stucky, G. D. (eds.); Materials for Nonlinear Optics: Chemical Perspectives; American Chemical Society; Washington, (1991).
3. A. A. Syed, and S.R. Taqui, Polyanilines: Materials and Applications. In: F. Mohammad, Specialty Polymers: Materials and Applications. Vol. 1. I.K. Publishing House, New Delhi, 21-69, (2007).
4. J.H. Jung, B.H. Kim, B.W. Moon, J. Joo, S.H. Chang, and K.S. Ryu, *Phys. Rev. B.* 64, 35101 (2001).
5. Dimitriev, O. P, Doping of polyaniline by transition metal salts, *Macromolecules* , 37(9): 3388-3395 (2004).
6. Zheng Z, Huang L, Yan Lu et.al, Polyaniline functionalized graphene nanoelectrodes for the regeneration of PC 12 cells via electrical stimulation. *Int. J. Mol. Sci.* 2019, 20(8), (2013).
7. Aghazadih H, Yazdi M, Kolahi A, Yekami M et. al. Synthesis, characterization and performance enhancement of dry polyaniline-coated neuroelectrodes for electroencephalography measurement. *Current Applied Physics*, 27; 43-50, (2021).
8. Abdelnasir S, Mungroo M, Shahabuddin S et. Al. , Polyaniline conjugated Boron nitrate nanoparticles exhibiting potent effects against pathogenic brain eating Amoebae; *ACS Neuroscience*; 12 (19) 3579-3587, (2021).
9. Lalegül-Ülker Ö, Elçin Y M: Magnetic and electrically conductive silica-coated iron oxide/polyaniline nanocomposites for biomedical applications, *Mater. Sci. Eng. C*, 119, 111600, (2021).
10. MacDiarmid, A.G, Polyaniline and polypyrrole: where are we headed?, *Synth. Met.* , 84(1-3): 27-34 (1997).
11. Parvatikar, N., Jain, S., Kanamadi, C.M., Chougule, B.K., Bhoraskar, S.V. and Ambika Prasad, M.V.N, Humidity sensing and electrical properties of polyaniline/cobalt oxide composites, *J. Appl. Polym. Sci.* , 103(2): 653-658 (2007).
12. Ahmed, S.M. and Ahmed, S.A, Spectral studies of highly optically transparent polyblends of poly (*o*-toluidine) doped with salicylidene-*o*-aminophenol, *Scientific Research and Essay* , 3(7):299-307(2008).
13. McCall RP, Ginder JM, Leng JM, Ye HJ, Manohar SK, Masters JG, Asturias GE, MacDiarmid AG, Epstein AJ: *Phys Rev B*, 41:5202 (1990).
14. Pron A., Rannou P. Processible conjugated polymers: from organic semiconductors to organic metals and superconductors. *Prog. Polym. Sci.* 27(1):135-190 (2002)
15. Kumar A., Ali V., Kumar S. Studies on conductivity and optical properties of poly (otoluidine)-ferrous sulphate composites. *Int. Polym. J. Anal. Charact.* 16(5):298- 306 (2011)
16. Tauc, J. Amorphous and Liquid semiconductors. New York, Plenum Press, 159 (1974).
17. Bredas J., Street G.B. Polarons, bipolarons, and solitons in conducting polymers. *Polarons and Bipolarons*, *Acc. Chem. Res.* 18(10):309-315 (1985).
18. Elmansouri A., Outzourhit A., Ameziane E. L. Active & Passive Electronic Components. Doi:10.1155/2007/17846 (2007).
19. Laska J., Widlarz. J. Spectroscopic and structural characterization of low molecular weight fractions of polyaniline. *Polymers*, 46(5):1485-1495 (2005).
20. Perez M Benjamin et al., Synthesis of silicon-substituted hydroxyapatite using hydrothermal process; *Ceramica y Vidrio (Elsevier)*, 59 (2) 50-64, (2020).



21. Moon S., Park J. K. Structural effect of polymeric acid dopants on the characteristics of doped polyaniline composites. *Synth. Met.*, 92(3):223-228 (1998).
22. Liu H., Hu X. B., Wang J. Y., Boughton R. I. Structure, Conductivity and Thermopower of Crystalline Polyaniline Synthesized by the Ultrasonic Irradiation Polymerization Method. *Macromolecules*, 35(25):9414-9419 (2002).
23. RahmanMM ,Mahtab T, Mukhlish MZB, Faruk MO; Enhancement of electrical properties of metal doped polyaniline synthesized by different doping techniques. 78, 5379-5397 (2021)
23. Reghu M, Cao Y, Moses D &Heeger A J, *Phys Rev B*, 47, 1758 (1993).
24. Reghu M, Yoon C O, Cao Y, Moses D &Heeger A J, *Phys Rev B*, 48, 17685 (1993).
25. Raghavendra S C, Khasim S, Revanasiddappa M, Prasad A & Kulkarni A B, *Bull Mater Sci*, 26, 733 (2003).

