Electrical and optical properties of nanocrystalline bismuth sulphide thin films prepared in PVA matrix by chemical drop method

A.Hussain*, A.Begum, A.Rahman

Department of Physics, Gauhati University, Guwahati - 781 014, (INDIA)

E-mail: hussainmakak@gmail.com

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ABSTRACT

Nanocrystalline Bi_2S_3 thin films were prepared by chemical drop method using polyvinyl Alcohol (PVA) as a matrix solution. Characterization of the films was carried out using X-ray diffraction (XRD), Scanning electron microscopy (SEM), optical absorption, composition analysis and electrical conductivity measurement. Average grain size calculated from the XRD spectra were found between 3nm -10nm. Surface morphology and particles sizes were also known from SEM image. EDAX gave the composition ratio of the prepared films. The absorption edge shifted towards the lower wavelength. The band gap obtained from the absorption spectra was found to change from 3.88 eV to 3.82 eV on changing the grain size from 3nm to 10nm. The electrical conductivity at room temperature was found to be in the range $10^{-6}\Omega^{-1}m^{-1}$.
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INTRODUCTION

In the last few years, nanocrystalline semiconducting thin films occupied an important place in research work due to their future applications. The optical, electrical and magnetic properties of a material change on changing the grain size and thickness of the film. So, it offers the possibility of materials enhancement device characteristics[1,2]. The particles with diameter in the range of 1nm-100 nm are in intermediate state between atomic and bulk species and their electronic structures are different from bulk materials[3,4]. The band structures of semiconducting materials are affected by the size of the nanocrystals and therefore properties are depending on the crystal size. Bi_2S_3

belongs to group V-VI compound semiconductor with gap energy in the range (1.3-1.7eV) which lies in the visible region of the spectra[5-8]. The calculated work function of Bi_2S_3 micro belts at the highly oriented {001} surfaces has been reported to be 4.93eV[9]. This indicates the potential application of this material for anode material and understanding the field emission characteristics and photochemical behaviours. It is very useful for solar energy conversion devices[10-12], photoelectronics devices, photo electrochemical devices, thermoelectric coolers, electric switching, solar selective coating etc[13,14]. Bi_2S_3 thin films have been reported to be prepared by different techniques such as ultrasonic method[15,16], microwave irradiation[17,18], hydrothermal synthesis[19-21], chemical depo-

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active evaporation[26]. Here in our work, we are using
chemical drop method which is simple, inexpensive
and convenient for large area deposition. With this
method, size of the particles can be easily controlled
by changing the concentration of different constitu-
ents of the solution. In the present investigation, we
have obtained thin films nanocrystalline Bi_2S_3 embed-
ded in PVA matrix and study their structural, surface
morphological, optical and electrical properties.

EXPERIMENTAL DETAILS

For the preparation of nanocrystalline Bi_2S_3 thin
films in polyvinyl alcohol (PVA), $Bi(NO_3)_3$ and Na_2S
were used as Bi^{+3} and S^{-2} ions sources respectively.
For this, 5wt% of PVA matrix solution was prepared
in double distilled water and stirred with the help of a
magnetic stirrer at a constant temperature 348K until
a transparent solution was formed. To this solution,
0.03M (molarity) of Bi_2S_3 was added in the ratio of
2:1 and the stirring was continued at the same tem-
perature for 3 hrs and brought down at the room tem-
perature (300K). To this mixture solution, 0.03M of
Na_2S was added drop by drop until the solution turned
into dark brown. The resultant solution was kept for
12 hrs in a dark chamber undisrupted for stabiliza-
tion. The stabilized solution was cast over the glass
substrates drop by drop and dried at room tempera-
ture (300K). This way the films containing Bi_2S_3 em-
bedded in a PVA matrix were obtained. Three sets of
films with different molarities (0.015M, 0.02M
0.03M) of Bi_2S_3 were obtained using the above men-
tion procedure. Films of higher molarity could not be
prepared under the present condition because
$Bi(NO_3)_3$ of more than 0.05M could not be dissolved
in PVA solution. For the measurement of electrical
conductivity of the films Al and In electrodes were
vaccum deposited making gap type structure. Elec-
trical conductivity measurement were performed over
a voltage range of 2V-7V using a stabilized power
supply and a Keithley digital electrometer in the tem-
perature range 298K to 388K and the same tem-
perature was varied using a temperature controller.
Temperatures of the samples were measured by
means of a thermocouple.

RESULTS AND DISCUSSION

XRD studies

The X-ray diffractogram of the PVA- Bi_2S_3 struc-
tures exhibit broadened diffraction profile. A broad peak
has been observed around $2\theta = 19.6^0$ as shown in fig-
ure 1. XRD spectrum of pure PVA shows similar peak
around the same angle. This indicates that the XRD
peak observed in PVA- Bi_2S_3 complex is due to the
PVA matrix. Since the Bi_2S_3 particles are of nanosize
and sparsely distributed in the PVA matrix, the diffracted
beams from Bi_2S_3 were not sufficiently intense to give
any detectable peak. Also some peaks if present were
merged with the broad peak obtained from PVA. The
crystallite size of the nanocrystalline films was estimated
using Scherrer's formula[2]

$$d = \frac{4}{3} \frac{0.9\lambda}{\beta\cos\theta} \qquad (1)$$

where λ is the wavelength of the X-ray used, β is the
full width at half maximum of diffraction peak and θ is
the Bragg's angle. The crystallite sizes were found to
be 10.8nm, 4.7nm and 3.6nm for molarities 0.015M,
0.02M and 0.03M of Bi_2S_3 respectively. It is observed
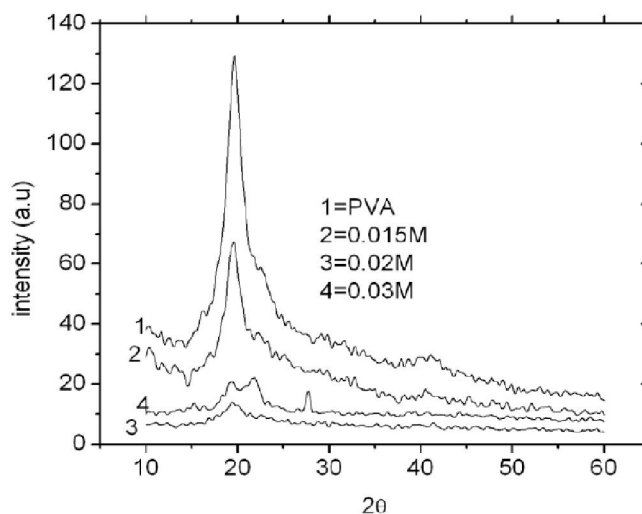that crystallite size decreases with increase in molarity.

**Figure 1 : X-ray diffraction patterns of PVA-Bi_2S_3 thin films
of different molarities.**

SEM analysis

Scanning Electron Microscopy is the convenient
technique to study the surface morphology of thin films.
Figure 2, Figure 3 and Figure 4 shows the surface mor-
phology of a typical PVA- Bi_2S_3 complex of different

molarity deposited at room temperature. It is observed that grains of Bi_2S_3 are not uniformly distributed throughout the PVA matrix. But the film is smooth without any
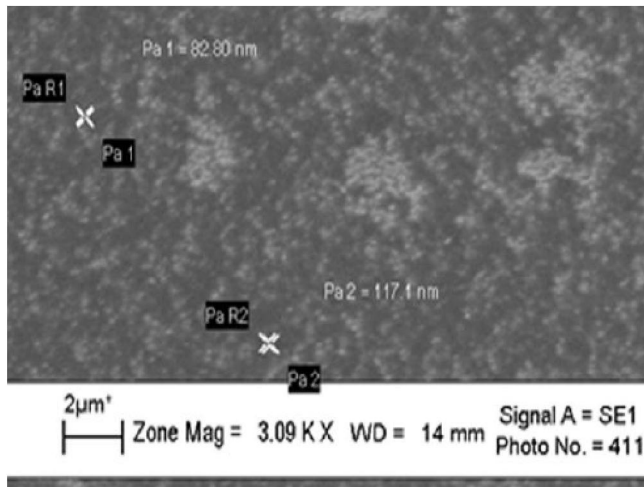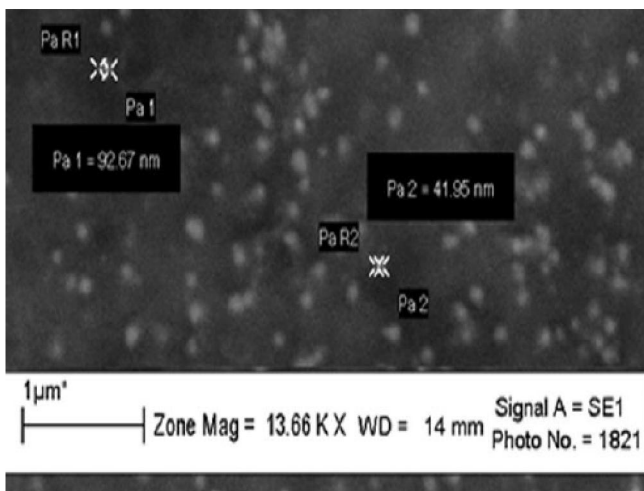

Figure 2 : SEM photograph of 0.015M.

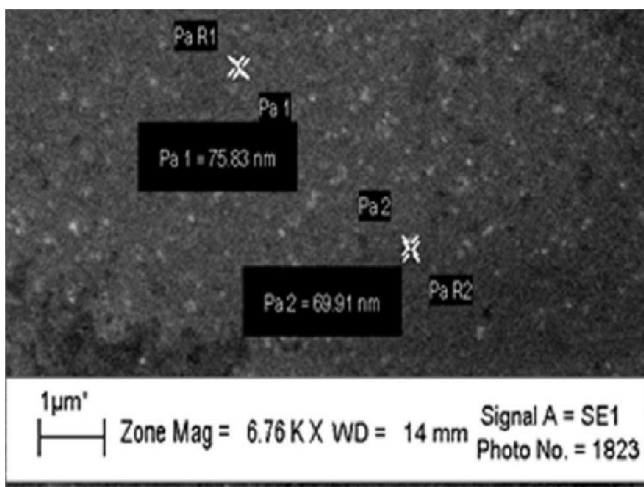**Figure 3 : SEM photograph of 0.02M.**

Figure 4 : SEM photograph of 0.03M.

void or crack. Therefore, average grain sizes were estimated of different grains within the film and found to be in the range of 41.95-117 nm. It is quite clear from the results that the average grain size estimated by SEM is larger than the average grain size measured by XRD.

EDAX study

Figure 5 gives the quantitative analysis by EDAX of Bi_2S_3 thin films deposited on a glass substrate at room temperature The elemental analysis was carried out only for Bi and S, the average atomic percentage of Bi:S was 77:22, (i.e. 3 : 1 ratio), showing that the sample was S deficient.
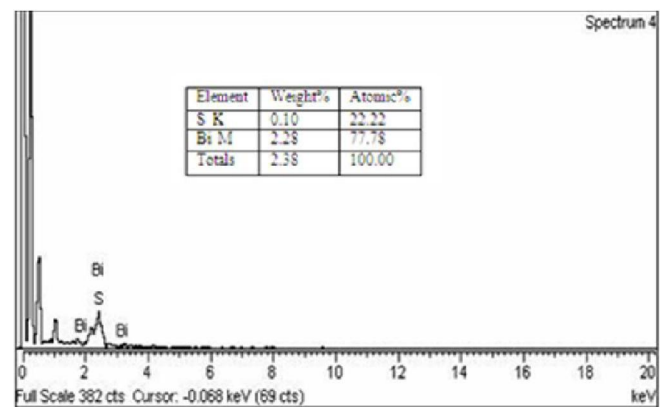

Figure 5 : EDAX spectrum of 0.015M.

Absorption studies

Figure 6 shows the absorption spectra of three different Bi_2S_3 thin films prepared in PVA matrix. The absorption edge shows a clear shift towards lower wavelength. This blue shift of the absorption edge indicates decrease of the crystallites sizes of the particle causing a change in the optical band gap energy. The nature of the transition is determined by the relation

$$\alpha = a \frac{(h\nu - E_g)^n}{h\nu} \qquad (2)$$

where 'a' is constant and E_g is the separation between the conduction band and valence band. If the plot of $(\alpha h\nu)^{1/2}$ vs $h\nu$ is linear, then the transition is known as an indirect band edge transition and if the plot of $(\alpha h\nu)^2$ vs $h\nu$ is linear, then such a transition is known as direct band edge transition. The linear nature of the plot indicates the existence of the direct transition. The extrapolation of the linear portion of such a plot to $\alpha = 0$ yields the band gap as shown in figure 7. The absorption coefficient 'α' was measured from relation

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$$\alpha = 2.303\left(\frac{A}{t}\right) \qquad\qquad (3)$$

where 'A' is the absorbance and 't' is the thickness of the film. The band gap obtained from the figure 7 was 3.82eV, 3.85eV and 3.88eV for molarity 0.015M, 0.02M and 0.03M respectively.
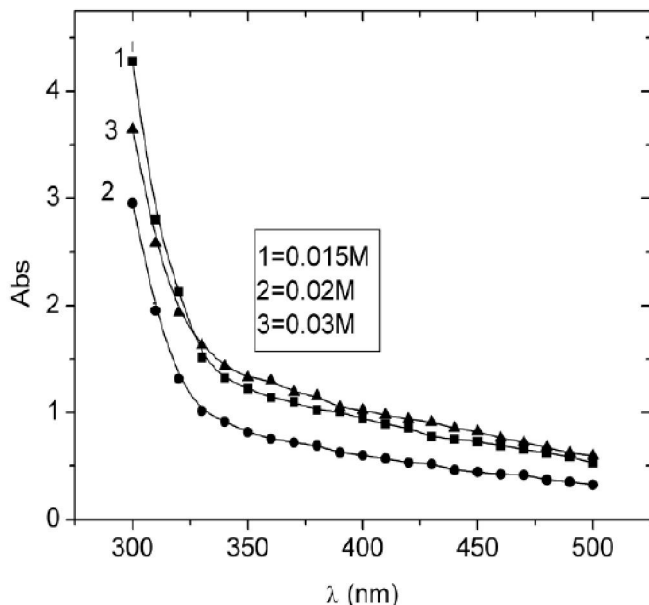

Figure 6 : UV-absorption spectra of Bi_2S_3 nanocrystalline films for different molarities
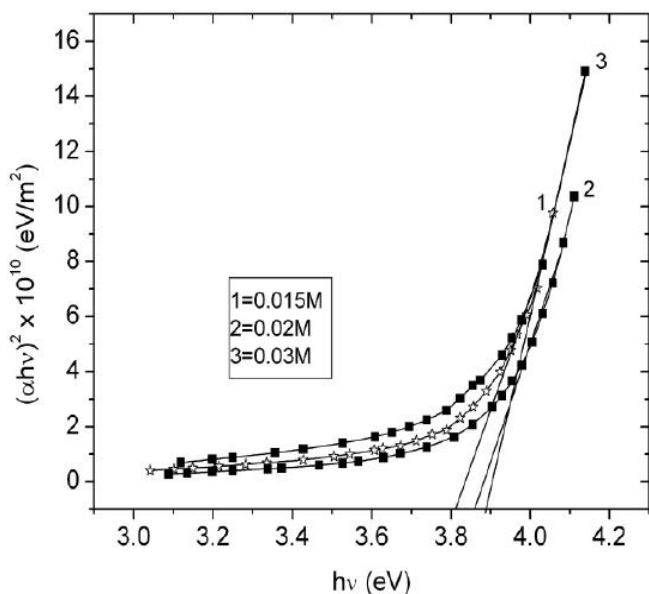

Figure 7 : Energy band determination of Bi_2S_3 films for different molarities from the hv vs $(\alpha h v)^2$ graph

Electrical conductivity

The electrical conductivity measured on gap type sample using Al and In as electrode materials has been shown in figure 8 and Figure 9 respectively. The conductivity has been observed to increase in all the sample as the temperature raised from 248K attaining a maximum around 323K, after which the conductivity was found to decrease and reached a minimum around 333K beyond which the conductivity showed a sharp increase again. This variation of conductivity has been thought to be due to phase transition with change in temperature. The temperature variation of conductivity of PVA was also studied with same electrode and has been observed to exhibit same pattern of variation of conductivity as stated above. The value of conductivity of PVA was of the order of $10^{-7}\Omega^{-1}m^{-1}$ while that of the Bi_2S_3-PVA complex was of the order of $10^{-6}\Omega^{-1}m^{-1}$. Thus, it may be inferred that the conductivity of Bi_2S_3 thin films grown in PVA matrix is largely influenced by the conductivity of PVA. More than one straight line are obtained in the $log(\sigma)$ vs 1/T curves (region I and region II) with different activation energies, indicating different conduction processes such as electronic and ionic conduction[27,28]. Ahmed et al[29] reported conductive processes to be electronic in co-operation with ionic in Vanadate doped PVA. They have also observed a phase transition regions from 360K to 380K. Abdel-Malik et al[30] explained current transport mechanisms in pure and doped PVA films in terms of both schottky and Pool-Frenkel effects. The Thermal activation energies were calculated using the relation
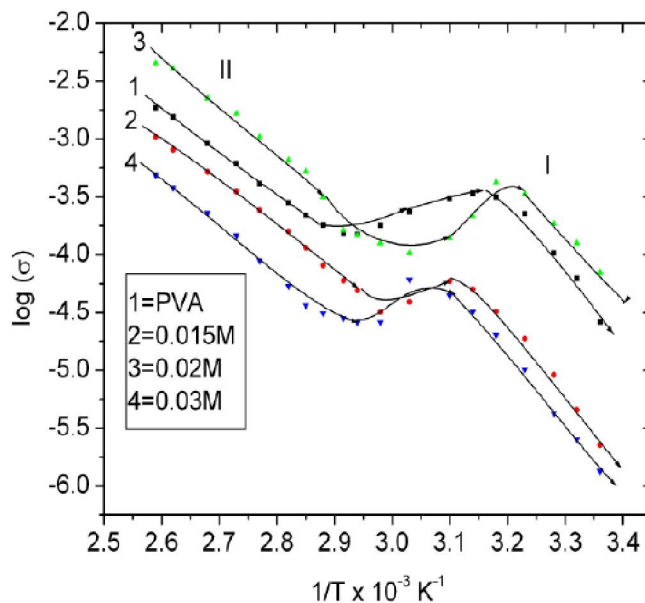

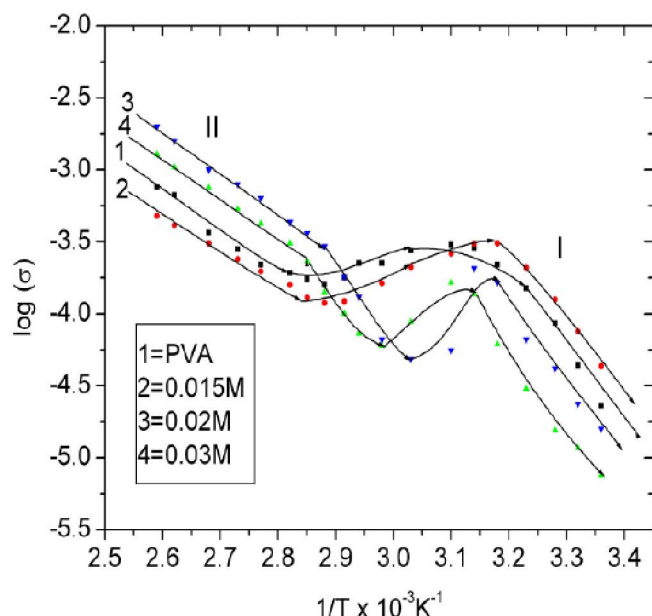**Figure 8 : Variations of $log(\sigma)$ vs 1/T of Al-PVA-Bi_2S_3-Al gap type**

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Figure 9 : Variations of log(σ) vs 1/T of In-PVA-Bi₂S₃-In gap type

$$\sigma = \sigma_0 e^{\frac{-E_a}{2KT}} \qquad (4)$$

where E_a is the activation energy, σ_o is a constant, k is the Boltzman's constant and T is the absolute temperature. Activation energies of PVA and different PVA-Bi_2S_3 films were calculated in the regions I and II. Average activation energies obtained from the slopes in the region I and II of pure PVA were 1.166eV and 0.657eV respectively and the same for nanostructured Bi_2S_3 grown in PVA are 1.36eV and 0.62eV.

CONCLUSIONS

Thin films of Bi_2S_3 prepared by chemical drop method in PVA matrix were found to be nanocrystalline. The crystallites sizes measured by XRD studies were found to be within 3.6-10.8nm and from SEM within 41.95-117nm for the same set of samples. The crystallite size has been found to decrease with increase of molarity. The band gap energy has been found to increase with decrease in crystallite size showing a blue shift in the absorption spectra. The electrical conductivity of pure PVA and PVA-Bi_2S_3 were found in the range of $10^{-7}\Omega^{-1}m^{-1}$ and $10^{-6}\Omega^{-1}m^{-1}$ respectively. The PVA matrix has exhibited phase transition around 320K to 350K. Electronic as well as ionic conduction processes are thought to be operative.

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REFERENCES

[1] A.Tanaka, S.Onari, T.Arai; Phys.Rev., **B47**, 1237 (**1993**).

[2] Biljana Pejova, Ivan Grozdanov; Mat.Chem.and Phys., **99**, 39-49 (**2006**).

[3] K.Akamatsu, S.Deki; Nanostructure Mater, **8**, 1121 (**1998**).

[4] R.Kubo; J.Phys.Soc.Jpn., **17**, 975 (**1962**).

[5] C.D.Lokhande; Mater.Chem.Physics, **27**, (**1991**).

[6] D.Jason Riley, Jonathan P.Waggett, K.G.Upul Wijayantha; J.Mater.Chem., **14**, 704 (**2004**).

[7] M.Gratzel; Nature, **414**, 338 (**2001**).

[8] D.Cummins, G.Boschloo, M.Ryan, D.Corr, S.N.Rao, D.Fitzmaurice; J.Physics.Chem, B, **104**, 11449 (**2000**).

[9] Yu Zhao, Xi Zhu, Yanyan Huang, Sunki Wang, Jinlong, Yi Xie; J.Phys.Chem.C, **111(33)**, 12141-12148 (**2007**).

[10] A.B.Novoselova (Ed); Physical and Chemical Properties of Semiconductor Handbook, Nauka, Moscow, 97 (**1978**).

[11] N.Parhi, B.B.Nayak, B.S.Acharya; Thin Solid Films, **254**, 47 (**1995**).

[12] I.M.Chapnik; Phys.Stat.Sol.(B), **137**, K95 (**1986**).

[13] S.R.Gadakh, C.H.Bhosale; Mater.Res.Bull., **35**, 1097 (**2000**).

[14] V.V.Killerdar, C.D.Lokhande, C.H.Bhosale; Thin Solids Films, **289**, 14 (**1996**).

[15] S.Y.Wang, Y.W.Du; J.Crystal Growth, **236**, 627 (**2002**).

[16] H.Wang, J.J.Zhu, J.M.Zhu, H.Y.Chen; J.Physics. Chem., B, **106**, 3848 (**2002**).

[17] X.H.Liao, J.J.Zhu, H.Y.Chen; Mater Sci.Eng., B, **85**, 86 (**2001**).

[18] X.H.Liao, H.Wang, J.J.Zhu, H.Y.Chen; Mater Res. Bull., **233**, 799 (**2001**).

[19] M.W.Shao, M.S.Mo, Y.Cui, G.Chem, Y.T.Qian; J.Crystalgrowth, **233**, 799 (**2001**).

[20] M.X.Zhang, Z.H.Yang, X.M.Huang, S.Y.Zhang, W.C.Yu, Y.B.Jia, G.I.Zhou, L.Chem; Solid State Communication, **119**, 143 (**2001**).

Full Paper

[21] S.H.Yu, J.Yang, Y.S.Yu, Z.H.Han, Y.Xie, Y.T.Qian; Mater.Res.Bull., **33**, 1611 **(1998)**.

[22] R.S.Mane, C.D.Lokahande, B.R.Sankapal; Mater. Res.Bull., **35**, 587 **(2000)**.

[23] R.S.Mane, C.D.Lokahande; Mater.Chem.Phys., **65**, 1 **(2000)**.

[24] S.H.Yu, L.Shu, J.A.Yang, Z.H.Han, Y.T.Qian, Y.H.Yang; J.Mater Res., **14**, 4157 **(1999)**.

[25] S.H.Yu, L.Shu, L.Yang, Y.Xie, Y.T.Qian, C.S.Wang; Matter.Lett., **35**, 116 **(1998)**.

[26] J.Lukose, B.Pradeep; Solid State Communication, **14**, 4157 **(1991)**.

[27] A.K.Jonscher; ibid, **1**, 1213 **(1967)**.

[28] K.C.Kao, W.Hwang; Electrical Transport in Solids, Pergamon Press, Oxford, **(1981)**.

[29] M.A.Ahmed, M.S.Abo-Ellil; Journal of Materials Science: Materials in Electronics, **9**, 391-395 **(1998)**.

[30] T.G.Abdel-Malik, R.M.Abdel-Latif, A.Sawaby, S.M.Ahmed; Journal of Applied Sciences Research, **4(3)**, 331-336 **(2008)**.