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STRUCTURAL AND OPTICAL CHARACTERIZATION OF BARIUM SULPHIDE THIN FILMS GROWN BY SOLUTION GROWTH TECHNIQUE.

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Abstract
Three thin films of barium sulphide were deposited on glass slides using solution growth technique. The bath compositions include barium chloride ($BaCl_2$) which was the source of Ba^{2+}, sodium thiosulphate ($Na_2 S_2O_3.5H2O$), source of S^{2-} and EDTA served as a complexing agent. The structural compositions of these films were examined using the microscope (HUND WETZLAR H600) and camera (RICOH 35mm SLR, XR-X300) at magnification of x400. Fourier transform infrared (FTIR) spectroscopy and spectrophotometer were used to determine the optical properties like absorbance, transmittance, reflectance, refractive index, extinction coefficient and optical conductivity. The results of characterization show that these films have poor absorbance and reflectance. The transmittance range of the films from UV-NIR is 60-90%. The range of the refractive index is 1.3-1.6; extinction coefficient has range of 0.001-0.012 while optical conductivity has a range of 1.0 $x10^{12}$ s^{-1} - 2.5 $x10^{12}$ s^{-1}.

Keywords: Barium sulphide, Fourier transform infrared (FTIR) spectroscopy, optical properties, thin films, solution growth technique.

INTRODUCTION

Solar energy is a source of free, natural and non polluting energy that man can harness for useful applications. Thin films have been found important for various solar energy devices such as mirror filters, anti reflection coating photosynthetic coating, thermal and solar control coatings [Tabor 1979, Meinel and Meinel 1979]. Some are moderately selective while others are non-selective. Those films whose optical properties such as absorbance, transmittance, emittance, reflectance etc. are dependent on wavelength are said to be spectrally selective films. For such films, the optical or radiative properties vary quantitatively with different parts of the electromagnetic spectrum.

Several methods for the deposition of thin films include thermal evaporation, electron beam evaporation, activated reactive evaporation epitaxy and ion plating [Campbel 1967, Duta 1985]. Other techniques include chemical vapor deposition

[Chopra and Das 1983, spray pyrolysis (Onyia and Okeke 1989), electrochemical deposition, anodization and solution growth technique (Nnabuchi and Okeke 2004, Ezema 2004, 2005).

In this work chemical bath deposition (solution growth technique) was adopted to deposit three thin films on glass substrates at varying parameters. The structural characterization of these films was done using microscope (HUND WETZLAR H600) and camera (RICOH 35mm SLR, XR-X300) at magnification of x400. The optical properties of the films examined are absorbance, reflectance, transmittance, extinction coefficient, refractive index and optical conductivity. Also in addition the thicknesses of the films were calculated.

MATERIALS AND METHODS

The reaction bath for the deposition of barium sulphide (BaS) thin films in this work includes barium chloride ($BaCl_2$) sodium thiosulphate ($Na_2\ S_2\ O_3.5H_2O$), EDTA and distilled water. $BaCl_2$ was the source of Ba^{2+}, $Na_2S_2O_3.5H_2O$ was the source of S^{2-} while EDTA was the complexing agent. The three films were obtained from the variation of bath compositions and concentration as shown in Table 1 below:

Table 1: Variation of bath composition and concentration of BaS thin films.

Reaction bath	Dip time (hr)	Temp (K)	pH	$BaCl_2$		$Na_2S_2O_35H_2O$		EDTA		H_2O (ml)
				Mol (m)	Vol (ml)	Mol (m)	Vol (ml)	Mol (m)	Vol (ml)	
D_7	48	Room	6.0	0.10	2	1.0	2	0.1	2	34
D_{10}	48	Room	6.2	0.01	2	0.5	2	0.1	2	34
D_{11}	20	Room	6.0	0.10	2	1.0	2	0.1	2	34

The ionic equations for the reaction are:

$$BaCl_2 + EDTA \leftrightarrow [Ba\ (EDTA)]^{2+} + 2Cl^-$$
$$BaCl_2 + TEA \leftrightarrow [Ba(TEA)]^{2+} + 2Cl^-$$
$$[Ba(EDTA)]^{2+} \leftrightarrow Ba^{2+} + EDTA$$
$$[Ba(TEA)]^{2+} \leftrightarrow Ba^{2+} + TEA$$
$$Na_2S_2O_35H_2O \leftrightarrow Na_2O_3 + 5H_2O + S^{2-}$$
$$Ba^{2+} + S^{2-} \leftrightarrow BaS\downarrow$$

As shown in Table 1, three samples were prepared using EDTA as complexing agent.

The spectral absorbance of the films was obtained using PYE-UNICAM UV SP8-100 spectrophotometers in the UV-VIS-NIR regions. The percentage transmittance in the infrared region was measured directly with infrared spectrophotometers. Other optical properties were calculated using the appropriate formula. Structural characterization was carried out using microscope (HUND WETZLAR H600) and camera (RICOH 35mm SLR, XR-X300) to produce micrographs at magnification of x400.

Transmittance, $T=I/I_o$ (where I is the transmitted flux and I_o is the incident flux. Reflectance, R and absorption coefficient α were calculated using $R = 1 - A - T$

and α = ln(1/T) x10^6 m^{-1} respectively. Other optical properties are refractive index.

$$N = \frac{1-R^{1/2}}{1-R^{-1/2}}$$

Extinction coefficient, $K = \frac{\alpha\lambda}{4\pi}$ [Pankove 1971]

and optical conductivity $\sigma_{op} = \frac{\alpha n c}{4\pi}$, where *c* represents velocity of light.

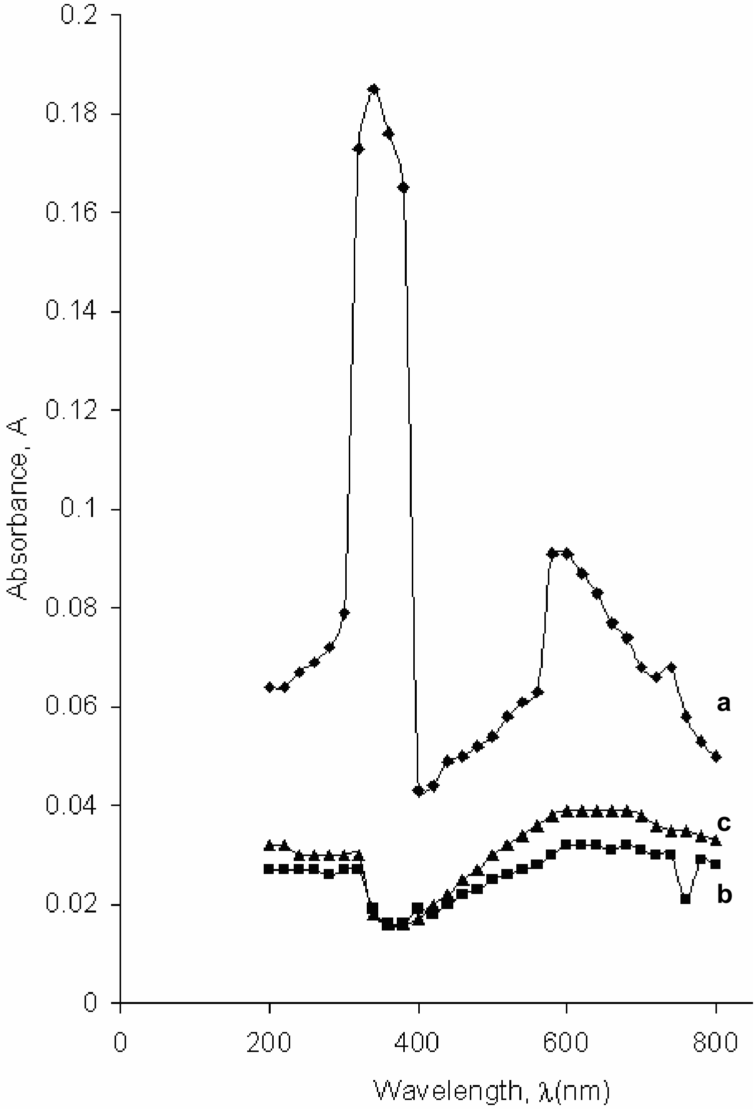

Fig. 1: Spectral absorbance of barium sulphide (BaS): a) D7, b) D10, c) D11 thin films.

RESULTS AND DISCUSSION

The spectral absorbance of barium sulphide films D_7, D_{10}, and D_{11} are shown in Fig. 1. The absorbance is generally low throughout the ultraviolet, visible and infrared regions. The value ranges from 0.02 to 0.04.

The range of spectral transmittance of the same set of films is 60-90% as shown in Fig. 2. This implies that it transmits greatly throughout the UV, VIS and IR regions. The shapes of the graphs are dissimilar showing that dip time and varying concentration of the reagents affected the transmittance spectra.

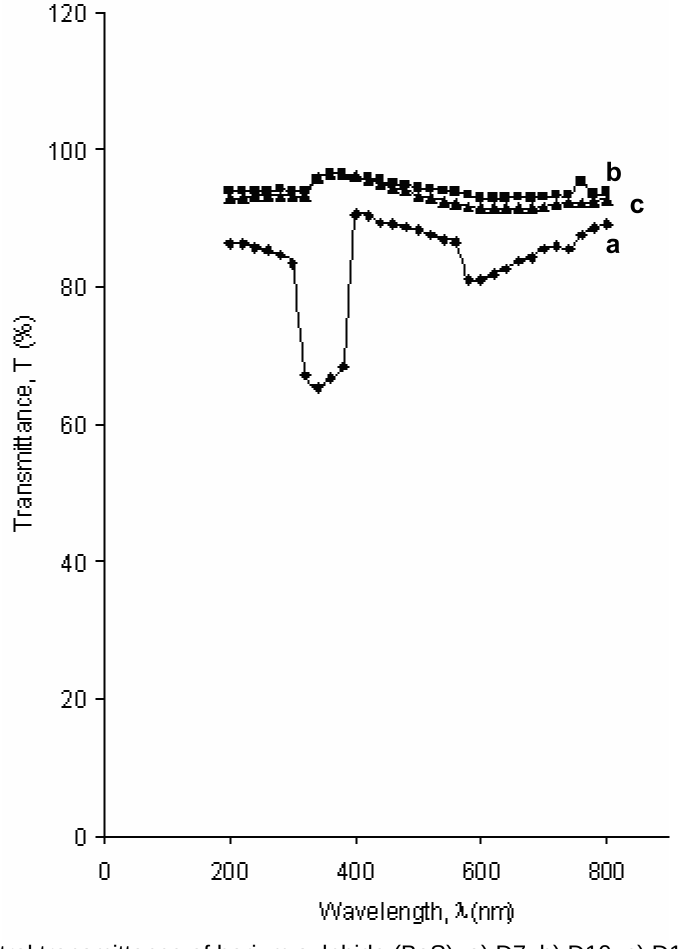

Fig. 2: Spectral transmittance of barium sulphide (BaS): a) D7, b) D10, c) D11 thin films.

Fig. 3 shows the reflectance spectra of films D_7, D_{10} and D_{11}. The difference in the molarities of $BaCl_2$ and $Na_2S_2O_3.5H_2O$ reagents and time of deposition were responsible for the large difference between the shapes of D_7 reflectance spectra on one side and D_{10} and D_{11} on the other side. The plots of K vs. $h\nu$ for D_7 and D_{11} are shown in Fig. 4. The extinction coefficient for D_{10} and D_{11} decreases as the photon energy increases except at 4eV where there are sharp rise and fall. The refractive index N vs. $h\nu$ plots for D_{10} and D_{11} are displayed in Fig. 5. The range of refractive index for D_{10} and D_{11} is ~ 1.32-1.55. Concentration of the reagents has significant effect on the shape of the graphs. Optical conductivity, σ_{op} vs. hν for D_7 is displayed in Fig. 6. The peak value is recorded at 3.8 eV. Fig. 7 shows the same for D_{10} and D_{11}. The range is ~1.0 $x10^{12}$ s^{-1} - 3.4 $x10^{12}$ s^{-1}. The minimum values are recorded at about 3.4 eV. Table 2 below is a display of the average values of these optical properties and thicknesses of BaS films. Fig. 8 shows the photomicrographs of BaS films deposited at 300K showing the structure of these films.

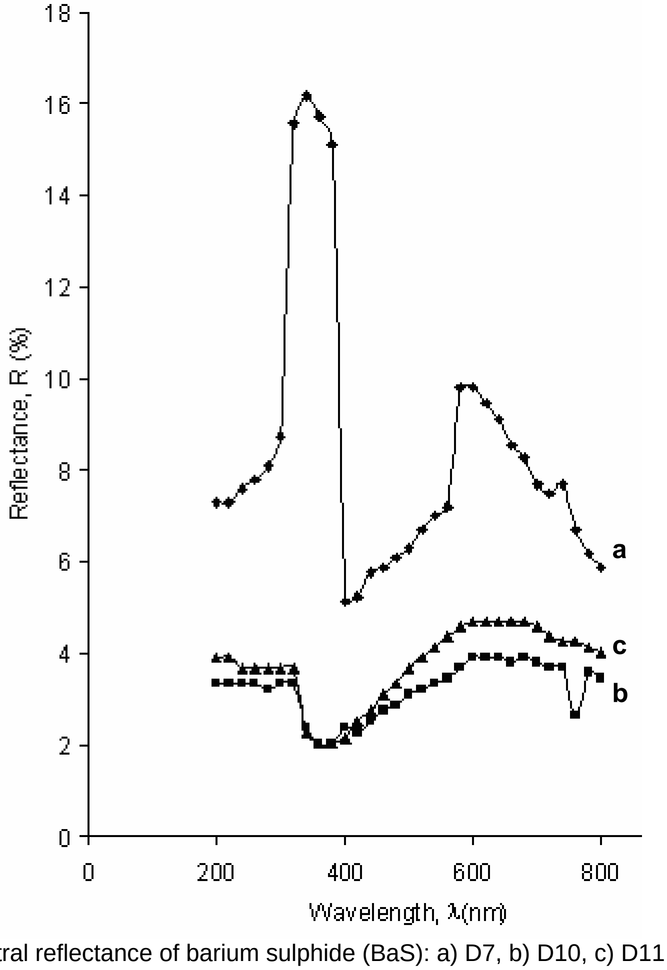

Fig. 3: Spectral reflectance of barium sulphide (BaS): a) D7, b) D10, c) D11 thin films.

Table 2: Optical properties and thicknesses of BaS films grown under varying conditions at 300K.

Reaction Bath	Dip time (hrs)	Average *N*	Average K $x10^{-3}$	Average σ_{op} $x10^{12}(s^{-1})$	Average α $x10^{6}(m^{-1})$	Average Thickness t (μm)
D_7	48	1.82	6.90	8.34	0.18	1.81
D_{10}	48	1.43	2.44	2.06	0.06	2.59
D_{11}	20	1.48	2.94	2.52	0.07	2.44

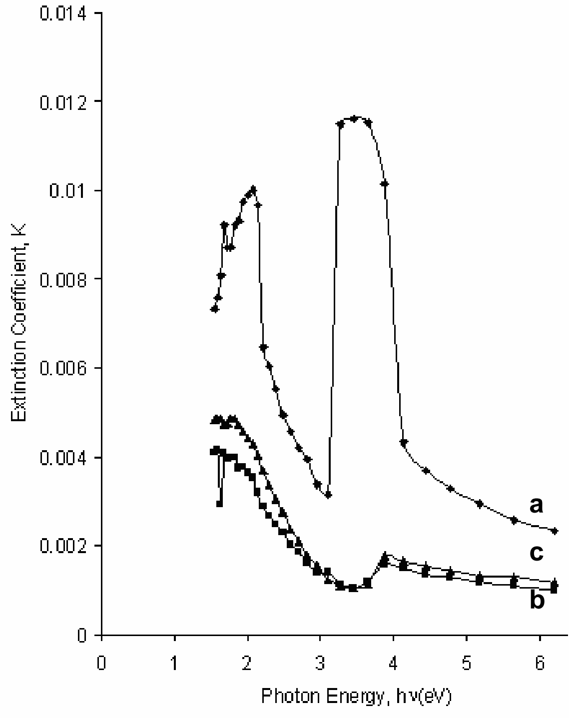

Fig. 4: Plots of extinction co-efficient against photon energy of barium sulphide (BaS): a) D7, b) D10, c) D11 thin films.

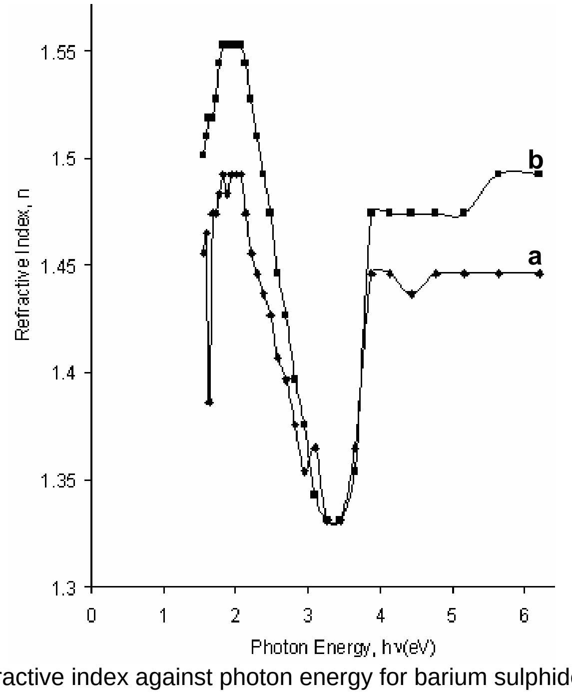

Fig. 5: Plots of refractive index against photon energy for barium sulphide (BaS): a) D10, b) D11 thin films.

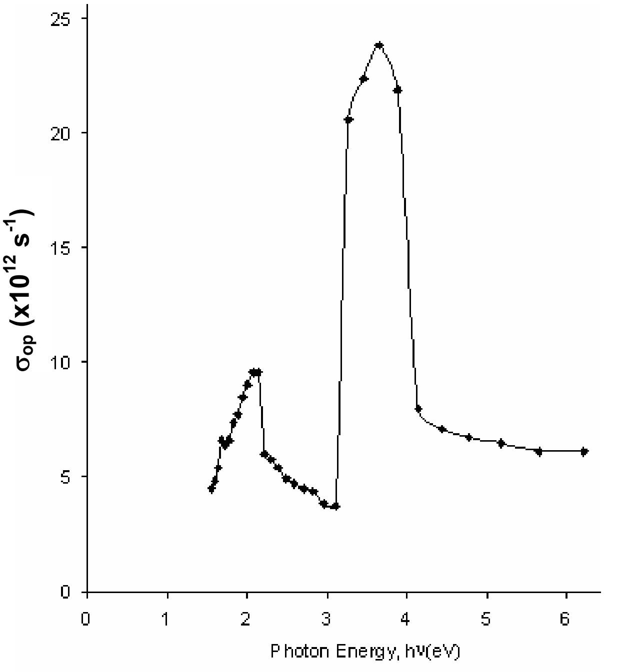

Fig. 6: Plot of optical conductivity against photon energy for BaS D7 thin film.

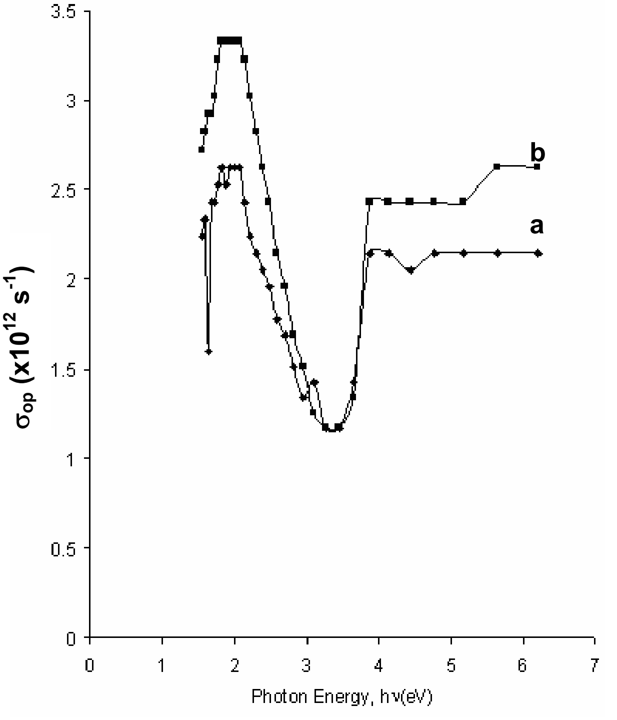

Fig. 7: Plots of optical conductivity against photon energy for BaS:
a) D10 and b) D11 thin films.

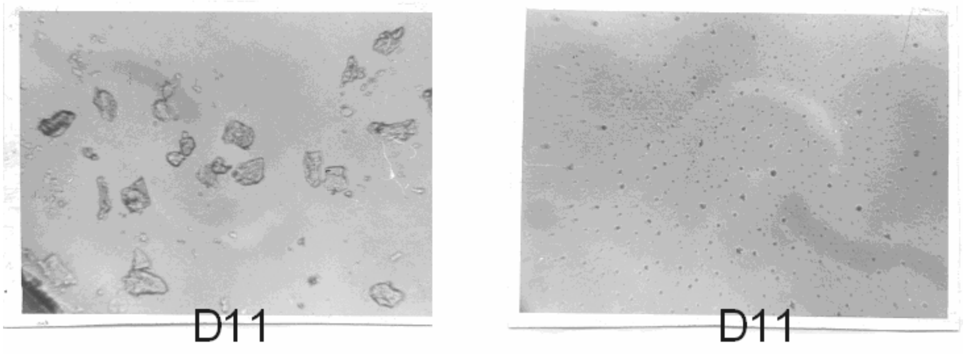

Fig. 8a: Photomicrographs of barium sulphide BaS - D11 thin films prepared at 300K.

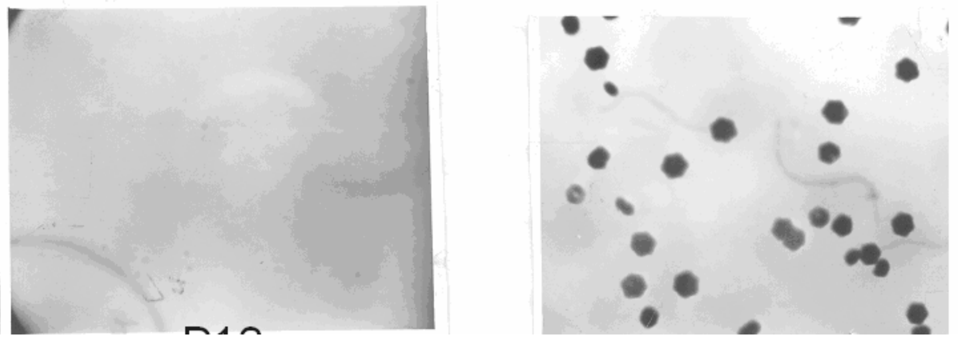

Fig. 8b: Photomicrographs of barium sulphide BaS - D10 thin films prepared at 300K.

From Table 2 it is clear that *N* has not much variation despite the variation in dip time for the different films. *K* and σ_{op} show great variations especially by D_7 film. Increase in bath concentration increases the thickness of the films very little.

CONCLUSION

It is possible to deposit three films of BaS thin films on glass substrates. The characterization shows that they have poor absorbance and reflectance. The transmittance range of the films from the UV to NIR is 60 to 90%. The range of the refractive index is 1.30-1.60, extinction coefficient has a range of 0.001-0.012, while optical conductivity has a range of $1.0\text{x}10^{12}s^{-1}$ to $25.0\text{x}10^{12}s^{-1}$. They are found suitable in so many solar applications such as solar energy collection, antireflection and photosynthetic coatings.

References

Campbel, O.S. (**1967**) “Preparation of thin films”, In: J. Thewlis (Ed.), *Encyclopaedic Dictionary of Physics Supplementary*, Vol. 2, Pergamon Press, Oxford, UK.

Chopra, K.L. and Das, S.R. (**1983**) “Thin Film Solar Cells”, Plenum Press, New York.

Dutta, V. (**1985**) “Physical vapour deposition”, In: K.L. Chopra and L.K. Malhotra (Eds.), *Thin Films Technology and Applications*, Tata Mc Graw-Hill Publications, New Delhi, India.

Ezema, F.I. (**2004**) “Fabrication, optical properties and applications of undoped chemical bath deposited ZnO thin films, *J. res. Sci. B.Z. Univ.,* **15** (4), 343-350.

Ezema, F.I. (**2005**) “Optical characterization of chemical bath deposited bismuth oxy iodide (BiOI) thin films, *Turk. J. Phys.* **29**, 105-114.

Meinel, B. and Meinel, M.P. (**1979**) “Applied Solar Energy: An Introduction”, Addison–Wesley and Co., Reading, UK.

Nnabuchi, M.N. and Okeke, C.E. (**2004**) “Characterization of optimized grown calcium sulphide thin films and their possible applications in solar energy”, *Pacif. J. Sci. and Technol.,* **5**(2), 72-82.

Onyia, A.I. and Okeke, C.E. (**1989**) “Fabrication and characterization of tin oxide (SnO_2) thin films using simple glass spray system”, *J. Phys D: Appl Phys*., **22**, 1515 -1518.

Pankove, J.I. (**1971**) “Optical Processes in Semi-conductors, Prentice-Hall Publications, New York, USA.

Tabor, H. (**1979**) “Selective surfaces in solar energy conversion: An introduction course”, In: A.E. Dixon and J.D. Leslie (Eds.), *Selected Lectures From The 5th Course on Solar Energy Conversion*, University of Waterloo, Ontario, Aug 6-19, 1979, Pergamon Press, Oxford, UK.