Characterization of Optimized Grown Calcium Sulphide Thin Films and their Possible Applications in Solar Energy

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ABSTRACT

Five thin films of calcium sulphide (CaS) were deposited on micro-slides using solution growth techniques. The bath compositions include: calcium sulphate ($CaSO_4$), sodium thiosulphate ($Na_2S_2O_3.5H_2O$), distilled water and ethylene diamine tetra acetic acid (EDTA), which served as a complexing agent. The films were deposited at different bath parameters, which include molarity of solution, volume of solution and water, time of deposition, and pH.

The absorbance of the films was measured using a PYE-UNICAM SP8-100 model spectrophotometer. Transmittance, reflectance, absorption coefficients, energy bandgap, refractive index, extinction coefficient, dielectric constant, and optical conductivity were calculated. The transmittance percentage of the films was measured with Fourier Transform Infrared (FTIR) Spectroscopy, and a spectrophotometer.

Light microscopes (HUNDWETZLAR H600) and cameras (RICOH 35mm SLR, XR – X300) were used to examine and produce micrographs of the samples at magnifications of X400, while energy dispersive X-ray fluorescence (EDXRF) was used to determine the elemental composition of the films.

The optical and solid-state characteristics revealed that films of calcium sulphate (CaS) have a low absorbance (~ 0.01 – 0.04), high transmittance (~ 70 – 99%), and low reflectance range (~ 1 – 15%) throughout the ultraviolet, visible, and infrared regions. The range of the thickness (t) of the films is (~ 2.64 – 2.98μm), and the refractive index (n) is ~ 1.37 – 1.43. Other values are optical conductivity (σ_{op}) ~ 1.71 x $10^{12}(S^{-1})$–2.11 x $10^{12}(S^{-1})$; extinction coefficient (K) ~ 2.10 x 10^{-3}–2.40 x 10^{-3}; absorption coefficient (α) ~ 0.05 x 10^6 –0.06 x $10^6(m^{-1})$; and energy bandgap (E_g) ~ 3.90 – 4.10eV. From the above results one can observe that CaS is suitable for use as a photosynthetic material and window coating.

(Key words: photovoltaic material, thin films, chemical deposition, coatings)

INTRODUCTION

Solar energy is a renewable source of energy, which is free and can be harnessed for useful applications. It can be harnessed to produce electricity either directly through the use of photocells, or indirectly through the use of electric generators. These photocells are products of thin film technology. Thin films are formed by the process of atom-by-atom, molecule-by-molecule, ion-by-ion, or cluster-by-cluster condensation (Anajemba, 1995).

The present level of advancement of modern civilization requires huge amounts of energy, while at the same time there is rapid depletion of conventional sources of energy such as petroleum, coal, natural gas, etc. It is therefore imperative, that alternative energy sources must be identified. In this work, we developed five thin films and characterized them. The results of the characterization showed their areas of application in solar energy.

The techniques for the deposition of thin films include thermal evaporation, electron beam evaporation, activated reactive evaporation, epitaxy, and ion plating (Campbell, 1967 and Dutta, 1985). Other techniques include chemical vapor deposition (Chopra et al, 1983), spray pyrolysis (Onyia et al, 1989), electrochemical deposition, anodization, and solution growth techniques (Ezema, 2000).

The solution growth technique was used to deposit five thin films of calcium sulphate on glass-slides at different bath parameters. The films were characterized to determine their solid state and optical properties, surface structure, elemental compositions and thickness. The areas of application of the films were determined based on the results of our characterization.

EXPERIMENTAL DETAIL

Calcium sulphide films were coated on micro-slides by the reaction of a solution of calcium sulphate ($CaSO_4$), sodium thiosulphate ($Na_2S_2O_3.5H_2O$), distilled water, and ethylene diamine tetra acetic acid (EDTA), which served as the complexing agent. The reaction details are presented below:

$$CaSO_4 + EDTA \rightleftharpoons [Ca(EDTA)]^{2+}] + SO_4^{2-}$$

$$Ca(EDTA)^{2+} \rightleftharpoons Ca^{2+} + EDTA$$

$$Na_2S_2O_3.5H_2O \rightleftharpoons Na_2O_3 + 5H_2O + S_2^{-}$$

$$Ca^{2+} + S^{2-} \rightleftharpoons CaS\downarrow$$

The five calcium sulphide films were deposited at different bath parameters as presented in Table 1.

After the deposition, a PYE-UNICAM SP8–100 model spectrophotometer was used to measure the absorbance of the films. The transmittance percentage of the films in the infrared region was measured directly with Fourier transform infrared (FTIR) spectrophotometers. The thickness (t) of the films was calculated using the following formula (Ezema and Asogwa 2004)

$$t = \frac{\left\{ \tan^{-1} \left(\frac{(n_o + n_s)^2 R - (n_o - n_s)^2}{\left(\frac{n_o n_s}{n} - n\right)^2 - \left(\frac{n_o n_s}{n} + n\right)^2 R} \right)^{1/2} \right\} \lambda}{2\pi n}$$

The structural characterization was done with a light microscope (HUND WETZLAR H600) and camera (RICOH 35mm SLR, XR–X300). The energy dispersive X-ray fluorescence (EDXRF) method was employed to determine the elemental compositions of the thin films.

THEORETICAL CONSIDERATIONS AND CALCULATIONS

(i) Transmittance, $T = I/I_o$ where I is the transmitted flux and I_o is the incident flux (Wooten, 1972)

(ii) Reflectance, $R = 1 – A – T$.

(iii) Absorption coefficient, $\alpha = \frac{\ln(1/T)}{t}$
$= \ln(1/T) \times (10^6 m^{-1})$.
(Digiulio et al, 1987)

(iv) Energy Bandgap, $E_g = h\nu - \alpha^2$.
h is Planck's constant and ν is the frequency (Abeles, 1972).

(v) Refractive index, $n = \frac{1 + R^{1/2}}{1 - R^{1/2}}$
(Robinson, 1952).

(vi) Extinction coefficient, $K = \frac{\alpha\lambda}{4\pi}$
(Pankove, 1971)

(vii) Dielectric constant, $\varepsilon = \varepsilon_r + \varepsilon_i = (n + ik)^2$.
ε_r is called the real dielectric constant and ε_i called the imaginary dielectric constant.

(viii) Optical conductivity, $\sigma_{op} = \frac{\alpha n c}{4\pi}$
c represents velocity of light.

Table 1: Preparation of Calcium Sulphide (CaS) Thin Films.

Reaction bath	Dip time (hr)	Temp. (^oC)	pH	$CaSO_4$		$Na_2S_2O_3.5H_2O$		EDTA		H_2O
				Mol (m)	Vol. (ml)	Mol (m)	Vol. (ml)	Mol (m)	Vol. (ml)	Vol. (ml)
B_1	48	Room	5.5	0.5	2	1.0	2	0.10	2	34
B_2	48	Room	6.5	0.5	2	1.0	2	0.01	2	34
B_3	48	Room	6.0	0.5	5	0.1	2	0.10	2	31
B_4	48	Room	6.5	0.5	2	0.5	2	0.01	2	34
B_9	48	Room	5.0	0.5	4	1.0	4	0.10	4	28

THEORETICAL CONSIDERATIONS AND CALCULATIONS

The spectral absorbance of three Calcium Sulphide films, B_1, B_2 and B_3 deposited at different bath parameters are displayed in Figure 1.

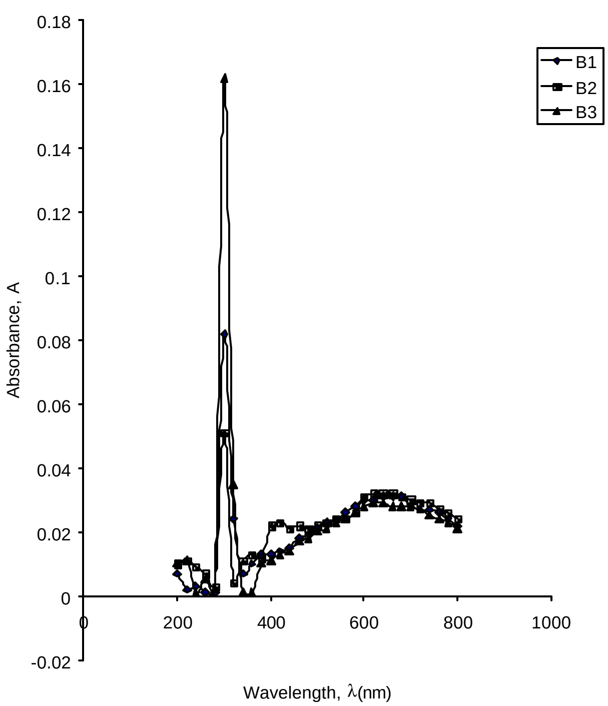


Fig. 1: Spectral Absorbance of Calcium Sulphide (CaS) - B1, B2 and B3.

The transmittance curves for the same set of films are presented in Figure 2, while Figure 3 is the graphical representation of reflectance for the three samples.

Generally the films exhibited low absorbance ranging from 0 – 0.17, high transmittance ranging from 70 – 100%, and low reflectance ranging from 0 – 15%.

Figures 4, 5 and 6 are infrared transmittance curves for the plain slide, B_1 film and B_3 film, respectively. Comparing the transmittance curves for the plain slide and B_1, B_3 films; it was observed that the CaS films reduced transmittance of light in the far infrared region.

The band gap of these films was 3.9eV, as shown in Figure 7. The plot of extinction coefficient vs. photon energy for films B_1, B_2 and B_3 are displayed in Figure 8.

Figure 9 shows a plot of refractive index against photon energy. The range is 1.2 – 2.4.

Figure 10 shows the plots of the real part of the dielectric constant against photon energy, while the plots of the imaginary part of the dielectric constant vs. photon energy are displayed in Figure 11. At the photon energy of 4eV, both the real and imaginary parts increased sharply. The plots of optical conductivity vs. photon energy for B_1, B_2 and B_3 are presented in Figure 12.

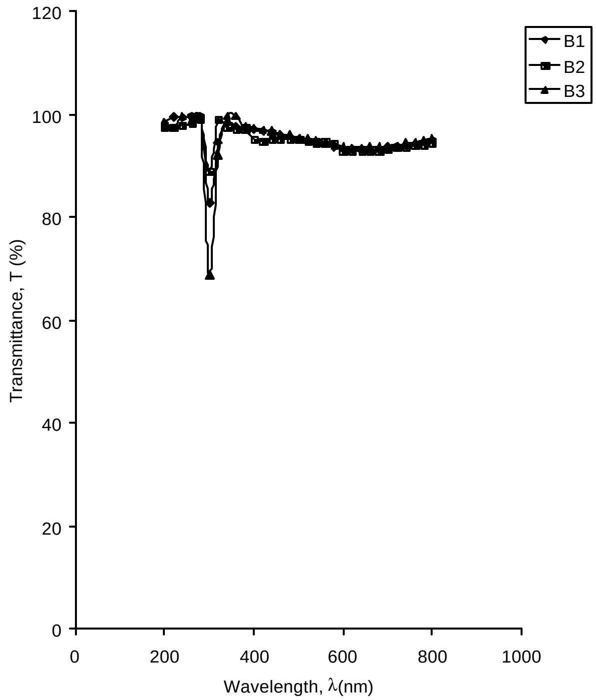


Fig. 2 : Spectral Transmittance of Calcium Sulphide (CaS) - B1, B2 and B3.

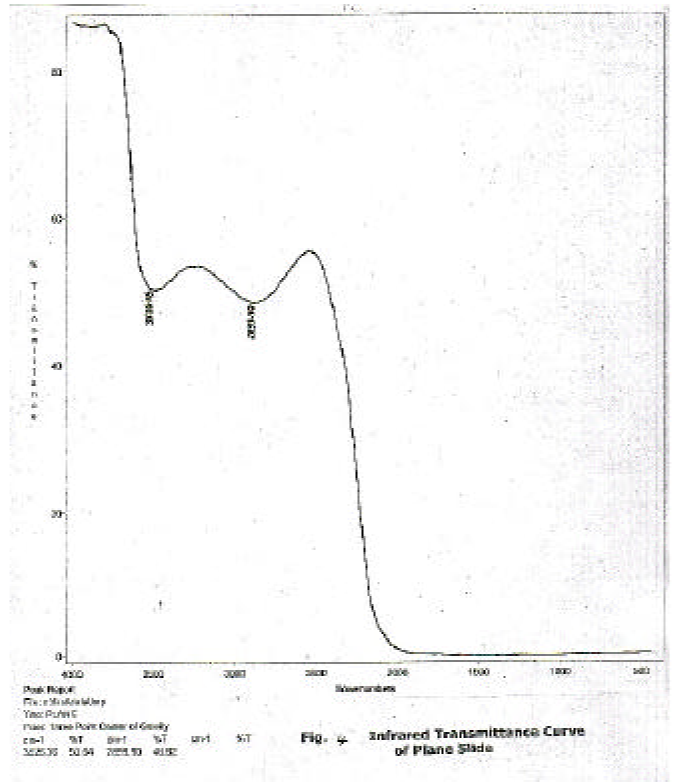


Fig. 4 Infrared Transmittance Curve of Plane Slide

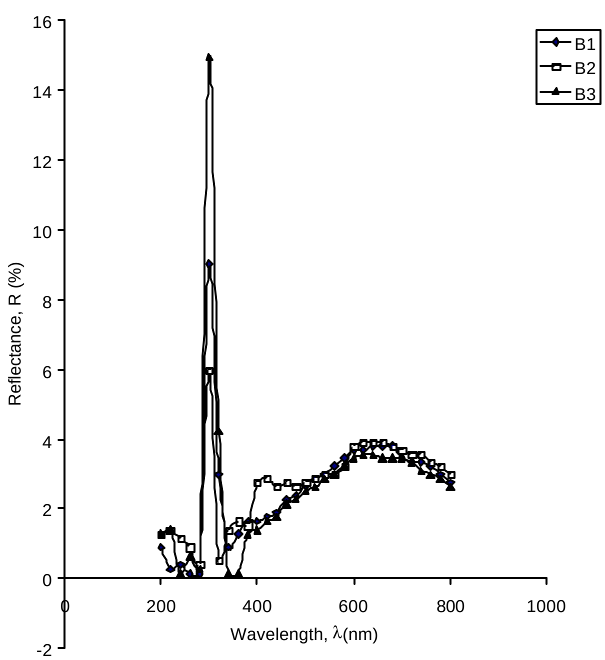


Fig.3: Spectral Reflectance of Calcium Sulphide (CaS) - B1, B2 and B3.

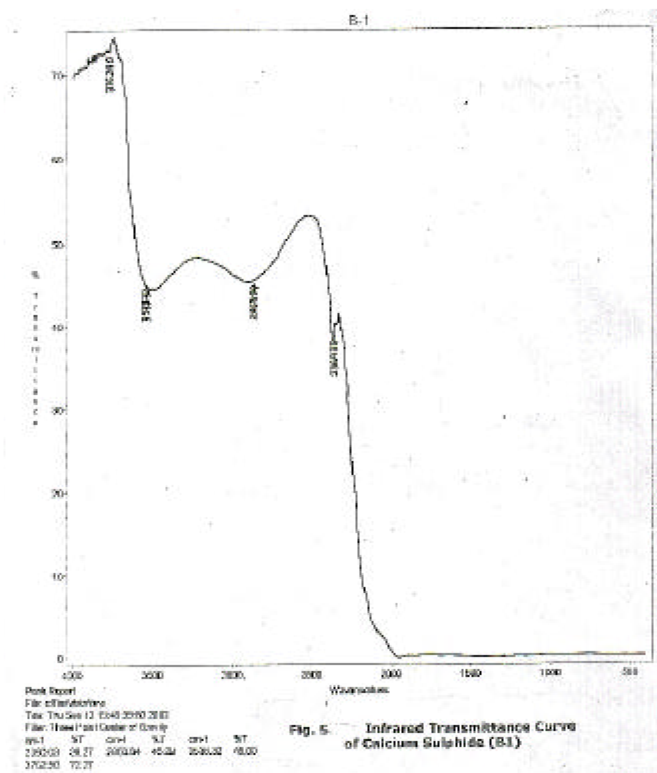


Fig. 5 Infrared Transmittance Curve of Calcium Sulphide (B1)

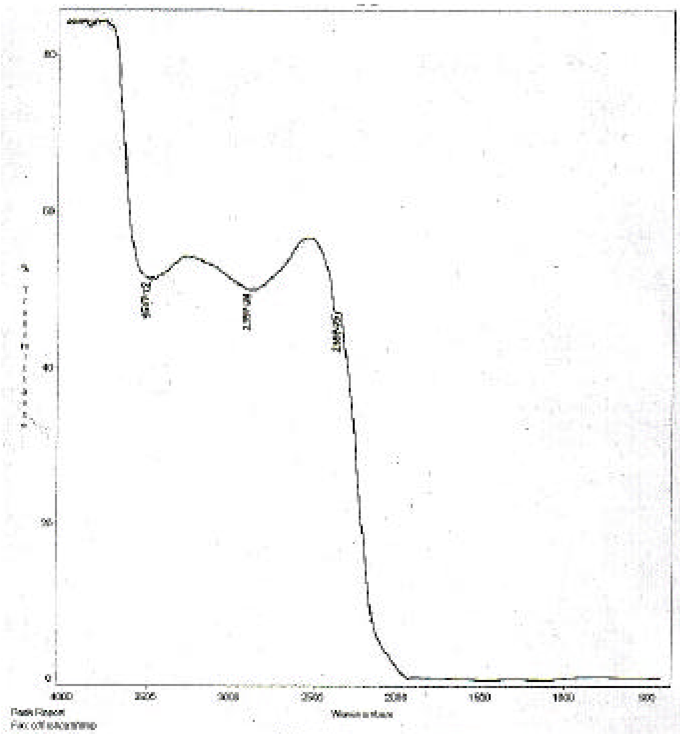


Fig. 6: Infrared Transmittance Curve of Calcium Sulphide (B3)

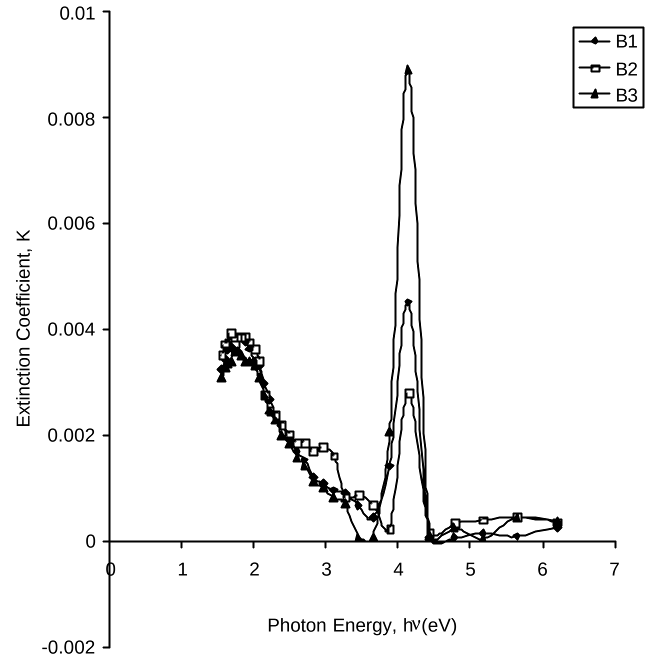


Fig. 8: Plot of Extinction Coefficient against Photon Energy for Calcium Sulphide - B1, B2 and B3.

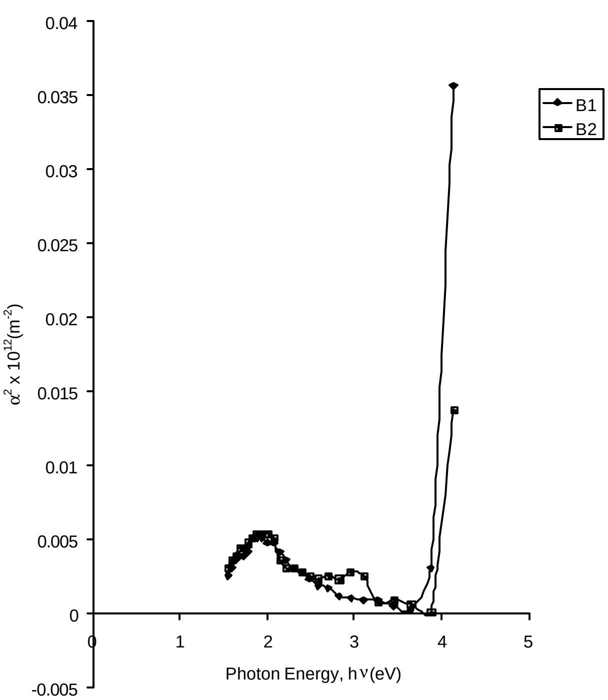


Fig. 7: Location of Energy gap for Calcium Sulphide (CaS) - B1 and B2.

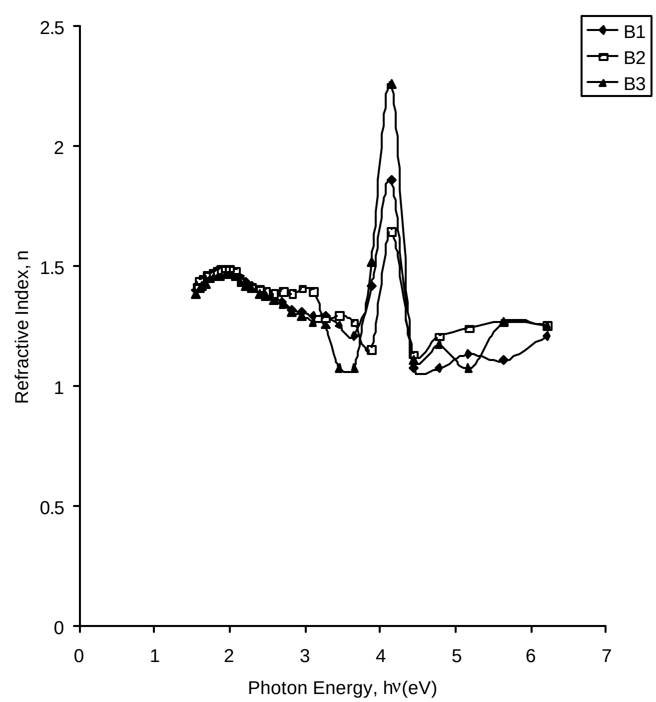


Fig. 9: Plot of Refractive Index against Photon Energy for Calcium Sulphide (CaS) - B1, B2 and B3.

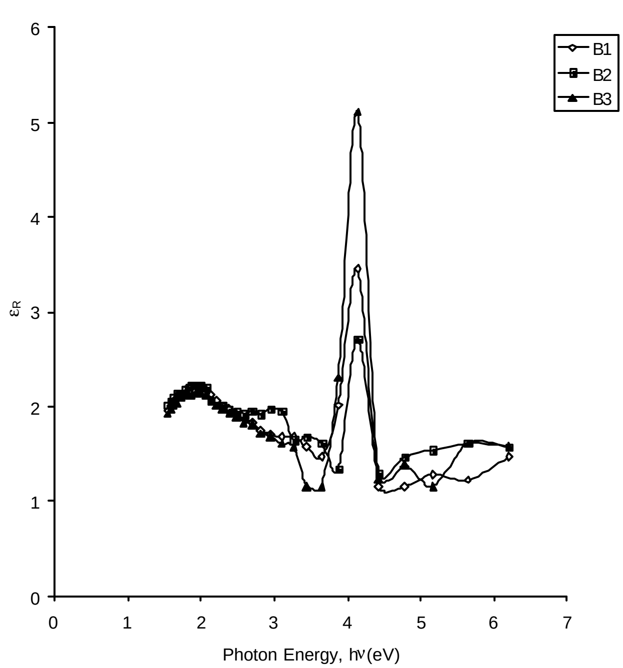


Fig.10: Plot of Real (ε_R) part of dielectric constant against Photon Energy for Calcium Sulphide- B1, B2 and B3.

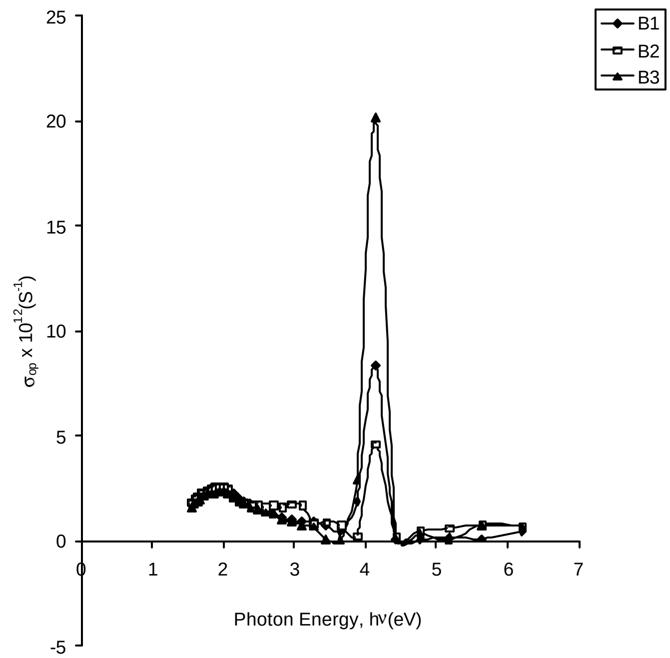


Fig. 12: Plot of Optical Conductivity against Photon Energy for Calcium Sulphide - B1, B2 and B3.

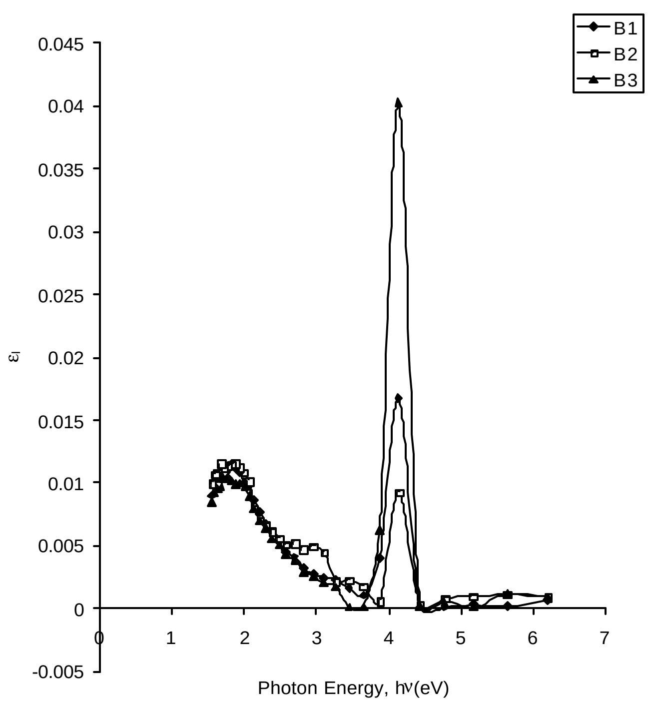


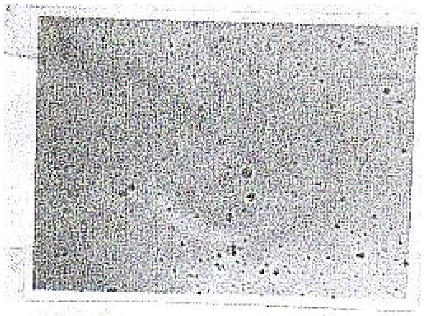
Fig.11: Plot of Imaginary (ε_I) part of dielectric constant against Photon Energy for Calcium Sulphide- B1, B2 and B3.

The photomicrographs of the films grown are displayed in Plate 1, while the average values of the optical, solid-state properties, and thickness of calcium sulphide films grown under varying bath parameters are presented in Tables 2 and 3 below.

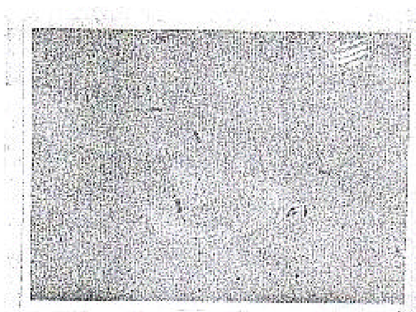
From Table 2, it can be observed that as thickness decreases, the extinction coefficient increases.

Additionally, from table 2, it can be observed that the extinction coefficient increases as the thickness decreases.

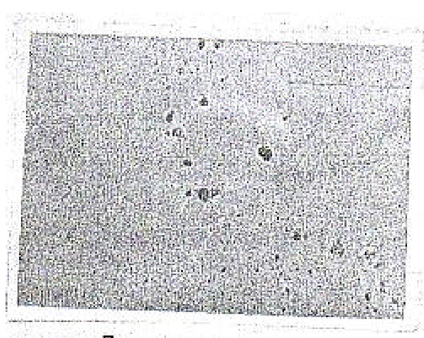
The energy dispersive x-ray fluorescence (EDXRF) method was employed to determine the elemental compositions of the thin films grown in this study. Tables 4, 5, and 6 present the analysis results for plain glass film B_4 and film B_9, respectively.



B1



B2



B3

Plate 1: Photomicrographs of the Films Grown in this Study (Films B1, B2, and B3)

Table 2: Optical Properties and Thickness of CaS Films Grown under varying Conditions at 300K.

Reaction bath	Dip time (hr)	Avg n	Avg k x 10^{-3}	Avg σ_{op} x 10^{12}(S^{-1})	Avg α x 10^{6}(m^{-1})	Avg Thickness t (μm)
B_1	48	1.37	2.10	1.71	0.05	2.93
B_2	48	1.39	2.20	1.74	0.05	2.79
B_3	48	1.37	2.20	2.03	0.05	2.92
B_4	48	1.38	2.10	1.76	0.05	2.98
B_9	48	1.43	2.40	2.11	0.06	2.64

Table 3: Solid State Properties of CaS Films Grown under varying Conditions at 300K.

Reaction Bath	Dip time (hr)	Bandg ap	Average ε_R	Average ε_I
B_1	48	3.90	1.95	0.01
B_2	48	3.90	1.93	0.01
B_3	48	3.90	1.92	0.01
B_4	48	3.90	1.90	0.01
B_9	48	4.10	2.04	0.01

CONCLUSIONS

It is possible to deposit calcium sulphide films at varying conditions by using a solution growth technique. The characterizations of these films have revealed their suitability in solar energy applications. Calcium sulphide films have very low percentage transmittance in the infrared region. If used as a window coating it could screen off the aspects of electromagnetic radiation responsible for heating up of the environment and thereby keep the temperature of the place very low.

Table 4: EDXRF Analysis Results of Blank Slide.

SAMPLE: Blank	IS5728	MATRIX: [AO (RES)= 11000]		WEIGHT [g/cm^2]: 0.942		
EL	E [KEV]	INT [C/S]	S	T	CONC [FRAC]	ERROR
K	3.312	0.052	1.65E+03	0.0025	1.18E-02	-LOD-
CA	3.690	0.518	1.96E+03	0.0033	8.06E-02	3.68E-03
TI	4.508	0.056	4.50E+03	0.0042	2.91E-03	-LOD-
BA	4.450	0.057	2.09E+03	0.0041	6.59E-03	-LOD-
V	4.949	0.039	6.74E+03	0.0054	1.04E-03	-LOD-
CR	5.411	0.042	8.76E+03	0.0067	7.03E-04	-LOD-
MN	5.895	0.050	1.11E+04	0.0083	5.26E-04	-LOD-
FE	6.400	0.222	1.38E+04	0.0103	1.53E-03	1.23E-04
CO	6.925	0.041	1.71E+04	0.0126	1.88E-04	-LOD-
NI	7.472	0.033	2.14E+04	0.0153	9.78E-05	-LOD-
CU	8.041	0.034	2.51E+04	0.0185	7.21E-05	-LOD-
ZN	8.631	0.042	3.01E+04	0.0221	6.21E-05	-LOD-
AS	10.532	0.055	4.27E+04	0.0361	3.50E-05	-LOD-
PB	10.540	0.047	2.50E+04	0.0361	5.05E-05	-LOD-
BR	11.907	0.037	5.93E+04	0.0480	1.28E-05	-LOD-
RB	13.375	0.070	6.46E+04	0.0619	1.72E-05	4.32E-06
SR	14.142	0.337	7.03E+04	0.0695	6.75E-05	4.37E-06
Y	14.933	0.043	7.60E+04	0.0775	7.09E-06	-LOD-
ZR	15.746	1.213	9.77E+04	0.0858	1.42E-04	3.86E-06
NB	16.584	0.047	1.06E+05	0.0942	4.63E-06	-LOD-
MO	17.443	0.64	1.15E+05	0.1029	5.27E-06	-LOD-
S	2.307	0.024	1.85E+03	0.0009	1.46E-02	2.43E-03

Table 5: EDXRF Analysis Results of Calcium Sulphide (B2).

SAMPLE: B2	IS5725	MATRIX: [AO (RES)= 11000]		WEIGHT [g/cm^2]: 0.942		
EL	E [KEV]	INT [C/S]	S	T	CONC [FRAC]	ERROR
K	3.312	0.048	1.59E+03	0.0025	1.13E-02	-LOD-
CA	3.690	0.522	1.89E+03	0.0033	8.37E-02	3.91E-03
TI	4.508	0.050	4.35E+03	0.0042	2.71E-03	-LOD-
BA	4.450	0.043	2.02E+03	0.0041	5.21E-03	-LOD-
V	4.949	0.042	6.52E+03	0.0054	1.16E-03	-LOD-
CR	5.411	0.037	8.46E+03	0.0067	6.30E-04	-LOD-
MN	5.895	0.037	1.08E+04	0.0083	3.99E-04	-LOD-
FE	6.400	0.217	1.33E+04	0.0103	1.55E-03	1.32E-04
CO	6.925	0.040	1.65E+04	0.0127	1.86E-04	-LOD-
NI	7.472	0.035	2.06E+04	0.0153	1.08E-04	-LOD-
CU	8.041	0.047	2.43E+04	0.0185	1.02E-04	-LOD-
ZN	8.631	0.044	2.91E+04	0.0222	6.62E-05	-LOD-
AS	10.532	0.056	4.12E+04	0.0362	3.65E-05	-LOD-
PB	10.540	0.047	2.41E+04	0.0362	5.22E-05	-LOD-
BR	11.907	0.038	5.73E+04	0.0481	1.35E-05	-LOD-
RB	13.375	0.061	6.24E+04	0.0621	1.53E-05	4.29E-06
SR	14.142	0.349	6.79E+04	0.0697	7.21E-05	4.45E-06
Y	14.933	0.050	7.34E+04	0.0777	8.58E-06	-LOD-
ZR	15.746	1.239	9.44E+04	0.0860	1.49E-04	3.99E-06
NB	16.584	0.050	1.02E+05	0.0945	5.07E-06	-LOD-
MO	17.443	0.054	1.11E+05	0.1032	4.59E-06	-LOD-
S	2.307	0.013	1.85E+03	0.0009	8.32E-02	1.60E-04

Table 6: EDXRF Analysis Results of Calcium Sulphide (B3).

SAMPLE: B3	IS5725	MATRIX: [AO (RES)= 11000]		WEIGHT [g/cm^2]: 0.942		
EL	E [KEV]	INT [C/S]	S	T	CONC [FRAC]	ERROR
K	3.312	0.064	1.59E+03	0.0026	1.51E-02	-LOD-
CA	3.690	0.579	1.89E+03	0.0032	9.36E-02	4.10E-03
TI	4.508	0.054	4.35E+03	0.0041	2.98E-03	-LOD-
BA	4.450	0.047	2.02E+03	0.0039	5.86E-03	-LOD-
V	4.949	0.043	6.52E+03	0.0052	1.25E-03	-LOD-
CR	5.411	0.038	8.46E+03	0.0065	6.80E-04	-LOD-
MN	5.895	0.037	1.08E+04	0.0080	4.23E-04	-LOD-
FE	6.400	0.222	1.33E+04	0.0099	1.64E-03	1.39E-04
CO	6.925	0.043	1.65E+04	0.0122	2.10E-04	-LOD-
NI	7.472	0.036	2.06E+04	0.0147	1.15E-04	-LOD-
CU	8.041	0.035	2.43E+04	0.0178	7.91E-05	-LOD-
ZN	8.631	0.035	2.91E+04	0.0213	5.51E-05	-LOD-
AS	10.532	0.054	4.12E+04	0.0347	3.71E-05	-LOD-
PB	10.540	0.047	2.41E+04	0.0348	5.42E-05	-LOD-
BR	11.907	0.037	5.73E+04	0.0462	1.35E-05	-LOD-
RB	13.375	0.070	6.24E+04	0.0596	1.83E-05	4.55E-06
SR	14.142	0.338	6.79E+04	0.0669	7.26E-05	4.62E-06
Y	14.933	0.047	7.34E+04	0.0746	8.39E-06	-LOD-
ZR	15.746	1.225	9.44E+04	0.0826	1.53E-04	4.14E-06
NB	16.584	0.047	1.02E+05	0.0908	4.96E-06	-LOD-
MO	17.443	0.054	1.11E+05	0.0908	4.84E-06	-LOD-
S	2.307	0.016	1.85E+03	0.0991	9.66E-02	1.90E-04

Films like B_1, B_2 and B_3, which transmit highly at $\lambda \sim 0.35–0.75 \mu m$ could be used as photosynthetic coatings. This is because they are likely to exhibit selective transmittance of photosynthetic active radiation (PAR).

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