__Original Research Article__

Effect of thiourea concentration on the structural, optical and electrical properties of Cu_2ZnSnS_4 thin films prepared by spray pyrolysis

ABSTRACT

Thin films of Cu_2ZnSnS_4 (CZTS), having different molar concentration of thiourea have been prepared on glass substrate by spray pyrolysis technique. The structural, optical and electrical properties of the CZTS thin films were carried out by X-ray diffraction (XRD), UV-vis spectroscopy and four probe method respectively. XRD analysis shows polycrystalline nature of CZTS films. A better crystallinity has been observed at thiourea concentration of 0.20 M. The optical study shows that band gap increases with increase in thiorea concentration. At thiourea concentration of 0. 20 M, the optical band gap is found to be 1.60 eV. It has also been observed that the sheet resistance of the sample having thiourea concentration of 0.20 M has minimum value of10.73 KΩ/□.

Keywords: [Cu_2ZnSnS_4 thin films, Spray pyrolysis, thiourea concentration]

1. INTRODUCTION

$CuInGaSe_2$ (CIGS) is considered as one of the most promising absorbent layers in solar cell fabrication [1, 2]. The US National Renewable Energy Laboratory (NREL) reported that CIGS thin film solar cells exhibited a conversion efficiency of 22.6% [3]. However, the use of less abundant elements such as, In and Ga, limits the development of CIGS solar cells due to high production cost [4, 5]. To overcome these drawbacks, Cu_2ZnSnS_4 (CZTS) is emerging as a substituent for CIGS. The crystal structure of CZTS is similar to the chalcopyrite semiconductor CIGS [6].

The quaternary compound copper zinc tin sulfide (Cu_2ZnSnS_4: CZTS), generally exists as a p-type semiconductor with tunable band gap ranging from 1.4 eV to 1.7 eV [7]. The most important property of this compound is that it has absorption coefficient greater than 10^4 cm^{-1} [8]. Further, the constituent elements of this compound are inexpensive, readily available and environment friendly. These factors made CZTS a potential material for the photo-absorbing layer in the fabrication of low cost thin film solar cells. It was reported that CZTS solar cell achieves an efficiency of 9.5% [3].

Thin films of CZTS can be prepared by using various techniques such as pulsed laser deposition [9], radio frequency magnetron sputtering [10], spray pyrolysis [11-15], electrochemical deposition [16], thermal evaporation [17], etc. In this work, we report the structural, optical and electrical properties of CZTS films prepared by spray pyrolysis technique at different thiourea concentrations. The thiourea concentration was varied in the precursor solution during the preparation of CZTS films.

2. MATERIAL AND METHODS

CZTS thin films were deposited using a homemade spray pyrolysis. Firstly, aqueous solutions of 0.05M Cupric Chloride dihydrated($CuCl_2.2H_2O$) as a source of Cu, 0.025M Zinc Acetate dihydrated[Zn $(CH_3COO)_2$. $2H_2O$] as a source of Zn, 0.025M Tin Chloride dihydrated($SnCl_2$. $2H_2O$) as a source of Sn and various molar concentration of thiourea [$CS(NH_2)_2$] as a source of S were prepared. Then, these separate solutions were mixed with continuous stirring for 15 minutes which resulted in a clear transparent and homogeneous precursor solution [18]. All the chemicals used in this work were of AR grade. The prepared solution was sprayed on the hot substrate with the help of a locally available general purpose nebulizer. The solution was sprayed at flow rate of 2 ml/min with the compressed air for 3 minutes. The aerosols generated by the nebulizer passed through the glass nozzle, which was nearly half a centimeter in diameter, to the hot substrate. The distance between nozzle and substrate was fixed at 1.5 cm. The temperature of substrate was fixed at 310°C using a temperature controller J-Tec model-903.

In this experiment, the thiourea concentration was varied from 0.20 to 0.35 M in the precursor solution. The structural characterization of the as-prepared CZTS thin films was performed using X-ray diffraction (XRD) technique employing X-ray wavelength, λ= 0.15405 nm, and the diffraction angle was varied from 10° to 80°. The optical properties were investigated by measuring transmittance T% of the films with Ocean Optics Spectrophotometer USB 2000, Singapore. To study the electrical properties, the sheet resistances were measured using a four-probe technique.

3. RESULTS AND DISCUSSION

3.1 Structural Characterization – Figure 1(a) shows the XRD pattern of CZTS thin film fabricated with 0.20M thiourea concentration at a temperature of 310°C. The peaks observed at 2θ= 28.53°, 47.48°, and 56.35° correspond to (112), (220), and (312) planes, respectively of CZTS with kesterite structure with reference to JCPDS card# 26-0575. Additionally, the broad peak at 2θ = 26.09° is possibly due to presence of amorphous phase of Cu_4SnS_4 corresponding to (220) plane. This was determined through a comparison of d-spacing made with respect to JCPDS card# 29-0584 as described below in Table 1. Symbol d denotes this broad peak, as shown in the inset of Figure 1(a). Figure 1(b) shows the XRD pattern of CZTS film prepared with 0.35M thiourea at the same temperature of 310°C. The pattern also shows the similar peaks but at slightly shifted positions. Through Gaussian fit of the observed peaks in XRD pattern, we obtained the peak positions.

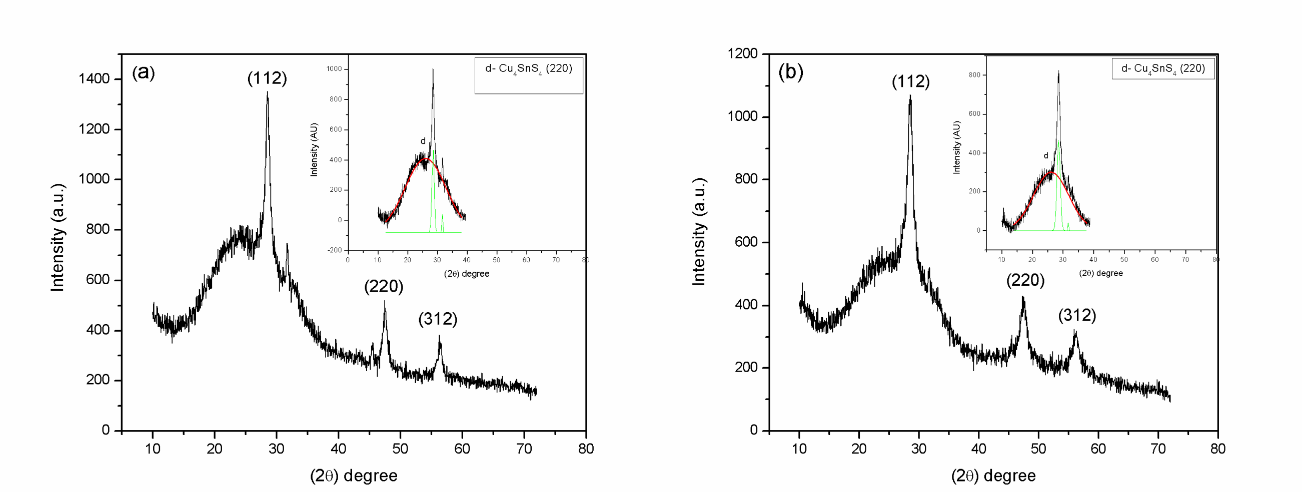

Fig.1. XRD pattern of CZTS thin films prepared with (a) 0.20M and (b) 0.35M thiourea. Insets to the figures show the Gaussian fit for the broad peak.

The peaks at about 28°, 47° and 56° were observed in both figures. It indicates the presence of polycrystalline CZTS film. The comparison of observed 2θ (d spacing) shows that as the concentration of thiourea in the precursor solution increased from 0.20M (figure 1(a)) to 0.35M (Figure 1(b)), the 2θ values slightly shifted as shown in table 1. For both concentrations, a broad peak at diffraction angle of about 26° was observed. This may be due to presence of an amorphous phase of Cu_4SnS_4. Since, the experiment was performed in non-vacuum conditions so we cannot ignore atmospheric oxygen for the formation of metal oxides, i.e ZnO. Improvement in crystallinity and minimization of secondary phase formations can be done by sulfurizing the deposited CZTS films with H_2S treatment at 550℃ for an hour in vacuum condition [19].

Table1. Peak position, observed and JCPDS- d spacing and (hkl) values obtained from XRD patterns of figure 1(a) and figure 1(b).

Figure	S.No.	Peak position (2θ) degree	Observed 'd' value	'd' value from JCPDS	JCPDS card number	(hkl)	phases
1(a)	1	26.09	3.3446	3.3420	29-0584	(220)	Cu_4SnS_4
	2	28.53	3.1250	3.1260	26-0575	(112)	CZTS
	3	47.48	1.9130	1.9190	26-0575	(220)	CZTS
	4	56.35	1.6314	1.6360	26-0575	(312)	CZTS
1(b)	5	26.62	3.3446	3.3420	29-0584	(220)	Cu_4SnS_4
	6	28.49	3.1303	3.1260	26-0575	(112)	CZTS
	7	47.45	1.9145	1.9190	26-0575	(220)	CZTS
	8	56.20	1.6354	1.6360	26-0575	(312)	CZTS

The crystallite size,D, of CZTS films was calculated using the Debye Scherrer's equation [20],

$$D = \frac{0.94\lambda}{\beta cos\theta}, \quad (1)$$

where λ, β, and θ represent the wavelength of X-ray, full width half maximum (FWHM) measured in radian and diffraction angle, respectively. The calculated values of relative intensities, FWHM, the D, dislocation density (δ), and texture coefficient (T_c) of above observed peaks were tabulated in Table 2. It shows that the intensities of all the peaks slightly shifted due to change in thiourea concentration. The FWHM of all observed peaks increases as the thiourea concentration increases from 0.20M to 0.35M and hence the crystallite size decreases. Similar pattern of decrease in crystallite size with increase in thiourea molar concentration was observed by Kiran Diwate et al [21]. It indicates that the sample prepared with 0.20M has better crystallinity than sample prepared with 0.35M of thiourea.The crystallite sizes of 11 nm and 7nm were observed for film prepared with 0.20 M thiourea and 0.35 M concentrations, respectively. Since instrumental line broadening and stresses are not taken into account, the correct grain sizes may be greater than above mentioned values. The decrease in crystallite size with increase in concentration of thiourea might be due to decrease in crystallinity of the film. The dislocation density ($\delta=1/D^2$) which gives the crystallographic defect or irregularity within a crystal structure was found to increase with increase in thiourea concentration as shown in Table 2.

The texture coefficient was calculated using the equation [20]

$$T_{c(hkl)} = \frac{I_{(hkl)}/I_{0(hkl)}}{\frac{1}{n}\sum_n I_{(hkl)}/I_{0(hkl)}}, \quad (2)$$

where $T_{c(hkl)}$ is the texture coefficient of (hkl) plane, $I_{(hkl)}$ is the intensity measured for (hkl) plane, $I_{o(hkl)}$ is the intensity of (hkl) plane taken from the standard data in JCPDS card fitting in the X-ray diffraction pattern material, and n is the diffraction peak number. Calculation shows texture coefficient values of greater than 1 for diffraction angles of both 28.53° and 56.35°. It infers that the samples show a preferential orientation along (112) direction. A closer look at the variation of T_c with thiourea concentration reveals that as thiourea concentration increases, T_c for diffraction angle 28.53° decreases from 1.3326 to 1.3147 which is shown in Table 2. It shows the orientation along (112) direction decreases with increase in thiourea concentration.

Table2. Calculation of grain size, dislocation density and texture coefficient

Thiourea conc. (M)	Observed d values (Å)	Observed Relative Intensity (%)	JCPDS d values (Å)	JCPDS Relative Intensity (%)	FWHM (degree)	D (nm)	δ (×10^2 nm)$^{-2}$	$T_{c(hkl)}$
0.20M	3.1250	100	3.1260	100	0.7722	11	0.8899	1.3326
	1.9130	26	1.9190	90	0.8756	10	1.0203	0.5478
	1.6314	15	1.6360	25	0.8426	11	0.8734	1.1194
0.35M	3.1303	100	3.1260	100	1.1857	7	2.1003	1.3147
	1.9145	29	1.9190	90	1.2212	7	1.9778	0.5078
	1.6354	18	1.6360	25	1.4052	6	2.4414	1.1077

3.2 Optical Characterization – Figure 2(a) represents the absorbance of the CZTS films prepared with different thiourea concentrations as a function of wavelength. From this figure, we see that absorbance starts to increase sharply at around 750 nm which is due to fundamental absorption of CZTS. A comparative study on variation of absorbance with thiourea concentration shows that the absorbance is higher for the sample prepared with 0.20M thiourea in comparasion to other thiourea concentrations. This might be due to greater amount of CZTS phase formation and better crystallanity nature of CZTS at 0.20 M thiourea concentration than at other concentrations. This result is found to be consistent with the structural analysis as discussed earlier through the observation of intense peaks in the XRD pattern of CZTS film prepared with 0.20M thiourea concentration. The direct band gap (E_g) of the each sample was determined by fitting the absorption data to the direct transition equation [22].

$$(\alpha h\nu)^2 = E_d(h\nu - E_g), \quad (3)$$

where α is the optical absorption coefficient, hν is the photon energy, E_g is the direct band gap,and E_d is a constant.

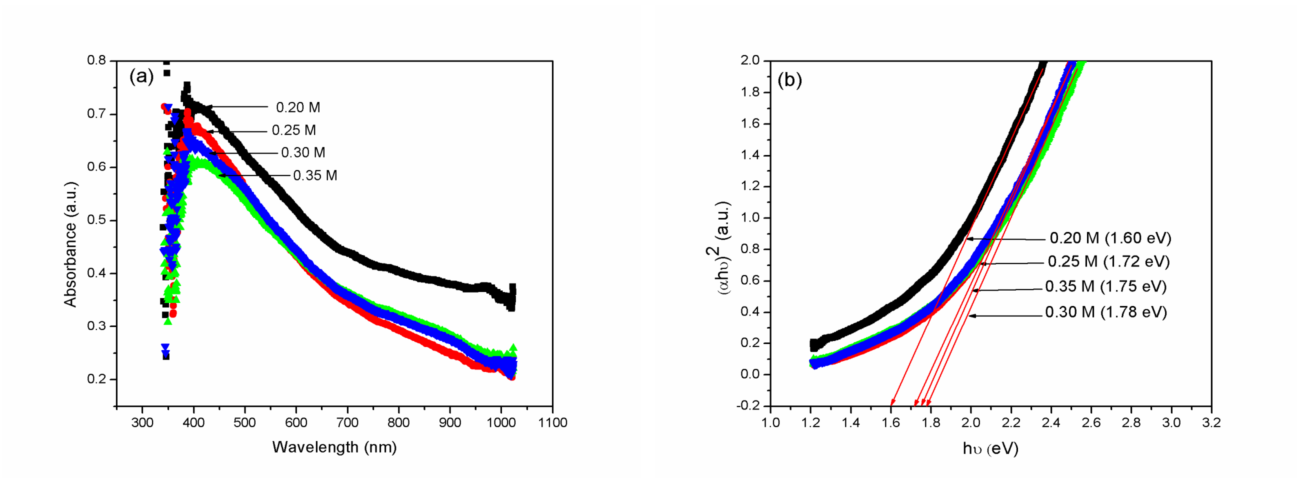

Fig.2. (a) Absorbance spectra and (b) band gaps of CZTS films prepared with different concentrations of thiourea.

Figure 2(b) shows the variation of $(\alpha h\nu)^2$ with photon energy, $h\nu$ (eV) of the prepared CZTS films. The optical band gap (E_g) of the films was determined by extrapolating the linear portion of $(\alpha h\nu)^2$ versus '$h\nu$' curve to $(\alpha h\nu)^2$ = 0 in the high absorption region. The band gap of CZTS film increased from 1.60eV to 1.78eV as the thiourea concentration increased from 0.20M to 0.35M shown in Table 3. The observed smallest band gap of 1.60 eV for film prepared with 0.20M thiourea was slightly higher than that reported by Kumar et al., [23]. The observation of increased band gap as thiourea concentration was increasing is possibly due to a decrease of particle size, which is consistent with our XRD results. The XRD results show as thiourea concentration increased from 0.20M to 0.35M the particle size decreased from 11 nm to 7 nm, which may lead to an increase in band gap. The greater value of band gap can be reduced by post sulfurization process.

Table 3. Band gap of CZTS films

S.N	Thiourea Concentration (M)	Band gap (eV)
1.	0.20 M	1.60 eV
2.	0.25 M	1.72 eV
3.	0.30 M	1.78 eV
4.	0.35 M	1.75 eV

3.3 Electrical Characterization – Figure 3 shows the variation of sheet resistance of CZTS films prepared with different thiourea concentrations. The sheet resistance was measured by the four probe method [24]. The result shows that as thiourea concentration increases, the sheet resistance of the CZTS film increases. This trend is possibly due to formation of larger particle size with CZTS film of 0.20 M thiourea concentration, having enhanced film crystallanity, than films prepared with other higher values of thiourea concentration: 0.25M, 0.30M and 0.35M. As thiourea concentration increases, the particle size decreases that leads to increase in grain boundaries. As charge carriers are scattered at the grain boundaries, this may increase resistivity of the material as well as sheet resistance of film deposited.

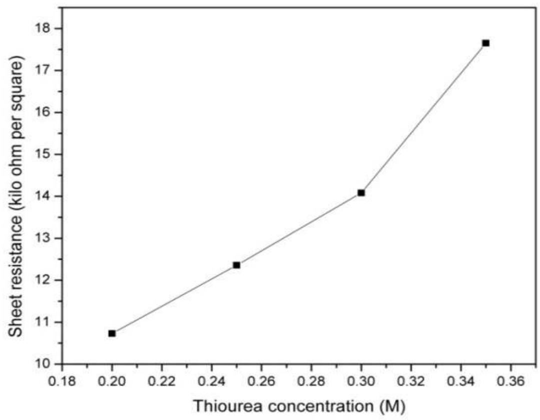

Fig.3. Sheet resistances of CZTS films prepared with various amounts of thiourea.

4. CONCLUSION

Thin films of CZTS were prepared by spray pyrolysis method. X-ray diffraction studies of as-prepared films indicate that the deposited films have kesterite structure. As the thiourea concentration increases from 0.20 M to 0.35 M the crystallite size decreases from 11nm to 7 nm. The lowest band gap of CZTS film prepared with 0.20M thiourea was 1.60 eV. Further, we observed that band gap increases from 1.60 to 1.75 eV as thiourea concentration increases from 0.20 M to 0.35 M. Electrical measurements show that sheet resistance of CZTS film increases from 10.73 to 17.65 kohm/□ when the thiourea concentration increases from 0.20 to 0.35 M.

REFERENCES

1. Ramanathan K, Contreras M, Perkins C, Asher S, Hasoon F, Keane J et al. Properties of 19.2% Efficiency ZnO/CdS/CuInGaSe_2 Thin-film Solar Cells. Prog. Photovolt: Res. Appl. 2003;11:225–30. DOI: 10.1002/pip.494

2. Nakada T, Mizutani M. 18% Efficiency Cd-Free Cu(In,Ga)Se_2 Thin-Film Solar Cells Fabricated Using Chemical Bath Deposition (CBD)-ZnS Buffer Layers. Jpn. J. Appl. Phys. 2002;41:165-67. DOI: 10.1143/JJAP.41.L165

3. Green M, Emery K, Hishikawa Y, Warta W, Dunlop E, Levi D, Ho-Baillie A. Solar cell efficiency tables (version 49). Prog. Photovolt: Res. Appl. 2016;25(1):3–13. DOI: 10 10.1002/pip.2855.

4. Andersson B. Materials Availability for Large-scale Thin-film. Prog. Photovolt. Res. Appl. 2000;8:61-76. DOI: 10.1002/(SICI)1099-159X(200001/02)8:1<61::AID-PIP301>3.0.CO;2-6.

5. Katagiri H. Cu_2ZnSnS_4 thin film solar cells. Thin Solid Films. 2005;480-481:426–32. DOI:10.1016/j.tsf.2004.11.024.

6. Lu X, Zhuang Z, Peng Q, Li Y. Wurtzite Cu_2ZnSnS_4 nanocrystals: a novel quaternary semiconductor. Chem. Commun. 2011;47:3141–43. DOI: 10.1039/c0cc05064d.

7. Hossain M. Prospects of CZTS Solar Cells from the perspective of material properties, Fabrication methods and current research challenges. Chalcogenide Lett. 2012;9(6):231–42.

8. Ito K, Nakazawa T. Electrical and Optical Properties of Stannite-Type Quaternary Semiconductor Thin Films. Jpn. J. Appl. Phys. 1988;27(11):2094-97. DOI: https://doi.org/10.1143/JJAP.27.2094.

9. Jin X, Yuan C, Jiang G, Liu W, Zhu C. Pulsed laser deposition of Cu_2ZnSnS_4 thin films from single quaternary sulfide target prepared by combustion method. Mater. Lett. 2016;175;180-83. DOI: https://doi.org/10.1016/j.matlet.2016.04.046.

10. Song N, Wen X, Hao X. Radio frequency magnetron sputtered highly textured Cu_2ZnSnS_4 thin films on sapphire (0001) substrates. J Alloys Compd. 2015;632;53-58. DOI: http://dx.doi.org/10.1016/j.jallcom.2015.01.192

11. Nakayama N, Ito K. Sprayed films of stannite Cu_2ZnSnS_4. Appl Surf Sci. 1996;92:171-75. DOI: 10.1016/0169-4332(95)00225-1.

12. Kamoun N, Bouzouita H, Rezig B. Fabrication and characterization of Cu_2ZnSnS_4 thin films deposited by spray pyrolysis technique. Thin Solid Films. 2007;515:5949–52. DOI: 10.1016/j.tsf.2006.12.144.

13. Kumar YB, Bhaskar P, Babu G, Raja V. Effect of copper salt and thiourea concentrations on the formation of Cu_2ZnSnS_4 thin films by spray pyrolysis. Phys. Status Solidi A. 2010;207(1):149–56. DOI: 10.1002/pssa.200925194.

14. Seboui Z, Cuminal Y, Kamoun-Turki N. Physical properties of Cu_2ZnSnS_4 thin films deposited by spray pyrolysis technique. J Renew Sustain Ener. 2013:5(023133):1-9. DOI: http://dx.doi.org/10.1063/1.4795399.

15. Bakr N, Khodair Z, Hassan S. Effect of Substrate Temperature on Structural and Optical Properties of Cu_2ZnSnS_4 (CZTS) Films Prepared by Chemical Spray Pyrolysis Method. Res J Chem Sci. 2015:5(10):51-61.

16. Farinella M, Inguanta R, Spano T, Livreri P, Piazza S, Sunseri C. Electrochemical deposition of CZTS thin films on flexible substrate. Energy Procedia. 2014;44;105-10. DOI: https://doi.org/10.1016/j.egypro.2013.12.015.

17. Garcia-Llamas E, Merino J.M, Gunder R, Neldner K, Greiner D, Steigert A et al. Cu_2ZnSnS_4 thin film solar cells grown by fast thermal evaporation and thermal treatment. Sol Energy. 2017;141;236-41. DOI: https://doi.org/10.1016/j.solener.2016.11.035.

18. Kamoun N, Bouzouita H, Rezig B. Fabrication and characterization of Cu_2ZnSnS_4 thin films deposited by spray pyrolysis technique. Thin Solid Films. 2007;515:5949–52. DOI: 10.1016/j.tsf.2006.12.144.

19. Das S, Frye C, Muzykov P.G , Mandal K.C. Deposition and Characterization of Low-Cost Spray Pyrolyzed Cu_2ZnSnS_4 (CZTS) Thin-Films for Large-Area High-Efficiency Heterojunction Solar Cells. ECS Trans. 2012;45(7);153-61. DOI: 10.1149/1.3701535.

20. Gupta G, Dixit A. Effect of precursor and composition on the physical properties of the low-cost solution processed Cu_2ZnSnS_4 thin film for solar photovoltaic application. J. Renewable Sustainable Energy. 2017;9(013502);1-13. DOI: http://dx.doi.org/10.1063/1.4974341.

21. Diwate K, Mohite K, Shinde M, Rondiya S, Paobake A, Date A et al. Synthesis and characterization of chemical spray pyrolysed CZTS thin films for solar cell applications. Energy Procedia. 2017:110:180-87. DOI: 10.1016/j.egypro.2017.03.125

22. Sze S.M, Kwok K. Ng. Physics of Semiconductor Devices. 3rd ed. New Jersey: John Wiley and sons; 2007.

23. Kumar YB, Babu G, Bhaskar P, Raja V. Preparation and characterization of spray-deposited Cu_2ZnSnS_4 thin films. Sol Energy Mater Sol Cells. 2009;93:1230–37. DOI: 10.1016/j.solmat.2009.01.001.

24. Van der Pauw L J. A method of measuring specific resistivity and hall effect of discs of arbitrary shape. Philips Res. Repts. 1958;13(1);1-9.