

SYNTHESIS AND CHARACTERIZATION OF UN-DOPED, RAFFIA PALM AND OIL BEAN DOPED LEAD CHLORIDE (PbCl_2) CRYSTAL IN SILICA GEL

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Abstract: The optical properties of un-doped, raffia palm and oil bean doped lead chloride (PbCl_2) have been studied by sol gel technique. The optical properties of lead chloride (PbCl_2) materials were determined using a JENWAY 6405 UV-VIS spectrophotometer, operating at a wavelength range of 200nm to 1200nm at an interval of 5nm. It was observed that the crystals are highly absorbing in the near infra-red to the infra-red region and as such are good materials for poultry and solar energy applications. The average refractive index (η) is between 0.1 and 3.0. The band gaps are from 2.4eV to 3.0eV, showing that the materials are wide band gap materials that could be applied in high temperature, high power, and high frequency materials. X-ray diffraction (XRD) studies showed that the materials are highly crystalline and of nano structures.

1.1 Introduction

Crystal growth is an interdisciplinary subject covering physics, chemistry, materials science, chemical engineering, metallurgy, crystallography, mineralogy, etc. In the past few decades, there has been a growing interest on crystal growth processes and doping technology, particularly in view of the increasing demand for materials for technological applications (Brice 1986, Nalwa and Miyata 1997). Modern day technology requires several types of doped semi-conductor materials, which have been attracting increasing interest for variety of applications (Samanta et al, 1996), In this work we used sol-gel techniques to grow un-doped and doped crystals of lead chloride (PbCl_2) using local materials as dopants.

1.2 Sol Gel Techniques

Sol gel consists of a three dimensional continuous network, which encloses a liquid phase; in a colloidal gel, the network is built from agglomeration of colloidal particles. The idea

behind sol-gel synthesis is to “dissolve” the compound in a liquid in order to bring it back as a solid in a controlled manner, (Okpala, 2003). The sol-gel method was developed in the 1960s, mainly due to the need of new synthesis methods in the nuclear industry.

1.3 Advantages of sol-gel growth technique

- It is extremely simple and inexpensive, good quality crystals can be grown even in small laboratories.
- Since the crystals are grown at or near room temperature, thermal strains are absent in the gel method.
- Crystals can be observed practically in all stages of their growth.
- The gel framework which is chemically inert and harmless acts like a three dimensional crucible in which the crystal nuclei are delicately held in the position of their formation and growth, thereby preventing damage.
- The effects of precipitation are eliminated as all nuclei are spatially separated.
- Gel medium considerably prevents convection currents and turbulence.
- Gel is soft and it yields a suitable environment for growing crystals.
- The purity of most crystals produced by this method is quite high; crystals generally contain only a few parts per million (atomic) of impurity.
- The gel method is capable of yielding crystals of high optical perfection and wide range of morphology.
- Gels also provide an efficient protection of samples during handling and transport without affecting their crystallographic analysis.
- Crystals are suspended in the gel network so that they do not form sediments and can grow free from strain exerted by the container.
- The grown crystals can be harvested easily without damaging the crystals.

1.4 Preparation of Materials

The raffia leaflets and oil beam seed were grounded to powder using manual grinding machine. These materials were placed on a crucible and burn in the absence of air, in a furnace of temperature 450⁰C (ash temperature) and allowed to cool. 100ml beaker was added with different quantities of sodium silicate solution; 30ml, 40ml, 50ml and 60ml with pH greater than eleven. It was titrated with some quantities of 1M of tartaric acid. The mixture formed gel at about pH 8.1-8.5. The set gel was added with 15ml of 1M of lead nitrate solution to give lead tartanate as in equation 1.1



The lead tartanate is generated in the gel as a white column, ring system of gradually increasing thickness. The precipitation of lead tartanate completed within a fortnight. 15ml of 1N of hydrochloric acid (HCl) and some pipette drops of locally produced impurities were placed over the set gel to give,



Fig. 3.1 Samples of gel formed.

1.5 Drying

The samples were first treated with all distilled water to avoid impurities and made slurry before it was introduced into a Buckner funnel, covered with filter paper, then attached to a suction flask, connected to a vacuum pump through its nozzle. When the pump was put on it

created a vacuum that allowed for the absorption of H₂O from the samples. The filter paper in the Buckner funnel prevented the solid from being sucked. The sample was then taken to the oven at an appropriate temperature of 100°C for 45 minutes. After which it was placed inside a desiccators to maintain dryness. CaCl₂ was used as desiccant.

1.6 Results and Discussion

Sample	(Na ₂ SiO ₃) (ml)	Pb(NO ₃) ₂ (ml)	Tartaric acid 7g in 100ml	impurity (ml)	P ^H
Un-doped A	30	quantity	15	,,,,,	8.4
B	20	„	15	0.5	8.5
C	30	„	15	0.8	8.1
D	50	„	15	1.0	8.5

Table 1.1 Quantity of reagent used in the growth

1.6a Graphs

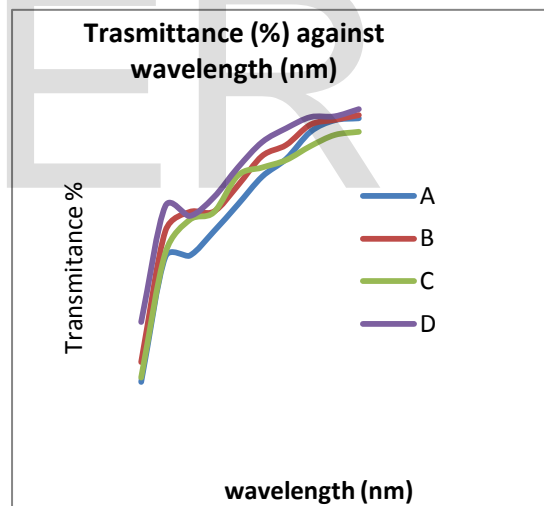
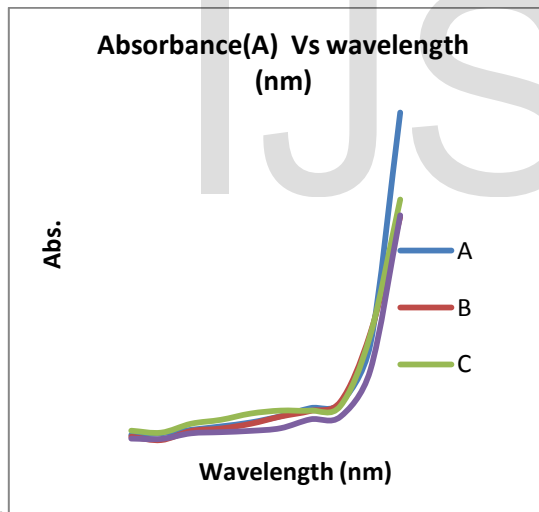


Fig 1.1 Graph of absorbance Vs Wavelength Fig. 1.2 Graph of Transmittance Vs Wavelength
 Figure 1.1 shows that sample A, have sharp increase in absorbance of about 2.20 in the visible/near infra-red. Sample D shows least absorbance in all the regions of the electromagnetic spectrum observed but sample C has the least absorbance in the ultraviolet/visible region. We observed that increase in the concentration of the impurities from raffia palm and oil beam seed coat lowered the absorbance of the crystal.

Sample D has highest transmittance from UV region to visible region and near infra-red region as in fig.1.2, followed by sample B in the UV region. Sample C maintained the same transmittance with A, from the UV to visible region down to infra-red region. This material could be used for poultry and solar energy applications.

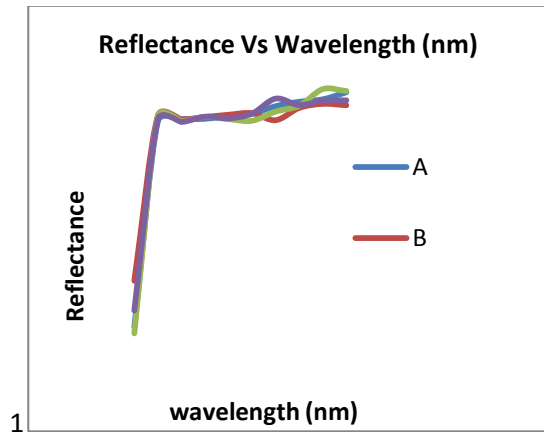


Fig. 1.3 graph of Reflectance Vs wavelength

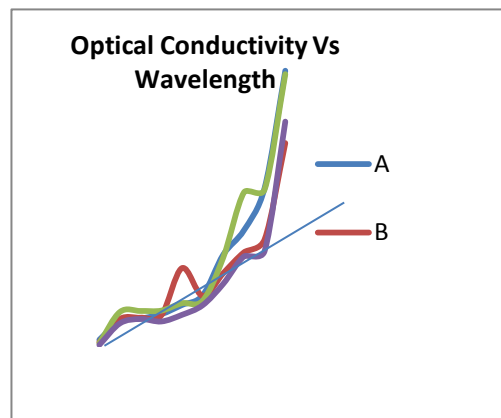


Fig 1.4 Graph of Optical conductivity Vs Wavelength

Figure 1.3, shows that A, B, C and D have high negative reflectance, 300nm to 600nm (mid visible), the sample showed the highest reflectance with sample C having the highest reflection of 0.256 at 500nm. Sample B have the least reflectance.

Optical conductivity against wavelength in figure 1.4 shows that sample A, B, C, and D maintained almost the same conductivity in the UV/region, from 350nm, their conductivity started increasing with sample B having a sharp increase in conductivity at 600nm which also decrease at 700nm.

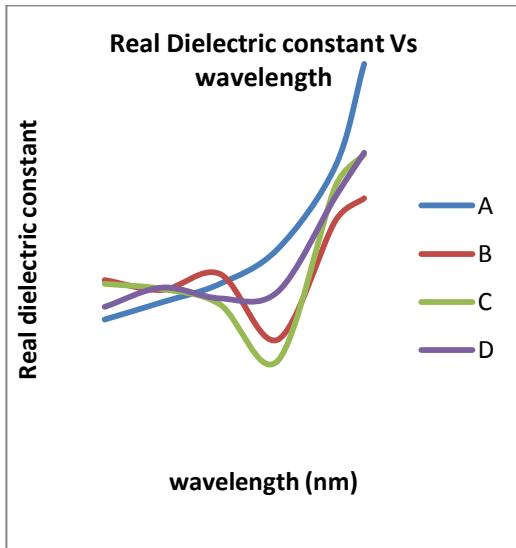


Fig.1.5 Graph of Real Dielectric Vs Wavelength

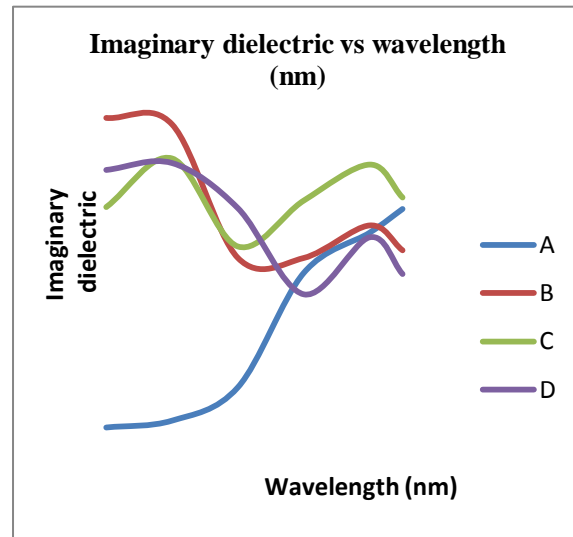


Fig.1.6 Graph of Imaginary dielectric Vs wavelength

Figure 1.5 shows that sample A has least value of real dielectric constant from 200nm to 500nm (UV- mid visible region), followed by sample D. Samples A, B, C and D witnessed some changes at 600nm, but Sample B, C and D decreases while sample A increased from 3.37 to 3.68. Sample A shows high real dielectric constant.

In Figure 1.6 sample A shows least dielectric constant in the ultraviolet region (200nm-350nm), from visible to near infra-red region, imaginary dielectric constant increases with increase in wavelength. Samples B, C and D behaved the same from 200nm-400nm, with sample C starting with least imaginary dielectric constant, followed by sample B and D. At 400nm sample B, C and D decreases in dielectric constant, with sample D showing the least followed by sample B, then C. from 800nm to 1000nm there was an increase in imaginary dielectric constant, but at 1100nm it started falling back which shows that the material is absorbed in near infra-red

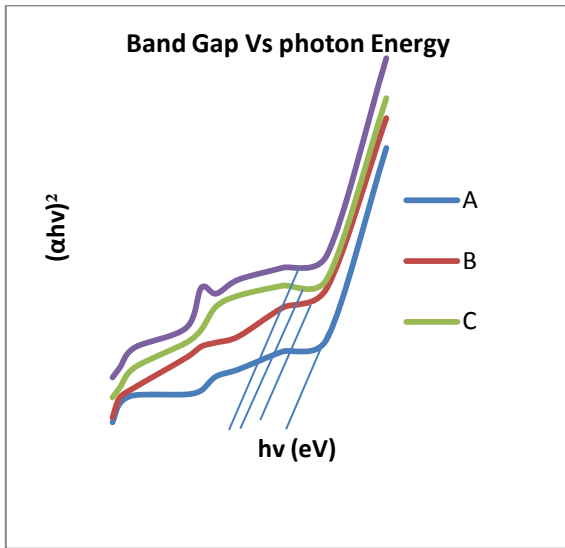


Fig.1.7 Graph of Photon energy Vs Band Gap

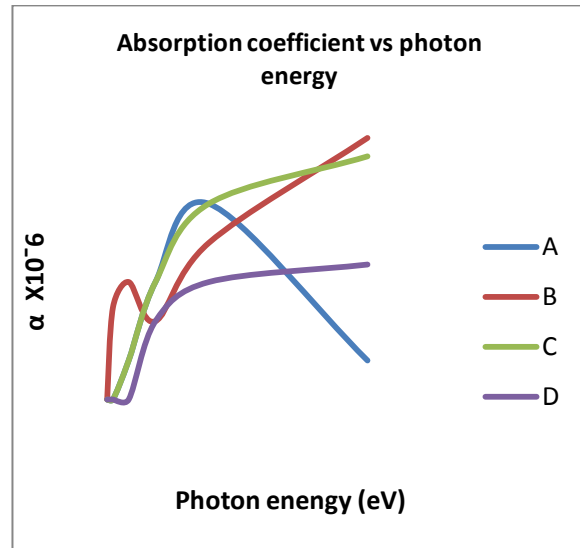


Fig.1.8 Graph of Absorption Coefficient Vs Photon Energy

Band gaps for the samples ranged from 2.4 to 3.0eV. Samples D have a large band gap of 3.0eV, followed by samples C and B. The least is the sample A which is un-doped with band gap of 2.4eV. The materials are all wide band gap materials which could be applied in high temperature, high power and high frequency materials and can be applied in solar energy and electronic technologies, (Okpala et.al., 2012; Ezema et.al., 2005)

1.6b X-ray Diffraction Result

Sample	Quantity of impurity (ml)	2θ	Crystallite size (nm)	FWHM
Un-dope PbCl ₂	/////	23.5, 26.41 27.72, 32.17	0.77, 1.65 0.27, 1.59	1.69, 0.82 5.16, 0.79
Doped PbCl ₂	0.5	6.88, 13.23 17.36, 28.07	2.77, 2.76 2.77, 2.86	0.49, 0.49 0.49, 0.49
Doped PbCl ₂	0.8	11.26, 10.49 13.67, 11.51	3.21, 3.21 3.21, 3.26	0.42, 0.42 0.42, 0.42
Doped PbCl ₂	1.0	9.88, 15.23 18.35, 29.06	2.77, 2.76 2.76, 2.82	0.49, 0.49 0.49, 0.49

Table 1.2 X-ray diffraction result

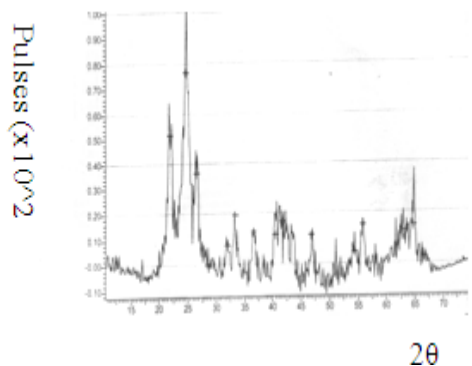


Fig. 1.9 XRD of Un-doped PbCl₂ Crystal

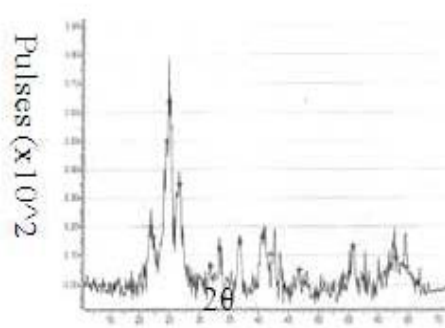


Fig. 1.10 XRD of 0.5 Doped PbCl₂ Crystal

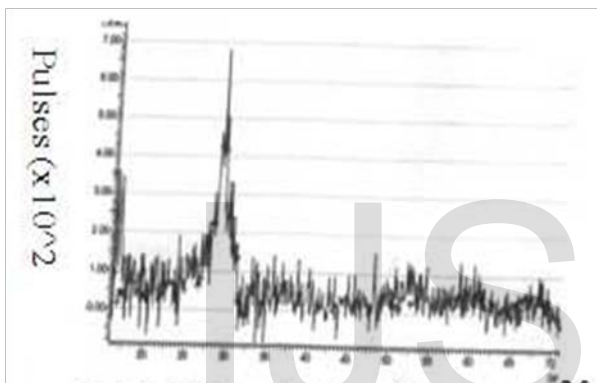


Fig. 1.11 XRD of 0.8 Doped PbCl₂ Crystal

1.7 Conclusion

Synthesis and Characterization of raffia palm and oil bean doped lead chloride (PbCl₂) crystal in silica gel have been carefully studied. Data for optical and solid state properties of the un-doped and doped lead chloride (PbCl₂) crystal were obtained using JANWAY 6405 UV-VIS Spectrophotometer. It was discovered that the materials have poor absorbance in the U.V. and visible regions but have high absorbance from the near infra-red to the infra-red regions and as such are good materials for poultry and solar energy applications.

They are wide band gap materials with band gaps from 2.4 to 3.0eV and can be applied in high temperature, high power and high frequency materials; solar energy and electronic technologies, (Okpala et.al., 2012; Ezema et.al., 2005).

References

1. Ban, T.D., Hamada, K., Hasegawa, H., Naiki, Y., Goto, (2003). Observation of Amyloid Fibril Growth Monitored by thioflavin T fluorescence, *Journal of Biochemistry* 278 (2), P. 16462-16465.
2. Brady, John B., and Boardman, Shelby J., 1995, Introducing Mineralogy Students to X-ray Diffraction through Optical Diffraction Experiments Using Lasers. *Jour. Geol. Education*, v. 43. Issue 5, 471-476.
3. Brady, John B., Newton, R. M., and Boardman, S. J., (1995). New Uses for Powder X-ray Diffraction Experiments in the Undergraduate Curriculum. *Jour. Geol. Education*, v. 43 Issue. 5, 466-470.
4. Brady, J. B., 1997, Making Solid Solutions with Alkali Halides (and Breaking Them) ,in:Brady, J., Mogk, D., and Perkins D. (eds.) *Teaching Mineralogy*, Mineralogical Society of America, p. 91-95.
5. Coutts, T.J., Ward, J.S., Emery, K., (2012). Model Performance of Polycrystalline thin film Tandem Cells, *Progressive in Photovoltaic Research and Applications*, 10. P195-203
6. David B. Tanner, optical effect in solid, lecture Note on Physics 7097, Department of Physics, University of Florida, Gainesville, USA.
7. Don Okpala, V. Uche (2013). Sol Gel Technique; A Veritable tool for Crystal Growth, *Pelagia Research Library* 4 (8), P.506-510.
8. Don Okpala, V. Uche (2013). Synthesis and Characterization of Local Impurities Doped lead Chloride (PbCl₂) Crystal in Silica Gel, *Pelagia Research Library* 4 (7), P. 477-487.
9. Dutrow, Barb, 1997, Better Living Through Minerals X-ray Diffraction of Household Products, in Brady, J., Mogk, D., and Perkins D. (eds.) *Teaching Mineralogy*, Mineralogical Society of America, p. 349-359.
10. E.A. and Reed, G.E., *J. Phys. Chem.*, Vol. 40, p.1161(1936), Vol. 41, p. 911-1937 Walter, A.T., *J. Polymer Sci.*, Vol. 13, p. 207-1954
11. Elsevier, B.V. (2009). *Federation of European Biochemical Societies* 583 (16), p. 2600-2609
12. Ezenwa, I.A., Ekpunobi, A.J., Ekwo, P. (2009). Growth and Characterization of Zinc Sulphide
13. Thin Films, By Chemical Bath Deposition, *Natural and Applied Science Journal* 10 (3), P. 234.
14. Ferry, J.D., et al., *Rev. Sci Instr.*, Vol. 112, p. 79 (1941); *J. Am. Chem. Soc.*, Vol. 64, p. 1323-1942; Vol. 70, p. 2244 (1948); *J. Coll. Sci.*, Vol. 9, p. 224 (1953); *J. Polymer Sci.*, Vol. 5, p. 195-1967.
15. Greenwood, N.N., Earnshaw, A. (1997). *Chemistry of the Elements*, 2nd Edition, Reed Education and Professional Publishing Ltd, Butterworth Heineman Linacre House Jordan Hill, Oxford.
16. Grolig, B., Kopp, J. (2003). *Optical Properties of Thin semiconductor Films* Jayant Dharma, Global Application Laboratory Manual, PerkinElmer Technical Center PerkinElmer, Inc Shelton, CT USA.
17. Hovis, Guy, L., (1997). Determination of Chemical Composition, State of Order, Molar Volume, and Density of a Monoclinic Alkali Feldspar Using X-ray Diffraction, in Brady, J., Mogk, D., and Perkins D. (eds.) *Teaching Mineralogy*, Mineralogical Society of America, p. 107-118.
18. John, M.P., King, N.T. (1980), Analysis Thin films and Interface, *Journal of Physics Today*, 33 (5), P. 34-39.
19. Lothian, G.F., (1958). *Absorption Spectrophotometry* 2nd Ed., Higher and Watts Ltd London, P.10- 20
20. Mahrov, B., Boschloo G., Hgfeldt A., Dloczuk L. and Dittrich T. (2004), *Photoelectron Spectroscopy*

Studies of $\text{Ru}(\text{dcbpyH}_2)_2(\text{NCS})_2/\text{CuI}$ and $\text{Ru}(\text{dcbpyH}_2)_2/\text{CuSCN}$ Interface for Solar Cell Applications

, Journal of Physical Chemistry B, 108 (31), P.11604-11610.

21. Moss, T.S.,(1961), Optical properties of Semiconductors, Butterworth and Co Pub. Ltd. London.
22. Muller, Richard S., Theodore, I. Kamins (1986). Device Electronics for Integrated Circuits. John Wiley and Sons.[ISBN 0-471-88758-7](#).
23. Ndukwe, I.C.,(1996). Solution Growth Characterization and applications of zinc Sulphide Thin films, Solar Energy 40, P.723.
24. Nellkon, M. (1997). Principal of Physics 7th Ed., Longman Group Limited, Longman House, Burnt Mill, Harlow, England, New York. P.478-500.
25. Ogueke, C.C., Nwosu, J.N., Onwuamanam, C. I., Iwouno, J.N.,(2010). Ugba, The fermented African Oil Bean Seeds; Its Production, Chemical Composition, Preservation, Safety and Health Benefits, Pakistan Journal of Biological Sciences, 13 (10), P. 489-496.
26. Okpala,, U.V., Ezema F.I., Osuji, R. U.,(2012). A study of Optical Properties of un-doped Potash doped Lead Chloride Crystal in Silica gel, Journal of nonmaterial's and Biostructures, vol. 7 (3), P. 861-870.
27. Okpala V. Uche, Ezema I. Felix, Osuji U. Rose, (2012), A study of Optical properties of un-Doped potash doped Lead Chloride Crystal in Silica Gel, Pelagia Research Library Vol.3, PP.103-109.
28. Perkins, Dexter, III, and Sorensen, Paul, Mineral Synthesis and X-ray Diffraction Experiments, in: Brady, J., Mogk, D., and Perkins D. (eds.) Teaching Mineralogy, Mineralogical Society of America, p. 81-90.
29. Weston, R.M (1962), In Photomicrography, J. Thewlis (ed) Encyclopedia Dictionary of physics Vol. 5, Pergamon press, London.
30. Woon-Jo J.,Cye Choon P.,(2003) Structural Electrical Properties of CuGaS_2 Thin Films