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A Study of the Optical Properties of Un-doped and Potash Doped Lead Chloride Crystal in Silica Gel

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ABSTRACT

The optical properties of potash doped lead chloride ($PbCl_2$) have been studied by sol gel technique. The optical properties of the 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 optically transparent. The average refractive index (n) is between 0.6 and 2.9. The refractive index greater than 2.0 makes the crystals good materials for protective coatings. The band gaps are from 3.9 to 5.0 showing that they are wide band gap materials and are good refractory materials.

Key words: Sol gel, Optical Properties, Silica Model and Local Impurities.

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INTRODUCTION

Sol-gel is a liquid based deposition technique [1,2]. It is a wet chemical technique widely used in the fields of materials science and ceramic engineering primarily for the fabrication of materials starting from a chemical solution which acts as the precursor for an integrate network (or gel) of either discrete particle or network of polymers [3]. A gel is a colloidal system in which the dispersed substance forms a continuous, ramifying, space-enclosing cohesive framework [4]. The gel medium prevents turbulence, and remaining chemically inert, provides a three-dimensional structure which permits the reagents to diffuse at a desirable controlled rate.

This research work is concentrated to the use of the sol-gel technique to grow some crystals of halide and chalcogenide compounds. Halides are binary compounds of which one part is a halogen and the other part is an element or radical that are less electronegative than halogen. A chalcogen is a chemical compound consisting of at least one chalcogen ion and one or more electropositive element. Chalcogen is reserved for sulphides, selenides and telluride. Chalcogenide thin films are potential candidates for high performance and low production cost optoelectronic and energy conversion devices including photo- electrochemical solar cell fabrication [5].

Sol gel is used in the manufacture of multi component glasses, coatings, fibres monoliths, thermal insulation materials, controlled particle size powders, as well as special types of ceramics such as electronic ceramics, superionic conductors and high temperature superconductors [6-9]. It is also used in the study of physical, chemical, electrical and magnetic properties of some materials as described in literature [10-13].

1.2. Lead Chloride Crystal ($PbCl_2$).

Lead chloride is a halide crystal which occurs naturally in the form of mineral cotunnite. It is used in the production of infra red transmitting glass and basic chloride of lead known as patteson's white lead [14], ornamental glass called aurene glass, stained glass. It is also used as an intermediate in refining bismuth (Bi) ore, it is used in the synthesis of organometallic (metallecene or plumbocenes), lead titanate and barium titanate [15,16]. The structure of $PbCl_2$ is orthorhombic dipyramidal. In this work, local potash which is a polymer in nature was used as dopant.

(a) Potash

Potash is a term coined by early American settlers who produced potassium carbonate by evaporating water filtered through wood ashes. The ash like crystalline residue remaining in the large iron pots was called 'potash' and was used in making soap. Potash (or carbonate of potash) is an impure form of potassium carbonate (K_2CO_3) mixed with other potassium salt. Potash has been used since antiquity in the manufacture of soap, glass and fertilizer [17]. Top-down approach was used to put potash into nano scale. Local potash is got by burning woods like tree fiber (ngu).

MATERIALS AND METHODS

In growing ($PbCl_2$), 100ml beaker was added with 25ml of sodium silicate solution of pH eleven. It was titrated with some quantity of 1M of tartaric acid. The mixture forms gel at pH 8. The set gel was added with 20ml of 1M of lead nitrate solution to give lead tartan ate as in equation (1.1),

$Pb(NO_3)_2 + H_6C_4O_6 \longrightarrow PbH_4O_6 + 2HNO_3$ ....(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. 20ml of 1N of hydrochloric acid (HCl) placed over the set gel to give,

$PbH_4C_4O_6 + 2HCl \longrightarrow PbCl_2 + H_6C_4O_6$ .... (1.2) [18]

And different concentrations of potash 0.5 and 0.8 normalities of locally produced impurity were also placed over the set gel. The HCl reacted with the colloidal precipitate of lead tartanate producing lead chloride ($PbCl_2$) which grew down into the gel as luminescent needles. The grown crystals were dried and adequately described through optical characterization (UV-VIS analysis) and structural analysis (XRD and FTIR). The quantity of the precursor materials used is as shown on table 1.

Table 1: Quantity of reagents used in the growth

Sample	Amount of sodium silicate (Na_2SiO_3) (g)	Amount of $Pb(NO_3)_2$ (ml)	Amount of tartaric	Concentration of K_2CO_3
A	25.0	20	Some quantity	Un-doped
B	25.0	20	"	0.5
C	25.0	20	"	0.8

DRYING

The samples were first treated with all glass 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 the vacuum pump through its nozzle. When the pump was put on it created a vacuum that allowed for the absorption of H_2O from the sample. The filter in the Buckner funnel prevented the solid from being sucked. The sample was then taken to the oven at an appropriate temperature of 104^0C for 30 minutes. After which it was placed inside the desiccators to maintain dryness. $CaCl_2$ was used as a desiccant.

RESULTS AND DISCUSSION

3.1. OPTICAL ANALYSIS.

The optical studies for the sol gel grown crystals were done using a JENWAY 6405 UV- VIS spectrophotometer operating at a wavelength range of 200nm to 1200nm at intervals of 5nm. In the optical absorption study, deionised water was used as reference. The crystal samples were dissolved in deionised water forming a colloidal solution which was then subjected to UV-VIS analysis.

Figures 1-4: Optical Analysis for Un-doped and Potash doped $PbCl_2$.

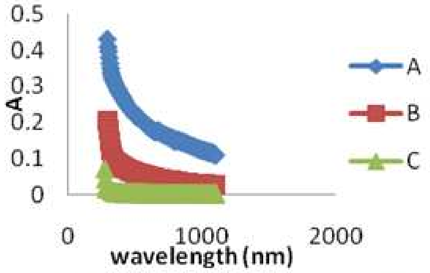


Figure 1: A plot of absorbance (A) against wavelength (nm)

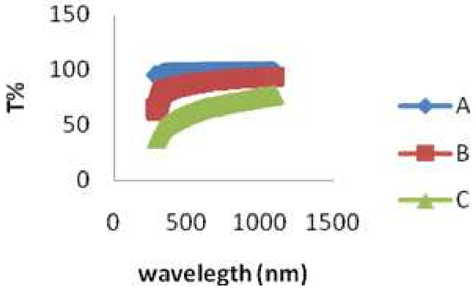


Figure 2: A plot of transmittance (T) against wavelength (nm)

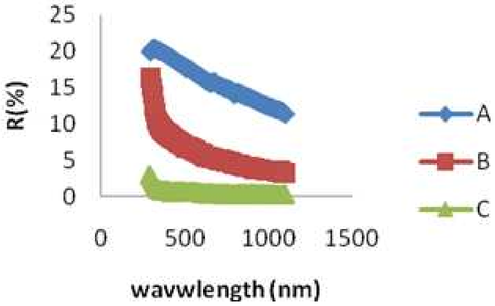


Figure 3: A plot of reflectance (R) against wavelength (nm)

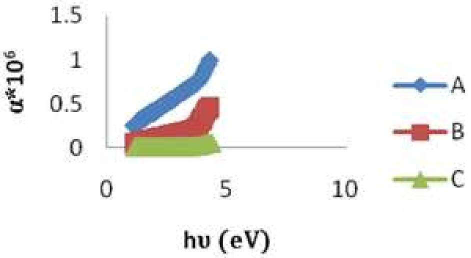


Figure 4: A plot of absorption coefficient (α) against photon

Figures 5-8: Graph of Optical constants for un-doped and Potash doped $PbCl_2$.

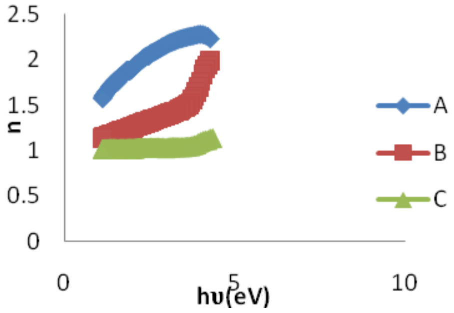


Figure 5: A plot of refractive index (n) against photon energy (eV)

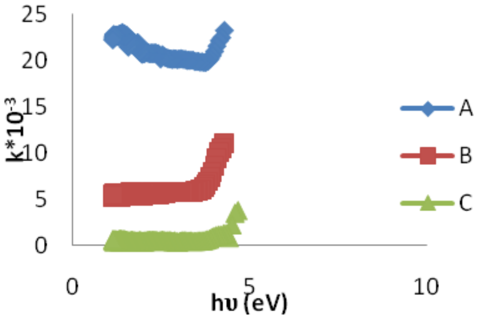
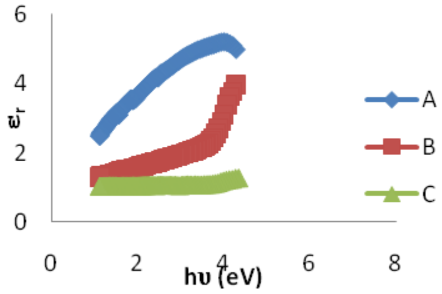


Figure 6: A plot of extinction coefficient (k) against photon energy (eV)



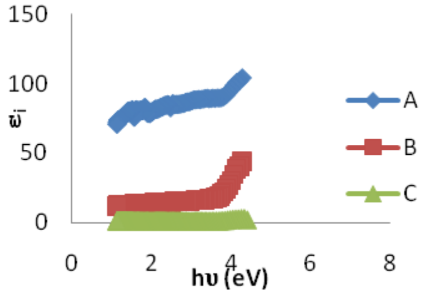


Figure 7: A plot of real dielectric (□$_r$) against photon energy (eV) **Figure 8: A plot of imaginary dielectric (□$_i$) against photon energy (eV)**

Table 2: Results of optical properties for un-doped and potash doped $PbCl_2$

S/n	Compd.	Appendix	Absorbance (A)	Transmittance (%T)	Reflectance (%R)	Absorption coefficient (α)	Usage
1	$PbCl_2$	1	Sample A is highly absorbing in the VIS region and decreased towards the IR but B and C are moderately absorbing in the VIS and decreased towards the IR region.	Sample A is highly transmitting from the VIS to the IR regions while samples B and C are moderately transmitting in VIS region and increased towards the IR.	Samples A and B are highly reflecting in the VIS and decreased towards the IR but sample C has very low reflectance in the VIS and no reflectance in the IR region.	Samples A and B have absorption coefficient between 0 and 1 while C has no absorption coefficient	The samples can be used in cold regions to warm rooms and in the coating of poultry roofs and walls [19].

Table 3: Result for optical constant for doped and un-doped $PbCl_2$

S/n	Compound	Sample	Refractive index (n)	Extinction coefficient (k x10^6m^{-1})	Real dielectric constant (€$_r$)	Imaginary dielectric (□$_i$)
1	$PbCl_2$	A B C	All the samples have very high absorption coefficient between 1 and 2.4	Sample A has the highest extinction coefficient followed by B but C has little or no extinction coefficient.	Samples A, B and C have real dielectric between 1 and 5.1.	Samples A and B have imaginary dielectric between 10 and 110 but C has no imaginary dielectric.

Figures 9-12: Optical band gaps for un-doped and doped lead chloride ($PbCl_2$)

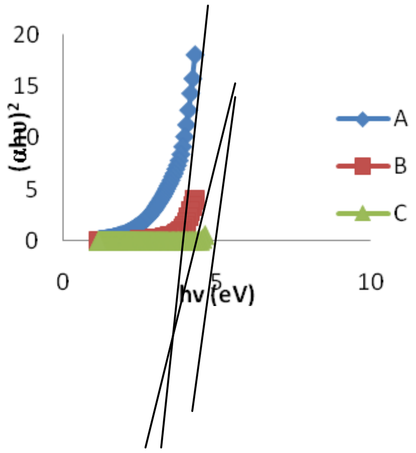


Figure 9: A plot of $(\alpha h\nu)^2$ against photon energy (eV)

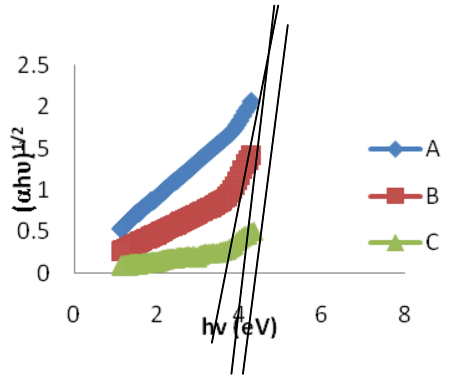


Figure 10: A plot of $(\alpha h\nu)1/2$ against photon energy

1

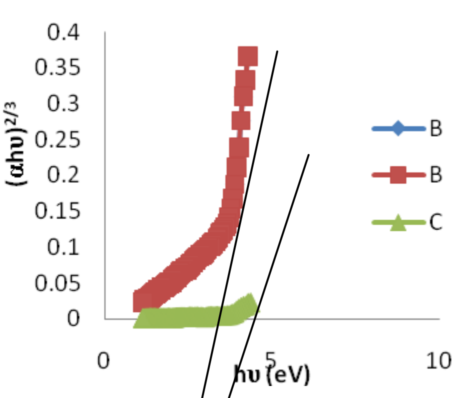


Figure 11: A plot of $(\alpha h\nu)^{2/3}$ against photon energy (eV)

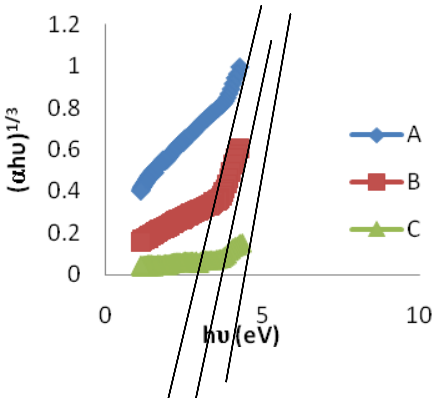


Figure 12: A plot of $(\alpha h\nu)^{1/3}$ against photon energy (eV)

Table 4: Result for optical band gaps for un-doped and potash doped $PbCl_2$

S/n	Compound	Sample	$(\alpha hv)^2$	$(\alpha hv)^{½}$	$(\alpha hv)_{1/3}$	$(\alpha hv)^{2/3}$	Usage
1	$PbCl_2$	A	3.9	3.3	4.0	4.0	Wide band gap materials can be used in high power, high temperature, and high frequency and optoelectronic devices [20].
2	$PbCl_2$	B	4.3	4.0	4.0	4.2	Wide band gap materials can be used in high power, high temperature, and high frequency, optoelectronic devices and as heat sink.
3	$PbCl_2$	C	5.0	4.2	4.5	4.6	Wide band gap materials can be used in high power, high temperature, and high frequency, optoelectronic devices and as heat sink [21].

3.2. X Ray Diffraction (XRD).

X ray diffraction analysis (XRD) was used to uniquely identify the crystalline phases present in the crystals and to study the structural properties. The XRD characterization of the samples was carried out using MD-10 Diffractometer, which recorded diffractograms using CuK□ radiation. Diffraction patterns of the samples were recorded in the 2θ range from 10^o to 72^o. XRD spectra in the figures revealed that the compounds grown are crystalline in nature. For each spectrum, the crystallite size D, was determined using the Debye Scherer formula [19,20-28] as given below:

$$D=K\lambda/ß\cos\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (1.3)$$

Where K = 0.9 is the shape factor, λ= 1.5409Å, θ is the diffraction peak angle (Bragg's Angle) in degrees and ß is the corresponding diffraction peak. The XRD result is shown on table 5.

Figures 13: 16 XRD Spectra for $PbCl_2$ crystals.

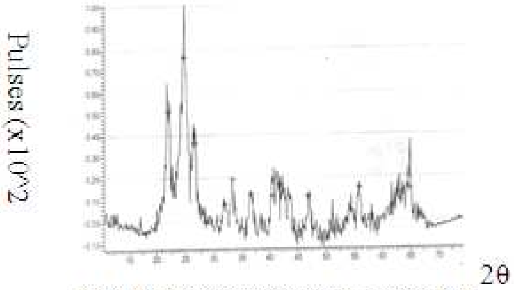


Figure 13: XRD spectra for potash un- doped $PbCl_2$.

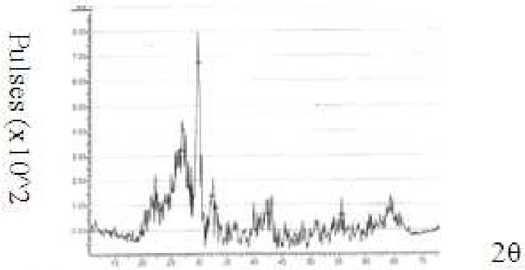


Figure 14: XRD spectra for 0.5N potash doped $PbCl_2$.

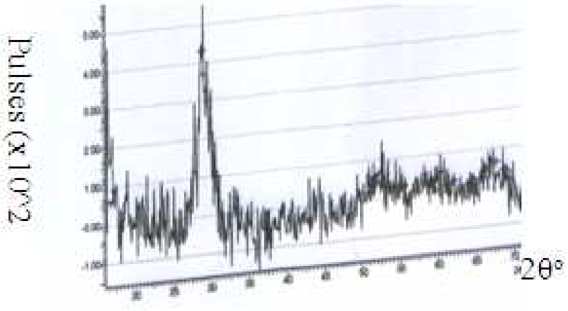


Figure 15: XRD spectra for 0.8N potash doped $PbCl_2$.

Table 5: XRD results for un-doped and potash doped $PbCl_2$

S/n	Compound	Sample	Concentration of impurity	2θ	Crystallite size (nm)	FWHM	Effect/result.
1	$PbCl_2$	A	**0**	24.59, 26.41, 28.82, 33.16	0.7740, 1.6968, 0.2651, 1.5903	1.7852, 0.8172, 5.2573, 0.8857	Presence of very sharp peaks and reduced crystallite size [19,22,23].
1	$PbCl_2$	B	**0.5**	29.73, 26.66, 32.20, 32.91	0.2248, 0.3417, 1.6575, 2.3983	0.8079, 4.0605, 0.8478, 0.5869	Presence of very sharp peaks and reduced crystallite size.
1	$PbCl_2$	C	**0.8**	20.00, 21.19, 21.85, 22.80	4.3298, 1.4055, 2.5058, 1.9950	0.3166, 0.9772, 0.5487, 0.6903	Presence of very sharp peaks and reduced crystallite size [24].

CONCLUSION

Sol-gel deposition technique has been successfully used to grow crystals of un-doped and potash doped lead chloride. Crystals grown in this study have made it possible for the following conclusions:

- Local materials from African environment can affect the optical and structural properties of semi conductor materials/crystals as seen in the crystallite sizes.
- The transparency of $PbCl_2$ decreased from 100-40% with increasing concentration of the dopant.
- The band gap lies from 3.9eV to 5.0eV, this shows that they are wide band gap semi conductors and can be employed in high power, high temperature, high frequency materials, optoelectronic devices and as heat sink, [20].
- The reduced particle size from 0.2nM to 2.5nM is a function of the broadness of the peaks and as such makes them good nano materials [19,22-25,29]
- The sharpness of the peaks indicate that they are highly crystalline and as such are semiconductor materials that can be employed in solar energy applications.

REFERENCES

[1] Hench L.L. and West J.K., *Chemical Reviews*, **1990**, 90:33.
[2] Klein L., *Springer Verlag*, **1994**.
[3] Allman iii R.M. *Wikipedia: the free Encyclopedia,**1983***,1.
[4] Thewils J., Encyclopedic Dictionary of Physics (Oxford: Pergamon Press) **2000** 3: 429.
[5] Santosh T.M. Pandurang C. P., Shrishail S. K. , Vikram S. K., and Lalasaheb P. D., *Pelagia Research Library* **2011**, 2(5)9.
[6] Roy R., *World Scientific, Singapore*, **1999**, 29.
[7] Ulrich D.R., *Chem. Eng. News*, **2004**, 29.
[8] Dardel G., Henning S. and Svensson L., *European Patent Specification* 0018955BI, **2003**
[9] Biecker F.J., Heckmann W, Fischer F., Mieke M., Schroeder J. and Stange A. *Structural Analysis of Granular Silica Aerogels, in: Physics Ut Vii*, Springer Verlag, Heidelberg, New York, **2001** pp123
[10] Bandgopadhyay S., Paul G.K. and Sen S.k., *Journal of Solar Energy Materials and Solar Cells*, **2002**, 71:103.
[11] Gracium G., Buiu O., Paszti F., Cobianu C. and Savaniu Vasile E., *Paper presented at Semiconductor Conference, IEEE Xplore 2.0.*, **2003,** 1:185.
[12] Yoshihara S., *Paper Presented at Semiconductor Conference, I.E.E.E. Xplore 2.0.*, **1997**, 2:173.
[13] Mandla A. and Li- Pin S., *Journal of Chemical Technology Research*, **2007** 4:383.
[14] Perry and Philips, *Handbook of Inorganic Compounds*, **1995**, 213.
[15] Aboujali L.A., Journal of Material Chemistry, **1998**, 8:1601-1606.
[16] Lowack R.H., *Journal of Organometalic Chemistry*, **1994**, 476: 25-32.
[17] Nichol R.B., *Potash and Phosphate Institute*, **2008**, 78.
[18] Ochuenwike C.C., *Unpublished M.Sc. Thesis, University of Nig., Nsukka*, (Enugu, Nigeria) **1986**, 77-80.
[19] Ezema F. I., *Journal of Applied Sciences*, **2006**, 6 (8) 1827-1823.
[20] Yacobi B.G., *Semiconductor Materials*, New York: Kluwer Academic Publisher, **2004**, 148-151.
[21] Haung J.H. and Liu C.P., *Thin Solid Films*, **2006**, 498: 152-156.
[22] Pradha A.K., Hunter D., Zhang K., Dadson J.B., Mohanty S., Williams T.M., Lord K., Rakhiimov R.R., Roy U.N., Cui Y, Burger A., Zhang J. and Sellmyer D.J., *Applied Surface Science*, **2005**, 252: 1628-1633.
[23] Amma B.S., Ramakrishna K. and Pattabi M., *Materials Chemistry and Physics*, **2005,** 112: 789-792.
[24] Chahal R.P., Mahendia S., Tomar A.K. and Kuma S., *Chalcogenide Letters*, **2010**, 7(8) 569-575.

[25] Kondawar S.B., *Arch.Apll.Sc.Res.*, **2010**, 2(3) 225-230
[26] Suresh K. B., Padmarkar A. S. and Suresh T. P., *Adv. Appl. Sci. Res.*, **2010**, 1(1) 29.
[27] Amrut S. L., Satish J.S., Ramchandra B. P. and Raghumani S. N., *Adv. Appl. Sci. Res.*, **2010**, 1 (2) 38.
[28] Hemant M., Balbir S. K. and Rajeev J., *Adv. Appl. Sci. Res.*, **2010,** 1(3)62
[29] Kaviyarasu K. and Prem A. D., *Adv. Appl. Sci. Res.,*, **2011**, 2(6)133