



## Review Of Research



### SYNTHESIS AND CHARACTERIZATION OF LEAD (II) CHLORIDE AND LEAD (II) CARBONATE NANO PARTICLES

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#### ABSTRACT:

Nanoparticles of Lead (II) Chloride and Lead (II) Carbonate were prepared using co-precipitation method. The white precipitate was obtained. The nano particles so obtained were characterized by powder X-ray diffraction, FT-IR Spectroscopy and UV-Visible spectroscopy techniques. The d-spacing and 2-Theta values from



XRD were compared with JCPDS values. The average grain sizes of nanoparticles were calculated from the Debye-Scherrer's formula. The stretching and bending frequencies of various molecular functional groups are studied from FT-IR spectrum. UV-Visible spectrum is used to determine the band gap of the samples.

**KEYWORDS:** Lead (II) Chloride and Lead (II) Carbonate, XRD, FT-IR, UV-Visible Spectroscopy.

#### INTRODUCTION

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale size-dependent properties are often observed. Thus, the properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. For bulk materials larger than one micrometer the percentage of atoms at the surface is insignificant in relation to the number of atoms in the bulk of the material. The interesting and sometimes unexpected properties of nanoparticles are therefore largely due to the large surface area of the material which dominates the contributions made by the small bulk of the material [1, 2]. Lead (II) Chloride is used in making many basic chlorides, such as Pattison's lead white, Turner's Patent Yellow, and Verona Yellow, used as pigments. Also, it is used as a flux for galvanizing steel; as a flame retardant in nylon wire coatings; as a cathode for seawater batteries; to remove H<sub>2</sub>S and ozone from effluent gases; as a sterilization indicator; as a polymerization catalyst for alpha-olefins; and as a co-catalyst in manufacturing acrylonitrile [3]. Lead (II) Carbonate, or

white lead, was one of the chief additives in lead paint. Lead carbonate is used as an additive in a variety of cements. Lead carbonate is also a part of both artistic and construction putty. There is a certain type of paper called lead carbonate paper, which is similar to more common carbon paper that is used commercially[4]. Because of the above said wide variety of applications of Lead (II) Chloride and Lead (II) Carbonate, we were interested to prepare these nanoparticles in our laboratory by using the co-precipitation method. These compounds were characterised by powder XRD, FT-IR and UV-Visible spectroscopic methods.

## MATERIALS AND METHOD

### Materials

The raw materials (Lead (II) nitrate, Sodium chloride, Sodium carbonate, distilled water and ethanol) used for this synthesis were purchased from the Modern Scientific Company, Madurai, India.

### Co-precipitation method

Chemical co-precipitation method is a simple low cost and easy method. From this method nanoparticle of Lead (II) chloride was prepared by adding solutions of lead (II) nitrate and sodium chloride. Precise amounts of reagent taking into account their purity were weighed and dissolved separately in distilled water into 0.5 M concentration. After obtaining a homogeneous solution, the reagents were mixed using magnetic stirring. The precipitate was separated from the reaction mixture and washed several times with distilled water and ethanol. The wet precipitate was dried and thoroughly ground using agate mortar to obtain the samples in the form of fine powder. Similarly, by using the above process Lead (II) carbonate nanoparticle was prepared from lead (II) nitrate and sodium carbonate solutions taking into 0.5 M concentration. The photographic view of the synthesised nano particles are shown in Fig. 1.



Fig. 1: Photographic view of the synthesised nano Particles

## RESULT AND DISCUSSION

### Characterization

The title compounds of Lead (II) Chloride and Lead (II) Carbonate were analysed by the powder XRD, FT-IR, UV-Visible spectroscopy techniques. The powder X-ray diffraction of the nano particles were carried out, using XPERT-PRO X-ray diffractometer with Cu K $\alpha$  ( $\lambda = 1.54060 \text{ \AA}$ ) radiation. The FT-IR spectra of the samples were recorded by using SHIMADZU FT-IR spectrometer in the range 4000–400  $\text{cm}^{-1}$ . The optical transmittance and absorbance spectrum of nano particles have been recorded with SHIMADZU-UV1800, double beam spectrometer. Transmittance and absorbance data were observed for the title compounds in the wavelength range 200–1200 nm in steps of 100 nm. The slit width chosen was 0.1 nm. The wavelength rate was in medium mode. The observed values of absorbance were recorded and stored in the memory of a computer and plotted.

### Powder XRD Analysis

The powder X-ray diffraction patterns were collected for Lead (II) Chloride and Lead (II) Carbonate nanoparticles using a XPERT-PRO X-ray diffractometer with Cu K $\alpha$  ( $\lambda = 1.54060 \text{ \AA}$ ) radiation. The XRD pattern of the title compound is depicted in Fig. 2. A good agreement between the experimental diffraction angle ( $2\theta$ ),  $d$  spacing and standard diffraction angle ( $2\theta$ ),  $d$  spacing of specimen is confirming standard of the specimen. Eighteen peaks at ( $2\theta$ ) values of lead (II) chloride and twelve peaks at ( $2\theta$ ) values of lead (II) carbonate are observed and tabulated in Table 1 & 2. The experimental values are compared with the standard powder diffraction card of Joint Committee on Powder Diffraction Standards (JCPDS), of lead (II) chloride (JCPDS file No. 26-1150) and lead (II) carbonate (JCPDS file No. 47-1734). The ( $2\theta$ ) &  $d$  spacing values are exactly matches with the JCPDS values of both compounds which confirm the formation of Lead (II) Chloride & Lead (II) Carbonate nano particles.

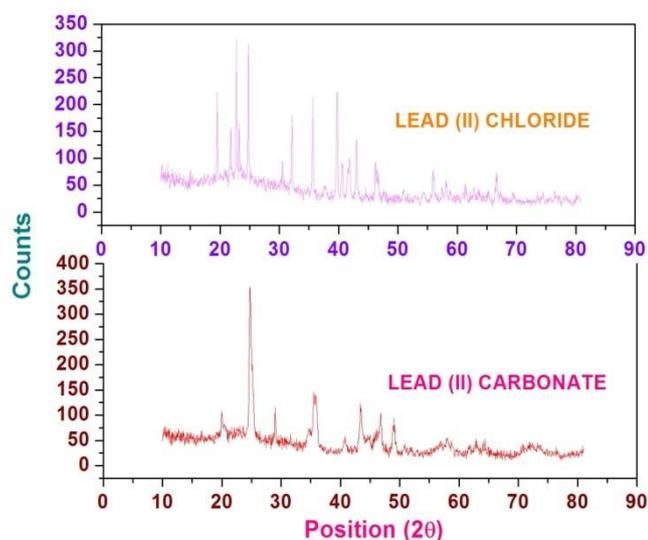


Fig. 2: Powder XRD patterns of Lead (II) Chloride and Lead (II) Carbonate nano particles

Table 1: Powder XRD data of Lead (II) Chloride nano particle

Experimental		Standard – JCPDS 26-1150	
Diffraction angle (2θ in degrees)	d spacing (Å)	Diffraction angle (2θ in degrees)	d spacing (Å)
19.51	4.54	19.61	4.52
21.80	4.07	21.89	4.05
22.74	3.90	22.84	3.89
23.22	3.83	23.32	3.81
24.76	3.59	24.85	3.57
30.57	2.92	30.64	2.91
32.12	2.78	32.22	2.77
35.66	2.51	35.22	2.51
37.71	2.38	37.68	2.38
39.77	2.26	39.72	2.26
40.62	2.22	40.71	2.21
41.87	2.15	41.94	2.15
43.03	2.10	43.12	2.09
46.22	1.96	46.30	1.95
50.94	1.79	51.00	1.78
54.36	1.68	54.26	1.68
55.88	1.64	56.00	1.64
58.17	1.58	58.17	1.58

Table 2: Powder XRD data of Lead (II) Carbonate nano particle

Experimental		Standard – JCPDS 47-1734	
Diffraction angle (2θ in degrees)	d spacing (Å)	Diffraction angle (2θ in degrees)	d spacing (Å)

19.96	4.44	20.08	4.41
24.70	3.60	24.78	3.59
28.97	3.08	29.03	3.07
35.53	2.52	35.55	2.52
35.97	2.49	36.04	2.49
40.76	2.21	40.73	2.21
43.43	2.08	43.42	2.08
46.78	1.94	46.94	1.93
48.98	1.85	48.95	1.85
58.30	1.58	58.02	1.58
62.95	1.47	62.95	1.47
71.59	1.31	71.31	1.32

### *XRD – Particle Size Calculation*

The XRD patterns of the prepared samples of Lead (II) Chloride and Lead (II) Carbonate nano particles are shown in Fig.2. The powder XRD studies reveal that nano sized crystalline nature of the compounds. The fine particle nature of the samples is reflected in the X-ray line broadening. The size of the synthesized nanoparticles are calculated using Scherrer equation [5]

$$D = 0.9 \lambda / \beta \cos\theta$$

Where

$\lambda$  - Wavelength of X- rays

$\beta$  - Half width at full maximum

$\theta$  - Diffraction angle

From the above relation the average grain size of the Lead (II) Chloride and Lead (II) Carbonate particles are found to be 54 nm and 41 nm respectively.

### *XRD – Dislocation Density*

The dislocation density is defined as the length of dislocation lines per unit volume of the crystal. In materials science, a dislocation is a crystallographic defect, or irregularity, within a crystal structure. The presence of dislocations strongly influences many of the properties of materials. The movement of a dislocation is impeded by other dislocations present in the sample. Thus, a larger dislocation density implies a larger hardness. The X-ray line profile analysis has been used to determine the dislocation density.

The dislocation density can also be calculated from

$$\delta = \frac{1}{D^2}$$

Where  $\delta$  - Dislocation density and

D - Crystallite size.

The number of unit cell is calculated from

$$n = \pi \left(\frac{4}{3}\right) \times \left(\frac{D}{2}\right)^3 \times \left(\frac{1}{V}\right) \quad (6.3)$$

**Table 3: Dislocation density and number of unit cells for Lead (II) Chloride nano particle**

<b>2θ (deg)</b>	<b>Crystallite size D (nm)</b>	<b>Dislocation Density <math>\times 10^{14}</math> (<math>m^2</math>)</b> $\delta = 1 / D^2$	<b>Number of Unit Cell <math>\times 10^5</math></b>
21.80	54.84	3.32	2.76
19.51	54.64	3.34	2.73
22.74	54.93	3.31	2.77s
23.22	82.46	1.47	9.37
24.76	55.13	3.29	2.80
30.57	55.82	3.20	2.91
32.12	42.03	5.66	1.24
35.66	56.56	3.12	3.03
37.71	17.07	34.3	0.08
39.77	34.35	8.47	0.67
40.62	28.70	12.13	0.39
41.87	43.24	5.34	1.35
43.03	43.41	5.30	1.36
46.22	58.54	2.91	3.35
50.94	29.82	11.24	0.44
54.36	15.28	42.82	0.05
55.88	36.57	7.47	0.81
58.17	36.97	7.31	0.84

**Table 4: Dislocation density and number of unit cells for Lead (II) Carbonate nano particle**

<b>2θ (deg)</b>	<b>Crystallite size D (nm)</b>	<b>Dislocation Density <math>\times 10^{14}</math> (<math>m^2</math>)</b> $\delta = 1 / D^2$	<b>Number of Unit Cell <math>\times 10^5</math></b>
19.96	41.01	5.95	1.33
24.70	41.35	5.85	1.36
28.97	41.72	5.75	1.40
35.53	28.27	12.51	4.36
35.97	28.26	12.52	4.36
40.76	21.54	21.55	0.19
43.43	34.78	8.27	0.81
46.78	35.20	8.07	0.84
48.98	14.94	44.82	0.06
58.31	5.80	297.16	0.00
62.95	15.94	39.36	0.08
71.60	4.99	402.06	0.00

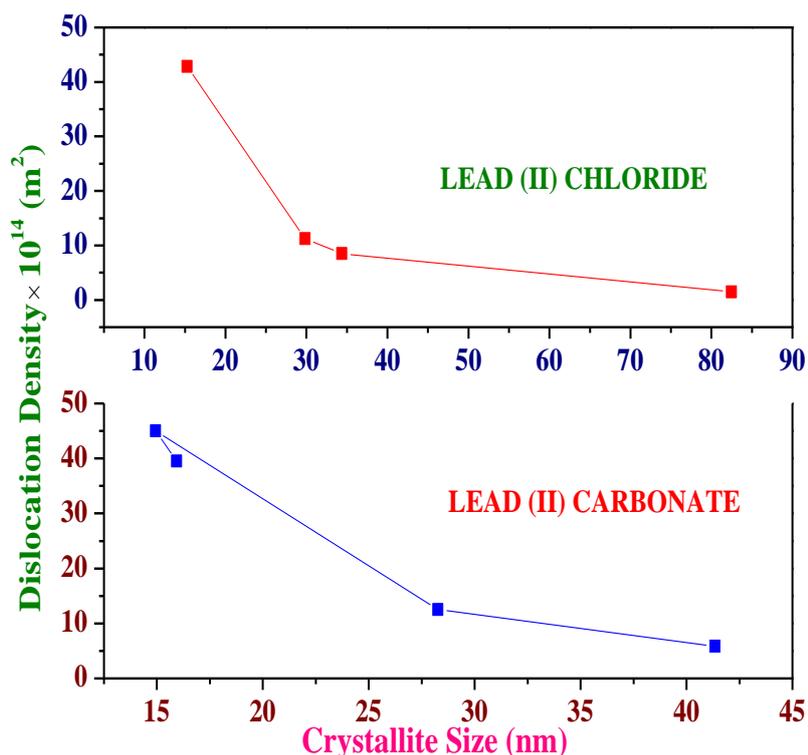


Fig. 3: Particle size Vs. Dislocation density graphs of the Lead (II) Chloride & Lead (II) Carbonate nano particles

The particle size versus dislocation density graphs of the Lead (II) Chloride and Lead (II) Carbonate nano particles are depicted in Fig.3. From the graph, it is observed that the dislocation density increases while the particle size decreases[5].

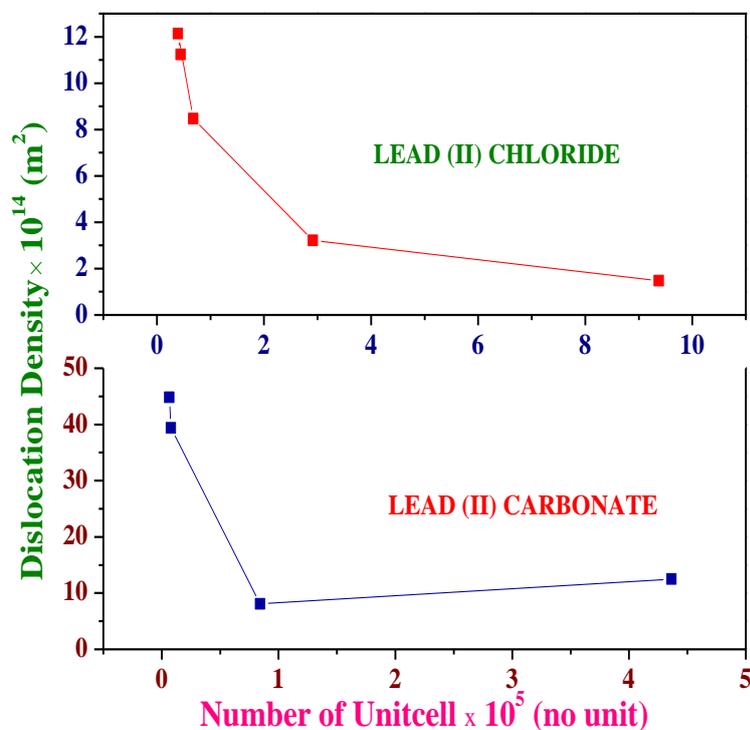


Fig. 4: Number of Unit cells Vs. Dislocation density graphs of the Lead (II) Chloride & Lead (II) Carbonate nano particles

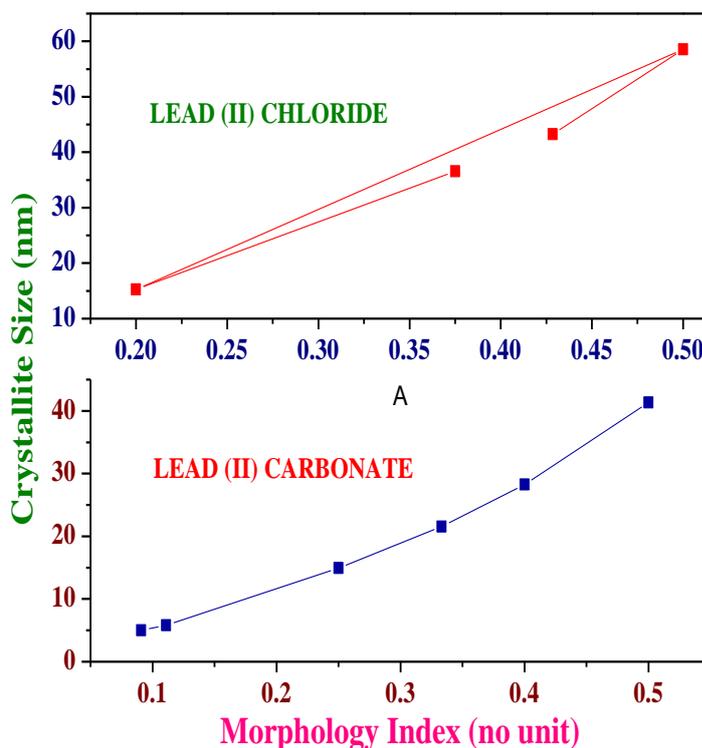
The number of unit cell versus dislocation density of the Lead (II) Chloride and Lead (II) Carbonate nano particles is depicted in Fig.4. From the graph, it is observed that the dislocation density increases while the number of unit cell decreases[5].

**XRD – Morphology Index**

A XRD morphology index (MI) is calculated from

$$M. I = \frac{FWHM_h}{FWHM_h + FWHM_p}$$

Where M.I. is morphology index,  $FWHM_h$  is highest FWHM value obtained from peaks and  $FWHM_p$  is value of particular peak’s FWHM for which M.I. is to calculate. The relation between morphology index and particle size [5] is shown in Table 5 &6.



**Fig.5: Morphology index Vs. Particle sizegraphs of the Lead (II) Chloride &Lead (II) Carbonate nano particles**

**Table5: Crystallite size and Morphology index of Lead (II) Chloride**

FWHM (β) radians	Crystallite size D (nm)	Morphology Index (unit less)
0.002	54.64	0.5
0.002	54.84	0.5
0.002	54.93	0.5
0.001	82.46	0.6
0.002	55.13	0.5

0.002	55.82	0.5
0.003	42.03	0.5
0.002	56.56	0.5
0.008	17.07	0.2
0.004	34.35	0.3
0.005	28.70	0.3
0.003	43.24	0.4
0.003	43.41	0.4
0.002	58.54	0.5
0.005	29.82	0.3
0.010	15.28	0.2
0.004	36.57	0.3
0.004	36.97	0.3

**Table6: Crystallite size and Morphology index of Lead (II) Carbonate nano particle**

<b>FWHM (<math>\beta</math>) radians</b>	<b>Crystallite size D (nm)</b>	<b>Morphology Index (unit less)</b>
0.003	41.00	0.5
0.003	41.34	0.5
0.003	41.71	0.5
0.005	28.27	0.4
0.005	28.26	0.4
0.006	21.54	0.3
0.004	34.77	0.4
0.004	35.20	0.4
0.010	14.93	0.2
0.027	5.80	0.1
0.010	15.93	0.2
0.034	4.98	0.09

The particle size versus morphology index graphs of the Lead (II) Chloride and Lead (II) Carbonate nano particles are depicted in Fig 4. From the graph, it is observed that the morphology index has direct relationship with particle size.

**XRD – Unit Cell Parameters**

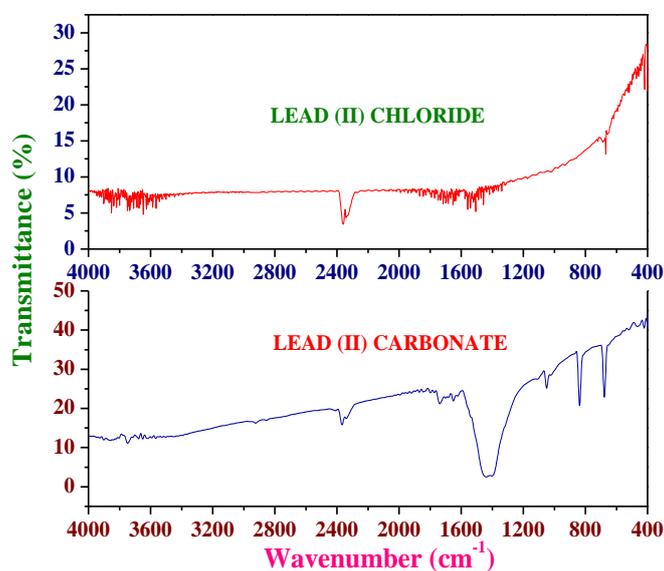
Unit cell parameter values of the title compounds were taken from JCPDS card number 26-1150 and 47-1734 respectively. They are provided in the Table 7.

**Table 7: XRD Parameters of Lead (II) Chloride and Lead (II) Carbonate Nanoparticles**

Parameters	Lead (II) Chloride	Lead (II) Carbonate
Structure	Orthorhombic	Orthorhombic
Particle size	54.9306 nm	41.3458 nm
Lattice Angles	$\alpha = \beta = \gamma = 90^\circ$	$\alpha = \beta = \gamma = 90^\circ$
Lattice Parameters	a = 7.622 Å b = 9.044 Å c = 4.534 Å	a = 5.178 Å b = 8.515 Å c = 6.146 Å
Volume of unit cell (V)	312.54 Å <sup>3</sup>	270.98 Å <sup>3</sup>
Dislocation density	$3.3141 \times 10^{14}$	$5.8497 \times 10^{14}$
Density	5.85 g/cm <sup>3</sup>	6.582 g/cm <sup>3</sup>

**FT-IR Spectroscopy Study**

The FTIR spectra of Lead (II) chloride and Lead (II) carbonate nano particles samples are shown in Fig.6.



**Fig.6: FTIR spectra of lead (II) Chloride and lead (II) Carbonate nano particles**

**Table 8: Observed vibrational wavenumbers ( $\text{cm}^{-1}$ ) and their assignments for Lead (II) Carbonate**

FT-IR $\bar{\nu}$ ( $\text{cm}^{-1}$ )	Assignments
1701 (w)	$\nu_{\text{as}}$ C = O
1651 (m)	$\nu_{\text{as}}$ C = O
1436 (s)	$\nu_{\text{as}}$ ( $\text{CO}_3$ ); $\nu_{\text{s}}$ ( $\text{COO}^-$ )
1111 (m), 1402 (s)	$\nu_{\text{s}}$ ( $\text{COO}^-$ )
1049 (s)	$\nu_{\text{s}}$ ( $\text{CO}_3$ )
837 (s)	$\delta_{\text{s}}$ ( $\text{CO}_3$ )
677 (s)	$\rho$ ( $\text{COO}^-$ ); $\delta_{\text{as}}$ ( $\text{CO}_3$ )
466 (m)	Lead cation

$\nu_{\text{s}}$ - symmetric;  $\nu_{\text{as}}$ - antisymmetric ;  $\rho$  – scissoring ;  $\delta$  – bending ;  $\delta_{\text{s}}$ - symmetric bending;  $\delta_{\text{as}}$  – antisymmetric bending.

In the FT-IR spectrum, the absorption band at  $466 \text{ cm}^{-1}$  assigned to Lead cation [5] . In the present study, the band observed at  $466 \text{ cm}^{-1}$  in FT-IR spectrum is assigned to the Lead cation.

#### **Vibration of carbonate group**

The absorption band at  $1420 \text{ cm}^{-1}$  and  $1051 \text{ cm}^{-1}$  is assigned to antisymmetric stretching and symmetric stretching mode of carbonate group. The observed band at  $850 \text{ cm}^{-1}$  and  $680 \text{ cm}^{-1}$  in IR spectrum are assigned to symmetric bending and antisymmetric bending mode of carbonate group [6]. In the present work, the absorption bands at  $1436 \text{ cm}^{-1}$  and  $1049 \text{ cm}^{-1}$  in IR spectrum identifies as the antisymmetric and symmetric stretching mode of carbonate group. Also the bands at  $837 \text{ cm}^{-1}$  and  $677 \text{ cm}^{-1}$  are assigned to the symmetric bending and antisymmetric bending mode of carbonate group respectively.

#### **C=O Vibration**

The absorption band occurs in the range  $1720 - 1680 \text{ cm}^{-1}$  is assigned to C=O antisymmetric stretching mode vibration [7]. In the present work, the absorption bands at  $1701 \text{ cm}^{-1}$  and  $1651 \text{ cm}^{-1}$  in the presence of C=O antisymmetric stretching mode vibration.

#### **COO<sup>-</sup> Vibration**

The absorption bands at  $1424 \text{ cm}^{-1}$ ,  $1400 \text{ cm}^{-1}$ ,  $1103 \text{ cm}^{-1}$  is due to the  $\text{COO}^-$  symmetric stretching and also the band at  $674 \text{ cm}^{-1}$  is due to the  $\text{COO}^-$  scissoring vibration [8]. In the present work, the band observed at  $1436 \text{ cm}^{-1}$ ,  $1402 \text{ cm}^{-1}$ ,  $1103 \text{ cm}^{-1}$  in the IR spectrum is attributed to symmetric stretching mode of  $\text{COO}^-$  group. Also, the scissoring vibration of  $\text{COO}^-$  group is appearing at  $674 \text{ cm}^{-1}$  in IR spectrum of Lead (II) Carbonate nano particle.

#### **O-H Vibration**

The absorption bands at  $1516 \text{ cm}^{-1}$ ,  $1543 \text{ cm}^{-1}$  and  $1649 \text{ cm}^{-1}$ ,  $1697 \text{ cm}^{-1}$  is assigned to O-H bending mode vibration [9, 10]. The Lead (II) Carbonate nano particle has the absorption bands at  $1512$ ,  $1541$ ,  $1649$ ,  $1651$  and  $1697 \text{ cm}^{-1}$  in IR spectra which is assigned to O-H bending mode vibration.

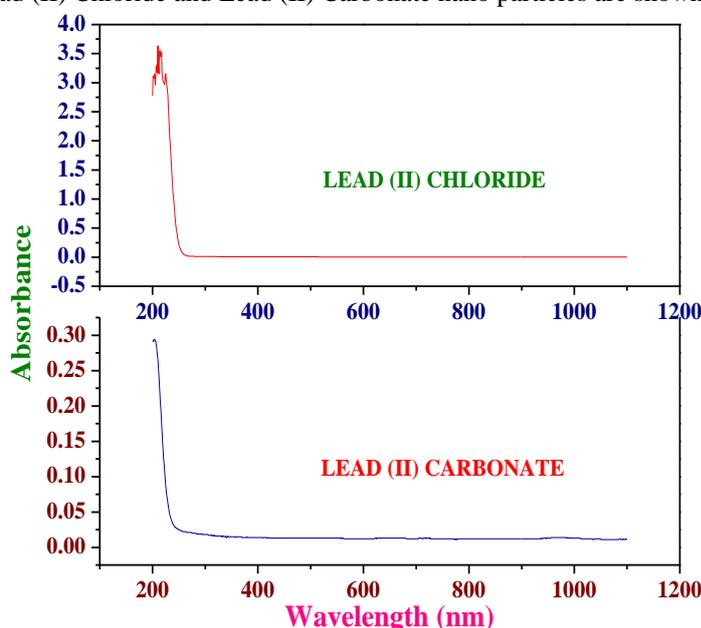
**Table 9: Observed vibrational wavenumbers ( $\text{cm}^{-1}$ ) and their assignments for Lead (II) Chloride**

Infrared Wavenumber ( $\text{cm}^{-1}$ )	Assignments
462	Lead cation
673	Chloride anion

In the FT-IR spectrum, the absorption band at  $462 \text{ cm}^{-1}$  is assigned to leadcation [5] and also the band at  $673 \text{ cm}^{-1}$  is assigned to chloride anion [4]. In the present work, the IR band at  $462 \text{ cm}^{-1}$  indicate the presence of Lead cation and also the band at  $673 \text{ cm}^{-1}$  indicate the presence of chloride anion.

#### UV-Visible Spectroscopy

The optical transmittance and absorption spectrum of title compounds have been recorded with SHIMADZU-UV 1800 double beam spectrometer in the range 200-1200 nm. The band gap values of Lead (II) Chloride and Lead (II) Carbonate nano particles were found to be as 5.19 eV and 5.62 eV respectively by using the UV-Visible spectroscopy. The absorption spectra of Lead (II) Chloride and Lead (II) Carbonate nano particles are shown in Fig.7.



**Fig.7. Wavelength Vs. Absorbance graph of Lead (II) Chloride & Lead (II) Carbonate Nano Particles**

From the absorption spectra of the title compounds, the lower cut-off wavelength is identified at 242 nm (Lead (II) Chloride) and 230 nm (Lead (II) Carbonate). The both nano particles have good transmittance in the visible region and it extends up to infrared region.

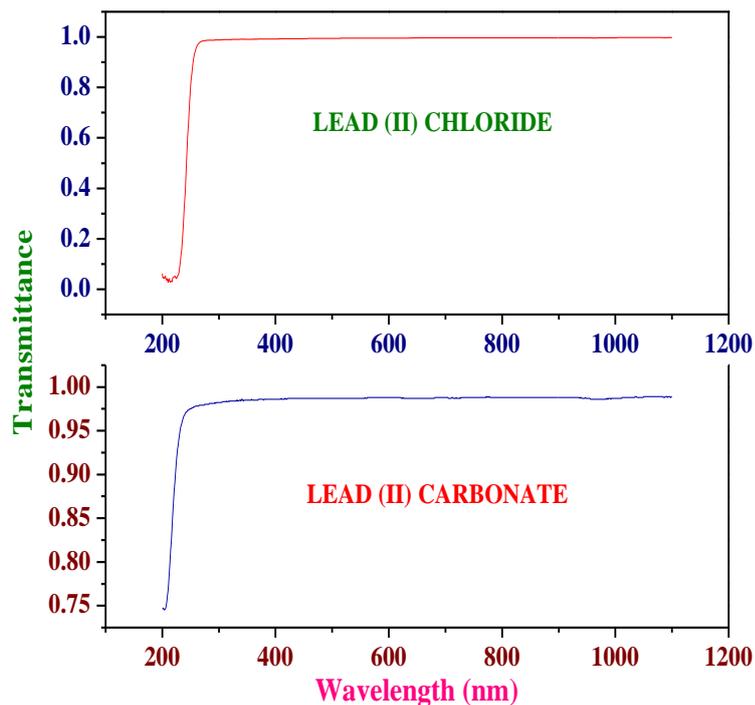


Fig.8.Wavelength Vs. Transmittance graph of Lead (II) Chloride &Lead (II) Carbonate Nano Particles

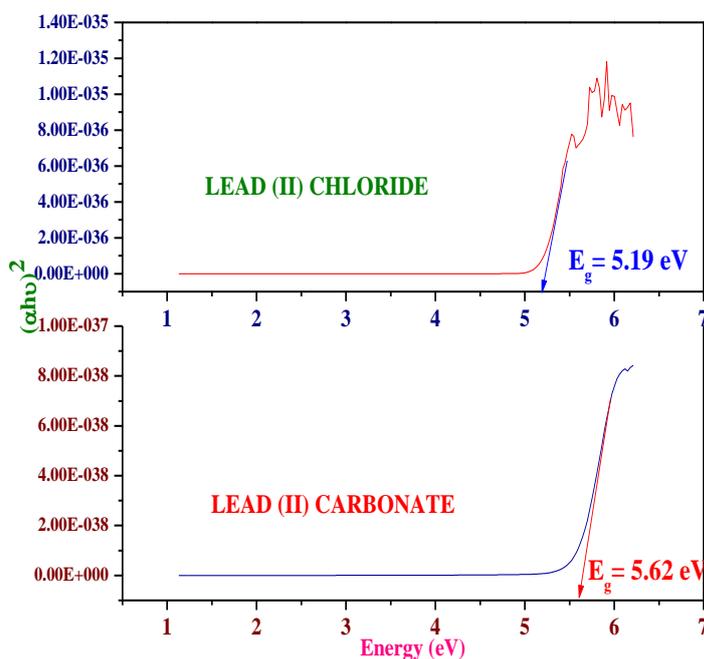


Fig. 9: Band gap graph of Lead (II) Chloride and Lead (II) Carbonate of Nano Particles

The energy gap value  $E_g$  could be determined by analyzing the optical data with optical absorption coefficient  $\alpha$  and the photon energy  $h\nu$  using Tauc's relation [11],  $(\alpha h\nu)^2 = A(h\nu - E_g)$ . The optical band gap was evaluated by plotting  $(\alpha h\nu)^2$  vs.  $h\nu$  as shown in Fig. 9, and extrapolating the linear portion of absorption edge  $(\alpha h\nu)^2$  the photon energy axis gives the optical band gap of the title compounds [12]. The optical band gap value of the Lead (II) Chloride and Lead (II) Carbonate nano particles are found to be as 5.19 eV and 5.62 eV from the Fig. 9.

## CONCLUSION

A variety of nanomaterial has been developed in last few years with interesting physical- chemical properties. In our work, nanoparticles of  $PbCl_2$  and  $PbCO_3$  were synthesized by Co- Precipitation method. They are subjected to various studies such as power XRD, FT-IR Spectroscopy and UV-Visible Spectroscopy. The XRD studies are used to determine particle size, dislocation density, number of unit cells and morphology index. The XRD study reveals that the Dislocation density is inversely proportional to the particle size and number of unit cells. Dislocation density increases while both particle size and number of unit cell decreases. The XRD morphology index (M.I) is calculated from FWHM of XRD data. It is observed that M.I has direct relationship with particle size. The FTIR spectroscopic study is employed here to identify the functional groups present in the nano particles of  $PbCl_2$  and  $PbCO_3$ . The band gap of prepared samples of Lead (II) chloride and Lead (II) carbonate nano particles were determined by using UV visible spectroscopy. From the UV-Visible spectra, the optical band gap of Lead (II) Chloride and Lead (II) carbonate are found to be 5.19 eV and 5.62 eV respectively.

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