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Synthesis and characterization of Lead (II) Phosphate nano particles

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ABSTRACT

Lead (II) Phosphate nano particles were synthesized via chemical co precipitation method from Lead Nitrate and Sodium Phosphate. The formed nano particle is characterized by powder X-ray diffraction, scanning electron microscopy, Ultra-violet spectroscopy and Fourier transform infrared spectroscopy, confirmed the preferential growth of Lead (II) Phosphate nano particles that width is 41.09 nm. The SEM image shows the synthesized Lead (II) Phosphate show well crystallized particles with spherical morphology. The FTIR spectrum is used to study the stretching and bending frequencies of molecular functional groups in the sample. From UV spectrum, the band gap of Lead (II) Phosphate nano particles is found to be 3eV. From AAS studies it is found that the absorbance is directly proportional to the concentration. The linear fit indicates that lead (II) Phosphate nanoparticles have been distributed in proper proportion.

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1.Introduction

Nanotechnology represents a rather broad interdisciplinary field of research and industrial activity involving particles less than 100 nanometers (nm) in diameter. Engineered materials made of such small particles exhibit novel properties that are distinctively different from their conventional forms and can affect their physical, chemical, and biological behavior. These nanoscale particles can be tubular (nanotubes), spherical, irregularly shaped, and may also exist in aggregated formations.

Nanoparticles have one dimension that measures 100 nanometers or less. Nanoparticles have a greater surface area per weight than larger particles which causes them to be more reactive to some other molecules. Nanoparticle research is currently an area of intense scientific interest due to a wide variety of potential applications in biomedical, optical and electronic fields. 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 (or micron), 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.

This paper is discussing about easy, simple and low cost preparation i.e. chemical co precipitation of Lead (II) phosphate nanoparticles and its characterizations - XRD, SEM, FTIR, UV and AAS studies.

4. Materials and Methods

Nano particles of Lead (II) Phosphate were prepared by chemical co precipitation method by adding Lead Nitrate and Sodium Phosphate. Precise amounts of reagents taking into account their purity were weighed and dissolved separately in distilled water into 0.1M 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.

X-ray diffraction is an ideal technique for the determination of crystallite size of the powder samples. The basic principle for such a determination involves precise quantification of the broadening of the peaks. XRD line broadening method of particle size estimation was chosen in this investigation for determining the crystallite size of the powder sample. XRD study of the powder samples was carried out at Centre for Electro Chemical Research Institute, Karaikudi. The morphology of the powder samples was studied by the scanning electron microscope (SEM) analysis taken at STIC Cochin. The infra red spectroscopic (IR) studies of Lead (II) phosphate nano particles were made by using 'SHIMADZU' FTIR 8400S model spectrometer through KBr method. The UV spectrum was taken in the absorbance mode in the wavelength range from 200 to 800 nm.

2. Results and discussion

2.1. XRD studies

2.1.1. XRD – Particle Size Calculation

The XRD patterns of the prepared samples of Lead (II) Phosphate are shown in fig.1. XRD studies reveal that the samples are nano sized and crystalline. The fine particle nature of the samples is reflected in the X-ray line broadening. The size of the synthesized Lead (II) Phosphate nano particles are calculated using Scherrer equation

$\mathbf{D} = \mathbf{0.9} \, \lambda \, / \, \beta \, \cos \theta$

where λ represents wavelength of X rays, β represents half width at full maximum and θ is the diffraction angle[6]. The average grain size of the particles is found to be 41.08 nm. The peak list in the XRD pattern is given in table-1.



Figure.1 XRD pattern of Lead (II) Phosphate Nano particles Table-1. Intensity of XRD peaks.

Pos. [°2Th.]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
21.3494	0.1673	4.16200	19.96
24.9931	0.1673	3.56287	20.35
27.1869	0.2007	3.28015	19.97
30.9326	0.2007	2.89096	100.00
32.1349	0.2844	2.78549	36.38
42.1808	0.2676	2.14244	15.89
46.5105	0.2676	1.95259	13.47
48.9632	0.2342	1.86036	21.62
61.7411	0.8029	1.50251	8.05
62.9132	0.4684	1.47731	10.29
73.7794	0.8029	1.28430	3.90
78.7871	0.6528	1.21375	1.65

2Theta = 30.9326

Theta = 30.9326/2 = 15.4663

 $D = (0.9 * 0.154) / (0.0035) * \cos(15.4663) = 41.08 \text{ nm}$

A good agreement between the Experimental diffraction angle [2 θ] and Standard diffraction angle [2 θ] of specimen is confirming standard of the specimen. Twelve peaks at 2 θ values of Lead (II) Phosphate is observed and tabulated in table-2 and compared with the standard powder diffraction card of Joint Committee on Powder Diffraction Standards (JCPDS), Lead (II) Phosphate file No. 73-0834. The d-spacing values of experimental is also confirming to the standard values.

Table.2. Experimental and standard diffraction angles of Lead (II) Phosphate specimen

Experimental		Standard – JCPDS 73-0834		
Diffraction angle	D spacing	Diffraction angle	D spacing	
$(2\theta \text{ in degrees})$	(Å)	$(2\theta \text{ in degrees})$	(Å)	
21.3494	4.1620	21.735	4.0857	
24.9931	3.5628	24.175	3.6785	
27.1869	3.8015	27.714	3.2163	
30.9326	2.8909	30.330	2.9446	
32.1349	2.7855	32.141	2.7827	
42.1808	2.1424	42.457	2.1273	
46.5105	1.9526	46.532	1.9501	
48.9632	1.8604	49.016	1.8569	
61.7411	1.5025	61.964	1.4964	
62.9132	1.4773	62.709	1.4804	
73.7794	1.2843	74.148	1.2777	
78.7871	1.2138	78.797	1.2136	

5.1.2. XRD - Expected 2θ Positions

The value of d (the interplanar spacing between the atoms) is calculated using Bragg's Law: $2d \sin \theta = n \lambda$

$$d = \frac{\lambda}{2 \sin \theta} \quad (n = 1)$$

Wavelength $\lambda = 1.5418$ Å for Cu Ka

The expected 2θ positions of all the peaks in the diffraction pattern and the interplanar Spacing d for each peak is calculated using following formula and the details are shown in table-3.

$$\frac{1}{d2} = \frac{4}{3} \frac{(h2 + hk + k2)}{a2} + \frac{l2}{c2}$$

Bragg's Law is used to determine the 2θ value: The expected 2θ and d values are close with the experimental 2θ and d values [6].

Table-3.	The	Lattice	plane	and	the	lattice	spacing	from	d
			fro	m XI	2 D				

hkl	20(deg)		D((Å)		
	Experiment	Expected	Experiment	Expected	
111	21.3494	21.724	4.1620	4.085	
002	24.9931	24.165	3.5628	3.678	
120	27.1869	27.702	3.8015	3.216	
121	30.9326	30.292	2.8909	2.947	
202	32.1349	32.121	2.7855	2.783	
400	42.1808	42.439	2.1424	2.127	
123	46.5105	46.514	1.9526	1.950	
410	48.9632	48.995	1.8604	1.857	
151	61.7411	61.936	1.5025	1.496	
413	62.9132	62.683	1.4773	1.480	
522	73.7794	74.110	1.2843	1.278	
106	78.7871	78.756	1.2138	1.213	

5.1.3. 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 (δ) in the sample has been determined using expression.

$$\delta = \frac{15 \ \beta \ COS\theta}{4aD}$$

Where δ is dislocation density, β is broadening of diffraction line measured at half of its maximum intensity (in radian), θ is Bragg's diffraction angle (in degree), a is lattice constant (in nm) and D is particle size (in nm). The dislocation density can also be calculated from

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

Where δ is dislocation density and D is the crystallite size. Results of the dislocation density calculated from both the formulas are given in table-4. The number of unit cell is calculated from

$$n = \pi (4/3) \times (D/2)^3 \times (1/V)$$
 ⁽⁴⁾

Where D is the crystallite size and V is the cell volume of the sample [6].

XRD							
20 (deg)	Particle	Dislocation D	Number of				
	Size	$\delta = 15\beta\cos\theta$	$\delta = 1 / D^2$	Unit Cell			
	D (nm)	/4aD					
21.3494	48.49	2.25×10^{14}	4.25×10^{14}	0.9704x10 ⁵			
24.9931	48.83	2.22×10^{14}	4.19×10^{14}	$0.9909 \text{ x}10^5$			
27.1869	40.91	3.16×10^{14}	5.97x10 ¹⁴	0.5827x10 ⁵			
30.9326	41.08	$3.12 \text{ x}10^{14}$	$5.93 \text{ x}10^{14}$	$0.5901 \text{x} 10^5$			
42.1808	31.96	$5.18 \text{ x} 10^{14}$	9.79 x10 ¹⁴	$0.2763 \text{ x}10^5$			
46.5105	32.41	$5.04 \text{ x}10^{14}$	9.52×10^{14}	$0.2894 \text{ x}10^5$			
48.9632	37.38	$3.78 \text{ x}10^{14}$	$7.15 \text{ x}10^{14}$	$0.4445 \text{ x}10^5$			
61.7411	11.65	$3.89 \text{ x}10^{15}$	$7.36 \text{ x}10^{15}$	$0.1345 \text{ x}10^5$			
62.9132	20.10	$1.31 \text{ x} 10^{15}$	$2.48 \text{ x}10^{15}$	$0.6912 \text{ x}10^5$			
73.7794	12.38	3.45×10^{15}	6.52×10^{15}	$0.0165 \text{ x}10^5$			
78.7871	15.81	$2.12 \text{ x}10^{15}$	$4.00 \text{ x}10^{15}$	$0.0336 \text{x} 10^5$			

 Table-4. Dislocation Density and Number of Unit Cell from

It is observed from these tabulated details, and from figures.2, 3 & 4, dislocation density is indirectly proportional to particle size and number of unit cell. Dislocation density increases while both particle size and number of unit cell decreases [6].











Figure.4 Particle Size Vs Number of Unitcells

5.1.4. XRD - Morphology Index

A XRD morphology index (MI) is calculated from FWHM of XRD data using the relation

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

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 be calculated. The relation between morphology index and particle size is shown in table-5. **Table-5. Relation between Morphology Index and Particle**

sizo

		SILC	
FWHM (β)	Particle	Size(D)	Morphology Index
radians	nm		(unitless)
0.00291	48.49		0.5453
0.00291	48.83		0.5453
0.00349	40.91		0.5292
0.00349	41.08		0.5
0.00494	29.19		0.4139
0.00465	31.96		0.4155
0.00465	32.41		0.4155
0.00407	37.38		0.4616
0.01397	11.65		0.1988
0.00815	20.10		0.2998
0.01397	12.38		0.1988
0.01135	15.81		0.2352



Figure.5 Morphology Index of Lead (II) Phosphate Nanoparticles.

It is observed that MI has direct relationship with particle size [2] and the results are shown in Figure.5.

5.1.5 XRD - Crystallinity Index

It is generally agreed that the peak breadth of a specific phase of material is directly proportional to the mean crystallite size of that material. Quantitatively speaking, sharper XRD peaks are typically indicative of high nano crystalline nature and larger crystallite materials. From our XRD data, a peak broadening of the nanoparticles is noticed. The average particle size, as determined using the Scherrer equation, is calculated to be 41.08nm. Crystallinity index equation is given by

Icry = Dp (SEM, TEM) / Dcry (XRD) ($Icry \ge 1.00$)

Where Icry is the crystallinity index; Dp is the particle size (obtained from either TEM or SEM (morphological analysis); Dcry is the particle size (calculated from the Scherrer equation). If Icry value is close to 1, then it is assumed that the crystallite size represents monocrystalline whereas a polycrystalline have a much larger crystallinity index [2]. The crystallinity index of the sample is 1.78 which is more than 1.0. The details are enumerated in Table-6.

Table-6. The crystallinity index of Lead (II) Phosphate

Nanoparticles						
Sample	Dp	Dcry	Icry	Particle Type		
	(nm)	(nm)	(unitless)			
Lead (II) Phosphate	73.33	41.08	1.78	Poly cry stalline		
Nanoparticles						

5.1.6. XRD – Unit Cell Parameters

Unit cell parameters values calculated from XRD are enumerated in table-7.

Table-7. XRD parameters of Lead (II) Phosphate Nanoparticles

Parameters	Values
Structure	Primitive
Space group	P63/m
Symmetry of lattice	Hexagonal
Particle size	41.08 nm
Lattice parameters	a = 9.826;c = 7.357
Vol.unit cell(V)	615.16
Density (ρ)	6.572
Dislocation Density	$3.12 \text{ x}10^{14}$
Mass	811.54amu

5.2. SEM studies

Scanning electron microscopy was used to analyze the morphology and size of the synthesized Lead (II) Phosphate nano particles. Fig.6, Fig.7, Fig.8 and Fig.9 show the SEM images of the Lead (II) Phosphate nano-particles at various magnifications. The SEM images of Lead (II) Phosphate nano particles show well crystallized particles with spherical shape. In this case the particles sizes are slightly increased and is also observed that the particles are distributed with agglomeration.



Figure.6 SEM image at 10000 magnifications



Figure.7 SEM image at 20000 magnifications



Figure.8 SEM image at 30000 magnifications



Figure.9 SEM image at 30000 magnifications

5.3. FTIR Studies

The FTIR spectrum of the Lead (II) Phosphate sample is shown in the fig.9. The FTIR spectrum for Lead (II) Phosphate shows a strong peak at 3450.41 cm⁻¹ corresponding to O-H group [1] and the peak at 1764.75 AND 1631.67 cm⁻¹ are due to water impurities [3] and H-O-H stretching [5]. Another peak with at 1382.87 cm⁻¹ is due to the P=O bond. The spectrum also show peaks at 1095.49 cm⁻¹ and 1058.85 cm⁻¹ indicating P=O double stretching bond[3] and the peak at 831.6 cm⁻¹ and 655.75 cm⁻¹ indicates asymmetric and symmetric stretch of P-O-P group[4]. The peaks at 536.17 cm⁻¹ represents the (PO₄)₃ group [3] and the peak at 447.45 cm⁻¹ is due to the presence of Lead [2].



Figure.9 FTIR spectra of Lead (II) Phosphate Nano particles 5.4. UV Studies

The band gap of the prepared sample Lead (II) Phosphate was determined by using UV visible studies. From the UV spectrum the optical band gap of Lead (II) Phosphate is 3eV. Fig.10 shows the graph to find the band gap of Lead (II) Phosphate.



Figure.10 Graph to find the band gap of Lead (II) Phosphate Nano particles

5.5. AAS Studies

The synthesized Lead (II) Phosphate nanoparticles have been analyzed by AAS with optical parameter settings Pb wavelength 283.3nm and Air – C_2H_2 flame type. The results are given in table-8. A calibration curve diagram for Concentration of Lead (II) Phosphate nanoparticles in parts per million (ppm) Vs Absorbance has been drawn and a linear fit has been got. It is observed from the fig.11 that the absorbance is directly proportional to the concentration. The linear fit indicates that Lead (II) phosphate nanoparticles have been distributed in proper proportion [2].



Figure. 11 Concentration Vs Absorbance Table-8 AAS Analysis Result

True	Standar	Sampl		Actual	Concentrati	Absorban
value	d	e	%R	Concentrati	on (ppm)	ce
				on %		
4.0000	4.1443	0.096	103.	28 7174	2 7620	0.0646
		9	5	36./1/4	2.7029	0.0040
6.0000	6.0775	0.142	101.			
		1	3	Weight Facto	or $= 1.000$	0000
8.0000	8.0149	0.187	100.	Volume Fact	or = 1.00	
		4	1	Dilution Fact	tor $= 1.00$	
10.000	9.8839	0.231	99.8	Correction F	actor = 1.000	000
0		1				

6. Conclusions

The Lead (II) Phosphate nano particles have been prepared by chemical co-precipitation method. XRD analysis suggests that the average particle size is in the nano range (41.08nm). The SEM picture reveals the well crystallized particles with spherical morphology. From the FTIR spectrum, the stretching and bending frequencies of the molecular functional groups in the sample are studied. From the UV spectra, the band gap was found. From AAS studies it is found that the absorbance is directly proportional to the concentration. The linear fit indicates that Lead (II) Phosphate nanoparticles have been distributed in proper proportion.

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