Synthesis and Characterization of Lead Chromate nanoparticles

Physics

KEYWORDS : XRD, SEM, FTIR, UV, AAS.

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ABSTRACT

Lead chromate nanoparticles were synthesized via chemical co-precipitation method from lead chloride and potassium chromate. The formed nanoparticle is characterized by powder x-ray diffraction, scanning electron microscopy, ultra-violet spectroscopy and fourier transform infrared spectroscopy, confirmed the preferential growth of lead chromate nanoparticles that width is 70.423nm. The SEM image shows the synthesized lead chromate show well crystallized particles with tetrahedral 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 chromate nanoparticles is found to be 4.4eV.

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 [1].

Lead Chromate is used as a pigment in oil and water colors and is used in printing fabric. It is also used in the chemical analysis of organic materials and as a constituent in pyrotechnic compositions. This paper is discussing about easy, simple and low cost preparation i.e. chemical co-precipitation of lead chromate nanoparticles and its characterizations – XRD, SEM, FTIR, UV and AAS studies.

2. Materials and Methods

Nanoparticles of lead chromate were prepared by chemical co-precipitation method by adding lead chloride and potassium chromate. 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.

3. Tests Conducted

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 Alagappa University, 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 chromate nanoparticles 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.

4. Results and discussion

4.1. XRD studies

4.1.1.XRD–Particle Size Calculation

The XRD patterns of the prepared samples of lead chromate are shown in figure.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 chromate nano particles are calculated using Scherrer equation

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

where λ represents wavelength of X rays, β represents half width at full maximum and θ is the diffraction angle [2]. The average grain size of the particles is found to be 70.423nm.

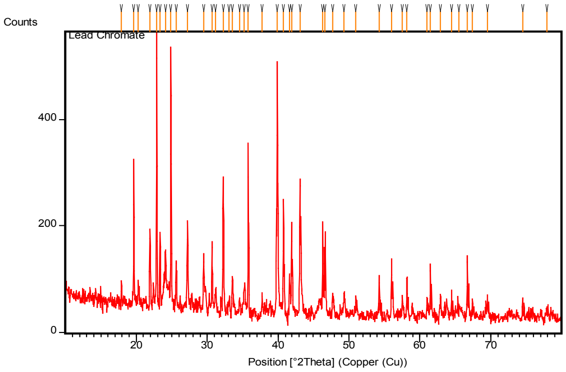


Figure.1 XRD pattern of lead chromate nanoparticles

A good agreement between the experimental diffraction angle [2θ] and standard diffraction angle [2θ] of specimen is confirming standard of the specimen. The peaks at 2θ values of lead chromate is observed and tabulated in table.1 and compared with the standard powder diffraction card of Joint Committee on Powder Diffraction Standards (JCPDS), lead chromate file No. 74-2304. The d-spacing values of experimental is also confirming to the standard values.

Table.1. Experimental and standard diffraction angles of lead chromate specimen.

Experimental		Standard – JCPDS 74-2304	
Diffraction angle (2θ in degrees)	D spacing (Å)	Diffraction angle (2θ in degrees)	D spacing (Å)
17.894	4.95304	17.901	4.9511
20.290	4.37375	20.242	4.3835
24.090	3.69186	23.914	3.7180
25.606	3.47604	25.510	3.4888
27.193	3.27670	27.155	3.2812
29.488	3.02672	29.455	3.0300
33.520	2.67129	33.690	2.6581
34.510	2.59675	34.480	2.5990
35.190	2.54814	35.180	2.5489
35.742	2.51014	35.732	2.5108
39.838	2.26100	39.856	2.2600
40.711	2.21448	40.608	2.2198
41.940	2.15241	41.884	2.1551
43.130	2.09575	43.185	2.0932
47.718	1.90437	47.808	1.9010
49.320	1.84635	49.260	1.8483
54.284	1.68851	54.180	1.6915
56.018	1.64030	56.006	1.6406
57.530	1.60067	57.448	1.6028
58.185	1.58427	58.166	1.5847
61.013	1.51742	61.120	1.5150
61.480	1.50702	61.387	1.5090
62.890	1.47664	62.594	1.4828
64.458	1.44438	64.277	1.4480
65.460	1.42466	65.328	1.4272
66.696	1.40126	66.885	1.3977
67.400	1.38838	67.472	1.3870
69.504	1.35134	69.768	1.3468
74.459	1.27320	74.536	1.2720
77.850	1.22596	77.639	1.2288

4.1.2. XRD - Expected 2θ Positions

The value of d (the interplanar spacing between the atoms) is calculated using Bragg's Law:**2d sin θ = n λ**

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

Wavelength λ = 1.5418 Å for Cu Kα

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.2.

$$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

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 [2].

Table.2. The Lattice plane and the lattice spacing from d from XRD

hkl	2θ(deg)		D((Å)	
	Experiment	Expected	Experi ment	Expected
011	17.89	17.9122	4.9530	4.9461
-111	20.29	20.2470	4.3737	4.3806
020	24.09	23.9048	3.6918	3.7180
200	25.60	25.5000	3.4760	3.4888
120	27.19	27.1436	3.2767	3.2810
012	29.48	29.4891	3.0267	3.0254
211	33.52	33.6900	2.6712	2.6569
112	34.51	34.5100	2.5967	2.5958
-212	35.19	35.1970	2.5481	2.5467
-221	35.74	36.2990	2.5101	2.4719
221	39.83	40.3790	2.2610	2.2310
310	40.71	40.5935	2.2144	2.2197
131	41.94	42.3836	2.1524	2.1300
212	43.13	43.2076	2.0957	2.0913
023	47.71	47.8570	1.9043	1.8984
132	49.32	49.2726	1.8463	1.8472
312	54.28	54.1950	1.6885	1.6904
240	56.01	55.9821	1.6403	1.6406
-214	57.53	57.5204	1.6006	1.6003
331	58.18	58.1533	1.5842	1.5844
024	61.01	61.1971	1.5174	1.5127
114	61.48	61.4691	1.5070	1.5066
-314	62.89	62.6542	1.4766	1.4809
-431	64.45	64.2525	1.4443	1.4479
430	65.46	65.3365	1.4246	1.4265
412	66.69	66.8928	1.4012	1.3970
204	67.40	67.5509	1.3883	1.3850
431	69.50	69.7502	1.3513	1.3466
440	74.45	74.5039	1.2732	1.2702
413	77.85	77.6916	1.2259	1.2276

4.1.3. 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.3. The number of unit cell is calculated from

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

Where D is the crystallite size and V is the cell volume of the sample [2].

Table.3. Dislocation Density and Number of Unit Cell from XRD.

2θ (deg)	Particle Size D (nm)	Dislocation Density (m^2) x10^{14}		Number of Unit Cell x10^5
		$\delta = 15\beta\cos\theta$ /4aD	$\delta = 1 / D^2$	
20.290	36.68	5.40	7.42	0.723
25.606	81.47	1.09	1.50	7.923
27.193	62.87	1.84	2.53	0.004
29.488	48.32	3.11	4.28	1.653
33.520	69.14	1.52	2.09	4.843
39.838	70.42	1.46	2.01	5.116
43.130	77.66	1.21	1.65	6.862
49.320	46.01	3.43	4.72	1.427
57.530	82.39	1.07	1.47	8.195
62.890	54.78	2.42	3.33	2.408
67.400	73.46	1.34	1.85	5.807
69.504	80.58	1.12	1.53	7.666
77.850	63.08	1.56	2.15	4.623

It is observed from these tabulated details, and from figure.2, figure.3 and figure.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 [2].

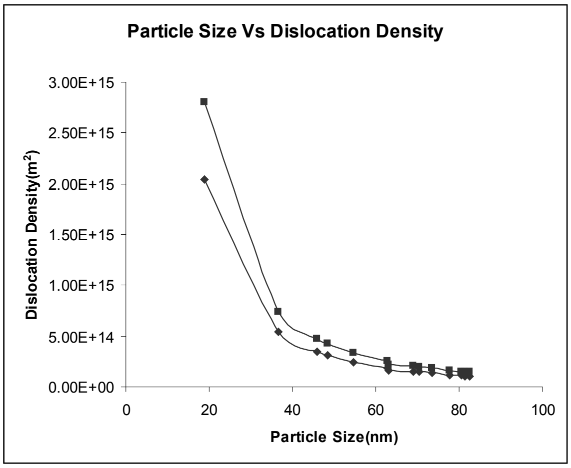


Figure.2 Particle size Vs Dislocation density for lead chromate nanoparticles.

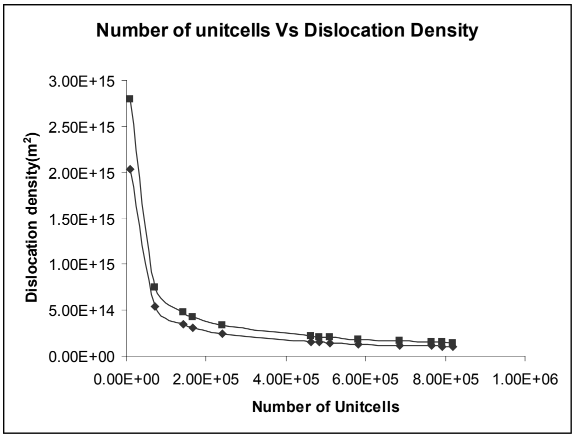


Figure.3 Number of Unit cells Vs Dislocation density for lead chromate nanoparticles.

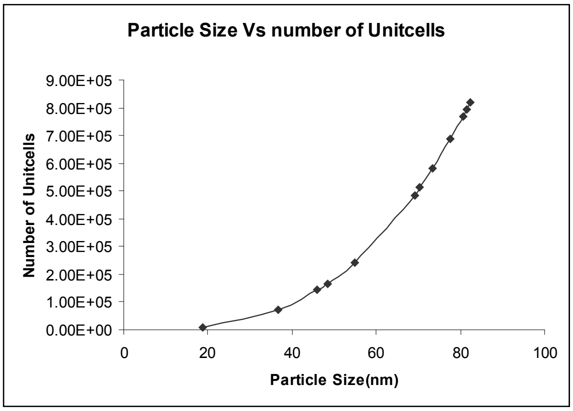


Figure.4 Particle Size Vs Number of Unitcells for lead chromate nanoparticles.

4.1.4. XRD – Morphology Index

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

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

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 be calculated. The relation between morphology index and particle size is shown in table.5.

Table.5. Relation between Morphology Index and Particle size.

FWHM (β) radians	Particle Size(D) nm	Morphology Index (unitless)
0.00383	36.688	0.236
0.00750	18.893	0.136
0.00174	81.477	0.405
0.00226	62.879	0.266
0.00296	48.327	0.286
0.00209	69.147	0.362
0.00383	37.887	0.236
0.00209	70.423	0.362
0.00191	77.665	0.383
0.00331	47.013	0.326
0.00157	99.992	0.430
0.00190	82.397	0.383
0.00296	54.782	0.266
0.00220	73.462	0.266
0.00200	80.584	0.362
0.00260	68.085	0.312

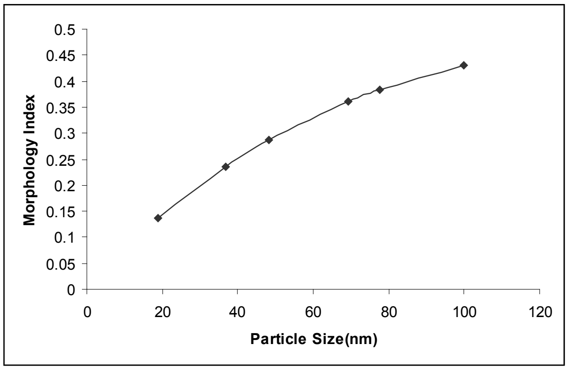


Figure.5 Morphology Index of lead chromate nanoparticles.

It is observed that MI has direct relationship with particle size [3] and the results are shown in Figure.5.

4.1.6. XRD – Unit Cell Parameters

Unit cell parameters values calculated from XRD are enumerated in table.6.

Table.6. XRD parameters of lead chromate nanoparticles.

Parameters	Values
Structure	Primitive
Space group	P21/c[14]
Symmetry of lattice	Monoclinic
Particle size	70.43 nm
Lattice parameters	a= 7.145;b = 7.436;c = 6.795
Vol.unit cell(V)	352.57
Density (ρ)	6.089
Dislocation Density	$x10^{14}$
Mass	323.19amu

4.2. SEM studies

Scanning electron microscopy was used to analyze the morphology and size of the synthesized lead chromate nanoparticles. Figure.6 and Figure.7 show the SEM images of the lead chromate nanoparticles at various magnifications. The SEM images of lead chromate nano particles show well crystallized particles with tetragonal shape. In this case the particles sizes are slightly increased and is also observed that the particles are distributed with agglomeration.

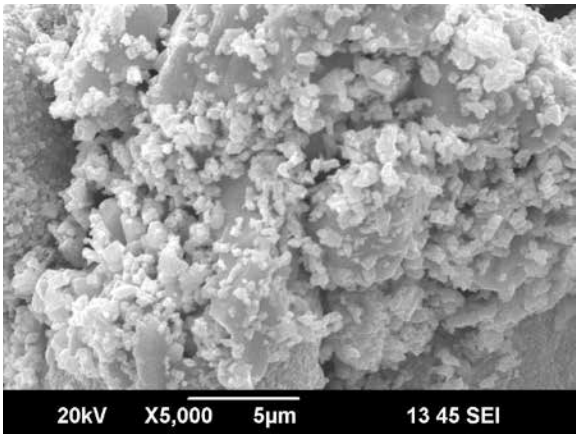


Figure.6 SEM image at 5000 magnifications.

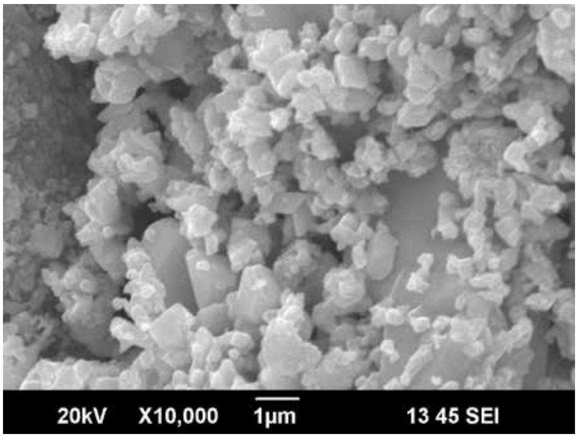
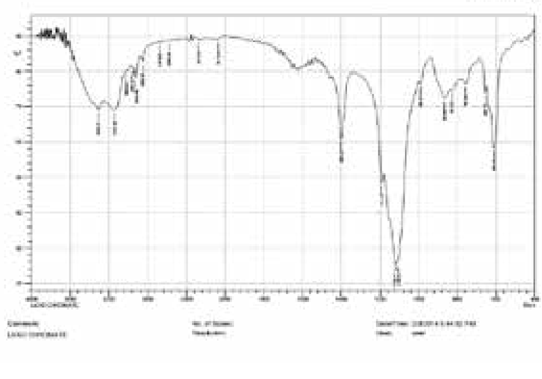


Figure.7 SEM image at 10000 magnifications.

4.3. FTIR Studies

The FTIR spectrum of the lead chromate sample is shown in the figure.8.The FTIR spectrum for lead chromate show peaks at 3315.41cm^{-1}, 3139.9 cm^{-1}, 3020.32 cm^{-1}corresponding to free O-H group [4] and the spectrum also shows peak at 1191.93cm^{-1} indicating the presence of lead and peak at 655.75cm^{-1} represents Cr-O stretching mode.

Figure.8 FTIR spectra of lead chromate nanoparticles.



4.4. UV Studies

The band gap of the prepared sample lead chromate was determined by using UV visible studies. From the UV spectrum the optical band gap of lead chromate is 4.4eV. Figure.9 shows the graph to find the band gap of lead chromate nanoparticles.

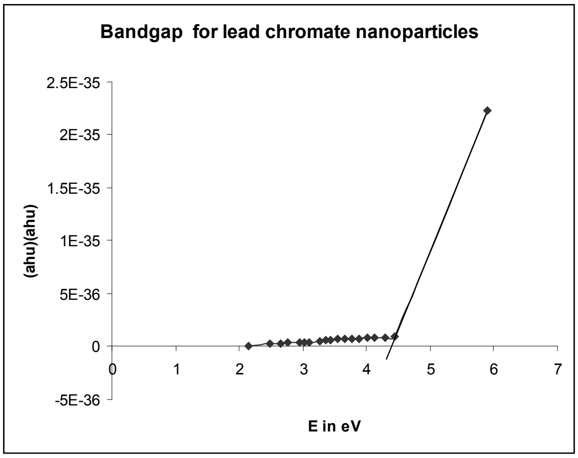


Figure.9 Graph to find the band gap of lead chromate nanoparticles.

5. CONCLUSIONS

The lead chromate nanoparticles have been prepared by chemical co-precipitation method. XRD analysis suggests that the average particle size is in the nano range (70.423nm). The SEM picture reveals the well crystallized particles with tetrahedral 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.

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