Research Paper

Volume : 2 | Issue : 7 | July 2013 • ISSN No 2277 - 8179

Synthesis And Characterisation Of Nanosized Cadmium Oxide

Chemistry

KEYWORDS : Synthesis, Thermal decomposition, Crystallite size, Density, fuel

Mahesha N — Department of Chemistry, Singhania University, Rajastan, India

Arunkumar Lagashetty — Department of Chemistry, Appa Institute of Engineering & Technology, Gulbarga, Karnataka, India

ABSTRACT

Low temperature synthesis of metal oxide nano materials using polymer as a fuel constitute simple and energy efficient synthetic route. Solid state combustion technique is used for the synthesis of oxide materials at nano dimension. Present work reports, solid state preparation of nanosized CdO by thermal decomposition of cadmium oxalate precursor employing polyvinyl alcohol as a fuel. The structure of as synthesised CdO is characterised by X-ray diffraction (XRD), bonding by Fourier transfer infrared (FTIR), morphology and particle size by Scanning Electron Microscope (SEM) tools. Crystallite sizes and density measurement of the sample is under taken. The crystallite sizes were calculated using X-ray line broadening and density measurements were under taken by various methods. Crystalline behaviour is observed by XRD pattern and metal –oxygen (Cd-O) bond formation was confirmed by FTIR study.

1. Introduction

Solid state combustion synthesis of materials at nano dimension enhances the synthetic chemistry. Although one can evolve a rational approach to the synthesis of oxides, there is always an element of serendipity. Several methods are used for the preparation of verity of oxides specially, traditional ceramic method, which involves mixing and grinding powders of the constituent oxides by heating them at high temperature with intermediate grinding when necessary. A wide range of conditions often bordering on the extreme, have been employed in materials synthesis; these include high temperatures or precursors, very low oxygen fugacites and rapid quenching. Recent method trend is to avoid brute force methods in order achieve better control of purity. The so called soft chemistry routes are indeed desirable because they lead to novel products at low temperature [1-2].

Solid state combustion synthesis method is known for its simplicity and materials can be prepared at laboratory grade as well as industry level [3-4]. The oxide ceramics obtained by combustion technique shows nanocrystalline nature and also good particle morphology [5-6]. Materials based on cadmium oxides have been extensively investigated because of their potential applications in many technological fields. Cadmium oxide is an important ceramic oxide used as a good adsorbent for heavy metals and catalytic applications.

Present work reports the synthesis of cadmium oxide nanoparticle using cadmium oxalate precursor employing combustion synthesis method. Polyvinyl alcohol (PVA) is used as a fuel for the conversion of cadmium oxalate in to cadmium oxide nanoparticles. Polyvinyl alcohol is a good surfactant and dispersant, hence the precursor will be well dispersed in the molton PVA which is needed for the initiation of combustion process. Initially it burns partially with fuel and it completes conversion of precursor in to cadmium oxide particles at high temperature. The prepared sample is well characterised for its structure by X-ray diffraction (XRD), morphology by Scanning Electron Microscope (TEM) and bonding by Fourier Transform Infrared study (FT-IR) techniques. Crystallite size and various densities of cadmium oxide are calculated.

2. Experimental

2.1 Materials and methods

Cadmium salt, oxalic acid and ammonia chemicals are used in the present study were of AR grade. Polyvinyl alcohol of molecular weight 125,000 was obtained commercially is used as fuel. Thermal decomposition method is adopted for the synthesis of cadmium oxide nanoparticles

2.2 *Preparation of cadmium oxalate precursor*

The hydrated cadmium oxalate precursor was prepared by dissolving eqimolar proportions of cadmium salt and oxalic acid in minimum volume of suitable solvent and was stirred for about 15 min on a magnetic stirrer. The slight brown coloured precipitate is obtained at 5-6 pH and is washed with cold distilled water. Finally, the precipitate is washed repeatedly with dry acetone and then dried under vaccume [7].

2.3 *Preparation of Cadmium Oxide*

The prepared cadmium oxalate precursor is mixed with polyvinyl alcohol in the weight ratio 1:5 [8] and ground well using pestle and mortar. The resultant mixture was transferred into a crucible and ignited in an electrical oven. The dispersed phase ignited with the evolution of large volume of gases. Here, PVA reacts with the precursor a partially decomposed product was obtained, after the complete evolution of gases. The temperature of the process does not exceed 300°C at any time. Chemical and physical characterisation of the partially decomposed products did not give any confirmable phases. The possible reason for a partially decomposed product formed may be attributed to the low temperature of the reaction giving rise to the insufficient energy needed for complete conversion. Hence, the partially decomposed sample mixture is further heated to get the desired product. Initially it burns with small flame shows the presence of cadmium metal. Further heating the sample forms crystalline product called cadmium oxide sample.

2.4 Density measurement

2.4.1 Density evaluation from X-ray data

$$d := 8\frac{M}{Na^3}$$

The X-ray density of the samples have been computed from the values of lattice

parameters using the formula [9-10].

Where 8 represents the number of molecules in a unit cell of a spinal lattice

M = Molecular weight of the sample N = Avogardo's number

a = Lattice parameter of the sample

The lattice constant for the cubic was calculated using the equation

$$d = \frac{a}{(h^2+k^2+l^2)^{1/2}}$$

2.4.2 Tap density

The as prepared cadmium oxide was crushed in agate mortar using a pestle and mortar. A known amount of this powder was filled into a graduated cylinder of 25ml capacity. The cylinder

was tapped until the powder level remains unchanged. The volume occupied by the powder was noted. The ratio between the weight of the substance and the volume gave tap density [11].

2.4.3 Powder density

The powder densities were measured using Archimedes principle [12] with a pycnometer and xylene as a liquid medium. The pycnometer of volume 25ml was used. The following weights were taken and used in the density calculation.

$$\rho_{sample} = \frac{(w_2 - w_1)\,\rho_{sol}}{(w_4 - w_3) + (w_2 - w_1)}$$

Weight of the bottle = W1g, Weight of the bottle + Substance = W2g, Weight of the bottle + Substance + Xylene = W3g, Weight of the bottle + Xylene = W4g, Density of Xylene = rsol, Density of sample = rsample

2.4.4 Crystallite size from X-ray data

Detailed knowledge of crystallite size, shape and strain in a finely divided powder often helps to correlate many physical properties of a system undergoing transformation in a solid-state reaction. X-ray line broadening analysis provides a method of finding bulk average size of coherently diffracting domains and r.m.s strain. The average crystallite size (D) from X-ray line broadening has been calculated using the Scherrer equation [13-14]. The instrumental broading was corrected using quartz as a internal standard.

$$D = \frac{0.9\lambda}{\beta_{1/2}\mathrm{Cos}\theta}$$

Where λ is the wavelength of the X-ray beam, β1/2 is the angular width at the half-maximum intensity and θ is the Bragg angular

2.5 *Characterisation*

The X-ray diffraction patterns were obtained employing a Geol JDX-8p spectrometer using CuKα radiation. The X-rays generator was operated at 30kV and 20mA. The scanning range, 2θ/θ were selected. The scanning speed =10 min-1 were employed for precise lattice parameter determination. High purity silicon powder was used as an internal standard. The shape, size and distribution of the powder, as prepared tin oxide sample, microstructure of the sample have examined using a Leica-440 Cambridge Stereoscan, scanning electron microscope image. The infrared spectra of the oxide sample were recorded on a Perkin –Elmer FTIR spectrophotometer [Model 1000] in the range 400 cm-1 to 4000cm-1.

3.0. Results and discussion

3.1. X-ray diffraction

Figure1 shows indexed XRD pattern of as prepared cadmium oxide. The pattern shows large number of peaks confirms the formation of cubic phase CdO sample. The d-spacing values of the sample matches well with standard 04-0640 JCPDS file. Unit cell parameters ware obtained by least–square refinement of the powder XRD data. This study reveals that the sample is monophasic and the values in the parenthesis indicate miller indices.

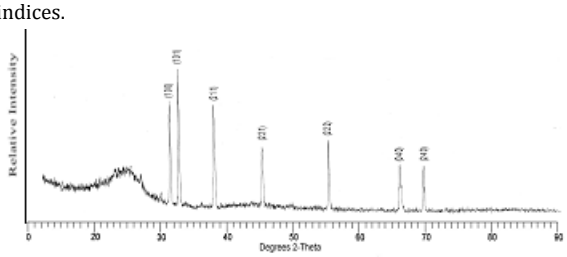

Figure1: XRD pattern of Cadmium oxide

3.2. Crystallite size and density

The crystallite size of the co sample is calculated from XRD data is 80 nm. The size obtained is dependent on solid-state transformation reaction, which generally adopts the habit of its precursor. Thus, the conversion of cadmium oxalate precursor into CdO is considered being topotactic in nature, indicating that the synthesis of precursor with very small particle sizes would be required for obtaining nanosized cadmium oxide sample. The densities of the sample calculated from XRD data, tap density and powder density is 4976 kg/m3, 5289 kg/m3 and 3740 kg/m3 respectively. The sample shows approximately same density may be attributed to their average shape which might have similar surface area.

3.3. Scanning Electron Microscopy

The morphology of as prepared cadmium oxide was studied by Scanning Electron Microscope tool. Figure 2 shows SEM image of as prepared CdO sample. Irregular shaped particles are grouped each other and some particles are spherical agglomerated. A uniform morphology and chemical homogeneity is also observed in the image.

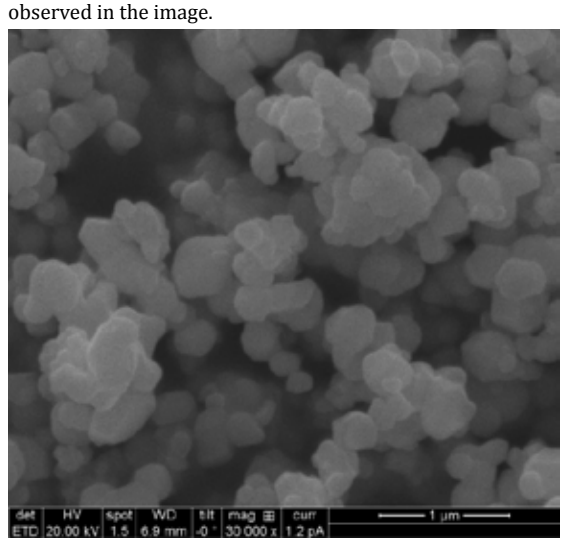

Figure-2: SEM image of Cadmium Oxide

3.4. Infrared studies

The bonding nature of the prepared cadmium oxide sample was studied by Fourier transform infra red tool. Figure 3 shows FTIR spectrum of as prepared CdO sample. The sample shows the absorption in the region 3630, 1464, 645 and 410 cm-1. The peak 3630cm-1 corresponds to water of absorption and the peak at 1460 cm-1 due to the presence of some overtones. The peaks at 645 and 410 cm-1 corresponds to metal-oxygen (Cd-O) vibrational modes of the spinal compound. (Metal oxides generally give absorption bands below 1000cm-1 arising from inter-atomic vibrations [15]).This conform the formation of CdO sample.

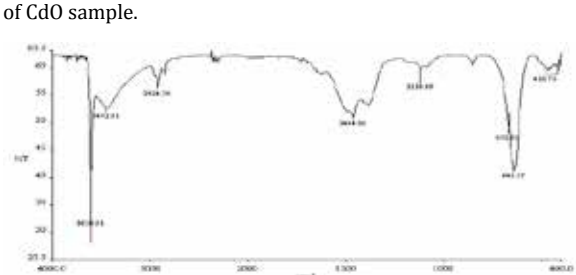

Figure 4: FTIR spectrum of as prepared Cadmium oxide sample

4. Conclusions

Solid state chemical conversion of cadmium oxalate precursor in to cadmium oxide nanomaterial. Polyvinyl alcohol is used as an efficient fuel in microwave ignition. This preparative technique is very simple and energy efficient to obtain materials at nano dimension. Hence, this method can adopt for the synthesis of other metal oxides at nano dimensions not only for laboratory preparation, this procedure may be extended for large-scale

synthesis. A characterization technique confirms the complete conversion of cadmium oxalate in to its oxide.

Acknowledgement
We are grateful to Prof. A Venkataraman, Department of Materials Science, Gulbarga University Gulbarga and Dr. Sanghshetty Kalyani, Department of Physics, Bheemanna Khandre Institute of Technology, Bhalki, Bidar for useful discussion in spectral analysis. We are also thankful to Sri Guruling, I.I.Sc, Bangalore for providing spectral data. Thanks are due to Chairman, Department of Chemistry, Singania University for constant support and encouragement.

REFERENCE

1. Rao, K.J. (1995): Perspectives in solid state chemistry, Narosa publishing house, New Delhi, | 2. Rao, C.N.R,; Gopalkrishnan, J. (1997): New directions in solid state chemistry, Cambridge University Press, Cambridge. | 3. Lagashetty A and Venkataraman A, (2004), Adsorption Study of lead ions on nanosized SnO2 synthesised by Self-Propagating Combustion reaction, Bull. Mat. Sci. 27(6)(2004)419. | | 4. Granquist, C.G. (1995): Hand book of Inorganic Electrochromic Materials, Elsevier, Amsterdam. | 5. Mallikarjuna, N. N,; Govindraj, B.; Lagashetty, A.; Venkataraman, A. (2003): Combustion derived ultrafine □-Fe2O3: Structure, morphology and thermal studies, J. Therm. Anal. & Cal. 71, 915. | 6. Lagashetty,A.; Mallikarjuna, N. N.; Venkataraman, A. (2003): Adsorption study of lead ions on □-Fe2O3 –thiourea complex composite, Ind .J. Chem.Tech., 10, 63. | 7. Mallikarjuna, N. N.;.Venkataraman, A. (2003): Combustion synthesis of nanosized □-Fe2O3:Structure, electrical and dielectric studies, Ind. J. Engg. & Mater. Sci., 10(2003)50 | 8. Lagashetty, A.; Havanoor, V.; Basavaraja, S.; Venkataraman, A. (2008): Combustion synthesis of LiMn2O4 by thermal decompositionoxalate precursor, Ind. J. Chem. Tech. 15,42. | 9. Smit, J.; Wijn,H. P. T.; Phillips, N. N.; Eindnoven, G. (1959): Ferrites, The Holland. | | 10. Venkataraman, A.; Hiremath, V. A.; Date, S. K.; Kulkarni, S. D. (2001): A new route to □-Fe2O3 synthesis, Bull. Mater. Sci. 24(6), 101. | 11. Kinsman, S. (1978): Systematic Materials Analysis" Vol. 4, (eds.) T.H. Richardson and R.V. Peterson Academic, New York p 200. | 12. Lagashetty, A..; Havanoor, V.; Basavaraja, S.; Balaji, S.D.; Venkataraman, A. (2007): Microwave-assisted route for synthesis of nanosized metal oxides, Sci. & Tech. Adv. Mater. 84, 84 | 13. West, A. R. (1989): Solid State Chemistry and its Application, John Weily, Newyork. | 14. Klug, A.; Alexander, L. (1962) : X-ray diffraction procedure, John Weily, Newyork. | 15. Rao, C. N. R.(1963): Chemical Applications of Infrared Spectroscopy, Academic Press, NewYork and London. |