



Investigating Structural, Thermal and Optical Properties of Lead Oxide Nano-Particles Synthesized by Sol-Gel Combustion Method

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ABSTRACT: Metal and metal oxide nanoparticles (NPs) have piqued the interest of material scientists in recent years due to their unique physicochemical properties which are dependent on their size, shape, and chemical surroundings. The sol gel combustion is one of the most straightforward and practical technique for getting tiny and similar size and shape of the powder out of all the current lead oxide nanoparticle synthesis techniques. In this study, PbO nanoparticles are prepared using the sol-gel method followed by an auto combustion process. This research is aimed at the particle size, shape, thermal analysis, and optical properties of nanostructured PbO. Several microscopic, spectroscopic, and thermogravimetric analysis are employed for the structural characterization of lead oxide nanoparticles. Tiny lead oxide particles with a diameter of 60 nanometres have been prepared. The prepared sample's optical band gap was discovered to be 2.44 electronvolt. Thermal investigations indicate the thermal behaviour and stability of synthesized lead oxide powder and are described in details.

KEYWORDS: Combustion, Lead oxide, Nanoparticles, Optical property, Sol-gel, Thermal properties.

INTRODUCTION

"There is Plenty of Room at the Bottom," which means more elements can fit in the same amount of area when things are shrunk in size. As a result, Richard Feynman introduced nanotechnology to the world with this speech. At the time, he thought that direct atom manipulation would be a more potent form of synthetic chemistry. [1]. Nanoscales are typically fewer than 100 nanometers (nm) in size, and nanotechnology is the study, control, and manipulation of materials at these scales [2]. The synthesis of nanomaterials has received significant attention in recent decades in a variety of scientific and industrial sectors [3,4]. In order to approach nanotechnology from the perspective of materials science, nanomaterial study makes use of developments in materials synthesis and metrology in support of microfabrication research [5]. Because of special chemical and physical properties and potential use Due to their special physical and chemical characteristics as well as their potential use in a wide range of industries, including paints, rechargeable batteries, gas sensors, fuel cells, pigments, and more, nanomaterials are of interest to researchers [6-8]. The commercialization of nanomaterials is accelerating, and they are becoming conventional [9, 10]. Due to their distinctive optical and electrical characteristics, inorganic nanomaterials (such as quantum dots, nanorods, and nanowires) may be employed in optoelectronics [11]. The mechanical, magnetic, chemical, and other characteristics of nanomaterials composed of metals, semiconductors, or oxides are of immense interest [12,13]. Nanoparticles have been used to create quantum dots and chemical catalysts like nanomaterial-based catalysts. Numerous nanoparticles have been the subject of recent study for biomedical uses, including medication delivery, tissue engineering, and biosensors [14,15].

Lead oxide nanoparticles have a wide range of uses because of their lengthy life cycles [16]. Lead oxide nanoparticles are most frequently used in nanodevices. Lead oxide (PbO) is a crucial industrial material because of its special electrical, mechanical, and optical characteristics, as well as because of its prospective use in nanodevices and functionalized materials [17]. PbO nanoparticles are distinctive in their properties and have a wide range of uses, such as illuminating materials, gas sensors, storage devices, UV blockers, and oxide glass modifiers [18–20]. A significant glass modifier called lead oxide improves the glass's thermal and optical properties as well as its chemical and mechanical stability [21]. Rare earth doped B₂O₃-PbO (Lead Borate) glasses have drawn huge attention because of its potential uses in thermoluminescence and solid-state lasers [22,23]. An exciting material for



antireflection coatings in solar cell manufacture is lead oxide thin film [24]. There are numerous variations of lead oxide, including PbO, Pb₃O₄, Pb₂O₃, and PbO₂. PbO itself comes in three different forms: litharge-, massicot-, and amorphous-PbO. While -PbO is stable at high temperatures, the opposite is true for -PbO. Around atmospheric pressure, -PbO undergoes a phase change to -PbO at 489 °C [25,26], while the pure -phase can only be produced between 240 and 260 °C [27].

The process of generating lead oxide using different methods is continuous in order to enhance its attributes as its use in batteries is expanding and advancements are made to raise its discharge capacity and life cycle, as well as its use in electronic devices and other applications. In this study, an open lab combustion procedure is tried after a sol gel process. It is preferred to use the combustion process to produce uniform and fine particle sizes. In order to ascertain its structure, shape, stability, optical, and thermal qualities, it is thereafter subjected through several tests.

EXPERIMENTAL

Synthesis of Lead Oxide Nanoparticles

Synthesis part in the present study carried out with two steps involving sol-gel preparation followed by its combustion. Prepared powder sample is then characterized to verify the functional group and to obtain the morphology and many more. Overall workflow of the present study can be illustrated in Figure 1.

All the materials used in the preparation of lead oxide nanoparticles were of the AR (Analytical Reagent) grade and have been used without additional purification as received.. The materials used for synthesis were Lead (II) acetate - Pb(C₂H₃O₂)₂, Polyvinyl alcohol (PVA) - CH₂CH(OH), Ethanol - CH₃CH₂OH and Distilled Water - H₂O. Double-distilled water was used in all experiments.

Sol-Gel preparation: Lead acetate and PVA of weight 8 grams and 32 grams were taken into a mixture of 160 ml of distilled water and 240 ml of ethanol to form an aqueous solution. Aqueous mixture was then put on the magnetic stirrer for 30 minutes to produce transparent solution called sol. Then heating was started at 80°C and continued for 2 hours, which resulted in the conversion of the sol into a thick milky gel. In this conversion, about 180 - 200 ml of sol has been evaporated. Figure 2 depicts the procedure of sol and gel prepared for the current study.

Combustion of prepared gel: However, combustion of any gel can be risky and dangerous especially if the material is toxic. Still, we attempted to do combustion in open lab. Nevertheless, instead of doing the burials in the furnace, they were done in the open laboratory. Even then, instead of doing the combustion in the furnace, it was done in the open laboratories which is unique part of present study.

To do so, a steel cooking pot full of sand was taken and kept on the electric coil stove. Prepared gel was taken into a ceramic crucible and placed into the sand. The obtained gel was taken in a ceramic crucible and buried in the sand and started to heat up. As the temperature rose, the gel started to boil. There came a point where all the water in the gel have been evaporated. When the sand temperature reached 300, the gel had completely dried up and a brown coloured mixture was seen. As the temperature crossed 450, the ceramic crucible caught fire and flaming continued for some time. When flaming stopped, it was seen that a fine powder of grey colour was ready. Figure 3 depicts the stepwise combustion procedure followed in the current study.

Characterization of Nanoparticles

Prepared sample is then observed under various characterization methods such as X-ray diffraction (XRD) which is done using RIGAKU (miniflex-600) instrument with Cu K α radiation having wavelength $\lambda=1.540598 \text{ \AA}$ in the 2θ range $10^\circ-80^\circ$ for determination of crystal structure, crystalline grain size and composition. Fourier Transform Infrared (FTIR) spectroscopy was done using BRUKER alpha spectrometer used to determine the interaction of reducing and stabilizing agents on the surface of nanomaterials. Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) are recorded using TA Model SDT 2790 Instrument for measuring change in mass.

The phases present in the material are studied with physical correlation between the crystallinity, size and juxtaposition using scanning electron microscopy (SEM), which is carried out using a Zeiss Supra 55 apparatus at 10 kV. Ultraviolet - Visible (UV-Vis) spectroscopy of lead oxide nanoparticles was done. For this, powder sample was taken into HCl solution and ultrasonic bath was given to it for 10 minutes for proper dissolution.



RESULTS AND DISCUSSION

X-Ray Diffraction

Crystalline structure of prepared lead oxide powder was then recorded by X-ray Diffraction (XRD) pattern. Equation (1) is used to calculate the particle size of the lead oxide from the broadening of the X-ray diffraction peaks.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where, D is particle size diameter, θ is the diffraction angle, β = angular width measured at half the maximum intensity and λ = wavelength of x-ray used (1.540598 Å).

The XRD pattern of the calcined powder is shown in Figure 4. The observed X-ray diffractogram was indexed by comparing it to the lead oxide standard JCPDS 38-1477 (Joint Code for Powder Diffraction Standards) data [28]. This indicated that the obtained product was PbO. Very sharp and strong peaks indicate a very good crystallization of the product. The prominent peaks present in the graph show the crystalline nature of PbO indicated by the black star and extra peaks represent the other lead oxide groups. The grain size calculated from Debye Scherrer's formula from the major diffraction peaks of the corresponding lead oxide and average size was found to be 93.00 nm [29].

FTIR and Thermal Analyses

Understanding the functional group of any organic molecule is made easier with the use of FTIR spectroscopy. In order to further prove the formation of PbO, the products were characterized by the FTIR spectroscopy of prepared nanocrystals and is shown in Figure 5. The FTIR spectrum was recorded in the range 400-1000 cm^{-1} and the absorption peak appears at 492 cm^{-1} which is assigned to the Pb-O bond [25]. There is absorption peak occurred throughout the spectrum in the range of 4000 to 600 cm^{-1} hence confirms the formation of pure lead oxide nanocrystals. The spectrum of 800 to 400 cm^{-1} range is shown by zooming in the graph indicating the Pb-O stretching region.

Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) recorded for sample can be shown in Figure 6. No discernible weight change was seen in the PbO powder throughout the TGA analysis until 390 °C. Analysis has been done up to 600°C for 60 minutes, maximum weight reduction has occurred was 2 weights % as powder sample was already combusted and dried. The possible reasons of getting the weight loss are the oxidation which was occurred at 390 °C corresponding to the conversion of PbO into Pb₂O₃ or the transformation of PbO into Pb occurs during the reduction step [30].

The findings of the DTA study point to either PbO phase shifts or minor reduction and oxidation effects. In DTA analysis, both (exothermic and endothermic) the processes or transformations are observed. Exothermic phenomenon occurred from $T = 290$ °C to $T = 360$ °C and peak is depicted at $T = 320$ °C. Similarly, endothermic process has been depicted from $T = 430$ °C to $T = 510$ °C with a well-defined peak at $T = 460$ °C. Equation (2) is used to calculate the temperature change.

$$\Delta T = T_s - T_r \quad (2)$$

where T_s and T_r are the temperature of sample and reference respectively. A peak forms on the temperature change against time or furnace temperature curve during TGA analysis [31].

The partial oxidation of the PbO powder to Pb₂O₃, which converts back to PbO at higher temperatures, causes the exothermic process. The endothermic peak at 560 °C is caused by the phase transition from litharge to massicot [32,33].

SEM study

Scanning electron microscopy (SEM) is used to investigate the particle morphology of lead oxide nanoparticles. The mean diameter was calculated by measuring either diameter or the thickness of over 50 grains using the "J image" program. As it is obvious in Figure 7, the sample includes lead oxide particles with average size range of 60 nm to 1000 nm. May be due to agglomeration in the particles, the size of some of them has been found to be 1000 nanometres range. However, there are a lot of tiny particles whose size has been found in 60 to 70 nanometres.

UV-Vis Spectra

UV-Visible spectroscopy, which analyses the visible and ultraviolet spectra, is used to confirm the synthesis of nanoparticles. For all of the sample sets, the absorbance measurement mode is chosen, and the medium scan speed is set. The UV-Spectrometer is used to analyse the lead oxide nanoparticles in the 200 to 1000 nm wavelength range. The location of the absorption peak provides further evidence that the sol-gel combustion synthesis results in the production of lead nanoparticles. Figure 8 (a) and (b) depict the UV-



Vis absorption and band gap spectra of prepared lead oxide nanoparticles. The absorption peaks around 357 nm are correlated to pure lead oxide. The size of the nanoparticles has an impact on the UV-Vis spectra (usually depends on the size), and as particle size increases, so does the maximum wavelength of absorption [34]. The energy gap has been taken out with the help of the Tauc plot and was found to be 2.44 eV which is an acceptable band gap value for the massicot lead oxide [19].

CONCLUSION

This research article introduces a novel method for synthesising nanostructured lead oxide. The gel was created, then open lab combustion was performed by keeping the gel in the ceramic crucible buried in the sand pot. This technology will aid in the production of huge quantities of lead oxide nanoparticles. Because lead oxide is known for its toxicity, the synthesis can be done out in the open, away from the populace. Combustion produces particles of uniform and fine size. The size of the nanomaterial prepared is in the nanoscale. To confirm the formation of lead oxide, as well as to assess the crystal structure and particle size, X-ray diffraction measurements were performed. The position and intensity of lines in the diffraction pattern confirm the orthorhombic structure. XRD determined a crystal size of 93 nm, which is quite near to the standard size of lead oxide nanoparticles.

Thermo Gravimetric analysis determines the material's stability by revealing changes in a sample's chemical properties as a function of temperature. DTA is used to record the temperature difference between the sample and the reference. The TGA curve indicates no mass change across the whole temperature range. The microstructure and grain size of lead oxide are examined using a scanning electron microscope (SEM). The micrograph of the chemical reveals a mixture of particles of various sizes. The grain size can reach 1000 nm due to agglomeration, however tiny particles as small as 60-70 nm have also been discovered. The optical spectra in HCl solution indicated a wide absorption region with a 357nm absorption peak. Using the tauc plot, the optical band gap energy was calculated and determined to be 2.44 eV.

Metal oxide stoichiometry, structure, and phase purity can all be better controlled using this approach. The approach has also been discovered to be easy and quick. Due to its unique qualities, nanotechnology is a developing topic in the current global market, and the usage of nanoparticles has demonstrated significant applicability in every industrial sector. More properties of this powder can be studied by making a pellet or thin film so that it can be used in the suitable electronic device.

DISCLOSURE STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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REFERENCES

1. Feynman, R., 1960. There's plenty of room at the bottom, engineering and science. California: California Institute Of Technology.
2. Kannan, N. and Subbalaxmi, S., 2011. Green synthesis of silver nanoparticles using *Bacillus subtilis* IA751 and its antimicrobial activity. *Res. J. Nanosci. Nanotechnol*, 1(2), pp.87-94.
3. Keating, C.D. and Natan, M.J., 2003. Striped metal nanowires as building blocks and optical tags. *Advanced Materials*, 15(5), pp.451-454.
4. Chen LJ, Zhang SM, Wu ZS, Zhamg ZJ, Dang HX (2005). Preparation of PbS-type PbO nanocrystals in a room-temperature ionic liquid. *Mater. Lett.*, 59: 3119-3121.
5. Singh, M., Manikandan, S. and Kumaraguru, A.K., 2011. Nanoparticles: a new technology with wide applications. *Research Journal of Nanoscience and Nanotechnology*, 1(1), pp.1-11.
6. Sadri, R., Hosseini, M., Kazi, S.N., Bagheri, S., Abdelrazek, A.H., Ahmadi, G., Zubir, N., Ahmad, R. and Abidin, N.I.Z., 2018. A facile, bio-based, novel approach for synthesis of covalently functionalized graphene nanoplatelet nano-coolants toward improved thermo-physical and heat transfer properties. *Journal of colloid and interface science*, 509, pp.140-152.
7. Hübler, A.W. and Osuagwu, O., 2010. Digital quantum batteries: Energy and information storage in nanovacuum tube arrays. *Complexity*, 15(5), pp.48-55.



8. Ghasemi, S., Mousavi, M.F., Shamsipur, M. and Karami, H., 2008. Sonochemical-assisted synthesis of nano-structured lead dioxide. *Ultrasonics sonochemistry*, 15(4), pp.448-455.
9. Eldridge, T., 2014. Achieving industry integration with nanomaterials through financial markets. *Nanotechnology Now*.
10. McGovern, C., 2010. Commoditization of nanomaterials. *Nanotechnol. Perceptions*, 6(3), pp.155-178.
11. Zeng, S., Baillargeat, D., Ho, H.P. and Yong, K.T., 2014. Nanomaterials enhanced surface plasmon resonance for biological and chemical sensing applications. *Chemical Society Reviews*, 43(10), pp.3426-3452.
12. Stephenson, C. and Hubler, A., 2015. Stability and conductivity of self assembled wires in a transverse electric field. *Scientific reports*, 5(1), pp.1-9.
13. Lyon, D. and Hubler, A., 2013. Gap size dependence of the dielectric strength in nano vacuum gaps. *IEEE Transactions on Dielectrics and Electrical Insulation*, 20(4), pp.1467-1471.
14. Valenti, G., Rampazzo, E., Bonacchi, S., Petrizza, L., Marcaccio, M., Montalti, M., Prodi, L. and Paolucci, F., 2016. Variable doping induces mechanism swapping in electrogenerated chemiluminescence of Ru (bpy) 3²⁺ core-shell silica nanoparticles. *Journal of the American Chemical Society*, 138(49), pp.15935-15942.
15. Keravitayanan, P., Carrow, J.K. and Gaharwar, A.K., 2015. Nanomaterials for engineering stem cell responses. *Advanced healthcare materials*, 4(11), pp.1600-1627.
16. Karami, H., Karimi, M.A. and Haghdar, S., 2008. Synthesis of uniform nano-structured lead oxide by sonochemical method and its application as cathode and anode of lead-acid batteries. *Materials Research Bulletin*, 43(11), pp.3054-3065.
17. Xi, G., Peng, Y., Xu, L., Zhang, M., Yu, W. and Qian, Y., 2004. Selected-control synthesis of PbO₂ submicrometer-sized hollow spheres and Pb₃O₄ microtubes. *Inorganic Chemistry Communications*, 7(5), pp.607-610.
18. Konstantinov, K., Ng, S.H., Wang, J.Z., Wang, G.X., Wexler, D. and Liu, H.K., 2006. Nanostructured PbO materials obtained in situ by spray solution technique for Li-ion batteries. *Journal of power sources*, 159(1), pp.241-244.
19. Arulmozhi, K.T. and Mythili, N., 2013. Studies on the chemical synthesis and characterization of lead oxide nanoparticles with different organic capping agents. *AIP advances*, 3(12), p.122122.
20. Barriga, C., Maffi, S., Bicelli, L.P. and Malitesta, C., 1991. Electrochemical lithiation of Pb₃O₄. *Journal of power sources*, 34(4), pp.353-367.
21. Almeida, J.M.P., Almeida, G.F.B., Hernandez, A.C. and Mendonça, C.R., 2016. Architecture of lead oxide microcrystals in glass: a laser and etching based method. *CrystEngComm*, 18(31), pp.5959-5964.
22. Pisarski, W.A., Goryczka, T., Pisarska, J. and Ryba-Romanowski, W., 2007. Er-doped lead borate glasses and transparent glass ceramics for near-infrared luminescence and up-conversion applications. *The Journal of Physical Chemistry B*, 111(10), pp.2427-2430.
23. Rodriguez Chialanza, M., Castiglioni, J. and Fornaro, L., 2012. Crystallization as a way for inducing thermoluminescence in a lead borate glass. *Journal of Materials Science*, 47(5), pp.2339-2344.
24. Calnan, S., 2014. Applications of oxide coatings in photovoltaic devices. *Coatings*, 4(1), pp.162-202.
25. Salavati-Niasari, M., Mohandes, F. and Davar, F., 2009. Preparation of PbO nanocrystals via decomposition of lead oxalate. *Polyhedron*, 28(11), pp.2263-2267.
26. Radhakrishnan, S., Kamalasanan, M.N. and Mehendru, P.C., 1983. Sensitization of photoconductivity in tetragonal lead monoxide. *Journal of Materials Science*, 18(7), pp.1912-1916.
27. Hai, K., Tang, D. and Wang, X.G., 2013. Effect of an oxidizing environment on the phase structure of lead oxide nanowires. *AIP Advances*, 3(2), p.022120.
28. SMRR, 2002. <http://www.cristal.org/smrr/results/solutions/smrr-4.gif> (Accessed on: May 2018)
29. Jenkins, R. and Snyder, R.L., 1996. Introduction to X-ray Powder Diffractometry, John Wiley & Sons Inc. 89–91 Table 1. Commercially available molybdenum based alloys.
30. Liptay, G., Erdey, L., Paulik, F. and Paulik, J., 1971. Atlas of thermoanalytical curves:(TG-, DTG-, DTA-curves measured simultaneously). Heyden and Son.
31. Porter, R.S. and Johnson, J.F., 2013. Analytical Calorimetry: Proceedings of the Symposium on Analytical Calorimetry at the meeting of the American Chemical Society, held in Chicago, Illinois, September 13–18, 1970. Springer Science & Business Media.

32. Sorrell, C.A., 1972. PbO transformation induced by water. Journal of the American Ceramic Society, 55(1), pp.47-47.
33. Bersani, M., Morten, B., Prudenziati, M. and Gualtieri, A., 1997. Interactions between lead oxide and ceramic substrates for thick film technology. Journal of materials research, 12(2), pp.501-508.
34. Li, S., Yang, W., Chen, M., Gao, J., Kang, J. and Qi, Y., 2005. Preparation of PbO nanoparticles by microwave irradiation and their application to Pb (II)-selective electrode based on cellulose acetate. Materials chemistry and physics, 90(2-3), pp.262-269.

FIGURES:

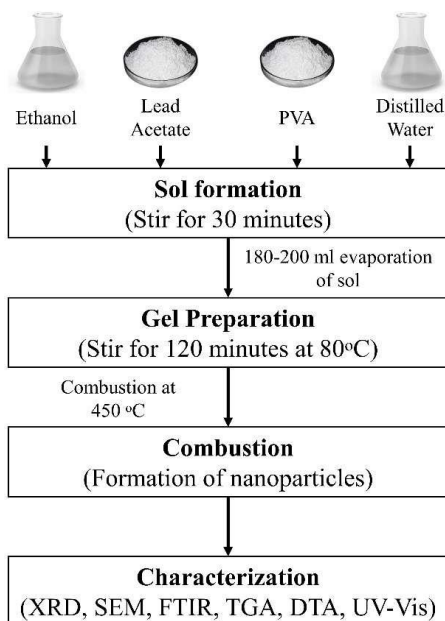


Figure 1: Overall workflow of present study

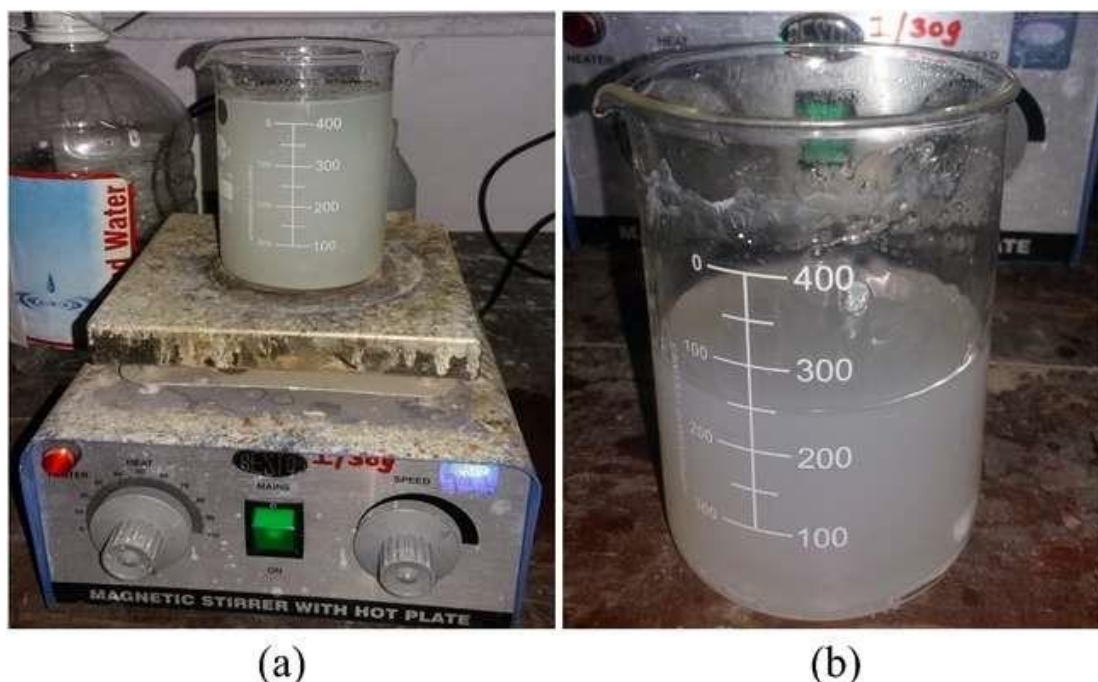


Figure 2: Sol and Gel preparation (a) Sol after 30 minutes of stirring (b) Gel after 2 hours of continue heating

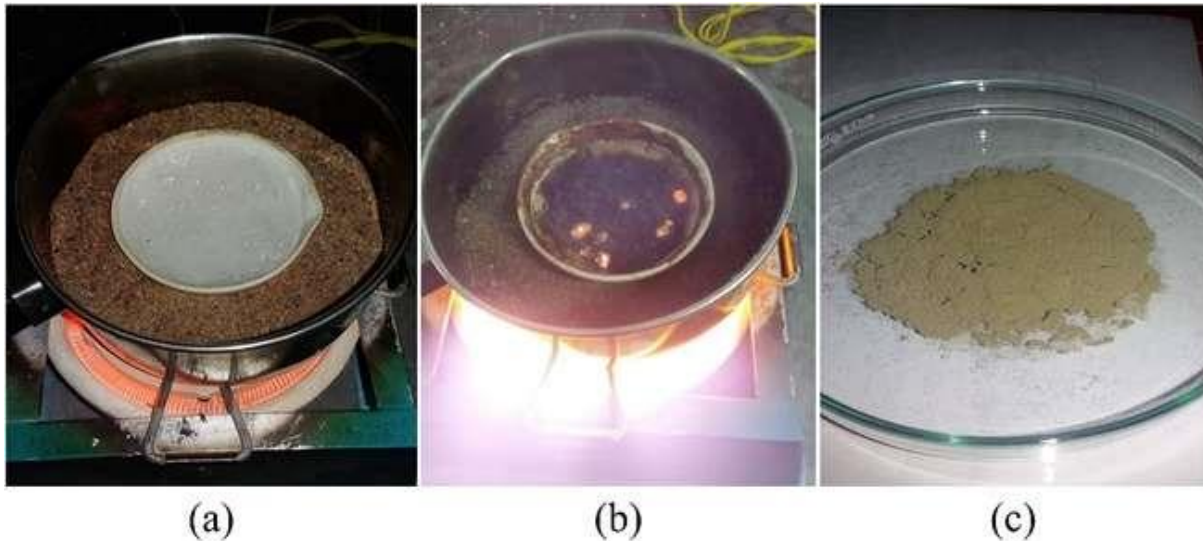


Figure 3: Combustion process carried out in present study (a) Initial stage – heating of gel (b) Middle stage – combustion at 450 °C (c) final stage – obtained nano powder

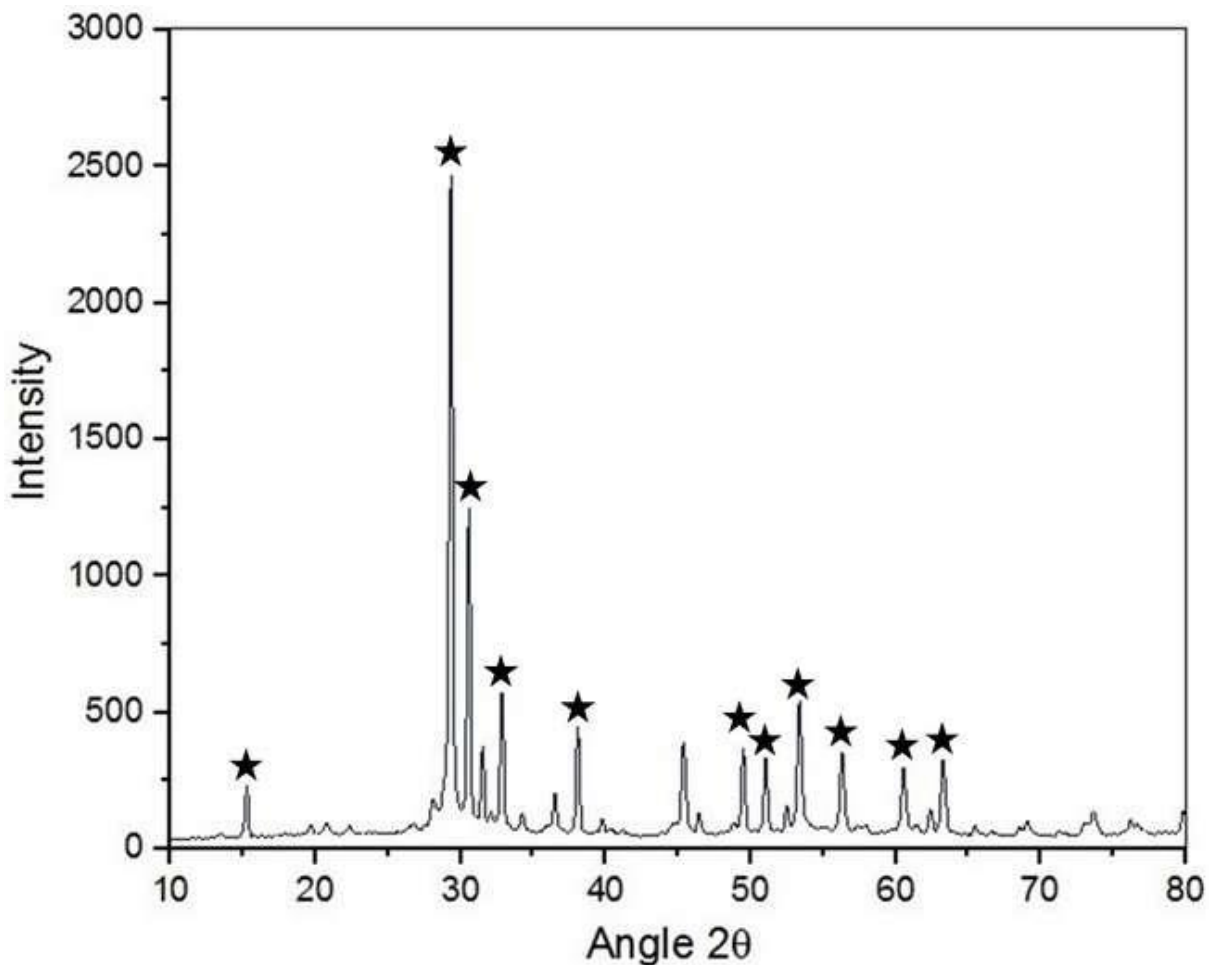


Figure 4: X-ray Diffraction pattern of prepared Lead Oxide

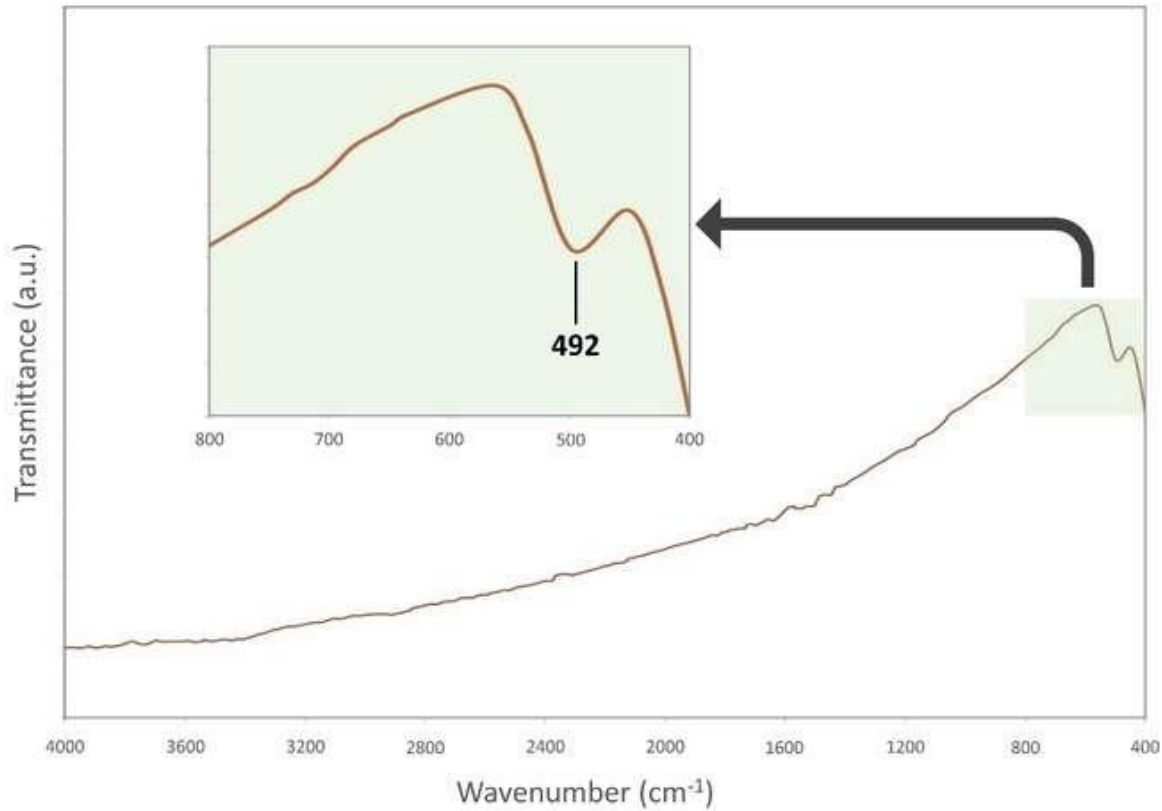


Figure 5: FTIR spectra of prepared Lead Oxide

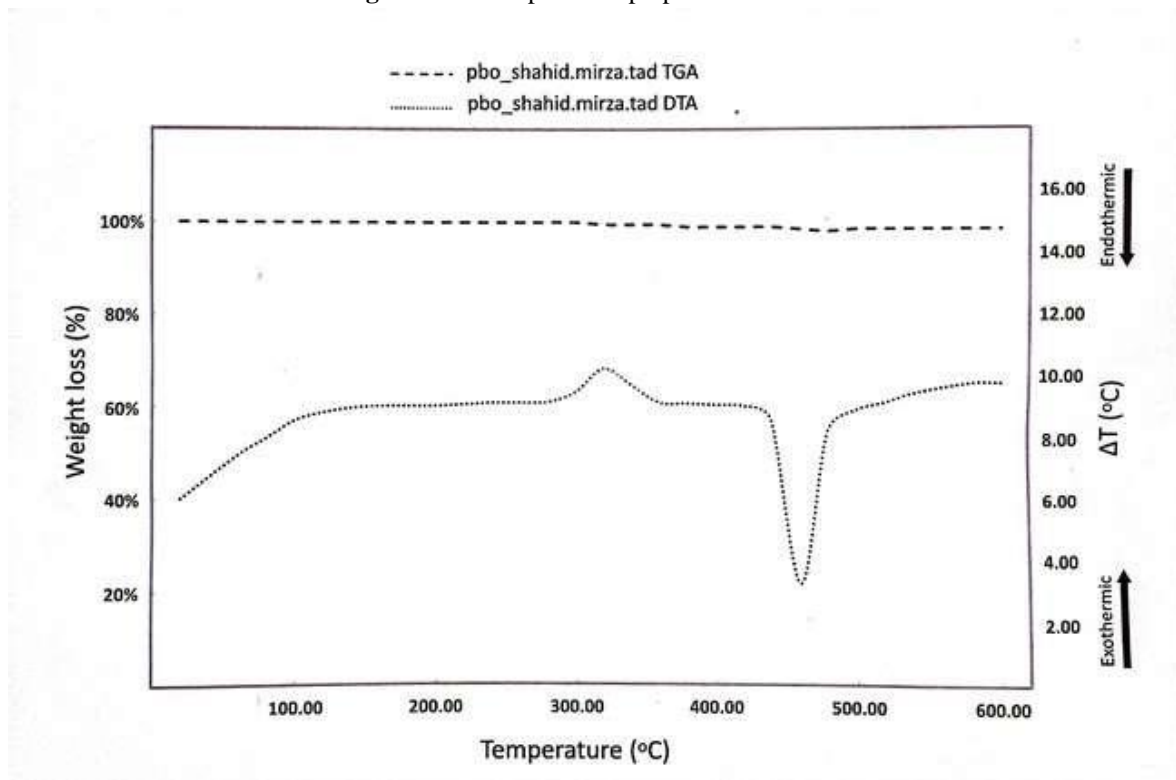


Figure 6: TGA and DTA characteristics of prepared Lead Oxide

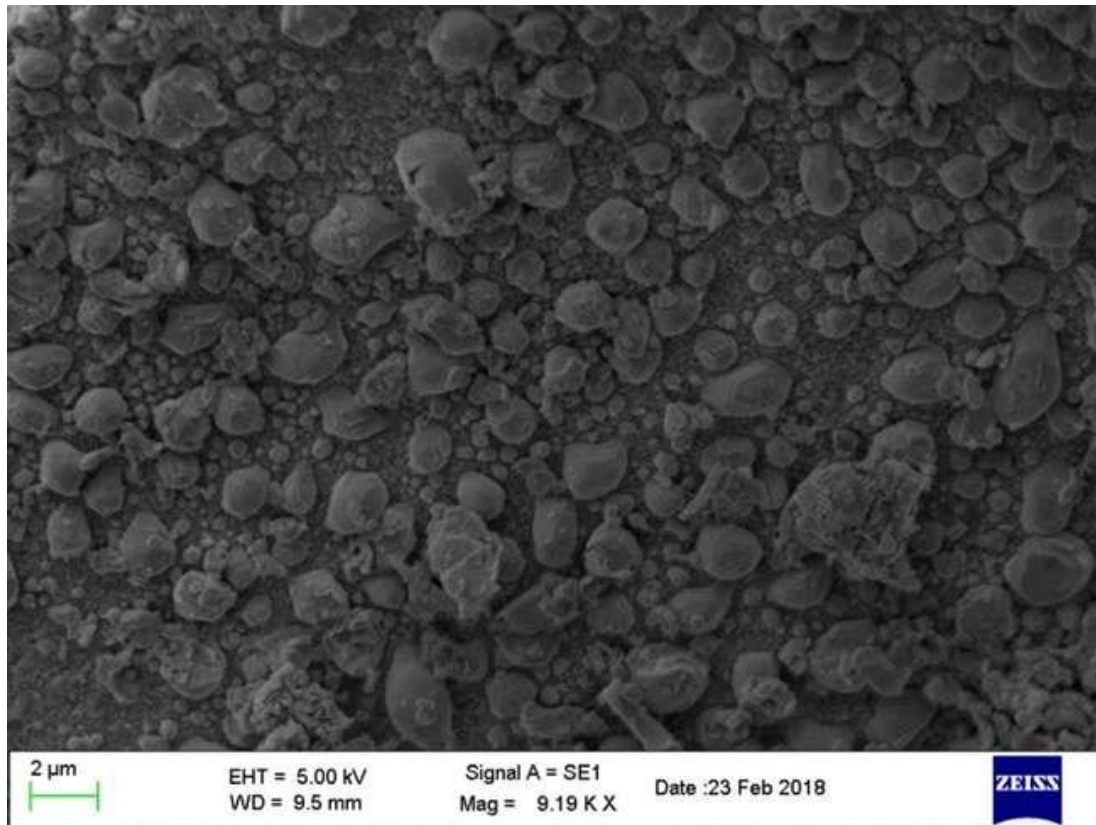


Figure 7: Scanning electron microscopy of prepared Lead Oxide

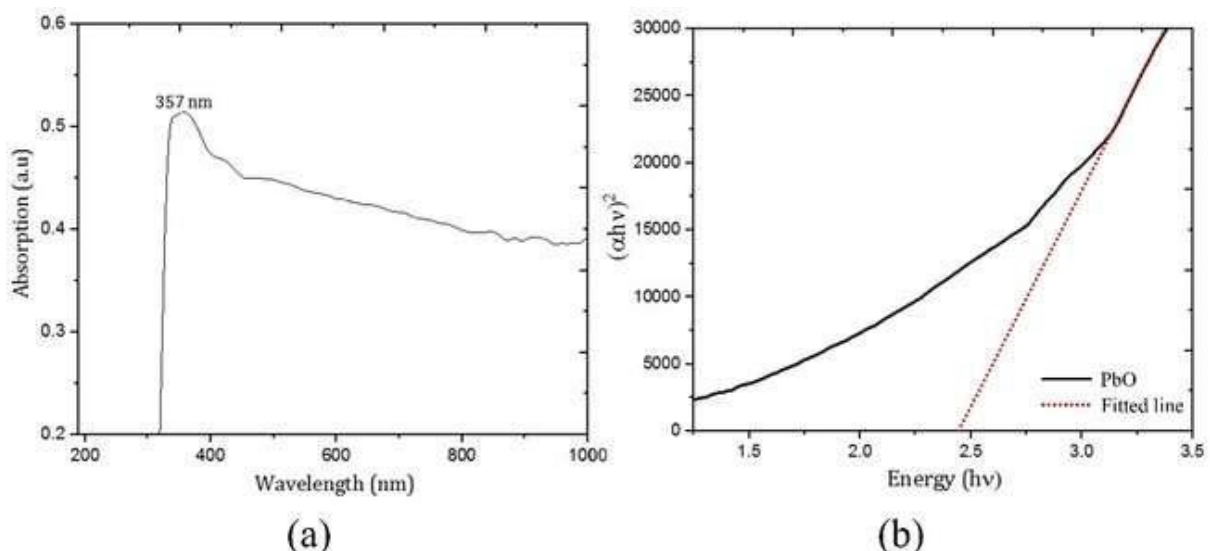


Figure 8: Optical study of prepared Lead Oxide (a) UV-Vis spectra (b) Tauc plot

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