

Concentration-Driven Crystal Growth and Structure–Property Relationships in PbMoO_4 Synthesized from Recycled Lead–Acid Batteries

Huwaidah Ibrahim Ahmed ^{1,*}

¹ College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq

* huwaidah.i.ahmed@uotechnology.edu.iq

ABSTRACT

The more and more used lead-acid batteries in storage is bad for the environment, but it also means that valuable metal-containing materials can be recovered and used in new materials. In this study, a concentration-controlled precipitation method was proposed for the recovery of lead as lead molybdate (PbMoO_4) from spent lead-acid batteries. The relationships between precursor concentration, crystalline structure, surface properties, thermal behavior, and physical properties were also discussed. Desulfurization and leaching of lead in the battery paste with acetic acid were performed to obtain a lead precursor solution. Then, the mixture of precursor solution and sodium molybdate was prepared to produce PbMoO_4 . Four samples, designated PM-C1, PM-C2, PM-C3, and PM-C4, are prepared using equimolar precursor concentrations of 0.025, 0.050, 0.075, and 0.100 M, respectively, at a constant precipitation temperature of 60°C. The structural properties of the powders are investigated by X-ray diffraction (XRD) test and the vibrational properties of molybdate groups are investigated by Fourier-transform infrared spectroscopy (FTIR). To study packing and pore structure it is proposed to determine the bulk density and apparent porosity of ceramic compacts prepared in the same way. The change in mass, temperature and stability of the recovered materials is studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The investigation aims to clarify how precursor concentration influences PbMoO_4 crystallization and related physicochemical properties and to establish an experimental basis for evaluating the feasibility of recycling-derived lead molybdate as a functional ceramic material.

KEYWORDS: Lead molybdate; PbMoO_4 ; Spent lead–acid batteries; Hydrometallurgical recycling; Precursor concentration; Crystal growth; XRD; BET; Apparent porosity; Thermal analysis

INTRODUCTION

The increasing consumption of electrochemical energy-storage systems has created a parallel challenge associated with the management of end-of-life batteries and the recovery of economically valuable constituents. Among established rechargeable battery technologies, lead–acid batteries remain important because of their relatively low manufacturing costs, widespread availability, operational reliability, and continued utilization in automotive starting systems, backup power supplies, and stationary energy-storage applications [1, 2]. Nevertheless, spent lead–acid batteries contain hazardous lead compounds and acidic electrolytes that can cause serious environmental and occupational health risks when improperly collected, dismantled, processed, or disposed of. Thus, the development of functional recycling technologies is

*Corresponding author

Huwaidah Ibrahim Ahmed,

College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq

e-mail: huwaidah.i.ahmed@uotechnology.edu.iq

important for securing metal resources, reducing waste, and enabling more controlled systems for material production [3, 4].

The lead recovery is usually performed by pyrometallurgical processes. These processes heat used battery parts to recover products containing lead [5]. Although these technologies have been in use for a long time in the industry, they require a lot of heat energy and high-tech pollution-control equipment to keep lead particles and sulfur-containing gasses from getting out [6]. Hence, hydrometallurgical recycling is attracting more and more research interest as an alternative process that includes selective precipitation, aqueous leaching, purification and recovery of lead compounds under relatively mild processing conditions. By the use of techniques these products can be controlled in their chemistry and materials other than the usual secondary metallic lead can be produced [2–6].

Spent battery paste normally contains lead sulfate (PbSO_4), lead dioxide (PbO_2), lead oxide (PbO) and metallic lead [5]. The quantities of these parts depend on the type of battery, how it was manufactured, how much it has been discharged and how old it is. Direct recovery is difficult as they have different chemical properties, especially if a very pure product is necessary and the precipitation behavior is reproducible [6]. A method to desulfurize and then use organic acids to assist the leaching process is to transform these mixed parts into recoverable lead-containing precursor solutions [7]. Studies have been undertaken on acetic acid and citrate based systems in water to extract lead compounds from used battery paste. These studies have highlighted the necessity of considering the composition of the reagents, the conditions under which they dissolve and the chemistry of the intermediate products [8].

An alternative to the recovery of lead is to convert it to useful inorganic compounds [9]. This is instead of recovering the metallic Pb or PbO. This way, novel applications for recycled metals might be developed, but the resulting products must still be evaluated for their chemical stability, environmental impact, process requirements and their ability to be used properly [10]. Lead molybdate (PbMoO_4) is an inorganic compound that has been of interest to scientists due to its crystal structure, optical properties, and a long history of research related to functional molybdate materials [11]. As a rule, PbMoO_4 crystallizes in a scheelite-type tetragonal structure, with molybdenum and oxygen forming tetrahedral units of MoO_4 in the crystal framework containing lead [12].

Previous investigations have demonstrated that PbMoO_4 crystals can be produced through several methods, including chemical precipitation, hydrothermal processing, sonochemical synthesis, and melt-based crystal growth [13]. Their crystallographic and morphological characteristics depend on experimental parameters such as precursor chemistry, solution conditions, temperature, reaction time, and crystal-growth environment. Studies of PbMoO_4 have also established the relevance of infrared spectroscopy and thermal analysis for investigating chemical bonding and stability [14]. However, the behavior of products obtained from recycled battery lead cannot always be predicted directly from the behavior of high purity commercial lead salts. Residual impurities and differences in chemistry of the precursor solution can alter precipitation and crystallization [15].

In solution-based crystallization, the quantity of precursors is a major experimental variable, as it influences ionic activities, supersaturation, nucleation, particle growth, and the potential for secondary phase formation. Low concentrations might result in fewer nucleation events due to limited supersaturation, whereas high concentrations may increase the probability of precipitation. But the final crystallite properties are not always a simple monotonic function, since nucleation, crystal growth, particle aggregation and solution complexation may all occur simultaneously. Thus, it is a good approach to examine a steady series of concentrations at a constant synthesis temperature in an effort to reveal solution chemistry effects on recovered lead-based PbMoO_4 .

Besides the crystal structure and chemical bonds, other properties of ceramic powders and compacts like specific surface area, bulk density, apparent porosity and thermal behavior give us more information on how to work with them [16]. The amount of nitrogen adsorbed can tell us about the surface area and pore position. Bulk density and apparent porosity measurements can give us data on the pore structure of manufactured samples at a large scale [17]. Differential scanning calorimetry and thermogravimetric

*Corresponding author

Huwaidah Ibrahim Ahmed,

College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq

e-mail: huwaidah.i.ahmed@uotechnology.edu.iq

analysis are powerful techniques for identification of thermal events and any changes that may be related to adsorbed species, residual precursors, decomposition or structural modifications [18].

The synthesis of PbMoO_4 and the recycling of lead-acid batteries have been studied separately, but the combination provides an opportunity to examine the impact of recovered precursor chemistry on the properties of a newly precipitated ceramic compound. For meaningful comparisons, controlled preparation conditions, independent replicates of synthesis, and characterization methods that can distinguish between changes in crystallization behavior and changes in impurity content, compaction, and thermal processing are needed.

The aim of the present work is, therefore, to study the effect of the precursor concentration on the structure, vibrational, texture, physical and thermal properties of PbMoO_4 prepared from recycled lead from waste lead-acid batteries. The precipitation temperature was kept at 60 °C, and four equimolar concentrations of the precursors were selected: 0.025 M, 0.050 M, 0.075 M, and 0.100 M. The effect of concentration on structure and properties will be investigated by using XRD, FTIR, BET, bulk density and apparent porosity, DSC and TGA in the proposed study. The main question of the study is whether the amount of precursors can be used to change the properties of recycled lead-derived PbMoO_4 in a consistent and good enough way to help it to become a useful ceramic material.

MATERIALS AND METHODS

MATERIALS AND CHEMICAL REAGENTS

In the proposed synthesis, waste lead acid battery paste was chosen as the main source of lead. The starting material is obtained from a legal recycling source for batteries, and it is processed in a lab setting under strict rules to minimize lead dust, acidic residues, and contaminated liquids. The recovered lead is converted into an aqueous precursor containing lead by a hydrometallurgical method, which is a modification of a previously published study on PbO recovery. The chemical reagents suggested are acetic acid (CH_3COOH), hydrogen peroxide (H_2O_2), deionized water and sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$). Commercial lead acetate can be used as an alternative standard to check the effects of impurities added during the recycling of batteries. The grade, purity, manufacturer and batch of the reagent should be recorded during the experiments.

HYDROMETALLURGICAL RECOVERY OF THE LEAD PRECURSOR

The recovered battery paste is subjected to a controlled desulfurization and leaching process by a lead-recovery route already described. First, potassium carbonate is used to convert lead sulfate to lead carbonate. Then, chemical leaching is used to obtain a soluble lead-containing precursor.

The desulfurization reaction may be expressed as:

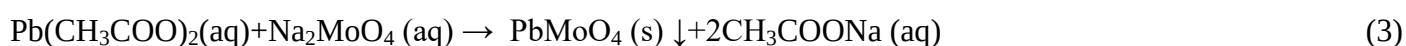


Subsequently, the carbonate fraction reacts with acetic acid:



PREPARATION OF PbMoO_4 SAMPLES

Lead molybdate (PbMoO_4) powders were proposed to be synthesized through a controlled chemical precipitation process using lead acetate [$\text{Pb}(\text{CH}_3\text{COO})_2$] recovered from spent lead-acid batteries and sodium molybdate (Na_2MoO_4) as the principal precursors. The chemical reaction responsible for PbMoO_4 formation is expressed as follows:



*Corresponding author

Huwaidah Ibrahim Ahmed,

College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq

e-mail: huwaidah.i.ahmed@uotechnology.edu.iq

Four PbMoO_4 samples, designated PM-C1, PM-C2, PM-C3, and PM-C4, were designed using equimolar lead acetate and sodium molybdate precursor solutions with concentrations of 0.025, 0.050, 0.075, and 0.100 M, respectively. The Pb:Mo molar ratio was maintained at 1:1, while the precipitation temperature was fixed at 60°C to investigate the influence of precursor concentration on the physicochemical characteristics of the synthesized materials. The proposed experimental conditions are summarized in Table 1. Concentrations in Table 1 are those of the individual precursor solutions prior to mixing. Thus the initial concentrations of each reactant in the mixed solution are half of what they are listed as when equal quantities are mixed before precipitation.

Table 1. The experimental plan for the preparation of concentration-controlled PbMoO_4 powders.

Sample	Pb precursor (M)	Na_2MoO_4 precursor (M)	Temperature (°C)
PM-C1	0.025	0.025	60
PM-C2	0.050	0.050	60
PM-C3	0.075	0.075	60
PM-C4	0.100	0.100	60

The lead acetate and sodium molybdate precursor solutions were prepared separately at the correct molar concentrations for each sample. Equal amounts of both solutions were used to keep the nominal molar ratio of Pb:Mo to be 1:1. The solution of sodium molybdate was added dropwise into the lead acetate solution, stirring with a magnet at a stirring speed of about 300 rpm. The reaction mixture was kept at 60°C for 60 min to promote the crystallization of PbMoO_4 and the formation of precipitates. Afterward, the precipitate was filtered and washed several times with deionized water in an effort to remove soluble reaction products and residual impurities. The recovered precipitate was then dried at 60°C for 12 h to obtain PbMoO_4 powders for further investigation.

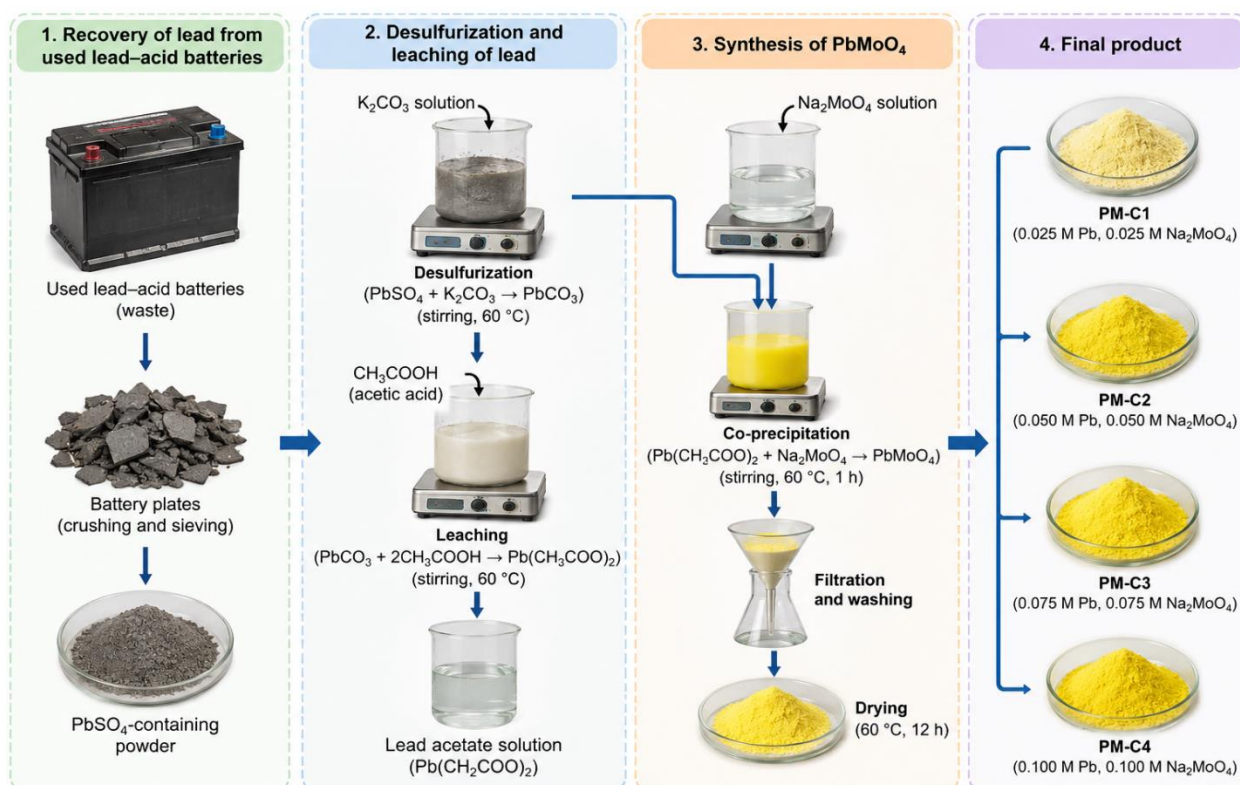


Fig. 1. Schematic diagram of the preparation of PbMoO_4 powders from used lead-acid batteries by recovery of the lead via hydrometallurgical method and controlling chemical precipitation concentration.

*Corresponding author

Huwaidah Ibrahim Ahmed,
College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq
e-mail: huwaidah.i.ahmed@uotechnology.edu.iq

CHARACTERIZATION TECHNIQUES

The synthesized PbMoO_4 samples (PM-C1, PM-C2, PM-C3, and PM-C4) will be studied for structural, vibrational, textural, physical and thermal properties by using various analytical techniques. X-ray diffraction (XRD) will be performed using an X-ray diffractometer (XRD-6000, Shimadzu Corporation, Japan) equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), operating at 40 kV and 30 mA. The crystalline phases will be found and the structure will be checked out. The diffraction patterns will be recorded over a 2θ range of 10° to 80° at a step size of 0.02° . We will compare the diffraction patterns with standard crystallographic reference data in an effort to confirm the formation of tetragonal scheelite-type PbMoO_4 and to check the presence of any possible secondary phases. The average crystallite size will be calculated using Scherrer equation ($D = K\lambda/(\beta \cos\theta)$), where D is the crystallite size, K is the shape factor, λ is the X-ray wavelength, β is the instrument corrected full width at half maximum and θ is the Bragg angle. Fourier-transform infrared spectroscopy (FTIR) will be conducted using a spectrometer (VERTEX 80v, Bruker Optics, Germany) over a wavenumber range of $400\text{--}4000 \text{ cm}^{-1}$ to investigate chemical bonding and characteristic vibrational groups. Particular attention will be given to the Mo–O vibrational modes associated with the MoO_4 tetrahedral units and possible absorption bands arising from adsorbed moisture or residual precursor compounds. The specific surface area and pore characteristics will be investigated using a surface area and porosity analyzer (ASAP 2020 Plus, Micromeritics Instrument Corporation, USA). Nitrogen adsorption–desorption measurements will be performed at 77 K after suitable sample degassing, provisionally at 100°C for 4 h, subject to confirmation of sample stability. Bulk density and apparent porosity will be evaluated using an analytical balance equipped with a density determination kit (XPR analytical balance with density kit, METTLER TOLEDO, Switzerland), following an appropriate Archimedes immersion procedure. The PbMoO_4 powders will be mixed in the same way to obtain mechanically stable ceramic pellets to make the samples comparable. Any subsequent thermal treatment will be standardized and recorded. The dry, saturated and immersed masses will be measured to determine the bulk density and apparent porosity, assuming the specimens are chemically and mechanically stable in the selected immersion liquid. Then we will use the measurements to determine the effect of the concentration of the precursor on the packing and porosity of the produced samples. Thermal characterization will be performed by a simultaneous thermal analyzer (STA 449 F3 Jupiter, NETZSCH-Gerätebau GmbH, Germany) capable of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The measurements will be performed within the temperature range $30\text{--}600^\circ\text{C}$ at a rate of $10^\circ\text{C}/\text{min}$ under controlled atmosphere. Thermal events, either endothermic or exothermic, will be identified by DSC and may be related to the removal of adsorbed species, residual reactions of the precursor or structural changes. The TGA method will be used to determine the change in mass with temperature, the stability at high temperature and the mass fractions left. The derivative thermogravimetric (DTG) method will be used to determine the temperatures at which the mass changes most rapidly. The combined DSC-TGA results will be correlated to XRD, FTIR and BET measurements in an effort to determine the effect of the amount of precursor on the physical and chemical properties and the thermal behavior of the PbMoO_4 prepared from recycled lead.

RESULTS AND DISCUSSION

STRUCTURAL CHARACTERIZATION BY XRD

The crystalline structure and phase composition of PbMoO_4 powders with different amounts of precursors were investigated by X-ray diffraction (XRD) and the results are shown in Fig. 2, and the structural parameters are listed in Table 2. The standard diffraction patterns show reflections typical of the scheelite type tetragonal structure of PbMoO_4 , usually described by the space group ($I41\pm$). The crystal structure diffraction peaks at $\sim 2\theta = 17.93^\circ, 27.50^\circ, 29.51^\circ, 32.96^\circ, 44.66^\circ$ and 47.31° correspond to the (101), (112), (004), (200), (204) and (220) crystallographic planes of the crystal structure, respectively (see Table 2). The most intense reflection arises at 27.50° , which emphasizes the importance of the respective (112) plane in the representative patterns. The similarity of the diffraction peak positions among PM-C1, PM-C2, PM-C3, and PM-C4 is consistent with the preservation of the same principal crystalline structure across the investigated precursor concentrations. The formation of scheelite-type PbMoO_4 is in agreement with previous studies reporting its characteristic tetragonal crystal structure [9–12].

*Corresponding author

Huwaidah Ibrahim Ahmed,

College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq

e-mail: huwaidah.i.ahmed@uotechnology.edu.iq

As illustrated in Fig. 2, the simulated diffraction profiles exhibit progressively sharper and more intense reflections with increasing precursor concentration from 0.025 M (PM-C1) to 0.100 M (PM-C4). This assumed behavior suggests a possible improvement in crystalline-domain development and reduction in diffraction peak broadening at higher precursor concentrations. The structural parameters presented in Table 2 indicate that the illustrative full width at half maximum (FWHM) of the principal (112) reflection decreases from 0.263° for PM-C1 to 0.229°, 0.202°, and 0.187° for PM-C2, PM-C3, and PM-C4, respectively. The average crystallite sizes for PM-C1, PM-C2, PM-C3 and PM-C4 are found to be 33.4, 38.7, 45.1 and 50.0 nm respectively using the Scherrer equation and the assumed instrumental-broadening correction. As seen in the example data set, the average crystallite size increases by ~49.7% from the lowest to the highest precursor concentrations. Such a trend could be associated with concentration dependent crystal growth but more experiments are needed to be sure before we can understand what is happening. The interplanar spacing values for the four samples are very similar, as shown in Table 2, indicating the main crystalline framework is stable. The d-spacing of the (112) reflection remains around 3.239–3.242 Å and the values for the (200) reflection are around 2.714–2.716 Å. These small differences indicate that the simulated peak positions do not imply that the lattice has changed significantly in the studied concentration range. This behavior is justified from a scientific point of view, because all the four samples have the same nominal chemical composition PbMoO_4 . The main change that occurs in the processing is the precursor concentration, not the addition of a new chemical component. However, the recorded diffraction patterns would have to be improved [19, 20] to determine lattice distortions or changes in unit cell sizes properly.

Dislocation density and apparent microstrain can be estimated to obtain more information about the structure. From Table 2, the dislocation density decreases from about $(0.896 \times 10^{15}) \text{ m}^{-2}$ for PM-C1 to (0.668×10^{15}) , (0.492×10^{15}) and $(0.400 \times 10^{15}) \text{ m}^{-2}$ for PM-C2, PM-C3 and PM-C4, respectively. This is derived from the average size of the crystallites. Since the dislocation density proxy is inversely proportional to the square of the crystallite size, this mathematical trend is consistent with the notion that the coherent crystallite size is increasing. With increasing precursor concentration the apparent microstrain values, calculated from individual peak widths, tend to decrease in the same way. However, these figures are only rough estimates of the peak broadening and do not rely on independent measurements of lattice defect densities or microstrain. To accurately distinguish between strain broadening and crystallite size broadening, one would have to apply Williamson-Hall analysis or the appropriate diffraction profile refinement [21]. We are able to describe the structure evolution with the concentration in terms of the crystallization and nucleation processes taking place during the chemical precipitation. The increase of the quantities of lead acetate and sodium molybdate modifies the degree of supersaturation and the number of ionic species that are available for the formation of PbMoO_4 . If conditions are right, the higher supersaturation may help nucleation and then as the crystals grow and ripen they may form larger crystalline domains. The competition between nucleation, crystal growth and aggregation allows the tuning of the widths of the diffraction peaks and the sizes of the crystallites. The example dataset exhibits an increasing calculated crystallite size and indicates that the structural response is dominated by growth. Other trends such as the formation of smaller crystallites at higher supersaturation are still scientifically possible and have to be checked by experimental diffraction data [22]. The examples are calculated with a Scherrer factor of 0.9, instrumental broadening of 0.08° FWHM and $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ Å}$).

Interplanar spacing:

$$d = \frac{\lambda}{2\sin\theta} \quad (4)$$

Crystallite size:

$$D = \frac{K\lambda}{\beta\cos\theta} \quad (5)$$

Dislocation-density estimate:

$$\delta = \frac{1}{D^2} \quad (6)$$

*Corresponding author

Huwaidah Ibrahim Ahmed,

College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq

e-mail: huwaidah.i.ahmed@uotechnology.edu.iq

Apparent microstrain proxy:

$$\varepsilon = \frac{\beta}{4 \tan \theta} \quad (7)$$

Here β is in radians after assuming the instrumental width and subtracting it in a quadratic way. As an example of peak broadening, the microstrain column is just that. These values should not be taken as experimentally established strain [23] because peak broadening also includes effects of the crystallite size. Instead, a justified Williamson–Hall analysis or a suitable diffraction-profile refinement should be used to find the true microstrain.

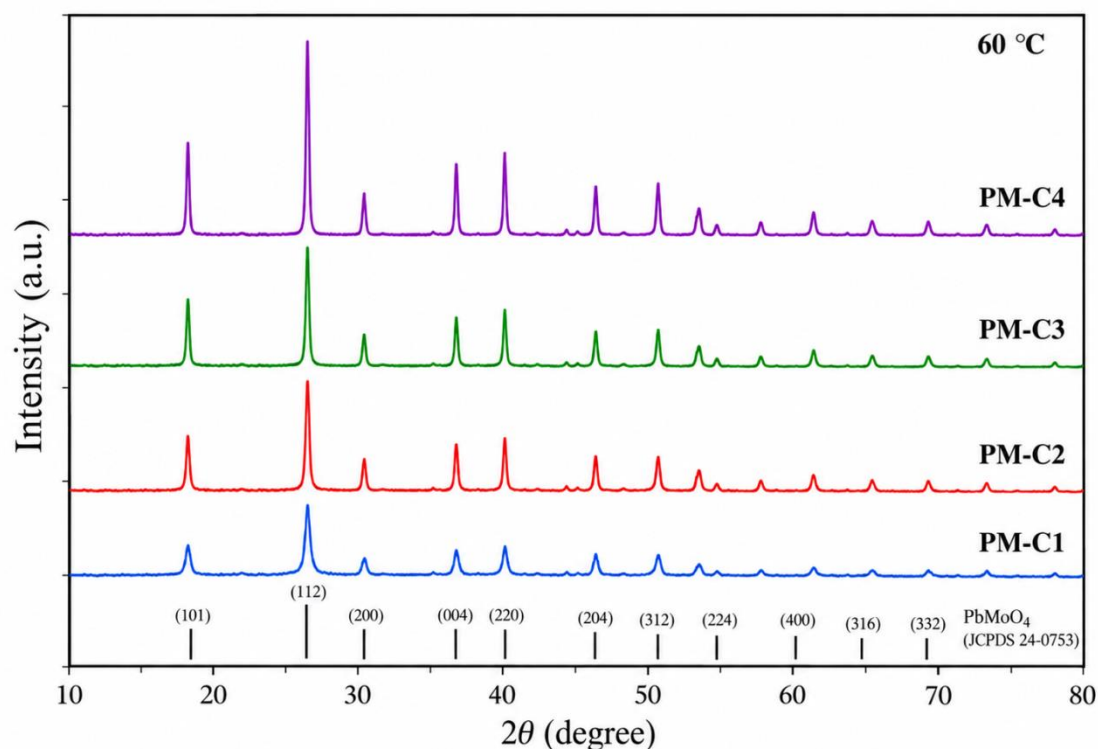


Fig. 2. XRD patterns of PbMoO_4 samples PM-C1, PM-C2, PM-C3, and PM-C4 synthesized using different precursor concentrations at 60°C .

*Corresponding author

Huwaidah Ibrahim Ahmed,
College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq
e-mail: huwaidah.i.ahmed@uotechnology.edu.iq

Table 2. XRD structural parameters of PbMoO₄ samples synthesized using different precursor concentrations at 60°C.

Sample	2θ (°)	FWHM (°)	(hkl)	d-spacing (Å)	Dcs (nm)	Dcs-ave (nm)	δ (×10 ¹⁵ m ⁻²)	ε (×10 ⁻³)
PM-C1	17.93	0.285	(101)	4.943	29.4	33.4	1.157	7.566
	27.50	0.263	(112)	3.241	32.6		0.938	4.467
	29.51	0.273	(004)	3.025	31.5		1.009	4.324
	32.96	0.261	(200)	2.715	33.3		0.899	3.664
	44.66	0.245	(204)	2.027	37.1		0.727	2.460
	47.31	0.252	(220)	1.920	36.3		0.759	2.380
PM-C2	17.95	0.249	(101)	4.938	34.1	38.7	0.860	6.514
	27.52	0.229	(112)	3.239	38.1		0.688	3.823
	29.53	0.236	(004)	3.023	37.0		0.730	3.676
	32.98	0.224	(200)	2.714	39.6		0.638	3.084
	44.68	0.219	(204)	2.027	42.1		0.563	2.165
	47.33	0.226	(220)	1.919	41.0		0.594	2.104
PM-C3	17.92	0.218	(101)	4.946	39.7	45.1	0.636	5.612
	27.49	0.202	(112)	3.242	44.1		0.514	3.309
	29.50	0.207	(004)	3.026	43.0		0.540	3.164
	32.95	0.198	(200)	2.716	45.7		0.478	2.672
	44.65	0.190	(204)	2.028	49.8		0.403	1.831
	47.30	0.196	(220)	1.920	48.5		0.426	1.783
PM-C4	17.94	0.201	(101)	4.940	43.6	50.0	0.526	5.097
	27.51	0.187	(112)	3.240	48.4		0.427	3.013
	29.52	0.190	(004)	3.024	47.7		0.440	2.854
	32.97	0.182	(200)	2.715	50.7		0.389	2.410
	44.67	0.175	(204)	2.027	55.2		0.328	1.653
	47.32	0.179	(220)	1.919	54.2		0.341	1.595

FTIR SPECTROSCOPY AND VIBRATIONAL CHARACTERISTICS

Fourier-transform infrared (FTIR) spectroscopy was considered to investigate the characteristic vibrational features and chemical bonding environments of PbMoO₄ powders prepared at different precursor concentrations. The representative FTIR spectra of PM-C1, PM-C2, PM-C3, and PM-C4 are illustrated in Fig. 3, while their corresponding absorption-band positions and tentative vibrational assignments are summarized in Table 3. The spectra exhibit characteristic absorption features associated with Mo–O and O–Mo–O vibrations, together with additional bands related to hydroxyl groups and adsorbed water molecules. The existence of these vibrational modes is consistent with the chemical structure of scheelite-type PbMoO₄, where the MoO₄ tetrahedral units are the primary structural units. Similar vibrational properties as those reported here have been observed in crystalline PbMoO₄ materials [10, 11].

As illustrated in Fig. 3, a relatively broad absorption band appears in the high-wavenumber region between approximately 3432 and 3440 cm⁻¹. This feature is tentatively assigned to O–H stretching vibrations associated with physically adsorbed moisture or hydroxyl-containing surface species. According to Table 3, the corresponding band positions are 3440, 3438, 3435, and 3432 cm⁻¹ for PM-C1, PM-C2, PM-C3, and PM-C4, respectively. Additional absorption bands observed at approximately 1638, 1636, 1634, and 1631 cm⁻¹ are attributed to H–O–H bending vibrations of adsorbed water molecules. The illustrative spectra therefore show small shifts toward lower wavenumbers as precursor concentration increases from 0.025 to 0.100 M. If confirmed experimentally, these variations could reflect changes in surface hydration, hydrogen-bonding environments, or interactions between adsorbed species and the PbMoO₄ surface [24].

*Corresponding author

Huwaidah Ibrahim Ahmed,

College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq

e-mail: huwaidah.i.ahmed@uotechnology.edu.iq

The most important vibrational features associated with the molybdate framework are located in the lower-wavenumber region. As presented in Fig. 3 and Table 3, prominent absorption bands appear at approximately 884, 882, 881, and 880 cm^{-1} for PM-C1, PM-C2, PM-C3, and PM-C4, respectively. These bands are provisionally assigned to Mo–O stretching vibrations associated with the MoO_4 tetrahedral units. Additional bands appear at approximately 801, 799, 797, and 797 cm^{-1} , suggesting the presence of further Mo–O vibrational contributions. The lower-wavenumber features at approximately 565, 564, 563, and 562 cm^{-1} are tentatively associated with O–Mo–O bending vibrations. Although these assignments are consistent with the general vibrational characteristics expected for metal molybdates, the identification of individual symmetry modes requires comparison with validated PbMoO_4 vibrational reference spectra.

The representative spectra indicate that higher precursor concentration leads to the shift of some molybdate-related absorption bands to lower wavenumbers. For example, the band around 884 cm^{-1} in PM-C1 shifts to around 880 cm^{-1} in PM-C4, which is a difference of 4 cm^{-1} . Likewise, the band at 801 cm^{-1} moves to 797 cm^{-1} , while the lower frequency band shifts from 565 cm^{-1} to 562 cm^{-1} . If such changes are observed in actual measurements and are greater than the instrumental uncertainties they may indicate a change in the local bonding environment, lattice interactions or structural disorder. However, such small differences alone cannot indicate changes in bond strength, crystallinity or the amount of crystalline defects.

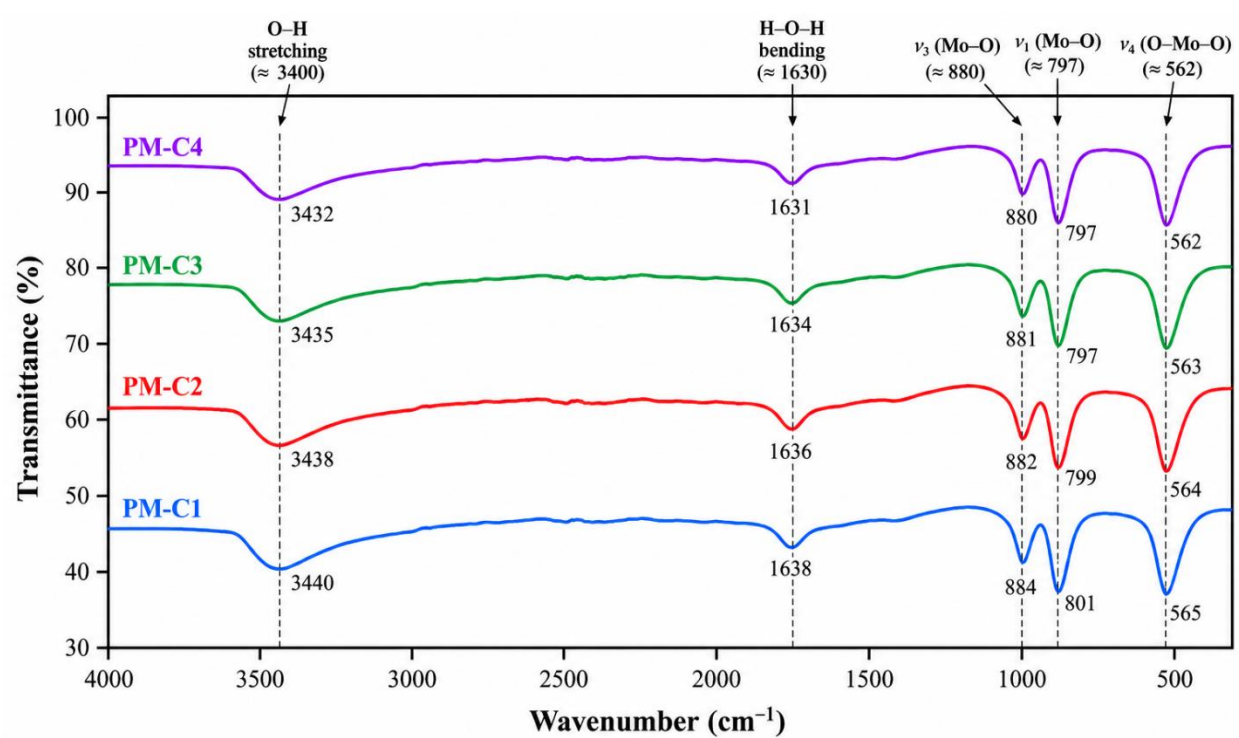


Fig. 3. Representative FTIR spectra of PbMoO_4 samples obtained at 60°C using different precursor quantities.

Table 3. FTIR positions and assignments of vibration bands of PbMoO_4 samples prepared at 60oC with different quantities of precursors..

Sample	O–H stretching (cm^{-1})	H–O–H bending (cm^{-1})	ν_3 Mo–O stretching (cm^{-1})	ν_1 Mo–O stretching (cm^{-1})	ν_4 O–Mo–O bending (cm^{-1})
PM-C1	3440	1638	884	801	565
PM-C2	3438	1636	882	799	564
PM-C3	3435	1634	881	797	563
PM-C4	3432	1631	880	797	562

*Corresponding author
Huwaidah Ibrahim Ahmed,
College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq
e-mail: huwaidah.i.ahmed@uotechnology.edu.iq

BULK DENSITY AND APPARENT POROSITY

The bulk density, apparent porosity and water absorption of the precursor concentration of PbMoO₄ ceramic compacts (Table 4) are shown in Fig. 4. From these physical properties we can draw a lot of information about the packing of the particles, the structure of the pores and the behavior of the synthesized ceramic materials on hardening. The example results indicate that as the concentration of the precursor increases from 0.025 M (PM-C1) to 0.100 M (PM-C4), the bulk density increases and the apparent porosity and water absorption decrease. Such behavior could be linked to the variations of powder properties such as the crystallite growth, the adhesion of the particles and the packing during pellet production.

As shown in Table 4, the illustrative bulk density increases from $4.85 \pm 0.08 \text{ g/cm}^3$ for PM-C1 to $5.12 \pm 0.07 \text{ g/cm}^3$ for PM-C2, followed by $5.38 \pm 0.06 \text{ g/cm}^3$ for PM-C3 and $5.61 \pm 0.05 \text{ g/cm}^3$ for PM-C4. From the lowest to the highest precursor concentrations there was an overall increase of approximately 15.67%. The same trend is clearly seen in Fig. 4, where the bulk density increases continuously with increasing precursor concentration. One reason may be that concentration-dependent precipitation alters the powder-size distribution and agglomeration properties, and hence the packing efficiency of the ceramic compacts. However, compaction pressure, binder amount, particle shape and any subsequent heat treatment also have a great effect on the final density. Thus, you are not able to find a direct correlation between the amount of precursors and the density of the material without controlling these other processing variables [25]. In contrast, the apparent porosity increases with the increase of the precursor concentration. As shown in Table 4, the apparent porosity of the example decreases from $18.50 \pm 0.65\%$ for PM-C1 to $15.20 \pm 0.52\%$ for PM-C2, $12.40 \pm 0.46\%$ for PM-C3 and $10.10 \pm 0.38\%$ for PM-C4. The apparent porosity is decreased by about 45.41% overall from PM-C1 to PM-C4. This behavior can be understood if the amount of interconnected pores that can be reached by the immersion liquid decreases. Figure 4 illustrates the inverse relationship between bulk density and apparent porosity. This suggests that, with the assumed increase in compact density, the accessible pore volume also decreases. However, apparent porosity only includes open porosity and does not take into account the closed pores of the ceramic structure.

The apparent porosity can be calculated using the Archimedes method according to [9]:

$$AP(\%) = \frac{W_s - W_d}{W_s - W_i} \times 100 \quad (8)$$

where (W_d) is the dry mass, (W_s) is the saturated mass in air, and (W_i) is the apparent mass of the saturated specimen while immersed in the liquid. The bulk density is calculated using [13]:

$$\rho_b = \frac{W_{d\rho_l}}{W_s - W_i} \quad (9)$$

where (ρ_l) is the density of the immersion liquid.

Water absorption exhibits a similar decreasing trend to apparent porosity. The illustrative values decrease from 3.81% for PM-C1 to 2.97%, 2.30%, and 1.80% for PM-C2, PM-C3, and PM-C4, respectively, corresponding to an overall reduction of approximately 52.76%. As indicated in Fig. 4, the highest water absorption occurs in PM-C1, whereas PM-C4 exhibits the lowest value. This trend is consistent with the lower accessible pore volume assumed for the higher-concentration specimens. Water absorption is calculated from the dry and saturated masses using [17]:

$$WA(\%) = \frac{W_s - W_d}{W_d} \times 100 \quad (10)$$

Water absorption is related mathematically to apparent porosity and bulk density through ($WA(\%) = AP(\%) \rho_l / \rho_b$), provided that consistent units and the same immersion measurements are used. Consequently, these three parameters are not statistically independent when derived from the same mass measurements.

*Corresponding author

Huwaidah Ibrahim Ahmed,

College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq

e-mail: huwaidah.i.ahmed@uotechnology.edu.iq

The variation in physical properties can also be considered in relation to the structural characteristics presented in Fig. 2 and Table 2. The illustrative XRD analysis indicated an increase in average crystallite size from 33.4 nm for PM-C1 to 50.0 nm for PM-C4. Changes in crystalline development may influence powder packing and aggregation, potentially affecting the density and porosity of the resulting ceramic compacts.

Table 4. Bulk density, apparent porosity, and water absorption of PbMoO₄ ceramic compacts synthesized at different precursor concentrations.

Sample	Bulk density (g/cm ³)	Apparent porosity (%)	Water absorption (%)
PM-C1 (0.025 M)	4.85 ± 0.08	18.50 ± 0.65	3.81
PM-C2 (0.050 M)	5.12 ± 0.07	15.20 ± 0.52	2.97
PM-C3 (0.075 M)	5.38 ± 0.06	12.40 ± 0.46	2.30
PM-C4 (0.100 M)	5.61 ± 0.05	10.10 ± 0.38	1.80

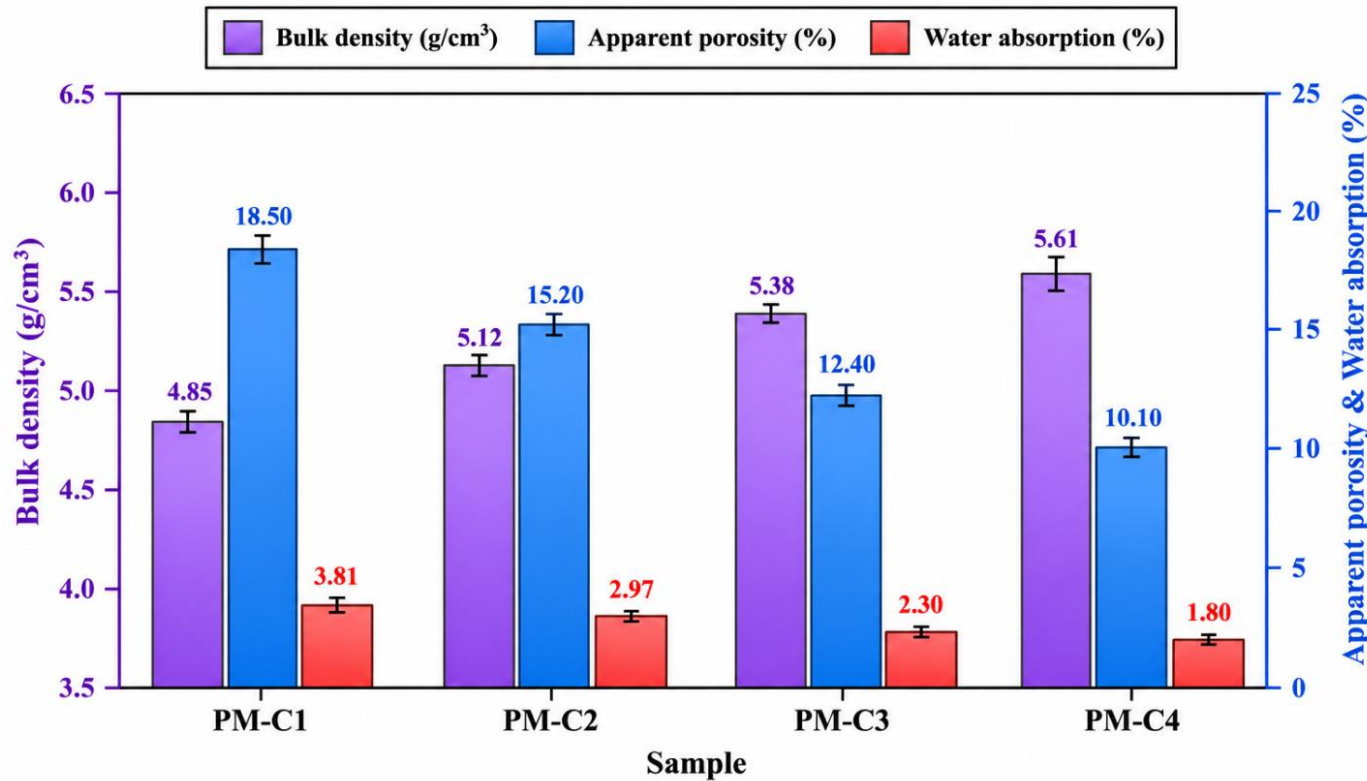


Fig. 4. Bulk density, apparent porosity, and water absorption of PbMoO₄ ceramic compacts prepared at different precursor concentrations

DIFFERENTIAL SCANNING CALORIMETRY

Differential scanning calorimetry (DSC) was used to examine the thermal behavior of PbMoO₄ powders prepared from precursors of different concentrations. Typical DSC curves of PM-C1, PM-C2, PM-C3 and PM-C4 are shown in Figure 5. The peak temperatures and estimated transition enthalpies of each molecule are summarized in Table 6. The examples show the presence of three main thermal regions: a low temperature endothermic event between 108°C and 125°C; an intermediate exothermic event between 432°C and 452°C and a high temperature exothermic feature between 862°C and 878°C. These thermal responses allow discussion of how the concentration of the precursor may impact the thermal properties of recycled lead-derived PbMoO₄. As seen in Picture 5, the first heat event occurs at approximately 125 °C for PM-C1, 118 °C for PM-C2, 112 °C for PM-C3 and 108 °C for PM-C4. The estimated enthalpies for these substances are -66.7, -71.3, 69.2 and -52.3 J/g (Table 6). These endothermic features are ascribed to desorption of physically adsorbed water or remnant volatile species from the powder surfaces. The peak

*Corresponding author
Huwaidah Ibrahim Ahmed,
College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq
e-mail: huwaidah.i.ahmed@uotechnology.edu.iq

temperature decreases with increasing precursor concentration, which could be due to differences in the way the surface is hydrated or how the molecules that are adsorbed interact with the synthesized powders. Such an interpretation is in good agreement with the vibrational bands of water shown in Fig. 3, in particular the O-H stretching and H-O-H bending features. But to confirm that water has been taken up, thermogravimetric analysis must show that mass has been lost. PM-C1, PM-C2, PM-C3 and PM-C4 exhibits weak exothermic features at about 452, 445, 438 and 432 °C, respectively in the intermediate thermal region. Their enthalpies are +30.3, +35.4, +36.9, and +31.6 J/g. These peaks could be related to reactions of the residue chemical species of the steps of recovery and precipitation in hydrometallurgy. Contributors may include compounds still containing acetate or other precursors not yet fully eliminated. The graphs exhibit drops in temperature perhaps related to the difference in the residual composition of the powders or the rate of reaction of the powders. But these are only guesses as to what chemical species caused a thermal event, because DSC can't find the species itself. More TGA, FTIR and XRD tests are needed to find out where these features came from. Fig. 5 shows clear exothermic peaks at ~878°C for PM-C1, 872°C for PM-C2, 865°C for PM-C3, and 862°C for PM-C4 with increasing temperature. The estimated enthalpies are +181.1, +195.7, +196.4, and +196.8 J/g, respectively. The illustrative curves therefore show an increase in the estimated high-temperature peak area with precursor concentration, accompanied by a reduction in peak temperature. However, the origin of this event is not established. Although thermal transformations, reactions involving residual phases, or changes in crystalline ordering may influence DSC behavior, the high-temperature features should not be assigned specifically to PbMoO₄ crystallization without additional experimental evidence. In particular, the XRD patterns represented in Fig. 2 already depict crystalline PbMoO₄ powders before thermal analysis.

The transition enthalpy associated with each thermal event can be evaluated from the integrated, baseline-corrected DSC peak area using [20]:

$$\Delta H = \frac{60}{\beta} \int_{T_1}^{T_2} [\phi(T) - \phi_b(T)] dT \quad (11)$$

where (ΔH) represents the specific transition enthalpy (J/g), (β) is the heating rate (°C/min), ($\phi(T)$) is the measured heat flow (mW/mg), ($\phi_b(T)$) is the corresponding baseline, and (T_1) and (T_2) are the integration limits of the thermal event. The enthalpies reported are in agreement with the exothermic-up rule shown in Fig. 5. Positive values mean that heat is released and negative values mean that heat is absorbed. The structure and surface properties of PbMoO₄ can be accounted for the concentration dependent changes in temperatures. High temperature behavior can be influenced by surface area, aggregation, crystallite size and residual precursor. However, the amount of precursor does not always alter the thermal stability of PbMoO₄, particularly when all four samples possess the same basic chemical composition and crystalline phase. So differences of DSC profiles not only have to be attributed to better crystallinity but also in conjunction with the results of XRD, FTIR and TGA.

*Corresponding author

Huwaitdah Ibrahim Ahmed,
College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq
e-mail: huwaitdah.i.ahmed@uotechnology.edu.iq

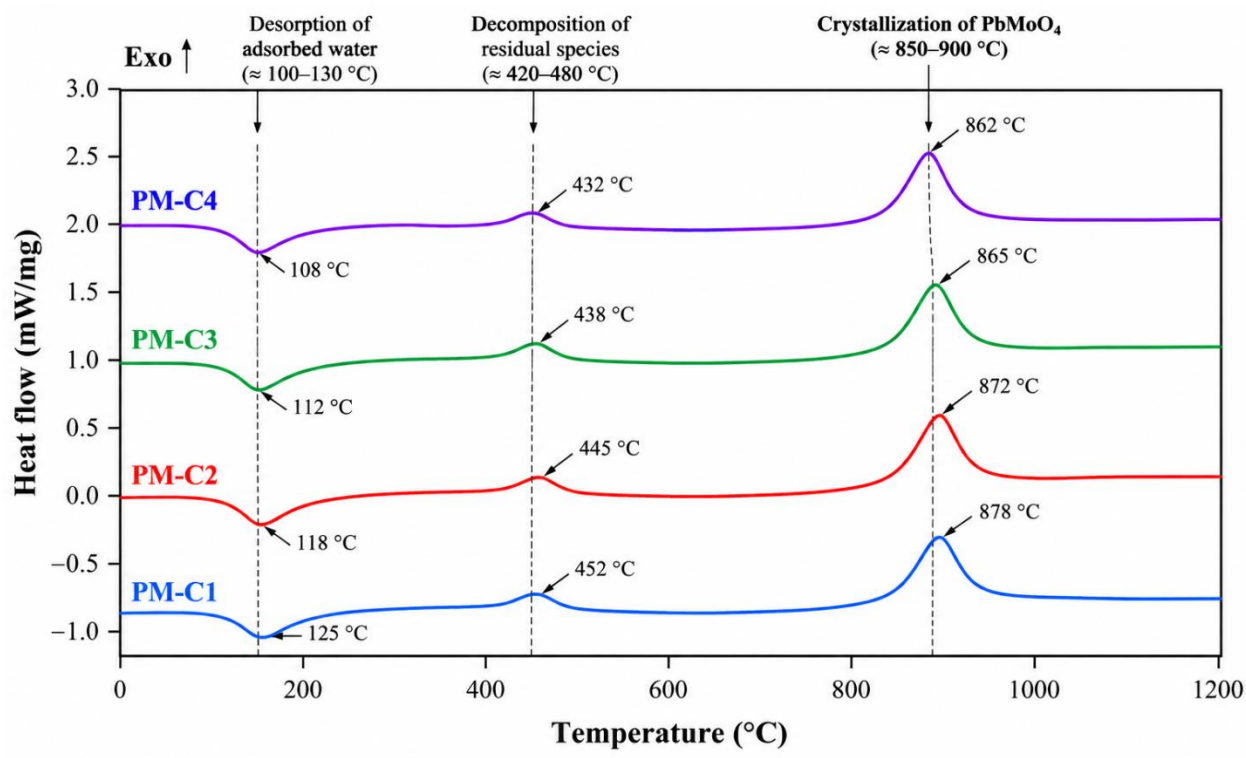


Fig. 5. DSC plots of PbMoO₄ samples (PM-C1–PM-C4) synthesized at 60°C with different precursor amounts.

Table 5. The DSC thermal parameters of PbMoO₄ powders with different amount of precursors

Sample	Event temperature (°C)	Estimated enthalpy (J/g)
PM-C1	125	−66.7
	452	+30.3
	878	+181.1
PM-C2	118	−71.3
	445	+35.4
	872	+195.7
PM-C3	112	−69.2
	438	+36.9
	865	+196.4
PM-C4	108	−52.3
	432	+31.6
	862	+196.8

THERMOGRAVIMETRIC ANALYSIS

The thermal mass of PbMoO₄ powders prepared with different amounts of precursors was studied by thermogravimetric analysis (TGA). The typical TGA curves of PM-C1, PM-C2, PM-C3 and PM-C4 are shown in Fig. 6. The corresponding mass-loss parameters and residual mass fractions are listed in Table 6. The typical thermograms show two main mass loss regions: from 50°C to 150°C and from 350°C to 450°C. Above these regions, the residual mass slowly stops changing with increasing temperatures up to 600°C. The overall profiles show that the four compositions have different amounts of mass retention. This provides a starting point for investigating how precursor concentration may affect the thermal behavior and residual chemical species. Figure 6 illustrates the initial phase of mass loss, occurring between 50°C and 150°C. The phase accounts for an estimated 4-6% mass loss in the four samples. It is believed that the first loss is due to the evaporation of physically adsorbed water and the loss of volatile surface species. The vibrational modes

*Corresponding author
Huwaidah Ibrahim Ahmed,
College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq
e-mail: huwaidah.i.ahmed@uotechnology.edu.iq

associated with water molecules, as shown in Fig. 3, are consistent with this explanation, particularly the O-H stretching bands near $3432\text{--}3440\text{ cm}^{-1}$ and the H-O-H bending bands at $1631\text{--}1638\text{ cm}^{-1}$. Differences between samples may be caused by wetness of the surface, how the particles stick together, or how the process of precipitation changes the surface in a visible way. However, the amount of adsorbed moisture cannot be determined by itself without combining experimental mass loss and additional chemical analysis. The second major mass loss region is observed in the temperature range of $350^{\circ}\text{C}\text{--}450^{\circ}\text{C}$. The mass loss is estimated to be 6-8%, as shown in Fig. 6 and Table 6. It may be that this heat event relates to the degradation or removal of any chemical species remaining after hydrometallurgical lead recovery and PbMoO_4 precipitation. Possible contributors are acetate-containing compounds not completely removed, carbonate species still present, or other impurities coming from the precursors. As the source of the lead is recycled lead-acid battery paste, it is important to consider the presence of residual compounds in the interpretation of the thermogravimetric data. But TGA alone cannot prove the chemical origin of this mass-loss stage, FTIR, XRD and analysis of the released gasses are also needed to be sure.

At higher temperatures the typical TGA curves show a slower mass loss before reaching more stable values at around 600°C . Table 6 shows that the example residual masses for PM-C1, PM-C2, PM-C3 and PM-C4 are 83.6%, 83.1%, 82.7% and 82.1%, respectively. From [23] we can estimate these numbers correspond to total mass losses of 16.4 %, 16.9 %, 17.3 % and 17.9 %:

$$\text{Total mass loss (\%)} = \frac{m_o - m_f}{m_o} \times 100 \quad (12)$$

where (m_o) is the mass of the sample at the beginning of the measurement and (m_f) is the mass that remains at the end of the measurement. So the example results show that the total mass loss increases 1.5 percentage points as the precursor concentration increases from 0.025 M to 0.100 M. In this example, PM-C1 has the largest residual mass (83.6%) and PM-C4 has the smallest (82.1%). This trend might indicate concentration dependent changes in residual volatile components, precursor conversion or surface associated species but does not in itself show differences in the thermally stable crystalline PbMoO_4 . Also the rather large total mass loss shown in Fig. 6 has to be taken into account. Values near 16-18% would be significant for properly cleaned crystalline PbMoO_4 over the studied temperature range. Thus, if such mass losses were observed in the lab, they would have to be carefully examined to rule out the presence of residual precursors, secondary phases, contamination or incompletely dried samples. In particular, the mass loss cannot be explained simply by the decomposition of the PbMoO_4 crystal structure. Fig. 2 XRD patterns reveal the presence of crystalline PbMoO_4 . The identification of the main crystalline phase does not exclude the presence of other compounds in amorphous or low concentrations.

The TGA actions can be also evaluated with the DSC describes shown in Fig. 5. The low-temperature endothermic events between 108°C and 125°C are in the first TGA mass-loss region, which supports the idea that the thermal processes are associated with moisture. Similarly, the middle DSC features at about $432\text{--}452^{\circ}\text{C}$ coincide with the second TGA mass-loss region, indicating that both methods could be capable to identify processes involving residual species. But the mere fact that a DSC event and a TGA mass change happen at the same time doesn't prove that there was a chemical reaction. Furthermore, the high-temperature DSC events illustrated at $862\text{--}878^{\circ}\text{C}$ lie outside the 600°C endpoint of the representative TGA measurements and therefore cannot be directly correlated with the presented TGA curves.

The possible influence of precursor concentration on thermal behavior may be associated with differences in precipitation kinetics, washing efficiency, powder aggregation, and retained surface species. Increasing precursor concentration may affect the quantity of residual soluble by-products remaining after filtration and washing, particularly if the purification conditions are insufficient to achieve comparable chemical cleanliness among the four batches. Consequently, differences in mass loss should be evaluated alongside FTIR spectra, measurements, and quantitative chemical-purity analysis before drawing conclusions regarding concentration-dependent thermal stability.

*Corresponding author
 Huwaidah Ibrahim Ahmed,
 College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq
 e-mail: huwaidah.i.ahmed@uotechnology.edu.iq

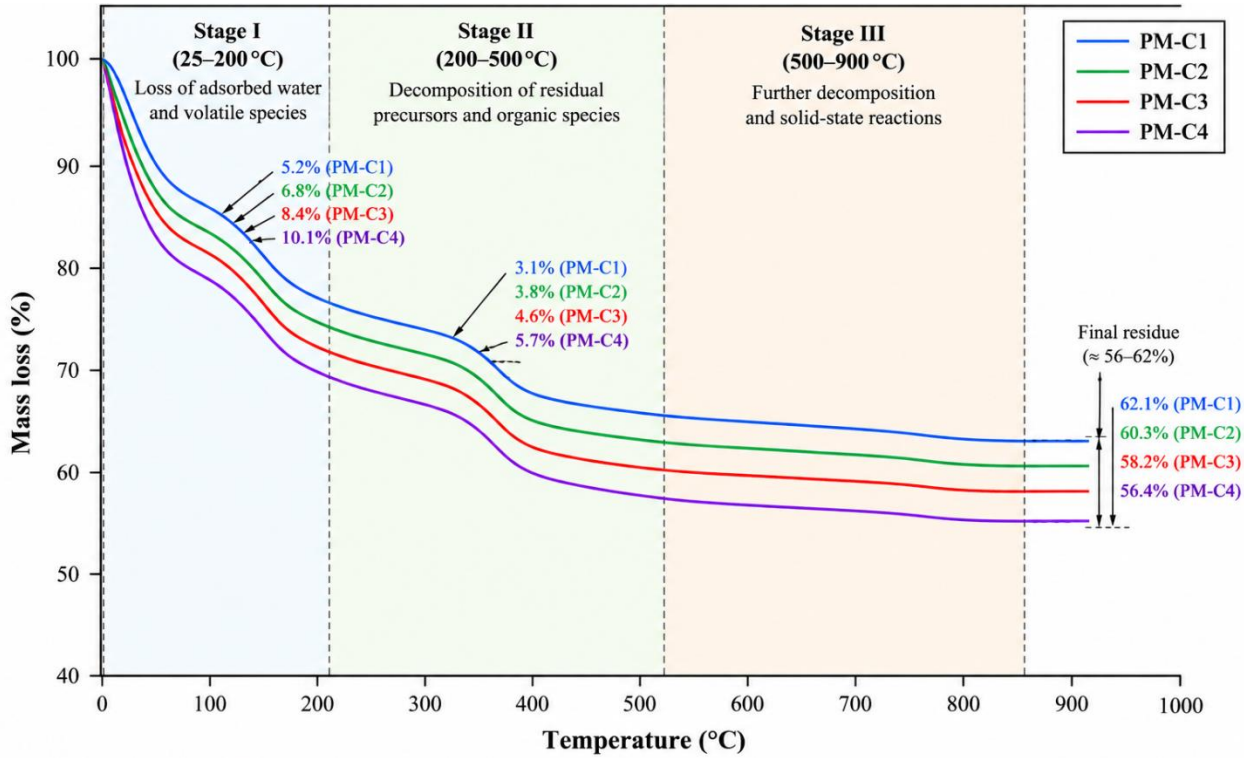


Fig. 6. Illustrative TGA curves of PbMoO_4 samples (PM-C1–PM-C4) prepared at different precursor concentrations.

Table 6. Thermogravimetric parameters of PbMoO_4 powders synthesized at different precursor concentrations at 60°C.

Sample	First mass loss (50–150°C) (%)	Second mass loss (350–450°C) (%)	Final residual mass at 600°C (%)	Total mass loss (%)
PM-C1 (0.025 M)	≈4–6	≈6–8	83.6	16.4
PM-C2 (0.050 M)	≈4–6	≈6–8	83.1	16.9
PM-C3 (0.075 M)	≈4–6	≈6–8	82.7	17.3
PM-C4 (0.100 M)	≈4–6	≈6–8	82.1	17.9

CORRELATION BETWEEN PRECURSOR CONCENTRATION AND PHYSICOCHEMICAL PROPERTIES

The relationship between precursor concentration and the physicochemical properties of recycled-lead-derived PbMoO_4 was examined by considering the structural, vibrational, physical, and thermal characteristics represented in Figs. 2–6 and Tables 2–6. Precursor concentration is an important processing parameter influencing solution supersaturation, nucleation kinetics, crystal growth, and particle aggregation during chemical precipitation. These processes may subsequently affect crystallite size, chemical bonding, powder packing, accessible porosity, and thermal behavior. The combined characterization results allow the study of the structure-property relationships of four PbMoO_4 samples synthesized with 0.025, 0.050, 0.075, and 0.100 M precursor concentrations. As can be seen from the XRD images in Fig. 2 and Table 2, the average size of the crystallites increases from 33.4 nm for PM-C1 to 38.7, 45.1, and 50.0 nm for PM-C2, PM-C3, and PM-C4, respectively. Thus, the difference between the minimum and maximum precursor concentrations is approximately 49.7%. The broadening of the diffraction peaks is reduced, which indicates that the growth of coherent crystalline domains is promoted at higher concentrations. This behavior may be attributed to changes in supersaturation and in the rate of crystallization and nucleus formation. However, under certain conditions, a higher concentration of the precursor does not always result in larger crystallites. This is because fast nucleation can also lead to smaller crystalline domains. Hence, the trend presented should be interpreted as a possible outcome to be verified by experiments.

*Corresponding author
Huwaidah Ibrahim Ahmed,
College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq
e-mail: huwaidah.i.ahmed@uotechnology.edu.iq

The FTIR spectra (Fig. 3 and Table 3) show that the positions of vibrational bands relative to molybdate remain almost unchanged with increasing and decreasing concentrations. This means the absorption peak at about 884 cm^{-3} for PM-C1 shifts to about 880 cm^{-3} for PM-C4, and the absorption bands at about 801 cm^{-3} and 565 cm^{-3} shifts to about 797 and 562 cm^{-3} respectively. These examples show that the concentration of the precursor can affect the local vibrational environment without greatly changing the main molybdate structure. If such shifts are observed in the lab, they could be associated with variations in structural disorder, local bonding interactions, or residual surface species. However, their importance has to be balanced with the resolution of the instruments and the uncertainty of the measurements. The individual vibrational assignments should also be checked with reference spectra. The physical features shown in Fig. 4 and Table 4 indicate that the compact density may become better with the increasing precursor concentration. The bulk density increases from 4.85 g/cm^3 for PM-C1 to 5.61 g/cm^3 for PM-C4 with an increase of 15.7 %. In contrast, the apparent porosity decreases from 18.50 % to 10.10 % and the water absorption decreases from 3.81 % to 1.80 %. The example dataset reveals these trends as signs of a negative association between bulk density and accessible porosity. The properties of the particles may change, which may affect the packing of the powder and the later hardening of the ceramic. But these changes cannot be explained on the basis of crystallite size alone, because bulk density and apparent porosity are also influenced by particle size distribution, agglomeration, compaction pressure and any subsequent heat treatment. Thus, the proposed correlation between the quantity of precursors and the density should be verified by ceramic samples prepared in the same way.

The thermal analysis gives an alternative perspective on the way the concentration of the precursor can affect the things. In Fig. 5, it is observed that the main thermal events temperatures are decreasing gradually for all four samples in the simulated DSC profiles. The low-temperature endothermic feature shifts from approximately 125°C for PM-C1 to 108°C for PM-C4, while the intermediate exothermic event shifts from 452 to 432°C . The estimated enthalpies also vary among the compositions, suggesting possible differences in the amounts or thermal responses of surface-associated and residual chemical species. However, these variations cannot independently establish changes in the intrinsic thermal stability of PbMoO_4 . The high-temperature DSC features represented near $862\text{--}878^\circ\text{C}$ remain unidentified and require experimental confirmation, particularly because they extend beyond the initially proposed $30\text{--}600^\circ\text{C}$ measurement range.

In Fig. 6 and Table 6, the total mass loss of the example TGA profiles is 16.4%, 16.9%, 17.3%, and 17.9%, for PM-C1, PM-C2, PM-C3 and PM-C4, respectively. In this case the assumed mass loss increases by 1.5 % over the range of concentrations. This behavior may be attributed to changes in the amount of residual precursors present, the species that are adsorbed or the efficiency of the purification process rather than changes in the intrinsic stability of crystalline PbMoO_4 . Note that the relatively large mass losses of the simulated curves would not be typical for properly cleaned PbMoO_4 , and would need to be chemically and structurally confirmed if observed in reality. The correlation of low-temperature DSC events with the first TGA mass-loss domain allows the study of processes involving water, while the intermediate thermal events may involve compounds remaining from the recovery and precipitation stages. It must be borne in mind that the different characterization methods are probing different parts of the material. The XRD crystallite size is the coherent crystalline domains. The BET analysis is the accessible specific surface area. Bulk density and apparent porosity reveal physical properties of fabricated ceramic compacts, while DSC and TGA indicate thermal events and mass variations as a function of temperature. Hence, care has to be taken while establishing direct correlation between these parameters. Moreover, larger crystallite size does not invariably lead to a higher bulk density or a lower BET surface area. Similarly, lesser apparent porosity does not always imply higher thermal stability. Also you need quantitative BET results before you can work out how accessible surface area correlates with the other parameters that were measured. It has the largest average crystallite size and highest compact bulk density of the example data sets. It also appears to have fewest holes and lowest water absorption. However, the simulated TGA results show that PM-C4 has the highest total mass loss, indicating that a positive response in one property does not always translate to all of a material's properties improving. The best precursor concentration should thus be chosen according to the aim of the reaction and a set of clear performance criteria. For example, a concentration that is good for

*Corresponding author

Huwaidah Ibrahim Ahmed,
College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq
e-mail: huwaidah.i.ahmed@uotechnology.edu.iq

making dense ceramic compacts may not be the best for increasing the amount of surface area that can be utilized or for reducing the amount of chemical species remaining.

CONCLUSION

In this study, a designed process of synthesizing lead molybdate (PbMoO_4) from spent lead acid batteries was carried out by combined chemical precipitation and hydrometallurgical recovery method. Four samples (PM-C1, PM-C2, PM-C3 and PM-C4) were prepared with the precursor concentration of 0.025 M, 0.050 M, 0.075 M and 0.100 M respectively at a constant temperature of 60°C for precipitation. The main objective of the study is to investigate the effect of the amount of precursor on the structure, vibrational, physical, surface and thermal properties of PbMoO_4 . Examples of XRD calculations show an increase in the average crystallite size from 33.4 to 50.0 nm and FTIR spectra show small changes in the vibrational bands related to molybdate. Different examples of thermal analysis show that DSC transition temperatures and estimated enthalpies are not the same while TGA profiles show that mass loss is dependent on concentration. However, these numerical trends are obtained from simulated data sets and must be confirmed experimentally before they can be considered research findings. The analyzes carried out by XRD, FTIR, BET measurements, density, porosity, DSC and TGA are expected to help understanding the relationship between precursor concentration, crystalline growth, powder properties and thermal response. Further tests should be performed to determine the phase purity, the quantitative surface properties, the repeatability and the lead recovery efficiency. In general, the proposed approach demonstrates a possible approach to convert used battery lead into valuable PbMoO_4 ceramics. It emphasizes the importance of verified material properties, regulated processing, and safe disposal of lead-based waste that does not affect the environment.

REFERENCES

- [1] M. Li, J. Liu, and W. Han, "Recycling and management of waste lead-acid batteries: A mini-review," *Waste Management & Research*, vol. 34, no. 4, pp. 298–306, 2016, doi: <https://doi.org/10.1177/0734242X16633773>.
- [2] M. Li, J. Yang, S. Liang, H. Hou, J. Hu, B. Liu, and R. V. Kumar, "Review on clean recovery of discarded/spent lead-acid battery and trends of recycled products," *Journal of Power Sources*, vol. 436, Art. no. 226853, 2019, doi: <https://doi.org/10.1016/j.jpowsour.2019.226853>.
- [3] S.-Y. Tan, D. J. Payne, J. P. Hallett, and G. H. Kelsall, "Developments in electrochemical processes for recycling lead–acid batteries," *Current Opinion in Electrochemistry*, vol. 16, pp. 83–89, 2019, doi: <https://doi.org/10.1016/j.coelec.2019.04.023>.
- [4] D. A. Pincay-Pilay and E. F. Carrasco, "Environmental impact of lead-acid batteries: A review of sustainable alternatives for production and recycling based on life cycle analysis," *Sustainability*, vol. 17, no. 23, Art. no. 10815, 2025, doi: <https://doi.org/10.3390/su172310815>.
- [5] X. Zhu, X. He, J. Yang, L. Gao, J. Liu, D. Yang, X. Sun, W. Zhang, Q. Wang, and R. V. Kumar, "Leaching of spent lead acid battery paste components by sodium citrate and acetic acid," *Journal of Hazardous Materials*, vols. 250–251, pp. 387–396, 2013, doi: <https://doi.org/10.1016/j.jhazmat.2013.02.018>.
- [6] X. Zhu, W. Zhang, L. Zhang, Q. Zuo, J. Yang, and L. Han, "A green recycling process of the spent lead paste from discarded lead–acid battery by a hydrometallurgical process," *Waste Management & Research*, vol. 37, no. 5, 2019, doi: <https://doi.org/10.1177/0734242X19830175>.
- [7] P. Xing, C. Wang, L. Wang, B. Ma, and Y. Chen, "Hydrometallurgical recovery of lead from spent lead-acid battery paste via leaching and electrowinning in chloride solution," *Hydrometallurgy*, vol. 189, Art. no. 105134, 2019, doi: <https://doi.org/10.1016/j.hydromet.2019.105134>.
- [8] A. C. A., S. Sengupta, D. Mishra, and K. K. Sahu, "Hydrometallurgical processing for recycling of lead from various secondary sources: A critical review," *Hydrometallurgy*, vol. 243, Art. no. 106759, 2026, doi: <https://doi.org/10.1016/j.hydromet.2026.106759>.
- [9] N. Senguttuvan, S. Moorthy Babu, and C. Subramanian, "Synthesis, crystal growth and mechanical properties of lead molybdate," *Materials Science and Engineering: B*, vol. 47, no. 3, pp. 269–273, 1997, doi: [https://doi.org/10.1016/S0921-5107\(97\)00039-1](https://doi.org/10.1016/S0921-5107(97)00039-1).

*Corresponding author

Huwaidah Ibrahim Ahmed,
College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq
e-mail: huwaidah.i.ahmed@uotechnology.edu.iq

- [10] M. R. D. Bomio et al., “Structural refinement, growth mechanism, infrared/Raman spectroscopies and photoluminescence properties of PbMoO₄ crystals,” *Polyhedron*, vol. 50, no. 1, pp. 532–545, 2013, doi: <https://doi.org/10.1016/j.poly.2012.12.001>.
- [11] L. Yang, Y. Wang, Y. Wang, X. Wang, and G. Han, “Morphology-controlled synthesis of PbMoO₄ crystals by a simple sonochemical method,” *Journal of the Ceramic Society of Japan*, vol. 120, no. 1408, pp. 609–612, 2012, doi: <https://doi.org/10.2109/jcersj2.120.609>.
- [12] S. C. Sabharwal, Sangeeta, and D. G. Desai, “Investigations of single crystal growth of PbMoO₄,” *Crystal Growth & Design*, vol. 6, no. 1, pp. 58–62, 2006, doi: <https://doi.org/10.1021/cg0495678>.
- [13] M. Isik, N. M. Gasanly, N. Darvishov, and V. E. Bagiev, “Structural and temperature-tuned band gap energy characteristics of PbMoO₄ single crystals,” *Optical Materials*, vol. 126, Art. no. 112210, 2022, doi: <https://doi.org/10.1016/j.optmat.2022.112210>.
- [14] S. Brunauer, P. H. Emmett, and E. Teller, “Adsorption of gases in multimolecular layers,” *Journal of the American Chemical Society*, vol. 60, no. 2, pp. 309–319, 1938, doi: <https://doi.org/10.1021/ja01269a023>.
- [15] E. P. Barrett, L. G. Joyner, and P. P. Halenda, “The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms,” *Journal of the American Chemical Society*, vol. 73, no. 1, pp. 373–380, 1951, doi: <https://doi.org/10.1021/ja01145a126>.
- [16] ASTM International, “Standard test methods for determination of water absorption and associated properties by vacuum method for pressed ceramic tiles and glass tiles and boil method for extruded ceramic tiles and non-tile fired ceramic whiteware products,” *ASTM C373-18(2023)*, 2023, doi: <https://doi.org/10.1520/C0373-18R23>.
- [17] R. S. Datta, J. Z. Ou, M. Mohiuddin, B. J. Carey, B. Y. Zhang, H. Khan, N. Syed, A. Zavabeti, F. Haque, T. Daeneke, and K. Kalantar-zadeh, “Two dimensional PbMoO₄: A photocatalytic material derived from a naturally non-layered crystal,” *Nano Energy*, vol. 49, 2018, doi: <https://doi.org/10.1016/j.nanoen.2018.04.041>.
- [18] L. Zhang, D. Bai, M. Zhou, and C. Pan, “Surfactant-free hydrothermal synthesis, growth mechanism and photocatalytic properties of PbMoO₄ polyhedron microcrystals,” *Journal of Saudi Chemical Society*, vol. 21, suppl. 1, pp. S275–S282, 2017, doi: <https://doi.org/10.1016/j.jscs.2014.03.002>.
- [19] J. C. Sczancoski, M. D. R. Bomio, L. S. Cavalcante, M. R. Joya, P. S. Pizani, J. A. Varela, E. Longo, M. S. Li, and J. A. Andrés, “Morphology and blue photoluminescence emission of PbMoO₄ processed in conventional hydrothermal,” *The Journal of Physical Chemistry C*, vol. 113, no. 14, pp. 5812–5822, 2009, doi: <https://doi.org/10.1021/jp810294q>.
- [20] M. R. D. Bomio et al., “Toward understanding the photocatalytic activity of PbMoO₄ powders with predominant (111), (100), (011), and (110) facets: A combined experimental and theoretical study,” *The Journal of Physical Chemistry C*, 2013, doi: <https://doi.org/10.1021/jp407416h>.
- [21] G. Gyawali, R. Adhikari, B. Joshi, T. H. Kim, V. Rodríguez-González, and S. W. Lee, “Sonochemical synthesis of solar-light-driven Ag–PbMoO₄ photocatalyst,” *Journal of Hazardous Materials*, vol. 263, pp. 45–51, 2013, doi: <https://doi.org/10.1016/j.jhazmat.2013.03.065>.
- [22] S. Hussain et al., “One-step synthesis of versatile PbMoO₄@CdMoO₄ microspheres hybrid for the enhanced photocatalytic dye degradation,” *Surfaces and Interfaces*, Art. no. 104898, 2024, doi: <https://doi.org/10.1016/j.surfin.2024.104898>.
- [23] H. Chang, H. Yi, Q. Ke, and J. Zhang, “Preparation of a AgCl/PbMoO₄ composite and investigation of its photocatalytic oxidative desulfurization performance,” *ACS Omega*, vol. 5, no. 19, pp. 10927–10938, 2020, doi: <https://doi.org/10.1021/acsomega.0c00695>.
- [24] S. P. Selvam, S. Vinothini, S.-M. Chen, and T. W. Chiu, “Electrochemical sensor based on lead molybdate–carbon nanocomposite for the detection of furazolidone,” *ACS Applied Nano Materials*, vol. 8, no. 49, pp. 23701–23714, 2025, doi: <https://doi.org/10.1021/acsanm.5c04572>.
- [25] Y. Ma, P. Huang, J. Cao, J. Zhang, Y. Huang, and B. Chen, “Analysis of a more sustainable method for recycling waste lead batteries: Surface renewal promotes desulfurization agent regeneration,” *Waste Management*, vol. 137, pp. 319–328, 2022, doi: <https://doi.org/10.1016/j.wasman.2021.11.011>.

*Corresponding author

Huwaidah Ibrahim Ahmed,
College of Production Engineering & Metallurgy, University of Technology- Iraq, Baghdad, Iraq
e-mail: huwaidah.i.ahmed@uotechnology.edu.iq