

New Synthesis of Solid-Solution Lead Hydroxyapatite (PbHAP) by Ceramic and Semi-Ceramic Methods

¹Mohammed A.B. Abdul jabar and ²Ignatov A.V

¹College of Science, Al-Karkh University of Science, Hayfa Street, Baghdad 10001, Iraq.

²Faculty of chemistry, Donetsk National University, University Street 24, 83001-Donetsk, Ukraine.

mohammedbaset1980@gmail.com*

(Received on 7th January 2019, accepted in revised form 12 July 2019)

Summary: The synthesis of solid solutions lead hydroxyapatite, $\text{Pb}_{10}(\text{PO}_4)_{6-y}(\text{OH})_2$, were successfully synthesized by solid-state reaction (ceramic method) ($y = 0.95; 0.96; 0.97; 0.98; 0.99$ and 1.00) and precipitation (semi ceramic method) ($y = 0.97; 0.98; 0.99$ and 1.00) methods at 800°C for 50 hours. The X-ray powder diffraction (DRON-3m diffractometer), electron microscopy scanning (SEM) and energy dispersive X-ray micro-analysis which characterized all samples. It has been established that $\text{Pb}_{10}(\text{PO}_4)_{5.82}(\text{OH})_2$ and $\text{Pb}_{10}(\text{PO}_4)_{5.88}(\text{OH})_2$ are the best synthesis for lead hydroxyapatite in the solid-state reaction method, and $\text{Pb}_{10}(\text{PO}_4)_{5.88}(\text{OH})_2$ is the precipitation method.

Keywords: Lead, Hydroxyapatite, Solid Solutions, X-ray Diffraction.

Introduction

Due to a variety of isovalent and heterovalent substitutions, the interest in lead hydroxyapatite has grown in recent years. Although much less intensively studied, lead hydroxyapatite may be the following candidate for development in many fields such as medical biomaterials, luminescent, laser constituents, environmental sensors, solid electrolytes, sorbents, catalysts, etc [1-4]. Control of practical size, chemical composition and morphology can influence the properties of lead hydroxyapatite. Common synthetic methods for the preparation of many types of apatite structures including: solid-state synthesis, wet chemical methods and hydrothermal synthesis [5-8]. Lead hydroxyapatite, $[\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2]$, designated as PbHAP] particles have earlier been synthesized by numerous examiners via solid-state reaction and precipitation methods.

Many studies have synthesized lead hydroxyapatite, $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ system by ceramic (as a solid-state reaction) [9-11] and semi-ceramic (precipitation) methods [12-15]. Many researchers have prepared PbHAP $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ from $\text{Pb}_{10}(\text{PO}_4)_6\text{O}$ at 425°C under 1000 atm using a solid state method. In another study [10], lead hydroxyapatite, $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ (PbHAP) synthesized by solid-state reaction of $\text{Pb}_{10}(\text{PO}_4)_6\text{O}$ at 300°C and by precipitation method of $\text{Pb}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{HPO}_4$ followed by solid state reaction at 300°C . In addition, lead hydroxyapatite is prepared at the room temperature, 300, 600 and 900°C by solid state reaction from PbO and $\text{NH}_4\text{H}_2\text{PO}_4$ [11]. Researchers in other study [12], obtained lead hydroxyapatite, $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ via a $\text{Pb}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{HPO}_4$ precipitation reaction at pH 12 and 37°C . Moreover,

solid solution PbHAP was synthesized from a semi-ceramic containing PbHPO_4 and NaOH (Hydroxide Sodium) which had been stayed at 40°C for 7 days [13], from solutions containing Lead(II) acetate $\text{Pb}(\text{CH}_3\text{COO})_2$ and many phosphates stayed at 100°C for 4-24 hours [14] and from many solutions containing basic $\text{Pb}(\text{NO}_3)_3$ and H_3PO_4 [15].

A change of lead hydroxyapatite was prepared by authors in this study. A hot solution of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ [lead (II) acetate trihydrate] (0.25 dm^{-3}) was mixed with di-sodium hydrogen phosphate (0.25 dm^{-3}). The initial concentration for lead and sodium salts was 0.01 and 0.06 mol dm^{-3} correspondingly, and the Pb:P molar ratios was 5:3. Colorless complex was separated during the addition of the Pb^{2+} salt to the Na salt. The precipitate was dehydrated at 100°C for 24 hours [16]. The semi-ceramic (precipitation) method used acetamide has prepared crystalline lead hydroxyapatite, $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$. The acetamide concentration of the lead hydroxyapatite composition was $0.4 - 1.6 \text{ mol dm}^{-3}$ [17]. Lead hydroxyapatite have been prepared from the compounds: H_3PO_4 and $\text{Pb}(\text{NO}_3)_2 \cdot 5\text{PbO}$, latter of which was produced through drying up of basic lead nitrates like $2\text{Pb}(\text{NO}_3)_2 \cdot 5\text{Pb}(\text{OH})_2$ and $\text{Pb}(\text{NO}_3)_2 \cdot 5\text{Pb}(\text{OH})_2$. The prepared lead hydroxyapatite was calcinated at 773, 973 and 1173 K for 3 hours, the XRD patterns showed the apatite composition, but PbHap was partly heated at 1173 K [18].

The synthesis of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ doped with 30 mol% Pb ($\text{Ca}_{6.6}\text{Pb}_{3.4}(\text{PO}_4)_6(\text{OH})_2$) was prepared from dropwise adding of a Lead(II) nitrate

*To whom all correspondence should be addressed.

(Pb(NO₃)₂) solution to calcium nitrate (Ca(NO₃)₂) solution at 80 °C, pH = 11. After the adding, the solution was stirred for 2.5 hours at the similar temperature. The precipitate was separated by filtration, repetitively washed with distilled boiling water and dehydrated at 100 °C for 24 hours [19]. Lead hydroxyapatite (Pb₅(PO₄)₃(OH)) was prepared according to the semi-ceramic (precipitation method) reaction: $5\text{Pb}^{2+} + 3\text{PO}_4^{3-} + \text{OH}^- \rightarrow \text{Pb}_5(\text{PO}_4)_3\text{OH}$. Lead (II) acetate (Pb(CH₃COO)₂·H₂O), ammonium acetate (CH₃COONH₄), mono-ammonium phosphate NH₄H₂PO₄ and ammonium hydroxide (NH₄OH) were used as initial reagents. The produced precipitates heated at 100 °C for 48 hours [20]. Many researchers were able to prepared lead hydroxyapatite (Pb₁₀(PO₄)₆(OH)₂) from aqueous solutions at 80 °C by adding 200 mL aqueous solutions of 0.05M Lead (II) nitrate (Pb(NO₃)₂) and potassium dihydrogen phosphate (KH₂PO₄) were treated with a 0.25 mL/min rate to a glass beaker, which contained 100 mL of distilled water, pH of 8 was kept using 2M potassium hydroxide (KOH) [21].

Ultrapure water was used to synthesis the lead hydroxyapatites by bubbled the solutions with the nitrogen (gaseous state) to eliminate dissolved CO₂ gas. The lead-calcium solution (pH 5.2–5.4) was prepared by mixing lead (II) nitrate (Pb(NO₃)₂) (0.040 M, 12.5 mL) with solid calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O) (0.00–295 g) and treated the solution with ultrahigh purity water. Cloudy white suspension was centrifuged after that and then washed with ultrapure water five times to eliminate any remaining calcium nitrate. The remaining precipitate was then filtered and dehydrated immediate at 80 °C [22].

We turn our consideration in the current study to lead hydroxyapatite Pb₁₀(PO₄)₆(OH)₂ (PbHAP) which is prepared using two methods: ceramic (solid state reaction) and semi-ceramic (precipitation) methods. X-ray powder diffraction and scanning electron microscope (SEM) investigated the compound structures.

Experimental

Materials

For the synthesis of lead hydroxyapatite (PbHAP) Pb₁₀(PO₄)₆(OH)₂, the samples were prepared using a mixture of lead oxide PbO (chemically pure) and dibasic ammonium phosphate (NH₄)₂HPO₄ (analytical grade) composed by stoichiometry: $5\text{PbO} + 3(\text{NH}_4)_2\text{HPO}_4$ used as initial reagents. All samples were synthesized using two methods: ceramic (y=

0.95; 0.96; 0.97; 0.98; 0.99 and 1.00) and semi-ceramic (precipitation) (y= 0.97; 0.98; 0.99 and 1.00).

Instrumentation

All synthesized materials were characterized by the following classical techniques: X-ray powder diffraction was performed using a DRON-3 diffractometer using monochromatic Cu K α -filtered radiation ($\lambda= 1.54178$). The pattern was scanned using the X-ray energy dispersive spectrometer INCA Penta FETx3 (OXFORD Instruments, England) in steps of $2\theta= 0.05^\circ$, in the range 15–140° for each step and Scanning electron microscope SEM (JSM-6490LV (JEOL, Japan) for a counting duration of 3 seconds). The Match program and PDF-2 database (ICCD) (International Center for Diffraction Data) [23] and the PDF-4 (ASTM) database (American Society for Testing and Materials) were used for phase investigation.

Procedure

In the ceramic synthesis method, the starting materials suspended in stoichiometric ratios were mixed for 20 minutes in an agate mortar and calcined for 3 hours in alundum crucibles at a temperature of 300 °C, after which the temperature rose to 800 °C, calcination that was performed for 5 hours. The samples were homogenized after calcination and analyzed through X-ray phase analysis (XRD) to determine the composition of the phase. The samples were then calcined again at a temperature of 800 °C, subjected to homogenization and examined using XRD method. To achieve a constant phase composition, this cycle of operations was performed. Consequently, the total calcination time was 50 hours at a temperature of 800 °C.

In the semi-ceramic method, stoichiometric amounts of the initial materials weighed on an analytical balance were dissolved in nitric acid HNO₃ (diluted), after which the resulting solution was vaporized, and the precipitate residue was calcined in the temperature range 500–800 °C. The samples total calcination time at a temperature of 800 °C as well as the ceramic synthesis method was 50 hours.

Result and Discussion

X-ray diffraction patterns of samples of different value y prepared by solid state reaction (ceramic method) show that the phase composition constancy of solid solutions obtained after 50 hours of

calcination. The results of this system's phase analysis samples are shown in Fig. 1 and Table-1.

Table-1: Phase composition samples of the systems $Pb_{10}(PO_4)_{6*y}(OH)_2$, which prepared by solid state reaction (ceramic method).

y	The relative intensity ($I/I_{max} \times 100, \%$) of the maximum phase with the structure		
	$Pb_{10}(PO_4)_6(OH)_2$	$Pb_3(PO_4)_2$	Another phase
0.95	100	6	2
0.96	100	5	1
0.97	100	-	-
0.98	100	-	-
0.99	100	13	3
1.00	100	23	2

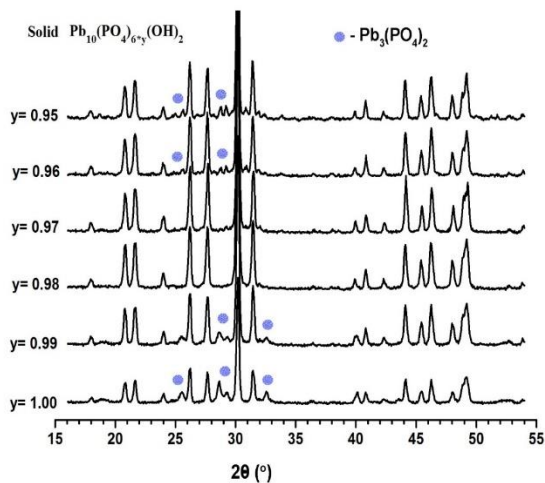


Fig. 1: The X-ray diffraction patterns of $Pb_{10}(PO_4)_{6*y}(OH)_2$, prepared by ceramic method (solid state reaction).

As can be seen from data, the best synthesis for lead hydroxyapatite prepared by the solid state reaction method is $Pb_{10}(PO_4)_{5.82}(OH)_2$ ($y=0.97$) and $Pb_{10}(PO_4)_{5.88}(OH)_2$ ($y=0.98$), only the phase peaks with lead hydroxyapatite structure are present in the X-ray patterns and there are no peaks of other phases (pure lead hydroxyapatite reflections) [24]. In other compositions, $Pb_{10}(PO_4)_{5.70}(OH)_2$ ($y=0.95$), $Pb_{10}(PO_4)_{5.76}(OH)_2$ ($y=0.96$), $Pb_{10}(PO_4)_{5.94}(OH)_2$ ($y=0.99$) and $Pb_{10}(PO_4)_6(OH)_2$ ($y=1.00$) in addition to the lead hydroxyapatite peaks, there are also lead phosphate peaks $Pb_3(PO_4)_2$ with an intensity of 6-23%. We also found reflections whose intensity is approximately 3% compared to lead hydroxyapatite's maximum intensity reflective structure. We can assume that either the reflections of the superstructure

or the component of reflection that is not part of the structure isomorphous.

XRD patterns of samples of different value y prepared by precipitation method (semi-ceramic method) show that the phase composition of solid solutions obtained after 50 hours of calcination is constant.

The results of this system's phase analysis samples are shown in Fig. 2 and Table-2.

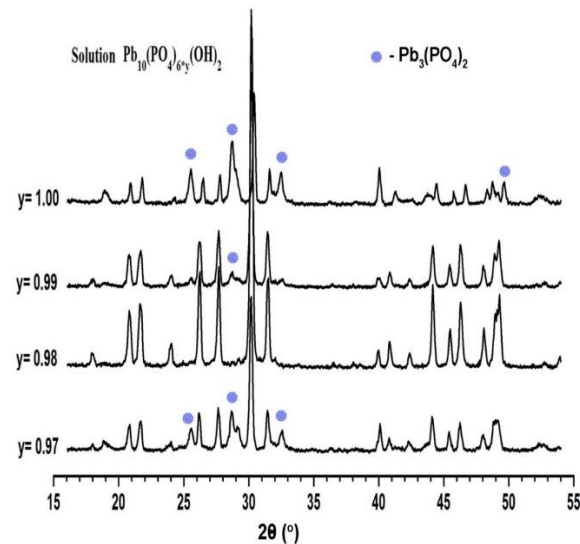


Fig. 2: The X-ray diffraction patterns of $Pb_{10}(PO_4)_{6*y}(OH)_2$ (PbHAP), prepared by semi ceramic (precipitation) method.

As shown in Fig. 2 and Table-2, the best synthesis for lead hydroxyapatite prepared by precipitation method (semi ceramic method) is $Pb_{10}(PO_4)_{5.88}(OH)_2$ ($y=0.98$), only the phase peaks with lead hydroxyapatite structure are present in X-ray patterns and there are no peaks of other phases (pure lead hydroxyapatite reflections).

Table-2: Phase composition samples of the systems $Pb_{10}(PO_4)_{6*y}(OH)_2$, which prepared by semi ceramic (precipitation) method.

y	The relative intensity ($I/I_{max} \times 100, \%$) of the maximum phase with the structure		
	$Pb_{10}(PO_4)_6(OH)_2$	$Pb_3(PO_4)_2$	Another phase
0.97	100	14	2
0.98	100	-	-
0.99	100	7	1
1.00	100	30	2

In other synthesis of lead hydroxyapatite prepared by the same method $Pb_{10}(PO_4)_{5.82}(OH)_2$ ($y=$

0.97), $\text{Pb}_{10}(\text{PO}_4)_{5.94}(\text{OH})_2$ ($y=0.99$) and $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ ($y=1.00$), in addition to the peaks of lead hydroxyapatite, there are also peaks of lead phosphate $\text{Pb}_3(\text{PO}_4)_2$ with an intensity of 7-30%.

In addition, we found reflections whose intensity is about 2% compared to lead hydroxyapatite's maximum intensity reflective structure. It can be assumed that either the reflections

of the superstructure or the component of reflection that is not part of the structure isomorphous [25].

The chemical compositions (wt%) for solid solution $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ were examined by SEM (scanning electron microscopy) of elements (Pb, P and O) and achieved in 24 points on five sections. All results are presented in Tables 3, 4 and Fig. 3 and 4.

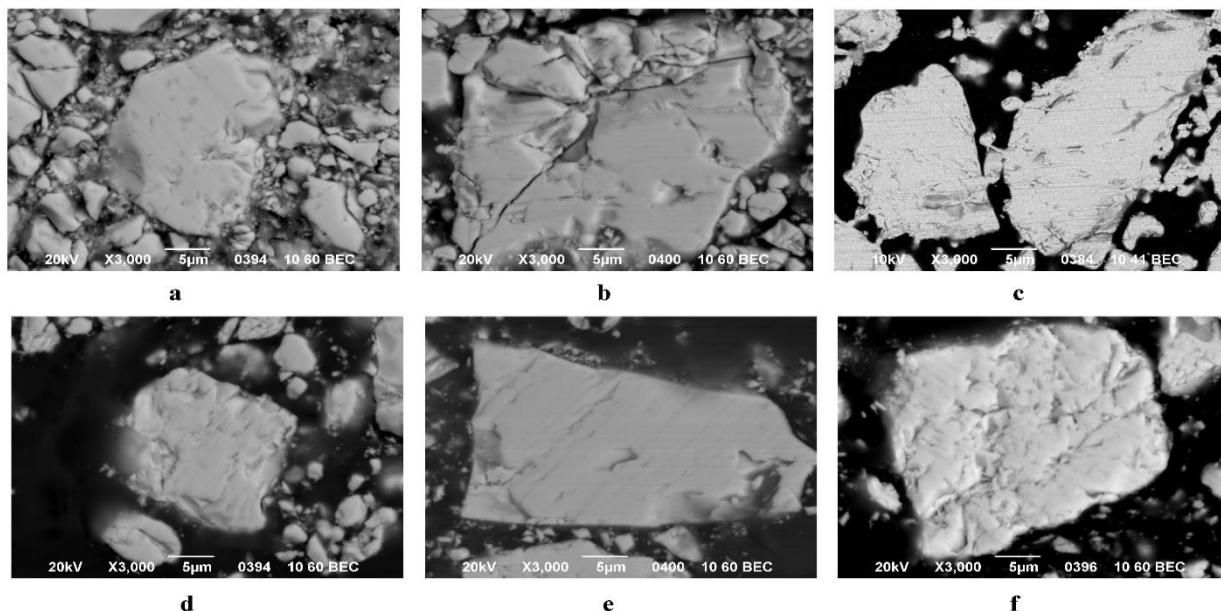


Fig. 3: Scanning Electron Microscope (SEM) photographs of $\text{Pb}_{10}(\text{PO}_4)_{6-y}(\text{OH})_2$ for (a) $y=0.95$, (b) $y=0.96$, (c) $y=0.97$, (d) $y=0.98$, (e) $y=0.99$ and (f) $y=1.00$ (wt%), which synthesized by solid state reaction (ceramic method) at 800°C .

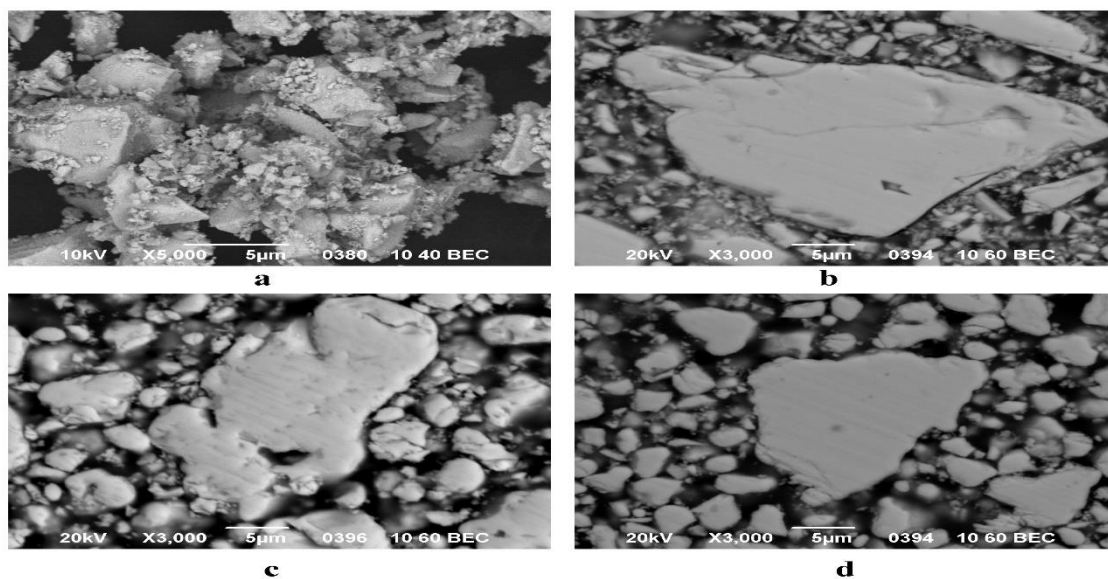


Fig. 4: Scanning Electron Microscope (SEM) photographs of $\text{Pb}_{10}(\text{PO}_4)_{6-y}(\text{OH})_2$ for (a) $y=0.97$, (b) $y=0.98$, (c) $y=0.99$, (d) $y=1.00$ (wt%), which synthesized by semi ceramic (precipitation) method at 800°C .

Table-3: Results of the SEM of $Pb_{10}(PO_4)_{6-y}(OH)_2$ for $y=0.95, y=0.96, y=0.97, y=0.98, y=0.99$ and $y=1.00$ (wt%), which synthesized by solid state reaction (ceramic method) at 800 °C.

y	P		Pb		H		O	
	Calcd	found	Calcd	Found	Calcd	found	Calcd	found
0.95	7.020	7.009	78.267	78.260	0.080	-	15.710	15.698
0.96	7.004	6.984	78.099	78.087	0.080	-	15.679	15.672
0.97	6.989	6.983	77.931	77.926	0.080	-	15.646	15.638
0.98	6.975	6.968	77.765	77.759	0.080	-	15.612	15.607
0.99	6.960	6.947	77.599	77.594	0.080	-	15.579	15.573
1.00	6.945	6.943	77.434	77.432	0.080	-	15.546	15.544

Table-4: Results of the SEM of $Pb_{10}(PO_4)_{6-y}(OH)_2$ for $y=0.97, y=0.98, y=0.99$ and $y=1.00$ (wt%), which synthesized by semi ceramic (precipitation) method at 800 °C.

y	P		Pb		H		O	
	Calcd	found	Calcd	Found	Calcd	found	Calcd	found
0.97	6.989	6.979	77.931	77.921	0.080	-	15.646	15.636
0.98	6.975	6.966	77.765	77.757	0.080	-	15.612	15.608
0.99	6.960	6.942	77.599	77.592	0.080	-	15.579	15.569
1.00	6.945	6.938	77.434	77.429	0.080	-	15.546	15.537

According to scanning electron microscopy data (Table-3 and 4 and Fig. 3 and 4), the elements for both methods (ceramic and semi-ceramic) are distributed almost uniformly across the surface of the particles, indicating the processes of replacement of homogeneous samples occurring [26].

The data above showed that the measured element values (Pb, P, and O) were approximate to the calculated element values.

It is noted that by scanning electron microscopy (SEM), it is not possible to measure the chemical compositions (wt%) of the hydrogen element (H) in solid solution $Pb_{10}(PO_4)_{6-y}(OH)_2$ because many reasons: first, hydrogen element does not have fundamental electrons. Second, H's orbital 1s electrons are valance electrons that are involved in chemical bonding with other elements and cannot distinguish between electrons of hydrogen valence and other elements [27].

The measurement of the hydrogen element is therefore impossible to determine by scanning electron microscope (SEM) or by X-ray photoelectron spectroscopy (XPS).

Conclusion

All samples were examined by X-ray powder diffraction, electron microscopy scanning (SEM) and energy-dispersive X-ray microanalysis. Samples of lead hydroxyapatite (PbHAP) $Pb_{10}(PO_4)_{6-y}(OH)_2$ were obtained for 50 hours at 800 °C. Two methods successfully prepared solid solutions lead hydroxyapatite $Pb_{10}(PO_4)_{6-y}(OH)_2$: ceramic and semi-ceramic.

In the ceramic method, two compositions $Pb_{10}(PO_4)_{5.82}(OH)_2$ ($y=0.97$) and $Pb_{10}(PO_4)_{5.88}(OH)_2$ ($y=0.98$) were obtained with only pure lead hydroxyapatite reflections, while the solid solution $Pb_{10}(PO_4)_{5.88}(OH)_2$ ($y=0.97$) only pure lead hydroxyapatite reflections were obtained in the semi-

ceramic method obtained. Other compositions with various phases were also obtained (not pure lead hydroxyapatite). There are many reasons for the presence of these reflections from our point of view: first, heated air water vapor entered the composition. Second, some ingredients have reacted sideways, interfering with the main reaction, and third, the presence of vacancies in the compositions that have not yet been identified.

For the improvement of new practical materials with lead hydroxyapatite, we recommended obtained results from this study.

Conflict of Interests

The researchers declare that there is no conflict of interests about the publication of this paper.

Acknowledgements

We appreciated all the support which was presented by Department of Inorganic Chemistry, Donetsk National University, Donetsk, Ukraine during preparing, measuring and analyzing the samples in this paper.

References

1. J. Zhang, H. Liang, R. Yu, H. Yuan and Q. Su, Luminescence of Ce^{3+} -activated chalcogenide apatites $Ca_{10}(PO_4)_6Y$ ($Y = S, Se$), *Mater. Chem. Phys.*, **114**, 242 (2009).
2. S. Kale, S. Kahandal, S. Disale and R. Jayaram, Conventional and microwave-assisted multicomponent reaction of alkyne, halide and sodium azide catalyzed by copper apatite as heterogeneous base and catalyst in water, *Curr. Chem. Lett.*, **1**, 69 (2012).
3. D. Grossin, S. Rollin-Martinet, C. Estournès, F. Rossignol, E. Champion, C. Combes, C. Rey, C. Geoffroy and C. Drouet, Biomimetic apatite

- sintered at very low temperature by spark plasma sintering: Physico-chemistry and microstructure aspects, *Acta Biomater.*, **6**, 577 (2010).
- H. Yoshioka, Y. Nojiri and S. Tanase, Ionic conductivity and fuel cell properties of apatite type lanthanum silicates doped with Mg and containing excess oxide ions, *Solid State Ion.*, **179**, 2165 (2008).
 - P. Ptáček, *Apatites and their Synthetic Analogues-Synthesis, Structure, Properties and Applications*, chapter 4, published by IntechOpen, p. 177 (2016).
 - A. R. West, *Solid State Chemistry and its Applications*, 2nd ed., John Wiley & Sons, p. 582 (2014).
 - L. E. Smart and E. A. Moore, *Solid State Chemistry: An Introduction*, Fourth Edition, CRC Press, p. 494 (2012).
 - C. K. Haweel, B. Abdul-Majeed and M. Eisa. Beneficiation of Iraqi Akash at Phosphate Ore Using Organic Acids for the Production of Wet Process Phosphoric Acid, *Al-Khwarizmi Engineering Journal*, **9**, 24 (2013).
 - G. Engel and W. E. Klee, Infrared spectra of the hydroxyl ions in various apatites, *J. Solid State Chem.*, **5**, 28 (1972).
 - K. C. Blakeslee, R. A. Condrate and A. Robert, Vibrational spectra of hydrothermally prepared hydroxyapatites, *J. Am. Ceram. Soc.*, **54**, 559 (1971).
 - T. Negas and R. S. Roth, High temperature dehydroxylation of apatitic phosphates, *J. Res. Nat. Bur. Stand.*, **72A**, 783 (1968).
 - T. S. Narasaraju, R. P. Singh and V. L. Rao, A new method of preparation of solid solutions of calcium and lead hydroxylapatites, *J. Inorg. Nucl. Chem.*, **34**, 2072 (1972).
 - R. Klement, Basische Phosphate zweiwertiger Metalle II. Blei-hydroxylapatit, *Z. Anorg. Allg. Chem.*, **237**, 161 (1938).
 - V. M. Bhatnagar, Synthesis, X-ray and infrared studies of lead phosphates, *Rev. Roum. Chim.*, **16**, 1513 (1971).
 - S. Sugiyama, T. Nakanishi, T. Ishimura, T. Moriga, H. Hayashi, N. Shigemoto and J. Moffat, Preparation, characterization, and thermal stability of lead hydroxyapatite, *J. Solid State Chem.*, **143**, 296 (1999).
 - S. Brückner, G. Lusvardi, L. Menabue and M. Saladini, Crystal structure of lead hydroxyapatite from powder X-ray diffraction data, *Inorganica Chimica Acta.*, **236**, 209 (1995).
 - A. Yasukawa, T. Kunitomo, K. Kamiuchi, K. Kandori and T. Ishikawa, Preparation of lead hydroxyapatite particles using acetamide, *J. Mater. Chem.*, **9**, 1825 (1999).
 - S. Sugiyama, T. Nakanishi, T. Ishimura, T. Moriga, H. Hayashi, N. Shigemoto, J. Moffat, Preparation, characterization, and thermal stability of lead hydroxyapatite, *J. solid state chem.*, **143**, 296 (1999).
 - D. Ellis, J. Terra, O. Warschkow, M. Jiang, G. Gonzalez, J. Okasinski, M. Bedzyk, A. Rossi and J. Eon, A theoretical and experimental study of lead substitution in calcium hydroxyapatite, *Phys.Chem. Chem. Phys.*, **8**, 967 (2006).
 - Y. Zhu, B. Huang, Z. Zhu, H. Liu, Y. Huang, X. Zhao and M. Liang, Characterization, dissolution and solubility of the hydroxypyromorphite-hydroxyapatite solid solution $[(Pb_xCa_{1-x})_5(PO_4)_3OH]$ at 25 °C and pH 2-9, *Geochem Trans*, **17**, 1 (2016).
 - A. Giera, M. Manecki, O. Borkiewicz, S. Zelek, J. Rakovan, T. Bajda, and T. Marchlewski, *Monoclinic structure of hydroxylpyromorphite $Pb_{10}(PO_4)_6(OH)_2$ -hydroxylmimetite $Pb_{10}(AsO_4)_6(OH)_2$ solid solution series*, Geophysical Research Abstracts (EGU General Assembly), **18** (2016).
 - J. Hopwood, G. Derrick, D. Brown, C. Newman, J. Haley, R. Kershaw and M. Collinge, The Identification and Synthesis of Lead Apatite Minerals Formed in Lead Water Pipes, *Journal of Chemistry*, **1** (2016).
 - I. Mayer, A. Semadja, V. Weiss, Lead phosphate apatites substituted by rare earth, sodium, and potassium ions, *J. Solid State Chem.*, **34**, 223 (1980).
 - K. Brandenburg and H. Putz, Match software for phase identification from powder diffraction data. <http://www.crystalimpact.com>.
 - E. Get'man, S. Loboda, A. Ignatov, V. Prisedsky, M. Abdul Jabar and L. Ardanova, Isomorphous Substitution of Rare-Earth Elements in Lacunary Apatite $Pb_8Na_2(PO_4)_6$, *J. Am. Chem. Soc.*, **55**, 2165 (2016).
 - E. Getman, A. Ignatov, S. Loboda, M. Abdul Jabar, L. Pasechnik, A. Gegailo, *Ukr. Chem. J.*, **77**, 30 (2011).
 - N. Stojilovic, Why Can't We See Hydrogen in X-ray Photoelectron Spectroscopy? *J. Chem. Educ.*, **89**, 1331 (2012).