

The Identification and Synthesis of Barium-Substituted Lead Hydroxyapatite Structure ($\text{Pb}_{10-x}\text{Ba}_x(\text{PO}_4)_6(\text{OH})_2$) by Ceramic Method

Mohammed A. Abdul Jabar

College of Science/ Al-Karkh University of Science/ Hayfa Street/ Baghdad / Iraq

p-ISSN: 1608-9391

e-ISSN: 2664-2786

Article information

Received: 14/ 7/ 2022

Accepted: 3/ 11/ 2022

DOI: 10.33899/rjs.2023.177294

corresponding author:

Mohammed A. Abdul Jabar

mohammed.a.baset1980@gmail.com

ABSTRACT

The substitution of barium ion (Ba^{2+}) with lead ion (Pb^{2+}) in the following composition: $\text{Pb}_{10-x}\text{Ba}_x(\text{PO}_4)_6(\text{OH})_2$ has been investigated by an X-ray diffractometer. Samples with the range $x=0$ up to $x=5$ were calcined at $800\text{ }^\circ\text{C}$ for 25 hours, and the samples with the range from $x=6$ up to $x=10$ were calcined at $1100\text{ }^\circ\text{C}$ for 15 hours. The solid solutions hydroxyapatite samples are synthesized by the ceramic method. It was established that the sample with $x=0$ showed only reflections of composition $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$, while the sample with $x=10$ showed only reflections of composition $\text{Ba}_{10}(\text{PO}_4)_6(\text{OH})_2$. The Samples with $x = 1-9$ showed more reflections called "unknown phase" besides those of pure hydroxyapatite.

Keywords: Lead, Apatite, Barium, Substitution, Solid solution.

INTRODUCTION

Hydroxyapatites (HAP) (space group P63/m) have a composition described by the formula $M(1)_{10-x}M(2)_x(BO_4)_{10}X_2$, where M (1) and M (2) are metal cations (Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , Cd^{2+} , etc.), while B are P^{5+} , V^{5+} , As^{5+} , Cr^{6+} , etc., and X is OH^- , F^- , Cl^- , Br^- , I^- , O^{2-} , etc (Sugiyama *et al.*, 1999; Ptáček, 2016; Abdul Jabar *et al.*, 2018).

Hydroxyapatites are compounds with many unique properties that determine their wide practical applications (Zhu *et al.*, 2015; Tbeen *et al.*, 2021). For twenty years, researchers and scientists all over the world became increasingly interested in various hydroxyapatite compounds such as calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), lead hydroxyapatite ($Pb_{10}(PO_4)_6(OH)_2$), cadmium hydroxyapatite ($Cd_{10}(PO_4)_6(OH)_2$), barium hydroxyapatite ($Ba_{10}(PO_4)_6(OH)_2$), strontium hydroxyapatite ($Sr_{10}(PO_4)_6(OH)_2$), and others for several reasons, including that these compounds have a variety of practically important properties and can be used in many fields such as nanochemistry, bio-medical, industrial and green chemistry (Liu *et al.*, 2011; Savankova *et al.*, 2014; Zhu *et al.*, 2016). Hydroxyapatites allow many substitutions for many elements with others inside the hydroxyapatite structure; Therefore, these compounds are one of the main important aspects of the crystal chemistry of hydroxyapatites (Getman *et al.*, 2011; Abdel-Aal *et al.*, 2022). As the substitutions within these compounds lead to changes in the crystal structure of these compounds, it is considered one of the main factors responsible for determining the physical and chemical properties of materials (Flis *et al.*, 2010; Getman *et al.*, 2016; Abdul Jabar *et al.*, 2020; Haider *et al.*, 2022).

Lead hydroxyapatite compounds are one of the most important apatite structures (Iconaru *et al.*, 2018). Several studies which prepared lead hydroxyapatite [$PbHAP$ ($Pb_{10}(PO_4)_6(OH)_2$)] compounds have shown that lead can be substituted with several elements such as strontium, calcium, and others by many methods (solid-state reaction, precipitation, sol-gel, etc.) with a different range of temperatures ranging from 600 – 1100 °C (Fleet *et al.*, 2010; Giera *et al.*, 2016; Hopwood *et al.*, 2016).

In our study, we synthesized lead-barium hydroxyapatite $Pb_{10-x}Ba_x(PO_4)_6(OH)_2$, which preparation by solid-state reaction.

MATERIALS AND METHODOLOGY

To investigate the substitution of barium ion (Ba^{2+}) with lead ion (Pb^{2+}) in the lead-barium Hydroxyapatite Structure ($Pb_{10-x}Ba_x(PO_4)_6(OH)_2$), we synthesized all samples ($x = 0.0; 1.0; 2.0; 3.0; 4.0; 5.0; 6.0; 7.0; 8.0; 9.0$ and 10) by the ceramic method (solid-state reaction). All following materials: PbO (chemically pure), $BaCO_3$ (analytical grade), and $(NH_4)_2HPO_4$ (analytical grade) provided by Sin bias (Ukraine), were used as initial reagents. The samples were obtained using the technique described: $(10-x) PbO + 6(NH_4)_2HPO_4 + xBaCO_3 \rightarrow Pb_{(10-x)}Ba_x(PO_4)_6(OH)_2 + \dots\dots$

Since many materials absorb water and carbon dioxide stored in the laboratory, these materials have been heated to remove before use. Lead oxide (PbO), Barium carbonate ($BaCO_3$), and diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) were calcined at 400 °C for 4 hours. After the calcining process, all materials are placed in a desiccator containing freshly heated silica gel, cooled to room temperature, and immediately used for weighing.

The initial substances were ground in an agate mortar for 20 minutes and calcined in alundum crucibles at 400 °C for 3 hours, after which the temperature was raised to 800 °C for samples with $x=0.0, 1.0, 2.0, 3.0, 4.0, \text{ and } 5.0$ and 1100 °C for samples with $x=6.0, 7.0, 8.0, 9.0, \text{ and } 10.0$, calcination lasting 4 hours. Then the samples were crushed, and tablets were pressed from the obtained powders and calcined at 800 and 1100 °C for 4–5 hours. After the calcination process, they were crushed and examined by X-ray phase analysis to establish the phase composition. And then, all tablets were again pressed from the powders and calcined at the same temperature. This procedure was continued until the samples' phase composition became consistent. Consequently, the overall calcination time at 800 °C was 25 hours, whereas, at 1100 °C, it was 15 hours.

All samples were investigated by X-ray phase analysis on a DRON-3 diffractometer using Cu K_{α} radiation ($\lambda=1.54178$). The rotation speed of the counter during survey shooting to determine the phase composition of the samples was 2 degrees per minute. We used software such as the Match program and the PDF-2 (ICCD) and PDF-4 (ASTM) databases for phase examination (Brandenburg *et al.*, 2014; Roisnel, 2000; Rodriguez-Carvajal, 2016).

RESULTS AND DISCUSSION

The results shown in this section are mainly discussed and explained with the data on the system $(Pb_{10-x} Ba_x (PO_4)_6(OH)_2)$, which have not been published in any journal or conference before.

The Fig. (1) below shows the X-ray diffraction patterns of different samples ($x = 0.0; 1.0; 2.0; 3.0; 4.0; 5.0; 6.0; 7.0; 8.0; 9.0$ and 10) of the composition $(Pb_{10-x} Ba_x (PO_4)_6(OH)_2)$, which were prepared by the ceramic method (solid-state reaction) after calcinating the samples with the composition from $x=0$ to $x=5$ under a temperature of $800\text{ }^{\circ}\text{C}$ for 25 hours and samples with the composition from $x=6$ to $x=10$ under the temperature of $1100\text{ }^{\circ}\text{C}$ for 15 hours (Abdul Jabar *et al.*, 2020).

It can be seen from the Fig. (2) that the sample with $x=0$ showed only reflections of the phase with the pure lead hydroxyapatite structure $Pb_{10}(PO_4)_6(OH)_2$. Samples with the composition $x=1-6$, in addition to reflections of the lead hydroxyapatite structure, reveal more reflections called the "unknown phase". The relative intensity of the "unknown phase" reflections (peaks) is between 3 and 12 % compared to the maximum intensity of reflections of the hydroxyapatite structure since their intensity is independent of x (Getman *et al.*, 2011).

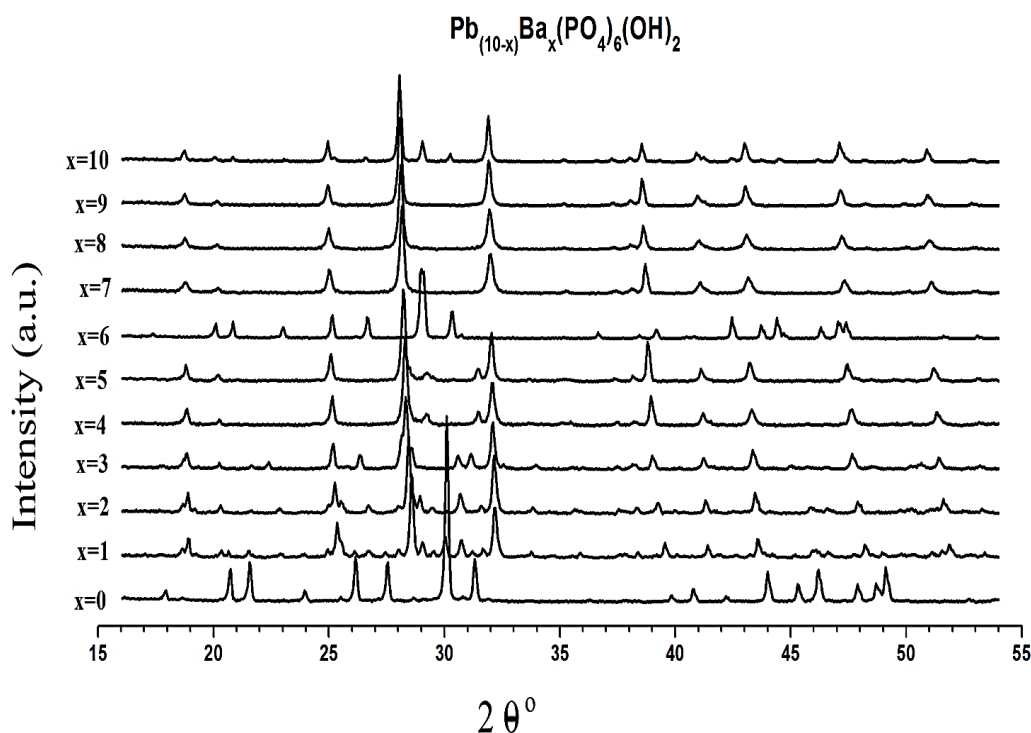


Fig. 1: Patterns of X-ray diffraction from samples (X=0-10) of the composition $(Pb_{10-x} Ba_x (PO_4)_6(OH)_2)$.

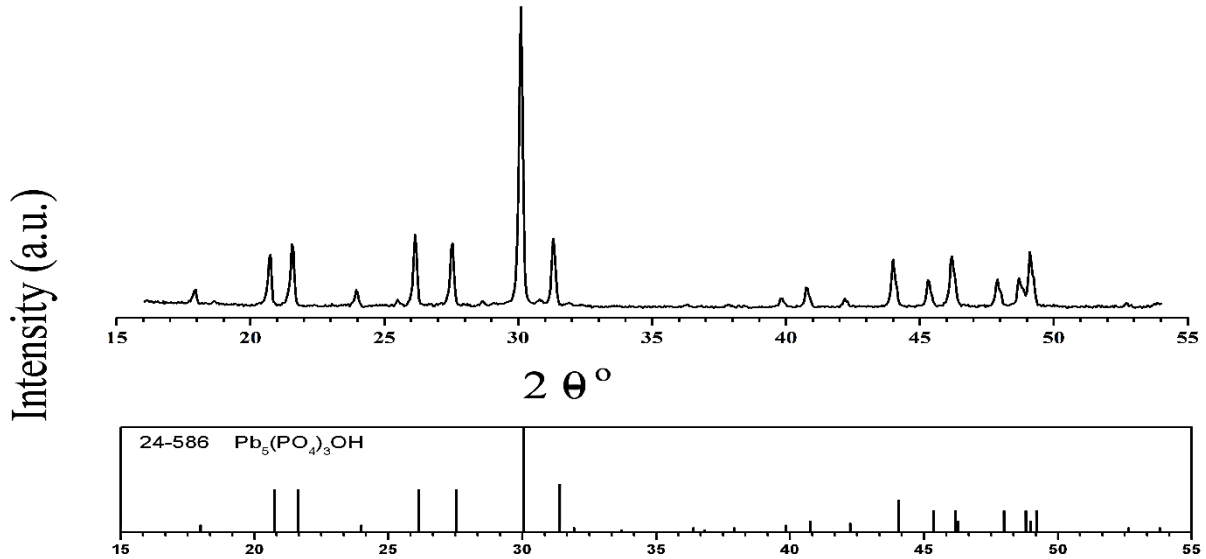


Fig. 2: Pattern of X-ray diffraction of the composition $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$, ($x=0.0$).

These unknown reflections, according to our opinion, have many reasons, including the inability to prevent the water in hot air from interacting with the components of hydroxyapatite; many side reactions that interfere with the hydroxyapatite compound inside the furnace; the presence of gaps within the composition of hydroxyapatite due to the differences in the ionic radii between the lead ions ($\text{Pb}^{2+}=119$) and barium ion ($\text{Ba}^{2+}=135$); that these reflections are superstructural; and finally it can be assumed that these reflections are reflections of secondary components that are not symmetrically included in the structure of the hydroxyapatite synthesis (Getman *et al.*, 2016).

In the samples with a range of compositions $x = 7 - 9$, the X-ray diffraction patterns show many reflections of the structure of barium hydroxyapatite $\text{Ba}_{10}(\text{PO}_4)_6(\text{OH})_2$, the intensity of which naturally increases with the value of x (Abdul Jabar *et al.*, 2018).

Fig. (3) demonstrates that the sample with $x=10$ exclusively displayed reflections of the pure barium hydroxyapatite structure $\text{Ba}_{10}(\text{PO}_4)_6(\text{OH})_2$.

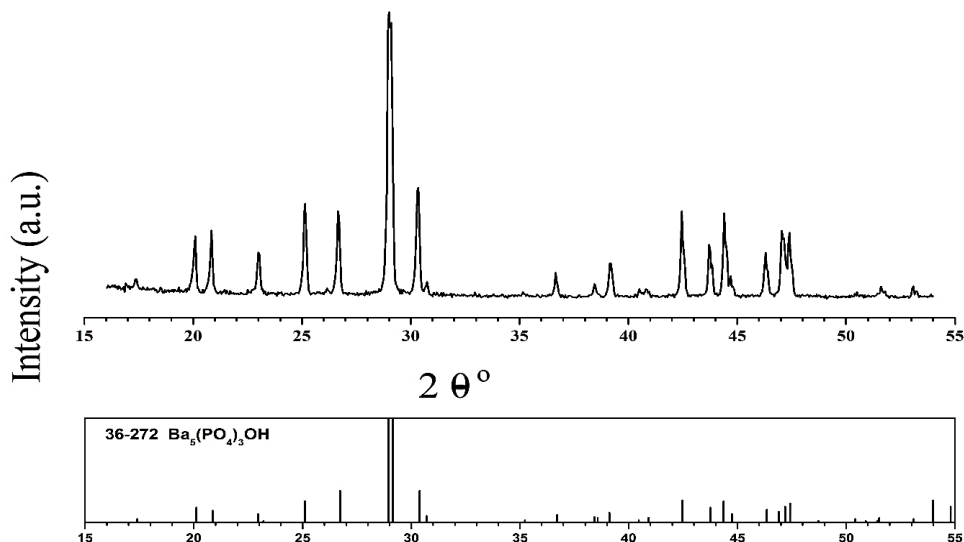


Fig. 3: Pattern of X-ray diffraction of the composition $(\text{Ba}_{10}(\text{PO}_4)_6(\text{OH})_2)$, ($x=10$).

CONCLUSION

In conclusion, X-ray diffraction was used to investigate the substitution of lead by barium in the structure of lead-barium hydroxyapatite ($\text{Pb}_{10-x}\text{Ba}_x(\text{PO}_4)_6(\text{OH})_2$) ($0 \leq x \leq 10$), following the scheme $\text{Pb}^{2+} + 2\text{OH}^- \rightarrow \text{Ba}^{2+} + 2\text{OH}^-$.

Pure Lead hydroxyapatite ($x = 0$) and barium hydroxyapatite ($x=10$) were successfully prepared by the ceramic method at 800 and 1100 °C, respectively. The time used to prepare the lead hydroxyapatite compound was (25 hours), while the time used to prepare the barium hydroxyapatite compound was (15 hours).

In the samples from $x = 1-9$, besides the pure lead-barium hydroxyapatite reflections, various side reflections appeared that overlapped with the pure lead-barium hydroxyapatite reflections. The reasons for the existence of these various repercussions can be explained by the following:

1. Incomplete substitutions in these samples.
2. The formation of additional side compounds such as nitrogen oxides or carbon dioxide gas is due to oxygen interference in hydroxyapatite compounds.
3. A vacancy (\square) could occur during the substitution process between lead and barium in the hydroxyapatite compound due to variations in the ionic radii of the lead (1.19 Å) and barium (1.34 Å) ions.

This paper is a preliminary introduction to many types of research still being worked on to develop alternative structures between lead, barium, strontium, and other elements, which can be useful for predicting the behavior of luminescent properties in different hydroxyapatite structures.

So, we recommend using the results of this study to improve the new process materials using lead-barium hydroxyapatite.

REFERENCES

- Abdel-Aal, E.; Abdel-Ghafar, H.; El-Sayed, D.; Ewais, E.M. (2022). Synthesis of high hardness hydroxyapatite particles using surfactant assisted hydrothermal method. *Int. J. Innov. Sci. Technol.*, **2**(1), 35-50.
- Abdul Jabar, M.; Getman, E.; Ignatov, A. (2018). New gadolinium-substituted lead sodium apatite structure. *Funct. Mater.*, **25**(4), 713-719.
- Abdul Jabar, M.; Ignatov, A. (2020). New synthesis of solid-solution lead hydroxyapatite (PbHAP) by ceramic and semi-ceramic methods. *J. Chem. Soc. Pak.*, **42**(3), 363-268.
- Brandenburg, K.; Putz, H. (2014). Match software for phase identification from powder diffraction data. Computer program.
- Fleet, M.; Liu, X.; Shieh, S. (2010). Structural change in lead fluorapatite at high pressure. *Phys. Chem. Minerals*, **37**, 1-9.
- Flis, J.; Borkiewicz, O.; Bajda, T.; Maneckia, M.; Klasaa, J. (2010). Synchrotron-based X-ray diffraction of the lead apatite series $\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2\text{-Pb}_{10}(\text{AsO}_4)_6\text{Cl}_2$. *J. Synchrotron Rad.*, **17**, 207-214.
- Getman, E.; Loboda, S.; Ignatov, A.; Abdul Jabar, M. (2011). Study the crystal structure of the composition $\text{Pb}_{8-x}\text{Eu}_x\text{Na}_2(\text{PO}_4)_{6-2-x/2}\text{O}_{x/2}$. *Scientif. Notes Tauride National University. V.I. Vernadsky. Sci. J.*, **24**(3), 48-56.
- Getman, E.; Loboda, S.; Ignatov, A.; Prisedsky, V.; Abdul Jabar, M.; Ardanova, L. (2016). Isomorphous substitution of rare-earth elements in lacunary apatite $\text{Pb}_8\text{Na}_2(\text{PO}_4)_6$. *J. Am. Chem. Soc.*, **55**(5), 2165-2173.
- Giera, A.; Manecki, M.; Bajda, T.; Rakovan, J.; Kwaśniak-Kominek, M.; Marchlewski, T. (2016). Arsenate substitution in lead hydroxyl apatite's: A Raman spectroscopic study. *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **152**, 370-377.
- Haider, T.; Mahmood, A. (2022). Study the susceptibility of epoxy-based composite materials reinforced with powders of different elements and compounds to be used as materials with a positive environmental impact. *Raf. J. Sci.*, **31**(12), 19-39.

- Hopwood, J.; Derrick, G.; Brown, D.; Newman, C.; Haley, J.; Kershaw, R.; Collinge, M. (2016). The Identification and synthesis of lead apatite minerals formed in lead water pipes. *J. Chem.*, **2016**, 1-11.
- Iconaru, S.; Motelica-Heino, M.; Guegan, R.; Beuran, M.; Costescu, A.; Predoi1, D. (2018). Adsorption of Pb (II) Ions onto hydroxyapatite Nano powders in aqueous solutions. *Materials*, **11**(11), 2204-2221.
- Liu, X.; Fleet, M.; Shieh, S.; He, Q. (2011). Synthetic lead bioapatite: X-ray structure at ambient pressure and compressibility up to about 20 GPa. *Phys. Chem. Minerals*, **38**, 397-406.
- Ptáček, P. (2016). "Apatite's and their Synthetic Analogues - Synthesis, Structure, Properties and Applications". Intech Open, Croatia, 512 p.
- Rodriguez-Carvajal, J. (2016). Foolproof. 2k. Computer program.
- Roisnel, T. (2000). WinPLOTR: a Windows tool for powder diffraction patterns analysis. *Materials Science Forum, Proceedings of the Seventh European Powder Diffraction Conference (EPDIC 7)*, **378-381**, 118-123.
- Savankova, T.; Akselrud, L.; Ardanova, L.; Ignatov, A.; Getman, E.; Gladyshevskii, R.; Loboda, S. (2014). Synthesis, crystal structure refinement, and electrical conductivity of $Pb_{(8-x)}Na_2Sm_x(VO_4)_6O_{(x/2)}$. *J. Chem.*, **2014**, 1-7.
- Sugiyama, S.; Nakanishi, T.; Ishimura, T.; Toshihiro, M.; Hiromu, H.; Naoya, S.; Moffat, J. (1999). Preparation, characterization, and thermal stability of lead hydroxyapatite. *J. Solid State Chem.*, **143** (2), 296-302.
- Tbeen, M.; Al sheikh, A. (2021). Size dependent thermo elastic properties of nano lead sulfide (PbS) under high pressure. *Raf. J. Sci.*, **30**(3), 12-20.
- Zhu, Y.; Huang, B.; Zhu, Z.; Liu, H.; Huang, Y.; Zhao, X.; Liang, M. (2016). 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**(2), 1-18.
- Zhu, Y.; Zhu, Z.; Yang, F.; Huang, Y.; Zhao, X. (2015). Synthesis of the Lead-Calcium HAP solid solutions. *Russ. J. Appl. Chem.*, **88**(1), 178-183.

تحديد وتوليف هيكل هيدروكسيباتيت الرصاص المستبدل بالباريوم $(Pb_{10-x}Ba_x(PO_4)_6(OH)_2)$ بطريقة السيراميك

محمد عبد الباسط عبد الجبار
كلية العلوم / جامعة الكرخ للعلوم

الملخص

تم فحص استبدال أيون الباريوم (Ba^{2+}) بأيون الرصاص (Pb^{2+}) في التركيب التالي: $Pb_{10-x}Ba_x(PO_4)_6(OH)_2$ بواسطة جهاز مقياس حيود الأشعة السينية. تم تكليس العينات ذات المدى بين $x=0$ وحتى $x=5$ عند 800 درجة مئوية سيليزية ولمدة 25 ساعة، وتم تكليس العينات ذات المدى بين $x=6$ وحتى $x=10$ عند 1100 درجة مئوية سيليزية ولمدة 15 ساعة. تم تحضير عينات المحاليل الصلبة للهيدروكسيباتيت بطريقة السيراميك. ثبت أن العينة مع $x = 0$ أظهرت فقط انعكاسات تكوين $Pb_{10}(PO_4)_6(OH)_2$ ، بينما أظهرت العينة ذات $x = 10$ انعكاسات التركيب $Ba_{10}(PO_4)_6(OH)_2$ فقط. أظهرت العينات ذات المدى بين $x=1$ وحتى $x=9$ عن انعكاسات أكثر تسمى "طور غير معروف" إلى جانب انعكاسات هيدروكسيباتيت النقي.

الكلمات الدالة: رصاص، اباتيت، باريوم، استبدال، محلول صلب.