Full Paper

SciRad SCIENTIAE RADICES

Thermal treatment effect on the particle size distribution of alkaline earth metals hydroxyapatite

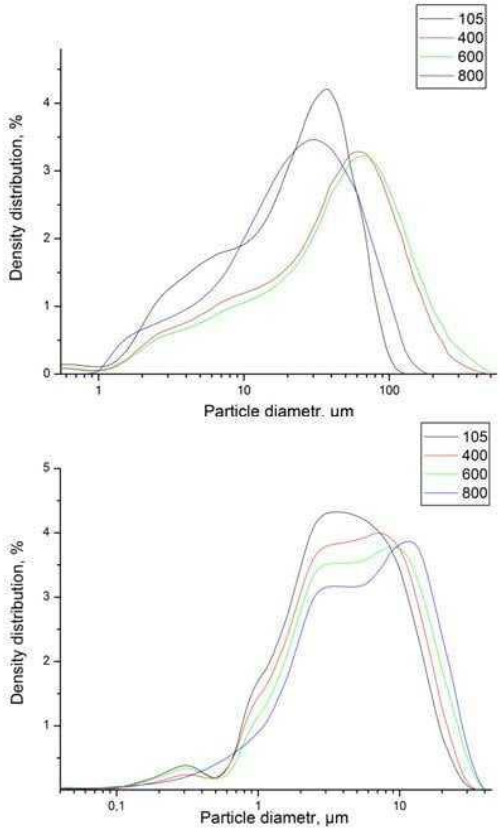
Volodymyr Diichuk[(1)], Iryna Diichuk[(2)] ✉

[(1)] Yurii Fedkovych Chernivtsi National University, Chernivtsi, Ukraine,
[(2)] Bukovinian State Medical University, Chernivtsi, Ukraine

✉ Correspondence to: v.diychuk@chnu.edu.ua

Phase composition
$Ca_5(PO_4)_3OH$
$Sr_5(PO_4)_3OH$
$Ba_5(PO_4)_3OH$, $Ba_3(PO_4)_2$
$Mg_5(PO_4)_3OH$, $MgHPO_4 \cdot 3H_2O$

$$D = \frac{K\lambda}{\beta \cos\theta}$$



Abstract: Hydroxyapatites of certain alkaline earth metals were synthesised, and their phase composition was determined using X-ray phase analysis. Thermal modification of the studied compounds was performed at temperatures not exceeding 800°C. The laser

diffraction method determined the size distribution of the samples subjected to thermal treatment. It was found that the mean particle size ranged from 5,48±1,28 to 126,71±3,68 μm. It has been demonstrated that particle aggregation and fragmentation processes are possible depending on the synthesised compounds' qualitative and quantitative phase composition and the modification temperature.

Keywords: hydroxyapatites, phase composition, thermal treatment, particle size distribution

Received: 2023.07.20
Accepted: 2023.09.28
Published: 2023.10.11
DOI: 10.58332/scirad2023v2i4a01

Introduction

The modern development of functional materials requires the study of various methods for forming their properties. Thermal treatment is one of the key methods applied to modify the properties of materials affecting their structure, morphology, dispersion, surface condition, and other parameters [1-3].

Hydroxyapatites have wide applications in various fields [4-6]. Calcium hydroxyapatite is the most extensively studied and used in medicine and biomaterials science as bone graft substitutes to promote bone regeneration, as coatings on implants to enhance osseointegration, dental restorations, drug delivery, and so on [7-9]. Calcium phosphates are also used in the pharmaceutical and cosmetic industries [10, 11], for water purification [12], etc.

Hydroxyapatite can be synthesized using precipitation, sol-gel processes, hydrothermal synthesis, and others [13, 14]. It can also be extracted from natural sources, such as animal bones and scales which are rich in hydroxyapatite content [15 16].

The particle size of hydroxyapatites is of significant importance for their applications, as it directly affects their sorption, catalytic, antimicrobial, and other properties [17-19]. Despite considerable research on the effect of temperature on the properties of hydroxyapatites, information regarding the impact of thermal treatment on particle sizes remains quite limited.

Therefore, this study aimed to investigate the dependence of particle size distribution of alkaline earth metal hydroxyapatites on the temperature of thermal treatment. Hydroxyapatites of alkaline earth metals were synthesized, and their phase composition was determined. The obtained samples were heat treated, and particle size distribution was studied.

Results and discussion

The phase composition of the synthesized compounds.

The surface properties of substances depend on their phase composition, structure, morphology, dispersion, and so on [20, 21]. During thermal treatment, processes such as thermal decomposition, pore formation, increased specific surface area, or conversely, sintering, decreased specific surface area, and as a result, surface activity passivation can occur [22]. In this context, it was interesting to study how different modes of thermal treatment affect the particle size of the synthesized materials.

The results of the XRD phase composition study of synthesized compounds of alkaline earth metals are shown in Table 1.

Table 1. The phase composition of the synthesized compounds after drying at 105°C.

Compounds of …	Phase composition
Calcium	$Ca_5(PO_4)_3OH$
Strontium	$Sr_5(PO_4)_3OH$
Barium	$Ba_5(PO_4)_3OH$, $Ba_3(PO_4)_2$,
Magnesium	$Mg_5(PO_4)_3OH$, $MgHPO_4 \cdot 3H_2O$

The thermal treatment of the investigated compounds was carried out at temperatures not exceeding 800°C. The change in the mass to the mass of samples dried at 105 °C was studied. The most minor mass loss during heat treatment was observed for barium compounds: 0.4% at 400°C, 1.9% at 600°C and 2.5% at 800°C. These results indicate a loss of volatile sorbed components at 400 °C and changes in structure or phase composition at 600°C and above. Similar behaviour was observed for calcium and strontium compounds. The mass loss of magnesium compounds during processing in the temperature range from 400 to 800°C was from 3.8 to 4.1%. Such a significant mass loss at 400°C is caused by the decomposition of the crystallohydrate phase (Table 1).

Particle size distribution of thermally modified samples.

The effect of processing temperature on the size distribution of calcium hydroxylapatite particles is shown in Fig. 1.

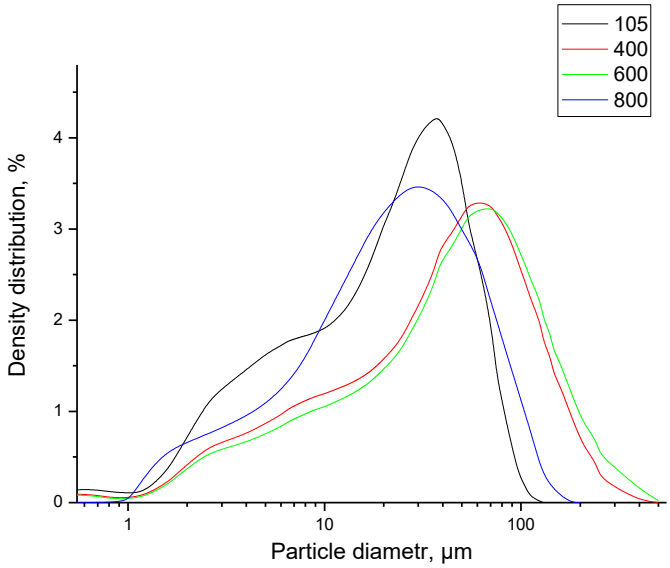


Fig. 1. Size distribution of calcium hydroxylapatite particles after thermal treatment at 105, 400, 600, and 800°C.

As seen from Figure 1 and Table 2, for calcium hydroxyapatite dried at 105°C, 90% of the particles (D90 or 90th percentile) have a size not exceeding 51.95 μm. Increasing the processing temperature to 400 and 600°C leads to particle agglomeration, with D90 values of 114.51 μm and 129.29 μm, respectively. The sizes of samples modified at 800°C do not differ significantly from those dried at 105°C, with D90 measuring 60.71 μm.

Table 1. Particle size distribution of thermally modified compounds

Compounds of …	Modification temperature, °C	Mean size, μm	D90, μm
Calcium	105	24,66±2,60	51,95
	400	52,52±2,86	114,51
	600	59,85±2,89	129,29
	800	28,05±2,85	60,71
Strontium	105	11,19±2,17	21,65
	400	17,17±2,25	33,81
	600	22,48±2,22	44,41
	800	10,01±1,95	18,57
Barium	105	5,48±1,28	11,48
	400	6,11±2,82	12,90
	600	6,92±3,00	14,95
	800	7,68±2,84	16,35
Magnesium	105	10,15±1,75	17,95
	400	11,89±1,84	21,44
	600	11,17±1,89	20,31
	800	126,71±3,68	295,91

A similar character of particle size distribution after thermal treatment is observed for strontium hydroxylapatite (Fig. 2, Table 2).

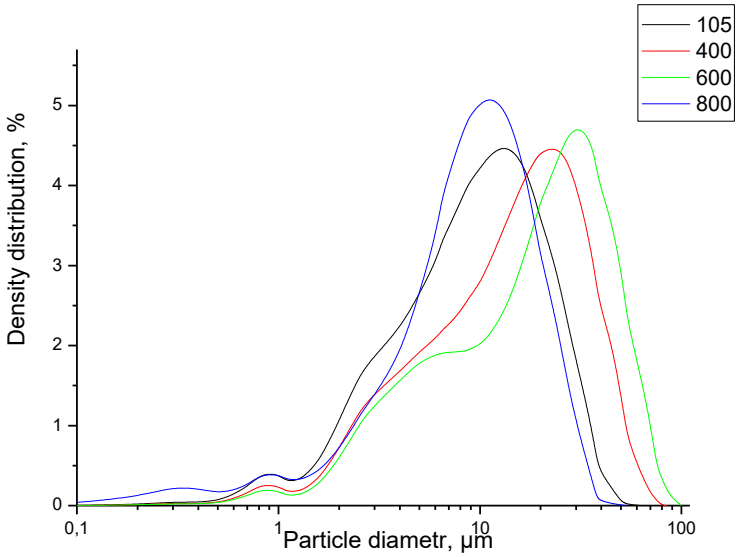


Fig. 2. Size distribution of strontium hydroxylapatite particles after thermal treatment at 105, 400, 600, and 800°C.

For samples dried at 105°C, the 90th percentile did not exceed 21.65 μm, while increasing the modification temperature to 400 and 600°C resulted in particle agglomeration (33.81 μm and 44.41 μm, respectively). Treatment at 800°C affects a decrease in particle size (D90 - 18.57 μm). Light scattering analysis agrees well with light microscopy images of the particles.

Therefore, according to the results of X-ray phase analysis, the synthesised calcium and strontium compounds are in the form of hydroxyapatites, which confirms a similar particle size distribution pattern during thermal processing.

The synthesised barium compounds also contain barium phosphate in addition to hydroxyapatite (Table 1). The particle size distribution after thermal treatment is shown in Figure 3 and Table 2.

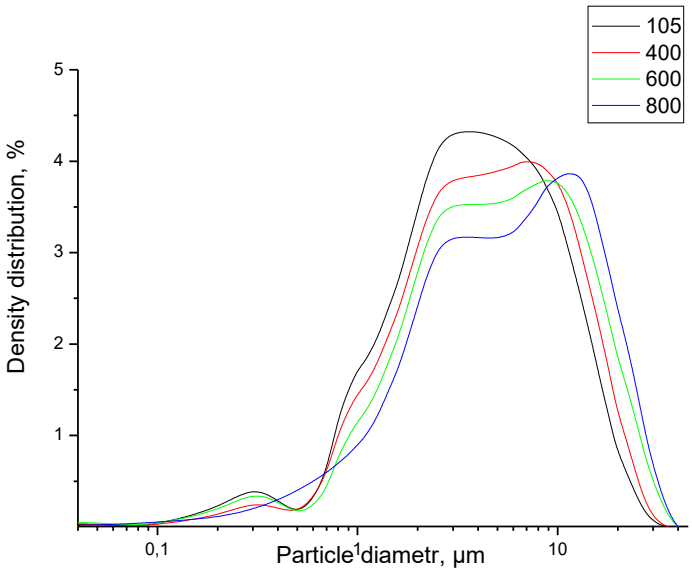


Fig. 3. Particle size distribution of barium phosphorus-containing compounds after thermal treatment at 105, 400, 600 and 800°C.

As evident from the obtained data for barium phosphorus-containing compounds, increasing the modification temperature leads to a slight increase in particle size (D90 ranging from 11.48 to 16.35 μm) for all investigated temperatures.

The particle size distribution for magnesium compounds after thermal processing differs from one of the other investigated compounds (Fig.4., Table 2).

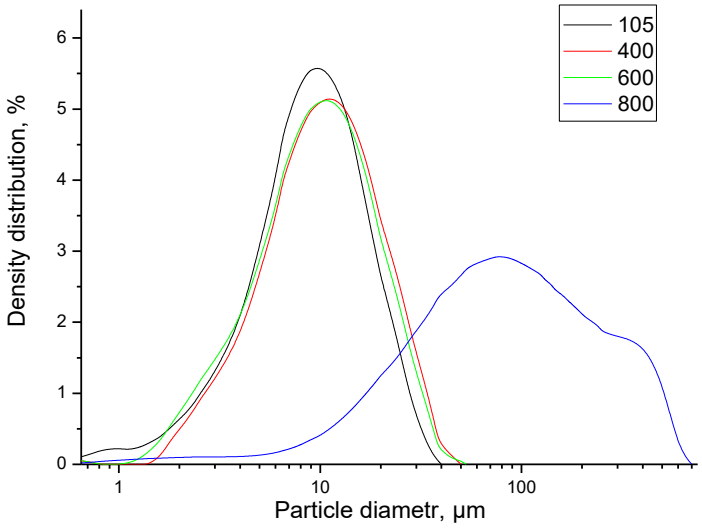


Fig. 4. Particle size distribution of magnesium phosphorus-containing compounds after thermal treatment at 105, 400, 600 and 800°C.

During the thermal processing of magnesium compounds at 400°C and 600°C, the particle sizes do not differ significantly from the sizes of samples dried at 105°C (ranging from 17.95 to 21.44 μm). However, increasing the modification temperature to 800°C leads to a more than 10-fold increase in particle size, with a D90 value of 295.91 μm under these conditions. The obtained results indicate that significant changes in the structure and morphology of the synthesized magnesium compounds occur during thermal processing at 800°C.

The size of the crystallites calculated from XRD data with the Debye-Scherrer equation was estimated as 3-8 nm for all studied phases which proves the complex internal structure of the particles, not seen by other methods.

Material and methods

Studied compounds were synthesized by the sedimentation of the corresponding salts from ammonium-alkaline solutions similar to the synthesis of calcium hydroxyapatite described in [23] according to the reaction:

$$10Me(NO_3)_2 + 6(NH_4)_2HPO_4 + 8NH_4OH = Me_{10}(PO_4)_6(OH)_2 + 20NH_4NO_3 + 6H_2O$$

where Me: Ca, Sr, Ba or Mg.

The phase composition of the dried at 105°C samples was investigated by XRD phase analysis. It was performed with a monochromatic Cu kα x-ray source.

Then the samples were thermally treated at 400, 600, and 800°C for 3 hours until a stable weight was reached.

The particle size determination of thermally modified compounds was performed using a laser diffractometer PSA 1190 by Anton Paar company.

Conclusions

It has been shown that depending on the qualitative and quantitative phase composition and the temperature of modifications, both particle aggregation and fragmentation processes of the synthesised compounds are possible. The synthesised compounds of calcium and strontium had a similar phase composition - hydroxyapatites, as a result, similar pattern particle size changes during thermal treatment. Barium compounds were in the form of hydroxyapatite and sulfate. Thermal treatment at 105 to 800°C led to insignificant particle aggregation. Magnesium compounds consisted of hydroxyapatite and trihydrate hydrogen phosphate phases. Thermal modification up to 600°C had little effect on

particle sizes, while at 800 °C, significant particle agglomeration occurred, with particle size exceeding more than 10 times.

Therefore, thermal modification can be used for controlled change in the dispersion, structure, morphology and other parameters of alkali-earth metals hydroxyapatites to manage their properties.

Acknowledgements

The authors acknowledge the administration and employees of the Chemical Engineering and Technology Faculty of the Cracow University of Technology for the XRD phase analysis and Donau Lab Ukraine for particle size analysis.

References

[1] Regonini, D.; Jaroenworaluck, A.; Stevens, R. & Bowen, C.R.; Effect of heat treatment on the properties and structure of TiO2 nanotubes: Phase composition and chemical composition. *Surface and Interface Analysis*, **2010** 42 (3), 139-144. DOI: 10.1002/sia.3183

[2] Salman, O.O.; Gammer, C.; Chaubey, A.K.; Eckert, J.; Scudino, S.; Effect of heat treatment on microstructure and mechanical properties of 316L steel synthesized by selective laser melting. *Materials Science and Engineering: A*, **2019**, 748, 205-212. DOI: 10.1016/j.msea.2019.01.110

[3] Shunmuga Priya, R.; Priyanka Chaudhary; Ranjith Kumar, E. et al.; Effect of heat treatment on structural, morphological, dielectric and magnetic properties of Mg–Zn ferrite nanoparticles. *Ceramics International*, **2022**, 48 (11), 15243-15251. DOI:_10.1016/j.ceramint.2022.02.056

[4] Sans, J.; Arnau, M.; Sanz, V.; Turon, P.; Alemán, C.; Hydroxyapatite-based biphasic catalysts with plasticity properties and its potential in carbon dioxide fixation. *Chemical Engineering Journal*, **2022**, 433(2) 133512, DOI: 10.1016/j.cej.2021.133512

[5] Fiume E.; Magnaterra G., Rahdar A.; Verné E.; Baino F.; Hydroxyapatite for Biomedical Applications: A Short Overview. *Ceramics* **2021**, 4 (4), 542-563. DOI: 10.3390/ceramics4040039

[6] De Lima, C.O.; de Oliveira, A.L.M.; Chantelle, L.; Silva Filho, E.C.; Jaber, M.; Fonseca, M.G.; Zn-doped mesoporous hydroxyapatites and their antimicrobial properties. *Colloids and Surfaces B: Biointerfaces*, **2021**, 198, 111471. DOI: 10.1016/j.colsurfb.2020.111471

[7] Shi, H.; Zhou, Z.; Li, W.; Fan, Y.; Li, Z.; Wei, J.; Hydroxyapatite Based Materials for Bone Tissue Engineering: A Brief and Comprehensive Introduction. *Crystals*, **2021**, 11 (2), 149. DOI: 10.3390/cryst11020149

[8] Lett, J. A.; Sagadevan, S.; Fatimah, I.; Hoque, E.; Lokanathan, Y. et al.; Recent advances in natural polymer-based hydroxyapatite scaffolds: Properties and applications. *European Polymer Journal*, **2021**, 148, 110360 DOI: 10.1016/j.eurpolymj.2021.110360

[9] Lara-Ochoa, S.; Ortega-Lara, W.; Guerrero-Beltrán, CE.; Hydroxyapatite Nanoparticles in Drug Delivery: Physicochemistry and Applications. *Pharmaceutics*. **2021**, 13 (10), 1642. DOI: 10.3390/pharmaceutics13101642

[10] Wagner, M.; Hess, T.; Zakowiecki, D.; Studies on the pH-Dependent Solubility of Various Grades of Calcium Phosphate-based Pharmaceutical Excipients. *Journal of Pharmaceutical Sciences*, **2022** 111 (6), 1749-1760. DOI: 10.1016/j.xphs.2021.12.005

[11] Carella, F.; Degli Esposti, L.; Adamiano, A.; Iafisco, M.; The Use of Calcium Phosphates in Cosmetics, State of the Art and Future Perspectives. *Materials* **2021**, 14, 6398. DOI: 10.3390/ma14216398

[12] Brazdis, R.I.; Fierascu, I.; Avramescu, S.M.; Fierascu, R.C.; Recent Progress in the Application of Hydroxyapatite for the Adsorption of Heavy Metals from Water Matrices. *Materials* **2021**, 14, 6898. DOI: 10.3390/ma14226898

[13] Pu'ad, N.A.S.M.; Haq, R.H.A.; Noh, H.M.; Abdullah, H.Z.; Idris, M.I.; Lee, T.C.; Synthesis method of hydroxyapatite: A review, *Materials Today: Proceedings*, **2020**, 29 (1), 233-239. DOI: 10.1016/j.matpr.2020.05.536

[14] Agbeboh, N.I.; Oladele, I.O.; Daramola, O.O.; Adediran, A.A. et al.; Environmentally sustainable processes for the synthesis of hydroxyapatite. *Heliyon*. **2020,** 6 (4), e03765. DOI: 10.1016/j.heliyon.2020.e03765

[15] Bee, S.-L.; Hamid, Z.A.A; Hydroxyapatite derived from food industry bio-wastes: Syntheses, properties and its potential multifunctional applications. *Ceramics International*, **2020,** 46 (11), 17149-17175. DOI:10.1016/j.ceramint.2020.04.103

[16] Abdelraof, M.; Farag, M.M.; Al-Rashidy, Z.M. et al.; Green Synthesis of Bioactive Hydroxyapatite/Cellulose Composites from Food Industrial Wastes. *J Inorg Organomet Polym,* **2022**, 32, 4614–4626. DOI: 10.21203/rs.3.rs-1670361/v1

[17] Dinda, G.P.; Shin, J.; Mazumder, J.; Pulsed laser deposition of hydroxyapatite thin films on Ti–6Al–4V: Effect of heat treatment on structure and properties. *Acta Biomaterialia*, **2009**, 5 (5), 1821-1830. DOI: 10.1016/j.actbio.2009.01.027

[18] Liu, Q.; Matinlinna, J. P.; Chen, Zh.; Ning, Ch. et al.; Effect of thermal treatment on carbonated hydroxyapatite: Morphology, composition, crystal characteristics and solubility. *Ceramics International*, **2015**, 41 (5), 6149-6157. DOI: 10.1016/j.ceramint.2014.11.062

[19] Fukada, M.; Chhetri, T.; Suresh, A.; Upendran, A.; Afrasiabi, Z.; Size and Morphology-Mediated Antiproliferative Activity of Hydroxyapatite Nanoparticles in Human Breast Cancer Cells. *Journal of Nanotechnology*, **2023**, 1-8. DOI: 10.1155/2023/5381158

[20] Oh, S.Ch.; Xu, J.; Tran, D.T.; Liu, B.; Liu, D.; Effects of Controlled Crystalline Surface of Hydroxyapatite on Methane Oxidation Reactions. *ACS Catal.,* **2018**, *8* (5), 4493-4507. DOI: 10.1021/acscatal.7b04011

[21] Huda, S. A.; Keshk, A. A.; Ghareeb, R. Y.; Ibrahim, A. A. et. al.; Physico-chemical and biological responses for hydroxyapatite/ZnO/graphene oxide nanocomposite for biomedical utilization. *Materials Chemistry and Physics*, **2022**, 283, 125988. DOI: 10.1016/j.matchemphys.2022.125988

[22] Tripković, D.; Wang, J.; Küngas, R. et. al.; Thermally Controlled Activation and Passivation of Surface Chemistry and Oxygen-Exchange Kinetics on a Perovskite Oxide *Chemistry of Materials* , **2022,** *34* (4), 1722-1736. DOI: 10.1021/acs.chemmater.1c03901

[23] Narasaraju, T.S.B.; Phebe, D.E; Some physico-chemical aspects of hydroxylapatite. *Journal of Materials Science,* **1996**, 31, 1–21. DOI: 10.1007/BF00355120