

RESEARCH ARTICLE

## Survey and Evaluation of Hardystonite Nanostructure (HTN) Bioactivity in Biomedical Engineering

Hassan Gheisari Dehsheikh <sup>1</sup>, Ebrahim Karamian <sup>2</sup>, Mohammad Farokhi Alakouhi <sup>3</sup>

<sup>1,2,3</sup> Advanced Materials Research Center, Department of Materials Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Iran

<sup>1</sup> Institute of Biomaterials and Biomedical Engineering, University of Toronto, Toronto, ON, Canada

### ABSTRACT

#### ARTICLE INFO

##### Article History:

Received 2022-03-17

Accepted 2022-05-26

Published 2023-02-15

##### Keywords:

Hardystonite,

Bioactivity,

Hydroxyapatite,

Nanomaterials,

SBF.

Hardystonite (HT) is a monoclinic pyroxene mineral with the composition  $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ . Lately, hardystonite (HT) has been introduced as a bioceramic due to its bioactivity and biocompatibility. It has better strength and toughness than that of hydroxyapatite (HA). In this project, the bioactivity of hardystonite (HT) powder was evaluated and investigated. Hardystonite (HT) powder was synthesized using zinc (Zn) calcite ( $\text{CaCO}_3$ ), and nanosilicium ( $\text{SiO}_2$ ) powders that were mechanically activated for different times. After that, the prepared powders were blended with ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and put on at various temperatures. In this part, for the survey of bioactivity evaluation, the obtained hardystonite (HT) powders were pressed and immersed in Kokubo solution (SBF). The results indicated that nano-structure hardystonite powder had a crystalline size of 40 nm. The apatite formation ability, bioactivity, and good mechanical behavior make it a good candidate for bone implant materials and open new insights in biomedical engineering.

#### How to cite this article

Gheisari Dehsheikh H., Karamian E., Farokhi Alakouhi M., Survey and Evaluation of Hardystonite Nanostructure (HTN) Bioactivity in Biomedical Engineering. J. Nanoanalysis., 10(1): 414-418, Winter 2023. 10.22034/jna.2022.1955260.1297

## INTRODUCTION

The composition of hydroxyapatite (HA) is very similar to bone; its very weak mechanical behavior limits the use of this material in load bearing applications [1, 2]. So, finding some substitutions is necessary for load bearing in medical applications. Recently, some research has indicated that some

compounds from the magnesia– silica and calcite systems are bioactive and used in dental prostheses [3, 6]. Hardystonite (HT) and enstatite are such good biomaterials that belong to the olivine group. HT is a machinable bioceramic with chemical formula of  $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ . That is a different polymorph. A metastable form, clinoenstatite, can be formed from

\*Corresponding Author Email: [Hassan.gh.d@gmail.com](mailto:Hassan.gh.d@gmail.com)



This work is licensed under the Creative Commons Attribution 4.0 International License.

To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

protoenstatite, depending on temperature, pressure, and internal stresses in size [7]. For changes of enstatite structure can cause volume changes and produce intrinsic stress, and this material used in medical applications [8].

On the opposite, HT does not have destroyed volume changes and, due to its good bioactivity, may be used as a good enstatite bioceramic. While HT has good biocompatibility and better mechanical behavior than those of HA, its bioactivity is poor [9]. Moreover, nanostructured bioceramics have better bioactivity than micron-sized structures [10]. The goal of this project was to study the hardystonite (HT) nanostructure bioactivity of SiO<sub>2</sub>, CaCO<sub>3</sub>, and Zn in the presence of chlorine ions. Also, the bioactivity of the single-phase nanostructured HT powder was investigated by the standard method.

## EXPERIMENTAL

### *Materials and Methods*

The composition of hydroxyapatite (HA) is very similar to bone; it's very weak mechanical behavior limits the use of this materials in load bearing applications [1, 2]. So, finding some substitutions is necessary for load bearing in medical applications. Recently, some research has indicated that some compounds from the magnesia– silica and calcite systems are bioactive and used in dental prostheses [3, 6]. Hardystonite (HT) and enstatite are such good biomaterials that belong to the olivine group. HT is a machinable bioceramic with chemical formula of Ca<sub>2</sub>ZnSi<sub>2</sub>O<sub>7</sub>. That is a different polymorph. A metastable form, clinoenstatite, can be formed from protoenstatite, depending on temperature, pressure, and internal stresses in size [7]. For changes of enstatite structure can cause volume changes and produce intrinsic stress, and this material used in medical applications [8].

On the opposite, HT does not have destroyed volume changes and, due to its good bioactivity, may

be used as a good enstatite bioceramic. While HT has good biocompatibility and better mechanical behavior than those of HA, its bioactivity is poor [9]. Moreover, nanostructured bioceramics have better bioactivity than micron-sized structures [10]. The goal of this project was to study the hardystonite (HT) nanostructure bioactivity of SiO<sub>2</sub>, CaCO<sub>3</sub>, and Zn in the presence of chlorine ions. Also, the bioactivity of the single-phase nanostructured HT powder was investigated by the standard method.

## RESULTS AND DISCUSSION

The X-ray diffraction pattern and crystallite size of nanostructured HT powder are shown in Fig. 1a and b. All the X-ray peaks showed HT structure. As it is clear in Fig. 1b, the crystallite sizes of the HT powder obtained were 40 nm.

To determine the magnesium and calcium ion concentrations in the simulated body fluid, an atomic absorption spectrometer test was performed. The results of the atomic absorption spectrometer test and the pH of the simulated body fluid are shown in the Fig. 2. As can be seen, the pH and magnesium ion concentration and decreasing the calcium ion concentration in the simulated body fluid were the overall consequences of soaking the samples. The findings revealed that on the first day of soaking, the ion concentration and pH of the simulated body fluid solution had the most changes. With increasing soaking time, calcium ion concentration decreased with a smooth slope due to the consumption of these ions and the formation of apatite on the surface of HT samples.

Fig. 2d compares the FTIR of the surfaces of the prepared HT bulk samples before and after soaking in the simulated body fluid solution. The bands related to the investigation bands of HT appeared at 1010, 971, 882, and 842 cm<sup>-1</sup> (SiO<sub>4</sub>), at 621, 531, and 512 cm<sup>-1</sup> (SiO<sub>4</sub> bending), and at 481 cm<sup>-1</sup> for modes of octahedral ZnO<sub>6</sub>, which is in better agreement with previous studies [12]. After immersing the samples in

the simulated body fluid solution for different times, new absorption bands relating to O–H, C–O, and P–O were observed. The bands at 3650 and 1632  $\text{cm}^{-1}$  belonged to hydroxyl ion groups in the HT.

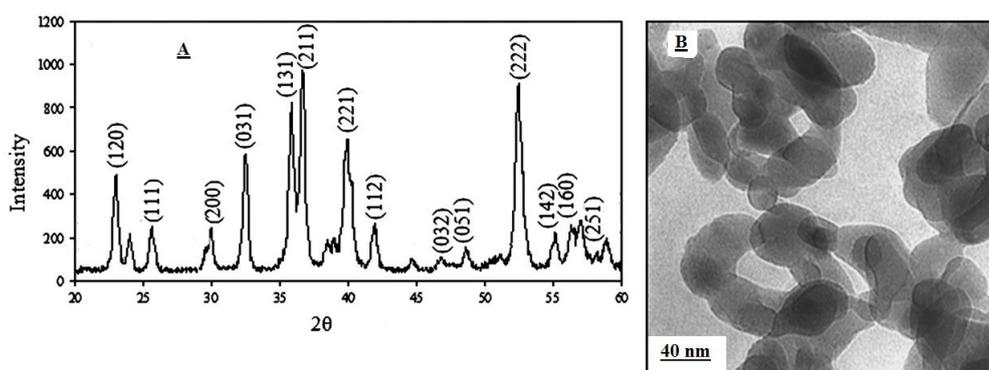


Fig. 1. (A), X-ray diffraction pattern and (B) transmission electron microscopy (TEM) image of the obtained HT powder after 10 h of mechanical activation

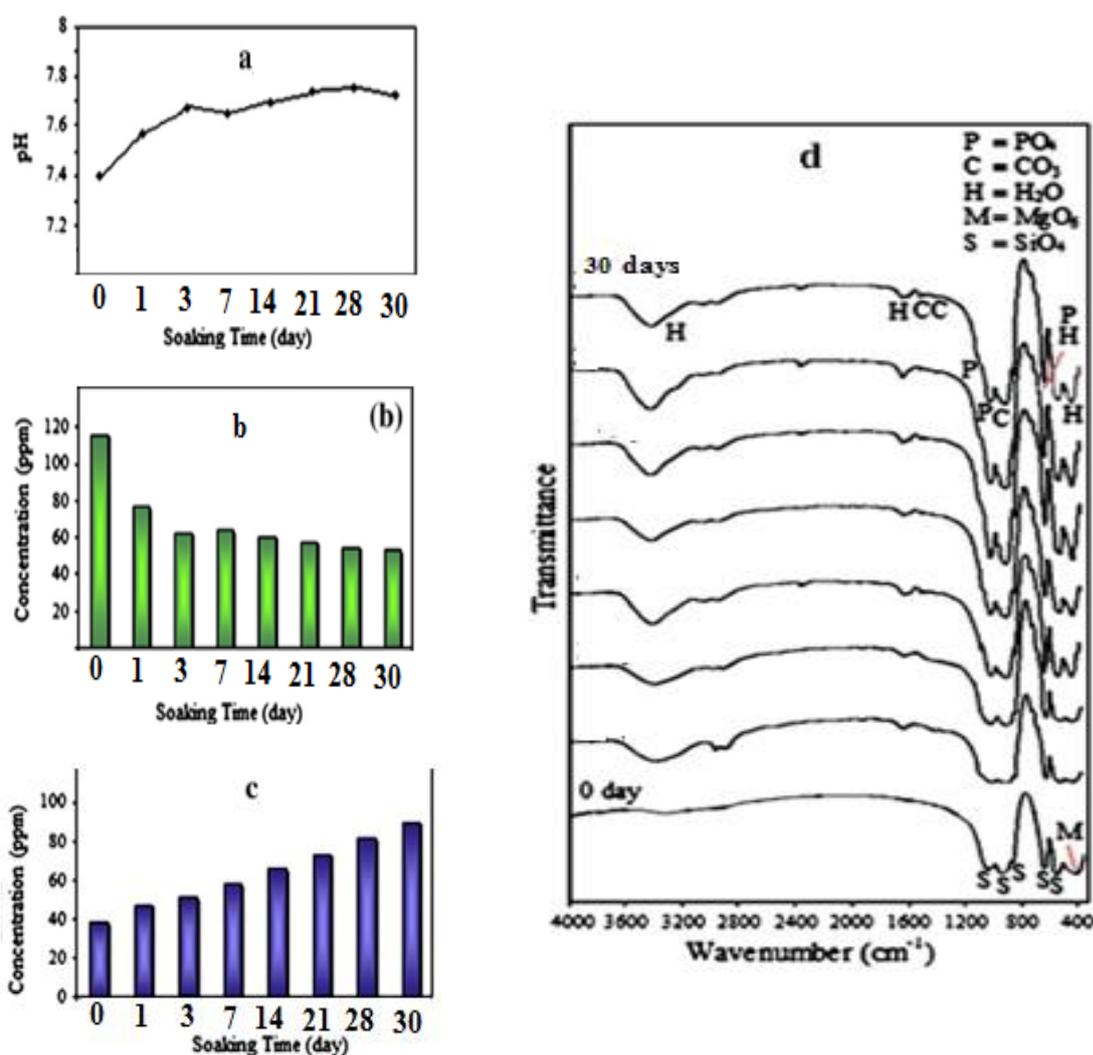


Fig. 2. The variations of (a) pH, (b) Ca, and (c) Mg ion concentration of the simulated body fluid, after soaking the nanostructure HT ceramics and (d) FTIR spectra of nanostructured HT soaked in the SBF for different periods of time.

Those bands at 1471 and 1431  $\text{cm}^{-1}$  fit with bands in the carbonate groups of apatite. Also, the band at 881  $\text{cm}^{-1}$  was assigned to carbonate groups that could be distinguished at higher soaking times in the simulated body fluid solution. Also, the bands related to phosphate groups were situated at 1110–1040, 611, and 581  $\text{cm}^{-1}$ . With increasing the soaking time, the absorption bands of all O–H, C–O, and P–O bands got stronger because the formation of a higher amount of HT on the surface of HT samples. Fig. 3 indicates the surfaces morphology and energy dispersive spectroscopy spectra of the HT samples after immersion in the simulated body fluid solution for 21 and 30 days. After 14-day soaking, small particles were observed on the surface of the HT samples with cauliflower shape. The energy dispersive spectroscopy spectra showed that these particles are composed of Ca and phosphorus. By increasing the soaking time, the HT grew and their size increased. Moreover, the energy dispersive spectroscopy (EDS) spectra proved the presence of Ca and phosphorus in this specimen. With

the results of FTIR patterns and changes in the ion concentration in the simulated body fluid solution, it is expected that the formed deposits were hydroxyapatite (HA).

The bone-bonding ability of a material is evaluated by examining the ability of apatite to form on its surface in a simulated body fluid with ion concentrations nearly equal to those of human blood plasma. It was proposed that the examination of apatite formation on a material in simulated body fluid solution is useful for predicting the in vivo bone bioactivity of a material. Our findings suggested that nanostructured HT powder had apatite formation ability and was bioactive. With dissolution of HT in a simulated body fluid solution, some preferable locations were formed on the ceramic surface, which improved the apatite formation ability of nanostructured HT. Finally, the release of Mg ions from nanostructure HT ceramics into a simulated body fluid solution medium was quantitatively estimated to support its in vitro bioresorbability.

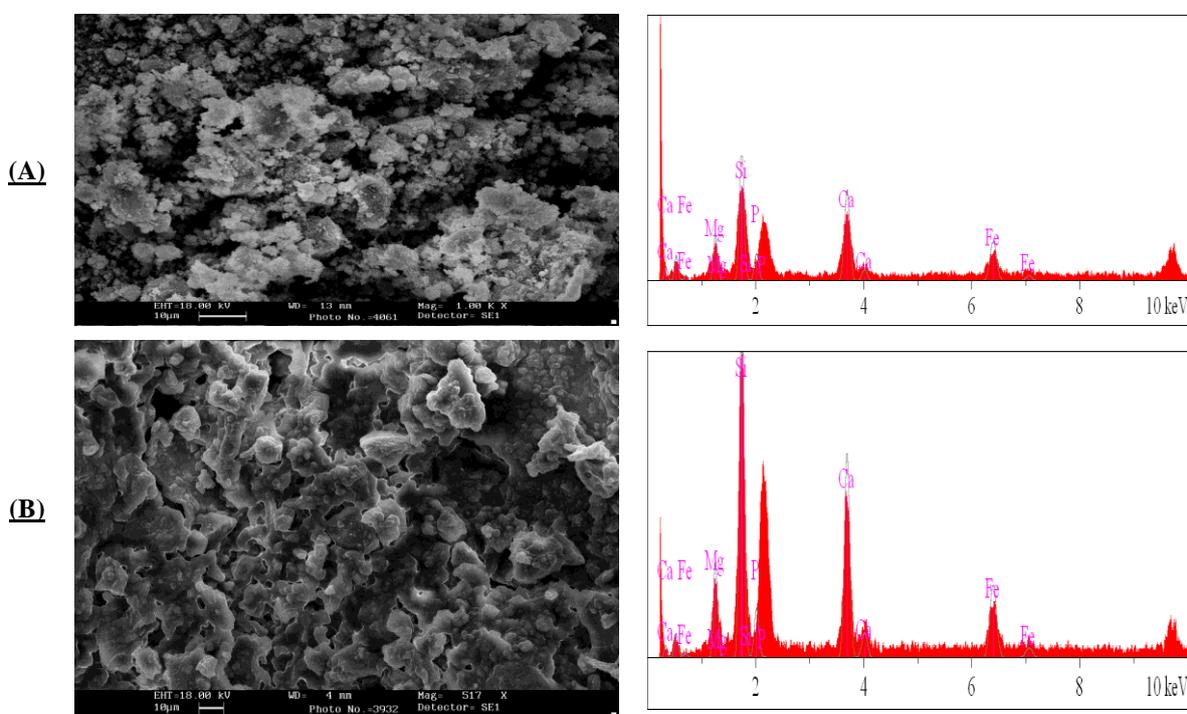


Fig. 3. SEM micrographs and EDS spectra of the surfaces of nanostructured HT after immersion in SBF for (A) 14 days and (B) 30 days.

## CONCLUSION

In this research paper, the behavior of nanostructured HT ceramic in the simulated body fluid solution was studied to evaluate its bioactivity. These results indicated that prepared nanostructure HT with a crystallite size of about 40 nm was bioactive and had the ability to form apatite layers. In addition to the atomic absorption spectrometer the AAS test of simulated body fluid showed that nanostructured HT ceramic released Mg ions into the simulated body fluid and had biodegradation behavior. In sum, our findings indicated that nanostructure hardystonite (HT) bio-ceramic is bioactive and might make a good candidate for biomedical purposes.

## REFERENCES

- [1] H.Gheisari , E.Karamian and M.Abdellahi , A novel hydroxyapatite –Hardystonite nanocompositeceramic , Ceramics International.2015; 4 (2): 5967–5975.
- [2] H.Gheisari and E.Karamian , Preparation and characterization of hydroxyapatite reinforced with hardystonite as a novel bio-nanocomposite for tissue engineering ,2014; 1(2): 298- 301.
- [3] Thakkar KN, Mhatre SS, Parikh RY. Biological synthesis of metallic nanoparticles. *Nanomed J.* 2010; 6(2): 257–262.
- [4] Hosseini-Abari A, Emtiazi G, Ghasemi SM. Development of an eco-friendly approach for biogenesis of silver nanoparticles using spores of *Bacillus athrophaeus*. *World J Microbiol Biotechnol.*2013; 29(12): 2359–2364.
- [5] Hosseini-Abari A, Emtiazi G, Lee SH, Kim BG, Kim JH. Biosynthesis of silver noparticles by *Bacillus stratosphericus* spores and the role of dipicolinic acid in this process.*Appl Biochem Biotechnol.* 2014; 174(1): 270-282.
- [6] E.Karamian , M.Abdellahi and H.Gheisari , Internationals of Materials Research , Fluorine-substituted HA reinforced with zircon as a novel nano-biocomposite ceramic: Preparation and characterization .2015; 3(1): 1-8.
- [7] Hassan Gheisari Dehsheikh, Salman Ghasemi-Kahrizsang, “Performance improvement of MgO-C refractory bricks by the addition of Nano-ZrSiO4”, *Materials Chemistry and Physics*, 2017; 4(2): 369-376.
- [8] Salman Ghasemi-Kahrizsangi, Hassan Gheisari Dehsheikh, Ebrahim Karamian, “Impact of Titania nanoparticles addition on the microstructure and properties of MgO-C refractories”, *Ceramics International*, 2017; 5(1): 15472- 15477.
- [9] Salman Ghasemi-Kahrizsangi, Hassan Gheisari Dehsheikh, Mehdi Boroujerdnia,” Effect of micro and nano-Al2O3 addition on the microstructure and properties of MgO-C refractory ceramic composite”, *Materials Chemistry and Physics*, 2017; 2(3): 230-236.
- [10]Mousom Bag, Sukumar Adak, Ritwik Sarkar,” Study on low carbon containing MgOC Refractory: Use of nano carbon, *Ceramics International.* 2012; 3(3): 2339-2346.
- [11]Mousom Bag, Sukumar Adak, Ritwik Sarka, “Nano carbon containing MgO-C refractory: Effect of graphite content, *Ceramics International.* 2012; 4(1): 4909-4914.
- [12]Salman Ghasemi-Kahrizsangi, Ebrahim Karamian, Hassan Gheisari Dehsheikh, Ahmad Ghasemi-Kahrizsangi, “A Review on Recent Advances on Magnesia-Doloma Refractories by Nano-Technology”, *Journal of Water and Environmental Nanotechnology.* 2017; 3(2): 206-222.