Impact of HAP on The Ti Implant’s Morpho-Structural Characteristics and Corrosion Resistance for Biomedical Applications

Garv Chawla1, L.Bangi1,a)

1GARV Wellness & Detox Center, Maharashtra, India

Corresponding author: a)[shibangidas147@gmail.com](mailto:shibangidas147@gmail.com)

**Abstract:** The naturally occurring mineral hydroxyapatite (HA) is important for agriculture and biology. It is best recognized for playing a crucial part in the skeletons of both humans and other animals. Strength and structural integrity are imparted by HA, which is mostly composed of calcium and phosphorus and comprises the primary mineral component of bones and teeth. In order to provide a composite structure that strikes a balance between the flexibility and rigidity necessary for skeletal function, HA and type-I collagen work in concert within bones. Dental enamel's exceptional hardness and semi-translucency, which are essential for both functional and esthetic dental qualities, are attributed to HA crystals.Titanium and its alloys have become well-known as adaptable biomaterials in biomedical applications because of their remarkable mechanical qualities, resistance to corrosion, and biocompatibility.Because of their biocompatible oxide layer and surface topography, titanium implants help with osseointegration, which is essential for the long-term survival of implants used in orthopedic and dental procedures. Even with their benefits, problems like high melting temperatures, machining difficulties, and dark coloration still exist, requiring continuous improvements in material processing and design.A key factor in determining whether biomaterials are appropriate for use in medicine is their biocompatibility, or their capacity to blend in with host tissues without causing inflammation or unfavorable immunological reactions. Because titanium and its alloys resist corrosion, they are more biocompatible because their structural integrity is preserved and harmful biological reactions are avoided over a prolonged length of time.Overall, the special qualities of titanium and hydroxyapatite alloys highlight their vital roles in biological systems and cutting-edge biomedical technologies, underscoring continuous research initiatives to enhance their functionality and broaden their applications in agriculture and medicine.

**Keywords:** hydroxyapatite, titanium alloys, biocompatibility, osseointegration, biomedical applications

# Introduction

Anaturally occurring mineral with biological and agricultural significance is hydroxyapatite. Hydroxyapatite makes up the bones of both humans and animals. Hydroxyapatite is produced in nutrient recovery operations by treating waste streams that include calcium [(1)](https://www.sciencedirect.com/topics/chemical-engineering/hydroxyapatite).The typical apatite lattice structure of HA is (A10(BO4)6C2), where A, B, and C are specified by Ca, PO4, and OH. HA is an inorganic mineral. With a weight percentage of 18% phosphorus and 39.68% calcium, pure HA has a Ca/P mole ratio of 1.67 [(2)](https://pubmed.ncbi.nlm.nih.gov/19024998/) The human body contains HA crystals, primarily in the teeth and bones. As a bioactive ceramic, the HA crystals make about 65–70% of the weight of a human bone [(3)](https://pubmed.ncbi.nlm.nih.gov/15468865/) Moreover, type-I collagen and HA are the inorganic and organic components of the bone's architecture, respectively.When it comes to the dental function, HA crystal makes up 70% to 80% of the dentin and enamel by weight. The hardest material in the human body is enamel, which is made up of comparatively large HA crystals that are 25 nm thick, 40 to 120 nm broad, and 160 to 1000 nm long.Enamel is not made of collagen like bone is [(Aparna et al., 2021; Poornima et al., 2021; Verma & Muthuswamy Pandian, 2021)](https://paperpile.com/c/tEfKbJ/zybz+ktf7+QEtj) [(4)](https://pubmed.ncbi.nlm.nih.gov/28171719/) Collagen's role is replaced by enamelins and amelogenins, which offer a framework for mineralization. Furthermore, the main component of enamel, HA, gives the impression of semitranslucency by blocking the pores on the enamel surface and reducing diffuse reflection of light [(5)](https://www.ncbi.nlm.nih.gov/books/NBK513314/) Titanium is a bioinert substance, meaning that it has little to no negative effects on the surrounding tissue [(Laghari et al., 2023; Ramakrishnan et al., 2023)](https://paperpile.com/c/tEfKbJ/C2YJi+tI9Fs) [(6)](https://www.ncbi.nlm.nih.gov/pmc/articles/PMC9104688/). Since the early 1980s, the amount of titanium (Ti) and Ti alloys has increased significantly. Due to its unique qualities and wide range of biomedical applications, it has emerged as the most widely acknowledged metallic biomaterial [(Chokkattu et al., 2022; Ramamurthy et al., 2022)](https://paperpile.com/c/tEfKbJ/DhsvF+8dojP) [(7)](https://books.google.com/books?hl=en&lr=&id=-RzhDwAAQBAJ&oi=fnd&pg=PP4&ots=vtGRV4C8b7&sig=bjFiBmVf0f-a0Wzv_hE2WfdBRc8).Because of its low modulus of elasticity, low specific weight, remarkable resistance to corrosion, amazing strength-to-weight ratio, good tribological properties, and remarkable biocompatibility, titanium has been hailed as one of the most promising biomaterials for design [(Chokkattu et al., 2022; Ramamurthy et al., 2022)](https://paperpile.com/c/tEfKbJ/DhsvF+8dojP) [(8)](https://www.ncbi.nlm.nih.gov/pmc/articles/PMC9640965/).Due to their impact on the quality of their interaction with the bone, titanium implant surface smoothness and roughness are also significant characteristics [(Marya et al., 2022)](https://paperpile.com/c/tEfKbJ/oIUHg) [(9)](https://openurl.ebsco.com/EPDB:gcd:1:7707601/detailv2?sid=ebsco:plink:scholar&id=ebsco:gcd:36895213&crl=c).Titanium alloys have properly corrosion resistance , eventhough thiscould be altered through the presence of proteins including albumin, and therefore there maybe an boom in thequantity of titanium launched into the tissues [(Jain & Verma, 2022; Marya et al., 2022)](https://paperpile.com/c/tEfKbJ/oIUHg+NygUg) [(10)](https://www.sciencedirect.com/science/article/abs/pii/S1742706115300441).The interfacial quarter among the titanium alloy implant and residing bone is crucial withinsidethe improvement of osseointegration. This area, thatis thin (20–50 nm), is the area into which boom elements are launched from the bone cells, and this initiates thestairs that bringabout bone formation [(Wadhwani et al., 2022)](https://paperpile.com/c/tEfKbJ/hoH9j) [(11)](https://www.tandfonline.com/doi/abs/10.1080/03602532.2016.1277737) This alloy has various benefits, such as a thermal expansion coefficient that is comparable to that of bone, strong corrosion resistance, low density, and good biocompatibility. It also has good mechanical qualities, including as modulus of elasticity, fatigue strength, ultimate tensile strength, yield tensile strength, or and thermal conductivity [(Sreevarun et al., 2023)](https://paperpile.com/c/tEfKbJ/20eod) [(12)](https://www.researchgate.net/profile/A-Loureiro/publication/283863116_Properties_and_applications_of_titanium_alloys_A_brief_review/links/578e0d7a08ae35e97c3f5e6e/Properties-and-applications-of-titanium-alloys-A-brief-review.pdf). Titanium offers exceptional osseointegration because of its surface topography, which has a moderate level of roughness (1-2 µm) that promotes osseointegration and great wettability [(Adel et al., 2023)](https://paperpile.com/c/tEfKbJ/EjMxY). However, a few drawbacks of Ti-alloys should be noted, including their dark color, difficulties in machining and casting, and high melting temperature [(Solanki et al., 2023)](https://paperpile.com/c/tEfKbJ/oQW8o) [(13)](https://www.ncbi.nlm.nih.gov/pmc/articles/PMC10608008/#B14-materials-16-06624). The ability of a biomaterial to function and show an adequate host response without causing an allergic or inflammatory reaction in a specific application is called biocompatibility [(Merchant et al., 2022; Pandiyan et al., 2022)](https://paperpile.com/c/tEfKbJ/DI0sB+WVXzN). A living organism or system (microenvironment) is called a "host" and the host's behavior toward foreign biomaterial is called a "host response." For example, bacterial colonization resistance [(Ganapathy 2021; Merchant et al., 2022; Pandiyan et al., 2022)](https://paperpile.com/c/tEfKbJ/DI0sB+WVXzN+TzxNN) [(14)](https://www.ncbi.nlm.nih.gov/pmc/articles/PMC8865884/). Although these biomaterials have good mechanical and biological properties, corrosion resistance is still critical for overall processing success [(Subramanian & Harikrishnan, 2023)](https://paperpile.com/c/tEfKbJ/AHXds). It has long been known that corrosion products formed as a result of the interaction between metal and the environment have a significant effect on the biocompatibility and long-term stability of prostheses/implants [(Ganapathy 2021)](https://paperpile.com/c/tEfKbJ/5ptXU).The excellent corrosion resistance of titanium and its alloys used in implants results from the formation of an oxide film with a thermodynamically stable, continuous, strongly adhesive and protective surface [(Chokkattu et al., 2023)](https://paperpile.com/c/tEfKbJ/fcvUC). Because titanium metal itself is very reactive and has a very high affinity for oxygen, this useful surface oxide film forms spontaneously and immediately when a fresh metal surface is exposed to air and/or moisture [(Muthuswamy Pandian et al., 2022)](https://paperpile.com/c/tEfKbJ/LTQOW) [(15)](https://www.researchgate.net/profile/Rafik_Karaman/post/how_can_i_get_the_ions_concentration_of_Titanium_after_its_corrosion_in_oral_environment/attachment/59d623d079197b80779821e8/AS:309275526664193@1450748439455/download/Titanium+2.pdf)**.**

# Materials and Methods

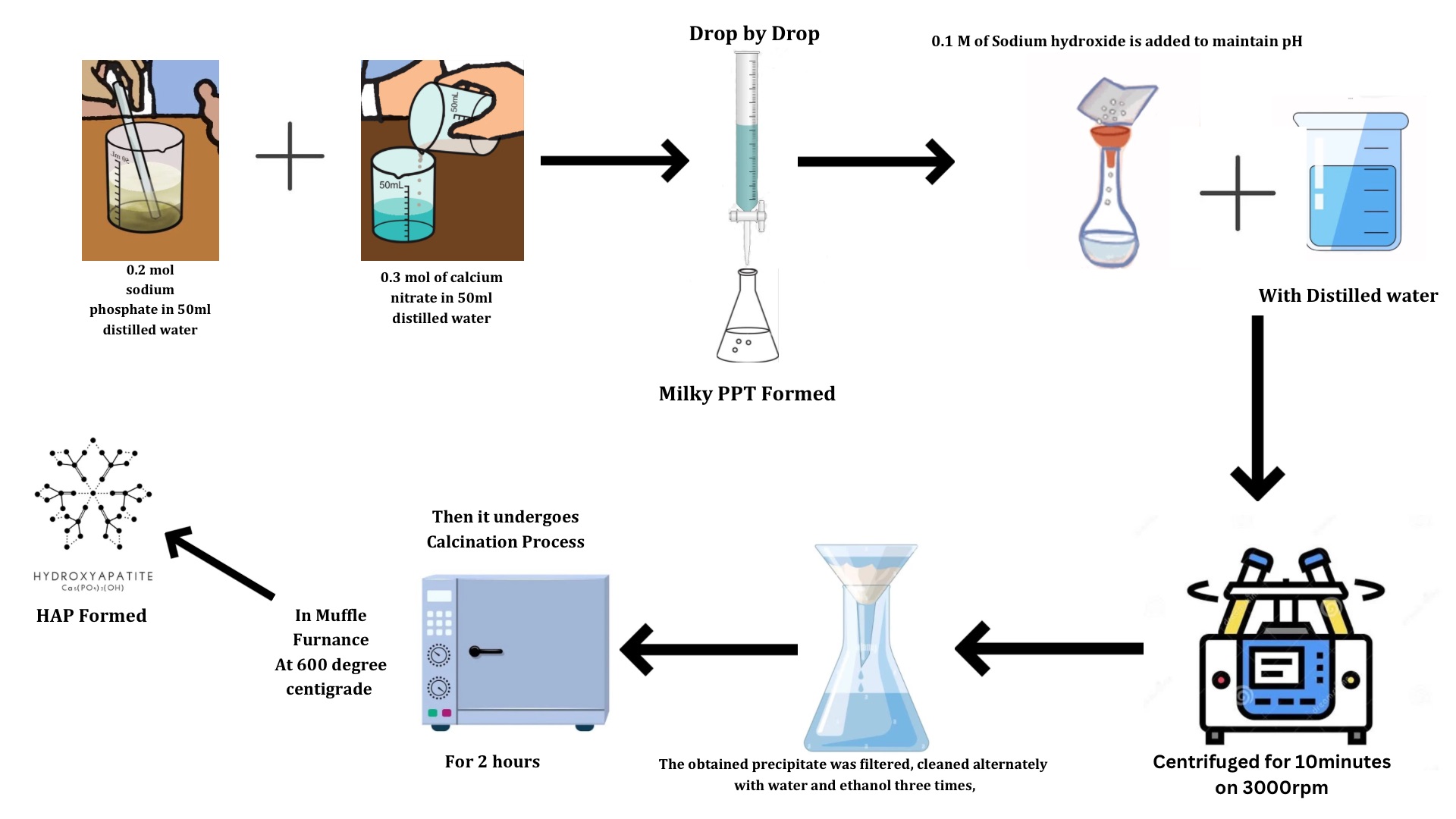


Figure 1: Flowchart

Na3PO4(0.2 M, 100 mL) was stirred at room temperature (18-22 "C) in a 2 L beaker with Ca(NO3)2 (0.3 M, 100 mL) added drop wise over one hour, resulting in a "milky" suspension of HAP. The Ca/P molar ratio was kept at 1.67 corresponding to the stoichiometry of HAP. The pH was maintained through the addition of NaOH (0.1 M) within the range 9.4-9.5. This "milky" suspension was then stirred overnight at room temperature using a magnetic stirring bar. The obtained precipitate was filtered, cleaned alternately with water and ethanol three times, oven dried at 65 "C for six hours, and then calcined at 600 "C for a further two hours making full synthesis complete within less than 24 hours.

# Results

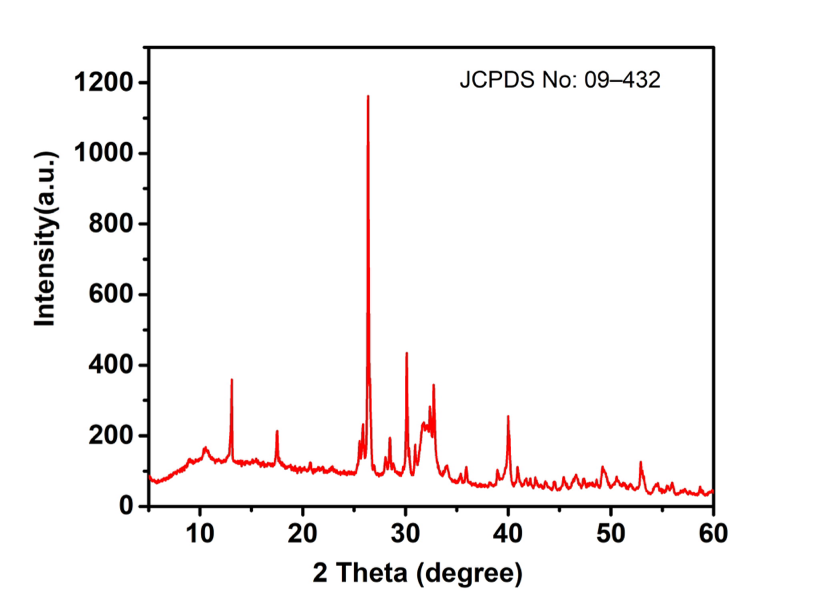
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Figure 2: Intensity vs. 2 Theta

XRD Pattern of HAP-Figure 1.-The pattern show high crystallinity and all the diffraction peaks are well fitted to the hexagonal structure of hydroxyapatite.X-ray diffraction patterns of HAp which shows Formation of hexagonal Hydroxyapatite crystalline phase in HAp is assessed by the identified reflections such as (200), (111), (002), (210), (211), (112), (300), (202), (310), (311), (113), (203), (222), (312), (123), (321), (402), (004) and (322).

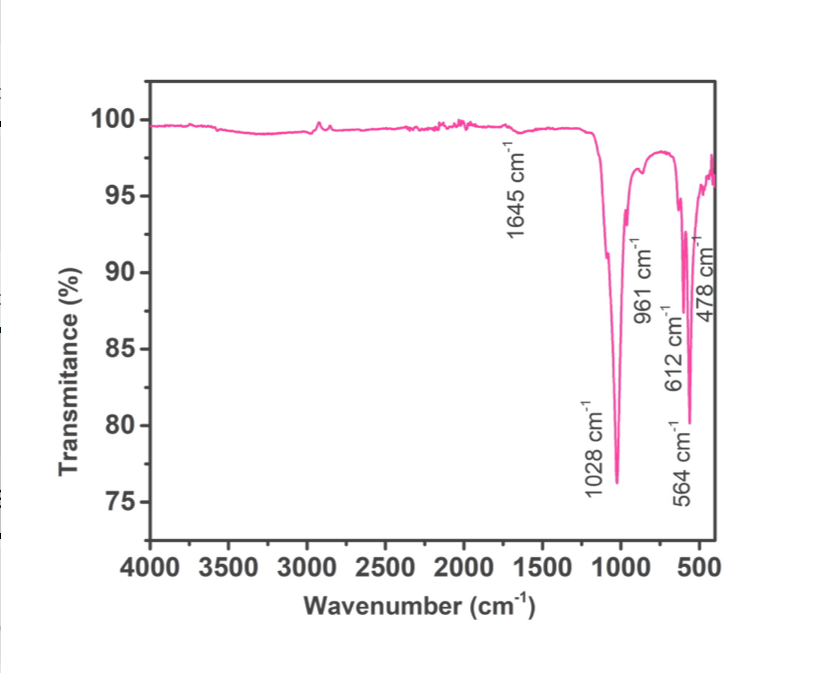


Figure 2: Transmitance vs. Wavenumber

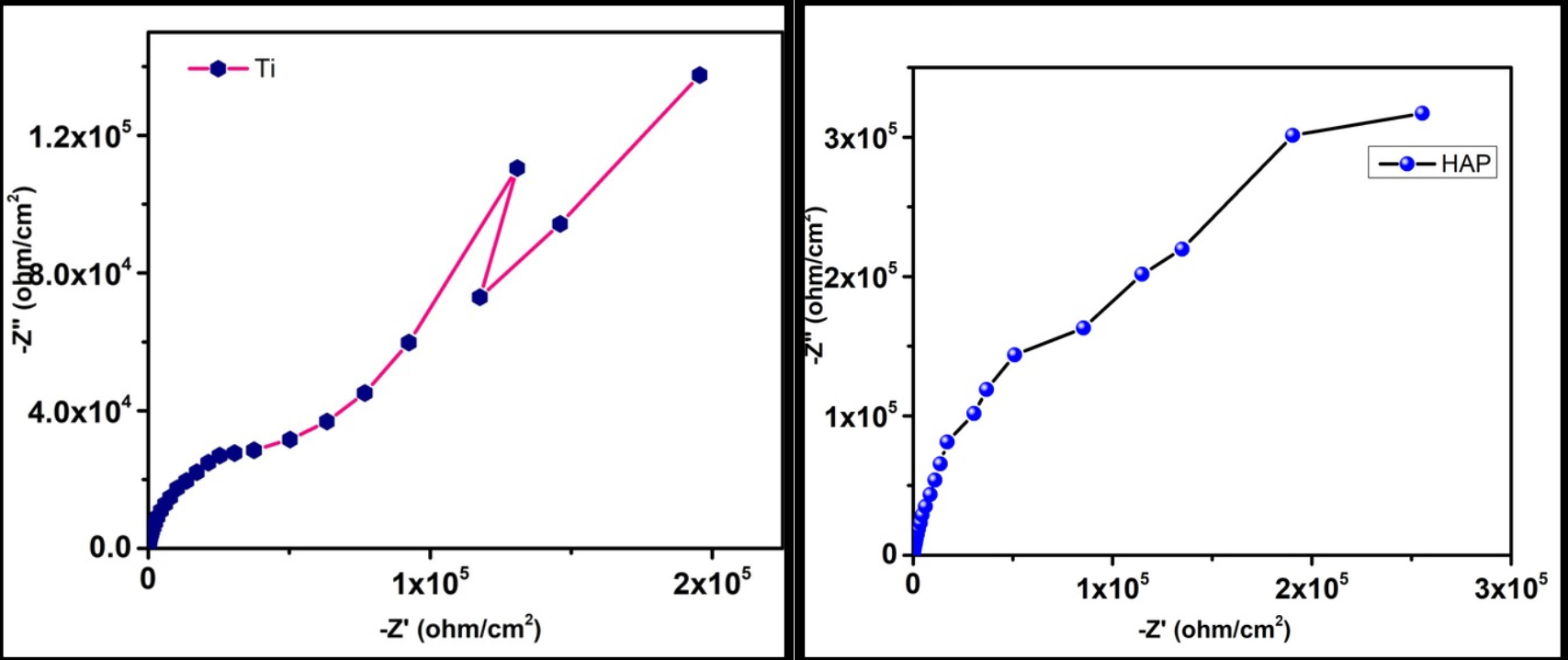
The FTIR spectrum of HAP nanoparticles is shown in Figure. The specific bands of the phosphate group, PO4 3, characteristic to hydroxyapatite structure were observed at 564, 612, 660.2, and1000e1100 cm1 [17]. The band at 478cm1 may be attributed to OePeO bond. The absorption band at 1645 cm1 and the bands at 3551.45 and 3608 cm1 indicated the presence of the hydroxyl groups. The absorption band at 3404.9 in Fig. 1(b) indicated the presence of the hydroxyl groups in the modified hydroxyapatite.The broadness of the band means that a change was occurred in the hydroxyapatite, the absorption band was broadened due to the modification of hydroxyapatite.



1. (b) (c)

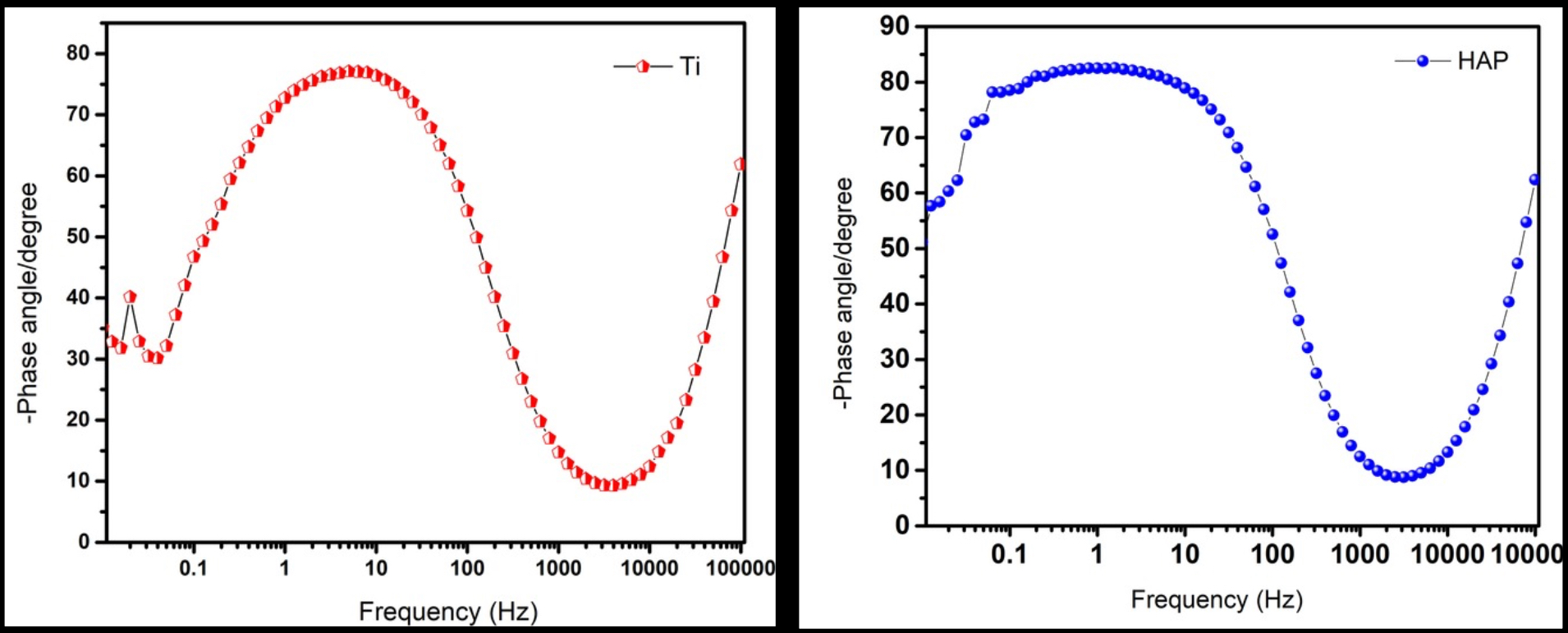
Figure 3: (a) (b) (c) SEM

Figure 3-Shows a HRTEM micrograph of synthetic Hap. The crystals exhibit elongated morphology like rods in nanoscale less than 100 nm.The H-RTEM indicates the configuration of smooth rod-like structures of the samples with an average diameter of ~ 20nm along with nanosphere HAP. The morphology of the HAP crystal varies with the synthesis process, precursors and other parameters.It is observed that when the MW power is increased, it results in nano-rods structures instead of an elongated needle like structure.The HAP rods produced by the MW method are promising materials as biomaterial for bone implant application.



1. (b)

Figure 4: (a) (b) Impedence spectrum of uncoated Ti impants and HAP coated Ti Impants.Semicircle pattern of uncoated Ti implant is less than HAP coated Ti implants which indicates lowerconductivity and higher resistance towards corrosion



1. (b)

Figure 5- (a) (b)Phase angle spectrum of uncoated Ti impants and HAP coated Ti Impants.Lower Frequency at uncoated Ti impant and coate HAP Ti impant shows the difference in phase value.

# Discussion

## XRD PATTERN

MW-assisted preparations of HAP samples were found to be significantly efficient and economic. Hence, a growing interest in MW-assisted processing of biomaterials is always a concern of interest (Chehelgerdi et al., 2023). The X-ray diffraction pattern of the microwave irradiated HAP particles as presented in . The X-ray pattern exactly matches with the characteristic peaks of pure HAP in accordance with JCPDS data No: 09–432. The peaks were purely crystalline in nature with the hexagonal HAP phase and no other secondary phases such as calcite or TCP were present. The wide peaks around (002) and (211) designates that the crystallite size was the order of a nanometer scale. Using Debye-Scherrer formulation the average crystallite size was found to be of the order of 26 nm and the percentage of crystallinity based on previous studies for the samples prepared by microwave irradiation method was 92%. Huang et al. investigated the effects of micro-sized MW synthe- sized HA (μHA) versus nano-sized conventionally precipitated HAP on the osteogenic differentiation of rat bone marrow- derived mesenchymal stem cells (rBMSCs) . It was found that the cells expressed higher levels of osteoblast-related mar- kers with nano-HAP than μ-HAP stimulation. These results further confirm that the size of HAP is an important factor for osteogenic differentiation of rBMSCs and also provides a new approach to study stem cell differentiation and to obtain more differentiated cells. For the purpose of drug delivery, MW was used to prepare HAP in the form of self-assembled hollow structures and was applied in studies including drug deliv- ery <https://www.researchgate.net/figure/XRD-pattern-of-HAP-nanoparticles_fig3_333570304>.

## FTIR PATTERN

The crystals exhibit elongated morphology with a length of about 400–500 m and diameter of 40–50 m. FTIR spec-trum of the synthetic Hap is shown in Figure 2. The band assignment shows the peaks assigned to PO3− at 1035, 4960, 601, and 561 cm−1 and the O–H vibration modes at 3573 and 634 cm−1.1415.According to the theory of viscoelasticity for polymeric materials the dynamic storage modulus (E′) increases with increasing loading frequency (Saadh et al., 2024). This is also the case in our nano-composite alginate gels withhydroxy-apatite

# Hrtem Pattern

An essential technique for examining the microstructure of titanium implants coated with hydroxyapatite (HAp) particles is high-resolution transmission electron microscopy (HR-TEM), which offers information on the crystalline structure, interface quality, and general integrity of the material. Because the HAp coating is chemically comparable to human bone mineral, its main purpose is to improve the implant's bioactivity and osseointegration characteristics

<https://pubmed.ncbi.nlm.nih.gov/23142624/> With typical d-spacing values that validate the crystalline nature of the HAp layer, HR-TEM displays intricate lattice fringes that match the hexagonal structure of HAp <https://pubmed.ncbi.nlm.nih.gov/12361617/>. Furthermore, the quality of adhesion at the interface between the HAp particles and the titanium substrate can be determined, and this is important for the mechanical stability and biological function of the coating <https://pubmed.ncbi.nlm.nih.gov/19006399/>.

# Impedance Spectrum

The electrochemical impedance analysis (EIS) was conducted in a potentiostat environment, with measurements taken across a frequency spectrum from 100,000 Hz to 0.01 Hz, with a voltage amplitude of 10 mV. For accurate results, we repeated the electrochemical test three times.The coatings made at speeds of 2000 and 3000 RPM are heated to temperatures of 500 and 600 °C for a duration of 2 hours and examined using electrochemical impedance spectroscopy (EIS) and Tafel polarisation studies to verify their corrosion resistance properties.The HAP coating has demonstrated greater resistance to electrical current at lower frequencies compared to the uncoated and alkaline-treated alloys, which supports the rise in resistance to corrosion of the HAP coatings on Ti-6Al-4V [(Muthuswamy Pandian et al., 2022; Ramakrishnan et al., 2023)](https://paperpile.com/c/tEfKbJ/LTQOW+C2YJi).

# CONCLUSION

Hydroxyapatite (HAP) coatings on titanium (Ti) implants enhance their morpho-structural characteristics and corrosion resistance, making them more suitable for biomedical applications. The bioactive nature of HAP promotes better integration with bone tissue, improving biocompatibility and fostering cell adhesion and proliferation due to enhanced surface roughness. The high crystallinity and stability of HAP coatings maintain the structural integrity of the implants, while providing a protective barrier that reduces ion release and corrosion rates. This improved chemical stability enhances the long-term performance and reliability of Ti implants, reducing failure rates and contributing to better clinical outcomes. Overall, HAP coatings significantly improve the functionality and longevity of Ti implants in orthopedic and dental applications, although the coating process must be carefully optimized to maximize these benefits.

# FUTURE SCOPE

Future research on the effects of hydroxyapatite (HAP) on the morpho-structural properties and corrosion resistance of titanium (Ti) implants for biomedical purposes is both diverse and promising. Research can concentrate on improving HAP coatings to improve the mechanical stability and corrosion resistance of Ti implants, potentially prolonging their lifespan and performance in the human body, in response to the growing need for more robust and biocompatible implants. It is possible to investigate cutting-edge methods like surface alterations and nanostructuring to enhance osseointegration and lower the likelihood of implant failure. Furthermore, by comprehending the nanoscale interaction between HAP and Ti, advances in personalized medicine—where implants are customized to meet the demands of specific patients—may result.Research on bioactive coatings and how they affect implant surfaces should continue to yield advances in lowering infection rates and enhancing patient outcomes in general. The creation of next-generation biomedical implants might be completely transformed by combining these discoveries with 3D printing and regenerative medicine.

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