# The Effects of Zinc Oxide on the Thermal& Mechanical Properties of Direct Synthesis Hydroxyapatite

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## Abstract

Effects Zinc oxide(ZnO) of on the mechanical (bending strength and hardness) and thermal stability of hydroxyapatite( HA) that directly synthesized by mechanical milling in a planetary ball mill, using orthophosphoric acid solution ($H_3PO_4$) and calcium hydroxide $Ca(OH)_2$ was evaluated. High purity zinc oxide was added in ratios of 10, 30 and 50 percent by weight. HA/ZnO exhibited increasing in microhardness, and bending strength with increasing amount of ZnO addition. X-ray diffraction after sintering at 1100°C for synthesis of hydroxyapatite showed unstable compound, decomposed to β-TCP, while X-ray for the hydroxyapatite/ ZnO contained thermally stable HA phase and different amounts of ZnO , depending on the amount of ZnO added.

**Keywords**: Zinc oxide , Hydroxyapatite( HA) , Mechanical Activation, Milling.



## 1- Introduction

Mechanosynthesis method is an alternate routine to prepare hydroxyapatite through that reaction stimulate by mechanical grinding[1]. The reactants in a mill, are crushed between wall and ball (horizontal or planetary ball mill. Mixtures imbibe quantity of frictions or collisions energy in case through that deliver the energy required for reaction[2]. Mechanosynthesis can be achieved below wet or dry situations. Wet mechanosynthesis contains crushing in an aqueous interruption of the initial resources (wet abrasion or mechanochemical–hydrothermal route) with a fluid-to-powder proportion reaching normally from 60 to 95 wt.% )[3]. In dry mechanosynthesis, powders mixture without any solvent are straight crushed. In papers record and charters regarding mechanosynthesis grinding of calcium phosphates, was achieved in wet environments[4].The reactions want high temperatures in mechanochemical treating, will happen in a ball mill at lower temperatures without some requisite for outside heating [5].

Technical inquiry through scientists materials must been always focused to ameliorative the performance and properties of materials[6] . Important developments in chemical, physical and mechanical properties have been realized done chemistry alterations and thermal, thermo mechanical and mechanical treating procedures[7].

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), categorized as a biomaterial, is a fabricated material accustomed substitute parts of a alive organization or to purpose in near interaction with alive tissues [8]. This material is current in considerable quantities in the mineralized tissue of vertebrates, i.e. 60‑70% of the inorganic part of the human bone [9]. The mechanical properties of hydroxyapatite are not perfect sufficient to be applied as an graft in load-bearing locations, similar artificial teeth or bones[10].

One path to disband this trouble is to join it with a hard phase, creating a compound and improve its mechanical confines by strengthening it with appropriate material[10]. In this method, a material is achieved with heightened belongings, without harm to its

biocompatibility[11]. Zinc oxide presentation several aids for bone development and an antimicrobial activity for grafts , stimulates growth of bone prevents bone recommencement presentation antimicrobial opposition[12]. The obtainability of zinc concludes the performance and this can be deliberate by the microstructure (crystal size, form ,and crystallinity, of zinc [13] . Innermost trainings mingle zinc from an aquatic sol in apatite crystallization and determination several difficulties. Zinc meaningfully reductions the mineral evolution amount through adsorbing to the external [14].

Synthesis of hydroxyapatite using a mechanochemical process was investigated in this research work. Initially, the objective was to synthesize HA directly without the need for a two-stage process where mechanical activation for 6 hours was followed by a heat treatment process at 1100$^{o}$C [15].The milling parameters were systematically investigated, and these included the milling duration, the types of milling media and ball toward powder ratio. The use of milling media, i.e. the balls and the jars, was restricted to the same material as compared to dissimilar materials which had been reported in the literature[16].

The ultimate objective of the present work was to synthesize a single phase hydroxyapatite directly by mechanical milling using orthophosphoric acid solution ($H_3PO_4$), and calcium hydroxide, $Ca(OH)_2$, equally the originators without any need for heat treatment, and communicate the mechanical, structural, and bioactive belongings of hydroxyapatite- zinc oxide biomaterials by different installation of zinc oxide.



## 2- Materials and Procedures

### 1-Raw Materials

In this work commercially precursors utilized orthophosphoric acid solution ($H_3PO_4$) and calcium hydroxide , ($Ca(OH)_2$, and zinc oxide. Fluka,96%).

### 2- Hydroxyapatite Preparation:

In effective production hasten to produce single-phase HA only, first 100 mL of ethanol was located into a amplitude Pyrex of 100 mL. additional powder $Ca(OH)_2$ 2.96 g of (50.0296 mol Ca) into ethanol and made dense suspension was stirred magnetically for 5 min at room temperature. Supplementary $H_3PO_4$ , 4 mL of (50.0592 mol P) into the suspension of calcium hydroxide. wet mixed in a planetary ball mill (SFM-1, QM-3SP2) with runs at 400 rpm. The wet mixture was oven dried at 100 ◦C for 24 hours to be sure that all moisture was removed. Orderly to evade heat extreme, 30 minutes milling intervals with 2 minutes pause milling was carried out. The milling media to start off with was alumina(ball and jar) and the ball-to-powder ratio (BPR) was fixed at 10:1 , a milling duration of 6 hours . Fig. 1 shows the typical processes used to produce the hydroxyapatite powder.

### 3- Hydroxyapatite(HA)- zinc oxide(ZnO) Preparation:

The fine powders of the zinc oxide(ZnO) was mingled with the powder of hydroxyapatite(HA) was obtained from the method described earlier in a mode that the definitive combinations consist of 10 , 30 , and 50 wt% of the (ZnO) . The combinations were fully standardized till 4 hours through ball milling. Prepared pellets (13 mm diameter, 26 mm height) were by uniaxial cold pressing in hardened steel dies, using uniaxial pressure device (CT340-CT440) at pressure of 150 MPa.

The pellets were sintered at1200 ˚C for 2 hours with an average heating rate of 7 ˚C/min.

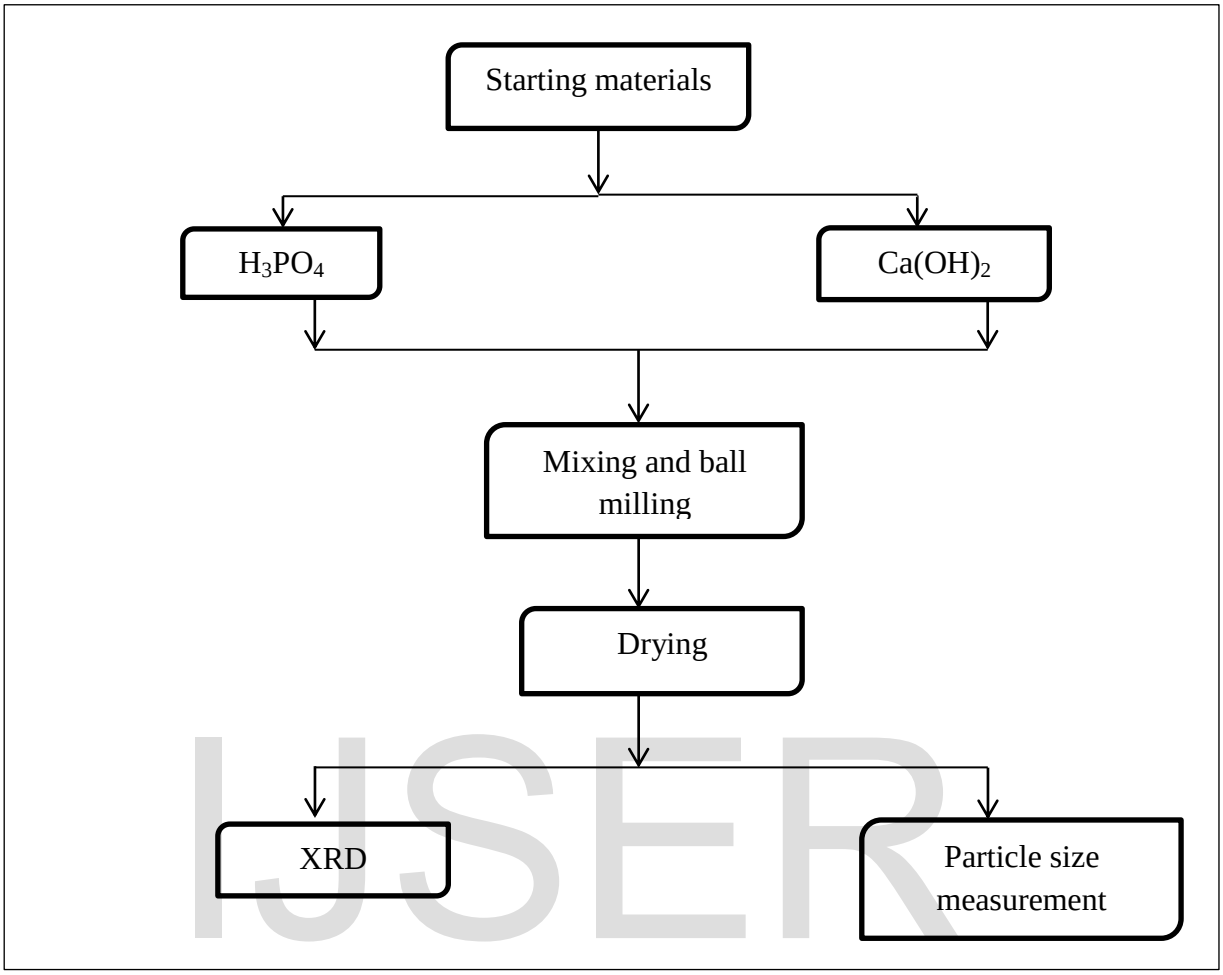



Fig. 1 Schematic diagram of preparation hydroxyapatite powder.

## 3- Characterization

### 1-X-ray diffraction (XRD)

X-ray diffract meter (Shimadzo, 6000) at room temperature using Cu kα radioactivity (λ = 1.5405 Å), and 40 KV/30 mA was used as the main analytical tool**.**

### 2- particle size analyzer

Particle size for prepared (HA) powder was measured using laser particle size analyzer (Bettersize2000).

### 3- Mechanical Properties

Bending strength and microhardness for the (HA) and for (HA)/(ZnO) samples were tested. The computerized universal experimentation machine with a speed test of 0.5 mm/min using to determine bending strength test using rectangular bar samples prepared with dimensions of (Length=50mm,Width=10mm,Height=5mm), the samples prepared according to the ASTM –D790 in steel die. The test was made

according to ASTMC1161 procedure. The subsequent equation consuming to intentional strength of bending.

$$(\sigma b)=3\, p_f L/2wt^2 \quad \text{……..(1)}$$

Where $\sigma b$, is the bending strength (Mpa), pf, fracture load (N), w, the sample width (mm), t, the sample thickness (mm) [17].

Microhardness for all samples were tested using Digital microvickers hardness tester (TH-717) at 9.8 N with a dwelling time of 15 second. Disc samples prepared with dimensions of (Diameter=13mm, Height=5mm), samples prepared in steel die. The test was made according to ASTM standard C1327-90. Vickers hardness was deliberated by the subsequent equation.

$$H_v=1.\,854(p/d^2) \quad \text{……..(2)}$$

Wherever, $H_v$, Vickers hardness (Mpa), p, pregnancy (N), D, diagonal length of the indentation impression (μm) [18] .

## 4- Results and Discussion

### 1-X-ray diffraction (XRD)

Fig. 2 displays the result for complete reaction for the batch, a single-phase HA can be successfully obtained . The powder of hydroxyapatite was scanned in diffraction angle (2Θ) from 5◦ to 50◦. This result is matched with (JCPDS) card No. (09-0432). Fig. 3 shows XRD patterns of sintered HA at 1000 ˚C. Hydroxyapatite is thermally unstable compound, decomposed at temperature 1000 $^{o}$C to β-TCP. The resulting of decomposition is started at 800 ˚C, to give correct calcium orthophosphate of the composition stoichiometric $Ca_3\ (PO_4)_2$ phase when matching its peaks with (JCPDS) card No. (09-0169).

Fig. 4 (A) and( B) illustration XRD configurations for HA-ZnO models contained 10 , and 50 wt% of the (ZnO) sintered at 1200 ˚C for 2 hours. The powder of HA-ZnO was scanned in diffraction angle (2Θ) from 10◦ to 60◦. Phase stability for the crystallized apatites still shows at higher temperatures sintering without decomposition and different amounts of ZnO phase when matching its peaks with (JCPDS) card No.(13-0311).

This also provides direct evidence that (ZnO) incorporations into apatite, enriched thermal stability of amorphous calcium phosphate up to 1000 $^{o}$C. leading to higher crystallization temperatures[19] .

### 2- Particle Size Analyzer

Fig5 shows the particle size analysis of HA powder to give an average particle size of 7μm .

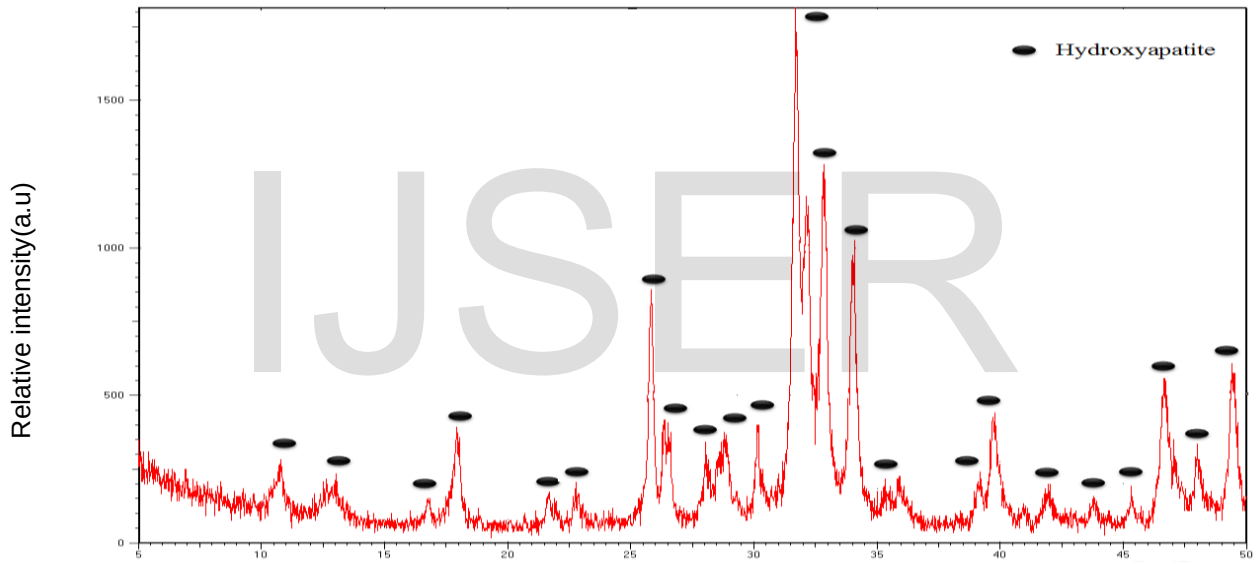
### 3- Bending Strength and Vickers Hardness

Fig 6,and 7 show the relation between the HA-ZnO samples with different weight percent of ZnO and bending strength , and Vickers hardness. The increase in bending strength and hardness is detected as the content of ZnO increases in the models

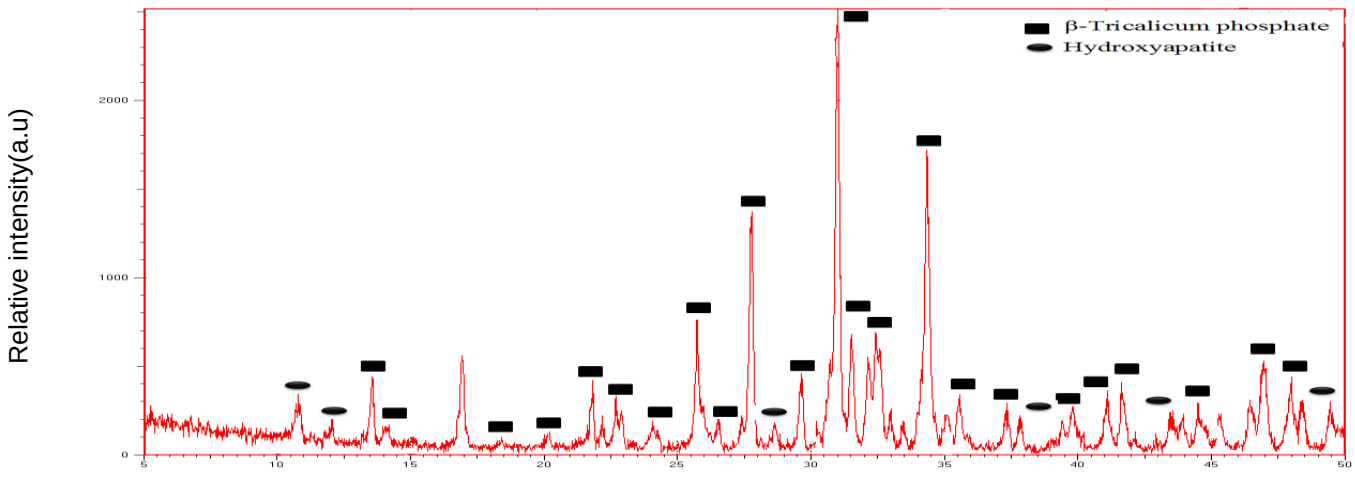
compare to the pure hydroxyapatite. This is a lucid significance of exactly how the addendum of ZnO to the syntheses improves their heftiness[20].The results shown in table 1.

**Table 1 Summary of the mechanical properties for the HA-ZnO samples.**

| | HA% | ZnO % | Bending strength(MPa) | Vickers hardness(Mpa) |
|---|---|---|---|---|
| **Sample 1** | 100 | 0 | 32.5 | 3.7 |
| **Sample2** | 90 | 10 | 35.5 | 5.2 |
| **Sample3** | 70 | 30 | 38.0 | 5.8 |
| **Sample4** | 50 | 50 | 41.6 | 6.4 |




Figure(2) XRD patterns of hydroxyapatite( HA) that directly synthesized by mechanical milling.




Figure(3) XRD configurations of hydroxyapatite sample sintered at 1000 °C.

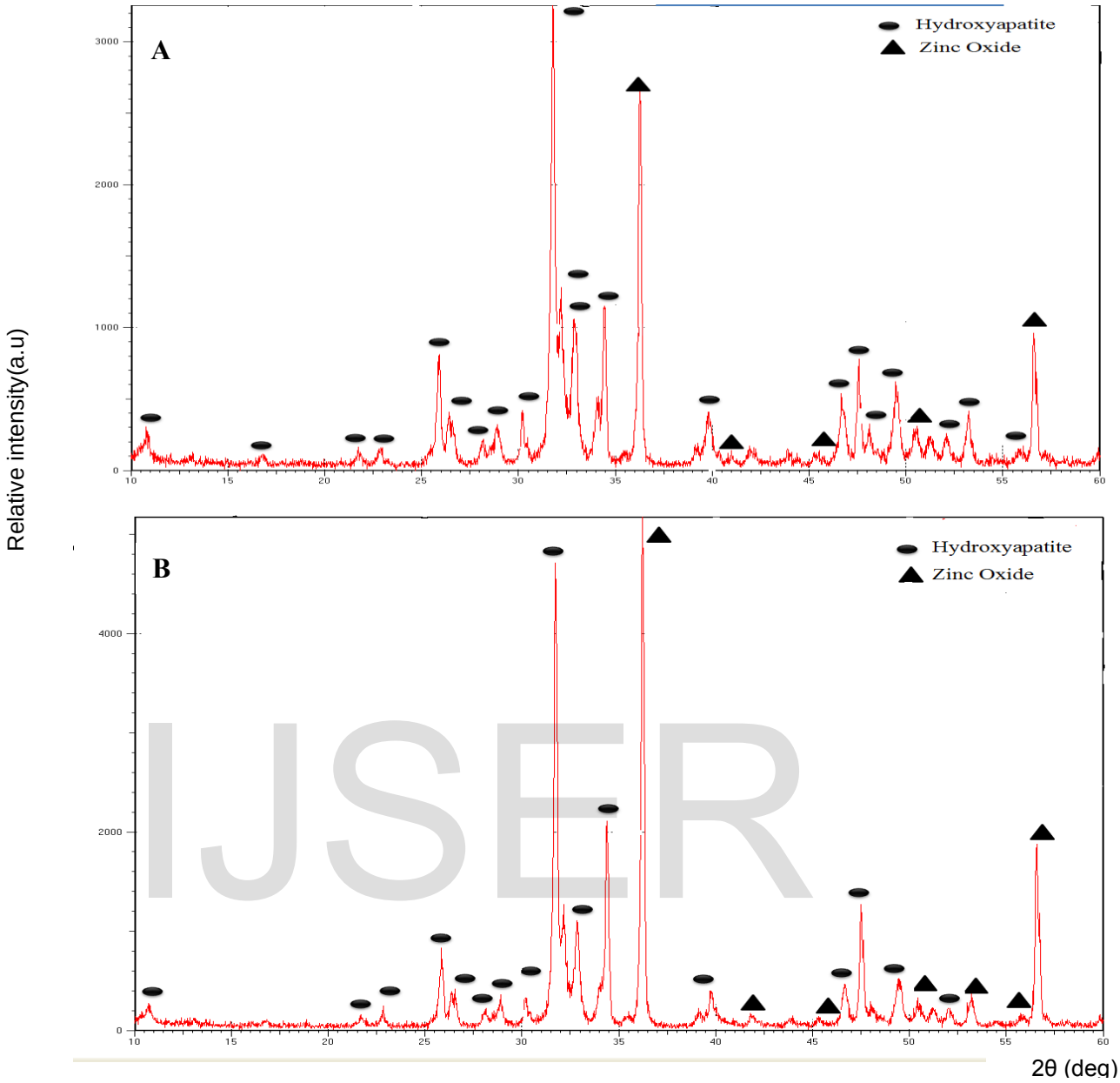
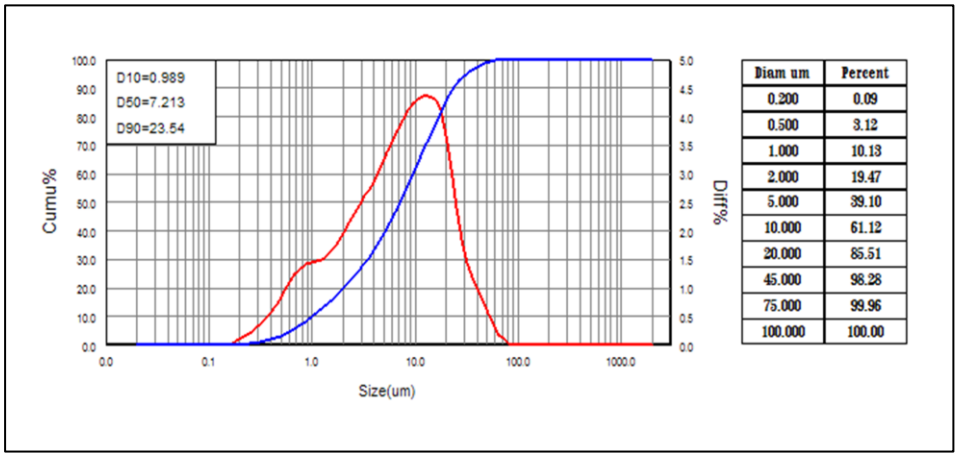
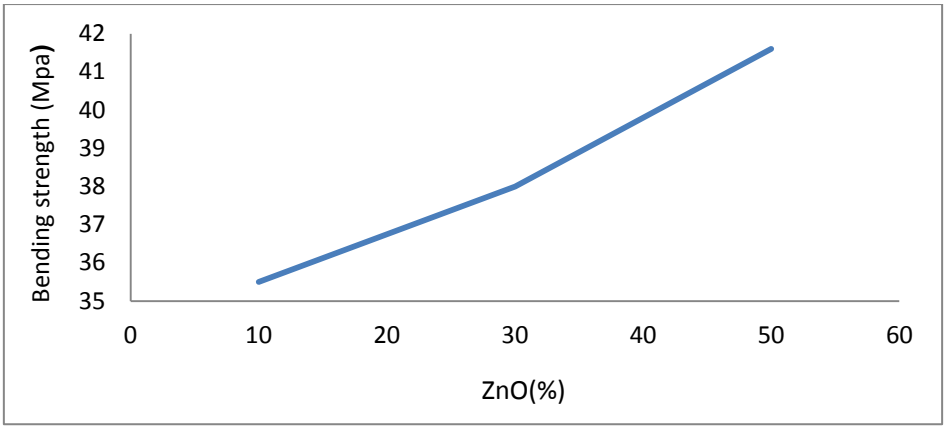



Figure (4) XRD configurations for the( HA-ZnO) samples of A (30%), B (50%) of the (ZnO) sintered at 1200 ˚C.

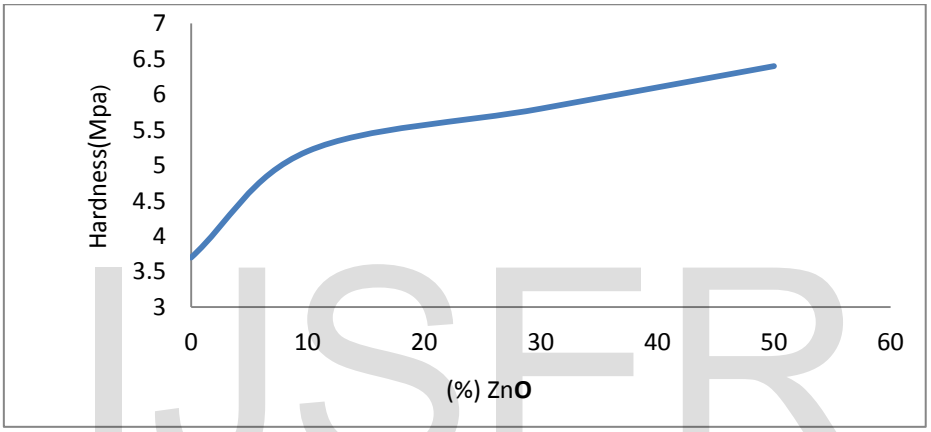



| Diam um | Percent |
|---|---|
| 0.200 | 0.09 |
| 0.500 | 3.12 |
| 1.000 | 10.13 |
| 2.000 | 19.47 |
| 5.000 | 39.10 |
| 10.000 | 61.12 |
| 20.000 | 85.51 |
| 45.000 | 98.28 |
| 75.000 | 99.96 |
| 100.000 | 100.00 |

Figure (5) Particle size analysis of HAP powder.




Figure(6) Variation of bending strength of the HA-ZnO samples with ZnO percentage.






Figure(7) Variation of Vickers hardness of the HA-ZnO samples with ZnO percentage.

## 5- Conclusion

**1-** Finer powder hydroxyapatite( HA) directly synthesized by mechanical milling in a planetary ball mill, using orthophosphoric acid solution ($H_3PO_4$) and calcium hydroxide $Ca(OH)_2$ . The optimization was confirmed principally with X-ray diffraction (XRD) which indicated that only a single phase hydroxyapatite was the final product in this milling reaction.

**2-** High purity zinc oxide (ZnO) was added in ratios of 10, 30 and 50 percent by weight. It was found that addition of (ZnO) to the hydroxyapatite matrix in the rate of (10, 30 ,50 ) wt.% lead to increase the mechanical properties( hardness & bending strength).

**3-** HA ceramic prepared from mechanochemical synthesis powders is thermally unstable compound, decomposed at sintering temperature 1000 °C to β-TCP.

**4-** After sintering process for HA-ZnO samples at 1200°C for 2 hours. X-Ray results on upper temperatures still displays stability of crystallized apatites phase without decomposition with different amounts of ZnO phase .

**5-** The(ZnO) incorporations into apatite enhance the thermal stability the HA-ZnO samples tested up to 1000 $^{o}$C of, unlike apatites produced by mechanical milling.

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