Development and Physical, Chemical and Mechanical Characterization of Doped Hydroxyapatite

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Abstract— In this study, we made an attempt to synthesize doped bioactive hydroxyapatite (HAp) ceramic powder using a simple Chemical method and studied its physical and mechanical properties. Different quantities (2wt% and 5 wt%) of Magnesium chloride Hexahydrate , Zinc oxide, Titanium oxide were incorporated as dopants into Hap at the time of synthesis. The synthesized powder samples were analyzed for their phases using X-ray diffraction technique, Fourier Transform Infrared Spectroscopy. The synthesized powders were uniaxially compacted and then sintered at 1250ºC for 1hr in air. Vicker's hardness testing was performed to determine the hardness of the sintered structures. Fracture toughness of sintered samples was calculated using Inverted Optical Microscope with Image Analysis software.

Index Terms— Dopants, Fracture toughness, FTIR, Hydroxyapatite, Sintered structure, Vicker's hardness, XRD.

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1 INTRODUCTION

Among different forms of calcium phosphates, the bioactive hydroxyapatite (Ca_{10} (PO4)$_6$(OH) $_2$) phase has been most extensively researched due to its outstanding biological responses to the physiological environment. Hydroxyapatite is brittle in nature and load bearing capacity and strength of HAp is low so we could not use it in load bearing implant (total bone replacement) where tensile stress is developed. To overcome the above stated limitations of Hap, many researchers were tried to generate nano grained HAp powder [1, 2] in different methods. There is a significant difference of properties between natural and apatite crystals found in bone mineral and the conventional synthetic HAp. Bone crystals are formed in a biological environment through the process of biomineralization. In addition, the bone mineral also contains trace ions like Na+, Mg++, K+, which are known to play a important role in overall performance [1]. It has also been shown that the bioactivity of conventional synthetic HAp ceramics is inferior to the bone [1, 3-8]. During recent years, many researchers were tried in developing HAp powder doped with metallic ions by Ball milling, dry and wet milling process to increase the strength and ductility of HAp powders [1,3]. In this study, we have used a simple chemical route process that could produce HAp powder with a fairly short synthesis time. We have introduced three metal ions ,in different weight percentage, which are known to be present as the bone mineral during synthesis of HAp powder. This paper presents the synthesis and characterization of physical, mechanical and crystal structure of pure and doped HAp ceramic in detail.

2 EXPERIMENTAL PROCEDURE

2.1 Materials and methods

Pure and doped HAp powders were synthesized through water based Chemical route method. In this method, Calcium hydroxide [Ca(OH)2](MERCK,INDIA) and Orthophosphoric Acid [H3(PO)4] (MERCK,INDIA) were used as raw materials to produce apatite particles .

$$10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 \downarrow + 18H_2O$$

The apatite powder produced was aged for 24 hr. Then, the apatite particles in the suspension were filtrated, washed with ethanol three times, and dried at 100ºC for 24 hr in air. The dried powder was ground with a mortar and pestle into fine powder and subjected to calcinations at 800ºC temperature for 2 hrs using electrically heated furnace (NASKAR & Co., Model No.-EN170QT) at a constant heat rate of 5ºC/min, followed by cooling inside the furnace. In order to synthesize HAp powder doped with Magnesium, Zinc and Titanium, measured quantities of Magnesium Chloride Hexahydrate ($MgCl_2$,6H_2O,MERCK, INDIA, 96% pure), Zinc Oxide (ZnO, MERCK, INDIA, 99% pure) and Titanium Oxide (TiO2, MERCK,INDIA, 98% pure) were incorporated into the Calcium Hydroxide suspension before the addition of $H_3(PO)_4$ solution separately. The dopants were used in the amount of 2wt% and 5 wt% to see their effects on powder morphology and properties of the sintered ceramics.

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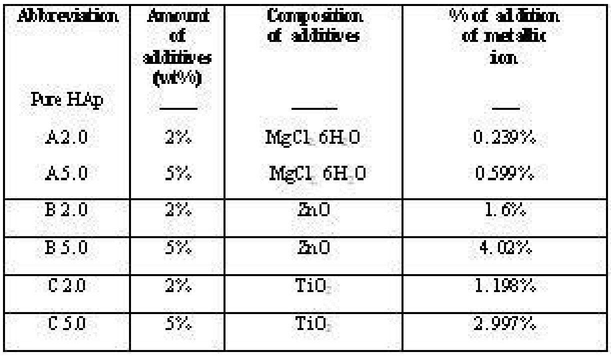
The resultant powders were then calcined at 800ºC for 2 hr. in a electrically heated furnace. A constant heating rate of 5ºC/min. was used, followed by cooling inside the furnace. Various composition of doped HAp is presented in TableI.

TABLE I

ABBREVIATION,AMOUNT(WT%),COMPOSITIONOF ADDITIVES AND PERCENTAGE OF ADDITION OF METALLIC IONS



Abbreviation	Amount of additives (wt%)	Composition of additives	% of addition of metallic ion
Pure HAp	___	___	___
A2.0	2%	$MgCl_2\,6H_2O$	0.239%
A5.0	5%	$MgCl_2\,6H_2O$	0.599%
B 2.0	2%	ZnO	1.6%
B 5.0	5%	ZnO	4.02%
C 2.0	2%	TiO_2	1.198%
C 5.0	5%	TiO_2	2.997%

3. POWDER CHARACTERIZATION

3.1 X-ray diffraction

X-ray diffraction (XRD) technique was used to study the effect of calcination temperature and dopants on the phase evolution and phase indentification. The dried calcined powders at 800ºC were ground into fine powder using a mortar and pestle to break down the powder agglomerates before analyzing in an X-ray diffractometer. Powder samples were placed in the specimen holder of a Rigaku diffractometer (Model- Miniflex, Rigaku Co., Tokyo, Japan) separately, and then analyzed, using Kb filtered Cu Kα radiation in the step scanning mode with tube voltage of 30KV and tube current of 15mA. The XRD patterns were recorded in the 2θ range of 0-80º with scan speed 1deg/min. The calcined powders doped with 2 wt% and 5 wt% of [$MgCl_2$, $6H_2O$] ZnO and TiO2, separately, were also analyzed for their phases in the same manner.

3.2. Fourier transform infrared spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) relies on the fact that most molecules absorb light in the infrared region of the electromagnetic spectrum , this absorption corresponds specifically to the bonds present in the molecule. In our experiment, we have done FTIR of as prepared calcined HAp powder and calcined HAp powder doped with different wt% of [$MgCl_2$, $6H_2O$] ZnO and TiO_2.FTIR measurement were performed in mid IR region (5000-400 cm-1) using KBr pallets in a Perkin- Elmer, Model No- 1615 (USA) instrument.

3.3.Powder Compaction And Sintering Study

As synthesized pure and doped crystalline HAp powders were uniaxially pressed using a steel mold having an internal diameter of 12-13 mm at a pressure of 173MPa, with a 2-ton press for 2 min from PEECO hydraulic pressing machine (PEECO Pvt Ltd, M/C NO.-3/PR-2/HP-1/07-08). Green ceramic structures were measured for their density and then sintered in a chamber furnace at 1250ºC for 1 hr at a constant heating rate of 5ºC/min.

A sintering cycle was developed to achieve better densification and to avoid cracking in the sintered specimens, by introducing several soaking temperature and tailoring the rate of heating and cooling.

Sintered ceramic structures were measured for their density and then subjected to mechanical characterization. Sintered samples intended for densification study, hardness measurement. Green and sintered ceramic specimens were measured for their geometric density from the ratio between the mass of specimen and its volume(determined by dimensional measurement).

3.4. Mechanical Characterization

Hardness Test was carried out using a Vickers diamond indenter on an automated hardness tester (Model No-LV-700AT, LECO Co, MI). During the hardness test, a load of 0.3 Kgf, 1Kgf and 3Kgf was applied on two samples of each of the composition type were tested for their hardness at three different locations with three different loads. The average of these readings were computed, reported and compared.

To determine the Fracture Toughness, we used Inverted Optical Microscope (OLYMPUS Co. Ltd., Model No-GX51F) interfacing with computer. We measured the average crack length (c) using Image Analysis Software .The cracks were developed by the indentation at the time of hardness testing. Fracture Toughness (K_{1c}) was calculated using simple equation considering radial-median crack geometry:-

$$K_{1c}=0.016(E/H)^{1/2}\,P/(c)^{3/2}$$

Two samples of each of the composition type were measured the fracture toughness.

4. RESULT AND DISCUSSION

4.1.Phase Identification

4.1.1 XRD Analysis

X-ray diffraction data of the amorphous powder, powder calcined at 800ºC temp. and Mg, Zn and Ti doped HAp powder at different wt% calcined at 800 ºC ,were recorded in 2θ range. The obtained XRD patterns of pure HAp and HAp powder doped with different wt% of Mg, Zn and Ti were presented in Fig1.The pure HAp powder calcined at 800 ºC exhibited several high intensity peaks corresponding to various planes of HAp i.e. (0 0 2), (2 1 1), (1 1 2), (3 0 0) and (2 0 2) as revealed by our analysis, with reference PDF card No.- 74-0566 for hydroxyapatite. Compared to XRD pattern of pure HAp, c/a ratio of HAp crystal structure and % of volumetric strain of HAp crystals (Table: I) changed due to addition of Mg, Zn and Ti. No phase change was noticed in their XRD patterns.XRD figures 1(a),(b),(c),(d) shows the XRD traces of the dried amorphous and calcined powders, with and without dopants. The XRD patterns of the pure HAp and doped powders calcined at 800ºC clearly show the presence of the most prominent peak at 2θ angle of ~31.7ºC, corresponding to hydroxyapatite (2 1 1) plane. Presence of this broad peak suggests that crystallites of HAp phase were formed as a result of calcinations at 800ºC. Almost identical patterns were recorded for all these compositions, which suggest that the presence of 2 wt% and 5 wt% of [$MgCl_2$,$6H_2O$] ZnO and TiO_2 as dopants did not alter the phase purity of crystalline HAp.

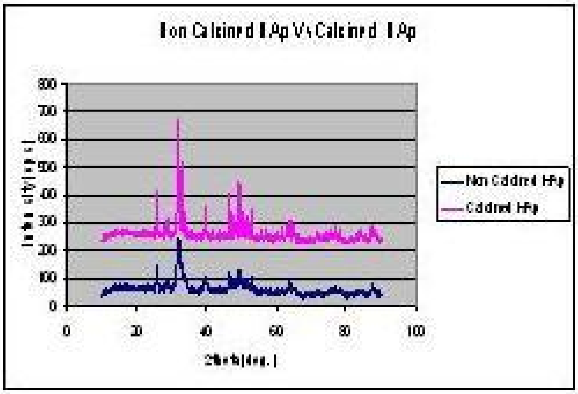


Figure 1(a). XRD patterns of Non Calcined HAp and Non Calcined HAp

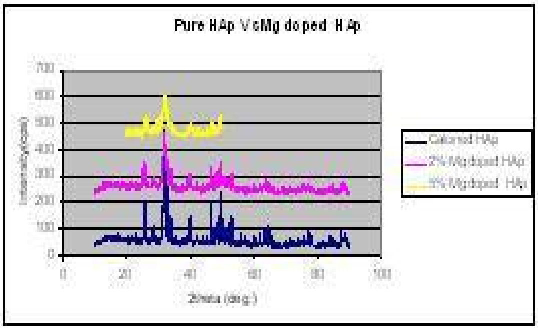


Figure 1(b). XRD patterns of Calcined HAp and Mg doped HAp(2wt% and 5wt%)

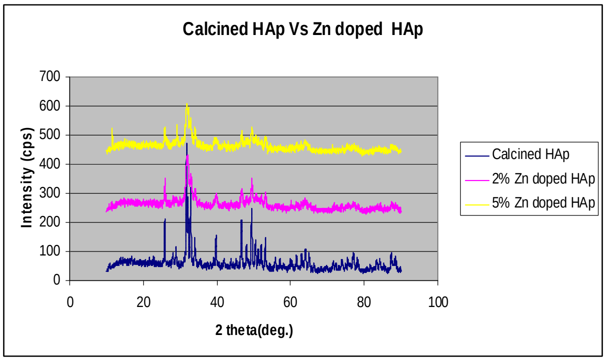


Figure 1(c). XRD patterns of Calcined HAp and Zn doped HAp(2wt% and 5wt%)

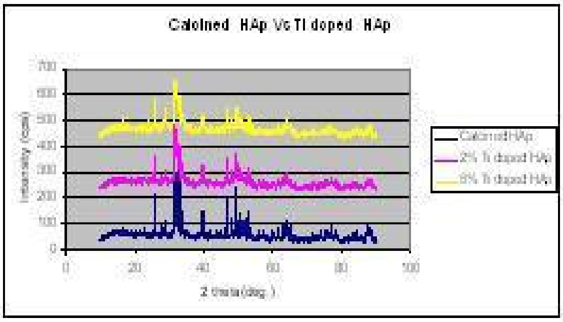


Figure 1(d). XRD patterns of Calcined HAp and Ti-doped HAp(2wt% and 5wt%)

Atomic radius of Mg (150 picometer),Zn (135 picometer) and Ti(144. 8 picometer) are different so they changed c/a ratio by replacing cations and developed volumetric strain.

TABLE II

C/A, UNIT CELL VOLUME AND PERCENTAGE OF VOLUMETRIC STRAIN

Composition	c/a ratio of a crystal	Unit cell volume (Å^3)	% Volumetric strain
Pure HAp (before Calcination)	0.731	529. 672	_____
Pure HAp(after Calcination)	0.731	531. 697	_____
5% Mg doped HAp (calcined)	0.734	533. 853	0. 789 % increase
2% Mg doped HAp (calcined)	0.729	527. 725	0.368% decrease
5% Zn doped HAp (calcined)	0.739	535. 059	1.017% increase
2% Zn doped HAp (calcined)	0.733	531. 0451	0. 259 % increase
5% Ti doped HAp (calcined)	0.720	526. 323	0. 632% decrease
2% Ti doped HAp (calcined)	0.720	526. 323	0. 632% decrease

4.1.2. FTIR ANALYSIS:

The obtained FTIR patterns of pure HAp and HAp powder doped with different wt% of Mg, Zn and Ti were presented in Fig2.The Fig 2(a) shows that FTIR of pure HAp powder calcined at 800ºC. In this FTIR plot of pure calcined HAp powder we got bulge shaped peak at 3436 which reveals the presence of hydroxyl group. The Fig 2(b) shows that FTIR of 5wt% and 2 wt% Mg doped HAp powder calcined at 800ºC. In these two FTIR plots hydroxyl group peak is very short and tending to disappear. This may due to the evaporation of the surface moisture of the powder. The Fig 2(c) shows that FTIR of 5wt% and 2 wt% Zn doped HAp powder calcined at 800ºC. In these two FTIR plots we got bulge shaped peak at 3436 which shows the presence of hydroxyl group. FTIR, spectra of HAp powder and ZnO doped Hap powder present almost similar bands. The Fig 2(d) shows that FTIR of 5wt% and 2 wt% Ti doped HAp powder calcined at 800ºC.

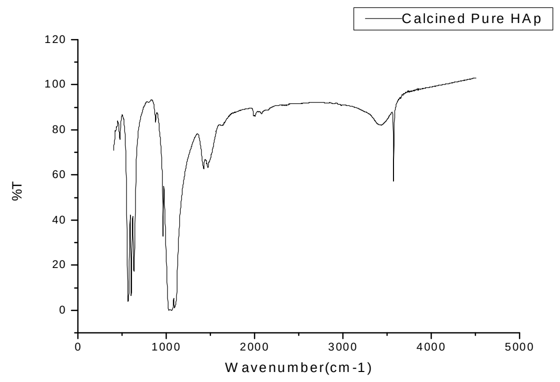


Figure 2(a). FTIR patterns of Calcined HAp

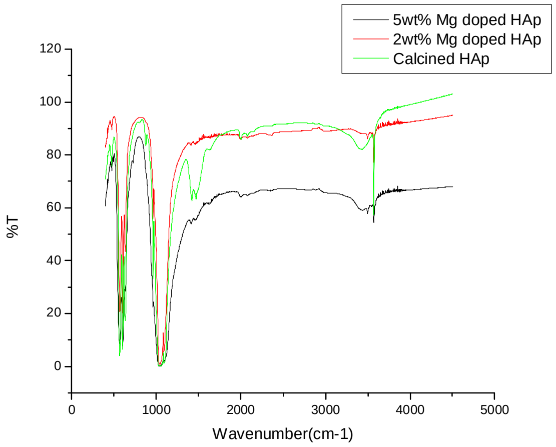
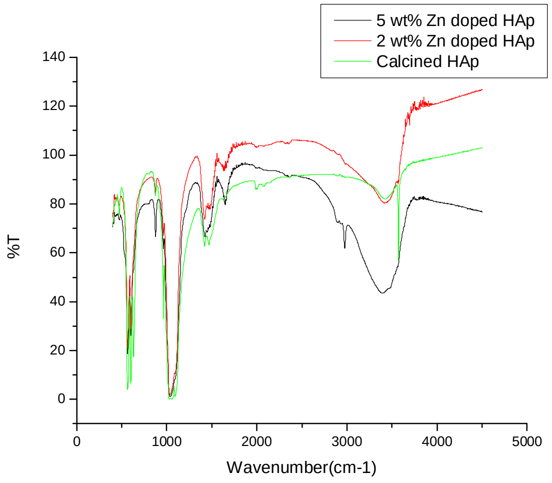


Figure 2(b). FTIR patterns of Calcined HAp and Mg doped HAp(2wt% and 5wt%)



2.(c)

Figure 2(c). FTIR patterns of Calcined HAp and Zn doped HAp(2wt% and 5wt%)

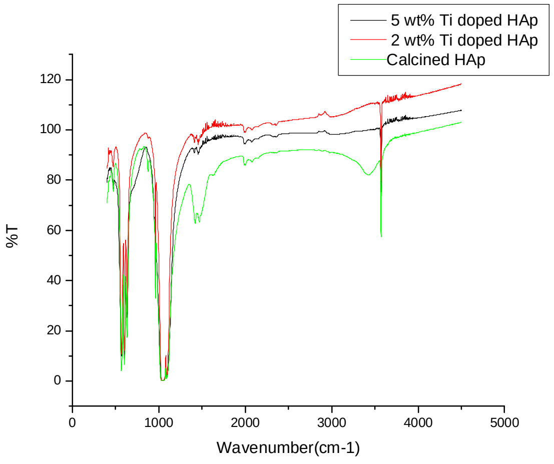


Figure 2(d). FTIR patterns of Calcined HAp and Ti doped HAp(2wt% and 5wt%)

4.2.Sintering study

Green ceramic structure prepared via uniaxial pressing were measured for their green density and were subjected to pressureless sintering. Average green density of all compositions are presented in Table III .The average diameters of all specimens before sintering is 12.15+_0.05 mm and thickness 5.4+_0.05 mm. Each sintered specimen was measured for its density and linear ,diametric and volumetric shrinkage and average of each of these compositions were calculated and presented in Table IV. Average diameter of sintered specimens is 10+_0. 05mm and thickness 4.5+_0.05mm. There was no major variation in shrinkage among the various compositions. Results of our sintering study showed that sintering at 1250ºC helps in the densification of pure and doped crystalline HAp ceramics which is in line with literature on conventional HAp sintering [5,6,10].We also performed some sintering study at 1200ºC which showed relatively lower densification(85. 25%).Sintering studies were not done above 1300ºC, as it is already established that sintering of HAp ceramics above 1300ºC leads to significant phase change, unwanted grain growth and deterioration of their properties. An average sintered density of 2.9 g/cc were recorded in pure HAp specimens sintered at 1250ºC which is equivalent to 93.9% of theoretical density of HAp. In this work, presence of Mg, Zn and Ti separately as dopants during powder synthesis again altered the sintered density of HAp powder. It is evident from the Table V that the Hap doped with $[MgCl_2, 6H_2O]$ and TiO_2 did not show the highest sintered density. Presence of 2% ZnO in the HAp powder showed the best sintered density of 3.12 g/cc when sintered at 1250ºC.

TABLE III

GREEN DENSITY AND PERCENTAGE OF THEORETICAL DENSITY

Compositions	Green density(g/cc)	% of Theoretical density
Pure HAp(calcined)	1.66	52.41%
5%Mg doped HAP (calcined)	1.69	53.36%
2%Mg doped HAP (calcined)	1.597	50.43%
5%Zn doped HAP (calcined)	1.64	51.78%
2%Zn doped HAP (calcined)	1.66	52.42%
5% Ti doped HAP (calcined)	1.65	52.01%
2%Ti doped HAP (calcined)	1.56	49.26%

TABLE IV
SINTERED DENSITY,PERCENTAGE OF DIAMETRIC,LINEAR AND VOLUMETRIC SHRINKAGE

Composition	Average Sintered Density(g/cc)	% Diametric Shrinkage	% Linear Shrinkage	% Volumetric Shrinkage
Pure HAp	2.98	18.32%	18.72%	45. 8%
A2.0	2.87	18.27%	18.35%	45.34%
A5.0	2.87	16.64%	16.64%	43.45%
B 2.0	3.10	18.98%	18.61%	46.54%
B5.0	2.85	17.31%	18.42%	44.15%
C2.0	2.89	18.87%	19.38%	46.94%
C5.0	2.78	16.54%	17.22%	42.31%

TABLE V
PERCENTAGE OF CONVENTIONAL HAP DENSITY OF ALL COMPOSITIONS

Composition	% of conventional HAp density
Pure HAp	93.9%
A 2. 0	90. 72%
A 5. 0	90. 52%
B 2. 0	97. 99%
B 5. 0	90. 096%
C 2. 0	91. 14%
C 5. 0	87. 82%

4.3.MECHANICAL CHARACTERIZATION

4.3.1.VICKERS HARDNESS TESTING

The average hardness of each of these composition was calculated and plotted as a function of the different indentation loads (0.3Kgf, 1 Kgf and 3 Kgf) shown in Fig 4. It is clear from the figures that the presence of Mg, Zn and Ti dopants in crystalline HAp influence its hardness.

In almost each compositions 2wt% of doping caused higher hardness values with highest load (3kgf).In other loads also hardness for 2wt% dopant concentration was higher than that with 5%.This feature may be attributed to higher density.

Results of our hardness testing proved that the hardness of crystalline HAp ceramics in influenced by the presence of Mg, Zn and Ti as dopants during synthesis. As seen in graph of hardness in Fig 4 in 3 Kgf load we can present the Table VI.

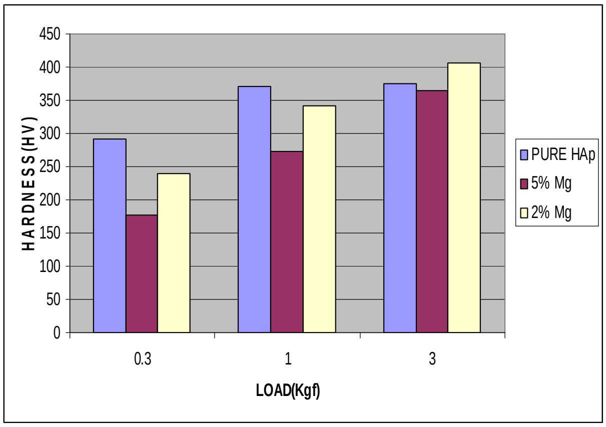


Figure 3(a).Graphical representation of Hardness of Calcined HAp and Mg doped HAp(2wt% and 5wt%)

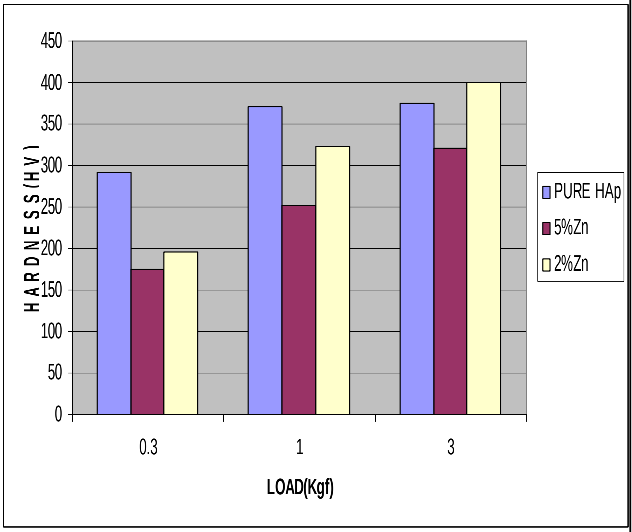


Figure 3(b).Graphical representation of Hardness of Calcined HAp and Zn doped HAp(2wt% and 5wt%)

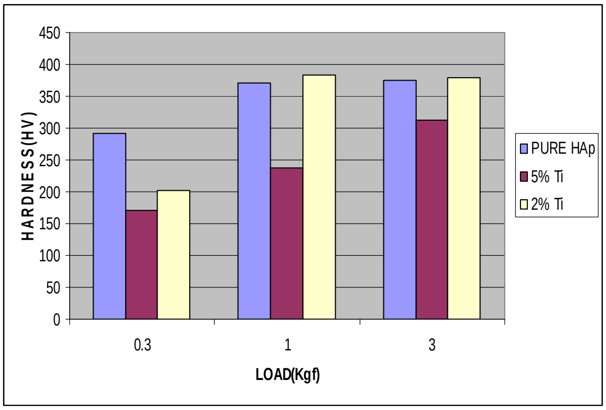


Figure 3(c).Graphical representation of Hardness of Calcined HAp andTi doped HAp(2wt% and 5wt%)

TABLE VI

AVERAGE HARDNESS AND PERCENTAGE OF HARDNESS VARIED

Composition	**Average Hardness (HV)**	**% of Hardness increase/decrease**
Pure HAp	374. 31	—
A 2. 0	399.42	6.71% increase
A 5. 0	365.54	2.34% decrease
B 2. 0	399.71	6.78% increase
B 5. 0	320.593	14.35% decrease
C 2. 0	378.78	1.19% increase
C 5. 0	311.78	16.7% decrease

We can conclude from the above chart that percentage of hardness increased 6.71%, 6.78% and 1.19% respectively for 2 wt% of Mg, Zn and Ti dopants , but for 5 wt% of dopants of Mg, Zn and Ti % of hardness was decreased.

4.3.2.FRACTURE TOUGHNESS

Pure and doped crystalline HAp ceramics sintered at 1250ºC were calculated for their fracture toughness with the Inverted Optical Microscope using Image Analysis Software. The average fracture toughness and their standard deviation of each of these composition was calculated and presented in Table VII. For radial-median crack system c/a ratio (where c=average crack length, d= average diagonal) should be more than 2. 5 and it was followed here.

The average crack length was 271.18µm for pure HAp, 225.05µm for 2% Mg doped HAp, 171.56µm for 5% Mg doped HAp, 210.83µm for 2% Zn doped HAp, 240.63µm for 2% Ti doped HAp and 82µm for 5% Ti doped HAp. We could not calculate the average crack length of 5% Zn doped HAp because the crack propagation was not found clearly from the site of indentation. The crack propagation path and the lateral crack growth of some specimens during the time of indentation with 3 kgf load are shown in Fig 4.

TABLE VII

AVERAGE FRACTURE TOUGHNESS AND STANDARD DEVIATION

Composition	Average Fracture Toughness (MPa√m)	Standard deviation
Pure HAp	0. 4988	0. 039823
A 2. 0	0. 63552	0. 07592
A 5. 0	0. 9993	----
B 2. 0	0. 7084	0.09215
B 5. 0	-----	-------
C 2. 0	0. 5973	0. 084834
C 5. 0	5.0735	0. 972112

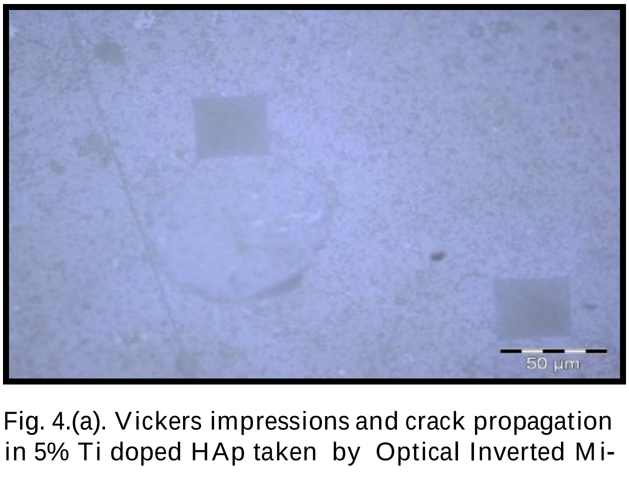


Fig. 4.(a). Vickers impressions and crack propagation in 5% Ti doped HAp taken by Optical Inverted Microscope

We can conclude from the above chart that in most of the cases fracture toughness of are close to 1 or just less than 1. In the case of 5% Ti doped HAp(C 5. 0) fracture toughness was highly increased. Pure HAp has inherent brittleness property. We can overcome this brittleness property with these compositions. Fracture toughness is increased for 2wt% and 5 wt% of all compositions than pure HAp powder. It was also noticed 5 wt% of all compositions is better than 2 wt% of all compositions in the case of fracture toughness.

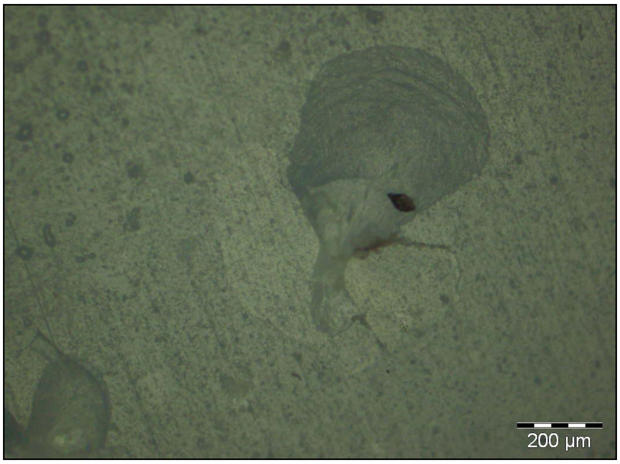


Fig. 4.(b). **Lateral crack propagation in Pure doped HAp**

From the Fig 4(a) in case of 5% Ti doped HAp we have got very clear impression of rhombus with sharp edges. The impression resembles metal like impression with small cracks at the edges. In contrary, pure HAp impression was not so clear and at identical load (3Kgf) it suffered severe chipping due to propagation and coalescence of lateral cracks. It was also noticed that fracture toughness values of 5% Ti HAp showed large scatter. We got the lowest value of fracture toughness of 5%Ti doped HAp was 1.4359MPa√m and highest value was 9.74MPa√m.

5. CONCLUSION

In our study, we prepared pure dense HAp and 2wt% and 5 wt% of Mg, Zn and Ti doped dense HAp powder using chemical route method. In XRD study, all compositions of doped and pure HAp powder we have got HAp phase. Pure HAp and all compositions of doped HAp powder we have got uniform pattern of shrinkage and almost of all cases we have got densification above 90%. Hardness was increased for 2wt% of all compositions of doped HAp powder; it may be attributed to better densification. Pure HAp is brittle material, all compositions of doped HAp powder fracture toughness was increased. For 5wt% of Ti doped HAp powder fracture toughness was highly increased and has got clear impression with small cracks. In all compositions of doped HAp powder mechanical property was increased, density was high and average toughness values were increased. This is marked improvement from practical point of view compared with pure HAp powder.

6. Acknowledgment

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