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# Micro hardness studies of pure and doped brushite crystals

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**Abstract** : Vicker's micro hardness studies on pure and doped brushite ($CaHPO_4.2H_2O$) crystals are reported. The micro hardness value ($H_v$), work hardening coefficient (n), and first order elastic stiffness coefficient ($C_{11}$) are reported for brushite crystals doped with Ni, Cd, Mg and Pb. It has been observed that the micro hardness has a load dependent part and a load independent part.

**Keywords** : Urinary stones, doped brushite crystals, Vicker's micro hardness

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## 1. Introduction

Bio-mineralization in human systems affects a large population world-wide and the number of cases reported is ever on the increase [1]. Of the various crystals formed in the human body, deposition of matter in renal systems has become a common diseases resulting in the wastage of a number of man hours [2]. Calcium phosphates are the most common crystals in urine. They are often identified at the center of calcium oxalate and calcium phosphate mixed stones [3]. A variety of calcium phosphate stones *viz.*, $CaHPO_4.2H_2O$- (Brushites), $CaHPO_4$, $Ca_8H(PO_3)_2OH$ and $Ca_3(PO_4)_2$ are found to grow in biological systems of mammals. Of these different stones, crystallization of $CaHPO_4.2H_2O$ plays an important role in the formation of metabolic and non-metabolic urinary stones [4]. Brushites are significant for their role in the nucleation of calcium oxalate crystals [5].

Investigations made on urinary stones have proved that at least 14 different trace elements are present in these crystalline components of matter [6]. The prominent among these trace elements are Cd, Ni, Mg and Pb. These trace elements may enter the body through atmospheric pollutants and food. Cadmium and lead are known toxic elements present in the human body and they enter the body along with food particles. Accumulation of cadmium is severe to the body since its presence in liver and kidney leads to renal tubular damage [7]. The increases in lead and nickel content in the body of gout patients results in renal failure due to nephrolithiasis [8]. The presence of an impurity element in crystalline solid changes its elastic properties. The change in hardness of the element with dopant is very interesting.

Fragmentation of stones has become an invasive technique of stone therapy. The stones can be crushed inside the bladder, ureter or kidney. Hardness of the stones stumbles the process of such bloodless surgery. Extra corporal shockwave lithotripsy (ESWL) has become a primary treatment modality for urinary stone diseases [9]. Because of their differences in chemical composition and structural features the efficacy of stone fragmentation may vary considerably [10]. Hardness of a material is a measure of the resistance it offers to local deformation [11]. A proper knowledge of the hardness of these crystals containing different trace elements will be useful in managing the disease more effectively. The variations of hardness on doping the crystal with these dopents are discussed in this paper. Micro hardness

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measurements have aided the determination of the elastic constants of the crystal. Knowledge of the elastic properties of stones is also essential in optimising the parameters like frequency and intensity required for stone fragmentation by ultrasound lithotripsy.

The gel technique was employed to synthesize the brushite crystals. The gel medium has very close resemblance to the mucus medium in which the stones happen to grow in biological systems. *In-vitro* crystallisation in gel medium is popular in the study of crystallization of urinary stones [12].

## 2. Experimental

The crystals were grown in a gel medium of sodium metasilicate gel having density 1.03g $cm^{-3}$ and pH 5 6, by titrating the gel against 1.18M potassium dihydrogen phosphates. After gelation, 1.68M calcium nitrate solution was added as supernatant solution. Liesegang rings were formed within a few days. They arise due to the rhythmic precipitation of the supernatant solution through the gel medium. In a few days, these rings disappear and in that region spherulitic crystals were observed. Platy crystals were also found to grow just below the region where spherulites were found in the medium [13]. To dope the crystals with ingredients such as lead, nickel, magnesium and cadmium the supernatant solution was mixed with appropriate amounts of lead nitrate, nickel chloride, magnesium chloride and cadmium chloride solutions. Elemental analysis on the doped crystals confirmed the presence of the respective dopents on the doped samples.

Crystals with different morphologies were found to grow in each system. Good quality crystals of medium size (5 x 2 x 0.5 mm) were obtained for pH 5.61 and gel density 1.03 gm/$cm^3$. The growth period varied from 60 to 75 days.

All the samples were analysed by using X-ray diffraction (XRD) and inductively coupled plasma emission spectroscopy (ICPEAS). The microhardness studies were carried out on pure and doped crystals using Vicker's hardness tester.

### *A. X-ray diffraction analysis :*

Powder XRD pattern for the pure sample has been recorded using a Rigaku Dmax/2C (Japan) diffractometer fitted with nickel filtered Cu $K_\alpha$ radiation (Figure 1). The calculated d values from XRD of the crystals (Table 1) were in good agreement with standard values [14]. The following are the lattice parameters of brushite crystals obtained from the XRD data.

Crystal system : Monoclinic,

Space group : Ia,

Cell dimensions : $a = 5.812$ Å, $b = 15.180$ Å, $c = 6.239$ Å, $\beta = 116.41°$,

No : of molecules in unit cell : 4.

### *B. Micro hardness studies :*

Micro hardness studies on smooth plane surfaces were carried out using Leitez hardness tester type P1191 fitted with a Vicker's

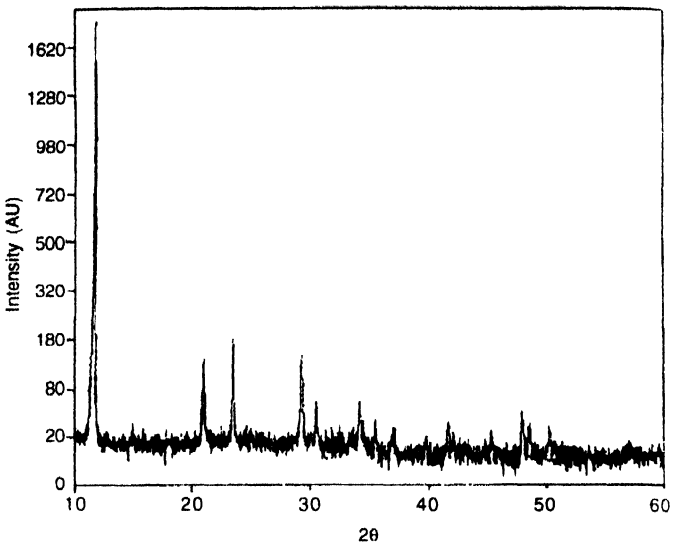


**Figure 1.** XRD Pattern of $CaHPO_4.2H_2O$.

**Table 1.** Calculated and standard d values of Brushites

| Observed d value (A°) | ASTM d value (A°) | hkl plane |
|---|---|---|
| 7.5899 | 7 62 | 020 |
| 4 2329 | 4.27 | 121 |
| 3 0452 | 3 06 | 141 |
| 2 9243 | 2 93 | 121 |
| 2 6223 | 2 63 | 200 |
| 2.5315 | 2 53 | 060 |
| 2.4163 | 2 47 | 220 |
| 2 2674 | 2 27 | 042 |
| 2 1702 | 2 17 | 152 |
| 2 0847 | 2.09 | 112 |
| 2 0216 | 2 03 | 071 |
| 2 001 | 2 01 | 170 |

pyramidal diamond intender. The (100) planes of samples were identified and indentations were made on these faces using the diamond intender. The indentation time was maintained at 30 seconds. The load was varied from 5g to 100g. For each load five indentations were made at a distance greater than 4 times the length of diagonal. The Vicker's micro-hardness number $H_v$ was calculated loads using the relation.

$$H_v = 1.8544\,(P/d^2)\ \text{kg/mm}^2,$$

where $P$ is the applied load in kg and $d$ is the average diagonal length of the Vicker's impression in mm after unloading. Both pure and doped samples were tested for its hardness.

Variations of hardness with load for the pure and doped samples of pure and doped brushites are shown in Figure 2. The

samples exhibited practically zero brittleness up to a load of 200g, which is the maximum for the instrument.

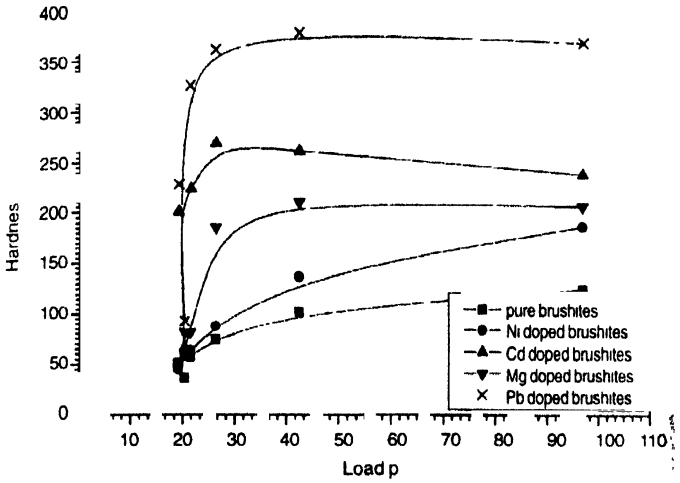


**Figure 2.** Hv *vs P* curve for pure and doped brushites

## 3. Results and discussion

The hardness and elastic properties of doped crystals show variations from the pure crystals. Figure 2 depicts the variations in microhardness with applied load for the different crystals. All the curves show a unique pattern in the low load region. Below a threshold load, the behaviour of the doped as well as the pure crystals are identical. In this region the microhardness dependence with external stress is linear. For higher loads the micro-hardness becomes load independent. This is similar to the proportional resistance model (PSR model) proposed by [15, 16]. In the PSR model micro hardness has two contributions.

*(i) The indentation load dependent part :*

Mayer's power law [17] can be applied to this part, which is in the low load region.

$$P = Ad^n \tag{1}$$

A plot of 'log p' *versus* 'log *d*' graph provides a straight line (Figure 3), the slope of which gives the work hardening coefficient $n$. The best linear fit of this curve is taken to evaluate the work hardening coefficient $n$ (Table 2). A is a constant parameter for a given material.

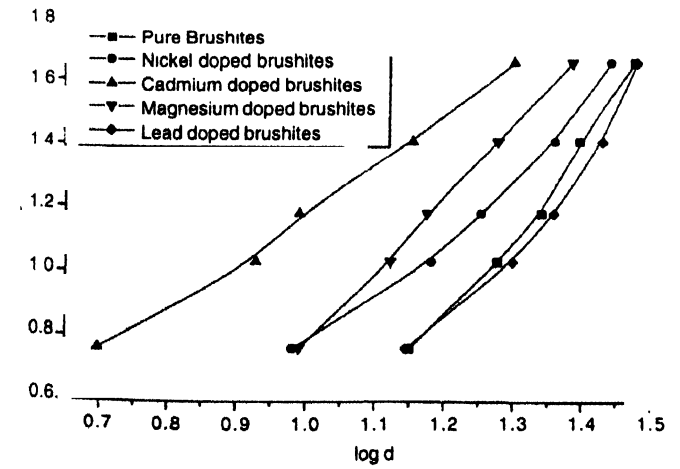


**Figure 3.** log *p vs* log *d* curve for pure and doped brushites

**Table 2.** Mayer's law parameters determined for pure and doped brushite crystals

| Crystal | Work hardening coefficient-n | A |
|---|---|---|
| Pure brushites | 2.8529 | 1.3040 |
| Nickel doped brushites | 7.9155 | 3.3120 |
| Cadmium doped brushite | 5.5992 | 0.8103 |
| Magnesium doped brushites | 3.4298 | 1.0216 |
| Lead doped brushites | 4.5885 | 2.6192 |

It is found that the work hardening coefficient is the lowest for pure brushites while it increases for all the doped samples. All the crystals have $n > 2$, which confirms that they are soft materials as per the Onstrich concept [18]. Accordingly the lattice is soft if $n > 2$ and if $n > 2$ that lattice is hard. A hard lattice will show brittle characteristics in the high load region. Interestingly no crack lengths were observed when the samples were loaded to different loads. Thus all the crystals can be assigned with soft lattices.

From clinical experience, it has been concluded that of all urinary stones, brushites come under the middle order in the ease to fragment. The toughest ones being calcium oxalate monohydrate and cystine [19, 20]. The work hardening coefficient $n$ is highest for Ni doped crystals, followed by Cd and Pb doped crystals and interestingly the least for Mg doped. The inhibiting property of Mg in brushite crystals is well established by Shiv Kumar *et al* [21]

*(ii) The indentation load independent part :*

In the high load region, classical Mayer's law was insufficient as the microhardness tends to be load independent. A polynomial equation represents the experimental data. The indentation test load $P$ is related to indentation size $d$ as :

$$P = a_1 d + a_2 d^2 = a_1 d + \left(P_c / d_0^2\right) d^2, \tag{2}$$

where $a_1$ is the proportionality constant in the load dependent region and $a_2$ that in the load independent region, $P_c$ is the critical applied test load above, which micro hardness becomes load independent and $d_0$ is the corresponding diagonal length. The first term in eq. (2) represents the surface energy contribution. Eq. (1) can be rearranged to give

$$(P/d) = a_1 + \left(P_c / d_0^2\right) d. \tag{3}$$

Hence, a plot of '*P/d*' *versus* '*d*' will give a straight line and the slope of which gives the value of load independent micro hardness $\left(P_c / d_0^2\right)$, when multiplied this by the Vicker's conversion factor 1.854 gives the load independent micro

hardness. In this region too the micro hardness is the least for the pure samples and high for the doped ones (Table 3). The micro hardness of brushites has considerable variation from there respective pure samples. Doping with magnesium decreases the $H_0$ values whereas all other dopents like lead, cadmium and nickel increased the $H_0$ value when compared to the pure brushites. Thus the dopents have a considerable influence on the hardness of the urinary crystals. As the pollutants like nickel, lead and cadmium increase in the body the hardness of the formed stones is on the increase making it difficult for the removal by shock wave lithotripsy.

**Table 3.** PRS model parameters and load independent microhardness values and first order elastic constants of pure and doped brushites

| Crystal | $pc/d_0^2$ (Pa) | H (Pa) | $C_{11}$ (Pa) |
|---|---|---|---|
| Pure brushites | 1 29 | 2 40 | 4.6277 |
| Nickel doped brushites | 1 14 | 2 12 | 3 7246 |
| Cadmium doped brushites | 2.91 | 5.41 | 19 1909 |
| Magnesium doped brushite | 2.13 | 3 95 | 11 0673 |
| Lead doped brushites | 1 44 | 2 67 | 5 5769 |

The first order elastic stiffness coefficient $C_{11}$ of the samples are calculated using Wooster's empirical relation [22].

$$C_{11} = H_0^{7/4}. \tag{4}$$

## 4. Conclusion

Hardness variations in the load dependent and load independent regions for pure and doped brushite crystals are reported for the first time. Elastic properties of pure and doped brushite crystals are interestingly related to the impurity addition in crystals. All the crystals show remarkable changes in micro hardness, work hardening coefficient and first order elastic stiffness coefficient. Microhardness studies carried out on the doped crystals shows that the difference in size of the ions constituting the mixed crystal is responsible for internal elastic ion interaction in the lattice and these types of strain gives rise to imperfections affecting the microhardness of the doped crystal. The presence of the cations of Pb, Ni, Cd, and Mg in place of Ca ions induces strain in the lattice due to the different ionic radius of the dopent resulting in the increase in the work hardening coefficient. In the load independent part too the value of Vicker's microhardness is the least for the pure samples and it increases for the doped crystals. This study reveals that the dopents have a definite influence of brushite crystals and their presence increases the hardness of the crystals making the stone removal harder by way of crushing it inside the body.

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