COMPUTER SIMULATION OF SELECTED AND CONVERGENT BEAM ELECTRON DIFFRACTION PATTERNS FOR HYDROXYAPATITE

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Abstract

In this work, the structural characteristics of the hydroxyapatite (HAP) are studied by simulation of selected area (SAD) and convergent beam (CBED) electron diffraction patterns. Experimentally HAP shows SAD patterns that present an incompatibility with the crystallography of its reported space group, because the existence of forbidden reflections 001 (l odd). Since forbidden reflections along the c* axis are a consequence of the existence of the screw axis of the symmetry 63 according with the simulation results, they indicate that experimentally this screw axis is lost during the sample electron beam interaction.

Keywords: Hydroxyapatite, CBED patterns, simulation of structure, forbidden reflections.

1. Introduction

Hydroxyapatite (HAP) is the main mineral component of bones, cement and teeth [1,2], its study is of great importance for its application in the field of biomaterials. Its chemical composition is $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, and shows a hexagonal unit cell with parameters $a = b = 0.9432$ nm, $c = 0.6881$ nm and $\gamma = 120^\circ$ [3]. Recently it has been reported [4] the transition from insulation to ionic superconductor around 300° C in HAP of dental enamel. The presence of the forbidden reflections along the c* axis in the selected area electron diffraction pattern (SAD) has been also reported [3], as shown in Figure 1 for the [0.01] direction. Apparently these reflections violate the symmetry specified by the space group of the HAP (No. 176: P6/m). Evenmore, these reflections are also presented in the SAD patterns along the directions [1.10] and [1.00] when a tilting sequence is done around the c* axis starting from [0.01]. All this has showed that the observance of these reflections are not produced by the well-known double diffraction effect [5].

Fig. 1. Experimental SAD along [1.00] from HAP. Note the presence of forbidden reflections 00l, (l odd) $V=200$ KeV
In this work we have calculated the SAD and CBED patterns by computer simulation for the analysis and study of the forbidden reflections along the c axis. Everything seems to indicate that experimentally they are a product of the interaction between the sample and the electron beam when the HAP samples are observed with the electron microscope.

2.- Experimental

Starting from the data generated by Brés et al. [3] for the atoms in the HAP unit cell (table 1), they were captured in the sub-program “cristal builders” of the program CERIUS [6] to obtain a graphic visualization of the HAP unit cell (Figure 2). From this model, an adjustment was obtained by the Rietveld method [7] with $R_{wp} = 9.85\%$. The resulted data was also captured in the data matrix of the program EMS [8] and the simulations of SAD and CBED diffraction were obtained. The CBED patterns were obtained in ZOLZ, FOLZ, HOLZ, SAD, and Kikuchi line’s patterns for different axes zone and thicknesses to compare them with their corresponding experimental ones.

### Table 1. Crystallographic data for hydroxyapatite.

<table>
<thead>
<tr>
<th>Hexagonal unit cell</th>
<th>Parameters $a = b = 0.9432, \text{nm}, , c = 0.6881, \text{nm}$</th>
<th>atomic positions</th>
<th>occupancy</th>
</tr>
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<tbody>
<tr>
<td>Elements</td>
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<tr>
<td>O(I) in 6(h):</td>
<td>0.3272 0.4837 1/4,</td>
<td>occ = 1</td>
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<td>O(II) in 6(h):</td>
<td>0.5899 0.4666 1/4,</td>
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<tr>
<td>O(III) in 12(i):</td>
<td>0.3457 0.2595 0.0736,</td>
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</tr>
<tr>
<td>P in 6(h):</td>
<td>0.3999 0.3698 1/4,</td>
<td>occ = 1</td>
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<tr>
<td>Ca(I) in 4(f):</td>
<td>1/3 2/3 0.0010,</td>
<td>occ = 1</td>
<td></td>
</tr>
<tr>
<td>Ca(II) in 6(h):</td>
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<td>occ = 1</td>
<td></td>
</tr>
<tr>
<td>O$_H$ in 4(e):</td>
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<td>occ = 1/2</td>
<td></td>
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<tr>
<td>H in 4(e):</td>
<td>0.0 0.0 0.0617,</td>
<td>occ = 1/2</td>
<td></td>
</tr>
</tbody>
</table>

3.- Results

When the simulation of the SAD pattern was carried out for different zone axes, we noticed that they show some similarity with the experimental pattern (Figure 3), although for the case of the simulated patterns the reflections 001 (l/odd) do not appear. Once the SAD patterns were calculated, the CBED patterns were calculated too for different thicknesses. In figure 4 a CBED pattern is presented in ZOLZ in the [0.01] direction confirming that there is a symmetry 6-fold, but any mirrors are presented. Note the similarity with the experimental one. In figure 5 the CBED pattern in ZOLZ in the [1.10] direction is shown. In this the absence for the forbidden reflections and the existence of two perpendicular mirrors, which are independent of the thickness (Figure 6) are observed. In this case, in the corresponding experimental pattern, the dynamical effects are not possible to observe. Figure 7 shows a CBED pattern in HOLZ for the main direction. We notice that either ZOLZ, FOLZ and SOLZ in [0.01] present a 6-fold symmetry but any mirror is presented. In the [1.10] and [1.00] directions show that ZOLZ has two mirrors, but FOLZ and SOLZ present only one. Figure 8 shows the Kikuchi lines together with ZOLZ and FOLZ, they can be compared with that one obtained experimentally[4].
Fig. 3. Simulated SAD pattern from HAP along [1.00] axis zone. Note the absence of the reflections 00l (l odd). V = 200 kV.

Fig. 4. CBED patterns from HAP in ZOLZ along [0.01] direction. A) experimental pattern, B) simulated. Notice the absence of the reflections 00l (l odd).

Fig. 5. CBED patterns in ZOLZ along [1.10] direction. A) experimental, B) simulated. Notice the absence of the reflections 00l (l odd).

Fig. 6. Segments of the CBED patterns for different thickness along the [0.01] direction. Note the presence of dynamic lines along this direction and the absence of forbidden reflections.
4. Discussion

Using the tables for the 31 diffraction groups given by Spence and Zuo [9] and taken in account the symmetries observed in Figure 4, 5 and 7, we have observed that ZOLZ indicated the symmetry 2mm and generates the diffraction group in projection 2mm₁, and the symmetry 6-fold generates the diffraction group in projection 6₁. Therefore, since we have a hexagonal system for HAP, it is found that the diffraction groups are 2₁ mm for the zone axis [1,0,0] and [1,1,0], and 6₁ for [0,0,1]. This would indicate us that HAP shows the point group 6/m in [0,0,1] and the point groups 6/ m and 6/mmm in [1,0,0] and [1,1,0]. Therefore the point group is 6/m.

To determine the space group, the formation of dynamic bands or crossings presented in ZOLZ must be analyzed. They would give us the elements of translational symmetries: screw and slip axes. In Figure 6 we notice that, for different thicknesses, the dynamic lines are presented after a thickness of 150 nm. Moreover the absences presented in the [1,0,0] and [1,1,0] SAD pattern correspond to the reflections 00l (l odd). All this indicates an screw axis 2₁ along “c” which is contained in the symmetry 6₃. Therefore, the space group of the hydroxyapatite is P6/m.

The weak intensity observed in the 00l (l odd) reflections could have several causes. A specific structural phenomenon has been reported by Reyes-Reyes and Reyes-Gasga [10,5] These authors have shown that the electron diffraction patterns do not exhibit forbidden reflections due to a modulated structure effect. Brés et al. [3] have proposed the possibility of structural disorder occurring in the screw axis when observing CBED patterns, so the forbidden reflections are the result of the chemical disorder in the HAP unit cell. They say that this is the reason why the dynamic lines are not evidenced along the c* axis in the disks ZOLZ and the presence of the forbidden reflections. Reyes-Gasga and García [11] have calculated the ballistic damages produced by the electron beam in a HAP sample; from these calculus it was realized that the OH ions are weakly bonded and do not need too much energy to be displaced. So, it would produce a break down of the original structure of the crystal, mainly the screw axis.

Fig. 7. CBED patterns in HOLZ
A) [1,1,0], B) [0,0,1] and C) [1,0,0].
Note the 6-fold in B), and the mirrors in A) and C).
L = 500 mm. V = 200 KeV
5. Conclusions

From the simulated patterns for HAP, the CBED patterns present the symmetries 6mm and m in the central disks, 6-fold and 2mm in ZOLZ, and the symmetries 6-fold and m in HOLZ. The non-existence of the reflections 00l (l odd) is characteristics of the space group P6/m. The probable structural disorder in the hydroxyl columns of ions of the HAP unit cell might be taken in account for the observance of the weak intensity in the otherwise forbidden 00l (l odd) reflections and for the poor visibility of FOLZ reflections in the experimental CBED pattern along the [0.01] zone axis. This disorder might destroy the screw axis of the symmetry 63.

6. Acknowledments

Ing. Manuel Aguilar Franco, C.D. Ana Guadalupe Rodríguez, Sr. Pedro Méxía Hernández, Sr. Carlos Flores Morales, Sr. Luis Rendón Vázquez, Fis. Roberto Hernández, Ing. Samuel Tehuacanero, Ing. Cristina Zorrilla, M. en C. Jacqueline Cañetas. This work was sponsored by CONACYT

7. References

8. Software EMS-Online http://cecm.insa-lyon.fr/CIOLS/

Fig. 8. Kikuchi lines pattern with ZOLZ y FOLZ
A) [0.01], B) [1.10], C) the experimental one in the [1.10] direction. L = 300 mm V=200 KeV