X-ray Structure Refinement and Vibrational Spectroscopy of Ca$_{8}$Gd$_{2}$ (PO$_4$)$_6$ O$_2$

R. Ayadi, M. Boujelbene and T. Mhiri

Laboratory of the Physico-Chemistry of Solid States. LR11 ES51. of Sfax. Road of Soukra km 4. Sfax3071.

Tunisia.

Email: rayda_ayadi@yahoo.fr

M. Boujelbene

Laboratory of the Physico-Chemistry of Solid States. LR11 ES51. of Sfax. Road of Soukra km 4. Sfax3071.

Tunisia.

* Corresponding author: m_boujelbene2010@yahoo.fr

T. Mhiri

Laboratory of the Physico-Chemistry of Solid States. LR11 ES51. of Sfax. Road of Soukra km 4. Sfax3071.

Tunisia.

Email: tahermhiri@yahoo.fr

Abstract

The present paper is interested in the study of compounds from the apatite family with the general formula Ca$_{10}$ (PO$_4$)$_6$A$_2$. It particularly brings to light the exploitation of the distinctive stereochemistries of two Ca positions in apatite. In fact, Gd-Bearing oxyapatite Ca$_8$Gd$_2$ (PO$_4$)$_6$O$_2$ has been synthesized by solid state reaction and characterized by X-ray powder diffraction. The site occupancies of substituents is 0.3333 in Gd and 0.3333 for Ca in the Ca(1) position and 0.5 for Gd in the Ca (2) position. Besides, the observed frequencies in the Raman and infrared spectra were explained and discussed on the basis of unit-cell group analyses.

KEYWORDS: Inorganic compounds; X-ray diffraction; Infrared spectroscopy; Raman spectroscopy.
1. Introduction

The structure of apatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, $A= F, \text{OH}, \text{O}, \text{Cl}, \ldots$ apatite in the space group $\text{P6}_3/m$ allows a wide range of cation substitution [1-16].

A compact arrangement of $\text{PO}_4$ tetrahedrons constitutes the skeleton of this structure which exhibits two kinds of tunnels parallel to the c-axis.

The first is occupied by four $M$ (1) cations at 4f sites, along a three–fold axis. These cations are coordinated by nine oxygen atoms. The second tunnel is occupied, on its periphery, by the six other $M$ (2) cations at 6h sites, along a six–fold axis. These $M$ (2) cations which are surrounded by six oxygen atoms and one $Y$ atom two alternated equilateral triangles at level 1/4 and 1/4 centered on a six–fold axis where the $Y$ atoms are located.

The formula assigned to the compound had to be $[\text{Ca}_4]^{8+}[\text{Ca}_4\text{Bi}_{1.6}\text{O}_4\text{O}_3]^{8+}\text{PO}_4\text{O}_4\text{O}_3$ with space group $\text{P6}_3/m$. Thus the lower oxygen content (1.8) compared to stoichiometric expected (2) (see the procedure), confirmed the volatilized of bismuth. Therefore, 16% de bismuth was volatilized. The refined results indicated that the $\text{Bi}^{3+}$ ions were mainly located in $\text{Ca}$ (2) site on 6h position and formed two triangles that rotated 60° from the c-axis. The oxygen atom $O_4$ was located in the center of these $\text{Bi}$-triangles [17].

The compounds $\text{BiCa}_4(\text{PO}_4)_3\text{O}$ and $\text{LaCa}_4(\text{PO}_4)_3\text{O}$ have been reported recently [18]. They are isostructural with $\text{BiCa}_4(\text{VO}_4)_3\text{O}$ (Merck. 98. 9%) and $\text{Ca}_4\text{CO}_3$ (Cerac. 99.95%), as shown in the following formula:

$\text{Gd}_2\text{O}_3 + 3 \text{P}_2\text{O}_5 + 8 \text{CaCO}_3 \rightarrow \text{Ca}_8\text{Gd}_2(\text{PO}_4)_6\text{O}_2 + 8 \text{CO}_2$ (gaz)

The resultant powder was subsequently heated at 740°C during 12 h, in slow cooling conditions.

X-ray powder diffraction (XRD) pattern was determined by means of a Panalytical XPERT PRO MPD diffractometer equipped with a detector Xcellerator operating with a secondary monochromator and using a CuKα radiation source ($Kα_1 = 0.15439$ nm and $Kα_2 = 0.15440$ nm). The diffraction pattern was recorded under ambient atmosphere over an angular range of 5-80° (2θ) with a step length of 0.033° (2θ).

The Fourier transform infrared (FT-IR) measurements were performed at room temperature. On a JASCO FT-IR 420 spectrometer over the 4000 - 400 cm$^{-1}$ region, in a KBr pellet. Furthermore, Raman spectra were measured with a LABRAMHR 800 triple monochromatic at room temperature under a $50 \times$ LF objective microscope, a He-Ne ion laser operating at about 300 mW was used (on the triple) as an excitation source (514.532 nm), with a spectral steps of 3 cm$^{-1}$.

2. Experiment

The $\text{Ca}_8\text{Gd}_2(\text{PO}_4)_6\text{O}_2$ compound was obtained by the solid-state reaction of $\text{Gd}_2\text{O}_3$ (Merck. 98. 9%), $\text{P}_2\text{O}_5$ (Merck. 98. 9%) and $\text{Ca}_4\text{CO}_3$ (Cerac. 99.95%), as shown in the following formula:

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3. Results and discussion

3.1 Refinement of the structure

The structure of the compounds in the solid are closely related to those of the common phosphate apatite. They have been frequently described in the literature [22]. They have been commonly determined by X-Ray powder diffracture using the Rietveld method refinement stating from the isostructural phase $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$.

The analysis of the final adjustments carried out for the observed and calculated diagrams indicated that there were non-indexed lines. The latter could be identified as minor impurities. The latter could be identified as $\text{Ca}_3(\text{PO}_4)_2$.

The final results of this refinement are presented in Table. 1, Table. 2 (for the structure parameters), Table. 3 (for the atomic positions) and Table. 4 (the bond length distances and angles). Besides Fig. 1 shows the observed, calculated and different X-ray profiles of the powder diffraction of these apatite phosphates.
Table. 1. Details of powder X-ray data collection and structure refinement of Ca₈Gd₂(PO₄)₆O₂.

| Formula | Ca₈Gd₂(PO₄)₆O₂ |
|---------|----------------|
| Halfwidth parameters | U = 0.019711  
V = -0.052960  
W = 0.035341 |
| Parameters asymmetry | Asy1 : -0.02951  
Asy 2 : -0.01187 |
| Reliability Factors | Rₓ : 0.055  
Rᵧ : 0.1152  
Rₚ : 0.132  
RWP : 0.133 |

Table. 2. Analytical data and lattice parameters of Ca₈Gd₂(PO₄)₆O₂.

| System | Hexagonal |
|--------|-----------|
| Cell parameters (Å) | a=b=9.418(7)Å  
c=7.65(5) Å  
α = β = 90° et  
γ = 120° |
| Volume (Å), Z | V=587.73(8) Å³  
Z = 2 |
| Zéro point | 0.023 |
| Count time [sec / step] | 35 s |

Table. 3. Atomic coordinates, occupancy factors after Riveted refinement of Ca₈Gd₂(PO₄)₆O₂.

| Atom | X   | Y   | z     | Ueq | B exp |
|------|-----|-----|-------|-----|-------|
| Ca (1) | 1/3 | 2/3 | -0.00096 (4) | 0.01426 (19) | 1/3 |
| Gd (1) | 1/3 | 2/3 | -0.00096 (4) | 0.01426 (19) | 1/3 |
| Ca (2) | 0.01231 (9) | ¼ | ¼ | 0.0401 (2) | 0.5 |
| Gd (2) | 0.01231 (9) | ¼ | ¼ | 0.0401 (2) | 0.5 |
| P | 0.39224(4) | 0.36716(5) | ¼ | 0.0350 (13) | 0.5 |
| O (1) | 0.3499 (9) | 0.4975(9) | ¼ | 0.0075 (11) | 0.5 |
| O (2) | 0.5969 (9) | 0.4688 (7) | ¼ | 0.0075 (11) | 0.5 |
| O (3) | 0.34489(5) | 0.26913 (5) | 0.07354(8) | 0.0075 (11) | 0.5 |
| O (4) | 0.00000 | 0.00000 | 0.32595(10) | 0.0075 (11) | 1/3 |
Table 4. Selected bond lengths (Å) and bond angles (°) in Ca₈Gd₂(PO₄)₆O₂.

| Atom   | Bond lengths (Å) |
|--------|------------------|
| Ca(1)-O₂ | 2.556(4)       |
| Ca(1)-O₃ | 2.836(5)       |
| Ca(1)-O₁ | 2.550(4)       |
| Ca(1)-O₄ | 2.547(6)       |
| Ca(1)-O₂ | 2.836(5)       |
| Ca(1)-O₁ | 2.556(5)       |
| Ca(1)-O₂ | 2.553(5)       |
| Ca(1)-O₃ | 2.832(5)       |
| Ca(2)-O₃ | 2.600(5)       |
| Ca(2)-O₂ | 2.403(4)       |
| Ca(2)-O₃ | 2.600(8)       |
| Ca(2)-O₃ | 2.687(8)       |
| Ca(2)-O₄ | 2.687(8)       |

| Atoms  | Bond lengths (Å) | Angles(°)               |
|--------|------------------|-------------------------|
| P-O₁   | 1.451(4)         | O₃-P-O₂ 104.12(8)       |
| P-O₂   | 1.583(6)         | O₂-P-O₃ 118.85(9)       |
| P-O₃   | 1.557(3)         | O₃-P-O₁ 109.71(5)       |
| P-O₃   | 1.557(3)         | O₂-P-O₁ 109.81(8)       |

Figure 1. The final Rietveld refinement plot of the Ca₈Gd₂(PO₄)₆O₂.
3.2. Discussion

Fig. 2. shows the analysis of the tetrahedra revealed that the average P-O distance (1.537(5) Å) is nearly the same than the average values observed in oxyapatite (1.535(4) Å). The angles O-P-O were, on the other hand, varied between 104.12° and 118.85°, with an average value (109.71°). This is very close to the one of a uniform tetrahedron (109.47°).

The cations M (1) (Ca1/Gd1) were coordinated to nine oxygen anions belonging to six distinct tetrahedral. Each polyhedron was linked to three PO₄ tetrahedra via corners and to three other tetrahedra via edges (Fig. 3.). The M (2) (Ca2/Gd2) cations are inserted into six -fold sites that constituted the walls of the tunnels. Each polyhedron was linked to four PO₄ tetrahedra via corners and to one PO₄ via edge and two of the free oxygen O₄ (Fig. 4.).

In the case of the M (1)-O distances, the nine distances have an average value of 2.658(5) Å, which is slightly larger than the one observed in calcium-Fluorapatite (2.414(13) Å). In the case of the M (2)-O distances, the average value is 2.558(4) Å, which is similar than in calcium Fluorapatite 2.535(12) Å [23].
4. Spectroscopy analysis

The IR and Raman spectra are shown in Fig. 5 and Fig. 6 respectively. The spectral data and proposed vibration assignment is listed in Table. 5. As shown in the Raman spectrum. One strong band at 963 cm\(^{-1}\), was observed, which can be attributed to \(\nu_1\) (PO\(_4\)). The position of these bands were similar to those (933 and 963 cm\(^{-1}\)) previously reported by Toumi [24]. The weaker peaks observed at 1040, 1058 and 1082 cm\(^{-1}\) and those recorded at 539, 607 and 642 cm\(^{-1}\) which can be accredited to the asymmetric stretching \(\nu_3\) and the asymmetric bending modes \(\nu_4\) of PO\(_4\) groups, respectively. They were observed at 575/600 cm\(^{-1}\) and at 545/575 cm\(^{-1}\) in Pb\(_{10}\) (PO\(_4\))\(_6\)F\(_2\) and Ca\(_{10}\) (PO\(_4\))\(_6\)F\(_2\) [25], respectively. Regarding the weak lines observed at 432 and 445 cm\(^{-1}\), they could be assigned to the symmetric bending \(\nu_2\) mode.

![Figure 5. Infrared spectrum of Ca\(_{8}\)Gd\(_2\) (PO\(_4\))\(_6\)O\(_2\).](image-url)
Figure 6. Raman spectrum of Ca$_8$Gd$_2$(PO$_4$)$_6$O$_2$.

Table 5. The External modes Raman and IR of Ca$_8$Gd$_2$(PO$_4$)$_6$O$_2$.

| Raman  | IR    | Assignments |
|--------|-------|-------------|
| 364    | 453   | $\nu_2$     |
| 432    |       |             |
| 445    |       |             |
| 524    | 571   | $\nu_4$     |
| 536    | 601   |             |
| 582    |       |             |
| 593    |       |             |
| 607    |       |             |
| 642    |       |             |
| 677    |       |             |
| 735    |       |             |
| 963    | 962   | $\nu_1$     |
| 1040   | 1015  | $\nu_3$     |
| 1058   | 1035  |             |
| 1082   | 1094  |             |
| 3478   | 3470  | $\nu_9$     |
5. Conclusion

The results from X-ray refinement has shown that the formula assigned to the new Gd substituted Ca-apatite was Ca₈Gd₂(PO₄)₆O₂. The analysis of data from vibrational spectroscopy has also provided support for the high symmetry P6₃/m space group.

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