



## X-ray Structure Refinement and Vibrational Spectroscopy of $\text{Ca}_8\text{Gd}_2(\text{PO}_4)_6\text{O}_2$

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### Abstract

The present paper is interested in the study of compounds from the apatite family with the general formula  $\text{Ca}_{10}(\text{PO}_4)_6\text{A}_2$ . It particularly brings to light the exploitation of the distinctive stereochemistries of two Ca positions in apatite. In fact, Gd-Bearing oxyapatite  $\text{Ca}_8\text{Gd}_2(\text{PO}_4)_6\text{O}_2$  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.

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## 1. Introduction

The structure of apatite  $\text{Ca}_{10}(\text{PO}_4)_6\text{A}_2$ , A= F, OH, O, Cl, ... apatite in the space group  $\text{P6}_3/\text{m}$  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 which is the larger 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  $\frac{1}{4}$  and  $\frac{3}{4}$  centred on a six-fold axis where the Y atoms are located.

The formula assigned to the compound had to be  $[\text{Ca}_4]^{4f} [\text{Ca}_{4.4}\text{Bi}_{1.6}]^{6h} (\text{PO}_4)_6[\text{O}_{1.8}]^{2a}$  with space group  $\text{P6}_3/\text{m}$ . Thus the lower oxygen content (1.8) compared to stoichiometric expected (2) (see the procedure), confirmed the volatilized of bismuth. Therefore, 16% of bismuth was volatilized. The refined results indicated that the  $\text{Bi}^{3+}$  ions were mainly located in Ca (2) site on 6h position and formed two triangles that rotated  $60^\circ$  from the c-axis. The oxygen atom  $\text{O}_4$  was located in the center of these Bi-triangles [17].

The compounds  $\text{Bi Ca}_4 (\text{PO}_4)_3 \text{O}$  and  $\text{La Ca}_4 (\text{PO}_4)_3 \text{O}$  have been reported recently [18]. They are isostructural with  $\text{Bi Ca}_4 (\text{VO}_4)_3 \text{O}$  [19]. Which is closely related to the apatite structure except for the number of cationic sites available.  $\text{Bi Ca}_4 (\text{VO}_4)_3 \text{O}$  crystallizes in hexagonal symmetry with space group  $\text{P6}_3/\text{m}$  have only two types of cationic sites [20,21] where as  $\text{Bi Ca}_4 (\text{VO}_4)_3 \text{O}$  is reported to have three types of cationic sites viz; Ca(1), Ca(2) and Ca (3). The formula can be written as  $\text{Ca} (1)_{0.9} \text{Bi} (1)_{0.1} \text{Ca} (2)_{2.1} \text{Bi} (2)_{0.9} \text{Ca} (3) (\text{VO}_4)_3 \text{O}$ . The Ca (1) and Ca (3) atoms occupy 2b and Ca (2) occupies 6c crystallographic sites. Both Ca (1) and Ca (2) atoms have 6-fold coordination and Ca (3) atom has 9-fold coordination with respect to oxygen. Ca (2) has an irregular hexa-coordinated polyhedron and the O (3) atom in the coordination sphere does not belong to any of the  $\text{PO}_4$  groups Bi atom occupies both Ca(1) and Ca (2) sites with more occupancy in the low symmetry Ca (2) site.

In the present work, we propose to investigate the structure of the phosphate apatite and the vibrational spectroscopy of the  $\text{Ca}_8\text{Gd}_2 (\text{PO}_4)_6 \text{O}_2$  compound.

## 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  $\text{CaCO}_3$  (Cerac. 99.95%), as shown in the following formula:



The resultant powder was subsequently heated at  $740^\circ\text{C}$  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 X'cellerator operating with a secondary monochromator and using a  $\text{CuK}\alpha$  radiation source ( $\text{K}\alpha_1 = 0.15439 \text{ nm}$  and  $\text{K}\alpha_2 = 0.15440 \text{ nm}$ ). The diffraction pattern was recorded under ambient atmosphere over an angular range of  $5-80^\circ$  ( $2\theta$ ) with a step length of  $0.033^\circ$  ( $2\theta$ ).

The Fourier transform infrared (FT-IR) measurements were performed at room temperature. On a JASCO FT-IR 420 spectrometer over the  $4000 - 400 \text{ cm}^{-1}$  region, in a KBr pellet. Furthermore, Raman spectra were measured with a LABRAMHR 800 triple monochromatic at room temperature under a  $50 \times \text{LF}$  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  $3 \text{ cm}^{-1}$ .

## 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 diffraction using the Rietveld method refinement starting 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  $\text{Ca}_8\text{Gd}_2(\text{PO}_4)_6\text{O}_2$ .**

Formula	$\text{Ca}_8\text{Gd}_2(\text{PO}_4)_6\text{O}_2$
Halfwidth parametres	U = 0.019711 V = -0.052960 W = 0.035341
Parametres asymetry	Asy1 : - 0.02951 Asy 2 : -0.01187
Reliability Factors	$R_F$ : 0.055 $R_B$ : 0.1152 $R_P$ : 0.132 $R_{WP}$ : 0.133

**Table. 2. Analytical data and lattice parameters of  $\text{Ca}_8\text{Gd}_2(\text{PO}_4)_6\text{O}_2$ .**

System	Hexagonal
Cell parameters (Å)	a=b=9.418(7)Å c=7.65(5) Å $\alpha = \beta = 90^\circ$ et $\gamma = 120^\circ$
Volume (Å), Z	V=587.73(8) Å <sup>3</sup> Z = 2
Zéro point	0.023
Count time [sec / step]	35 s

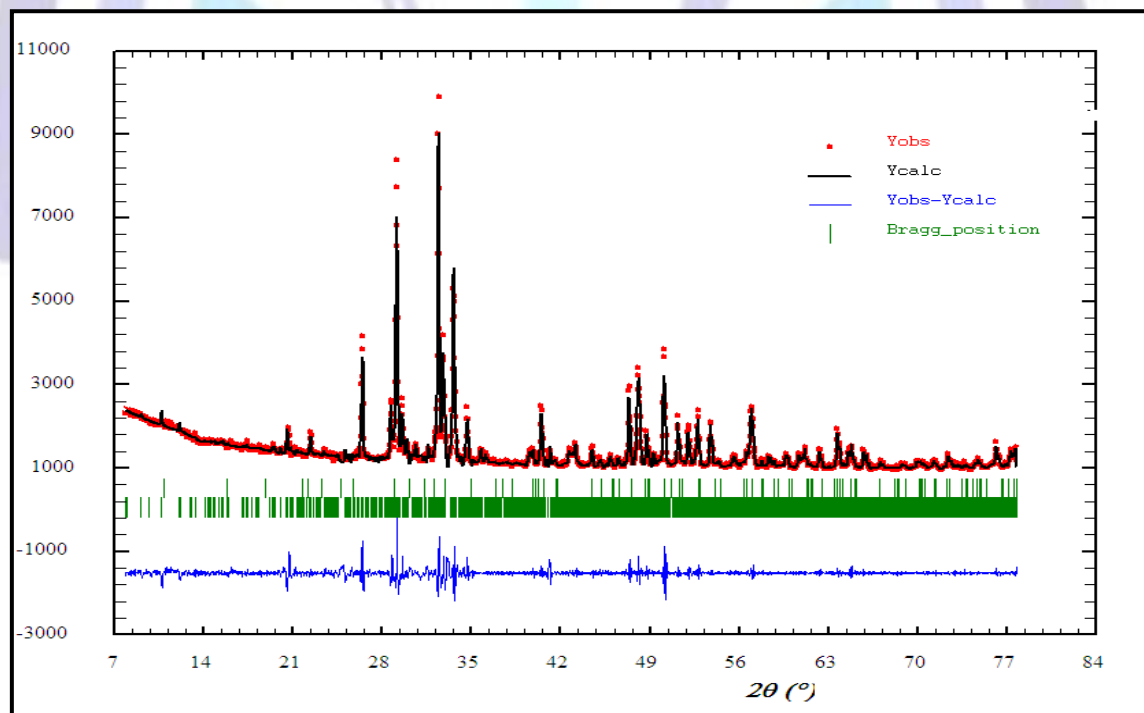
**Table. 3. Atomic coordinates, occupancy factors after Rietved refinement of  $\text{Ca}_8\text{Gd}_2(\text{PO}_4)_6\text{O}_2$** 

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  $\text{Ca}_8\text{Gd}_2(\text{PO}_4)_6\text{O}_2$ .**

Atom	Bond lengths (Å)
Ca(1)-O <sub>2</sub>	2.556(4)
Ca(1)-O <sub>3</sub>	2.836(5)
Ca(1)-O <sub>1</sub>	2.550(4)
Ca(1)-O <sub>1</sub>	2.547(6)
Ca(1)-O <sub>3</sub>	2.836(5)
Ca(1)-O <sub>2</sub>	2.556(5)
Ca(1)-O <sub>2</sub>	2.553(5)
Ca(1)-O <sub>3</sub>	2.832(5)
Ca(2)-O <sub>3</sub>	2.600(5)
Ca(2)-O <sub>2</sub>	2.403(4)
Ca(2)-O <sub>3</sub>	2.600(8)
Ca(2)-O <sub>3</sub>	2.687(8)
Ca(2)-O <sub>3</sub>	2.687(8)
Ca(2)-O <sub>4</sub>	2.372(8)

Atoms	Bond lengths (Å)	Angles(°)
P-O <sub>1</sub>	1.451(4)	O <sub>3</sub> -P-O <sub>2</sub> 104.12 (8)
P-O <sub>2</sub>	1.583(6)	O <sub>3</sub> -P-O <sub>3</sub> 118.85(9)
P-O <sub>3</sub>	1.557(3)	O <sub>3</sub> -P-O <sub>1</sub> 109.71(5)
P-O <sub>3</sub>	1.557(3)	O <sub>2</sub> -P-O <sub>1</sub> 109.81 (8)

**Figure. 1. The final Rietveld refinement plot of the  $\text{Ca}_8\text{Gd}_2(\text{PO}_4)_6\text{O}_2$ .**

### 3.2. Discussion

Fig. 2. as 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 PO<sub>4</sub> 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 PO<sub>4</sub> tetrahedra via corners and to one PO<sub>4</sub> via edge and two of the free oxygen O<sub>4</sub> (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].

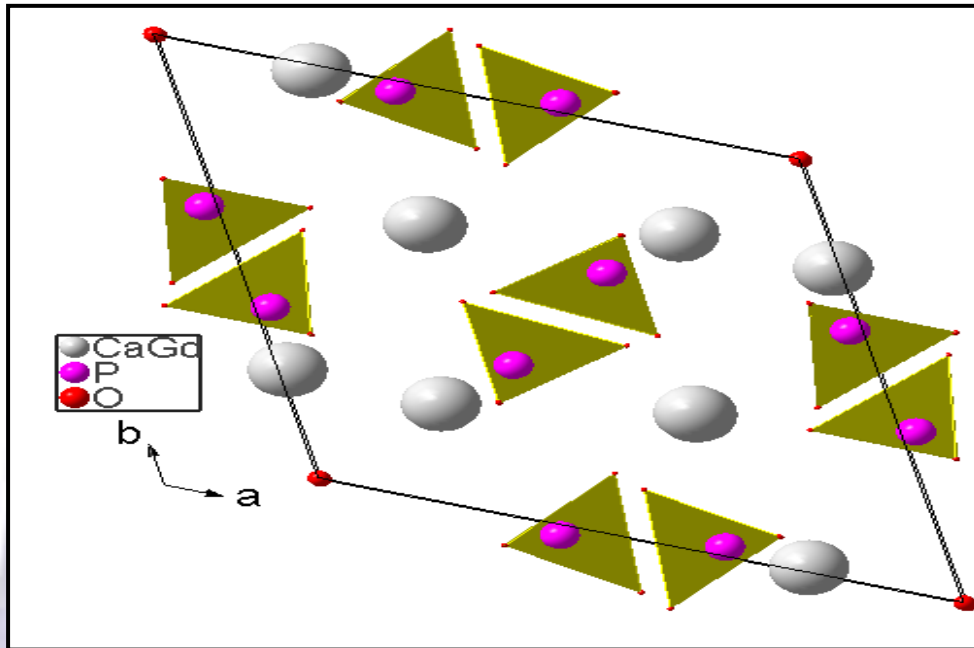


Figure. 2. Perspective view of Ca<sub>8</sub>Gd<sub>2</sub> (PO<sub>4</sub>)<sub>6</sub>O<sub>2</sub>.

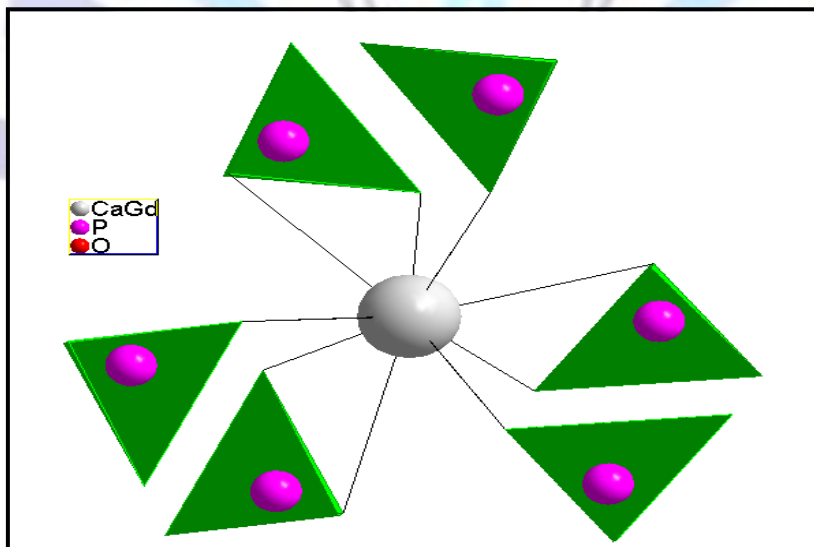


Figure.3. Coordination of the metal M (1).

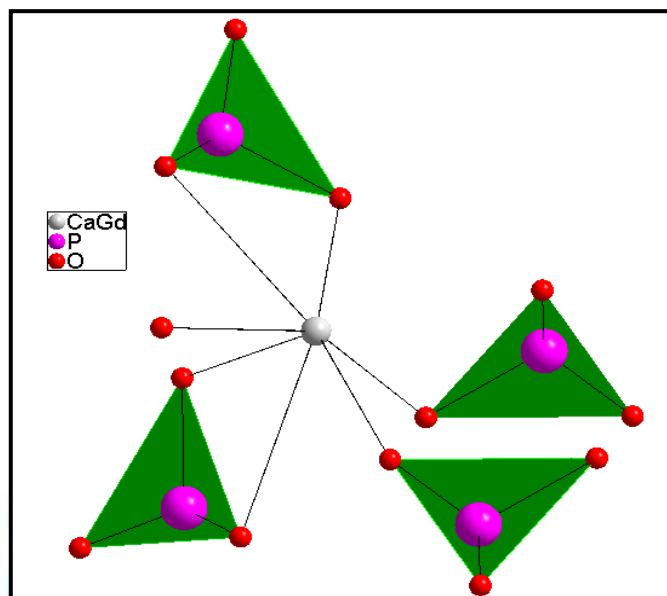


Figure.4. Coordination of the metal M (2).

#### 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  $963\text{ cm}^{-1}$ , was observed, which can be attributed to  $\nu_1(\text{PO}_4)$ . The position of these bands were similar to those ( $933$  and  $963\text{ cm}^{-1}$ ) previously reported by Toumi [24]. The weaker peaks observed at  $1040$ ,  $1058$  and  $1082\text{ cm}^{-1}$  and those recorded at  $539$ ,  $607$  and  $642\text{ cm}^{-1}$  which can be accredited to the asymmetric stretching  $\nu_3$  and the asymmetric bending modes  $\nu_4$  of  $\text{PO}_4$  groups, respectively. They were observed at  $575/600\text{ cm}^{-1}$  and at  $545/575\text{ cm}^{-1}$  in  $\text{Pb}_{10}(\text{PO}_4)_6\text{F}_2$  and  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$  [25], respectively. Regarding the weak lines observed at  $432$  and  $445\text{ cm}^{-1}$ . They could be assigned to the symmetric bending  $\nu_2$  mode.

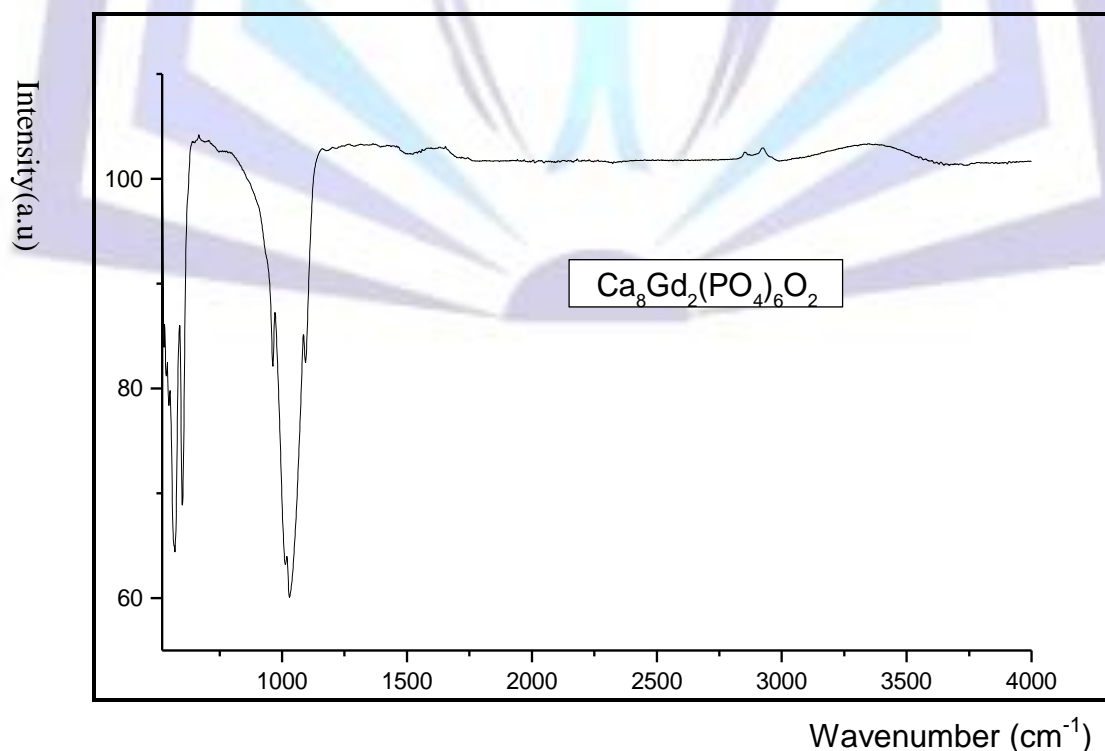
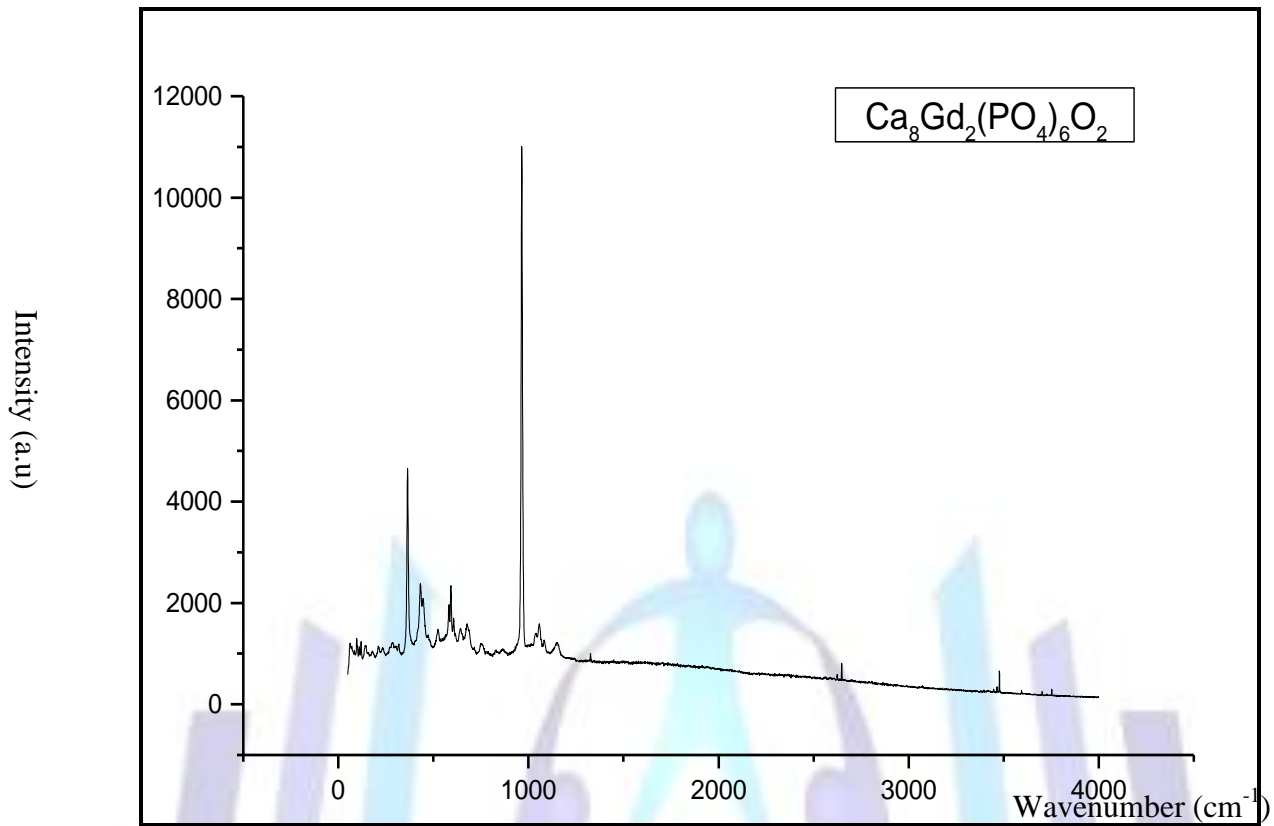


Figure. 5. Infrared spectrum of  $\text{Ca}_8\text{Gd}_2(\text{PO}_4)_6\text{O}_2$ .

Figure 6. Raman spectrum of  $\text{Ca}_8\text{Gd}_2(\text{PO}_4)_6\text{O}_2$ .Table 5. The External modes Raman and IR of  $\text{Ca}_8\text{Gd}_2(\text{PO}_4)_6\text{O}_2$ .

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



## 5. Conclusion

The results from X-ray refinement has shown that the formula assigned to the new Gd substituted Ca-apatite was  $\text{Ca}_8\text{Gd}_2(\text{PO}_4)_6\text{O}_2$ . The analysis of data from vibrational spectroscopy has also provided support for the high symmetry  $P6_3/m$  space group.

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