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Investigation of the structural and mineralogical changes of Tunisian phosphorite during calcinations

S. Elgharbi · K. Horchani-Naifer · M. Férid

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Abstract The thermal behavior of Tunisian phosphorite was investigated with X-ray powder diffraction (XRD), Fourier transform infrared (FT-IR), and Raman spectroscopies and DTA-TG measurements. The XRD patterns showed that the chief mineral constituents of calcined samples are calcium oxide and fluorapatite, while those in the raw phosphorite are calcite, dolomite, fluorapatite, and carbonate-fluorapatite. Physicochemical transformations result in the oxidation of organic matter, disappearance of calcite and dolomite crystalline phases, and partial dissociation of structural carbonates. The FT-IR and Raman spectra showed modifications of some bands; a decrease in the intensity of the ν_2 and ν_3 vibrations of carbonate groups and the appearance of new bands at 520 and 926 cm^{-1} after calcination of phosphorites at 800 °C. These bands were assigned to isomorphous substitutions of PO_4^{3-} in apatite by SiO_4^{4-} . Heat treatment alters the qualitative composition of the mineral as a result; the solubility of apatite in dilute citric acid was decreased.

Keywords Tunisian phosphorite · Calcinations · Fluorapatite · Calcite

Introduction

Most of the commercial phosphate rocks are of sedimentary origin and are mainly used in the manufacture of phosphate fertilizers. The composition of these rocks varies

from one deposit to another. These rocks are composed essentially of the apatite group in association with a wide assortment of accessory minerals mainly fluorides, carbonates (calcite and/or dolomite), clays, quartz, silicates, and metal oxides as well as organic matter.

Most of Tunisian phosphorites are considered to be carbonate-apatite or francolite with association of wide impurities such as calcite, dolomite, and quartz [1, 2]. It is more beneficial to remove the carbonate minerals because it consumes an additional acidulant (sulfuric acid) during the production of phosphoric acid by wet process. Also, if considerable amount of organic matter is present in the gangue material, it is necessary to eliminate this matter because it causes the reduction of sulfates in sulfide thus involving an intense corrosion of reactor during the manufacture of phosphoric acid [3].

Calcination was found to be one of the suitable methods to eliminate water and organic matter, to decompose all or part of carbonates [4]. By heating the ore to a high temperature ranging from 800 to 1000 °C, CaCO_3 and MgCO_3 are decomposed to CaO , MgO , and CO_2 . The upgrading by heat treatment has been considered by many authors [5, 6].

Calcination of phosphate ores is necessary for obtaining a phosphate product suitable for the production of light green phosphoric acid, which is in turn suitable for the production of pure, edible, super phosphoric acid. This last product is used in the preparation of pure chemical reagents, food, livestock, soft drinks, and other pharmaceutical preparations.

In a previous study, thermal treatment of mixtures of Tunisian phosphorite and additives of aluminum silicates was investigated [7]. The results show that the P_2O_5 solubility in various extracting agents in the case of the mixture of calcined and mechanically activated Tunisian phosphorite with Medet's steryl (Aluminum silicate waste)

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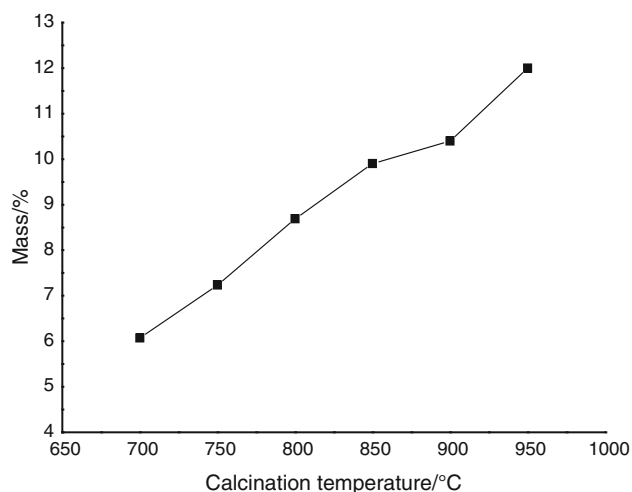


Fig. 1 Mass loss as a function of calcination temperature of Ras-Dhraa phosphorite samples

is higher than non activated Tunisian phosphorite and its mixtures. In another study [8], the authors investigated that an activation process of Tunisian phosphorite based on thermal treatment, mechanoactivated phosphorites, and ammonium sulfate as additive allows formation of fertilizers [8] but the thermal behavior of Tunisian phosphorite without additives has not been studied yet.

The aim of this study is to investigate the thermal behavior of Tunisian phosphorite. Structure and phase transformations of calcined solids are confirmed by XRD, FT-IR, and Raman spectroscopies. In addition, the solubility of the calcined products in 2 % citric acid solution was studied.

Materials and methods

Samples

Phosphorite used in this investigation was provided from the phosphate deposits in the Ras-Dhraa located between Nefta and Tozeur and belonging to large phosphate basin of Gafsa-Métlaoui.

Calcination

Calcination was performed by electric furnace. 2 g of phosphorite was put in platinum crucible, then the temperature was raised gradually (10 °C/min) from room temperature until reaching the required level. Samples were heated at 700, 750, 800, 850, 900, and 950 °C for 30 min and masses were obtained at room temperature after a fast cooling. As shown in Fig. 1, simultaneous

increase in calcination temperature, increases percentage of mass loss which is related to burning of organic components and decomposition of carbonate groups.

Methods

We determined phosphorus spectrophotometrically by measuring the color density of yellow complex phospho-vanado-molybdate at a wavelength of 430 nm, calcium and magnesium by calibration with a standard solution of EDTA, potassium and sodium by flame spectrophotometer, iron and aluminum by atom absorption spectrophotometry (AAS), silicon by mass analysis, fluorine with ion selective electrode, and volumetric analysis for CO₂.

XRD analyses were performed using an X'PERT Pro PANAnalytical diffractometer with CuKα radiation ($\lambda = 1.5418 \text{ \AA}$). The samples were scanned in the diffraction angle range (2θ) varying from 5° to 80° with steps of 0.02° for 5 min. The crystalline phases have been determined by comparison of the registered patterns with the international center for diffraction data (ICDD)-powder diffraction files (PDF).

Infrared spectra were measured from 400 to 4000 cm⁻¹ (wavenumber) by the standard KBr pellet method using a Fourier transform infrared spectrometer (Perkin-Elmer). A resolution of 4 cm⁻¹ was used collecting 20 scans for each sample.

Raman measurements were recorded at room temperature by using a LabRAM HR spectrometer (Jobin-Yvon). The Raman backscattering was recorded with 325 nm excitation wavelength. The beam was focused on the sample surface through an optical objective (40 × UVB objective (OBJ40 × UVB)).

Thermogravimetric (TG) and differential thermal analysis (DTA) were performed on a SETSYS Evolution 1750 SETARAM at a heating rate of 10 °C/min. A platinum crucible and 24.5 mg of sample were used.

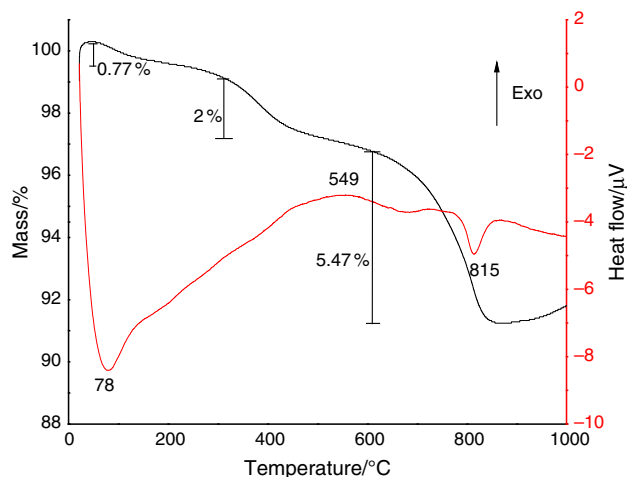
Results and discussion

Chemical composition

The results of chemical analysis are presented in Table 1. P₂O₅ content of phosphorite is 29 % and CaO is 49 %, the CaO/P₂O₅ ratio of 1.67 is slightly higher than that of 1.54 for a pure carbonate-fluorapatite. According to Slansky [9], if this ratio is >1.31, the increase may be due to either the substitution of PO₄ by CO₃ or to the presence of calcite or dolomite in the phosphorite. Chemical analysis confirms results obtained by IR spectroscopy and X-Ray analysis that Ras-Dhraa phosphorite contains calcite and dolomite.

Table 1 Chemical composition (mass%) of Ras-Dhraa phosphorite

	P ₂ O ₅	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	F	SiO ₂	CO ₂	SO ₃
Ras-Dhraa phosphorite	29.58	49.45	0.7	0.86	0.25	1.39	0.054	2.84	3.08	6.48	3.58

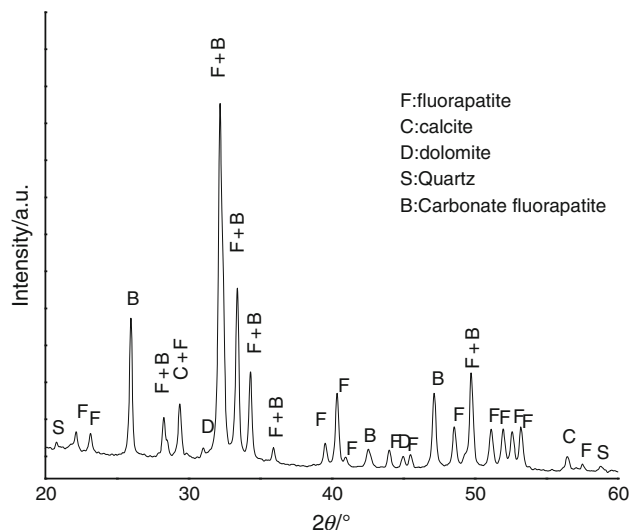
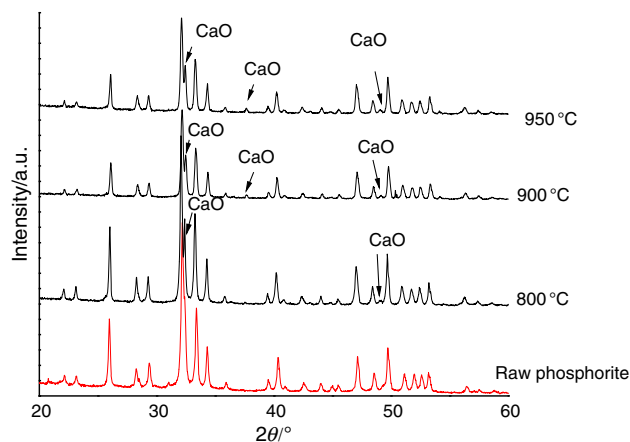
**Fig. 2** TG/DTA curves of Ras-Dhraa phosphorite

Thermal behavior of Ras-Dhraa phosphorite

The TG–DTA curves of Tunisian phosphorite are presented in Fig. 2. During thermal treatment of the phosphorites up to 900 °C, total mass losses are about 8.24 % and three mass losses of 0.77, 2, and 5.47 % are observed. The first mass loss corresponds to the removal of adsorbed water and was associated with an endothermic effect around 78 °C. The second was a weak exothermic peak at 549 °C and could be attributed to the simultaneous elimination of the chemical water in the structure and oxidation of the organic matter. The decomposition of the organic matter is accompanied by the release of sulfur gas because most of the phosphorites contain organic matter rich in sulfur.

The third mass loss corresponds to an endothermic peak at 815 °C which was associated to the dissociation of carbonate. In samples calcined at 800 °C and higher, XRD patterns (Fig. 4) reveal reflections corresponding to CaO. The data presented give evidence that carbonate located in the tetrahedral positions of the phosphate ion in the apatite structure is liberated as CO₂ [10] and CaO was formed.

We note that by raising the temperature over 700 °C, the mass loss continues and is not completed even at 850 °C. Thermal stability of apatite depend on carbonate substitution exactly on chemical composition [11]. Ras-Dhraa phosphorite was slightly carbonated samples, because previous study [12] concludes that temperature decreases for evolving carbonate with an increase in the carbonate content. The treatment of Tunisian phosphorite must be

**Fig. 3** X-ray diffractogram of Ras-Dhraa phosphorite**Fig. 4** X-ray diffractograms of raw and calcined phosphorites

performed at a temperature near or greater than 800 °C to remove the carbonate.

The thermal analysis data confirmed the formation of stable material at 900 °C. The fluorapatite was formed such proved by XRD patterns (Fig. 4).

X-ray diffraction characterization

XRD patterns of the raw and calcined phosphorites are depicted on Figs. 3 and 4. This method is used to identify

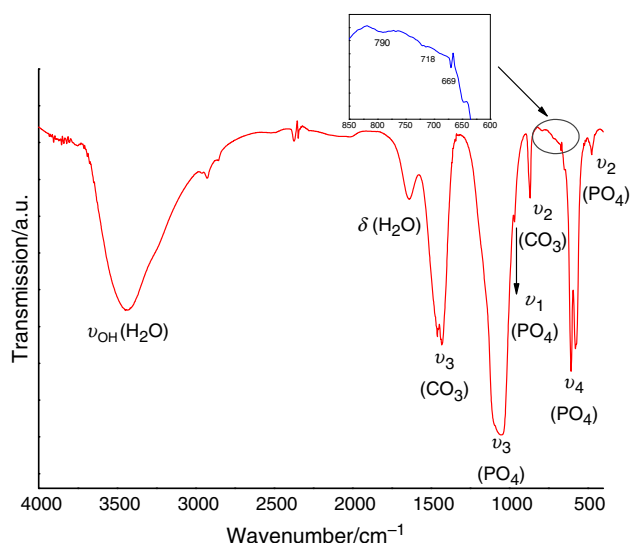
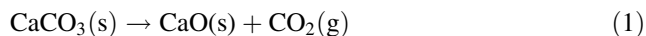


Fig. 5 FT-IR spectrum of Rhas-Dhraa phosphorite in the region 400–4000 cm^{-1}

the mineralogical constituents of each sample. As shown in Fig. 3, the main minerals in raw phosphorite are fluorapatite, carbonate-fluorapatite, calcite, dolomite, and quartz. The presence of carbonates associated with apatite was confirmed by XRD. In samples calcined at 700 and 750 °C, no change was observed in X-ray diffractograms.

XRD patterns of raw and calcined samples at 800, 900, and 950 °C are presented in Fig. 4. The relative intensities of the calcite, dolomite, and quartz reflections in the XRD patterns decreased due to the calcination of the phosphorite until a total disappearance at 800 °C. The lime reflections were formed at 800 °C and became clearly distinguishable at 900 °C. The main components in the calcined samples at temperature higher than 900 °C were fluorapatite and calcium oxide. As can be seen, carbonate-fluorapatite has changed to fluorapatite.

Calcium carbonate is decomposed as follows:



This lead to the formation of fluorapatite and CaO.

FT-IR spectroscopic characterization

The FT-IR spectrum at room temperature of Ras-Dhraa phosphorite (Fig. 5) shows the characteristic absorption bands of carbonate-fluorapatite [1]. Strong absorption band at 1049 cm^{-1} that can be ascribed to ν_3 mode of PO_4^{3-} and the ν_1 mode corresponds to the very narrow band at 966 cm^{-1} . The ν_4 mode gives two main bands at 605.5 and 577 cm^{-1} and the absorption peak at 474 cm^{-1} was attributed to the ν_2 mode. The substitution of carbonate into apatite is most readily detected by FT-IR spectroscopy.

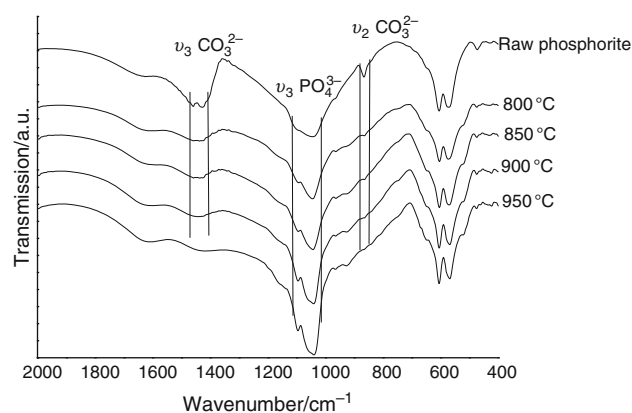


Fig. 6 FT-IR spectra of raw and calcined phosphorites at different temperatures

CO_3^{2-} ions can be present in two environments (the presence of two types of carbonates substitutions), carbonate ion can substitute both for OH^- (F^- , Cl^-) channel sites (A type) and for the phosphate ion (B type) with very complex substitutions mechanism and charge compensation [13].

The band at 870 cm^{-1} and the two bands at 1429.5 and 1458 cm^{-1} were assigned to ν_2 and ν_3 vibrations of CO_3^{2-} groups located in the B site of apatite (carbonate substituting phosphate) [14]. The observation of a weak band at 718 cm^{-1} (Fig. 5) is due to ν_4 mode of the calcite [15]. The absorption bands at 780–800 and 669 cm^{-1} are attributed to Si–O stretching of quartz mineral [16].

Characteristic bands of water vibrations are described by the bending δ (H_2O) deformation which appears at 1636 cm^{-1} and the stretching ν_{OH} (H_2O) vibration which appears as broad band at 3435 cm^{-1} .

FT-IR spectra of calcined phosphorites (Fig. 6) show the absorption bands characteristic of PO_4^{3-} groups at 571, 601, 962, and 1046 cm^{-1} . The changes in the apatite structure after calcination are slightly different in investigated temperatures. A decrease in the intensity of the ν_2 vibration of the carbonate group in the IR spectra at 800 °C was observed. Changes occur also in the relative intensities of the doublet components of ν_3 vibration at 1458 and 1429.5 cm^{-1} , this change is more pronounced in the spectrum of the product calcined at 800 °C (Fig. 6). The decreasing of intensities of ν_2 and ν_3 of the structural carbonate ions indicate that carbonate ions are partly released from the apatite structure during calcinations at 800 °C. The calcite ν_4 mode disappears at 800 °C; these results are confirmed by XRD analysis.

The carbonate substitution shows a strong effect on the ν_3 PO_4^{3-} region in the FT-IR spectrum [17]. At 800 °C, carbonate leaves the apatite structure and two main bands of ν_3 PO_4^{3-} becomes clearly distinguishable at 1040 and 1096 cm^{-1} .

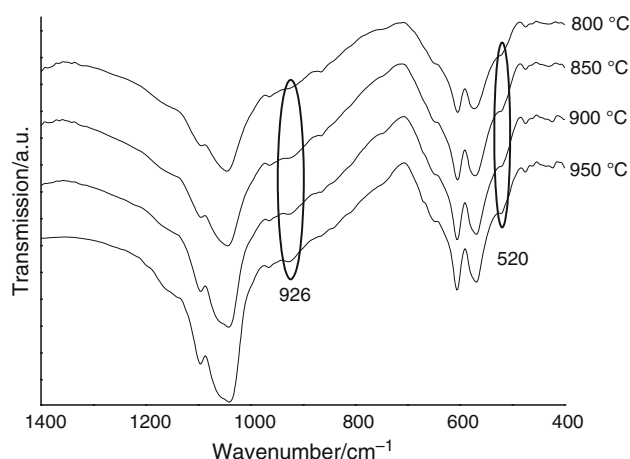


Fig. 7 FT-IR spectra of calcined phosphorites at different temperatures in the region 400–1400 cm^{-1}

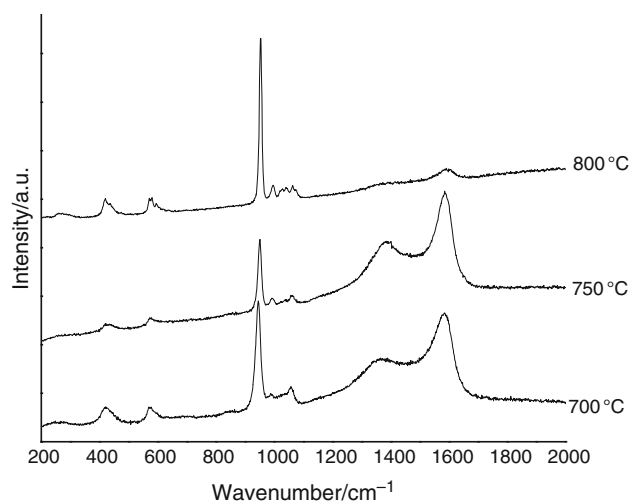


Fig. 9 Raman spectra of calcined phosphorites at 700, 750, and 800 $^{\circ}\text{C}$

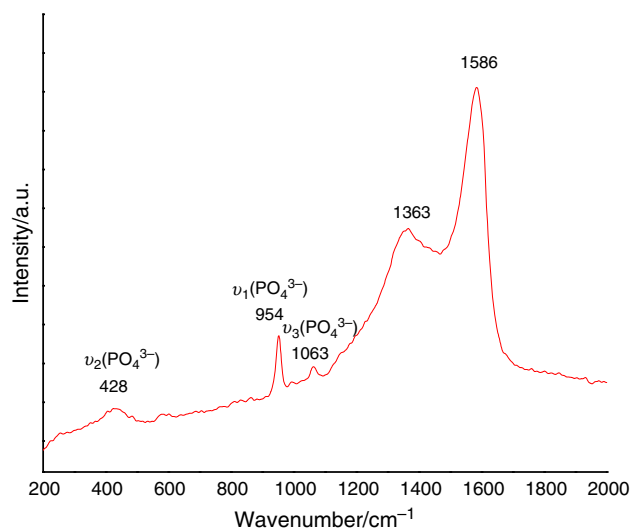


Fig. 8 Raman spectrum of Rhas-Dhraa phosphorite

Small bands are observed at 520 and 926 cm^{-1} in the FT-IR spectra of phosphorite calcined at 800 $^{\circ}\text{C}$ (Fig. 7). The band at 520 cm^{-1} indicates the presence of silicate phases (Si–O vibrations). During calcination of carbonaceous phosphorites, carbonates decompose by formation of free oxides and these free oxides are binding by formation of silicates [18]. The bands at 926 cm^{-1} indicate the isomorphous substitution of PO_4^{3-} by SiO_4^{4-} [19]. Free lime is formed at 900 $^{\circ}\text{C}$ as observed by the broad FT-IR band about 424 cm^{-1} [20]. These results demonstrate that from 800 $^{\circ}\text{C}$ carbonates in carbonaceous Tunisian phosphorites are decomposed by formation of free oxides.

Raman spectroscopy characterization

The color of the calcined phosphorites at 700 and 750 $^{\circ}\text{C}$ was between dark gray and black due to the presence of organic substances, which are not all combusted during thermal processing. After calcination of phosphorites at temperature higher than 800 $^{\circ}\text{C}$, the color of the materials obtained turns into white as a consequence of carbon removal.

Raman spectrum of raw material is ill defined because fluorescence signals; by heating of the raw material at different temperatures spectra became more defined.

The Raman spectrum of raw material is shown in Fig. 8, broad bands were observed in this figure indicating a poor degree of crystallization. The $\nu_1 \text{PO}_4^{3-}$ mode appears at 954 cm^{-1} . The weak band at 1063 cm^{-1} can be attributed to $\nu_3 \text{PO}_4^{3-}$ mode [17]. The $\nu_2 \text{PO}_4^{3-}$ mode shows a broad peak at 428 cm^{-1} .

The Raman spectra of calcined samples at 700, 750, and 800 $^{\circ}\text{C}$ are shown in Fig. 9; the typical $\nu_1 \text{PO}_4^{3-}$ symmetric stretching mode appears in all spectra. Bands at 944, 950, and 953 cm^{-1} and bands at 988, 992, and 995 cm^{-1} are assigned to the $\nu_1 \text{PO}_4^{3-}$ mode. The phosphate ν_1 mode band position increase from 944 to 953 cm^{-1} and from 988 to 995 cm^{-1} when the temperature is increased from 700 to 800 $^{\circ}\text{C}$. With increasing fluoride concentration $\nu_1 \text{PO}_4^{3-}$ band position increases [21]; hence, we can detect changes in apatite chemistry associated with raising temperature. Spectrum from raw material and the samples heated at 700 and 750 $^{\circ}\text{C}$ shows two broad bands at 1363 and 1586 cm^{-1} . The weak and broad band at 1363 cm^{-1} can be attributed to

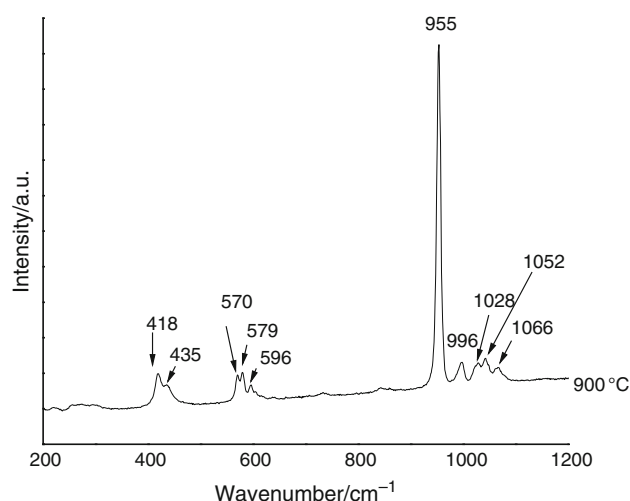


Fig. 10 Raman spectrum of calcined phosphorite at 900 °C

disordered carbon (designated as the D band) [22]. The sharp and intense band at 1586 cm^{-1} is characteristic of graphite and is known as the G band [22]. Spectrum of phosphate calcined at 800 °C shows a decrease in intensity of bands at 1586 and 1360 cm^{-1} , this result can be explained by the removal of organic matter after calcination of phosphorites at temperature higher than 800 °C .

The ν_2 and $\nu_4\text{ PO}_4^{3-}$ modes appear as very weak bands at 420 and 572 cm^{-1} , respectively, probably because of poor crystallization of samples heated at 700 and 750 °C , while $\nu_2\text{ PO}_4^{3-}$ mode shows two distinguishable peaks at 419 and 435 cm^{-1} and $\nu_4\text{ PO}_4^{3-}$ mode shows three bands around 569 , 579 , and 594 cm^{-1} for sample heated at 800 °C . These observations indicate that thermal treatment has improved the crystallinity. The $\nu_3\text{ PO}_4^{3-}$ mode appears as broad band at 1057 and 1060 cm^{-1} for samples calcined at 700 and 750 °C , whereas for sample calcined at 850 °C we observe three bands at 1028 , 1039 , and 1062 cm^{-1} . As we indicated previously, the $\nu_3\text{ PO}_4^{3-}$ domain appears to be the most affected by carbonate substitution. The phosphate ν_3 vibrations in apatite ($1020\text{--}1080\text{ cm}^{-1}$) occur near the region in which carbonate ν_1 is expected [23]. Carbonate, even at very low levels, causes significant broadening of the peak in the $1065\text{--}1080\text{ cm}^{-1}$ region, and this effect increases as the level of carbonate increases. In the Raman spectrum, the intensity of this band increased with the increasing temperatures, which allow as concluding that carbonate content decrease.

For phosphate ores calcined at temperature higher than 850 °C , clearly distinguishable peaks are observed (Fig. 10). The two bands at 955 and 966 cm^{-1} in the spectrum of phosphate calcined at 900 °C are attributed to the $\nu_1\text{ PO}_4^{3-}$ mode. The $\nu_2\text{ PO}_4^{3-}$ mode shows two distinguishable peaks at 418 and 435 cm^{-1} . The ν_4 mode of

Table 2 Solubility of calcined phosphorites at different temperatures

Temperature of treatment/ $^{\circ}\text{C}$ (30 min)	% P_2O_5 dissolved in a solution of citric acid 2 %
25	11.55
700	9.908
750	8.92
800	7.343
850	6.04
900	5.789
950	5.63

sample shows three bands around 570 , 579 , and 596 cm^{-1} . The $\nu_3\text{ PO}_4^{3-}$ mode shows three peaks at 1028 , 1052 , and 1066 cm^{-1} attributed to pure fluorapatite [24].

Effect of temperature on the solubility

The reactivity of phosphorite is related to the chemical and mineralogical composition of the apatite [25]. We determined the solubility by a solution of citric acid 2 % and the results are shown in Table 2. We note a decrease of the solubility with an increase of the temperature treatment, the proportion of the dissolved P_2O_5 in the sample without thermal treatment is equal to 11.55 %, and begin to decrease gradually with increasing the temperature of treatment, then it decreases sharply when treated up to 800 °C , this is consistent with previous researches [19] where carbonate-apatite transforms to less reactive fluorapatite. Decomposition of the adsorbed and combined water, the organic matter, and most of the combined carbon dioxide increase the phosphate grade in the calcined product. Decarbonation increases the grain porosity [26].

Conclusions

In this research, structural changes of Ras-Dhraa phosphorite after calcination were studied by powder X-Ray diffraction, FT-IR, and Raman spectroscopies. It was found that the main minerals of the calcined samples are calcium oxide and fluorapatite. From FT-IR spectroscopy, it was seen that SiO_4^{4-} substitutes into the calcium phosphate lattice when the carbonates are leaved from apatite structure. Raman study of calcined phosphorite highlight the effect of the carbonate substitution on the vibrational modes of the ions in the apatite lattice.

The calcination of Ras-Dhraa phosphorite at about $850\text{--}900\text{ °C}$ burn out organic matter, residual carbon, and carbonate. At this temperature, physical and chemical properties of the phosphorite are affected and the solubility decrease.

The calcined phosphorite is suitable for the manufacture of clear green phosphoric acid which is used as a source for producing super phosphoric acid and other high-grade chemical reagents.

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