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BRIEF COMMUNICATION

Introduction of Carbonate in the Rare Earth-Containing Oxyapatite

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The lanthanum-containing oxyapatite, $Ca_{10-x}La_x(PO_4)_6O_{1+x/2}\square_{1-x/2}$, treated in a CO_2 atmosphere at 950°C can be partially carbonated if $x < 2$; it remains uncarbonated when $x = 2$. The general formula of the carbonated apatites is $Ca_{10-x}La_x(PO_4)_6O_x(CO_3)_{1-x/2}\square_{1-x/2}$ $0 \leq x \leq 2$. The number of La^{3+} and O^{2-} ions on the one hand and the number of CO_3^{2-} ions and vacancies on the other hand are equal; each O^{2-} ion is joined to a close La^{3+} ion, and each CO_3^{2-} ion is next to a vacancy.

Introduction

In the calcium phosphate hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, OH^- ions are located in a channel formed by six calcium ions. CO_3^{2-} ions can substitute for OH^- ions: this apatite is called *A*-type carbonated apatite (*1*). Two anionic sites per unit cell are located in the channel. In calcium phosphate apatites, the total charge for these anionic sites equals two. Increasing the positive total charge in the cationic sites allows us to increase the negative total charge in the channel at the same time. So, for example, it is possible to prepare rare earth-containing dioxyapatite $Ca_8Ln_2(PO_4)_6O_2$, where *Ln* is a trivalent rare earth (*Ln* = La, Pr, Nd, Sm, Eu, Gd, Tb) (*2, 3*). Consequently, it would be possible to imagine the introduction of two CO_3^{2-} ions in apatites containing two rare earth elements. Nevertheless, a systematical study has shown (*4*) that the introduction of CO_3^{2-} ions in these dioxyapatites was unsuccessful.

This result prompted us to undertake a more accurate study of the carbonation of rare earth-containing apatite. For this, we used apatites which contained variable amounts of rare earth (0 to 2 per unit cell).

Among all the rare earths, lanthanum has the largest ionic radius (La^{3+} = 1.17 Å) and this could facilitate the introduction of a large ion such as CO_3^{2-} (CO_3^{2-} = 1.85 Å).

Materials and Methods

Pure and well-characterized oxyapatites containing lanthanum were first synthesized with the general formula (*3*)

$$Ca_{10-x}La_x(PO_4)_6O_{1+x/2}\square_{1-x/2} \quad 0 < x \leq 2.$$

The carbonation treatment of these oxy-

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apatites consisted in heating these samples at 950°C under a 1–100 bar pressure, in an atmosphere of pure and dried CO_2. Repeated treatments were needed to obtain a maximal carbonation.

The samples were studied by X-ray diffraction and infrared spectrometry. The CO_3^{2-} content was determined by thermogravimetric analysis at 1200°C.

Results and Discussion

A pressure increase does not favor the carbonation: so, only the results obtained at normal pressure will be described.

X-ray diffraction shows that all the samples formed are single phase. All the observed X-ray diffraction lines can be indexed in the hexagonal system. Lattice parameter variations are plotted on Fig. 1. The lattice parameters of apatite containing two lanthanum ions (La/(La + Ca) = 0, 2) remain unchanged after treatment: in this case, the carbonation treatment does not occur! For a given atomic ratio La/(La + Ca), the increase of the average ionic radius of the ions in the channel, changing from O^{2-} to CO_3^{2-} ($r_{O}^{2-} = 1.22$ Å, $r_{CO_3}^{2-} = 1.85$ Å), induces an increase of *a* and a decrease of *c*, in agreement with the well-known variation of the lattice constants in the apatitic structure (*5*). The smaller the CO_3^{2-} content, the smaller the variation between oxy- and carbonated apatite.

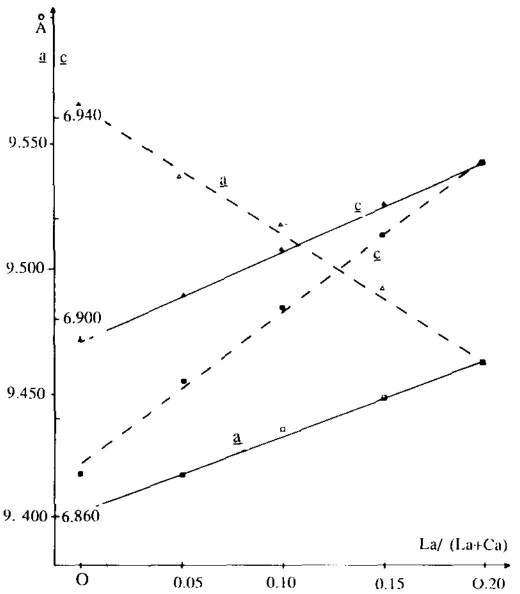

FIG. 1. Variations of lattice parameters versus La/(La + Ca) atomic ratio. —, oxyapatites; ---, carbonated apatites.

TABLE I

POSITIONS AND ASSIGNMENT OF INFRARED BANDS IN CARBONATED La-CONTAINING APATITE

Position (cm^{-1})	Assignment
960	v_1 PO_4^{3-}
450	v_2 PO_4^{3-}
1100	
1050	v_3 PO_4^{3-}
1015	
600	
	v_4 PO_4^{3-}
575	
1540	v_3 CO_3^{2-}
1465	
875	v_2 CO_3^{2-}
545	La–O

The positions and the assignments of the different infrared bands are reported in Table I. In addition to the well-known PO_4^{3-} bands, other ones appear. The two bands in the 1400–1600 cm^{-1} range and the small one at 875 cm^{-1} are characteristic of CO_3^{2-} ions in the channel of an *A*-type carbonated apatite. Another small band appears in all the samples at 545 cm^{-1}. This band which also exists in the untreated oxyapatite is ascribed to a La–O interaction. The fact that this La–O interaction remains after carbonation shows that the substitution of CO_3^{2-} for O^{2-} is incomplete.

Heating the carbonated apatite in air at 1100°C induces changes: CO_3^{2-} infrared bands disappear and lattice parameters become equal to those of the initial oxy-

TABLE II

CARBONATE AMOUNTS IN CARBONATED APATITE

La/(La + Ca) Atomic ratio	0.05	0.10	0.15	0.20
Weight loss (%)	3.01	2.08	1.25	0
CO_3^{2-} ion number observed	0.75	0.55	0.35	0
CO_3^{2-} ion number theoretical; if complete carbonation	1.25	1.50	1.75	2

apatite. Results of CO_3^{2-} analysis by TGA are summarized in Table II.

The theoretical and experimental values appear to be different; largest deviation of expected CO_3^{2-} content occurs for $x = 2$ in $Ca_{10-x}La_x(PO_4)_6O_{1+x/2}\square_{1-x/2}$: in this case, one predicts the introduction of two CO_3^{2-} ions; however, the experiments show no substitution.

Taking into account the general formula of the oxyapatites, the amount of CO_3^{2-} ions per unit cell, and the charge balance, the following formulas of lanthanum-containing carbonated apatite can be proposed:

$x = 0$ $Ca_{10}(PO_4)_6CO_3\square$
$x = 0.5$ $Ca_{9.5}La_{0.5}(PO_4)_6O_{0.52}(CO_3)_{0.73}\square_{0.75}$
$x = 1.0$ $Ca_{9.0}La_{1.0}(PO_4)_6O_{0.97}(CO_3)_{0.53}\square_{0.50}$
$x = 1.5$ $Ca_{8.5}La_{1.5}(PO_4)_6O_{1.41}(CO_3)_{0.34}\square_{0.25}$
$x = 2.0$ $Ca_{8.0}La_{2.0}(PO_4)_6O_2$

An examination of the carbonated apatite formulas show that on the one hand the number of CO_3^{2-} ions per unit cell equals the number of vacancies, and on the other hand the number of O^{2-} ions in the channel equals that of the La^{3+} ions. These observations must be correlated with the presence of the infrared band at 545 cm^{-1} after carbonation. This band can be assigned to the La–O interaction.

Previous work on rare earth (Ln^{3+})-containing oxyapatites have shown that Ln^{3+} ions are exclusively located around the channel in the cation II sites (*6, 7*). That position allows the formation of a strong bond between Ln^{3+} and O^{2-} ions and explains the infrared band at 545 cm^{-1}. The facts that this infrared band remains in the carbonated phase and that La^{3+} and O^{2-} ions are in equal number in the carbonated apatites clearly prove that the O^{2-} ions, close to the La^{3+} ions, do not react to form CO_3^{2-}. The only O^{2-} ions able to react are those which are distant and unbonded with La^{3+} ions.

Consequently, CO_3^{2-} ions and vacancies are in equal number in the channel: each CO_3^{2-} is connected with one vacancy; taking into account the large size of the CO_3^{2-} ion, it is likely that each CO_3^{2-} ion is located in a site next to a vacancy, which allows us to minimize the distortion of the structure.

In the apatite which contains two lanthanum ions and more generally in the apatites which contain two rare earth (Ln^{3+}) ions (i) no vacancy exists in the channel and (ii) each O^{2-} ion is joined to a Ln^{3+} ion: this explains the unsuccessful carbonation treatment of Ln-containing dioxyapatite.

Conclusion

A-type-carbonated apatites containing lanthanum can be obtained by a thermal treatment of oxyapatites at 950°C in a CO_2 atmosphere:

A general formula of these compounds can be proposed:

$$Ca_{10-x}La_x(PO_4)_6O_x(CO_3)_{1-x/2}\square_{1-x/2}.$$

In such a formula, the numbers of La^{3+} and O^{2-} ions are equal, and the number of CO_3^{2-} ions equals the number of vacancies. The carbonation is limited both by the fact that the O^{2-} ions bonded with the La^{3+} ions do not react and by the amount of vacancy. When the amount of La^{3+} ions increases, the amount of O^{2-} ions increases and the vacancy number decreases. Hence the introduction of an *A*-type carbonate ion into a dioxyapatite containing two La^{3+} ions, and more generally into a dioxyapatite containing two trivalent rare earth ions, is unsuccessful.

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