CORRELATION BETWEEN ELECTRICAL AND STRUCTURAL PROPERTIES OF POORLY CRYSTALLINE APATITE

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Abstract. The present work has been undertaken to compare the effect of maturation and chemical treatments by CO$_3^{2-}$ and F$^-$ ions on the crystallinity and the electrical properties of a synthetic poorly crystallised carbonate-apatites. The tendency of these materials to crystallise during maturation or following F$^-$ treatment was accompanied by improvement of their ionic conductivity, while a decrease of the crystallinity caused by CO$_3^{2-}$ ions occurred with reducing of the conductivity. Frequency dependant ionic conductivity was either attenuated gradually during maturation and rapidly succeeding F$^-$ treatment or accentuated following CO$_3^{2-}$ treatment. These results were explained by the short-range organisation of sites with time, and by occurrence of structural order or disorder in back of chemical treatments.

INTRODUCTION

Bioapatites are in general entitled as poorly crystalline carbonate apatites, whose crystallinity is affected under different conditions by chemical effects of foreign ions such as Mg$^{2+}$, Sr$^{2+}$, CO$_3^{2-}$ and F$^-$. For example, while carbonates and Mg$^{2+}$ ions lower the crystallinity, F$^-$ ions improve it$^2$. In addition, maturation is another way to get to the crystallinity, but in a procedure different from that caused by the ionic effects$^{1-2}$. For this reason, the present work establishes a comparison between effects of maturation, CO$_3^{2-}$ and F$^-$ ions on the crystallinity of synthetic poorly crystalline apatites. Investigation of electrical properties is to more elucidate these effects by examination of change in crystallinity by conductivity spectra, which proved out to be an adequate practice to visualise the occurrence of the order-disorder phenomena in solid electrolytes$^{3-5}$. 

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EXPERIMENTAL PROCEDURES

Carbonate-apatites were elaborated at ambient temperature by double decomposition of two aqueous solutions. The first solution was prepared by dissolving 40g of diammonium phosphate \((\text{NH}_4)_2\text{HPO}_4\) in 500ml of deionised water. The pH of this solution was adjusted to 8.34 by adding a concentrated basic solution \((\text{NH}_4\text{OH}, \text{d}=0.92)\), followed by the addition of 20g of monosodium carbonate \((\text{NaHCO}_3)\). The second solution was made by dissolving 17.7g of calcium nitrate \((\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O})\) in 250ml of deionised water. After co-precipitation, the pH reached 7.35. Precipitates were left for different maturation times at room temperature (ACM), then filtered, washed with deionised water and finally lyophilised.

5g of not dried precipitates matured one day (AC1 and AC2) were subjected to two different treatments without agitation at room temperature for 10 min. At first, AC1 apatite was treated in solution (10ml) containing 0.1M of \(\text{NH}_4\text{F}\) and 1M of \((\text{NH}_4)_2\text{HPO}_4\). In the second, carbonate treatment was realised on AC2 apatite in solution (10ml) containing 1M of \(\text{NH}_4\text{CO}_3\). Treated precipitates (AC1F and AC2C) were then filtered, rapidly washed with deionised water and finally lyophilised.

A RIGAKU D/Max-C X-ray powder diffractometer with a CuK\(\alpha\) monochromatic radiation in steps of 0.02 degree between 25 and 50° \((2\theta)\) was used to collect diffraction data (XRD). The electrical measurements were performed in alternative current between 10Hz and 2MHz by complex impedance method at room temperature with a Maxwell bridge. In order to have an homogeneous pellet, the powder was pressed to 3 tons/cm\(^2\). The continuity between the outside circuit and the pellet was maintained by platinum gel deposit at the surface.

RESULTS AND DISCUSSION

X-ray diffraction showed that the crystallinity of maturing apatites is poor but ameliorates gradually with time (Figure 1-a). One notes also that the treatment of AC1 in F\(^-\) rich medium (AC1F) is accompanied by a good resolution of its RX diagram, which indicates an improvement of the crystallinity of this material. However, treatment in CO\(_3^{2-}\) rich medium lowers the crystallinity as it is shown from the breadthness of the
Ionic conductivity of ACM in term of loge with different times of maturation is illustrated in figure 2-a. It can be noted that the conductivity increased with maturation. Also, complex impedance diagrams of AC1 and AC1F apatites conducted at room temperature (Figure 3-a) show clearly that F⁻ treatment get the conductivity better. However, CO₃²⁻ treatment reduce the conductivity as it was shown in figure 4-a. Thus, the crystallinity progression in ACM and AC1F or its regression in AC2C was accompanied respectively by improvement in ionic conductivity in ACM and AC1F or its decrease in AC2C. Moreover, we have previously demonstrated that the conductivity in such materials is mainly protonic⁶.

The frequency-dependant ionic conductivity or conductivity spectra of AC apatites exhibited the variation of logσ against logω, where σᵣ is the real part of the complex conductivity σ = σᵣ + iσᵢ and ω is the frequency. This dependence followed exactly the same advance of crystallinity and conductivity. In fact, while it became progressively less accentuated during maturation (figure 2-b), it varied oppositely in

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FIGURE 1: XRD of poorly crystallised apatites: (a) after different times of maturation and (b) following chemical treatments in F⁻ and CO₃²⁻-rich media.

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treated apatites (figures 3-b and 4-b). Actually, the same shape of these spectrum is precisely observed in other solid electrolytes$^{3-5,7-11}$. With regards to this, such evolution corresponds to the relaxation mode due to the coulomb interactions of the charge carriers and the disorder within the structure. Thus, structural disorder was shown both by this phenomenon and crystal strain as shown by line-broadening in the diffraction patterns.

The progressive amortisation of these events with maturation indicated a progressive establishment of structural order by a short-range organisation of sites. Also, F$^-$ treatment improves promptly the conductivity succeeding the establishment of the order as suggested by the decrease of frequency dependence of the conductivity. In fact, the incorporation of F$^-$ ions causes an increase in chemical stability due to the better fit of the F$^-$ ions within the imaginary Ca triangles in the apatite structure and an increase in crystallinity reflecting decrease in crystal strain as shown by a decrease in diffraction line-broadening in the diffraction patterns.

The great relaxation of AC2C apatite comparing with AC2 material clarifies the specific role of carbonates in the reactivity of carbonate apatite. In fact, they are more implicated than other ions in the change of the crystallinity as it is shown from the bad resolution of its XRD pattern, and thus, the structural disorder. The D$_{3h}$ symmetry of carbonates ions could lead to imperfect compatibility with tetrahedral geometry of phosphates groups after its substitution. Carbonate-apatite would be more unstable so more reactive. In the other hand, the enrichment of AC1 in F$^-$ in AC1F material was accompanied by a reduction of the relaxation phenomenon (figure 4) likely owing to the reject of carbonate ions caused by the incorporation of F$^-$ ions in the structure$^{1,2}$. The difference in the composition of calcified tissues in CO$_3^{2-}$ and F$^-$ ions define then their role in every organ, mainly its reactivity.
FIGURE 2: Electrical properties of ACM apatites in different times of maturation in term of (a): $\log \sigma$, and (b): conductivity spectra.

FIGURE 3: (a) Complex impedance Diagrams of AC1 and AC1F apatites and (b) their corresponding conductivity spectra.

FIGURE 4: (a) Impedance diagrams and (b) conductivity spectra of untreated AC2 and treated AC2C poorly crystalline apatites in carbonate medium.
SUMMARY

F⁻ ions are susceptible to better crystallinity of poorly crystallised apatite more than it could be done by maturation for long time by rapid establishment of the order within the structure. The contribution of F⁻ to the structural stability and physicochemical properties of apatites in term of ionic conductivity is similar to the effect of maturation; nevertheless, maturation may improve the crystallinity and establishment of the order gradually, so more appropriately. However, CO₃²⁻ ions lowers the crystallinity as a consequence of the disorder caused by the uncompleted compatibility of this ions to tetrahedral shape of phosphates groups.

Consequently, electric analysis by conductivity spectra enables significant information concerning the disorder of the apatitic structure in relation to its crystallinity. Further details for each case will be the subject of our future works.

REFERENCES

6. A. Bensaoud, A. Bouhaouss, M. Ferhat, Solid State Ionics (submitted)