

A. Bensaoud · A. Bouhaouss · M. Ferhat

Electrical properties in compressed poorly crystalline apatite

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Abstract A poorly crystallized apatite is prepared by co-precipitation at room temperature and dried by lyophilization. The electrical properties, in terms of ionic conductivity, improve after a second compression of the sample under 15 t/cm². Characterization by X-ray diffraction, infrared spectroscopy and conductivity spectra show that this improved conductivity following the compression processing could be related to the establishment of order within the apatitic network.

Keywords Apatite · Ionic conductivity · Compression · Relaxation · Order

Introduction

Apatites constitute a large domain of investigation because they are analogous to the mineral part of calcified tissues [1]. They form a large family of isomorphous solids where the representative structure is calcium phosphate hydroxyapatite, Ca₁₀(PO₄)₆(OH)₂. They are used as electrolytes for fuel cells [2], alcohol and carbon dioxide gas sensors [3, 4], ionic exchangers [5], catalysts [6], etc. Most of these applications are related to their electrical and structural properties. Indeed, for well-crystallized apatites, the ionic transport occurs along the *c*-axis within the cationic and anionic channels, which confer privileged ways of diffusion. The charge carriers can be anions (F⁻, OH⁻, O²⁻) [7, 8, 9, 10], cations (H⁺) [11] or both anions and cations (F⁻, Na⁺) [12]. Previous

electrochemical studies showed that HPO₄²⁻ groups contributed to the ionic conductivity of poorly crystallized apatite, involving the transfer of protons along H-bonded networks together with H⁺ transferring between adjacent phosphate groups along the chains PO₄³⁻...HPO₄²⁻...PO₄³⁻...HPO₄²⁻ [13]. The ionic conductivity of this material improved with maturation by progressive establishment of structural order and a short-range organization of sites [14]. Also, F⁻ treatment improved promptly the conductivity, succeeding the establishment of the order [15]. In both cases, an increase in the apatitic crystallinity was noticed. The ability of this material to conduct protons has been used in an environmental device for the removal of a hazardous pesticide and heavy metals from water [16, 17]. All of the previously mentioned works investigated effects of temperature, ionic substitutions and chemical treatments on the ionic conductivity of apatites in order to evaluate the charge carriers or to improve the conductivity. In the present work, the effect of compression on electrical properties of poorly crystallized apatite is studied. The aim is the improvement of the ionic conductivity of such materials with respect to applications in electrochemical and environmental devices.

Experimental

The present apatite (AP) was prepared by co-precipitation of two aqueous solutions. A solution of calcium nitrate [Ca(NO₃)₂·4H₂O] (250 mL, 0.075 M) was added to a solution of ammonium dihydrogen orthophosphate (NH₄H₂PO₄) (500 mL, 0.15 M) and sodium bicarbonate (NaHCO₃) (0.28 M). The mixture was agitated for a few seconds in order to produce good homogeneity. The pH after precipitation converged to 7.35. After leaving it to settle for 24 h without stirring, the precipitate was filtered and washed with deionized water, and finally lyophilized. Drying by lyophilization is chosen to keep the material in its nanocrystalline state by preventing the agglomeration of the crystallites; it is a purely physical procedure which does not induce any variation in the chemical composition. It also retains any labile ions.

The X-ray diffractometer used was an INEL CPS-120. Diffractograms were collected with monochromatic radiation Cu-Kα₁ (λ = 1.5406 Å) between 25° and 50°.

A. Bensaoud · A. Bouhaouss (✉) · M. Ferhat
Laboratoire de Chimie Physique Générale,
Université Mohammed V, Faculté des Sciences Rabat-Agdal,
B.P. 1014, Rabat, Morocco
E-mail: Bouhaouss@fsr.ac.ma
Tel.: +212-7-775440
Fax: +212-7-775440

A. Bouhaouss
GMRE, B.P. 8849, Rabat-Agdal, Rabat, Morocco

IR examination of the sample was made using an IR Avatar 360 FTIR spectrometer supplied with OMNIC software. The tablets were prepared by grinding 2 mg of the sample with 300 mg of KBr and pressed (5 t/cm^2) under vacuum conditions. Before every analysis, the background was collected and subtracted from the spectrum of the sample.

Electrical measurements were performed using alternating current in the frequency range 10 Hz–10 MHz by the complex impedance method using a Maxwell bridge at room temperature. To this end, a specimen of AP was pressed under 15 t/cm^2 pressure. This pellet was ground on an agate mortar and compressed again under the same pressure. The ground pellet will thereafter be called APB. The two opposite sides of both pellets (AP and APB materials) were coated with platinum, which plays the role of the irreversible electrode and assured contact for the impedance measurements.

As in the electric measurements, XRD and IR characterizations were made on the starting material (AP) and the ground tablet (APB). The IR absorption of the compressed sample (APB) is given in the same spectrum below that of the untreated sample (AP).

Results

Analysis of the AP and APB materials by X-ray diffraction reveals the existence of a pure apatite phase, indexable in space group $P6_3/m$. The observed hkl are the same of those in a pure hydroxyapatite giving by ASTM cards [18]. The diagram of the starting apatite AP presents a low resolution and is compared to bony mineral [1]. The compression processing did not result in apparent changes in the APB X-ray diagram. Nevertheless, some peaks became more intense and relatively more resolved (Fig. 1).

The IR absorption bands in the range $450\text{--}1350 \text{ cm}^{-1}$ are shown in Fig. 2. Several bands characterize the vibration of phosphate and carbonate groups in an apatitic structure. Indeed, the intense vibration at 1070 cm^{-1} , the shoulder at 960 cm^{-1} and the bands at 576 and 600 cm^{-1} correspond respectively to ν_3 , ν_1 and ν_4 modes of PO_4^{3-} groups. The band at 873 cm^{-1} is assigned to the ν_2 mode of CO_3^{2-} ions substituting PO_4^{3-} groups

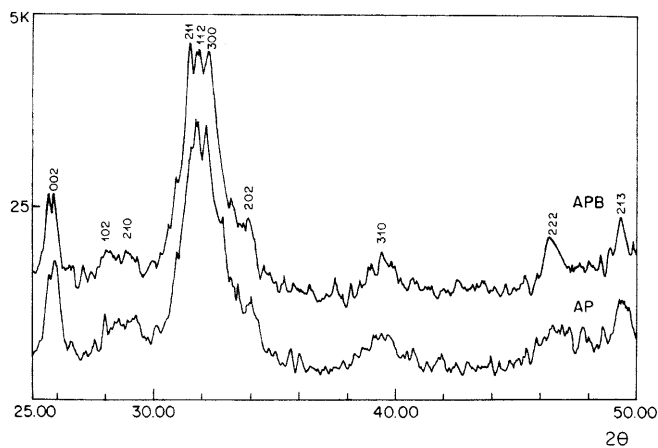


Fig. 1 X-ray diagrams of poorly crystalline apatites before (AP) and after the compression processing (APB). hkl planes are given with respect to the ASTM card [18]

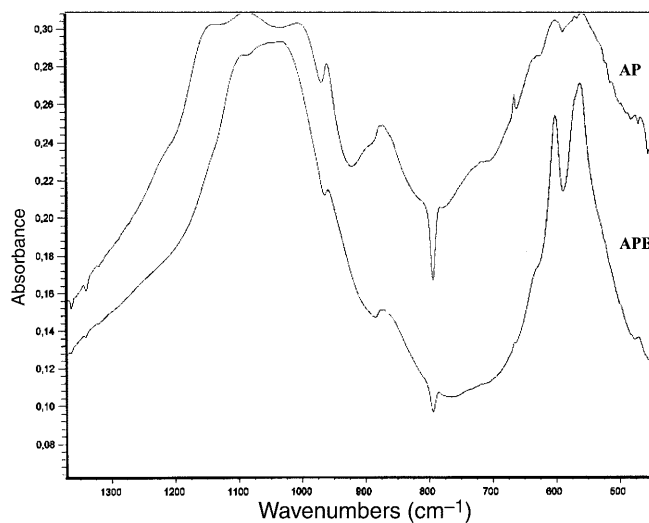


Fig. 2 Infrared spectra of poorly crystalline apatites before (AP) and after the second compression (APB)

[1]. The resolution of the IR spectra improves drastically, especially the $\nu_4 \text{ PO}_4$ band, which becomes more intense and finer following the second compression. The increased resolution of the vibrational bands of PO_4^{3-} groups could be due to the fact that the material passed to a more crystallized state.

The ionic conductivity, calculated from a Cole-Cole diagram, improves strongly following the second compression (Fig. 3). The starting material (AP) presents an arc with a high resistance, while the compressed material (APB) shows an arc with lower impedance, followed by a linear part characterizing the participation of irreversible electrodes. The representation of the conductivity in the frequency spectra highlights a change of its variation against the frequency (Fig. 4). Indeed, AP apatite presents a linear dependence of the conductivity vs. frequency, which becomes less important after the compression (APB).

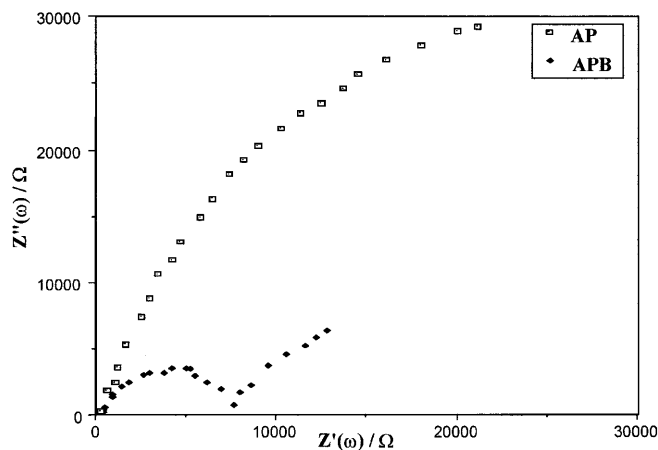


Fig. 3 Impedance diagrams of poorly crystalline apatites before (AP) and after the second compression (APB)

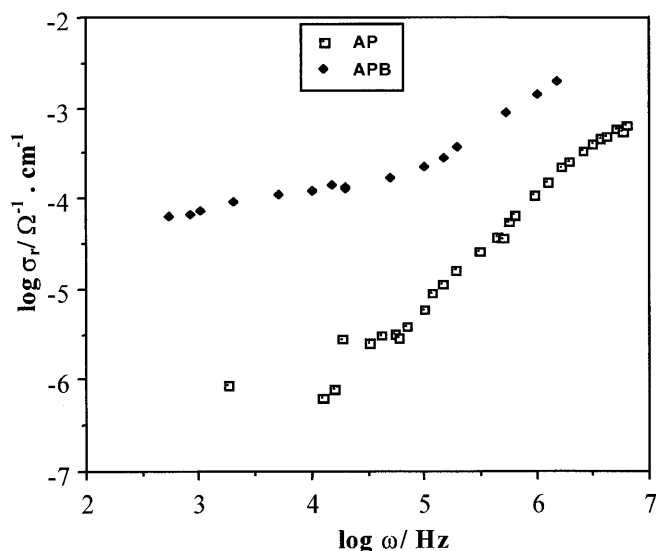


Fig. 4 Conductivity spectra of poorly crystalline apatites before (AP) and after the compression processing (APB)

Discussion

The poor crystallinity of apatite is unfavorable for proton diffusion owing to the disorder and the non-periodicity of sites where the diffusion should be privileged. From previous works [13, 14], the increase of the conductivity of APB following the compression is consistent with the improvement of some XRD diffraction peaks. It is most likely that the compression has improved relatively the crystallinity of the AP material.

The dramatic increase in the IR absorption following compression is more surprising. Trying to explain the effect of compression on the IR absorption, Hemley [19] proposed the formation of charge-transfer states between neighboring molecules. Some theories [20] focus on purely static charge, others focus on purely dynamic charge where displacements are induced [21, 22, 23]. For these materials, the charges are transferred by mobile protons along H-bonded networks. Indeed, one could discern from the IR spectra of both AP and APB apatites the existence of a negative band at 790 cm^{-1} , characterizing strong hydrogen bonds. Abe and al. [24] have found that the mobility of H^+ in some phosphate glasses increases markedly with the increasing strength of hydrogen bonding. In the present material, there exist many neighboring oxygens having a high ionic character, giving rise to strong hydrogen bonding. Thus, it is easy for protons to be mobile under an applied electrical field, provided the structure becomes more organized. The improvement of the ionic conductivity of APB apatite (Fig. 3) confirmed that the proton transfer became more favorable between apatitic groups after the compression processing.

To better understand this phenomenon, we have analyzed the a.c. conductivity spectra exhibited as variation of $\log \sigma'$ vs. $\log \omega$, where σ' is the real part of the complex

conductivity $\sigma = \sigma' + i\sigma''$ and ω is the frequency (Fig. 4). These spectra show a frequency dependence of a.c. conductivity according to the $\sigma' \propto \omega^s$ law. Actually, the same shape of these spectra is precisely observed in other solid electrolytes. 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 [10, 14, 25, 26]. Thus, it can be assumed that protons are randomly distributed between phosphate groups in the starting apatite (AP). The conductivity spectra show a slowing down of the relaxation phenomenon following the compression, especially in the lower frequencies. Obviously, the conductivity-frequency isotherm of sample APB became curved above 10^5 Hz and tends to be less dependent on the frequency. This can be explained by the fact that interactions between charge carriers become loosened owing to the establishment of order within the apatitic structure [25, 26]. Moreover, the plateau observed in the APB spectrum (Fig. 4) is mainly attributed to ion migration. In a previous work it was demonstrated that surface HPO_4^{2-} groups contributed to this conductivity. It is possible that the compression reduces the grain boundaries, makes the sites HPO_4^{2-} more organized, and favors the proton mobility. As far as we know, this feature is new and important, but needs to be studied more using other techniques. In our future work we will focus on further investigations to understand better such behavior.

Conclusion

In this preliminary work, we have demonstrated that poorly crystalline apatite presents a disordered network, exhibited by a relaxation phenomenon. The compression of this sample improves drastically its ionic conductivity, makes the IR bands more resolved, and decreases the relaxation, producing an establishment of order within the apatitic structure. The improvement in the ionic conductivity could be due to the reduction in the resistivity of grain boundaries.

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