



Structure electronic and ionic conductivity study versus Ca content in $\text{Ca}_{10-x}\text{Sr}_x(\text{PO}_4)_6\text{F}_2$ apatites

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ABSTRACT

Substitution effect on the crystallographic structure in $\text{Ca}_{10-x}\text{Sr}_x(\text{PO}_4)_6\text{F}_2$ solid solution are studied by X-ray diffraction patterns and Rietveld refinements. Full potential electronic structure calculations based on LCAO (linear combination atomic orbital) are also performed using the obtained crystallographic parameters. DOS modification and the charge transfer are estimated versus the calcium content. According to the complex impedance method, ionic conductivity changes are explained.

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1. Introduction

Morocco has various sedimentary phosphates deposits, which contain mineral apatites. These minerals show an interest for the environment safeguard due to their remarkable properties of fixing and retention of the pollutant elements (heavy metals, actinides, lanthanides, ...) [1–5].

Strontium and fluorine substitutions are involved in dental and bone pathologies, and in the preparation of bioceramics for tissues repair [6–9].

Therefore, we are interested in crystalline and electronic structure studies, which constitute a part of data necessary to understand their physical properties. Apatite minerals generally crystallize in the hexagonal system (SG: $P6_3/m$) as shown in Fig. 1. They have the general chemical formula $\text{Me}_{10}(\text{XO}_4)_6\text{Y}_2$, where Me generally represents a bivalent cation, XO_4 a trivalent anion and Y monovalent anion. They are characterized by the ability to accept substitution on all sites from a large array of elements and exhibit a high resistance to temperature and to irradiation processes. In nature, the apatite shows the ability to retain actinides (Pu, Am, ...) and corresponding fission products (Sr, Cs, Ba, ...) for up to one thousand million years. For this reason, it could be used in the future as a matrix for conditioning high radioactive separate

wastes. Many investigations on synthetic apatites containing this element, and with various substitutions, have been carried out in order to explain the effects of strontium on the apatitic structure and the physico-chemical properties of the material. Generally, the physicochemical properties depend on the substituted sites ($\text{Ca}_{(4f)}$, $\text{Ca}_{(6h)}$ or both sites). If the substituent does not have a valence equal to +2, both sites are concerned [6]. If the substituent is of M^{2+} type, the substitution depends on the relative size of the substituent. The substituent radius for the Ca^{2+} site and the apatite with hexagonal structure should be discussed when the size of the cation M^{2+} is between 0.95 and 1.35 Å [10]. Largest substituent prefer the $\text{Ca}_{(6h)}$ site [10,11]. Thus, in the current study, we also examine the substitution (Ca by Sr) effects on the electronic structure and ionic conductivity.

2. Materials and techniques

2.1. Sample preparation

Compounds of $\text{Ca}_{10-x}\text{Sr}_x(\text{PO}_4)_6\text{F}_2$ solid solution were prepared by precipitation wet method at 80 °C in ammoniacal solutions containing $(\text{NH}_4)_2\text{HPO}_4$, NH_4F and $\text{M}(\text{NO}_3)_2$ (where $\text{M} = \text{Ca}, \text{Sr}$) as reported in previous studies [12,13]. Different compositions were prepared by changing the strontium content x in the $\text{Ca}_{10-x}\text{Sr}_x(\text{PO}_4)_6\text{F}_2$. The mixture is then heated under agitation at 80 °C during 2 h of precipitation. After maturation, filtration, and drying of the precipitate, the obtained powder was heated in a continuous

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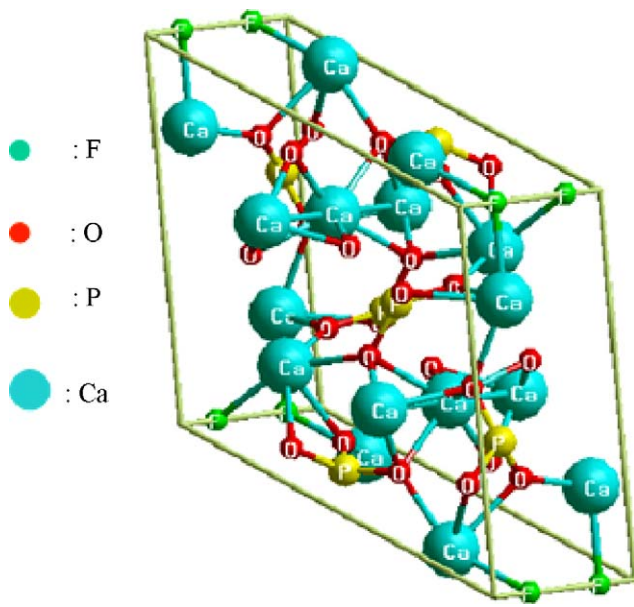


Fig. 1. Positions of atoms in the fluorapatite unit cell $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$.

pipe at 900°C during 3 h before different physicochemical characterizations. The fluorapatite structure has been confirmed by X-ray powder diffraction, infrared spectroscopy and chemical analysis.

2.2. Data acquisition and processing

X-ray powder data were collected using a D500 diffractometer operating at Cu K_α radiation and the Rietveld refinements were performed using the FullProf code [14,15]. The values (a and c cell parameters, atomic positions, site occupancies, thermal parameters) of the stoichiometric phosphocalcium fluorapatite were used as a starting model. Pseudo-Voigt function was used to fit the individual reflection profiles. In the final step of refinement, all atomic positions and site occupancies were refined simultaneously with thermal factor. Typical diffraction patterns and Rietveld refinement of $\text{Ca}_{10-x}\text{Sr}_x(\text{PO}_4)_6\text{F}_2$ solid solution are shown in Fig. 2.

2.3. Electronic structure calculations

To understand the ionic exchange properties of $\text{Ca}_{10-x}\text{Sr}_x(\text{PO}_4)_6\text{F}_2$ apatites, we have carried out an electronic structure calculation using the CRYSTAL code based on LCAO method [16]. The atomic orbitals were expressed as a linear combination of Gaussian-type functions. The basis sets used for calcium and fluorine were optimized in the CaF_2 system [17]. The basis set of phosphorus was optimized in the atomic state which is valid for ionic systems, whereas those for strontium and oxygen were optimized in the SrTiO_3 and Li_2O systems respectively [16,18]. The LCAO calculations are performed with the crystal structure parameters derived from our X-ray data gathered in Tables 1 and 2. The $P6_3/m$ space group for the $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ and $\text{Sr}_{10}(\text{PO}_4)_6\text{F}_2$ ordered compounds were used whereas $P6_3$ was used for the $\text{Ca}_4\text{Sr}_6(\text{PO}_4)_6\text{F}_2$ disordered compound, since the Ca and Sr atoms share the 6c site defined by $x = 0.239$, $y = 0.252$ and $z = 1/4$. In this compound, we do not consider a fully disordered system on 6c site for which the LCAO method is not convenient. To overcome this difficulty, we consider 6c as a quasi-chemically disordered site where 2 Ca atoms and 4 Sr atoms are put on the 6 available positions. All the remaining sites and their occupancies are kept unchanged according to the request formulae of $\text{Ca}_4\text{Sr}_6(\text{PO}_4)_6\text{F}_2$.

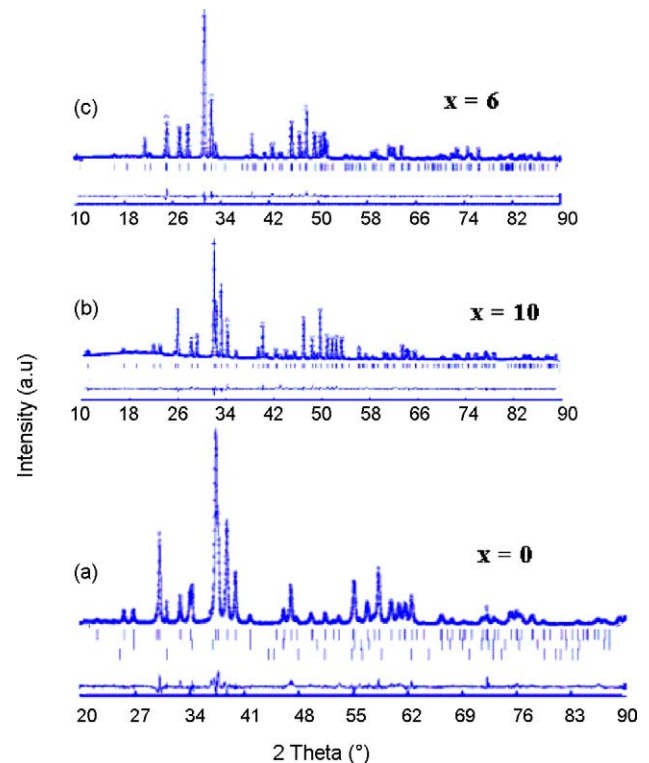


Fig. 2. Rietveld refinement of X-ray data of calcium-strontium apatite $\text{Ca}_{10-x}\text{Sr}_x(\text{PO}_4)_6\text{F}_2$, ($x = 0, 6$ and 10).

The inclusion of this quasi-disordered approximation leads to the space group change from $P6_3$ to $P2_1$ for our structure electronic calculations.

3. Results and discussion

3.1. Crystal and electronic structure

The typical diffraction patterns and the resulting refinement for synthetic $\text{Ca}_{10-x}\text{Sr}_x(\text{PO}_4)_6\text{F}_2$ samples are shown in Fig. 2, while the resulting crystal structure parameters are gathered in Table 1. The partial substitution of Ca by Sr ($x = 6$) leads to change the space group ($P6_3$) where the Ca atoms occupy the 2b site with $z = 0$, whereas the Sr atoms occupy the 2b site with $z = 0.5$. In addition, the 6c site is shared by Ca (2 atoms) and Sr (4 atoms) as described in Table 2. The cell parameters are $a = b = 0.9576$ nm and $c = 0.7116$, values slightly lower than those reported previously but very close to those reported for the $\text{Ca}_{2.7}\text{Sr}_{7.3}(\text{PO}_4)_6\text{F}_2$ system [19,20]. The Ca, Sr and P coordinates are also in a nice agreement with those reported previously, whereas the coordinates of the remaining atoms do not exhibit a good agreement [19]. Total substitution of Ca by Sr leads to recover the initial phase with the $P6_3/m$ space group where the Sr atoms occupy both 4f and 6h sites. As a result, this total substitution of Ca by Sr, with a higher atom radius, induces an increase of the a and c cell parameters and a change in the site coordinates occupied by P, O and F atoms. All of the present data agree well with those reported in Ref. [21].

Theoretical results from LCAO calculations led to the density of states (DOS shown in Fig. 3a). First, the analysis of the total DOS establishes that the Fermi level E_f fall in the gap, giving evidence of an insulating state of these compounds. The DOS, versus substitution, also exhibits several specific features in both the occupied as well as in the unoccupied states. Some of these features result from significant Ca or Sr atom contributions. The projected DOS on the Ca (Fig. 3b) and Sr atoms show no band gap

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