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Structural, electronic and thermodynamic properties of britholites $Ca_{10-x}La_x(PO_4)_{6-x}(SiO_4)_xF_2$ $(0 \leq x \leq 6)$: Experiment and theory

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ABSTRACT

The apatite-type compounds $Ca_{10-x}La_x(PO_4)_{6-x}(SiO_4)_xF_2$ with $0 \leq x \leq 6$ were prepared using a high temperature solid state reaction and were characterized by X-ray diffraction. The crystal structure, chemical bonding, electronic structure and formation energy of all relaxed structures were analyzed by density functional theory (DFT). The calculated results show that the predicted geometry can well reproduce the structural parameters. The incorporation of La^{3+} into the fluorapatite (FA) structure induced especially at the level of the S(2) sites a certain disorder which is responsible for the weakening in the stability with *x*. Excellent agreement were obtained between the calculated and experimental results. Moreover, the band structure indicates that despite the reduction of the band gap with *x* content all materials remain insulating.

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1. Introduction

The hydroxyapatite ($Ca_{10}(PO_4)_6OH_2$, HA) and to a lesser extent the fluorapatite ($Ca_{10}(PO_4)_6F_2$, FA) have been extensively studied because of to their physicochemical and biological properties and for their applications as biomaterials [1,2]. Furthermore, the ability of their structure to accommodate a great number of substitutions, both cationic and anionic substitutions, has widely expanded their field of application [3–5]. For example, the simultaneous substitutions of rare earth elements (Ln^{3+}, La^{3+}, Nd^{3+}, etc.) and SiO_4^{4-} for Ca^{2+} and PO_4^{3-}, result in a new family of compounds called britholites [6]. The discovery of the natural nuclear reactor of Oklo (Gabon) [7] has demonstrated that these compounds can retain minor actinides and long-lived fission products over several million years without suffering major damage [8–11], suggesting that they can be very suitable for the confinement of the nuclear waste [12].

Compared to FA, it is well known that the chemical and physical properties of the substituted counterparts are in direct correlation with the atoms in substitution. Therefore, britholites have been the aim of several experimental studies, using X-ray diffraction (XRD), infrared (IR) and Raman spectroscopy, nuclear magnetic resonance (NMR) and so on, in order to determine their thermal, chemical, physical and structural properties [13,14]. However, the interpretation of some experimental results is still somewhat difficult, such as the evolution of their stability with the substitution.

Nowadays, ab initio calculations have proved to be an effective way to analyze and model the structure of apatites at the atomic level in order to predict their physical and chemical properties. Several theoretical studies on the apatites have been reported for the interpretation of the electronic structure, charge distribution and atomic configuration using ab initio Hartree-Fock method [15], molecular dynamic simulation [16], and density functional theory [17–19]. Katsuyuki et al. [20,21] have proposed the thermodynamic treatment of total energies to analyze the defect stability under chemical equilibrium between the solid and aqueous solution. Rabone and de Leeuw have studied Sr^{2+} substitution for Ca^{2+} in fluorapatite and hydroxyapatite using classical potentials [22]. Other studies have focused on the position and orientation of the common anionic groups along the *c*-axis channel in apatites [19,23,24]. In addition, Meis et al. [25] have investigated the possibility of incorporating selectively plutonium and cesium in a mono-silicate neodymium-fluoroapatite using analytical potentials. These previous studies have established that the atomic scale simulation is useful and reliable for the study of apatites.

According to the properties of natural silicate-apatites and the strong bonds between lanthanides and fluorine anions as well as the rigidity of the PO_4 groups [6], the possibility of obtaining synthetic apatites with a definite composition allows the reparation of materials suitable for use as high performance matrices for long-lived radioactive wastes. The goal of this paper is to undertake

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a systematical analysis of the structural and electronic properties of the $Ca_{10-x}La_x(PO_4)_{6-x}(SiO_4)_xF_2$ $(0 \leq x \leq 6)$ in order to evaluate the influence of the substitutional atoms at the atomic level in order to help understand thermodynamic data, using first-principles DFT calculations. The obtained results will be compared to those experimentally determined.

2. Materials and methods

2.1. Sample preparation and characterization

The samples were prepared by utilizing a solid-state reaction from a stoichiometric mixture of $CaCO_3$, CaF_2, La_2O_3, SiO_2, and $Ca_2P_2O_7$ according to the following reaction:

$$3CaCO_3+\left(\frac{6-x}{2}\right)Ca_2P_2O_7+CaF_2+xSiO_2+xLa_2O_3 \rightarrow Ca_{10-x}La_x(PO_4)_{6-x}(SiO_4)_xF_2+3CO_2$$

The calcium diphosphate was obtained by heating a mixture of calcium carbonate and diammonium hydrogen phosphate at 900 °C for 10 h. Before use, the lanthanum oxide was calcined at 1000 °C for 12 h.

The starting reagents were thoroughly ground in an agate mortar. Then, they were pressed into pellets and heat-treated under an argon flow at 900 °C for 12 h. Thereafter, the pellets were manually crushed and homogenized. The resulting powders were again uniaxially pressed and heat-treated between 1200 and 1400 °C according to their SiO_2 content. The heating rate was of 10 °C/min. Finally, the samples were cooled naturally to room temperature. Samples were characterized by X-ray diffraction (XRD) using a Bruker D8 ADVANCE diffractometer operating with Cu-K_α radiation for a 2θ range from 9° to 80°, with a step size of 0.02° and a counting time of 10 s per step.

2.2. Density functional theory based calculations

The calculations have been performed using a plan-wave basis set and ultrasoft pseudopotentials as implemented in the QUANTUM-ESPRESSO package [26]. The wave functions are expanded in plane waves with an energy cutoff of 110 Ry. The exchange-correlation potential was treated in the framework of the generalized-gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [27]. The Brillouin-Zone (BZ) integrations have been carried out using sets of special points corresponding to a 4×4×2 Monkhorst-Pack mesh [28]. Each eigenvalue was convoluted with a Gaussian with a full width at half maximum of $\sigma = 0.02$ Ry. All structures were optimized by simultaneously relaxing the atomic basis vectors and the atomic positions inside the unit cells using Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [29]. The relaxation was considered to be complete when the atomic forces were less than 1.0 mRy/Bohr, and the total energy during the structural optimization iterative process was converged to less than 0.1 mRy. Unit-cell and initial positional parameters used in the optimization were referred from the Rietveld refinement results.

2.3. Crystal structure

Fluorapatite (FA) crystallizes in a hexagonal crystal structure with a $P6_3/m$ space group. The unit cell contains 42 atoms. In this structure, PO_4^{3-} tetrahedra form the network with two types of channels where the Ca atoms are located. The tunnels of the first kind are filled with four Ca(1), noted S(1) sites (4f position), along a three-fold axis. Each of these Ca atoms, which are aligned in columns parallel to the c-axis, is surrounded by nine oxygen atoms: three O(1), three O(2) and three O(3), forming a CaO_9-polyhedron with six short and three long Ca–O bonds. The second-type-tunnel, which is the largest, is lined by oxygen atoms and the six other Ca, noted S(2) sites (6h position), along a six-fold axis. These Ca coordinated by six oxygen atoms (O(1), O(2), four O(3), and a fluorine atom form an irregular CaO_6F-polyhedron. Otherwise, Ca(2) atoms are located at the vertices of two alternated equilateral triangles at $z = 1/4$ and $3/4$, which are centered on the six-fold axis, where the fluorine ions are located at 2a positions. A model for FA structure is given as a reference in Fig. 1.

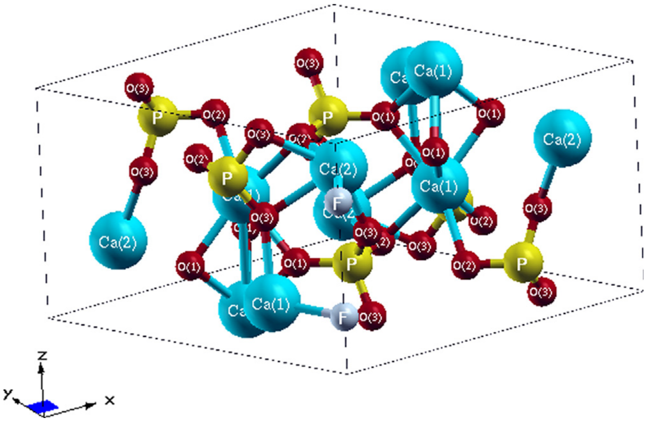

Fig. 1. Primitive unit cell of the fluoroapatite $Ca_{10}(PO_4)_6F_2$ with atoms labeled according to element and symmetric type.

3. Results and discussion

3.1. Lattice parameters and stability

The XRD patterns of the samples are shown in Fig. 2. All the XRD patterns showed reflections corresponding to an apatite phase, matching the ICDD standard (JCPDS 00-071-0880) for FA. No secondary phases were detected in any of the patterns.

Prior to the simulation, the XRD data were analyzed via the Rietveld method using the Fullprof program [30]. The computed together with experimental lattice parameters of the samples are given in Table 1 and are approximately 0.1–0.2 Å larger than the experimental ones. This overestimation is typical of the GGA functional. We notice that the increase of both a and c parameters with the simultaneous incorporation of La^{3+} and SiO_4^{4-} has a basically linear evolution in accordance with Vegard's law. This

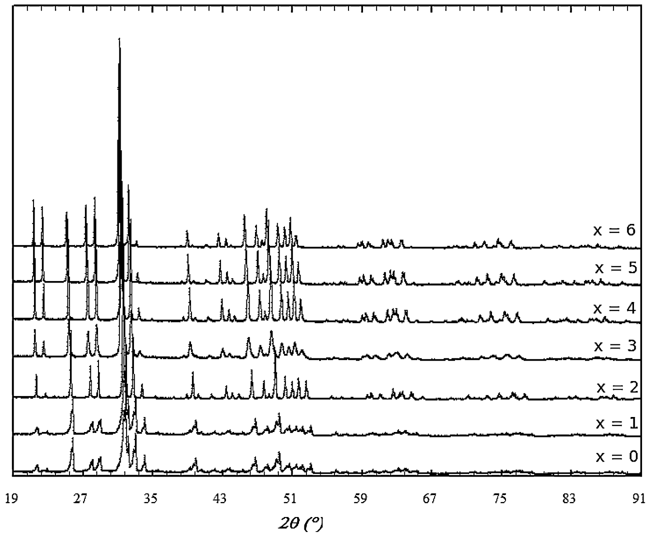

Fig. 2. XRD patterns of $Ca_{10-x}La_x(PO_4)_{6-x}(SiO_4)_xF_2$ sample, with $0 \leq x \leq 6$.

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