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Study of the ionic conductivity of $\text{Ca}_6\text{La}_4(\text{PO}_4)_2(\text{SiO}_4)_4\text{F}_2$ and $\text{Ca}_4\text{La}_6(\text{SiO}_4)_6\text{F}_2$ *Étude de la conductivité ionique de $\text{Ca}_6\text{La}_4(\text{PO}_4)_2(\text{SiO}_4)_4\text{F}_2$ et $\text{Ca}_4\text{La}_6(\text{SiO}_4)_6\text{F}_2$*

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ABSTRACT

In order to enhance our knowledge about the $\text{Ca}_{10-x}\text{La}_x(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{F}_2$ ($0 \leq x \leq 6$) series, whose chemical stability decreases as the substitution degree increases, $\text{Ca}_6\text{La}_4(\text{PO}_4)_2(\text{SiO}_4)_4\text{F}_2$ and $\text{Ca}_4\text{La}_6(\text{SiO}_4)_6\text{F}_2$ compounds were prepared through a solid-state reaction. Their ionic conductivity was measured by impedance spectroscopy. The results indicate that the conductivity increases with substitution, and fits the Arrhenius equation over the investigated temperature range. At high temperatures, a change in the activation energy has been observed, which has been related to the nature of the Ca/La–F bond, i.e. to the polarizability of lanthanum.

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R É S U M É

Dans le but d'améliorer nos connaissances sur la série $\text{Ca}_{10-x}\text{La}_x(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{F}_2$ ($0 \leq x \leq 6$), dont la stabilité chimique diminue lorsque le degré de substitution augmente, les composés $\text{Ca}_6\text{La}_4(\text{PO}_4)_2(\text{SiO}_4)_4\text{F}_2$ et $\text{Ca}_4\text{La}_6(\text{SiO}_4)_6\text{F}_2$ ont été synthétisés par réaction à l'état solide. Leur conductivité ionique a été mesurée par spectroscopie d'impédance complexe. Les résultats obtenus montrent que la conductivité augmente en fonction de la substitution et qu'elle suit la loi d'Arrhenius dans le domaine de température étudié. Aux températures élevées, un changement de l'énergie d'activation est observé. Il a été relié à la nature de la liaison Ca/La–F, et plus précisément à la polarisabilité du lanthane.

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1. Introduction

Apatites are a large group of minerals whose main representative is fluoroapatite (Ca_{10}Fap), crystallizing mainly in the hexagonal structure (space group $P6_3/m$), where the PO_4^{3-} groups build the framework and the Ca^{2+} ions occupy two non-equivalent sites, $S(1)$ and $S(2)$. Thanks

to its stability and flexibility, this structure can accommodate a great variety of substitutions – both cationic and anionic – leading to a wide variety of compounds having different properties, and making them fit for use in various application fields. Hydroxyapatite (Ca_{10}Hap), deriving from Ca_{10}Fap by the substitution of OH^- for F^- , is widely used as bone substitutes and coatings on metallic prostheses owing to its good biocompatibility, bioactivity and osteoconductive properties [1–4]. Furthermore, to improve its biological and physicochemical properties, many species contained in biological apatite have been

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incorporated into synthetic Ca₁₀Hap [4]. Apart from biomedical applications, Ca₁₀Hap and Ca₁₀Fap substituted with various ions have been used in catalysis [5], chromatography [6–8] or as adsorbents for the removal of heavy metals and many other species [9–13].

Another class of apatites – rare-earth-based apatites – has gained great interest from researchers for over several decades given their appealing properties. For example, compounds with various compositions, Ln_{9.33}(XO₄)₆O₂, Ln₁₀(XO₄)₆O₃ and Ln_{10–x}M_x(XO₄)₆O_{3–x/2}, where Ln is a rare-earth like La, Nd, etc., M is an alkaline earth like Ca, Sr, etc., and X is either Si or Ge, are extensively investigated thanks to their good ionic conductivity [14–18]. They are considered promising candidates to replace yttria-stabilized zirconia as solid oxide fuel cells (SOFCs) electrolytes at intermediate temperatures [19,20]. Also, oxyapatites doped with rare-earth ions, such as Eu³⁺, Tb³⁺, etc. have attracted the researchers' attention for their luminescence properties [21,22]. On the other hand, the compounds with the general formula Ca_{10–x}Ln_x(PO₄)_{6–x}(SiO₄)_xF₂ (Ln = La, Nd) have been the subject of both theoretical and experimental studies, because of their potential use as confinement matrices for the minor actinides and long-lived fission products [23–31]. Ardhaoui et al. [32,33], studying the thermodynamic properties of the latter series of compounds, have shown that their enthalpy of formation increased with the increase of the substitution of the pair (Ln³⁺, SiO₄^{4–}) for the pair (Ca²⁺, PO₄^{3–}). Furthermore, although a number of studies have been carried out on the structure [34–36] and properties [26–31] of the latter series, to our knowledge, no author has investigated its ionic conductivity.

In order to get a better understanding of the evolution of their properties with the substitution degree, a systematic study of lanthanide-substituted fluoro- and oxyapatites has been undertaken in our laboratory [36–41]. In this paper, we investigate the ionic conductivity of the Ca₆La₄(PO₄)₂(SiO₄)₄F₂ and Ca₄La₆(SiO₄)₆F₂ samples using impedance spectroscopy.

2. Experimental procedure

2.1. Sample preparation

Samples with the chemical formula Ca_{10–x}La_x(–(PO₄)_{6–x}(SiO₄)_xF₂, with $x = 0, 4$ and 6 , were synthesized via a solid-state reaction from CaCO₃, CaF₂, La₂O₃, SiO₂, and Ca₂P₂O₇. The latter compound was obtained by heating a stoichiometric mixture of CaCO₃ and (NH₄)₂HPO₄ at 900 °C for 10 h. To avoid the deviation from stoichiometry, lanthanum oxide was calcined at 1000 °C for 24 h just before use, because it is very sensitive to moisture and carbon dioxide from the air [42]. The starting materials in suitable proportions were weighed and thoroughly ground in an agate mortar. Then, they were pressed into pellets, which were firstly heat-treated under a dynamic atmosphere of argon at 900 °C for 12 h, in order to remove the volatile species. After this heat treatment, the pellets were manually crushed and homogenized, and the resulting powders were again uniaxially pressed. According to their

SiO₂ content and until a pure phase was obtained, the compacts have undergone one or more heat treatments at a temperature between 1200 and 1400 °C for 12 h under the same atmosphere. The heating rate was 10 °C/min.

After heat treatment, the density (d_{ex}) of a compact was determined from its dimension and weight, and the relative density was calculated using the formula:

$$\rho = \frac{d_{\text{ex}}}{d_{\text{theo}}} \quad (1)$$

The theoretical density (d_{theo}) was calculated for each composition, taking into account its molecular weight (W), the number of units per unit cell (Z) and the volume of the unit cell, according to the following equation:

$$d_{\text{theo}} = \frac{ZW}{A \times a^2 \times c \times \sin 120^\circ} \quad (2)$$

where A is Avogadro's number, and a and c are the lattice parameters.

In the following sections, the compositions with $x = 4$ and 6 will be labelled as Ca₆La₄Fap and Ca₄La₆Fap, respectively.

2.2. Sample characterization

The X-ray diffraction (XRD) patterns of the samples were obtained on a Bruker D8 ADVANCE diffractometer operating with Cu K α radiation. The samples were scanned in the 2θ range from 20 to 60° with a step size of 0.02° and a counting time of 10 s per step. The lattice parameters were refined by using the Rietveld method.

The MAS–NMR analyses were conducted on ³¹P and ²⁹Si nuclei using a Bruker 300 WB spectrometer at resonance frequencies of 121.50 and 59.62 MHz, respectively. The spinning rate of the sample at the magic angle was 8 kHz. ³¹P and ²⁹Si chemical shifts were referenced to external standards of an aqueous solution of 85% H₃PO₄ and tetramethylsilane (TMS), respectively.

Impedance measurements were carried out on samples with $x = 4$ and 6 , whose relative density was about 77%, using a Hewlett-Packard 4192-A impedance analyzer, operating at frequencies ranging from 5 to 13 MHz. Silver electrodes were painted on the two faces of the pellets with a silver paste, and then the painted pellets were heated at 300 °C for 1 h.

3. Results and discussion

3.1. Phase identification

Fig. 1 shows the XRD patterns of samples for $x = 0, 4$ and 6 . As seen, all the patterns exhibit only the reflections of an apatitic phase, indexed in the hexagonal system (space group $P6_3/m$) based on the fluoroapatite (JCPDS card #00-071-0880). No evidence of any second phase was found, indicating that the samples were single phased.

The insertion of La³⁺ and SiO₄^{4–} within the apatite lattice can be verified by comparing the lattice parameters of the substituted samples with those of Ca₁₀Fap. Both a and c are known to increase when Ca²⁺ and PO₄^{3–} ions are

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