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Mechanochemical synthesis and ionic conductivity of lanthanum phosphosilicate oxyapatites

Mécanosynthèse et conductivité ionique d'oxyapatites phosphosilicatées au lanthane

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ABSTRACT

Lanthanum phosphosilicate apatites with the chemical formula $Sr_{10-x}La_x(PO_4)_{6-x}(SiO_4)_xO$, where $0 \leq x \leq 6$, usually prepared by a solid-state reaction at about 1400 °C, were synthesized via the mechanochemical method at room temperature. The samples were characterized using powder X-ray diffraction, infrared spectroscopy and thermal analysis. The results showed that the prepared products were carbonated apatites and no secondary phase was detected. The realization of the milling under a controlled atmosphere can lead to oxyapatites containing no carbonates. The ionic conductivity of the $Sr_6La_4(PO_4)_2(SiO_4)_4O$ sample was investigated by using impedance spectroscopy. The highest ionic conductivity value of 1.522×10^{-6} S·cm^{-1} was found at 800 °C. In the investigated temperature range, the activation energy is of 0.85 eV.

Mots clés :
Oxyapatites
Terres rares
Mécanosynthèse
Conductivité ionique

RÉSUMÉ

Des apatites phosphosilicatées au lanthane de formule chimique $Sr_{10-x}La_x(PO_4)_{6-x}(SiO_4)_xO$ où $0 \leq x \leq 6$, généralement préparées par réaction à l'état solide à environ 1400 °C environ, ont été synthétisées par mécanosynthèse à la température ambiante. Les échantillons ont été caractérisés par diffraction des rayons X, spectroscopie infrarouge et analyse thermique. Les résultats ont montré que les produits obtenus étaient des apatites carbonatées et aucune phase secondaire n'a été détectée. La réalisation du broyage sous atmosphère contrôlée devrait conduire à des oxyapatites ne contenant pas de carbonates. La conductivité ionique de l'échantillon $Sr_6La_4(PO_4)_2(SiO_4)_4O$ a été étudiée par spectroscopie d'impédance. La valeur de la conductivité ionique la plus élevée, $1{,}522 \times 10^{-6}$ S·cm^{-1}, a été déterminée à 800 °C. Dans le domaine de température étudié, l'énergie d'activation est de 0,85 eV.

1. Introduction

Apatites are a large family of compounds with the general chemical formula $M_{10}(XO_4)_6Y_2$, where M represents a divalent cation, XO_4 an anion group and Y a monovalent anion. They crystallize mainly in the

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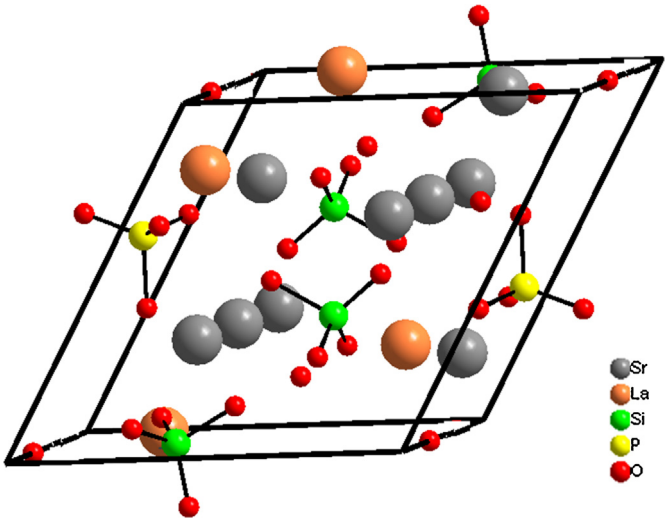

Fig. 1. (Color online). Positions of atoms in the strontium oxyapatite unit cell ($Sr_{10}(PO_4)_6O$).

hexagonal system with the $P6_3/m$ space group [1] (Fig. 1). The main representative member of the apatite family is the hydroxyapatite HA, $Ca_{10}(PO_4)_6(OH)_2$, that can be considered as a wonderful compound. Its chemical composition and crystallographic structure similar to that of the mineral phase of bone and teeth make it a material of choice in many medical applications [2–4]. Furthermore, as a result of its ability to accommodate a great number of substitutions: cationic, anionic or both cationic and anionic substitutions, practically a third of the periodic table elements can be incorporated within the apatite lattice [5,6], making the application field of the obtained materials practically unlimited [7–14]. Indeed, this flexibility of the apatite structure to accept a variety of species may confer to the prepared materials very diverse properties, resulting in a variety of applications that are either already planned or are still to be discovered.

For example, simultaneous substitutions can occur in the three sites (M, XO_4 and Y). In hydroxyapatite, the substitution of La^{3+}, SiO_4^{4-} and $O^{2-}$for Ca^{2+}, PO_4^{3-} and OH^-, respectively leads to new compounds, which have gained considerable interest as oxide ion conductors following the works of Nakayama et al. [15–17]. These compounds are usually prepared by a solid-state reaction at high temperatures. Also, several heat treatments are often required to achieve single-phase materials [18–21]. On the contrary, the mechanochemical synthesis involves only a solid-state reaction at room temperature [22,23]. Therefore, this method appears quite attractive for the preparation of this kind of materials [24,25]. Besides its low energy consumption, simplicity and speed, it is suitable for industrial production. Furthermore, the mechanical treatment leads to an increase in the specific surface area of powders, which should improve the densification of the materials [26].

The aim of this work was to attempt the preparation of the series ($Sr_{10-x}La_x(PO_4)_{6-x}(SiO_4)_xO$, where $0 \leq x \leq 6$) via the mechanochemical method. The obtained powders were investigated using XRD, FTIR and TGA/DTA. In addition, we have characterized the $Sr_6La_4(PO_4)_2(SiO_4)_4O$ sample by its ionic conductivity.

2. Experimental procedure

2.1. Preparation of powders

The samples were prepared by the mecanochemical process using a Retsch PM200 planetary micro mill. The synthesis reaction occurs as follows:

$$4\,SrO + (6\text{-}x)/2\;\; Sr_2P_2O_7 + x/2\;\; La_2O_3 + x\;\; SiO_2 \rightarrow Sr_{10-x}La_x(PO_4)_{6-x}(SiO_4)_xO \quad (1)$$

Appropriate amounts of strontium oxide (SrO), lanthanum oxide (La_2O_3), silica (SiO_2) and strontium diphosphate ($Sr_2P_2O_7$) in order to obtain (Sr + La)/(P + Si) atomic ratios of 1.67 were ground and homogenized in an agate mortar prior to grinding. Then, the mixture was introduced with several stainless steel balls, 10 mm in diameter in a 50 cm^3 stainless steel cell. The weight ratio of the ball-to-powder for all samples was 34:1. The rotating disc speed and cell speed were 500 and 1000 rpm, respectively. Following a previous study [24], the grinding duration was fixed at 25 h. In order to avoid excessive temperature inside the mill cell, milling was carried out in 30 minutes intervals with a 5 minutes pause.

The strontium diphosphate was obtained by heating a mixture of strontium carbonate and di-ammonium hydrogenophosphate at 900 °C for 10 h, while strontium oxide was obtained by calcination of the corresponding carbonate at 1100 °C for 24 h. To avoid deviation from stoichiometry, lanthanum oxide was calcined at 1000 °C for 24 h just before use. Indeed, when La_2O_3 is exposed to air, there is formation of $La_2(OH)_{6-2x}(CO_3)_x$, with $x \approx 1$ [27,28].

In the following sections, the compositions $Sr_{10}(PO_4)_6O$, $Sr_9La(PO_4)_5(SiO_4)O$, $Sr_8La_2(PO_4)_4(SiO_4)_2O$, $Sr_6La_4(PO_4)_2(SiO_4)_4O$, $Sr_5La_5(PO_4)(SiO_4)_5O$ and $Sr_4La_6(SiO_4)_6O$ will be labeled $Sr_{10}O$, Sr_9LaO, Sr_8La_2O, Sr_6La_4O, Sr_5La_5O and Sr_4La_6O, respectively.