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Uranium-doped britholites $Ca_xLa_y(SiO_4)_{6-u}(PO_4)_uO_t$:U synthesis, characterization and preliminary study of uranium diffusion

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Abstract

Natural apatitic phosphosilicates, generally called "britholites", were found to contain certain amounts of radioactive elements or fission products. Thus, britholites have been the object of a great interest because of their potential application as typical matrices for the conditioning of nuclear wastes. In the present report, uranium-doped oxy-silicophosphates $Ca_xLa_y(SiO_4)_{6-u}(PO_4)_uO_t$/U were synthesized by high-temperature solid-state reaction. The prepared compounds were characterized by X-ray diffraction method, Raman diffusion spectroscopy and X-ray microprobe. The uranium solubility in such compounds was studied. The uranium thermal diffusion in the britholite with the theoretical formula $Ca_5La_5(SiO_4)_3(PO_4)_3O_2$ was estimated. The bands present in the Raman spectra were identified and assigned to the corresponding vibration modes of SiO_4 and PO_4 anions. The diffusion coefficient of uranium in the studied apatite was found close to that calculated for europium and lanthanum in some other apatites.

Keywords: Phosphate–silicate apatite (britholite); Uranium solubility; Raman diffusion spectroscopy; X-ray microprobe; Diffusion coefficient; EDX microprobe

1. Introduction

Apatites form a large family of inorganic compounds, with the main formula $M_{10-a}(XO_4)_6Y_{2-b}$(*M*=Ca, Sr. . ., / *X*=P, Si, V. . . and *Y*=F, Cl, OH. . .). The *a* and *b* coefficients depend on the valence of the *M*, *X* and *Y* elements. The most common apatite compound in nature is $Ca_{10}(PO_4)_6F_2$, which crystallizes in the hexagonal system with the space group $P6_3/m$ [1]. This structure provides apatites great capacity to form solid solutions and, particularly, to accept several substitutes.

Apatites have been widely investigated because of their various applications in several domains such as agronomy (fertilizer), medicine (bone and teeth prosthesis), gemmology and technology (phosphors and laser materials; [2–5]). Apatitic phosphosilicates, generally called "britholites", are isomorphous to phosphate apatites and resulted from the substitution of (La^{3+}, SiO_4^{4-}) for (Ca^{2+}, PO_4^{3-}). Moreover, the structure of some natural britholite samples was found to remain stable, although it contains some radioactive elements or fission products [6,7]. For this reason, britholites have been the object of a great interest because of their possible use as typical materials for the storage of nuclear wastes [8].

Several papers reported the thermal diffusion of rare earth elements (La, Dy, Nd, Eu...) in hydroxyphosphate apatites [9,10]. Few reports dealt with the diffusion of actinides in such matrices [11]. Whereas no systematic study was focused on the diffusion of uranium in synthetic oxybritholites up to our knowledge.

Our scientific program was aimed on the study of an uranium-doped britholite with the theoretical formula $Ca_5La_5(SiO_4)_3(PO_4)_3O_2$. The choice of this stoichiometry rises from our previous work dealing with the determination of an apatitic single-phased domain in the CaO-La_2O_3-P_2O_5-SiO_2 system [12]. The as mentioned composition situated

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within the defined domain could be easily synthesized at the single-phase state. The present work reports the determination of the limit solubility, the valence and the thermal diffusion coefficient of uranium in this matrix.

The obtained results revealed that uranium could be incorporated in the studied apatite generally with the valence U^{4+}. The diffusion coefficient value of uranium in britholites was found to be close to that calculated for Eu or La in hydroxyapatites.

2. Experimental procedure

2.1. Samples preparation

Both uranium-doped and nondoped britholite samples were synthesized in crystallized powder form by high-temperature solid-state reaction. Stoichiometric mixtures of $CaCO_3$ (Prolabo, Normapur, ≥99.5%), La_2O_3 (Prolabo, Rectapur), SiO_2 (Alfa, ≥99.5%), $(NH_4)_2HPO_4$ (Prolabo, Normapur, ≥99.0%) and $(UO_2)(NO_3)_2 \cdot 6H_2O$ (Merck, ≥99.0%) were thoroughly ground in an agate mortar, pressed into disk pellets of 23 mm in diameter. The pellets were weighted and then fired at high temperature in a programmable furnace under an oxidant medium. The thermal treatment was the following: The pellet was firstly heated at 900 °C for 12 h. After quenching and grinding, a second heating at 1400 °C was carried out for a period of 24 h, accompanied with several intermediate grindings. The samples were then cooled down to room temperature at the cooling rate of the furnace estimated at 10 °C mn^{-1}.

2.2. Characterization methods

The purity of the obtained compounds was checked by X-ray diffraction method. The X-ray patterns were carried out on powdered samples via a "PW 3710 based" diffractometer ($K\alpha_1$ Cu=1.54060 Å).

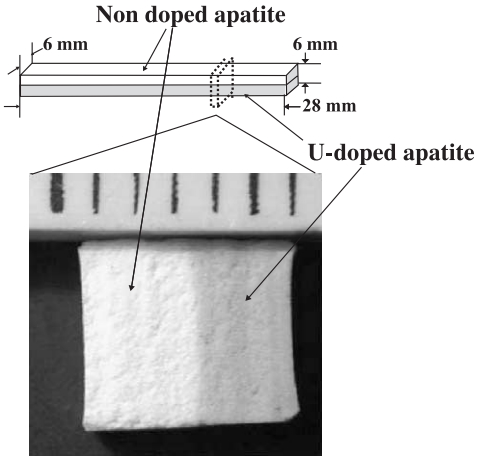

Fig. 1. Apatitic pellet dimensions and a photo of one plate and its constituting parts.

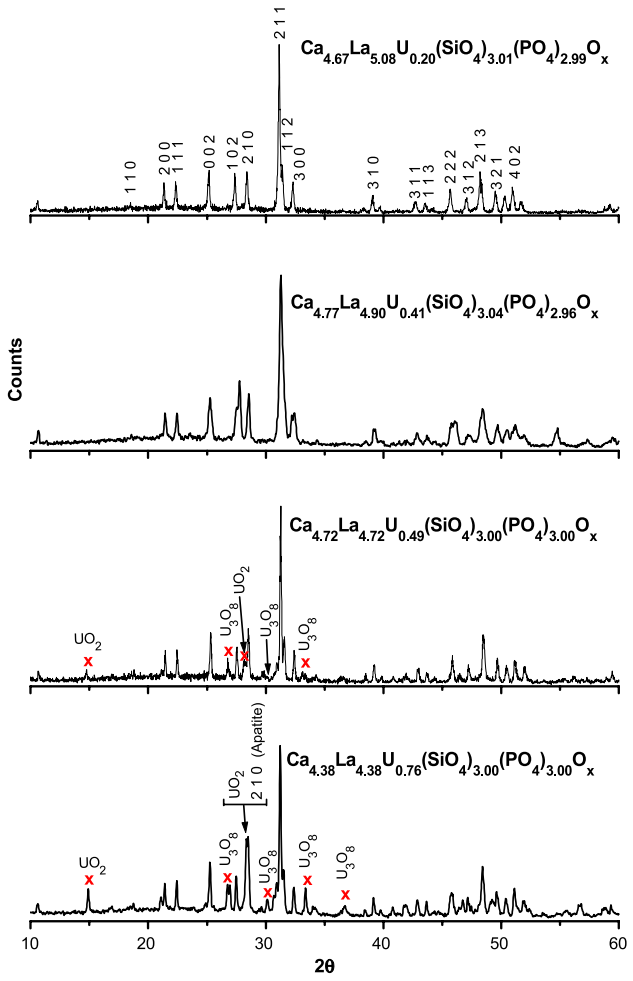

Fig. 2. X-ray patterns of some Uranium-doped britholites.

The uranium valence was checked by Raman diffusion spectrometry. Raman spectra were recorded with a Dilor XY microspectrometer equipped with a CCD detector, a 1800 line/mm grating and a Spectra Physics Ar Laser (514.5 nm).

For the uranium diffusion investigation, two samples—one U (2%) doped britholite and a nondoped one—were synthesized in the powdered form. After checking the purity of each compound, the powders were compacted to form a rectangular pellet made up of two parts associated through a plan interface. This pellet was then cut out into plates of 6 mm in width and 1 mm in thickness. The pellet weight is 0.1324 g (density ≈ 3.68 g cm^{-3}). Fig. 1 shows the pellet dimensions and a photo of one plate exhibiting the good homogeneity of its constituting parts.

These plates were then heated at various temperatures varying between 700 and 1200 °C during 48 and 72 h. The elementary analysis of the studied plates was determined via X-ray microprobe (CAMECA SX 100). During this work, measurements were taken by using the WDS technique. The probe generating the electron beam