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Evaluation of Fluorapatite as a Waste-Form Material: Fourth Quarter Report, June 1 - September 30, 2004

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Fourth Quarter Report 2004

Evaluation of Fluorapatite as a Waste-Form Material

06/01/04 – 09/30/04

Personnel

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Project Description

Fluorapatite, fluorinated calcium phosphate, has been identified as a potential matrix for the entombment of the zirconium fluoride fission product waste stream from the proposed FLEX process. If the efficacy of fluorapatite-based waste-storage can be demonstrated, then new and potentially more-efficient options for handling and separating high-level wastes, based on fluoride-salt extraction, will become feasible. This proposal will develop a dual-path research project to develop a process to fabricate a synthetic fluorapatite waste form for the ZrF_4 , FP waste stream, characterize the waste form, examine its performance under environmental conditions, and correlate the behavior of the waste form with natural analogs. Characterization of the material will be accomplished through probing the molecular-scale electronic and geometric structure of the materials in order to relate them to macroscopic properties, with the goal of developing techniques to evaluate and predict the performance of different waste-form materials. Time and funding permitting, other waste forms for the zirconium fluoride, fission product salt waste stream will be examined and benchmarked against the fluorapatite matrix baseline.

Highlights of Accomplishments

1. Fluorapatite containing Sr and Zn surrogates (replacing the Ca) have been synthesized, annealed and analyzed using various techniques such as SEM, IR, XPS, Raman, DSC, TGA, EDS, XRD and XANES.
2. Non-annealed samples of the same surrogate samples have been analyzed with the same techniques.
3. The phosphate in fluorapatite and hydroxyapatite is not replaced by the nitrate ions of the surrogates during synthesis.

Technical progress

The efforts of including surrogates into a fluorapatite matrix are progressing successfully and samples with various ratios of Ca to Sr and Zn have been synthesized on a large scale over the last couple of months. The prepared samples include:

1. Pure Fluorapatite
2. Ca: Sr = 4:1 Fluorapatite
3. Ca: Sr = 3:2 Fluorapatite
4. Ca: Sr = 2:3 Fluorapatite
5. Ca: Sr = 1:4 Fluorapatite
6. Sr-Fluorapatite

All samples were dried at temperatures of 150 C for 30 minutes and then annealed at up to 1200 C for 2 hours. The annealed samples were stiff and strong glass-like material. The samples were analyzed to determine their compositions and amorphous structures using IR, SEM and EDS. IR has been used to analyze annealed and un-annealed samples and the figure 1 shows a comparison between pure Ca-fluorapatite and pure Sr-fluorapatite.

There are clear differences between the two spectra shown in figure 1 in the vicinity of 3500cm^{-1} and 2000cm^{-1} . Individual peaks have not been assigned yet. Similar curves exist for all Ca:Sr ratios that have been synthesized.

Powder diffraction patterns were obtained for all of the above listed samples as well as for hydroxyapatite and natural fluorapatite. All samples show a basic $P6_3/m$ hexagonal structure with slight unit-cell parameter changes. Further analysis will be carried out to confirm the success of the synthesis and the percentage of impurities present in each sample.

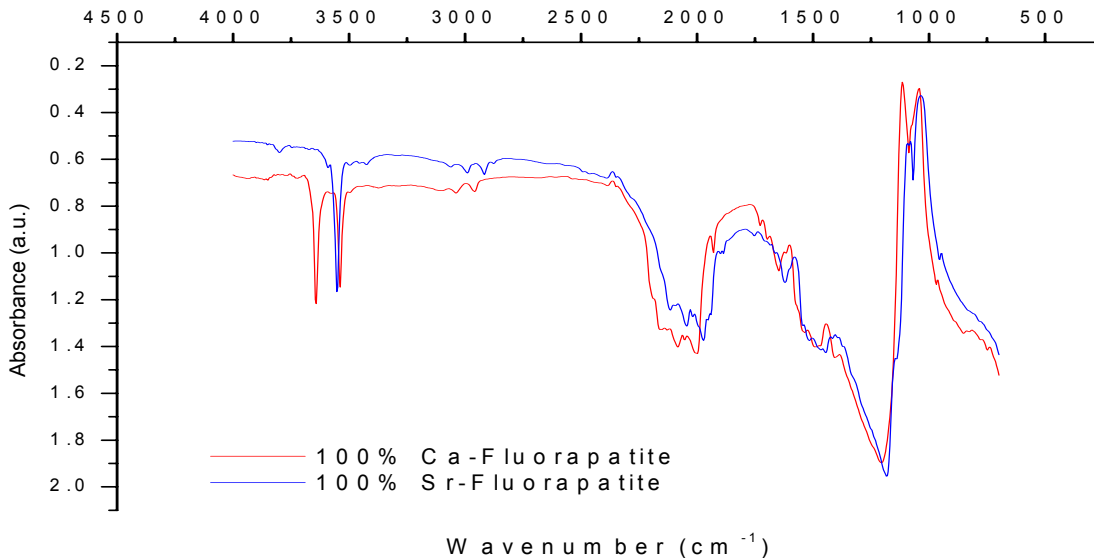


Figure 1: Two IR spectra are shown, one of pure Fluorapatite (100% Ca-Fluorapatite, red curve) and the other is of strontium Fluorapatite (100% Sr-Fluorapatite, blue curve).

Raman Spectroscopic analysis has been done for all samples and the following graph (figure 2) shows spectra of all samples. The basic peaks of natural fluorapatite can be observed in all samples except for slight shifts in peak positions as the Strontium ion quantity increases. The most intense peak has been shifted to lower energy with increasing Strontium ion quantity occupied in the apatite structure.

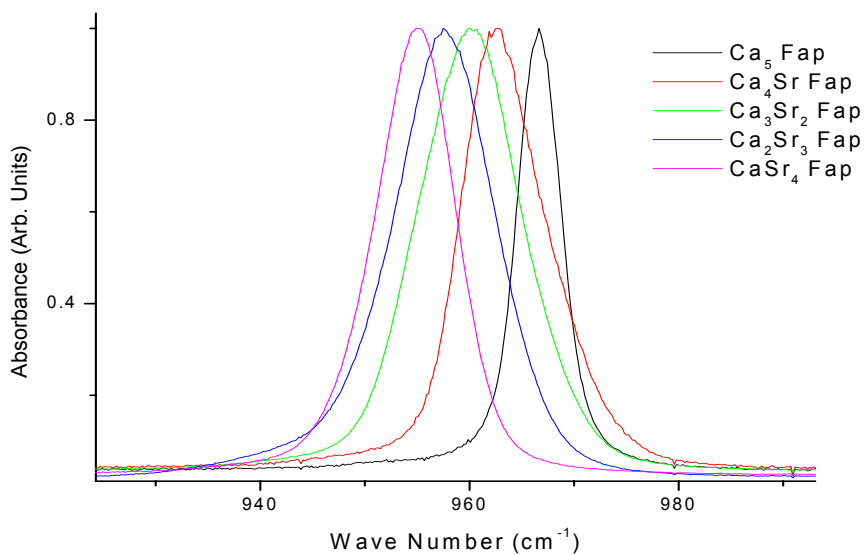


Figure 2. Raman Spectra for the range 940-980 cm^{-1}

Further more, XANES spectra were obtained for all samples including hydroxyl apatite and natural apatite near the Ca, Sr and Oxygen edges at the Advanced Light Source of LBNL at beam line 6.3.1.