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Development of Fluorapatite as a Waste Form: Final Report 1

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Development of Fluorapatite as a Waste Form

Final Report #1

Summary of optimal conditions of fluorapatite synthesis
and optimal waste loading; principal features of apatite-based ceramic

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1. Introduction

Some minerals incorporated into apatite group involving fluorapatite, chlorapatite, hydroxyl-apatite, carbonate- hydroxyl-apatite, carbonate-fluorapatite are commonly called as "apatite". In this report we will also use a brief name of these minerals-apatite specifying, if necessary, concrete mineral. Totally, apatite group includes 17 minerals. These are phosphates, arsenates and vanadates with common stehiometry formulae $A_5(XO_4)_3(F,Cl,OH)$, where A=Ba, Ca, Ce, K, Na, Pb, Sr, Y and X=As, P, Si, V; (PO_4) can substitute for (CO_3). All these minerals have a hexagonal structure [Fleisher, 1987]. Besides, there are several silicate and sulphate minerals of similar structure.

Apatite is most widespread mineral between phosphates [McConell,1973] and can be met almost in all the types of the rocks. Most coarse crystals appear in pegmatoid granites and marbles. As an accessory mineral it occur in granitic rocks and alkali syenites (fluorapatite), in basic rocks of gabbro group and pyroxenites (chlorapatite mainly). Fluorapatite often concentrates in nepheline-bearing syenites and in the rocks of melteigite-urtite series. Apatite, in this case, show a high content of Sr, Na and REE. In the most known Kukisvumchorr deposit coarse grains of this type apatite form a monomineral lens of 500m long in the Khibine alkaline massif (Kola Peninsula, Russia). The minerals also occur in many pneumatolite-hydrothermal deposits associated with the ultrabasic and alkaline intrusives. It is quite common for sulfide hydrothermal deposits, skarns, phyllites, crystalline schists and other metamorphic rocks. On the surface, in sedimentary rocks apatite forms buckles, concretions in the form of thin needles, oolites and, sometimes, cement of detritus. The rocks of this type, consisting mainly of apatite crystals are commonly named as phosphorites. They are chemical, biogenic or biochemical sediments. Detritus may be represented by another type of phosphorites- the rocks with high content of sea shell fragments, bones, the other organic remnants made up of apatite. Karst phosphorites in form of wandering mass resulted from chemical processes can be found in caves. In all the phosphorite types apatite occur in form of hydroxyl-apatite. Thus, apatite is a very widespread mineral which may be formed and is stable in practically any geological environment. It is interesting to note that calcium phosphate, which is very similar to apatite, is a major contributor in solid tissues of animals and men [Korago, 1992]. In form of the finest crystals enveloped by albumen it is developed in solid tissues of the bones.

One of the famous example showing chemical and radiation stability of apatite in nature is the Oklo (Gaboon, Africa) uranium deposit containing apatite. The chain reaction of uranium fission in the deposit took place about two billion years ago [Bros, 1996]. Apatite crystals were characterized by anomalous enrichment of [235]U and fission products.

Apatite is also stable during erosion, transport and redeposit of crystalline rocks. It occur in all the types of alluvial deposits (placers), except for highly differentiated quartz-rich deposits formed due to long intensive abrasion of deitritus during transportation or in placers experienced chemical weathering [Kukharenco, 1961]. The placers commonly contain fragments of prismatic apatite crystals as well as acute and rounded grains.

Apatite is soluble in acids. It is used to produce phosphoric acid, phosphorus and other chemical substances. Incorporation of rare-earth elements into apatite structure has been studied using luminescence method on apatite-like compound britholite, $(Ca,La,…)_{10}((SiO_4),(PO_4))_6O_{2-x}$ [Boyer et.al., 2000].

The samples of [244]Cm-doped synthetic silicate of $Ca_2La_8(SiO_4)_6O_2$ with apatite structure irradiated by Kr^+ ions and natural fluorapatite grains were used to study stability of apatite structure under radiation damage radiation [Weber *et.al.*, 1997]. The critical temperatures of amorphization (T_c) was estimated to be 15°C for 1 wt.% [239]Pu is 1%; and T_c=29°C for 10 wt.% [239]Pu. The temperature caused by radioactive decay in ceramic waste forms in near-field

environment of waste repository might reach more than 150°C during the first few hundred years. This implies that apatite-like compounds may preserve a crystalline structure over long time. The T_c of apatite and apatite-like silicates is significantly higher than that of zircons (from 218°C to 196°C for ^{239}Pu from 10 to 1.0 wt.% respectively). Therefore, the crystalline materials of apatite structure it is expected to be resistant to radiation damage even at higher Pu contents.

Fluorapatite was considered as the most thermodynamically stable mineral in apatite group [Orlovskiy et al., 1992,1995, 2002]. The substitution of OH⁻ for F⁻ causes significant increase of thermal and chemical durability of apatite. However, radiation damage effects in fluorapatite has not been studied experimentally yet.
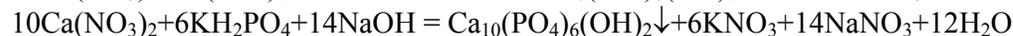
2. Review on methods of apatite synthesis

Apatite of various formulation can be obtained by different methods in the form of powder, granules, cement, crystalline ceramic, apatite coating etc. [Carpena et al. 1998]. All these apatite-based materials can be used for different purposes such as: engineering barriers; filling materials; conditioning matrices for mixed wastes etc. Thus, the French authors consider the apatite as universal host phase, which can accommodate all fission nuclides in the form of solid solution [Carpena et al. 1998]. They succeeded synthesizing: a) hydroxilapatite in the form of cement and ceramic; b) silicate-apatite, britholite, in the form of ceramic; c) silicate-phosphate apatite of complex composition, $Ca_9Nd_1(SiO_4)(PO_4)_5F_2$, crystallized from the melt heated to 1700°C for 2 hours [Carpena et al. 1998; Boyer et. al. 1997a-b]. Apatite-like compounds based on $Pb_{10}(VO_4)_6I_2$ as host matrix for iodine were also obtained [Audubert et al., 1997]. It was demonstrated that substitution of Ca^{2+} for Pb^{2+} and PO_4^{3-} for VO_3^{3-} increases unit cell parameters and provides substitution of OH⁻ for I⁻.

Hydroxyl-apatite can be obtained by calcination of three different initial precursors in presence of water vapor:
  1) $Ca_3(PO_4)_2 + CaCO_3 + H_2O(vapor) \rightarrow Ca_{10}(PO_4)_6(OH)_2$;
  2) $CaP_2O_7 + CaCO_3 + H_2O(vapor) \rightarrow Ca_{10}(PO_4)_6(OH)_2$;
  3) $CaHPO_4*2H_2O + CaO + H_2O(vapor) \rightarrow Ca_{10}(PO_4)_6(OH)_2$ at temperature $900 - 1300^{\circ}$C [Hench 1995].
In general, all methods of hydroxyl-apatite synthesis can be classified into following groups:
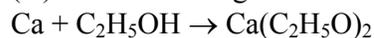(**A**)- based on using only soluble starting materials:
$10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 8NH_4OH = Ca_{10}(PO_4)_6(OH)_2\downarrow + 20NH_4NO_3$ or
$10Ca(NO_3)_2 + 6KH_2PO_4 + 14NaOH = Ca_{10}(PO_4)_6(OH)_2\downarrow + 6KNO_3 + 14NaNO_3 + 12H_2O$
 (**B**)- based on using poorly soluble $Ca(OH)_2$ and H_3PO_4 or its salts, including insoluble $Ca_3(PO_4)_2$:
$10Ca(OH)_2 + 6H_3PO_4 = Ca_{10}(PO_4)_6(OH)_2\downarrow + 18H_2O$
(**C**)- bases on using insoluble $CaCO_3$ and water solution of H_3PO_4
(**D**)- based on using alcoholate compounds:
$Ca + C_2H_5OH \rightarrow Ca(C_2H_5O)_2$
$Ca(C_2H_5O)_2 + H_3PO_4 \rightarrow Ca_x(PO_4)_y(C_2H_5O)_z*nC_2H_5OH$ (amorphous product which is converted into apatite after calcination in air).

It was reported [Carpena et al. 1998] that hydroxyl-apatite might be synthesized even at room temperature through the following reaction:

$\mathbf{a}Ca(H_2PO_4)_2 \cdot H_2O + \mathbf{b}Ca_3(PO_4)_2 + \mathbf{c}Ca_4(PO_4)_2O + H_2O(vapor) \rightarrow Ca_{10}(PO_4)_6(OH)_2$, where $\mathbf{b}=2-3\mathbf{a}$ and $c=1+2\mathbf{a}$.

The material obtained from this reaction looks like cement, however, it's sintering at $1200^{\circ}C$ allows obtaining high-density (low porosity) hydroxyl-apatite ceramic [Carpena et al. 1998].

Fluorine-silicate-apatite (called britholite) $Ca_{10-x}Ln_x(SiO_4)_x(PO_4)_{6-x}F_2$ can be prepared by the following interaction at $900^{\circ}C$:

$Ln_2O_3 + CaF_2 + CaCO_3 + SiO_2 + Ca_2P_2O_7 \rightarrow Ca_{10-X}Ln_X(SiO_4)_X(PO_4)_{6-X}F_2$.
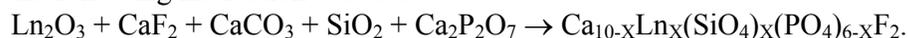
This process requires at least three grinding – calcination cycles to complete interaction [Boyer et al., 1997a]. Similar compounds can be obtained also by melting at $1700^{\circ}C$ for 2 hours [Boyer et al., 1997b]:

$8CaCO_3 + 5/2\ P_2O_5 + CaF_2 + 1/2\ Nd_2O_3 + SiO_2 \rightarrow Ca_9Nd(SiO_4)(PO_4)_5F_2 + CO_2$
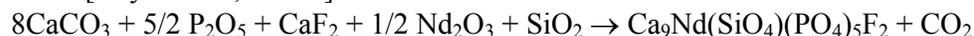
It is necessary to note that obtaining of homogenous apatite product through solid state interaction is difficult. In order to obtain single phase material it is necessary to repeat several times cycles of grinding and calcination (sintering). For example, the synthesis of apatite, $Ca_6La_4(SiO_4)_4(PO_4)_2O_x$, needs two or more "grinding – calcination" cycles [Boyer et al. 1997a].

Taking into account published data the simplest flowsheet of fluorapatite synthesis will include:
-   preparation of starting solutions: $Ca(NO_3)_2$, H_3PO_4, $(NH_4)HF_2$;
-   co-precipitation fluorapatite by NH_4OH;
-   filtering;
-   milling of fluorapatite precursor;
-   cold pressing into pellets;
-   final sintering in air.

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3. Fluorapatite synthesis at KRI

The following procedures were used for preparation of starting precursor materials:

Undoped fluorapatite, $Ca_5(PO_4)_3F$, and Sr-apatite, $Sr_5(PO_4)_3F$

1) Aqueous solution of $Ca(NO_3)_2$ was mixed with excess of phosphoric acid, H_3PO_4. For Sr-apatite dried $Sr(OH)_2$ was stirred and reacted with excess of phosphoric acid, H_3PO_4.
2) Excess of $(NH_4)HF_2$ was added.
3) Addition of NH_4OH has been done to achieve PH=7. This caused precipitation of "raw" apatite material.
4) The powder obtained was rinsed in distilled water and then dried in air at 150°C for 1 hour.
5) The "raw" apatite powder was ground in ball mill (with Al_2O_3 balls) in water medium for 3 hours.
6) Wet powders were filtered and dried in air at 25°C for 24 hours.
7) The precursors obtained were mixed with aqueous solution of 5 % polyvinyl-alcohol (weight ratio of powder and solution was 10:1) and then dried in air at 25°C for 24 hours.
8) Starting materials were cold pressed into pellets of 10 mm in diameter.

Nd-doped fluorapatite, $Ca_{9.0-9.9}Nd_{1.0-0.1}(PO_4)_5SiO_4F_2$, and $Ca_8NaNd(PO_4)_6F_2$

1) Aqueous solutions of $Ca(NO_3)_2$ and $Nd(NO_3)_3$ were prepared. Estimated Nd contents were approximately **13.0** and **1.4 wt.% el**. for two different samples of $Ca_{9.0-9.9}Nd_{1.0-0.1}(PO_4)_5SiO_4F_2$ and **13.0 wt.% el.** for $Ca_8NaNd(PO_4)_6F_2$.
2) Aqueous solution of $(NH_4)HF_2$ was mixed with dispersed SiO_2 (for of $Ca_{9.0-9.9}Nd_{1.0-0.1}(PO_4)_5SiO_4F_2$) or with Na_3PO_4 (for $Ca_8NaNd(PO_4)_6F_2$).
3) Stoichiometric amount of H_3PO_4 was added in both solutions of $(NH_4)HF_2$ (with additives) and then they were mixed with Ca-Nd-nitrates.
4) Addition of NH_4OH has been done to achieve PH=7. This caused precipitation of "raw" apatite material.
5) The powders obtained were rinsed in distilled water and then dried in air at 150°C for 1 hour.

6) The "raw" apatite powders were ground in ball mill (with Al_2O_3 balls) in water medium for 3 hours.
7) Wet powders were filtered and dried in air at 25°C for 24 hours.
8) The precursors obtained were mixed with aqueous solution of 5 % polyvinyl-alcohol (weight ratio of powder and solution was 10:1) and then dried in air at 25°C for 24 hours.
9) Starting materials were cold pressed into pellets of 10 mm in diameter.

Special furnace for apatite synthesis has been developed and fabricated at KRI (Fig.1). So far this furnace is placed in the fume-hood, however, it can be easily installed into glove box for the future experiments with real actinides and technetium.
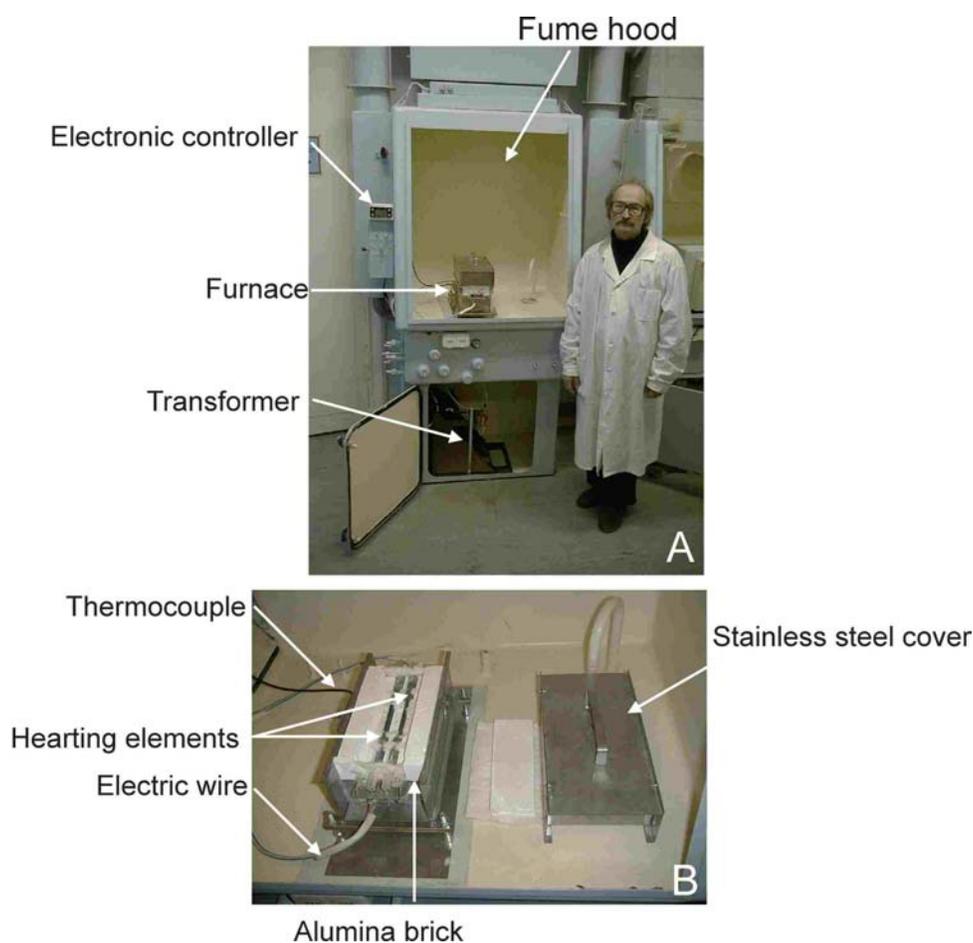

Figure 1. Special furnaces developed and build at KRI for the synthesis of apatite ceramic by sintering in air: a) general view; b) closer image. It allows operation at temperature up to 1600°C in air and provides heating rate from 3°C per hour and higher. Two SiC heating elements can be replaced easily even under conditions of glove-box.

All apatite samples were synthesized in air using sintering method:
- $Ca_5(PO_4)_3F$ and $Sr_5(PO_4)_3F$ - at 1300°C for 2 hours;
- Nd-doped apatite, $Ca_{9.0-9.9}Nd_{1.0-0.1}(PO_4)_5SiO_4F_2$, and $Ca_8NaNd(PO_4)_6F_2$, - at 1250°C for 4 hours.

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4. Samples obtained

Undoped fluorapatite, $Ca_5(PO_4)_3F$
Pellets of weight 0.9-1.1 gram each (diameter 8.4 mm) were characterized with low porosity (Fig.2). Bulk ceramic density was from 2.5 to 3.0 g/cm^3.

Sr-apatite, $Sr_5(PO_4)_3F$
Pellets of weight 1.0-1.5 gram each (diameter 8.6 mm) were characterized with low porosity similar to undoped $Ca_5(PO_4)_3F$. Bulk ceramic density was 3.9 g/cm^3.

Nd-doped fluorapatite, $Ca_{9.0-9.9}Nd_{1.0-0.1}(PO_4)_5SiO_4F_2$
Pellets of weight 0.8 gram each (diameter 8.0 mm) were characterized with essentially higher porosity in comparison with undoped sample (Fig.3). Bulk ceramic density was 3.2 g/cm^3 for sample doped with 13.0 wt.% Nd. Sample doped with 1.4 wt.% Nd was characterized with high porosity and low bulk density 2.0 g/cm^3.

Nd-doped fluorapatite, $Ca_8NaNd(PO_4)_6$
Pellets of weight 0.7-0.8 gram each (diameter 7.0-7.2 mm) were characterized with inhomogeneous structure. Peripheral zone of each pellet was porous, although central part was dense. Bulk ceramic density was 3.4-3.4 g/cm^3.
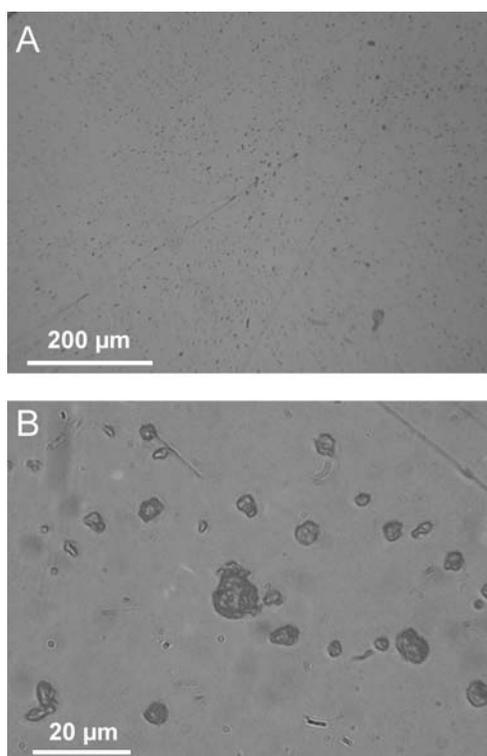

Figure 2. Reflected light image of undoped polycrystalline fluorapatite, $Ca_5(PO_4)_3F$. Black dots are void space. Sample is characterized with low porosity (density 2.9-3.0 g/cm^3). Phase composition from XRD is: 95-97 % fluorapatite and the rest is presumably, CaF_2.
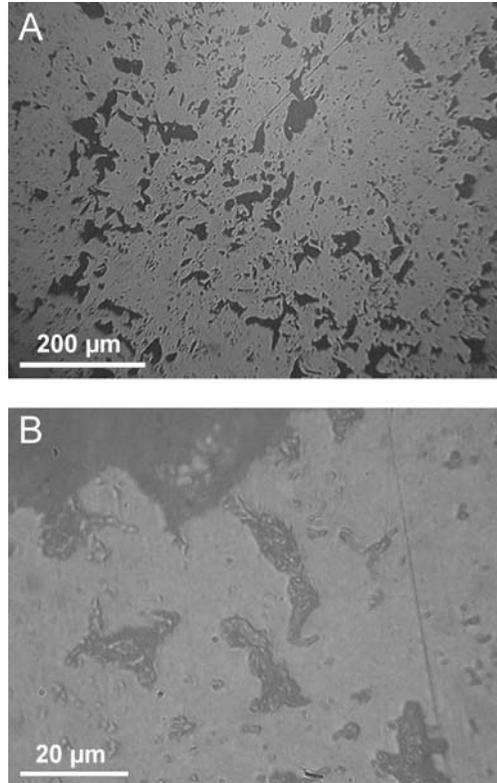
Figure 3. Reflected light image of ceramic based on Nd-doped (approximately 13 wt.% Nd) apatite, $Ca_9Nd(PO_4)_5SiO_4F_2$. Black dots are void space. Ceramic density is 3.1-3.2 g/cm^3. Phase composition from XRD indicates that sample consists of two main phases: apatite-structured phase - 60-65 wt.% and the rest is Nd-monazite, $NdPO_4$.

5. Results of XRD analyses

In according to results of XRD analysis synthesis of undoped fluorapatite, $Ca_5(PO_4)_3F$, was successful. The yield of apatite phase was 95-97 wt.% and the rest was, presumably, CaF_2. It is important to note that formation of fluorapatite phase (with low crystallinity level) has been observed already after precipitation from solution. Following sintering has just provided complete crystallization of fluorapatite.

Ceramic based on Sr-apatite, $Sr_5(PO_4)_3F$, was also successfully synthesized, although formation of minor phases: $Sr_2(PO_4)_2$ (approximately 15 wt.%) and $Sr_2P_2O_7$ (approximately 1 wt.%) was observed (Fig.4). These result demonstrates that appropriate yield of Sr-fluorapatite phase is very sensitive to stoichiometric amount H_3PO_4.

Significant amount of Nd-monazite, $NdPO_4$, was identified in both samples of 13 wt.% Nd doped ceramic based on $Ca_9Nd(PO_4)_5SiO_4F_2$ and $Ca_8NaNd(PO_4)_6F_2$ (Fig.5). This means that loading of approximately 13 wt.% Nd in starting precursor materials was not optimal. Synthesis of 1.4 wt.% Nd-doped ceramic based on $Ca_{9.9}Nd_{0.1}(PO_4)_5SiO_4F_2$ was unsuccessful. Although, apatite-structured phase was identified, the whole amount Nd admixture was converted into separated Nd-oxide, Nd_2O_3. We suggested, that this was caused by the failed stoichiometry of starting precursor due to the lack of H_3PO_4. Therefore, in the future experiments it will be important to identify optimal amount of actinides to be loaded into
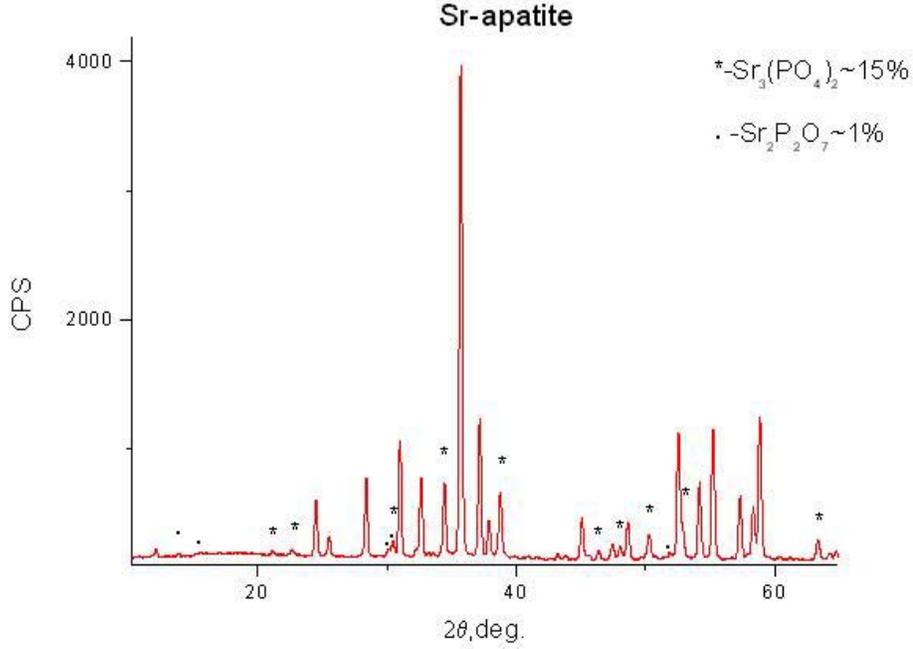
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Figure 4. Results of XRD analysis of ceramic samples based on Sr-apatite, $Sr_5(PO_4)_3F$. Formation of minor phases: $Sr_2(PO_4)_2$ (approximately 15 wt.%) and $Sr_2P_2O_7$ (approximately 1 wt.%) caused by excess of H_3PO_4 used for precursor preparation.

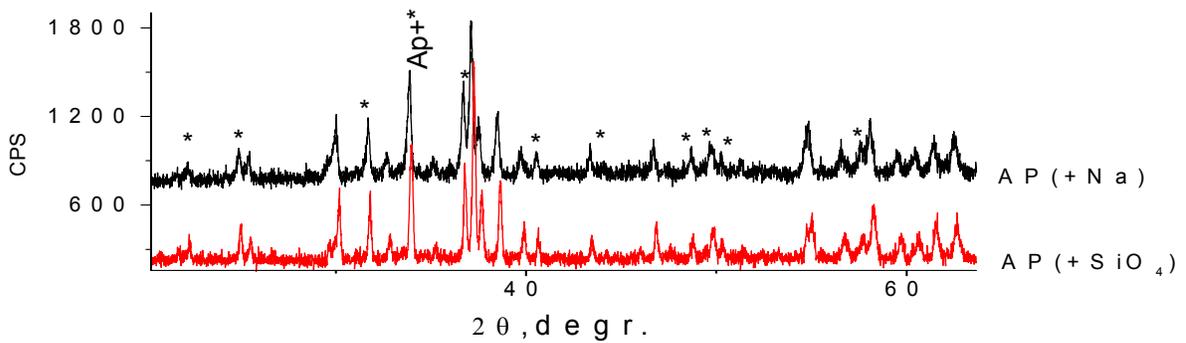
Figure 5. Results of XRD analysis of ceramic samples based on Nd-doped (approximately 13 wt.% Nd) fluorapatite: **black (AP+Na)** – $Ca_8NaNd(PO_4)_6F_2$ and **red (AP+SiO$_4$)** – $Ca_9Nd(PO_4)_5SiO_4F_2$. Non-marked peaks indicate apatite-structured phase. Both samples contains significant amount (35-40 wt.%) of Nd-monazite, $NdPO_4$ – marked by *.

apatite structure and develop simple control method of starting precursor stoichiometry, in particular, precise measurement of H_3PO_4 amount.

6. Samples delivered to UNLV

The following samples of fluorapatite obtained at KRI were sent to UNLV for additional investigation:
- 3 pellets of undoped fluorapatite, $Ca_5(PO_4)_3F$. Weight 0.9-1.1 gram each; diameter 8.4 mm; density 2.9-3.0 g/cm^3.

All other samples such as Sr-apatite and Nd-doped ceramics are also available for the future delivery to UNLV.

7. Conclusions

1) KRI has fabricated and tested special high temperature furnace for fluorapatite synthesis. This equipment might be installed into glove box in order to carry out experiments with real actinides and technetium. The same equipment might be fabricated and installed in Actinide laboratory at HRC by KRI technical staff;
2) Samples of undoped polycrystalline apatite, $Ca_5(PO_4)_3F$, of low porosity were successfully obtained by sintering in air at 1300°C. Part of these samples was already delivered to UNLV for additional study;
3) Samples of Sr-apatite, $Sr_5(PO_4)_3F$, of low porosity were successfully obtained by sintering in air at 1300°C. In order to improve yield of Sr-apatite phase in final ceramic it is important to control stoichiometry of starting precursor, in particular, amount of H_3PO_4. It was demonstrated that excess of phosphoric acid causes formation of minor phases $Sr_2(PO_4)_2$ and $Sr_2P_2O_7$ in the matrix of Sr-apatite ceramic;
4) It was found that formation of fluorapatite loaded with actinide surrogates is essentially affected by stoichiometry of starting precursor. Excess of actinide surrogate causes formation of separated monazite phase, $AnPO_4$ (where An is trivalent actinide surrogate, i.e. Nd, Eu etc). The lack of H_3PO_4 used for precursor preparation might cause formation of separated actinide-oxide phases into final ceramic matrices;
5) Future experiments should identify fluorapatite capacity to actinide incorporation. Other important goal of future work will be development of simple methods of control of starting precursor stoichiometry.

Dr. Boris E. Burakov , Principal Investigator