Available online at www.sciencedirect.com





Journal of the European Ceramic Society 23 (2003) 3049-3057

www.elsevier.com/locate/jeurceramsoc

# Synthesis and characterization of gadolinium phosphate neutron absorber

Paul A. Lessing\*, Arnold W. Erickson

Materials Department, Idaho National Engineering and Environmental Laboratory, PO Box 1625, Idaho Falls, ID 83415-2218, USA

Received 1 May 2002; received in revised form 23 December 2002; accepted 1 February 2003

### Abstract

Hydrated gadolinium phosphate (GdPO<sub>4</sub>·1H<sub>2</sub>O) was synthesized by reacting high purity dissolved salts (gadolinium nitrates or chlorides) with phosphoric acid. The hydrated powders were shown to be extremely insoluble in water with a  $K_{sp}$  measured to be between 2.07 E-14 and 4.76 E-13. Calcination to between 800 and 1000 °C resulted in the formation of GdPO<sub>4</sub> in a monazite (monoclinic) crystal structure. This was correlated with the first exothermic differential thermal analysis (DTA) peak (864.9–883.4 °C). The DTA also showed small peaks in the 1200–1250 °C range, that could be associated with a change from the monazite (monoclinic) crystal structure to the xenotime (tetragonal) crystal structure. However, calcination of a sample to 1400 °C, followed by relatively rapid cooling and XRD, showed the structure was still monazite (monoclinic). DTA results showed a melting point at 1899–1920 °C (endothermic peak). It was therefore concluded that the melting point probably was the melting of the monazite (monoclinic) phase, but may have been xenotime if a phase change at 1200–1250 °C was reversible and very rapid. The higher part of the melting range was achieved with material derived using the slightly higher purity nitrate salt. The results show that GdPO<sub>4</sub> is an excellent candidate for a chemically stable, water-insoluble neutron absorber for inclusion in spent nuclear fuel canisters. © 2003 Elsevier Ltd. All rights reserved.

Keywords: GdPO4; Nuclear applications; Powders-chemical preparation; Thermal properties

# 1. Introduction

This article reports the synthesis and characterization of anhydrous and hydrated crystalline phases of gadolinium phosphate (GdPO<sub>4</sub>·xH<sub>2</sub>O). These minerals are being considered as water insoluble neutron absorbers (i.e., "poisons") for inclusion in spent nuclear fuel canisters.<sup>1</sup> Gadolinium is preferred over other candidates (e.g. boron, hafnium) because it has the highest thermal neutron cross-section. Gadolinium metal probably cannot meet functional requirements over geologic time periods, while gadolinium compounds have been predicted to be highly insoluble in water. Therefore, relevant physical property data for GdPO<sub>4</sub>·xH<sub>2</sub>O is critical to aid in the engineering of structures containing these phases into successful neutron absorbers.

#### 1.1. Known methods to fabricate $GdPO_{4}$ compounds

GdPO<sub>4</sub> does not exist in pure form in nature and is not commercially available. However, a literature search indicated it could be fabricated via chemical processes starting from gadolinium-containing chemicals. Candidate starting chemicals that contain gadolinium are: Gd metal, Gd(OH)<sub>3</sub>, GdCl<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>, Gd(NO<sub>3</sub>)<sub>3</sub> (Note: hydrates of the salts are also implied.)

A generic method of fabricating metal phosphates is to dissolve a metal-salt in water and then react it by adding dilute phosphoric acid (in the proper molar ratio) to the solution, thus causing a precipitate. Aging of the precipitate in the liquid at low temperatures will usually form a hydrated compound. Heating the precipitate to high temperatures (e.g., 200–900 °C) in air will first drive off physically bound water, then cause a loss of the chemically bound waters. Eventually, anhydrous crystalline metal-oxide crystals will form that are stable at high temperatures. The best precursor choices

<sup>\*</sup> Corresponding author. *E-mail address:* pal2@inel.gov (P.A. Lessing).

 $<sup>0955\</sup>text{-}2219/03/\$$  - see front matter 0 2003 Elsevier Ltd. All rights reserved. doi:10.1016/S0955-2219(03)00100-6

are highly soluble gadolinium-containing salts, although  $Gd_2O_3$  might be used if it could be solubilized through the use of an acid solution.

Various rare-earth orthophosphates (La, Ce, Pr, Nd, Sm, Gd, Y, Dy, Er, or Yb) were synthesized by reaction of metal chlorides in solution with dilute H<sub>3</sub>PO<sub>4</sub> by Hikichi et al.<sup>2</sup> Hikichi conducted numerous reactions, including one where GdCl<sub>3</sub> reacted with H<sub>3</sub>PO<sub>4</sub> to form various orthophosphate phases (GdPO<sub>4</sub>·xH<sub>2</sub>O). In this study, mixtures of GdCl<sub>3</sub> solutions (0.05 mol/l) were rapidly added to dilute H<sub>3</sub>PO<sub>4</sub> solutions and magnetically stirred. After 1 h, the pH of the mixed solution was measured and the solution transferred to a flask with a tight stopper. The mixed solutions were then aged at temperatures of 20, 50, and 90 °C for 1-900 days. The pH of the various solutions was adjusted to a constant value (0.5, 1, 3, or 5) with  $H_3PO_4$ . Ultimately, the solutions were suction-filtered and washed five times with distilled water and finally with acetone. The precipitates were examined using X-ray diffraction and differential thermal analysis (DTA) techniques. Depending on the time, pH, and temperature conditions, various compounds were precipitated: H=hexagonal form of  $GdPO_4 \cdot 1/2H_2O$ ; A = amorphous phosphate, M = monazite form of GdPO<sub>4</sub>. For some of the other rare-earth precipitates, the phases W=weinschenkite form of  $RPO_4 \cdot 2H_2O$  and X = xenotime form of  $RPO_4$  were sometimes identified. The Hikichi results showed the hexagonal form of hydrated GdPO<sub>4</sub>·1/2H<sub>2</sub>O can be formed within 3 days. However, it takes many days (e.g., 900 days) to reliably form the dehydrated monazite form; although high temperature calcination could be used to quickly dehydrate the hexagonal form.

Crystallographic information is available for various rare-earth monazite and xenotime compounds<sup>3,4</sup> (including GdPO<sub>4</sub>). Monazite is monoclinic,  $P2_i/n$ , and xenotime is isostructural with tetragonal zircon (I4<sub>1</sub>/ amd). Both atomic arrangements are based on [001] chains of intervening phosphate tetrahedra and rare-earth polyhedra.

The Dictionary of Inorganic Compounds<sup>5</sup> lists three hydrated forms of GdPO<sub>4</sub>: hemihydrate (1/2 water) with a hexagonal lattice (rhabdophane-like structure), monohydrate (1 water), and 1.5 hydrate (1 1/2 water). The dictionary also seems to list three anhydrous crystalline forms of GdPO<sub>4</sub>: hexagonal (low temperature form), monoclinic (mid-temperature monazite-like form), and tetragonal (high temperature xenotime form). Evidently (from the Hikichi data), the hexagonal hemihydrate can be aged to yield the monoclinic monazite structure. Monoclinic and tetragonal structures are related, and one phase can be transformed to the other through a shift of atoms in their lattice positions (as opposed to a reconstructive phase change that is difficult to occur). The hexagonal form may not actually continue to exist after it is dehydrated during heating.

According to the limited summaries of literature found in the *Dictionary of Inorganic Compounds*, all of the following chemical reactions have been successfully accomplished, and the methods have been published in various literature sources:

Formation of hydrated GdPO<sub>4</sub>:

 $Gd(NO_3)_3 + H_3PO_4$  (aq.); results in 1.5 hydrate

 $Gd(NO_3)_3 + (NH_4)H_2PO_4$  (aq.)

 $GdCl_3 + H_3PO_4$  (aq.); pH 1–3 at 20 °C—results in hexagonal hemihydrate

 $GdCl_3 + Na_2HPO_4$  (aq.)

Formation of unhydrated

GdPO₄:

 $GdCl_3 + H_3PO_4$  (aq.); pH 1–3 at 50 °C, 900 h-results in monazite

 $Gd_2O_3$  + (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>; heat in platinum crucible in air at 1100 °C.

Kuo and Kriven<sup>6</sup> found it necessary to hot press xenotime-type YPO<sub>4</sub> at 1600 °C for 10 h in order to achieve 98% of theoretical density. This prompted Hikichi<sup>7</sup> to use a more complicated citric acid chelation route (polymeric precursor) to fabricate more easily sintered xenotime-type  $RPO_4$  (R = Y, Er, Yb, or Lu) powders. These powders were much finer and could be pressure-less sintered to >98% of theoretical density at relatively low temperatures (1300-1500 °C) in air. The cations (e.g.,  $Y^{+3}$ ,  $Gd^{+3}$ ) in the water solution should "chelate" or bond with a carboxyl groups (COOH) of the citric acid to prevent precipitation prior to complete reaction with the phosphate ion. In the Hikichi polymeric precursor method, anhydrous citric acid was added to a solution of R (NO<sub>3</sub>)<sub>3</sub>·nH<sub>2</sub>O (0.5 M) with the mixing mole ratio of citric acid: (R (NO<sub>3</sub>)<sub>3</sub>·nH<sub>2</sub>O) of 30:1. The pH of the mixed aqueous solution was adjusted to 5 with diluted NH<sub>4</sub>OH solution. Then, a solution of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> was added and, after aging and pH adjustment, a precipitate was formed. The precipitate was calcined at 850 °C for 1 h in air, ball-milled in ethyl alcohol for 2 h and then dried at 110 °C for 1 day. This resulted in sinterable xenotime-type powders that could be dry and isostatically pressed.

After consideration of the synthesis methods that could be used, the simple method of reacting dissolved salts with an acid to cause precipitation of a hydrated  $GdPO_4$  (that is then calcined) was selected. A different method would have been selected if ease of sintering had been a consideration.

# 2. Experimental method

## 2.1. Fabrication

Fabrication and characterization of hydrated forms of GdPO<sub>4</sub> were accomplished by reacting GdCl<sub>3</sub>·6H<sub>2</sub>O

or Gd(NO)<sub>3</sub>·6H<sub>2</sub>O (dissolved in water) with diluted H<sub>3</sub>PO<sub>4</sub>. The GdCl<sub>3</sub>·6H<sub>2</sub>O was obtained from Cerac, Inc.<sup>8</sup> and was 99.9% pure. The Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was obtained from PIDC<sup>9</sup> and was 99.95% pure. According to the CRC Handbook, GdCl<sub>3</sub>·6H<sub>2</sub>O is soluble in either cold or hot water, while Gd(NO)<sub>3</sub>·6H<sub>2</sub>O is very soluble in cold or hot water. Some other gadolinium salts are not water-soluble. Concentrated (86.4%) A.C.S. Reagent grade phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) obtained from J.T. Baker<sup>10</sup> was used. This material contained <0.0002% calcium, <0.0002% magnesium, <5 ppm heavy metals, and <0.005 ppm manganese.

## 2.1.1. Chemical reactions

The following reactions were investigated:

$$GdCl_36H_2O + H_3PO_4(aq.)$$

$$\rightarrow \text{ GdPO}_4 X/2H_2 O(\text{precip}) + 3\text{HCl(aq.)}$$
(1)

The system was aged for 3 days, pH 1–3 (excess  $H_3PO_4$ ) at 20 °C; followed by multiple washings and filtering to remove the precipitate from the soluble HCl and  $H_3PO_4$  in excess water. The precipitate was then dried at 50 °C.

$$GdPO_4X/2H_2O(precip) + heat \rightarrow GdPO_4$$
 (2)

Heating to 600, 800, and 1000  $^{\circ}$ C (in flowing air at 300 ml/h) was performed, followed by X-ray diffraction to determine if monazite or xenotime structure results. A heating rate of 400  $^{\circ}$ C/h was used, with a 1-h "hold" at the designated calcination temperature.

$$Gd(NO_3)_36H_2O + H_3PO_4(aq.)$$

$$\rightarrow \text{ GdPO}_4\text{Y}/2\text{H}_2\text{O} + 3\text{HNO}_3(\text{aq.}) \tag{3}$$

The system was aged for 3 days, pH 1–3 (excess  $H_3PO_4$ ) at 20 °C; followed by multiple washings and filtering to remove the precipitate from the soluble HNO<sub>3</sub> and  $H_3PO_4$  in excess water. The precipitate was then dried at 50 °C.

$$GdPO_4Y/2H_2O + heat \rightarrow GdPO_4$$
 (4)

Again, heating to 600, 800, and 1000 °C in flowing air was performed, followed by X-ray diffraction to determine if monazite or xenotime structure results. A heating rate of 400 °C/h was used, with a 1-h hold at the designated calcination temperature.

After multiple washings and filtering of each of the two types (chloride source and nitrate source) of precipitates (to remove excess HCl or HNO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> solubilized in the supernatant liquid), the precipitated GdPO<sub>4</sub>·xH<sub>2</sub>O compounds were separately placed in 100-ml capacity Pyrex<sup>TM</sup> flasks with a measured amount (100 ml) of high purity water for 4 days. The ratio of dried, chloride-derived powder to water was 0.452 g/100 ml (1.675 mmol/100 ml). The ratio of nitrate-derived powder to water was 0.497 g/100 ml (1.839 mMol/100 ml). After 4 days, samples of the supernatant water were decanted, carefully filtered (to remove any solid particles) using Whatman<sup>TM</sup> P2 type filter paper, and analyzed for both Gd and PO<sub>4</sub> ions using inductively coupled plasma spectroscopy. This measurement was made to give an indication of the solubility of the GdPO<sub>4</sub>·xH<sub>2</sub>O compound.

## 2.2. Characterization

After filtering, the hydrated precipitates were dried at 50 °C and then characterized using X-ray diffraction to determine phase content. Differential thermal analysis (DTA) was then used to determine the temperatures at which chemically hydrated water desorbs.

Other designated samples (slightly larger in volume) were calcined in air. An airflow rate of 300 ml/h was used. Separate samples were heated to 600, 800,1000, and 1400 °C and held at temperature for approximately 1 h. A heating rate of 400 °C/h was used. After cooling to room-temperature, these samples were characterized using X-ray diffraction to determine if they were phase pure and if they contained the monazite or xenotime structure. XRD patterns from the International Centre for Diffraction Data were referenced.<sup>11</sup>

Representative hydrated powders were examined using DTA during heating to very high temperatures. These tests were used to determine the melting point of these materials and if any high temperature phase transitions (e.g., dehydration reactions) or decomposition occurred prior to melting. In general, both monazite and xenotime-type RPO<sub>4</sub> compounds are quite stable with melting points<sup>12</sup> in air ranging between about 1896 °C (ErPO<sub>4</sub>-xenotime) to 2072 °C (LaPO<sub>4</sub>-monazite). Therefore, samples were sent for analysis to a company<sup>13</sup> with a special high temperature (up to 2400 °C using a graphite heating element), DTA instrument model "SETSYS DT TGA 24." For our GdPO4 samples, the SETSYS TG 24 system was arranged to use the following options: (a) DTA rod in WRh 30%/ WRh 6% for experiments up to 2400 °C, (b) carrier gas sweeping, (c) primary vacuum (purge), (d) primary vacuum device, and (e) automatic gas switching system by electro-valves.

The GdPO<sub>4</sub>·1H<sub>2</sub>O powders were analyzed in a tungsten crucible under helium low flow with a DTA rod 2400 calibrated by a sapphire melting. Literature (reference) values for the sapphire were: melting temperature =  $2054 \circ C \pm 6 \circ C$  and enthalpy =  $1089.6 \pm 39$ J/g. The samples were ramped from room temperature up to  $2100 \circ C$  at 20 K/min. The samples also were analyzed in two parts: room temperature up to  $400 \circ C$  at 10K/min under vacuum and room temperature up to 2200 °C at 20 K/min and from 2200 °C back down to room temperature at 20 K/min.

# 3. Results

# 3.1. Resulting phases

# 3.1.1. X-ray diffraction results

The nitrate-derived, as-precipitated (washed but not calcined) powder was characterized using X-ray diffraction. The results, as shown in Fig. 1, show the markers of GdPO<sub>4</sub>·1H<sub>2</sub>O (ICDD pattern No. 39-0232) exactly match all the peaks. Therefore, clearly the powder has one water of hydration.

The X-ray diffraction pattern for the precipitated, washed, and dried powder derived from the chloride salt showed the same result of GdPO4·1H<sub>2</sub>O (ICDD No. 39-0232), where there was a very good match all the major and minor peaks. The GdPO<sub>4</sub>·1.5H<sub>2</sub>O phase was not detected in our precipitated powders. This is demonstrated in Fig. 1 (for nitrate derived powder), where some GdPO<sub>4</sub>·1.5H<sub>2</sub>O peaks are missing. For instance, a major diffraction peak for GdPO<sub>4</sub>·1.5H<sub>2</sub>O phase is missing at 59.5 degrees (marked with arrow on figure).

It takes heating in air (calcination) at temperatures in excess of 800 °C to completely dehydrate the GdPO<sub>4</sub>·1H<sub>2</sub>O. This is shown in Fig. 2 for X-ray diffraction patterns taken powders calcined powders to both 800 and 1400 °C.

Fig. 2 shows the X-ray diffraction patterns for nitratederived powder calcined to 800 °C. The material has clearly dehydrated. A monoclinic (dehydrated) phase (monazite ICDD pattern No. 32-386) is now present. No other phases, like the more complex phosphate Gd<sub>4</sub> ( $P_2O_7$ )<sub>3</sub>, were present in the X-ray diffraction pattern. When both the nitrate-derived and chloride-derived powders were calcined to 1000 °C and even 1400 °C, the X-ray diffraction patterns retained their monoclinic/ monazite crystal structure.

# 3.2. Characterization results

#### 3.2.1. Solubility results

Liquid samples were taken, according to the experimental procedure section, over  $GdPO_4 \cdot 1H_2O$  powders derived via the nitrate or the chloride precursors. Inductively coupled plasma (ICP) spectrometry was used to measure gadolinium and phosphorous ion concentrations in the samples. The results are reported below in Table 1.

The Gd<sup>+3</sup> concentrations were used to calculate the solubility of GdPO<sub>4</sub>·1H<sub>2</sub>O in water. It was assumed that the phosphorus (PO<sub>4</sub>) concentration would be high because of a very low level contamination in the water or the glassware. These calculations are shown below.

For the chloride-derived powder:

(0.039  $\mu g~Gd^{+3}$  /ml) (1 mol  $GdPO_4{\cdot}1H_2O/$  1 mol  $Gd^{+3})$ 

 $(1 \text{ mole } GdPO_4 \cdot 1H_2O/270.24 \text{ g/mol}) =$ 

1.44 E-10 mole  $Gd^{+3}/$  ml or 1.44 E-7  $Gd^{+3}/$ L=[Gd<sup>+3</sup>]



Fig. 1. X-ray diffraction pattern of washed and dried powder precipitated from nitrate, showing 100% GdPO<sub>4</sub>·1H<sub>2</sub>O.



32-0386 (\*) - Gadolinium Phosphate - GdPO4

Fig. 2. X-ray diffraction patterns precipitated GdPO<sub>4</sub>·1H<sub>2</sub>O converts to the same monazite (monoclinic) phase GdPO4 (ICDD No. 32-386) when heated to either 800 or 1400 °C.

 Table 1

 Results of inductively coupled plasma spectrometry tests

Sample	$\mu g \ Gd/ \ ml$	$\mu g \ P/ \ ml$
Chloride-derived powder	0.039	3.566
Nitrate-derived powder	0.187	4.261
Nitrate spike	0.430	9.024
% Recovery	135.0	93.0
Mean % error	$7.9 \pm 0.8$	$11.1 \pm 0.5$

 $K_{\rm sp} = [Gd^{+3}] [PO_4^{-3}] = [Gd^{+3}]^2 = [1.44 \text{ E-7}] [1.44 \text{ E-7}] = 2.07 \text{ E-14}$ 

For the nitrate-derived powder:

 $(0.187~\mu g~Gd^{+\,3}~/ml)$  (1 mol  $GdPO_4{\cdot}1H_2O/$  1 mol  $Gd^{+\,3})$ 

 $(1 \text{ mole } GdPO_4 \cdot 1H_2O/270.24 \text{ g/mol}) =$ 

6.90 E-10 mol Gd<sup>+3</sup>/ ml or 6.90 E-7 Gd<sup>+3</sup>/ L=[Gd<sup>+3</sup>]

 $K_{\rm sp} = [Gd^{+3}] [PO_4^{-3}] = [Gd^{+3}]^2 = [6.90 \text{ E-7}] [6.90 \text{ E-7}]$ 7] = 4.76 E-13

### 3.2.2. DTA/TGA results

Two GdPO<sub>4</sub>·1H<sub>2</sub>O samples (GdPO4 -1 and GdPO4 -2) were analyzed. The GdPO4 -1 sample was derived from the nitrate precursor material while the GdPO4 -2 sample was derived from chloride precursor material. A calibration run was conducted where a standard material (high purity sapphire) was heated until it melted (beginning at 2052.7 °C). This is within the accepted range of the literature value of  $2054\pm 6$  °C; thus demonstrating that the instrument was very well calibrated. Fig. 3 is a thermogravimetric analysis (TGA) run at low temperatures that shows loss of weight most likely associated with physically adsorbed water. A very similar result was obtained for sample number 2. Figs. 4 and 5 are TGA and DTA runs for sample GdPO4 -1 where the most interesting feature is the high temperature endotherm at 1916.8–1920.3 °C associated with the melting point.

Fig. 6 shows a complete DTA "zoom" heating run on sample GdPO<sub>4</sub> -2. The first exothermic peak (864.85–883.36 °C) evidently is the loss of the one water of hydration when the monazite (monoclinic) crystal phase is formed. This corresponds very well with the calcination/XRD results. There are small peaks in the 1200–1250 °C range that possibly could be interpreted as a shift in the crystalline structure [monazite (monoclinic) to the xenotime (tetragonal)]. Finally, the large endothermic peak (1898.64–1901.40 °C) clearly is the melting point of the dehydrated GdPO<sub>4</sub>.

## 4. Discussion of results

The powder that was precipitated was identified using XRD as  $GdPO_4 \cdot 1H_2O$ . According to the literature results of Hikichi,<sup>2</sup> the precipitate that was anticipated for our aging conditions was the hexagonal form,  $GdPO_4 \cdot 1/2H_2O$ . Calcination to a temperature over 800 °C can be used to remove the 1 water of hydration to form dehydrated GdPO<sub>4</sub>. This was confirmed by the XRD results on the calcined powder, where the monoclinic/monazite



Fig. 3. DTA/TGA analysis for GdPO4 Sample No. 1 (nitrate precursor) at low temperatures.



Fig. 4. DTA/TGA analysis for GdPO4 Sample No. 1 (nitrate precursor) at high temperatures.



Fig. 5. DTA analysis for GdPO4 Sample No. 1 (nitrate precursor) showing melting point.



Fig. 6. DTA analysis for GdPO4 Sample No. 2 (chloride precursor) using "zoom" heating.

(ICDD No. 32-386) crystalline material was formed at temperatures over 800 °C. XRD data showed the monoclinic form existed after heating to 1400 °C and then fairly rapid (600  $^{\circ}$ C/h) cooling to room temperature. An additional test was performed to equilibrate the powder and then rapidly cool (a few seconds) it to ambient temperature. After cooling, only the monoclinic/monazite phase was detected using XRD. It was therefore concluded that it probably was melting of the monoclinic/ monazite phase; but, the phase may have been xenotime if there exists a monoclinic to tetragonal phase change at 1200–1250 °C that is both reversible and very rapid. Regardless of the resulting crystalline phase (monoclinic or tetragonal), dehydrated GdPO<sub>4</sub> is the form that likely would be used in most engineering applications because these phases will be physically and chemically stable after exposure to high temperatures.<sup>14</sup>

The melting point of sample GdPO4-1 was slightly higher (1916.8–1920.3 °C) than the value for sample GdPO4 -2. The higher melting point material (GdPO4 -1) was derived from a higher purity gadolinium precursor (Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was 99.95% pure). The slightly lower melting point material (GdPO4 -2) was derived from a slightly lower purity gadolinium precursor (GdCl<sub>3</sub>·6H<sub>2</sub>O was 99.9% pure). Either of the measured melting points is similar to those published for other rare-earth phosphate compounds. In general, RPO<sub>4</sub> compounds are quite stable with melting points,<sup>15</sup> in air, ranging between 1896 °C (ErPO<sub>4</sub>) and 2072 °C (LaPO<sub>4</sub>).

The solubility experiment yielded a  $K_{\rm sp}$  value between 2.07 E-14 and 4.76 E-13. This compares fairly well (about 10 times lower) to the value of 1.0 E-12 calculated <sup>16</sup> by using the "Geochemist's Workbench" thermodynamic software.<sup>17</sup>

## 5. Conclusions

In conclusion,  $GdPO_4$  can be synthesized by the simple method of reacting dissolved salts with phosphoric acid to cause precipitation of a hydrated  $GdPO_4$  (as described by Hikichi<sup>2</sup>). Either of the reactions:

 $GdCl_3 \cdot 6H_2O + H_3PO_4(aq.)$ 

$$\rightarrow$$
 GdPO<sub>4</sub>·1H<sub>2</sub>O(precip) + 3 HCl(aq.)

 $Gd(NO_3)_3 \cdot 6H_2O + H_3PO_4(aq)$ 

$$\rightarrow$$
 GdPO<sub>4</sub>·1H<sub>2</sub>O + 3 HNO<sub>3</sub>(aq.)

result in 100% single-phase  $GdPO_4$ ·1H<sub>2</sub>O powder. There is no readily apparent visible difference between the powders fabricated using either gadolinium nitrate or gadolinium chloride precursors.

Heating in air (calcination) to a temperature of over 800 °C is necessary to remove the one water of hydration. The DTA peak for water removal was centered at 883 °C to produce GdPO<sub>4</sub> in a monoclinic/monazite crystal structure. The hydrated powder (GdPO<sub>4</sub>·1H<sub>2</sub>O) is extremely insoluble in water with a  $K_{sp}$  measured between 2.07 E-14 and 4.76 E-13. The dehydrated monoclinic GdPO<sub>4</sub> (most likely monazite phase) is extremely stable with a measured melting point of 1899–1920 °C. The higher part of the melting range was achieved with a higher purity gadolinium precursor salt.

The results provide confirming data that  $GdPO_4$  can be easily synthesized and it is an excellent candidate to be used as a water insoluble neutron absorber (i.e., "poison") for inclusion in spent nuclear fuel canisters.

## Acknowledgements

This work was supported by the US Department of Energy, under DOE Idaho Operations Office Contract CE-AC07-99ID13727.

### References

- Hull, L., Pace, M., Lessing, P., Rogers, R., Mizia, R., Propp, A., Shaber, E. and Taylor, L. Advanced Neutron Absorbers for DOE SNF Standardized Canister—Feasibility Study, National Spent Nuclear Fuel Program, Document DOE/SNF/REP-057 Rev. 0, United States Department of Energy, Office of Environmental Management, August 2000.
- Hikichi, Y., Hukuo, K. and Shiokawa, J., Syntheses of rare earth orthophosphates. *Bulletin of the Chemical Society of Japan*, 1978, 51, 3645–3646.
- Ni, Y. and Hughes, J. M., Crystal chemistry of the monazite and xenotime structures. *American Mineralogist*, 1995, 80, 21–26.
- Kizilyalli, M. and Welch, A. J. E., Crystal data for lanthanide orthophosphates. J. Appl. Cryst, 1976, 9, 413–414.
- Dictionary of Inorganic Compounds-Volume Three. Chapman & Hall, London SE1 IHN, 1992.
- Kuo, D.-H. and Kriven, W. M., Characterization of yttrium phosphate and a yttrium phosphate/yttrium aluminate laminate. *J. Am. Ceram. Soc.*, 1995, **78**, 3121–3124.
- Hikichi, Y., Ota, T., Daimon, K., Hattori, T. and Mizuno, M., Thermal, mechanical, and chemical properties of sintered xenotime-type RPO4 (Re=Y, Ef, Yb, or Lu). *J. Am. Ceram. Soc.*, 1998, **81**, 2216–2218.
- Cerac Inc, PO Box 1178, Milwaukee, WI 53201-1178, USA. Tel.: +1-414-289-9800.
- PIDC (Pacific Industrial Development Corporation), Inc., 900 Victors Way, Suite 300, Ann Arbor, MI 48108, USA. Tel.: +1-734-930-9292.
- Mallinckrodt Laboratory Chemicals, A Division of Mallinckrodt Baker, Inc., 222 Red School Lane, Phillipsburg, NJ 08865, USA. Tel.: +1-908-859-6916.
- Powder Diffraction File, Release 1999, Data Sets 1-49 plus 70-86 PDF, International Centre for Diffraction Data (ICDD), 12 Campus Boulevard, Newtown Square, PA 19073-3273 USA.
- 12. Hikichi, Y. and Nomura, T., Melting Temperatures of Monazite and Xenotime. J. Am. Ceram. Soc., 1987, **70**(10), C252.

- 13. SETARAM, S.A. France, Applications Lab, 7, rue de l'Oratoire, F-69300 Caluire, France, Attn. L. Benoist, Lab Manager.
- 14. Norton, F. H., *Elements of Ceramics*, 2nd ed.. Addison-Wesley, Reading, MA, 1974.
- 15. Hikichi, Y. and Nomura, T., Melting temperatures of monazite and xenotime. J. Am. Ceram. Soc., 1987, 70(10), C252.
- Hull, L., Pace, M., Lessing, P., Rogers, R., Mizia, R., Propp, A., Shaber, E. and Taylor, L. National Spent Nuclear Fuel Program,

Advanced neutron absorbers for DOE SNF standardized canister—feasibility study, DOE/SNF/REP-057 Rev. 0, United States Department of Energy, Office of Environmental Management, August 2000.

 The Geochemist's Workbench<sup>TM</sup> is a registered trademark of The Board of Trustees of the University of Illinois. This set of software tools is available from RockWare Inc., 2221 East Street, Golden, CO 80401, USA. Tel.: +1-303-278-3534.