

# Phase Equilibria in the Fe<sub>2</sub>O<sub>3</sub>–P<sub>2</sub>O<sub>5</sub> System

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Four ferric phosphate compounds were identified in the  $Fe_2O_3$ - $P_2O_5$  system and the liquidus surfaces in the subsystems  $Fe_3PO_7$ - $FePO_4$ ,  $FePO_4$ - $Fe_4(P_2O_7)_3$ , and  $Fe_4(P_2O_7)_3$ - $Fe(PO_3)_3$  were determined. The results are significantly different from those presented by Wentrup in 1935.  $Fe_3PO_7$  is the stable ferric oxophosphate compound, not  $Fe_4P_2O_{11}$ , and  $Fe_3PO_7$  decomposes in air at 1090°C. The congruent melting point of  $FePO_4$  (1208°C) is similar to what was reported, but  $Fe_4(P_2O_7)_3$  melts congruently at 945°C, about 300°C lower than claimed by Wentrup.  $Fe(PO_3)_3$ , for which the melting temperature has not been previously reported, melts congruently at 1205°C. Eutectic points exist at 58.0 mol%  $Fe_2O_3$  (1070°C), 42.7%  $Fe_2O_3$  (925°C), and 37.0%  $Fe_2O_3$  (907°C). The latter two eutectic points bracket the conventional glass-forming range for iron phosphate melts under consideration as alternative hosts for nuclear wastes.

#### I. Introduction

CHEMICALLY durable iron phosphate glasses are compatible with a wide variety of other oxides and so have drawn much attention as alternative hosts for radioactive wastes.<sup>1–5</sup> Knowledge of phase equilibria in the iron phosphate system is of interest for understanding the effects of composition and temperature on glass formation, and for predicting crystallization behavior of iron phosphate melts and glasses.<sup>6</sup> In addition, iron phosphate compounds are finding increasing applications for use as electrode materials for Li batteries<sup>7,8</sup> and for catalysts,<sup>9,10</sup> and so the availability of accurate phase equilibrium information would be useful for the preparation and characterization of these materials.

Wentrup determined the original ferric phosphate phase diagram for the subsystems between  $Fe_2O_3$ ,  $Fe_4P_2O_{11}$ ,  $FePO_4$ , and  $Fe_4(P_2O_7)_3$  by recording heating and cooling curves of appropriate mixtures of  $Fe_2O_3$ ,  $FePO_4$ , and  $Fe_4(P_2O_7)_3$ .<sup>11</sup> One controversial compound in the original Wentrup diagram is the oxophosphate phase  $Fe_4P_2O_{11}$ . Wentrup reported the formation of a crystalline phase with this nominal composition, but did not characterize it. Korinth and Royen<sup>12</sup> used X-ray diffraction (XRD) to study mixtures of  $Fe_2O_3$  and  $FePO_4$  heated at  $800^\circ$ –  $900^\circ$ C and determined that the stoichiometry of the lowest phosphate compound was in fact  $Fe_3PO_7$  instead of  $Fe_4P_2O_{11}$ . Gleitzer and colleagues studied the solid-state equilibria and formation of ferric phosphate compounds at  $900^\circ$ C and confirmed that  $Fe_3PO_7$ , not  $Fe_4P_2O_{11}$ , is the stable oxophosphate compound.<sup>13,14</sup>

Another controversy associated with the Wentrup phase diagram concerns the FePO<sub>4</sub>–Fe<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub> system. The original phase diagram shows a melting temperature for ferric pyrophosphate, Fe<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub>, above 1200°C. However, research on glass formation in this system indicates that the melting temperature of the pyrophosphate must be closer to  $950^{\circ}$ – $1100^{\circ}$ C.<sup>15–19</sup> Many iron

Manuscript No. 28320. Received July 13, 2010; approved October 27, 2010. This work was financially supported by the National Science Foundation, grants DMR-0305202 and DMR-0502463. phosphate glass-forming compositions reported in the literature are centered on the  $Fe_4(P_2O_7)_3$ - $Fe(PO_3)_2$  system<sup>15,20,21</sup>; however, no investigation of the liquidus surface of this system has been reported.

Some information about the phase transition temperatures of the ferric phosphate compounds has been reported. FePO<sub>4</sub> was reported by Wentrup<sup>11</sup> to melt between 1230° and 1240°C, and Shafer et al.22 obtained a melting point of 1230°C using rapid heating in a strip furnace. Caglioti<sup>23</sup> mentioned the possible decomposition of Fe<sub>3</sub>PO<sub>7</sub> to Fe<sub>2</sub>O<sub>3</sub> and FePO<sub>4</sub> above 1100°C, and Korinth and Royen<sup>12</sup> later confirmed that Fe<sub>3</sub>PO<sub>7</sub> decomposes at 1200°C. Three overlapping endothermic differential thermal analysis (DTA) peaks between 1000° and 1150°C were reported for Fe<sub>3</sub>PO<sub>7</sub>, but were not explained, and the melting temperature of Fe<sub>3</sub>PO<sub>7</sub> was estimated from DTA to be  $1375^{\circ} \breve{C}$ .<sup>24</sup> Fe(III) in ferric phosphate systems often undergoes an endothermic reduction to Fe(II) when heated to the corresponding liquidus or decomposition temperatures, and P<sub>2</sub>O<sub>5</sub> can volatilize at high temperatures (generally above 1000°C) from melts, particularly from phosphate-rich compositions. These processes can make the interpretation of complex thermal curves more difficult, and may have contributed to the apparent errors in the Wentrup diagram.

Glasses with Fe<sub>2</sub>O<sub>3</sub> contents between 33 and 59 mol% form from melts held at 1300°C,<sup>20</sup> and glasses with Fe<sub>2</sub>O<sub>3</sub> contents between 50 and 63 mol% can form from melts at temperatures from 1150° to 1250°C.<sup>25</sup> Such studies provide some information about the liquidus surface of this system, although it is complicated by the reduction of some ferric ions to ferrous ions under typical melting conditions. No exact melting temperature for crystalline Fe(PO<sub>3</sub>)<sub>3</sub> has been reported, although glasses based on this composition have been prepared from melts quenched from 1250°C.<sup>21</sup>

In this paper, the existence of four ferric phosphate compounds is confirmed and the liquidus surface of the ferric phosphate system is determined between the compounds  $Fe(PO_3)_3$  and  $Fe_3PO_7$ . This information is then related to other reported studies of iron phosphate glass formation and compound formation.

# II. Experimental Procedures

# (1) Compound Preparation

Ferric phosphate compounds were prepared by solid-state reactions between stoichiometric mixtures of FePO<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> or NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> at different temperatures, as summarized in Table I. FePO<sub>4</sub> · *x*H<sub>2</sub>O (100%, Alfa Aesar, Ward Hill, MA), Fe<sub>2</sub>O<sub>3</sub> (Alfa Aesar,  $\geq$  99%), and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (Alfa Aesar, 98%) were used as raw materials. Samples obtained from these experiments were pulverized to < 53 µm and characterized by XRD (XRD Scintag XDS 2000, Scintag Inc., Cupertino, CA) with a slow scanning rate (1° every 1–2 min). Search and match of XRD patterns were achieved manually using DMSNT 1.37 (Scintag Inc.), which is based on a Hanawalt search method.

### (2) Phase Equilibria Studies

(A)  $Fe_3PO_7$ - $FePO_4$  System: Samples (<53 µm) weighing 100–200 mg were placed in an open alumina crucible for

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 Table I.
 Preparation Methods for Ferric Phosphate Compounds

Compound	Raw materials	Preparation conditions
Fe <sub>3</sub> PO <sub>7</sub>	FePO <sub>4</sub> +Fe <sub>2</sub> O <sub>3</sub>	12 h at 950°C, then 72 h at 1050°C
$Fe_4P_2O_{11}$	FePO <sub>4</sub> +Fe <sub>2</sub> O <sub>3</sub> , or Fe <sub>3</sub> PO <sub>7</sub> +FePO <sub>4</sub>	12-48 h holds at 800°, 900°, 1000°, and 1050°C-all unsuccessful
FePO <sub>4</sub>	$FePO_4 \cdot xH_2O$	12 h at 880°C
$Fe_4(P_2O_7)_3$	$FePO_4 + Fe(PO_3)_3$	12 h at 800°C, then 72 h at 940°C
Fe(PO <sub>3</sub> ) <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> +NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	Ammonia burn-off from thoroughly mixed batch at 500°C overnight, followed by 12-h hold at 800°C

DTA and thermogravimetric analysis (DTA–TGA, Netzsch STA 409C/CD, NETZSCH–Gerätebau GmbH, Selb, Germany). DTA–TGA was run at 10°C/min under flowing air. The data obtained were analyzed using the Netzsch Proteus software, version 4.3. The accuracy of the characteristic temperatures was determined to be  $\pm 5^{\circ}$ C by calibration and multiple runs. DTA–TGA was used to determine the phase-transition and decomposition temperatures of crystalline Fe<sub>3</sub>PO<sub>7</sub> and FePO<sub>4</sub>.

To study the decomposition of Fe<sub>3</sub>PO<sub>7</sub>, samples were heated in air for 10-12 h at temperatures between 1000° and 1350°C, and then quenched in water. These samples were dried, then either pulverized to < 53  $\mu$ m and analyzed by XRD, or mounted and coated with carbon for analytical scanning electron microscopy with energy-dispersive spectrometry (SEM-EDS, FESEM S4700, Hitachi High-Tech, Tokyo, Japan). Fe/P ratios were typically determined by EDS at low magnification (  $\times$  500) using a calibration curve based on the EDS analyses of the four ferric phosphate compounds. In general, analyses were obtained from at least five different spots on each sample and the average compositions are reported. The compositions of the melted regions of quenched samples obtained by EDS were used to determine the liquidus surface of the Fe<sub>3</sub>PO<sub>7</sub>-rich portion of this system, because these melts crystallize readily when quenched.<sup>25</sup> For the FePO<sub>4</sub>-rich portion of this system, similar analyses were performed on samples with the nominal composition (mol%) 51.4Fe<sub>2</sub>O<sub>3</sub>-48.6P<sub>2</sub>O<sub>5</sub> heated in air for 12 h at different temperatures between 1150° and 1205°C.

(B)  $FePO_4$ - $Fe_4(P_2O_7)_3$  System: One to two grams of samples with nominal Fe<sub>2</sub>O<sub>3</sub> contents of 44.5 and 47.5 mol%, quenched after heat treatments similar to those described above, were prepared and analyzed by SEM-EDS to determine the compositions of the resulting glassy phase. Fe<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub>-rich compositions are good glass formers, so the liquidus surface was studied by characterizing samples quenched from temperatures that bracket the expected liquidus temperature. Samples about 0.6-1.0 g in size with Fe<sub>2</sub>O<sub>3</sub> contents from 40.0 to 43.0 mol% were sealed under air in silica ampoules to minimize Fe(III) reduction and  $P_2O_5$  volatilization during subsequent thermal treatments. These sealed samples were heated for 12 h to different temperatures that bracketed the expected liquidus temperature, followed by a water quench. The temperature intervals were set at  $10^{\circ}$ C. These quenched samples were analyzed by optical microscopy (OM) and powder XRD, and the liquidus surface was determined to be the midpoint between the highest temperature where crystals were observed and the lowest temperature where no crystals were observed.

(*C*)  $Fe_4(P_2O_7)_3$ - $Fe(PO_3)_3$  System: P<sub>2</sub>O<sub>5</sub>-rich melts are good glass formers and so the P<sub>2</sub>O<sub>5</sub>-rich portion of the diagram was also studied by analyzing samples quenched from temperatures that bracket the expected liquidus temperatures. These samples (compositional intervals of ~1.5 mol% Fe<sub>2</sub>O<sub>3</sub>) were sealed in silica ampoules and heated in a similar way to what is described above for the Fe<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub>-rich samples. The quenched samples were studied by OM and micro-Raman spectroscopy (Horiba–Jobin Yvon LabRam-HR, Horiba Jobin Yvon Inc., Edison, NJ) using a He–Ne laser (632.8 nm). Raman spectra of crystalline Fe<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub> and Fe(PO<sub>3</sub>)<sub>3</sub> are more distinct than the respective XRD patterns, and so this technique was convenient for identifying isolated crystals in these quenched samples.

#### III. Results and Discussion

## (1) Ferric Phosphate Compounds

Single-phase samples of  $Fe_3PO_7$ ,  $FePO_4$ ,  $Fe_4(P_2O_7)_3$ , and  $Fe(PO_3)_3$  were prepared according to the processes outlined in Table I and confirmed by XRD. The compound  $Fe_4P_2O_{11}$  could not be obtained under the experimental conditions described in Table I. Instead, various mixtures of crystalline  $Fe_3PO_7$  and  $FePO_4$ , or  $Fe_2O_3$  and  $FePO_4$ , formed. The presence of  $Fe_3PO_7$  instead of  $Fe_4P_2O_{11}$  as the stable "iron-rich" oxophosphate compound in the ferric phosphate system is consistent with what was reported by Korinth and Royen.<sup>12</sup> but in disagreement with the conclusions of Wentrup.<sup>11</sup>

### (2) Phase Equilibria Studies

(A)  $Fe_3PO_7$ - $FePO_4$  System: Figure 1 shows the XRD patterns of samples of Fe<sub>3</sub>PO<sub>7</sub> quenched from 1000°, 1150°, and 1200°C after being held in air for 12 h. Crystalline Fe<sub>2</sub>O<sub>3</sub>, FePO<sub>4</sub>, and Fe<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, as well as a small amount of glassy phase, are present in the samples heated at or above 1150°C. Reactions 1 and 2 summarize the possible decomposition reactions that account for the formation of these phases:

$$Fe_3PO_7 \rightarrow Fe_2O_3 + Liquid (FePO_4 + Fe_2O_3)$$
 (1)

$$2 \operatorname{FePO}_4 \to \operatorname{Fe}_2 \operatorname{P}_2 \operatorname{O}_7 + 1/2 \operatorname{O}_2 \tag{2}$$

Figure 2 shows DTA and TGA curves for  $Fe_3PO_7$  and  $FePO_4$ heated in air. For  $Fe_3PO_7$ , overlapping endothermic DTA peaks are present at temperatures around 1100°C, consistent with literature reports about the thermal behavior of  $Fe_3PO_7$ .<sup>12,23,24</sup> Several processes, including the decomposition and melting of  $Fe_3PO_7$  (reaction (1)) and the reduction of Fe(III) (reaction (2)), may account for these endothermic events. The reduction of Fe(III) to Fe(II) accounts for the TGA weight loss. EDS analyses indicate that the overall Fe/P ratio of an Fe<sub>3</sub>PO<sub>7</sub> sample heat treated at 1200°C for 12 h was  $3.00\pm0.16$ , consistent with



**Fig. 1.** X-ray diffraction patterns of Fe<sub>3</sub>PO<sub>7</sub> quenched after 12 h in air from (a) 1000°C, (b) 1150°C, and (c) 1200°C.  $\Box$ , Fe<sub>3</sub>PO<sub>7</sub> (JCPDS: 37-0061); **▼**, FePO<sub>4</sub> (JCPDS: 84-0875); **⊽**, Fe<sub>2</sub>O<sub>3</sub> (JCPDS: 33-0664), and  $\bigcirc$ , Fe<sub>2</sub>P<sub>2</sub>O<sub>7</sub> (JCPDS: 72-1516).



Fig. 2. Differential thermal analysis and thermogravimetric analysis patterns for  $Fe_3PO_7$  and  $FePO_4$ .

the initial stoichiometry of the sample, and indicating that no significant loss of  $P_2O_5$  occurred from these iron-rich melts. Based on the results shown in Figs. 1 and 2, the decomposition temperature of Fe<sub>3</sub>PO<sub>7</sub> is estimated to be  $1090^{\circ} \pm 8^{\circ}$ C.

The DTA data for Fe<sub>3</sub>PO<sub>7</sub> in Fig. 2 reveal a solid-state phase transition between 840° and 880°C. This phase transition could be detected by DTA on cooling as well (not shown). Wentrup<sup>11</sup> reported a solid-state phase transition temperature of 869°C for his oxophosphate phase (Fe<sub>4</sub>P<sub>2</sub>O<sub>11</sub>). The identification of a solid-state phase transition at a similar temperature in Fe<sub>3</sub>PO<sub>7</sub> is taken as evidence that Wentrup misidentified Fe<sub>3</sub>PO<sub>7</sub> as Fe<sub>4</sub>P<sub>2</sub>O<sub>11</sub>. The DTA data for FePO<sub>4</sub> in Fig. 2 indicates that there are two solid-state phase transitions, at 710°±5°C ( $\alpha \rightarrow \beta$ ) and at 880°±5°C ( $\beta \rightarrow \gamma$ ). These transition temperatures are similar to those previously reported (707° and 889°C, respectively).<sup>11,22</sup>

Figure 3 shows backscattered electron images of an  $Fe_3PO_7$ sample quenched from 1200°C after being held there in air for 12 h. EDS analyses reveal that the bright sphere-like regions are free of phosphorus and appear to be Fe<sub>2</sub>O<sub>3</sub>. EDS and XRD indicate that the small crystals ( $<2 \mu m$ ) formed around the spherical particles include FePO<sub>4</sub>, Fe<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, and Fe<sub>2</sub>O<sub>3</sub>, the phases expected to precipitate from the liquid phase that forms at this temperature (reactions (1) and (2)). The average composition of the regions around the large Fe<sub>2</sub>O<sub>3</sub> particles was determined by EDS and is used as the composition of the liquid phase at the respective heat-treatment temperatures. Similar analyses were performed on other compositions in this system, and these experimental data are used for the liquidus surface for the  $Fe_3PO_7$ -FePO<sub>4</sub> system that is plotted in Fig. 4; error bars indicate uncertainties in the quantitative EDS analyses. By extrapolating the exponential line fitting these experimental points, the temperatures at which Fe<sub>3</sub>PO<sub>7</sub> and Fe<sub>2</sub>O<sub>3</sub> are predicted to fully melt are estimated to be 1380° and 1600°C, respectively. These temperatures are similar to those reported in the literature (1375°C for  $\text{Fe}_3\text{PO}_7^{24}$  and 1565°C for  $\text{Fe}_2\text{O}_3^{26}$ ).

The FePO<sub>4</sub>–Fe<sub>3</sub>PO<sub>7</sub> system has a eutectic point at  $58.0\pm1.2$  mol% Fe<sub>2</sub>O<sub>3</sub>, and the eutectic reaction occurs at  $1070^{\circ}\pm5^{\circ}$ C. The eutectic composition and temperature of the FePO<sub>4</sub>–Fe<sub>4</sub>P<sub>2</sub>O<sub>11</sub> system reported by Wentrup<sup>11</sup> were 58.0 mol% Fe<sub>2</sub>O<sub>3</sub> and 968°C. Wentrup appears to have misidentified Fe<sub>3</sub>PO<sub>7</sub> as Fe<sub>4</sub>P<sub>2</sub>O<sub>11</sub>, and may have misinterpreted endothermic evidence of Fe(III) reduction for eutectic melting. The eutectic temperature reported here was confirmed by observing the melting behavior of the eutectic composition. Glasses can be formed from melts with compositions around this eutectic point using rapid quench techniques, as reported elsewhere.<sup>25</sup>

(B)  $FePO_4$ - $Fe_4(P_2O_7)_3$  System: The same sample preparation and characterization methods described above were used to determine the liquidus surface of the FePO\_4-rich



**Fig. 3.** Backscattered electron images of  $Fe_3PO_7$  quenched after dwelling for 12 h at 1200°C; (a) and (b) are from the same sample but at different magnifications.

portion of the FePO<sub>4</sub>–Fe<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub> system. For the Fe<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub>rich part of this system, samples were sealed in silica ampoules to minimize the effects of phosphorus volatility at high temperatures. EDS analyses of a sample of Fe<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub> heated at 950°C for ~12 h in air and in a sealed ampoule indicate Fe/P ratios of  $0.75\pm0.05$  and  $0.70\pm0.02$ , respectively, compared with an expected ratio of 0.67. Figure 5 shows the XRD patterns collected from several compositions quenched from temperatures below their respective liquidus temperatures. These results were used to determine the liquidus temperatures and the eutectic point of the FePO<sub>4</sub>–Fe<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub> system.

Figure 6 shows the liquidus curves obtained by fitting the points obtained from the analyses described above. The FePO<sub>4</sub>-



**Fig. 4.** Phase diagram of the  $FePO_4$ – $Fe_3PO_7$  system. Dashed-dotted line is an extrapolation of the curve used to fit the experimental liquidus points.



Fig. 5. X-ray diffraction patterns of some compositions quenched from the indicated subliquidus temperature, compared with crystalline  $FePO_4$  and  $Fe_4(P_2O_7)_3$ .

 $Fe_4(P_2O_7)_3$  system has a eutectic point at  $42.7 \pm 0.4$  mol%  $Fe_2O_3$  and  $925^{\circ} \pm 8^{\circ}C$ . In contrast, Wentrup<sup>11</sup> reported a liquidus point at 46.5 mol%  $Fe_2O_3$  and  $954^{\circ}C$ .

(*C*)  $Fe_4(P_2O_7)_3$ - $Fe(PO_3)_3$  System: EDS analyses of a sample of Fe(PO\_3)\_3 heated in a silica ampoule to  $1250^{\circ}$ C for 4 h showed an Fe/P ratio of  $0.37 \pm 0.07$ , compared with an expected ratio of 0.33. The silica content in this sample was <2.0 mol%, as measured at a distance of 1 mm from the ampoule wall on a sample that was 11 mm in diameter. This analysis indicates that the nominal composition of this P<sub>2</sub>O<sub>5</sub>-rich sample was retained when melted in an ampoule.

Figure 7 shows the Raman spectra collected from crystals detected in samples from the  $Fe_4(P_2O_7)_3$ -Fe(PO<sub>3</sub>)<sub>3</sub> system quenched from temperatures below their respective liquidus temperatures. By comparing the Raman spectra of these samples to those collected from crystalline  $Fe(PO_3)_3$  and  $Fe_4(P_2O_7)_3$ , the equilibrium crystal phases at the quenching temperatures could be determined. A detailed discussion of the Raman spectra from iron phosphate compounds and glasses will be reported elsewhere.

Figure 8 shows the liquidus surface for the  $Fe_4(P_2O_7)_3$ -Fe(PO<sub>3</sub>)<sub>3</sub> system obtained from the OM–Raman and EDS analyses. The eutectic point is 37.0±0.3 mol% Fe<sub>2</sub>O<sub>3</sub> with a eutectic temperature of 907°±8°C. This appears to be the first report of the liquidus surface and eutectic composition in this subsystem.

#### (3) Discussion of the Liquidus Surface Determination

Figure 9 summarizes the liquidus surface of the ferric phosphate system between 25 and 75 mol%  $Fe_2O_3$ , and Table II summa-



Fig.7. Raman spectra of several partially crystallized samples quenched from the indicated temperatures and from crystalline  $Fe(PO_3)_3$  and  $Fe_4(P_2O_7)_3$ .

rizes the characteristic temperatures determined for this system. Four ferric phosphate compounds appear in this liquidus surface phase diagram;  $Fe_3PO_7$  decomposes during heating, and the others melt congruently. Eutectic points exist in each subsystem. Below the corresponding liquidus surface, neighboring solid compounds in the diagram are expected to coexist at equilibrium, although the details of the solid-phase equilibria were not studied in this work.

This work confirms the reports of Korinth and Royen<sup>12</sup> and Gleitzer and colleagues<sup>13,14</sup> that  $Fe_3PO_7$  ( $3Fe_2O_3-P_2O_5$ ) is the only ferric oxophosphate phase with an iron content between FePO<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>. The solid-state phase-transition temperature, decomposition temperature, and liquidus temperature determined in the present work are in good agreement with the respective temperatures reported in these earlier studies. The ferric oxophosphate phase reported in the Wentrup phase diagram,<sup>11</sup> Fe<sub>4</sub>P<sub>2</sub>O<sub>11</sub> (2Fe<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>), could not be produced. This finding has implications for the development of ferric oxophosphate compounds of interest for electrode materials. For example, the formation of Fe<sub>3</sub>PO<sub>7</sub> as an electrode material for Li batteries was accomplished by heating stoichiometric mixtures of Fe<sub>2</sub>O<sub>3</sub> and FePO<sub>4</sub> at 1050°C for 12 h.<sup>7</sup> This temperature is just below the eutectic temperature (1070°C) of the Fe<sub>3</sub>PO<sub>7</sub>-FePO<sub>4</sub> system determined in this study (Fig. 4).

Glass formation around the eutectic composition in the FePO<sub>4</sub>–Fe<sub>3</sub>PO<sub>7</sub> system has been evaluated and is described elsewhere.<sup>25</sup> The viscosities of those ferric phosphate melts near their respective liquidus temperatures were relatively low, necessitating the use of rapid quenching techniques (> $10^{3\circ}C/s$ ) to form glasses. These quench rates were much faster than those needed



Fig. 6. Liquidus surface of the  $FePO_4$ - $Fe_4(P_2O_7)_3$  system.



Fig. 8. Liquidus surface of the  $Fe_4(P_2O_7)_3$ -Fe(PO<sub>3</sub>)<sub>3</sub> system.



Fig. 9. Summary of the liquidus surface of the ferric phosphate system.

Table II. Summary of the Characteristic Temperatures in the Fe<sub>3</sub>PO<sub>7</sub>-Fe(PO<sub>3</sub>)<sub>3</sub> System

Fe <sub>2</sub> O <sub>3</sub> (mol%)	Temperature (°C)	Description
75.0	$1090 \pm 8$	Decomposition of Fe <sub>3</sub> PO <sub>7</sub>
$58.0 \pm 1.2$	$1070 \pm 5$	Eutectic melting (FePO <sub>4</sub> –Fe <sub>3</sub> PO <sub>7</sub> )
50.0	$1208 \pm 8$	Congruent melting of FePO <sub>4</sub>
$42.7 \pm 0.4$	$925 \pm 8$	Eutectic melting $(Fe_4(P_2O_7)_3 - FePO_4)$
40.0	$945 \pm 8$	Congruent melting of $Fe_4(P_2O_7)_3$
$37.0 \pm 0.3$	$907 \pm 8$	Eutectic melting (Fe(PO <sub>3</sub> ) <sub>3</sub> -
		$Fe_4(P_2O_7)_3)$
33.3	$1205\pm8$	Congruent melting of Fe(PO <sub>3</sub> ) <sub>3</sub>

to form glasses with compositions in the  $Fe(PO_3)_3$ - $Fe_4(P_2O_7)_3$ system. As shown in Fig. 9, the liquidus temperatures in the compositional range of approximately 36-43 mol% Fe<sub>2</sub>O<sub>3</sub> are below 950°C. This is the compositional range of greatest interest for vitrifying nuclear wastes<sup>17–19</sup> and the relatively low liquidus temperatures determined in this study are consistent with the glass-forming tendencies reported in the literature.

To the best of our knowledge, this is the first report of liquidus temperature information for ferric phosphate melts in the  $Fe_4(P_2O_7)_3$ -Fe(PO\_3)\_3 system. Part of the difficulty in obtaining accurate information about these materials is avoiding the vaporization of P<sub>2</sub>O<sub>5</sub>, particularly at the higher temperatures required as compositions approach  $Fe(PO_3)_3$ . Glass formation from phosphate-rich melts has been reported,<sup>21</sup> but those glasses appear to have lost some phosphate and were subject to some iron reduction during the melting process.

Efforts were made in this study to minimize the effects of phosphate volatility and the reduction of ferric phases, but the compositional uncertainties associated with both processes may affect these final results. The compositional dependence of the liquidus temperatures of the ferric phosphate melts shown in Fig. 9 can be used for guidance in understanding the behavior of iron phosphate melts. However, these melts will reduce in air at typical melting temperatures (1000°-1300°C), to produce glasses with about 20% ferrous ions.<sup>15</sup> Information about the liquidus temperatures of iron phosphate glass-forming melts is limited, but DTA studies of crystallization behavior of iron phosphate glasses reveal crystal melting temperatures near 900°C,<sup>6,19,27</sup> consistent with the liquidus temperature for the ferric phosphate compositions summarized in Fig. 9.

### VI. Conclusions

The liquidus surface of the Fe<sub>3</sub>PO<sub>7</sub>-Fe(PO<sub>3</sub>)<sub>3</sub> system was redetermined using sample preparation techniques that minimize the effects of sample volatilization and reduction. Significant differences are found when this work is compared with the earlier reports. In particular, Fe<sub>3</sub>PO<sub>7</sub> is the only ferric oxophos-

phate compound that forms and it decomposes in air at 1090°C. The liquidus temperature information in the FePO<sub>4</sub>-Fe<sub>3</sub>PO<sub>7</sub> subsystem is consistent with literature reports on processing materials of interest for electrodes in lithium electrochemical devices.  $Fe_4(P_2O_7)_3$  was found to melt congruently at 945°C, about 300°C lower than in earlier claims. For the first time, the liquidus surface of the  $Fe(PO_3)_3$ - $Fe_4(P_2O_7)_3$  subsystem has been reported. Fe(PO<sub>3</sub>)<sub>3</sub> melts congruently at 1205°C and a eutectic point exists at 37.0% Fe<sub>2</sub>O<sub>3</sub> (907°C). The liquidus temperatures of this subsystem are consistent with glass formation and crystallization behavior of compositions being developed for waste vitrification applications.

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