The synthesis of phosphate and vanadate apatites using an aqueous one-step method

Claude H. Yoder^{1*}, Maxwell D. Havlusch¹, Robyn N. Dudrick¹, Janse T. Schermerhorn¹,
Linh K. Tran¹, and Alix C. Dymier²

¹Department of Chemistry

Franklin and Marshall College

Lancaster, PA 17604

eEmail: cyoder@fandm.edu

²Carroll Laboratories of Orthopedic Surgery

Columbia University

New York, NY 10032-3072

Abstract

A modification of the aqueous addition method for the synthesis of apatites is described. This one-step method does not require addition of reagents and no adjustment of solution pH and therefore requires less equipment and less time than the traditional aqueous addition method. It can be used with a variety of starting materials to produce both phosphate and vanadate apatites with good purity and yield. The method generally produces smaller crystallites with average size in the 30-50 nm range. The effects of synthesis variables such as the nature of the reactants, control of pH, and digestion temperature and time are discussed.

Keywords: apatite, vanadate apatite, aqueous synthesis, one-step

1. Introduction

Apatites have been synthesized using many different methods. In his 1994 review of apatites, Elliott [1] described the syntheses of stoichiometric and non-stoichiometric apatites, including solid solutions, using primarily solution (precipitation, hydrolysis and hydrothermal) techniques and high temperature solid state reactions. The review by Sadat-Shojai et al. [2], almost 20 years later, includes dry (high-temperature solid state reactions and mechanochemical methods), wet (conventional chemical precipitation, hydrolysis, sol-gel, hydrothermal, emulsion, and sonochemical methods), high-temperature (combustion and pyrolysis methods), biogenic, and combination procedures. The proliferation of synthetic techniques for the preparation of apatites is surely partly due to an increased emphasis on apatites as biomaterials and the consequent efforts to control particle size and morphology.

Wet methods continue to be the most frequently used for the preparation of apatites [2] but suffer from possible lack of control of purity and crystallinity. Conventional chemical precipitation is particularly convenient for the preparation of insoluble ionic compounds for which soluble precursors can be found. The reaction is usually carried out by dropwise addition of one or more reagents to another reagent, all in solution. Because

of the dependence of the nature of the phosphate species present on the solution pH, the pH is generally adjusted to basic values of 8-10, where ortho phosphate is present to some extent (it is not dominant until the pH is above 12). After precipitation of the insoluble apatite phase the mixture undergoes a digestion period of generally several hours at temperatures of 60-90 °C, during which the pH is monitored and adjusted. During the digestion period the purity and size of the apatite crystallites are assumed to improve.

In our recent work on the syntheses of apatites containing the vanadate ion (VO_4^{3-}) rather than the phosphate ion, we have come across a variation of the aqueous addition method. This method, used primarily as a method of producing a homogeneous mixture of reactants for high-temperature syntheses of vanadate apatites, involves simple dissolution of the solid reactants in a flask. For example, in the preparation of CaVapOH ($\text{CaVapOH} = \text{Ca}_5(\text{VO}_4)_3\text{OH}$), Hara et al. [3] refluxed a mixture of CaSO_4 and Na_3VO_4 with excess NaOH for several hours, followed by evaporation of the water and calcination (heating) at 800 °C for 3 h. Significantly, Mayer, et al. [4] found that vanadate apatites (as well as phosphate and arsenate apatites) can be made without calcination by refluxing the sulfates of calcium, strontium, and lead with Na_3VO_4 in a solution “made strongly basic with NaOH.” We have found that heating a mixture of a solution of solid reactants, chosen according to the stoichiometry of the apatite, leads directly to pure apatite with sufficient crystallinity to produce relatively sharp powder X-ray diffraction patterns.

We report here on the phosphate and vanadate apatites prepared by this one-step procedure as well as our examination of the variables that affect the purity and crystallinity of the products.

2. Materials and Methods

All reagents were ACS-reagent grade. Distilled water was used for the preparation of solutions. The procedure for the preparation of CaApOH is as follows: Samples of 1.2g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 0.5g Na_3PO_4 , and 0.04g NaOH were placed in the bottom of a 125 mL Erlenmeyer flask equipped with a standard taper joint bearing a condenser with a thermometer inserted in the condenser and held slightly above the bottom of the flask (but in the solution) by a thin slice of suction tubing at the top of the condenser. The flask was placed on a heating/stir plate and 50 mL of distilled water was added. The solution was stirred magnetically and heated to 80 °C for approximately 3 hours. The pH was measured, but not adjusted, at the beginning and at the end of the 3 hours of digestion using Hydrion pH 1.0 – 12.0 paper. [In order to determine the effect of pH, the pH was adjusted with 3M NaOH for some samples at the beginning and during digestion.] Stirring was then discontinued and the solution was allowed to cool and settle overnight. The precipitate was suction filtered in a medium porosity glass filter crucible and washed 5 times with a total of about 150 mL of distilled water. The precipitate was dried in a vacuum drying oven at 110 °C for at least 4 hours and then ground with a mortar and pestle and stored in a closed, parafilm vial.

The general procedure for the method is derived from the stoichiometry of the desired apatite. For example, for the synthesis of CaApF ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) the mole ratio of the calcium to phosphate to fluoride sources is 5:3:1. Although F^- could be supplied by the cation salt (in this case CaF_2), that salt may be only slightly soluble, and generally it is advantageous to use ammonium or sodium fluoride as the source (the use of CaF_2 would also provide the fluoride ion in a ten-fold greater ratio than prescribed by the formula stoichiometry). At the scale used in this work, this ratio is obtained using 1.2 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 0.5 g Na_3PO_4 , and 0.043 g NaF for the synthesis of $\text{Ca}_5(\text{PO}_4)_3\text{F}$.

The procedure for CaVapOH was identical to that given above except for the use of 0.5 g of Na_3VO_4 and an excess of NaOH (0.25 g) and digestion at 90 °C for three hours. For the preparation of other vanadate apatites, the monovalent anion was generally used in 3 to 5-fold excess of that required by the stoichiometry. For example, the mole ratio dictated by the formula of $\text{Sr}_5(\text{VO}_4)_3\text{F}$ is 5:3:1, but the actual amount of NaF used in the reaction mixture corresponded to a ratio of 5:3:5.

Powder X-ray diffractograms were obtained using a PANalytical X'Pert PRO MPD (Multi-Purpose Diffractometer) Theta-Theta System with Cu-K α radiation. A step size of 0.02° 2-theta was used with a range from 5 to 70° 2-theta. X-ray diffraction was used to confirm the identity of the compound, to detect other phases present in the samples, and to obtain a qualitative idea of the crystallite size. The full width at half maximum (FWHM) of several lines of different Miller indices were obtained after profile-fitting of the peaks. Although the (002) line generally had the lower FWHM, the 222 line was

more representative of the entire line pattern for most apatites.

The presence of fluoride was ascertained using ^{19}F NMR spectra to determine the relative amount of fluoride in apatites. The apatite was dissolved in a minimum amount of 3 M or 6 M nitric acid. A sample of NaF in the same concentration of acid was used as a standard. A small portion of D_2O was added to the solution as a lock solvent. Spectra were obtained on an Agilent INOVA 500 MHz spectrometer at 25 °C.

Particle size and morphology were determined at Washington University (St. Louis, MO) using a Hitachi H-7500 transmission electron microscope at an energy of 80 keV. A sample of the apatite (3 mg) was mixed with 0.5 mL of methanol and sonicated for 5-10 min in order to suspend the powders. A 20 μL portion of solution was dropped onto the TEM grids on filter paper. The samples were allowed to dry for 30 min. Images of all the powders were taken at 200,000 X magnification.

3. Results

The primary difference between the traditional aqueous synthesis of apatites and the “one-step” method reported here is the absence of an addition step designed to improve the purity and crystallinity of the precipitated apatite.

Both methods begin with the selection of reagents, which are water-soluble and of relatively high purity. For the preparation of a calcium apatite (such as CaApOH), the cation source is most often calcium nitrate, but the sulfate, chloride or acetate could also be used, although the sulfate is limited in solubility (the solubilities [5] in g per 100 mL water at 25 °C are $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 0.3; $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 129; $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, 75; $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$, 35). If the apatite to be prepared contains a monovalent halide ion (such as SrApCl), the halide source is most conveniently the ammonium or sodium salt of the halide. If the desired apatite is a phosphate, the phosphate source could be an ortho phosphate such as Na_3PO_4 , a hydrogen phosphate such as $(\text{NH}_4)_2\text{HPO}_4$, or a dihydrogen phosphate such as NaH_2PO_4 . If the desired apatite is a vanadate (VO_4^{3-}), sodium ortho vanadate, Na_3VO_4 can be used, although ammonium meta vanadate NH_4VO_3 has also been utilized (see Table 2 below). Generally, the ammonium counter ion is preferred rather than a sodium or potassium salt, because of the possibility of incorporation of an alkali metal cation into the apatite, though the ammonium ion can also be incorporated [6]. Moreover, the formation of the byproduct NH_4NO_3 , formed in the reaction of calcium nitrate with an ammonium phosphate, decomposes on heating to volatile products, making it easy to remove even at relatively low temperatures in an oven or vacuum oven. The type of phosphate— PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- or even the acid H_3PO_4 —in solution is of little importance unless there is no attempt to control the pH of the solution.

Because the pH of the solution determines what species of phosphate is present, in using the aqueous addition method the pH is normally regulated at a value of about 9. At a pH

of 9, the phosphate species present in solution is primarily HPO_4^{2-} and although some synthetic apatites do contain the hydrogen phosphate ion, CaApOH is sufficiently insoluble to precipitate in the presence of a small concentration of PO_4^{3-} (CaHPO_4 has a molar solubility of ca. 6×10^{-3} [5] whereas CaApOH has a molar solubility of roughly 10^{-7} [7]).

The mode of addition of reactants is designed to favor formation of the product. In the preparation of calcium hydroxylapatite, the reactant calcium nitrate is generally added dropwise to a solution of sodium or ammonium hydrogen phosphate (or an ortho phosphate such as Na_3PO_4). Regardless of the mode of addition, the addition is done slowly, generally at no more than 2 mL/min, in order to maintain slow nucleation and thereby increase the crystallite size and to produce the thermodynamically-favored product. Although the addition is followed by a digestion period, the slow addition also increases the time available for slow formation and self-purification of the precipitate through continuous *in aquo* recrystallization. The digestion period, which is designed to increase the purity and particle size of the precipitate, is generally several hours at temperatures between 60 and 100 °C for CaApOH, but may extend to weeks when purity and particle size must be maximized.

Because of the absence of the addition sequence and control of pH, the one-step method is simpler and faster to execute than the traditional aqueous addition method and produces products that have approximately the same purity. In place of addition funnels, condenser, and round bottom flask (generally with standard taper joints) used in the

addition method, the one-step method uses an Erlenmeyer flask, which may be equipped with a condenser if warranted by the digestion temperature. For a three-hour digestion at 60 °C a condenser is generally not necessary. For most reactions minimal precautions were taken to exclude CO₂. Alkaline earth carbonates generally were not detected in the XRD patterns of the products, indicating that their levels were below about 1% of the products. If it is desirable to have products with the lowest possible amounts of incorporated carbonate, it is necessary to use reagents that have very low carbonate contamination, maintained by minimal exposure of both reagents and products to air and by using only water that has been purged with nitrogen (or boiled).

The one-step procedure was successfully employed for more than 100 reactions that involve the preparation of apatites containing calcium, strontium, barium, and lead as the divalent cation; hydroxide, fluoride, chloride, bromide, and iodide as the monovalent anion; and both phosphate and vanadate as the trivalent anion. Table 1 provides selected reactions that illustrate the effect of various synthesis variables. The table provides the reactants, digestion time and temperature, the pH observed at the end of the digestion period, as well as percent yields and the full width at half maximum (FWHM) for XRD lines of specific Miller indices to provide some indication of diffraction line widths and crystallinity.

The following variables related to the synthetic procedure were investigated:

3.1 Stoichiometry. Several reactions run with either an excess or deficiency of about 20% in the amount of one reagent relative to the stoichiometric amount (as indicated in the formula of the desired apatite) show that these deviations in stoichiometry produce products whose purity and XRD patterns are very similar to those products obtained using the correct stoichiometry. For example, CaApOH prepared with a stoichiometry using excess hydrogen phosphate and hydroxide ($\text{Ca}(\text{NO}_3)_2$: Na_2HPO_4 : NaOH = 5:4:2,) produced an XRD pattern similar to that obtained using the 5:3:1 stoichiometry with FWHM of the (002) and (222) lines of 0.341, 0.73 [5:4:2], and 0.253, 0.66 [5:3:1], respectively.

3.2 Nature of reactants. Cation sources such as CaSO_4 , CaCl_2 , and $\text{Ca}(\text{NO}_3)_2$ all produced calcium hydroxylapatite with Panalytical XRD scores (100 = perfect match to database pattern) of 89, 84, and 84, respectively. The use of either Na_3PO_4 or Na_2HPO_4 as the phosphate source produced XRD scores of 84 and 90, respectively, using $\text{Ca}(\text{NO}_3)_2$ as the source of calcium. The use of NaH_2PO_4 decreased the pH of the resulting mixture due to the acidity of the dihydrogen phosphate ion and generally resulted in lower yields.

3.3 Scaling. The method is amenable to scaling. For example, the use of twice the number of moles of reagents produced CaApOH in essentially the same purity and with a similar percent yield.

3.4 pH. CaApOH can be prepared at pH values of 5-11, although lower pH results in lower yields, presumably as a result of the solubility of the apatite in acidic

solutions as well as a decrease in the equilibrium amount of ortho phosphate ion. In some syntheses of CaApF the pH was adjusted to 8, in others there was no adjustment of pH. Both procedures resulted in XRD patterns with scores above 90. For apatites containing other cations, such as SrApOH, the pH was not adjusted. For the preparation of vanadate apatites there was also no adjustment of pH.

3.5 Digestion temperature and time. Reactions using digestion temperatures from 40 °C to reflux produced CaApOH; higher temperatures generally resulted in sharper XRD patterns (Figure 1). TEM images of CaApOH prepared using various digestion times and temperatures showed the presence of porous platelets with average lengths of 47 ± 20 nm, 32 ± 14 nm, and 31 ± 14 nm for digestion at 80°C for 3h, 80°C for 20 min, and 40°C for 3 h, respectively, indicating that a temperature difference of 40° in digestion time produces about the same difference in particle size as the difference between 3 hours and 20 minutes in digestion time at 80°C.

3.6 Incorporation of carbonate. Carbonated CaApF (CCaApF) was prepared using a 1:1 mole ratio of carbonate to phosphate. The XRD pattern of the CCaApF obtained had a score of 89 and showed no peaks due to calcite. In the preparation of CCaApOH, use of a 1:1 mole ratio of NaHCO_3 to Na_3PO_4 resulted in the formation of calcite as indicated by the presence of the most intense calcite peak at 29.4 ± 2 theta in the XRD pattern of the product. A sample of CCaApOH prepared with a NaHCO_3 to Na_3PO_4 mole ratio of 1 to 2 contained no calcite phase and contained 15 wt% incorporated carbonate. This percentage of carbonate is considerably greater than the

comparable percentage of carbonate incorporated (ca. 7%) at the same mole ratio using the traditional addition method.

3.7 Formation of apatites with $M = \text{Sr}, \text{Ba}, \text{Pb}$. The versatility of the method was demonstrated by the preparation of several strontium and barium apatites. SrApOH, SrApF and BaApCl were prepared in good yield (70-85%) and with good match to reported XRD patterns (scores from 85 to 90). For the preparation of alforsite (BaApCl) the use of excess chloride was required and this was supplied by BaCl₂ as the cation source, which was mixed with Na₃PO₄ in a 5 to 3 mole ratio. With Ba(NO₃)₂ as the cation source and NaCl as the chloride source in a 5 to 1 ratio (following the stoichiometry of the formula Ba₅(PO₄)₃Cl), the product was primarily Ba₃(PO₄)₂.

3.8 Formation of vanadate apatites. The one-step procedure is particularly well suited to the synthesis of vanadate apatites, which are more often prepared by high temperature solid state methods [8-15] or mechanochemical solid state methods [16, 17], than by aqueous addition [4,18-21] although some methods use aqueous addition followed by calcination [3, 9, 22]. Table 2 shows that the one-step method was used to synthesize a total of ten different types of vanadate apatites. It is interesting to note that CaVapCl, like its phosphate analog (CaApCl), could not be obtained in aqueous solution, likely due to its greater solubility relative to CaVapOH. The synthesis of BaVapOH and BaVapCl were not successful as a result of the formation of other vanadium byproducts such as Ba₃(VO₄)₂. As indicated in Table 1, the product of the synthesis of BaVapF also

contained about 30% $\text{Ba}_3(\text{VO}_4)_2$. The major product of the synthesis of SrVapCl and SrVapBr was V_2O_5 .

The stoichiometry used for the preparation of the vanadate apatites was somewhat different than that used for the synthesis of phosphate apatites: the ratio of cation source to Na_3VO_4 to monovalent anion was generally 5 to 3 to 5. The larger amount of hydroxide was thought to be helpful in reducing the amount of calcite that appeared in the product. However, later work showed that the 5:3:1 stoichiometry also produced apatite with no calcite when a newly-opened bottle of Sigma-Aldrich 99.99% NaOH was used.

3.9 Effect of calcination. The effect of heating the product to approximately 600° C (Bunsen burner or muffle furnace) on the width of the XRD lines can be significant, as shown in Figure 2 for the heating of CaApOH prepared using the one-step method. In general, calcination increases the size of crystallites. In vanadate apatites, however, it can also lead to decomposition of co-existing calcite (also possible with phosphate apatites) (Figure 2), and formation of calcium pyrovanadate ($\text{Ca}_2\text{V}_2\text{O}_7$) as well as calcium vanadate ($\text{Ca}_3(\text{VO}_4)_2$).

4. Discussion

The one-step method has been used to successfully produce most of the phosphate apatites previously prepared by the traditional aqueous addition method. It is also useful as a fast and simple method to prepare vanadate apatites in good yield. Because it uses less glassware and no addition of reagents, the method is simpler, easier, and faster than any of the other methods used to prepare apatites. The simplicity of the set-up produces less waste and less concern about safety in handling toxic reagents and products, such as those containing lead.

A comparison of the morphology of the products prepared by the traditional and one-step methods is shown in Figure 3, which shows TEM images of CaApOH prepared by the traditional method and by the one-step method. Based on these images (consistent with images of other samples), the average crystallite sizes for the two methods are 31 ± 14 nm (one-step) and 170 ± 143 nm (traditional). The crystallites obtained with the one-step procedure are porous, nearly equiaxed platelets, while those from the traditional method are larger, more elongated in one direction, and have more pointed terminations. The large standard deviation for the sample produced by the traditional method reflects the large range in sizes of the crystallites. The difference in the average crystallite size for the two methods is likely a consequence of the longer initial nucleation and crystallization time for the traditional method, the slow addition (generally 40-60 minutes for the complete addition), as well as the more dilute solution in which crystallization occurs. The same figure (Figure 3) also provides a TEM image of SrApOH prepared by the one-step method using Na_3PO_4 . Relative to the calcium analog prepared using NaH_2PO_4 ,

SrApOH formed elongated plates with triangular tips, slightly longer (average size = 58 ± 29 nm) than the one-step CaApOH crystals. The generally greater breadth of peaks in the XRD patterns (indicative of smaller crystallite sizes) of CaApOH prepared using the one-step method compared to the aqueous addition method is consistent with the sizes measured on the TEM images. Interestingly, the XRD patterns of CaApF made using the two techniques are nearly identical.

Given the deliberately slow addition of reagents in the aqueous addition method, it is not surprising that the one-step method produces smaller crystals. What is surprising, however, is the relative lack of sensitivity of the one-step method to what might appear to be product-defining synthesis variables. For example, the one-step method is relatively insensitive to the nature of the starting reagents and pH: both dihydrogen phosphate and ortho phosphate produce the desired product in spite of the significantly different pH values of the reaction mixtures. The very low concentration of PO_4^{3-} at a pH of 5, for example, is counterbalanced by the low solubility of most apatites. This insolubility allows precipitation of the apatite in the presence of small amounts of ortho phosphate (and high concentrations of the precipitating cation). The high concentration of the reactants (and presumed high rate of nucleation) in the one-step method may also partly account for the fact that apatite is produced with a digestion time of 20 minutes and also at a temperature of 40°C. Both the TEM images and the XRD patterns reveal, however, that higher temperatures and digestion times, as well as slow addition, do have an effect on crystal size.

Most of the observations of reaction variables can be rationalized by the significantly lower solubility of the apatite phase than that of other possible products such as the hydrogen phosphate, the hydroxide, or even the phosphate phase. There is one disadvantage to the one-step method—the difficulty, produced by the high concentrations of starting materials, in controlling the percentage of carbonate in carbonated CaApOH.

5. Conclusions

This work describes an aqueous one-step synthesis of apatites that is simpler to perform and produces products similar in purity and yield to that obtained with the traditional aqueous addition method. The method and the synthesis considerations described should be of interest not only for researchers of the preparation, structure, and properties of apatites but also for those in the biomaterials area. Many apatitic biomaterials are prepared at high temperatures or using more complicated procedures; this work indicates that a wide-range of precipitation conditions will produce similar products. The method is of particular value in the preparation of vanadate apatites, predominantly prepared by more onerous high-temperature methods. The one-step method will also be of interest to those looking for the advantages produced by smaller crystallite sizes.

Acknowledgements

The authors are indebted to the Camille and Henry Dreyfus Foundation for a Senior Scientist Mentor award (CHY) and to the Lucille and William Hackman Program at Franklin & Marshall College for funding. This material is based upon work supported by the National Science Foundation under Grant No. 0923224. The authors are indebted to

Annie Gitomer Schwartz (Washington University, St. Louis, MO) for assistance with TEM microscopy and to Jill D. Pasteris (Washington University, St. Louis, MO) for helpful suggestions.

References

- [1] J. C. Elliott, Structure and Chemistry of the Apatites and Other Calcium Orthophosphates, Elsevier, New York (1994).
- [2] M. Sadat-Shojai, , M-T. Khorasani, , E. Dinpanah-Khoshdargi, , A. Jamshidi, Acta Biomater. 9 (2013) 7591.
- [3] T. Hara, S. Kanai, K. Mori, R. Mizugaki, K. Ebitani, K. Jitsukawaw, K. Kaneda, , J. Org. Chem. 71 (2006) 7455.
- [4] I. Mayer, S. Wahnou, S. Cohen, Mater. Res. Bull. 14 (1979) 1479.
- [5] D. R. Lide, ed. Handbook of Chemistry and Physics, 90th edition, 4-55 (2009).
- [6] M. Vignoles, G. Bonel, R. A. Young. Calcified Tissue Int. 40 (1987) 64.
- [7] H. McDowell, T. M. Gregory, W. E. Brown, J. Res. Nat. Bur. Stand., 81A (1977) 273.
- [8] E. R. Kreidler, F. A. Hummel, Am. Mineral. 55 (1970) 170.
- [9] E. I. Get'man, L.I. Ardanova, V. I. Marchenko, T. S. Chagir, V. V. Trachevskii, Russ. J. of Inorg. Chem. 44 (1999) 1871.
- [10] E. I. Get'man, V. I. Marchenko, S. N. Loboda, N. V. Yablochkova, Russ. J. of Inorg. Chem. 52 (2007) 147.

- [11] E. I. Get'man, N. V. Yablochkova, S. N. Loboda, V. V. Prisedsky, V. P. Antonovich, N. A. Chivireva, J. Solid State Chem. 181 (2008) 2386.
- [12] J. Kang, Y. Yang, S. Pan, H. Yu Z. Zhou, J. Mol. Struct. 1056-1057 (2014) 79.
- [13] N. V. Yablochkova, E. I. Get'man, V. I. Marchenko, S. N. Loboda, Russ. J. Inorg. Chem. 53 (2008) 850.
- [14] Z. Dong, T. J. White, B. Wei, K. Laursen, J. Am. Ceram. Soc. 85 (2002) 2515.
- [15] H. P. Beck, M. Doulheche, R. Haberkorn, H. Kohlmann, Solid State Sci. 8 (2006) 64.
- [16] Y. Suetsugu, J. Nucl. Mater. 454 (2014) 223.
- [17] M. Zhang, E. R. Maddrell, P. K. Abratis, E. K. H. Salje, Mater. Sci. Eng. B. 137 (2007) 149.
- [18] J. G. Eon, C. B. Boechat, A. M. Rossi, J. Terra, D. F. Ellis, Phys. Chem. Chem. Phys. 8 (2006) 1845.
- [19] H. Pizzala, S. Caldarelli, J. G. Eon, A. Rossi, D. Laurencin, M. Smith, J. Am. Chem. Soc. 131 (2009) 5145.
- [20] C. B. Boechat, J. Terra, J. G. Eon, D. E. Ellis, A. M. Rossi, Phys. Chem. Chem. Physics, 5 (2003) 4290.
- [21] S. Nadir, S. Lacout, G. Montel, J. C. Trombe, Ann. Chim. France, 8 (1983) 463.
- [22] R. A. Gil, Phys. Chem. Chem. Phys. 2 (2000) 4225.
- [23] Noginov, M. A., Loutts, G. B., Anderson, A., Wang, J. C. OSA Trends Opt. Photo, 19 (1998) 419.

Figure captions

Figure 1. XRD pattern for CaApOH prepared with digestion (a) of 80°C for 3 hours, and (b) of 80°C for 20 minutes.

Figure 2. Product of attempt to prepare CaVapF. (a) product after calcination at 600°C for 2 h. CaVapOH is the main constituent. (b) XRD pattern of product containing calcite, CaVapOH, and $\text{Ca}_2\text{V}_2\text{O}_7$.

Figure 3. TEM images of: top, (a) CaApOH prepared using the one-step method with Na_3PO_4 as the phosphate source, (b) CaApOH prepared using the traditional aqueous addition method, and (c) SrApOH prepared using the one-step method with Na_3PO_4 as the phosphate source.

Figures

Figure 1

(a)

(b)

Figure 2

(a)

(b)

Figure 3

(a)

(b)

(c)

RD-31_002
11:10:47 AM 10/7/2015
TEM Mode: Imaging
100 nm
HV=80.0kV
Direct Mag: 200000x
X: 435.5 Y: -657.6 T: 0
AMT Camera System

Tables

Table 1. Synthesis conditions and characterization of products of one-step synthesis of phosphate and vanadate apatites[‡]

Apatite	Reactants	Digestion	pH at end, ± 1	XRD FWHM Miller indices for (002) and (222) lines, deg (2 theta)	% Yield
		temp, time (h)			
CaApOH	CaN, HP, OH	80, 3	7	0.253, 0.66	98
	CaN, H ₂ P, OH	80, 3	5	0.345, 0.55	61
	CaN, P, OH	90, 3	11	0.296, 0.58	96

	CaS, P, OH	80, 3	10	0.383, 0.58	83
	CaCl, P, OH	80, 3	9	0.312, 0.526	84
	CaCl,P,OH	80, 0.3	9	0.367, 0.77	91
CaApF	CaN,HP,F	80, 3	8	0.185, 0.422	100
	CaN,HP,F	40, 3	6	0.233, 0.387	69
	CaN,H ₂ P,F	80, 3	4	0.111, 0.418	12
SrApOH	SrN,P,OH	80,3	7	0.204, 0.502	70
SrApF	SrN,P,F	80,3	6	(002): 0.215, (213): 0.357	84
BaApCl	Ba,Cl,P	80,3	7	(120): 0.261, (410): 0.301	70
CaVapOH	CaN, V,	90, 3	11	0.172, 0.29	99

	OH				
CaVapF	CaS, V, F	90, 3	11	1.0, 0.186	82
SrVapOH	SrN, V, OH	90, 3	11	0.238, 0.524	99
SrVapF	SrN, V, F	90, 3	9	0.27, 0.46	98
BaVapF	BaN, V, F	90, 3	9	(002): 0.24	88*
PbVapOH	PbN, V, OH	90,3	11	0.165, 0.189	96***
PbVapF	PbN, V, F	90, 3	9	0.382, 0.423	70**
PbVapCl	PbN, V, Cl	90, 3	4	0.156, 0.240	91
PbVapI	PbN, V, I	90, 3	4	0.215, 0.390	90

‡Reactants designated as MN (M = Ca, Sr, Ba, or Pb) indicate the metal nitrate (such as $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), MS indicates the metal sulfate (such as CaSO_4), and MCl indicates the metal chloride (e.g., BaCl_2); P, HP, and H_2P denote Na_3PO_4 , Na_2HPO_4 , and $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$; OH is NaOH, and F is NaF and Cl is NaCl. *included ca. 30% $\text{Ba}_3(\text{VO}_4)_2$ **contained ca. 25% PbO ***contained ca. 5% PbO

Table 2. Methods used to prepare vanadate apatites.

	Reference	Method	reagents
CaVapOH	[3]	aqueous addition	Ca(NO ₃) ₂ , Na ₃ VO ₄ , NaOH
	[20. [22]	aqueous additon, calcination	Ca(NO ₃) ₂ , NH ₄ VO ₃
	[9]	aqueous addition, calcination	CaCO ₃ , NH ₄ VO ₃
	[4]	aqueous one-step	CaSO ₄ , Na ₃ VO ₄ , NaOH
	This work	aqueous one step	CaSO ₄ / Ca(NO ₃) ₂ , Na ₃ VO ₄ , NaOH
CaVapF	[8]	solid state	CaF ₂ , Ca ₃ (VO ₄) ₂
	[14]	solid state	CaF ₂ , V ₂ O ₅ , CaO
	This work	aqueous one step	Ca(NO ₃) ₂ , Na ₃ VO ₄ ,NaF
CaVapCl	[8]	solid state	CaCl ₂ , Ca ₃ (VO ₄) ₂
	[15]	solid state	CaCO ₃ , V ₂ O ₅ , CaCl ₂ ,
SrVapOH	[4]	aqueous one-step	SrSO ₄ ,Na ₃ VO ₄ , NaOH
	[13]	solid state	Sr(NO ₃) ₂ , NH ₄ VO ₃
	[11]	aqueous addition, calcination	Sr(NO ₃) ₂ , NH ₄ VO ₃
	[10]	solid state	Sr(NO ₃) ₂ , NH ₄ VO ₃
	This work	aqueous one step	Sr(NO₃)₂, Na₃VO₄, NaOH
SrVapF	[8]	solid state	SrF ₂ , Sr ₃ (VO ₄) ₂
	[23]	solid State	SrCO ₃ , V ₂ O ₅ , SrF ₂
	This work	aqueous one step	Sr(NO₃)₂, Na₃VO₄, NaF
SrVapCl	[8]	solid state	SrCl ₂ , Srv(VO ₄) ₂

	[15]	solid state	SrCO_3 , V_2O_5 , SrCl_2
BaVapOH	[13]	solid state	BaCO_3 , NH_4VO_3
BaVapF	[12]	solid state	BaCO_3 , V_2O_5 , BaF_2
	[8]	solid state	BaF_2 , $\text{Ba}_3(\text{VO}_4)_2$
	[23]	solid State	BaCO_3 , V_2O_5 , BaF_2
	This work	aqueous one-step	$\text{Ba}(\text{NO}_3)_2$, Na_3VO_4, NaF
BaVapCl	[8]	solid state	BaCl_2 , $\text{Ba}_3(\text{VO}_4)_2$
	[15]	solid state	BaCO_3 , V_2O_5 , BaCl_2
PbVapOH	[4]	aqueous one-step	PbSO_4 , Na_3VO_4 , NaOH
	[18]	aqueous addition	NH_4VO_3 , $\text{Pb}(\text{NO}_3)_2$
	This work	aqueous one-step	$\text{Pb}(\text{NO}_3)_2$, Na_3VO_4, NaOH
PbVapF	[8]	solid state	PbF_2 , $\text{Pb}(\text{VO}_4)_3$
	[14]	solid state	CaF_2 , V_2O_5 , PbO
	This work	aqueous one-step	$\text{Pb}(\text{NO}_3)_2$, Na_3VO_4, NaF
PbVapCl	[8]	solid state	PbCl_2 , $\text{Pb}_3(\text{VO}_4)_2$
	This work	aqueous one step	$\text{Pb}(\text{NO}_3)_2$, Na_3VO_4, NaCl
PbVapI	[17]	solid state	PbO , NH_4VO_3 , PbI_2
	[16]	solid state	PbO , V_2O_5 , PbI_2
	This work	aqueous one step	$\text{Pb}(\text{NO}_3)_2$, Na_3VO_4, NaI