Synthesis of monoclinic monazite, LaPO₄, by direct precipitation

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The direct synthesis of LaPO₄ and La₀.₉₆Sr₀.₀₄PO₄ monazite using nitrates and phosphoric acid to produce uniform and non-agglomerated monazite powders without the formation of any intermediate hydrated rhabdophane phase (LaPO₄·½H₂O) is described.

Monoclinic lanthanum phosphate (monazite) is a compound with a very high melting temperature (∼2000 K), very insoluble in water, and with high chemical stability; it has been proposed for use in broad applications. Its resistance to radiation damage and relative stability as a mineral over billions of years has led to the identification of monazite as a candidate material for the immobilization of radioactive waste elements by incorporation into the monazite crystal lattice.[1–3] When doped with some divalent elements, such as strontium, it potentially might be used in proton conducting systems as an intermediate temperature electrolyte.[4–7] Monazite acts as a highly efficient lamp phosphor when cerium or terbium are substituted into the crystal lattice.[8] Its ability to form weak interfaces with other oxides allows its use in two-phase mixtures of refractory oxides for fiber reinforced composite systems and machinable ceramics.[9]

Synthesis of monazite has been conducted *via* combustion synthesis,[10] aqueous precipitation utilizing rare earth chlorides,[11] nitrates,[12] *etc.*, polyol methods,[13] and solid state reactions of rare earth oxides.[14] A common route to the formation of monazite is *via* solid state synthesis, but this technique is slow, energy-intensive, and it is difficult to achieve a uniform composition. Solution routes yield the hexagonal derivative, LaPO₄·½H₂O (rhabdophane). Heating is then required to form monazite. Rhabdophane typically exhibits needle-like particle morphology, and as formed, contains excess phosphorus, which, if it is not properly removed by subsequent treatment, engenders liquid phase formation/problems within samples during sintering at high temperatures.[15] The polyol method to fabricate LaPO₄ monazite colloids at 160–180 °C requires further heat treatment to 400 °C or subsequent solvent washes to remove residual diethylene glycol.[13,16] Finally, synthesis of monazite involving chlorides produces undesirable byproducts, including HCl.[12] It thus becomes apparent, when considering the drawbacks of these synthesis routes, that a direct precipitation of monazite powders, eliminating byproducts or intermediates, would be more economical and desirably simple.

This novel method described herein for the direct synthesis of monoclinic monazite-type LaPO₄ by precipitation is an irreducibly simple process and would easily scale to large commercial quantities. The experimental parameters for two direct precipitation syntheses were discovered utilizing solid or aqueous additions of a lanthanum complex. While the particle morphologies of the two synthesis

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variants differed considerably, as will be discussed later, the crystal structures were confirmed by X-ray diffraction to be monoclinic monazite without the presence of any hexagonal rhabdophane.

Lanthanum nitrate hexahydrate [La(NO₃)₃·6H₂O₍ₛ₎], purchased from Fisher Chemicals, was chosen as the lanthanum containing reactant, and phosphoric acid [H₃PO₄₍ₗ₎], purchased from J. T. Baker, was chosen as the phosphorus source. In order to circumvent the formation of rhabdophane, the hydrated hexagonal form of LaPO₄, it is necessary to deny water to the precipitating crystals. Concentrated phosphoric acid was heated to a temperature of 150 °C, still below its boiling point. At this temperature, any free water is evaporated. La(NO₃)₃·6H₂O was added to the heated phosphoric acid both as a solid (Method I) and dissolved in water (Method II). Nevertheless, this latter process can be considered non-aqueous since there is instantaneous removal of water upon drop by drop addition of the nitrate solution to the 150 °C phosphoric acid

Solid La(NO₃)₃·6H₂O was directly dissolved in hot phosphoric acid (Method I), and the emission of NOₓ gas and water vapor occurred, followed by the precipitation of milky white solid particles within 30 minutes. Addition of the La nitrate, first dissolved in water, to hot phosphoric acid (Method II) was carefully conducted to limit any temperature drop and to ensure that violent reactions did not result from the addition of water to hot acid. Immediately upon contact with the phosphoric acid, water could be observed boiling off, confirming that the lanthanum was introduced into solution without available water present. Similar to the solid addition, Method II synthesis yielded a white precipitate after 30 minutes following the first addition of drops of the nitrate solution. Precipitated powders were allowed to settle before they were collected by diluting the product solution with water and filtering it *via* Whatman #1 Qualitative Filter Paper.

The powders from each synthesis route were analyzed by powder X-ray diffraction using a Siemens D5000 powder diffractometer with a Cu-Kₐ X-ray source (λ = 1.5418 Å) in order to confirm the crystal
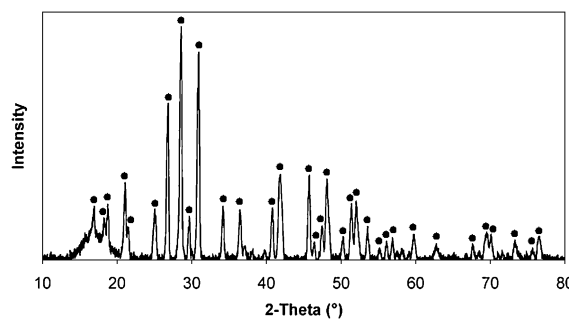

Fig. 1 XRD pattern of as-prepared LaPO₄ by direct, non-aqueous synthesis. Comparison to the powder diffraction pattern of monoclinic LaPO₄ (PDF 01-083-0651) is shown using dots for reference.

structure. Fig. 1 shows diffraction data collected for the powders made by Method II (similar data were obtained for Method I). XRD confirms the sole presence of the monoclinic monazite structure without any detectable hexagonal rhabdophane. In comparison, when the phosphoric acid was held at a lower temperature of 120 °C, a mixture of both rhabdophane and monazite forms, as identified by XRD patterns with distinct peaks appearing at 14.5° and 19.9° 2θ from the hexagonal rhabdophane. The broad peak from 15° to 20° 2θ was determined to be caused by the amorphous plastic sample holder, and was subsequently minimized in later runs. Previously published precipitation routes to monazite have typically found the formation of rhabdophane or mixtures of rhabdophane and monazite. At 150 °C, all water is allowed to be removed, and the formation of purely monoclinic monazite is then ensured. We have never observed any crystalline higher phosphates, such as LaP_3O_9, in our work, even though a vast excess of phosphate is available. Higher phosphates are known to be formed by solid state techniques so, perhaps, these are not stable low temperature phases.[17] Usually kinetics are fast enough in solution techniques to produce the thermodynamically most stable phases.

Further characterization of the monazite powders was conducted *via* scanning electron microscopy (SEM) on a Zeiss Ultra 55. Samples mounted on adhesive carbon tape were coated with a fine layer of carbon in order to reduce charging during SEM imaging. Secondary electron imaging was conducted utilizing an accelerating voltage of 10.0 keV. Fig. 2 compares the particle morphologies of the
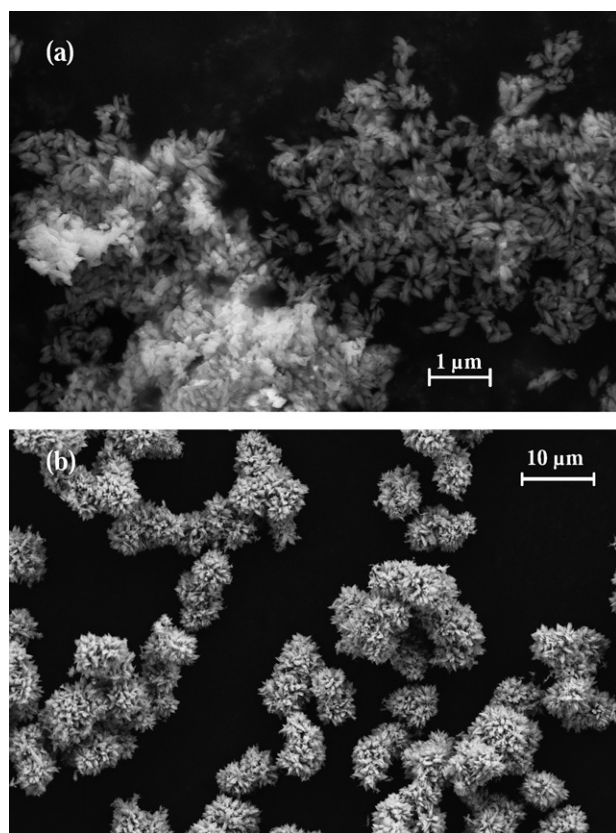
synthesized powders made by Methods I and II. Samples produced by Method I show very distinct rice-shaped particles of 200–400 nm that often appear in agglomerates. When grinding the powders, large and strong agglomerates were difficult to break up. Samples produced by Method II showed distinct floweret shaped particles ~5–10 μm in size, which may have been created by nucleation from a central nucleus (as for spherulites). The petals (again rice shaped) are approximately 0.6–1.0 μm in size within each floweret. Further investigation indicated that Method II yielded powders that were more mono-dispersed and more uniform than those produced by Method I. Therefore, powders from Method II were finer and smoother, compared to powders from Method I that were more granulated and coarse to the touch.

Experiments were conducted to confirm whether monazite could be fabricated using the same process but with the introduction of dopants. Since strontium-doped monazite has been proposed for use in proton conducting systems,[4–7] the direct synthesis methods described here were adapted to test the introduction of strontium into the crystals. $La(NO_3)_3 \cdot 6H_2O_{(s)}$ and $H_3PO_{4(l)}$ were used as reactants as described previously, while strontium nitrate $[Sr(NO_3)_{2(s)}]$, purchased from Fisher Chemicals, was chosen as the strontium source. Compositions included up to 4% atom substitution of strontium for lanthanum $[La_{0.96}Sr_{0.04}PO_4]$. The same synthesis routes described for Methods I and II were used, keeping the temperature of the acid at 150 °C. Solid strontium nitrate was either added sequentially or simultaneously with the lanthanum nitrate directly to the phosphoric acid, and yielded the same type of product as in Method I. In the liquid version (Method II), strontium and lanthanum nitrates were dissolved together in water before dropwise addition to the phosphoric acid. Once the reactants were combined together, dissolution immediately occurred, followed by precipitation of fine white particles as described previously. As in the undoped synthesis preparation, precipitates were allowed to settle before eventual dilution, filtration, and drying at room temperature.

X-Ray diffraction patterns for the Sr-doped products exhibited monazite patterns with the monoclinic structure. As shown in Fig. 3, all peaks indexed to pure monoclinic monazite, even with the incorporation of the strontium dopant. Just as before, XRD patterns obtained for the solid addition products matched those in Fig. 3 obtained for the nitrates dissolved in water prior to addition. No other phases are detectable.

Characterization of the Sr-doped monazite products was conducted by SEM, with samples prepared and examined in a similar
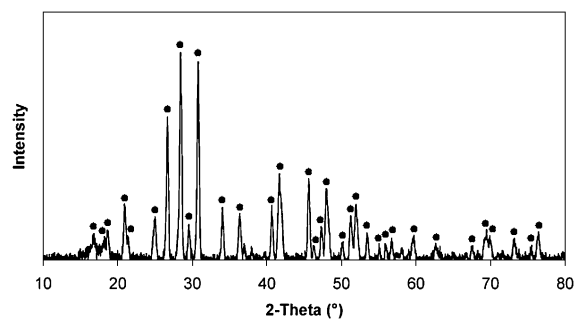

Fig. 2 SEM images of as-prepared $LaPO_4$. (a) Rice-shaped fine particles and agglomerates produced using Method I. (b) Uniform floret-shaped particles produced using Method II.

Fig. 3 XRD pattern of as-prepared Sr-doped $LaPO_4$ using Method II. Comparison to the reported powder diffraction pattern of monoclinic $LaPO_4$ (PDF 01-083-0651) is shown by dots for reference.
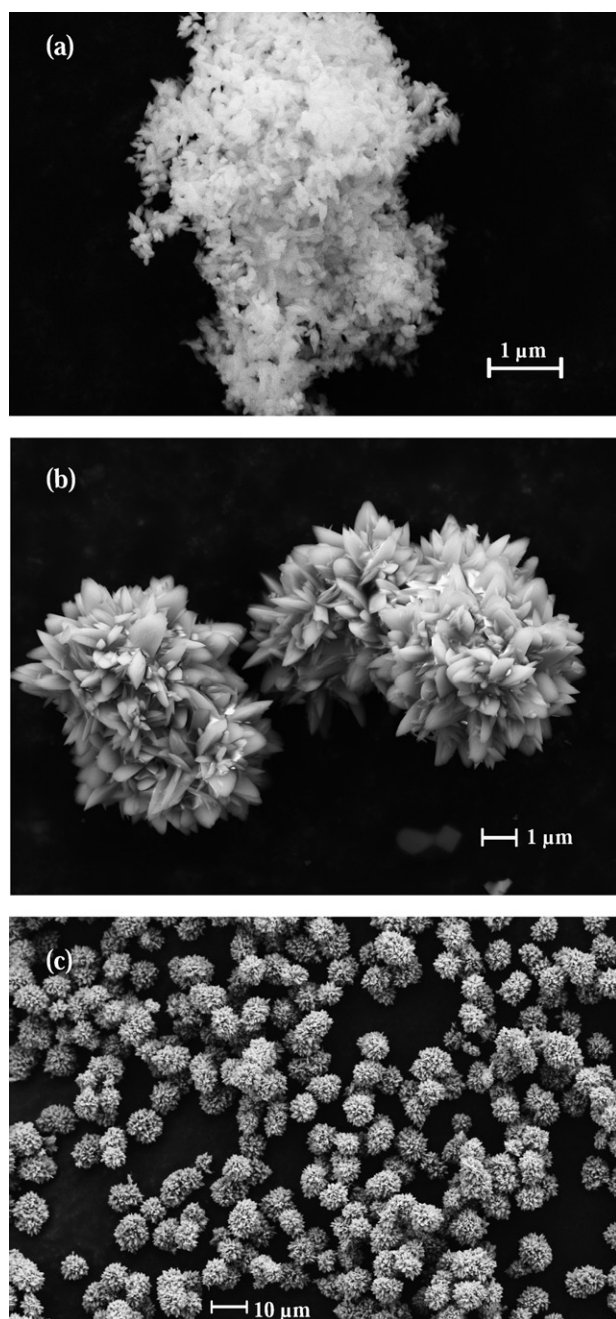
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Fig. 4 SEM images of as-prepared $La_{0.96}Sr_{0.04}PO_4$. (a) Method I with fine particles agglomerated. (b) Method II, showing distinct floret structure. (c) Method II showing uniform non-agglomerated nature of the $La_{0.96}Sr_{0.04}PO_4$ precipitates.

fashion as before. The crystal morphologies of the Method I and the Method II doped products resembled their respective undoped counterparts (Fig. 4). The same distinct rice-shaped morphology with particles of 200–400 nm formed for products of Method I, with strong agglomeration observed. Distinct floweret-shaped particles of size ~5–10 μm were again observed for the Sr-doped products of Method II. The uniform and fine nature of the precipitates can be contrasted with Sr doped monazite prepared *via* other low temperature routes.[6] Analysis from energy dispersive spectroscopy (EDS) on the SEM indicated that Sr was incorporated in the $LaPO_4$ powders, to at least 4 atom%. This new, easy processing route seems to increase the solubility of strontium and maybe other such dopants.

While the successful discovery of this direct synthesis route is encouraging and will find many applications, there still remain many questions to be explored, such as the influence this synthesis method may have on sintering and material properties of densified bodies of the material. With these direct synthesis pathways, it is conjectured that the dopant solubility of strontium and other compatible cations may be improved to facilitate better material properties, including higher proton conductivity. This process is also being explored for possible applications involving nuclear waste storage. This synthesis method offers a simplified material processing in a remote environment with a direct method to fabricate monazite with radioactive waste cations, and a process directly compatible with nitrate waste streams. The relevant findings are patent pending at the University of California, Irvine.

Acknowledgements

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