Nano materials from molten salts: Preparation of nano-sized lanthanide phosphates from chloride melts

V. A. Volkovich,[1] T. R. Griffiths[2] and R. C. Thied[3]

[1] Centre for Radiochemistry Research, Department of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom
[2] School of Chemistry, University of Leeds, Leeds, LS2 9JT, United Kingdom
[3] British Nuclear Fuels plc (BNFL), Sellafield R & D, Sellafield, Seascale, Cumbria,
CA20 1PG, United Kingdom

The formation of lanthanide phosphates in chloride melts has previously only been reported in NaCl, KCl and NaCl-KCl-based melts containing added lanthanide(III) chloride and using sodium or potassium *ortho*phosphates as precursors (1). The reaction was said to yield only the double phosphates of the composition $M_3Ln_2(PO_4)_3$ (M = Na, K; Ln = Ce, Pr, Nd, Sm, Eu, Gd). These phases were found to be essentially insoluble in molten chlorides (2).

Here we have studied the formation of phosphates of the lighter lanthanides (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy) by reaction of $LnCl_3$ with alkali metal phosphates in a LiCl-KCl eutectic melt between 450 and 650 ^oC and in a NaCl-KCl equimolar melt at 750 ^oC under an inert (Ar) atmosphere. *Ortho*-, *meta*- and *pyro*phosphate precursors have been employed.

The reaction in LiCl-KCl-$LnCl_3$ with sodium *ortho*phosphate at 550 ^oC yielded normal *ortho*phosphates of composition $LnPO_4$. These had the monoclinic (monazite type) structure when Ln = La, Ce, Pr, Nd, Sm, Eu and Gd, or tetragonal (xenotime type) structure if Ln = Tb or Dy. Precipitated lanthanide *ortho*phosphates, $LnPO_4$, can be separated from the alkali chloride melt as independent solid phases which are not significantly soluble in the melt. The mean crystallite size of precipitated phosphates was evaluated from X-ray powder diffraction patterns, employing Scherrer's equation, and found to be within 300 - 400 Å. The nature of the lanthanide did not noticeably influence the particle size of the precipitate. The influence of the concentration of added *ortho*phosphate and temperature on the precipitation of cerium phosphate has been studied in detail. Essentially complete precipitation of this lanthanide was possible at $PO_4^{3-} : Ce^{3+}$ mole ratio of *ca*. 5, Fig. 1A. Exceeding this ratio led to the additional precipitation of lithium phosphate, Li_3PO_4 Fig. 1B. There is no clear correlation between the particle size of the precipitate and the concentration of added phosphate. Increasing the temperature from 450 to 650 ^oC did not affect the composition of the precipitate but led to an increase in particle size of precipitated $CePO_4$. Addition of sodium *meta*- or *pyro*phosphate to LiCl-KCl-$CeCl_3$ melt resulted in the precipitation of monoclinic $CePO_4$. The particle size of $CePO_4$ depended on the phosphate precursor used and increased in the order *ortho*- < *meta*- ≤ *pyro*-. Lithium and potassium *ortho*phosphates have also been tested as precipitants and were found as efficient as Na_3PO_4.

The precipitation of lanthanide phosphates by reacting solid lithium phosphates with molten LiCl-KCl-$LnCl_3$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy) has been studied at 550 ^oC. Lanthanide chlorides were introduced into the melt as anhydrous $LnCl_3$ salts. The reaction with lithium *ortho*phosphate (at a phosphate-to-lanthanide mole ratio of 5) resulted in the formation of normal *ortho*phosphates, $LnPO_4$. The particle size of the precipitated phosphates was in the range 30 - 45 nm. The kinetics of the precipitation of Nd and Pr phosphates was studied using high temperature spectroscopy.

The precipitation of lanthanide phosphates by reacting sodium phosphates with molten NaCl-KCl-$LnCl_3$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy) has been studied at 750 ^oC. Lanthanide chlorides were introduced into the melt either as anhydrous $LnCl_3$ salts or by reacting corresponding oxides with chlorine in fused NaCl-KCl. The reaction with sodium *ortho*phosphate (at a phosphate-to-lanthanide mole ratio of 5) resulted in the formation of predominantly double phosphates, $Na_3Ln(PO_4)_2$ and normal *ortho*phosphates, $LnPO_4$. The particle size of the precipitated phosphates was in the range 10-50 nm. Some of the phases formed could not be identified by X-ray powder diffraction with certainty. In NaCl-KCl-$CeCl_3$ melts, increasing the initial $PO_4^{3-} : Ce^{3+}$ mole ratio from 1 to 10 led to a change in the composition of phosphate precipitate. At low mole ratio monoclinic $CePO_4$ was a main product and, at high mole ratio, tetragonal $Na_3Ce(PO_4)_2$. The phosphate formed at intermediate phosphate content is postulated as $Na_3Ce_2(PO_4)_3$. The reaction of sodium *meta*phosphate with NaCl-KCl-$CeCl_3$ melt yielded exclusively monoclinic $CePO_4$.

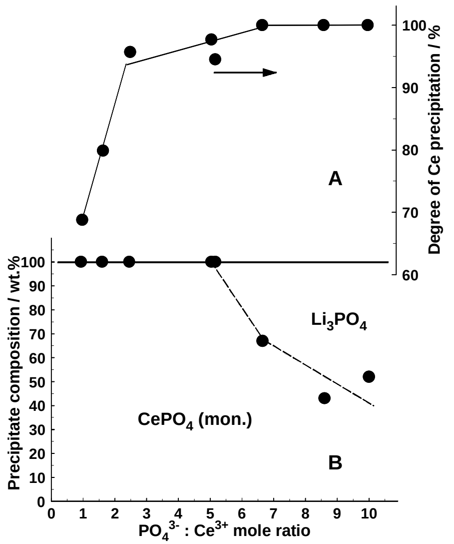

Fig. 1. Effect of $PO_4^{3=} : Ce^{3+}$ mole ratio on precipitation of cerium phosphate. A, yield of cerium into $CePO_4$ upon reacting LiCl-KCl-$CeCl_3$ melts with Na_3PO_4. B, estimated composition of the solid phase.

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