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

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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 orthophosphates as precursors (1). The reaction was said to yield only the two phosphates of the composition M₂Ln₃(PO₄)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 LnCl₃ with alkali metal phosphates in a LiCl-KCl eutectic melt between 450 and 650 °C and in a NaCl-KCl equimolar melt at 750 °C under an inert (Ar) atmosphere. Ortho-, meta- and pyrophosphate precursors have been employed.

The reaction in LiCl-KCl-LnCl₃ with sodium orthophosphate at 550 °C yielded normal orthophosphates of composition LnPO₄. 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 orthophosphates, LnPO₄, can be separated from the alkali chloride melt as independent solid phases which are not significantly soluble in the melt. The mean crystal 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 orthophosphate and temperature on the precipitation of cerium phosphate has been studied in detail. Essentially complete precipitation of this lanthanide was possible at PO₄³⁻ : Ce³⁺ mole ratio of ca. 5, Fig. 1A. Exceeding this ratio led to the additional precipitation of lithium phosphate, Li₃PO₄, 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 °C did not affect the composition of the precipitate but led to an increase in particle size of precipitated CePO₄.

Addition of sodium meta- or pyrophosphate to LiCl-KCl-CoCl₂ melt resulted in the precipitation of monoclinic CePO₄. The particle size of CePO₄ depended on the phosphate precursor used and increased in the order ortho- < meta- ≤ pyro-. Lithium and potassium orthophosphates have also been tested as precipitants and were found as efficient as NaPO₄.

The precipitation of lanthanide phosphates by reacting solid lithium phosphates with molten LiCl-KCl-LnCl₃ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy) has been studied at 550 °C. Lanthanide chlorides were introduced into the melt as anhydrous LnCl₃ salts. The reaction with lithium orthophosphate (at a phosphate-to-lanthanide mole ratio of 5) resulted in the formation of normal orthophosphates, LnPO₄. 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-LnCl₃ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy) has been studied at 750 °C. Lanthanide chlorides were introduced into the melt either as anhydrous LnCl₃ salts or by reacting corresponding oxides with chlorine in fused NaCl-KCl. The reaction with sodium orthophosphate (at a phosphate-to-lanthanide mole ratio of 5) resulted in the formation of predominantly double phosphates, Na₃Ln₃(PO₄)₃ and normal orthophosphates, LnPO₄. 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-CoCl₂ melts, increasing the initial PO₄³⁻ : Ce³⁺ mole ratio from 1 to 10 led to a change in the composition of phosphate precipitate. At low mole ratio monoclinic CePO₄ was a main product and, at high mole ratio, tetragonal Na₃Ce₄(PO₄)₃. The phosphate formed at intermediate phosphate content is postulated as Na₃Ce₃(PO₄)₃. The reaction of sodium metaphosphate with NaCl-KCl-CoCl₂ melt yielded exclusively monoclinic CePO₄.

Fig. 1. Effect of PO₄³⁻ : Ce³⁺ mole ratio on precipitation of cerium phosphate. A, yield of cerium into CePO₄, upon reacting LiCl-KCl-CoCl₂ melts with NaPO₄. B, estimated composition of the solid phase.

REFERENCES