P-11: Sonochemical Precipitation of Uranium and Lanthanide Oxides and Phosphates

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In this work, we examined feasibility of sonochemical precipitation of lanthanide and uranyl ions from their solutions in organic solvents, such as tetraglyme and triethylphosphate, with the aim of potentially using this procedure for removing radioactive elements from nuclear waste streams. The precipitated compounds should be easily converted to highly insoluble waste forms, such as mixed metal oxides and phosphates, for long-term deposition and safe storage. We used 2,4-pentanedionato (acac) complexes of lanthanide and uranyl ions as initial surrogate models for radionuclides and by sonolysis obtained amorphous precipitates that were converted to particular oxides and phosphates by calcination. All obtained precipitates were characterized by ICP-OES elemental analyses for metal content, nitrogen adsorption/desorption isotherms for surface areas, IR spectroscopy for the identification of residual organic groups, and by SEM images. Their thermal behavior was studied by TG/DSC analysis and resulting phases were identified by powder X-ray diffraction (XRD) analysis.

Sonolysis of a series of 2,4-pentanedionato complexes, $M(acac)_3$, M = Y, La, Ce, Pr, Nd, Eu, Dy, Er, and $UO_2(acac)_2$ was carried out in tetraglyme (tetraethyleneglycol dimethylether, TGL) or triethylphosphate (TEP) under Ar atmosphere on a Sonics and Materials VXC system with 500 W input power and working frequency of 20 kHz. Acetylacetonate precursors (0.50 g) were dissolved in TGL or TEP (50 cm^3), purged with Ar and cooled with a Julabo F 25-MP thermostat. Sonication was run for 8 h under Ar. The product was precipitated by the addition of hexane (20 cm^3) and the solid was separated from the solvents by centrifugation on a Heraeus Labofuge 400 at 3000 rpm. The powders were washed by isopropanol and light petroleum and left to dry in open air.

The sonolysis of $Ce(acac)_3$ in TGL provided an amorphous powder with major bands in its IR spectrum at 1560 a 1415 cm^{-1}, which correspond to $\nu_{as}(COO)$ a $\nu_s(COO)$ vibrations of acetates produced by the acac ligand decomposition. Calcination of the powder to 1000 °C in air led to the formation of cubic CeO_2 identified by its XRD powder pattern (PDF card 34-394). Similarly, sonolysis of $Pr(acac)_3$ afforded an amorphous product that was converted to Pr_6O_{11} (PDF card 42-1121) in several steps observed by TG/DSC thermal analysis. Similarly, the acac complexes of La, Nd, Eu, Dy, and Er provided upon sonolysis powders with high surface areas up 380 m^2/g (by BET analysis) and were subsequently transformed in an analogous manner to corresponding Ln_2O_3 oxides.

$UO_2(acac)_2$ was sonicated both in TGL and in TEP. The sonoreaction in an inert solvent TGL provided an amorphous powder with an IR band of uranyl stretching vibration at 929 cm^{-1}. Thermogravimetric analysis showed a total mass loss of 62.58 % in the stepwise conversion to U_3O_8 (PDF card 31-1424). On the other hand, by using a reactive solvent $OP(OEt)_3$ (TEP), we were able to obtain UP_2O_7 (PDF card 16-233) as the final product of calcination of the amorphous sonolysis product.

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References

Pinkas J., Reichlova V., Zboril R., Moravec Z., Bezdicka P., Matejkova J., 2008, Sonochemical synthesis of amorphous nanoscopic iron(III) oxide from $Fe(acac)_3$, Ultrasonic Sonochemistry 15, 256-264.

Pinkas J., Reichlova V., Serafimidisova A., Moravec Z., Zboril R., Jancik D., Bezdicka P., (2010), Sonochemical Synthesis of Amorphous Yttrium Iron Oxides Embedded in Acetate Matrix and their Controlled Thermal Crystallization toward Garnet ($Y_3Fe_5O_{12}$) and Perovskite ($YFeO_3$) Nanostructures, J. Phys. Chem. C 114, 13557-13564.