Synthesis and Crystal Structure of NZP-Type Thorium-Zirconium Phosphate

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Electronic Supplementary Information

Synthesis. $Th_{1/4}Zr_2(PO_4)_3$ microcrystal powder synthesis was carried out by sol-gel technology including organic complex formation and etherification processes (Pechini method) (Pechini, M.P. *US Patent* **1967**, *3330697*; Kakihana, M. *J. Sol-Gel Sci. Technol.* **1996**, *6*, 7). Reagent-grade $Th(NO_3)_4{\cdot}4.3H_2O$, $ZrOCl_2{\cdot}8H_2O$ and $NH_4H_2PO_4$ were used as starting materials in a molar ratio 1:8:12 (Th:Zr:P) with citric acid (CA) as polymer precursor and distilled water as solvent. Thorium nitrate has been dissolved in 1 M $ZrOCl_2$ aqueous solution and, later, citric acid (molar ratio $CA:M^{IV}$ = 15:1; M^{IV} = Th+Zr) was added. After homogenization of the solution, ethylene glycol (EG) (molar relation EG:CA = 4:1), dissolved in 1 M $NH_4H_2PO_4$, was dropped with permanent stirring. By heating at 100 °C, CA-EG esterification-polymerization was accelerated to produce a viscous gel that was dried at 150 °C. Then powder was sequentially heated at 600, 700, 800, 900, 1000 and 1100 °C during 24 hours in each stage. After each heating process, the powder have been grinded in agate mortar and their powder X-ray pattern was collected on a conventional powder diffractometer Shimadzu LabX XRD-6000 (Fig. 1). When T ≤ 800 ºC , the material is amorphous. At T = 900-1000 ºC a new compound ($Th_{1/4}Zr_2(PO_4)_3$), with $NaZr_2(PO_4)_3$ type structure, was obtained. When T ≥ 1100 ºC, the solid transform to a multiphase material, where several crystalline phases ($Zr_2P_2O_9$, ThP_2O_7, ZrP_2O_7, ThO_2, ZrO_2) were detected.

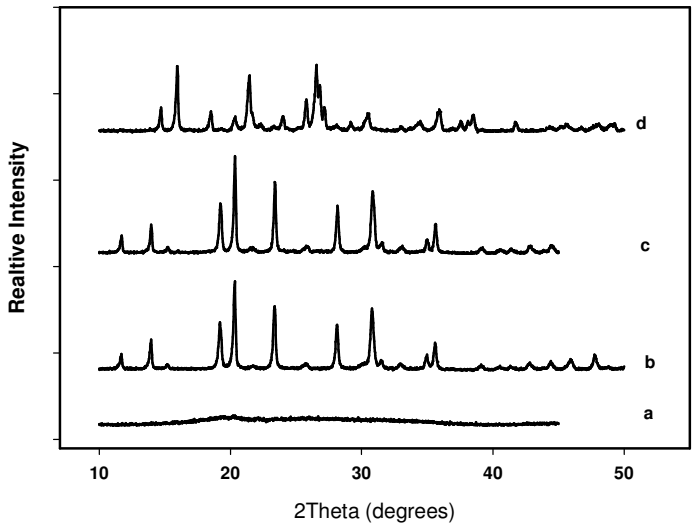

Figure 1. *Powder X-ray diffraction patterns of the samples as a function of treatment temperature: a) 800 °C, b) 900 °C, c) 1000 °C and d) 1100 °C.*

Analytical data for the sample obtained at 900 ºC. Infrared absorption spectra (Fig. 2) were recorded on a Shimadzu IR Prestige-21 FT spectrophotometer by the KBr pellet technique. The vibrations of the P-O bonds are observed from 500 to 640 cm^{-1} (ν_{as}), 920 to 980 cm^{-1} (ν_s), and about 1000 to 1160 cm^{-1} (ν_{as}). SEM (recorded with a JEOL JSM-6100 electron microscope operating at 20 kV) and TEM (recorded with JEOL-2000EX-II electron microscope operating at 200 kV) micrographs (Figs. 3 and 4) reveal a platelike morphology for irregular particles with size from 20 to 70 nm. Energy dispersive X-ray analysis are coherent with the $Th_{1/4}Zr_2(PO_4)_3$ composition.

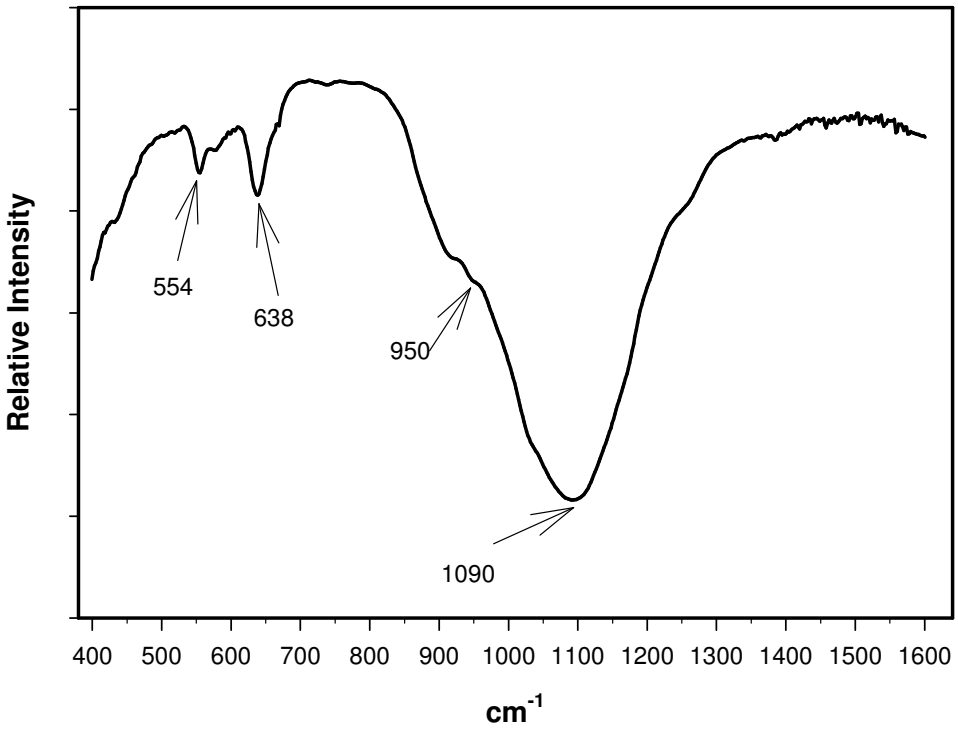

Figure 2. *IR spectra of $Th_{1/4}Zr_2(PO_4)_3$*

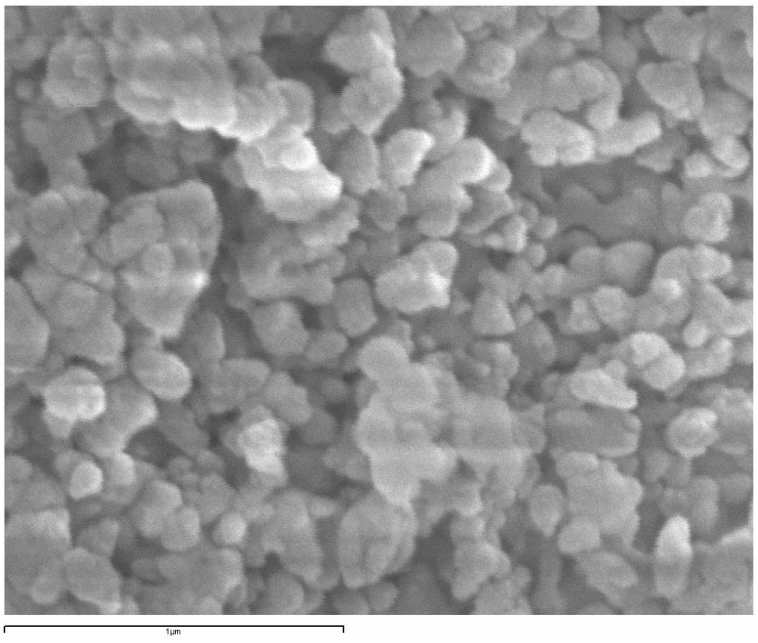

Figure 3. *SEM image of $Th_{1/4}Zr_2(PO_4)_3$ (50000x magnification).*

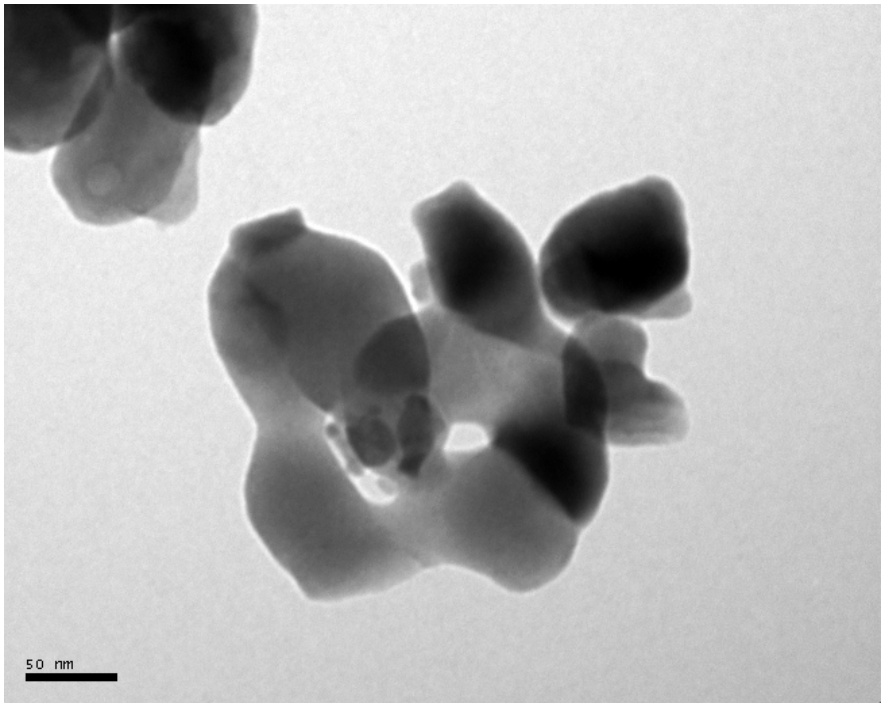

Figure 4. *TEM image of $Th_{1/4}Zr_2(PO_4)_3$ (200000*x *magnification).*

Powder diffraction data. $Th_{1/4}Zr_2(PO_4)_3$ X-ray powder diffraction pattern was recorded at beamline BM25A at the European Synchrotron Radiation Facility (ESRF), Grenoble (France). The sample was finely ground and loaded in a 0.5 mm diameter capillary. This capillary was mounted in a rotatory goniometer. Room-temperature data were collected in the continuous 2θ-scan mode from 3º to 60º using an incident wavelength of 0.82456 Å (calibrated with silicon powder; a = 5.430825 Å). The counts from the different channels were rebinned to produce an equivalent normalized step scan of 0.02º step intervals. The pattern was indexed using the program TREOR (Werner, P.E.; Eriksson, L.; Westdahl, M. *J. Appl. Crystallogr.* **1985**, *18*, 367) in the hexagonal system with lattice parameters $a = b = 8.749(1)$ Å, $c = 23.355(8)$ Å and figures of merit: $M_{17} = 19$, $F_{17} = 29$ (0.007, 79) and DICVOL04 (Boultif, A. & Louer, D. *J. Appl. Crystallogr.* **2004**, 37, 724) in the hexagonal system with lattice parameters $a = b = 8.741(2)$ Å, $c = 23.349(6)$ Å and figures of merit: $M_{20} = 25$, $F_{20} = 54$ (0.004, 87). Systematic absences were consistent with the space group $P\bar{3}c$ (No. 165). The structure refinement based on $Eu_{1/3}Zr_2(PO_4)_3$ structural model was carried out using the Rietveld method as implemented in the program GSAS (Larson, A.C.; Von Dreele, R.B. *General Structure Analysis System (GSAS)*; Los Alamos National Laboratory, Report LAUR, 1994; p 86). Initial least squares refinements of the profile included terms for the scale factor, background, lattice parameters, zero point, and peak shape. Atomic positions $Th_{1/4}Zr_2(PO_4)_3$ were refined with soft constraints consisting of Zr-O and P-O bond distances. The refinement of the positional parameters as well as their thermal parameters in isotropic approximation converged with the following final unit cell parameters: $a = b = 8.7311(4)$ Å, $c = 23.3090(19)$ Å, $Z = 6$ and $V = 1538.79(23)$ Å^3. Finally, 42 parameters were refined and gave good reliability factors $R_P = 0.071$ and $R_{WP} = 0.092$ (see Fig. 5).

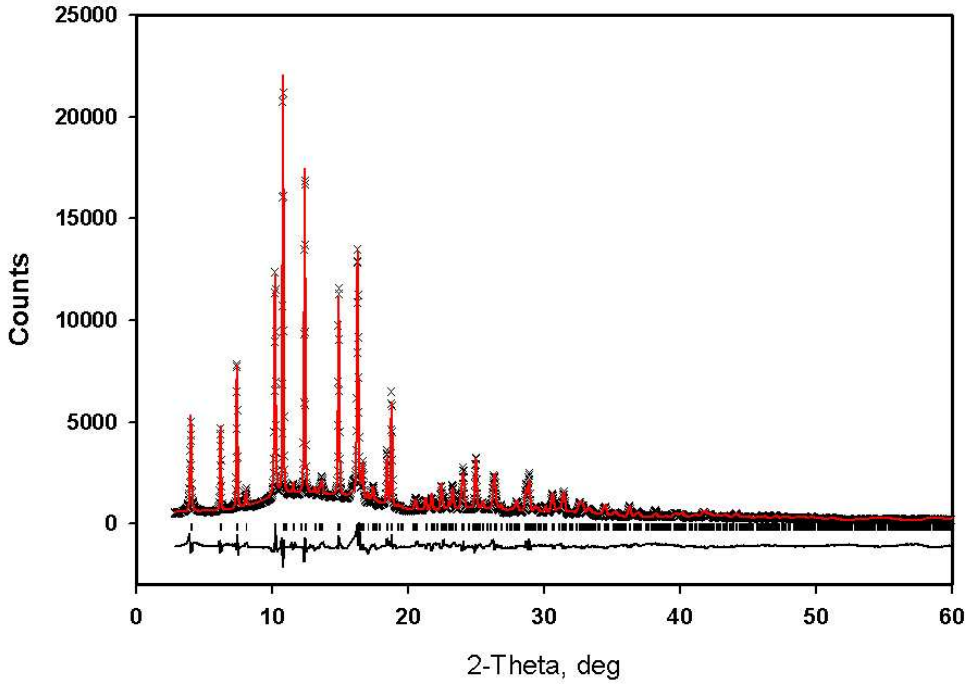

Figure 5. *X-ray diffraction powder patterns of* $Th_{1/4}Zr_2(PO_4)_3$. *Observed* (x), *calculated* (*line*) *and difference (below) profiles are plotted on the same scale. Bragg peaks are indicated by tick marks.*

Structural details. See "ThZrP-Oviedo-IC.cif" file.