

ELECTRONIC SUPPLEMENTARY INFORMATION

Acetate-citrate gel combustion: a strategy for the synthesis of nano sized Lutetium Hafnate phosphor powders

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I - Synthetic and experimental procedures

Synthesis of Lu₄Hf₃O₁₂ nano-particles via acetate-citrate gel combustion.

Hafnium tert-butoxide and lutetium acetate were used as metal precursors; since the Hf precursor is highly reactive towards water, it is necessary to handle with care this compound under nitrogen or argon in a dry box.

For each sample, a solution of lutetium citrate complexes was obtained in air by dissolving 0.62 g of lutetium acetate hydrated (99.9% - Multivalent Limited) previously dried in argon flux for 12h at 120°C in a quartz vessel, in 4.2 ml of water (Merck) containing 1.05 g citric acid (Sigma-Aldrich, 99.999%). The solution remained slightly opalescent under magnetic stirring over 2h at 80 °C.

0,525 ml of Hafnium tert-butoxide (99.99%, Multivalent) were added in nitrogen atmosphere to 0.5 ml of ethanol (99.8% v/v - Fluka) and a solution of Hf(CH₃COO)₄ was obtained by adding 1.4 ml of acetic acid (99-100%, Riedel de Hën) under magnetic stirring; the resulting solution was diluted by adding 2.8 ml of water.

Dopants solutions were obtained from Ce(III)(NO₃)₃•6H₂O (99.999%), Tb(III)(NO₃)₃•5H₂O (99.9%), Eu(III)(NO₃)₃•5H₂O (99.9%) and Bi(III)(CH₃COO)₃ (99.99%), all purchased by Sigma-Aldrich, dissolved in 10% v/v acetic acid, with a final trivalent ion concentration equal to 1.8 x 10⁻² M. The doping was achieved through the addition of proper amounts of these solutions into hafnium acetate solutions. Nominal concentrations of 0.1, 0.5 and 1 mol% were considered with respect to the total amount of Lu.

By dropping the Lu citrate sol into hafnium acetate, a colloidal system was was fastly obtained. The complete precipitation of the acetate-citrate gels was performed by drying the suspensions in rotating evaporator at 95 °C. The resulting powders were dried in vacuum over 2h, milled in agate mortar and sintered in quartz vessels with the following program: i) heating ramp from 40 to 450 °C in air (heating rate of 33 °C/h); ii) stasis at 450° in pure oxygen flux (duration 8 hours); iii) heating ramp from 450 to 1150 °C in pure oxygen flux (heating rate of 50 °C/h); iv) stasis at 1150 °C (duration 1 hour). The cooling down to room temperature was held in about 10 hours.

Characterization

SEM and TEM Analyses

Scanning electron microscopy (SEM) micrographs were obtained using secondary electrons by a Tescan Vega TS 5136XM operated at 20 kV, and equipped with EDAX Genesis 4000 XMS Imaging 60 SEM for microanalysis. The sample was prepared by dispersing the powders in acetone and dropping the suspensions on silicon polished wafers.

Transmission electron microscopy (TEM) observations were performed using a FEI Tecnai F20 Field Emission Gun (FEG) transmission electron microscope operated at 200 kV, both in transmission and diffraction mode. The particle size distribution was measured on more than 240 particles through the Digital Micrograph 3.7.1 by Gatan Software Team.

Powder X-Ray Diffraction Analysis

Powder X-ray diffraction (PXRD) measurements were carried out by a Bruker D8 Advance spectrometer (Cu-K α radiation) in the 10°- 110° 2 θ range, with a time step from 2 s for 0.02° $\Delta(2\theta)$ step.

Radio-Luminescence (RL) and Photo-Luminescence(PL)

X-ray excited RL measurements were performed by a home-made apparatus featuring a CCD detector (Jobin-Yvon Spectrum One 3000) coupled to a monochromator (Jobin-Yvon Triax 180) with 100 grooves/mm grating operating in the 200-1100 nm range. X-ray irradiation was realized with a Philips 2274 tube operated at 20 kV. Photoluminescence emission (PL) and excitation (PLE) spectra excited by a deuterium steady-state lamp (Oriel) were measured by a custom made 5000M Horiba Jobin Yvon spectrofluorometer. Single grating monochromators blazed at 300 nm and 500 nm were used in the excitation and emission part of the set-up, respectively. A TBX-04 Peltier-cooled detector was used working in photo-counting regime with extremely low noise (less than 20 counts-per-second). Excitation and emission spectra were corrected for the spectral dependence of the excitation energy and for the spectral dependence of detection sensitivity, respectively.

Thermal analysis

Thermo-gravimetric analysis (TG) and differential scanning calorimetry (DSC) were performed through a TGA/DSC1 STAR SYSTEM (Mettler Toledo) coupled with MS-THERMOSTARTM (Pfeiffer Vacuum) Mass Spectrometer. TG/DSC curves were measured in alumina crucibles, in air (80ml/min) and using a heating rate of 10 °C/min in the range 30-1200 °C.

Infrared Spectroscopy

FTIR spectra on powder samples were recorded in transmission mode by a Thermo-Scientific Nicolet iN10 MX FT-IR microscope, using a resolution of 2 cm⁻¹ and 256 scans, and a BaF₂ crystal plate as a substrate.

II - Supplementary Data

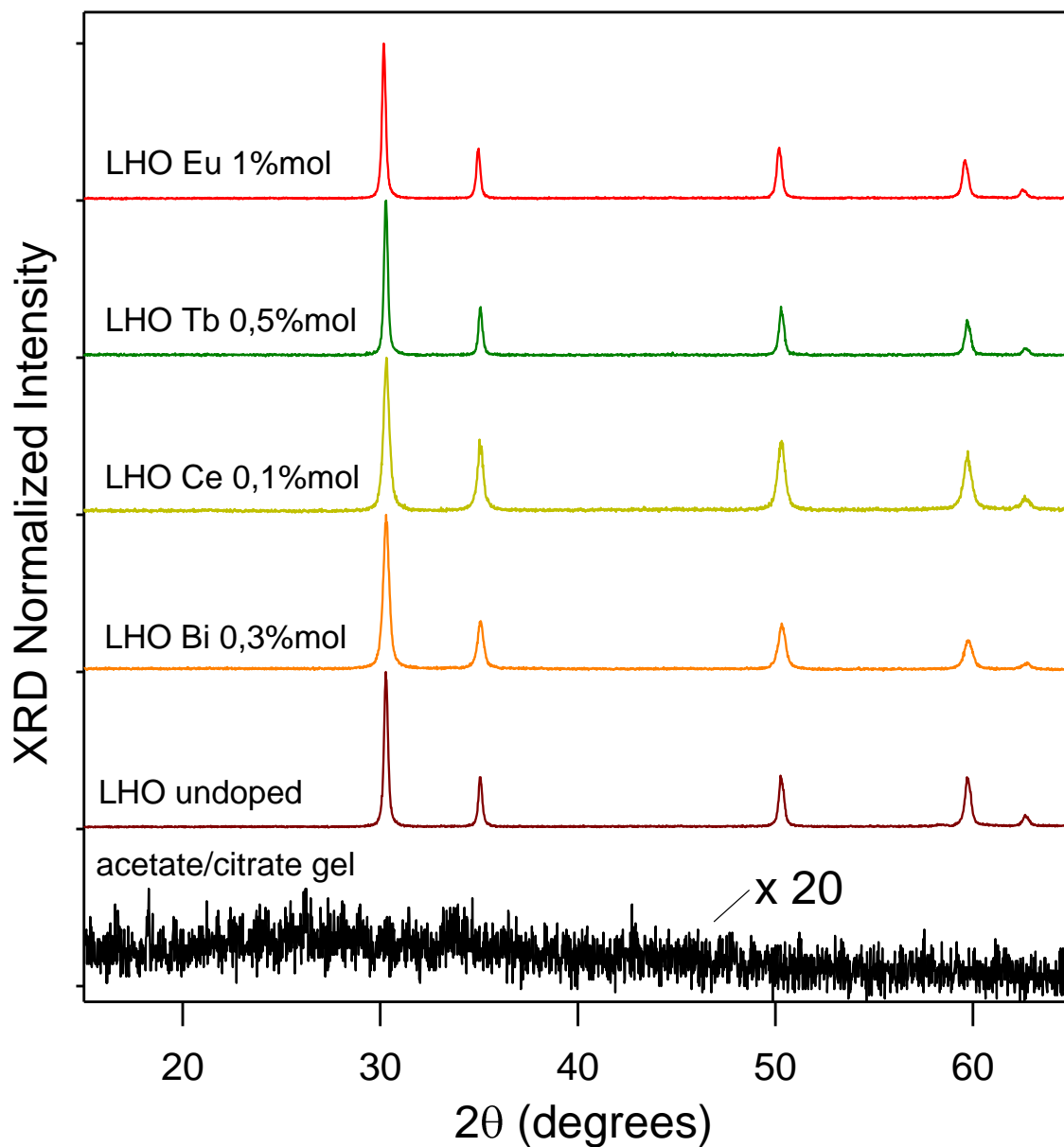


Fig. S1 – PXRD measurements of $\text{Lu}_4\text{Hf}_3\text{O}_{12}$ powders sintered at 1150°C in O_2 . The rhombohedral structure of the host is not altered by doping, whatever the ion and its concentration. Lu-Hf acetate-citrate gel powder (magnified 20 times) exhibit no significant feature, suggesting the amorphous structure of their organo-metallic network. Diffractograms are shifted on the ordinate axis for clarity.

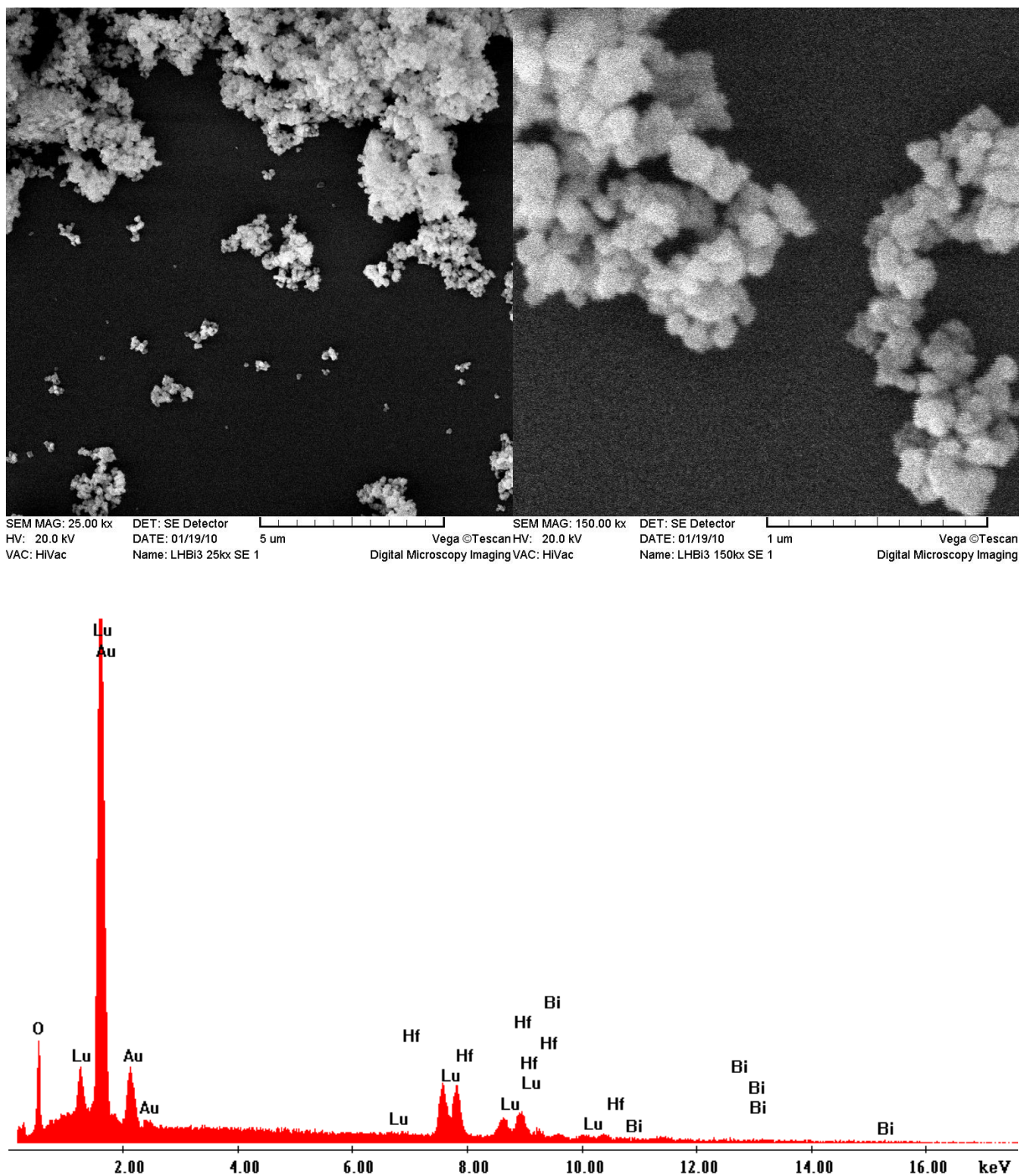


Fig. S2 - SEM micrographs of 0.3 mol% Bi^{3+} doped $\text{Lu}_4\text{Hf}_3\text{O}_{12}$ powders sintered at 1150 °C with two different magnifications (top panel) show the presence of particles with diameter of ~100 nm and forming aggregates. EDX elemental analysis for 3 mol% Bi^{3+} doped $\text{Lu}_4\text{Hf}_3\text{O}_{12}$ (lower panel) reveals Lu, Hf, O and the Au layer sputtered during sample preparation. The signal due to nominal Bismuth concentration of 3 mol% is below the detection limit.

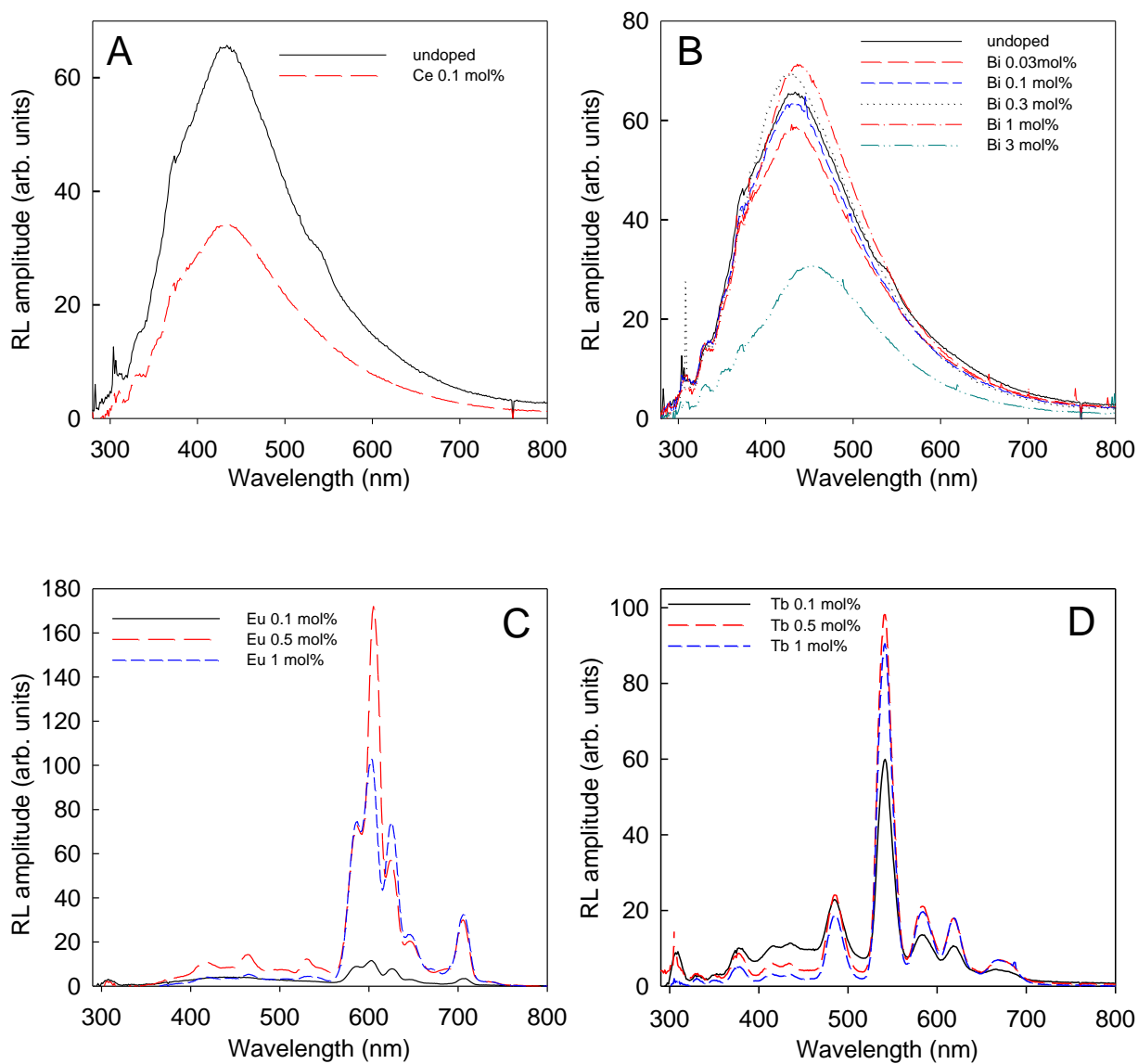


Fig. S3 – A) Comparison between RL spectra of undoped and Ce-doped (0.1 mol%) LHO samples. B) Comparison between RL spectra of undoped and Bi-doped LHO samples. C) RL spectra of Eu-doped LHO with three different Eu concentrations: 0.1 mol% (black full line), 0.5 mol% (red long dashed line) and 1 mol% (blue short dashed line). D) RL spectra of Tb-doped LHO with three different Tb concentrations: 0.1 mol% (black full line), 0.5 mol% (red long dashed line), and 1 mol% (blue short dashed line)

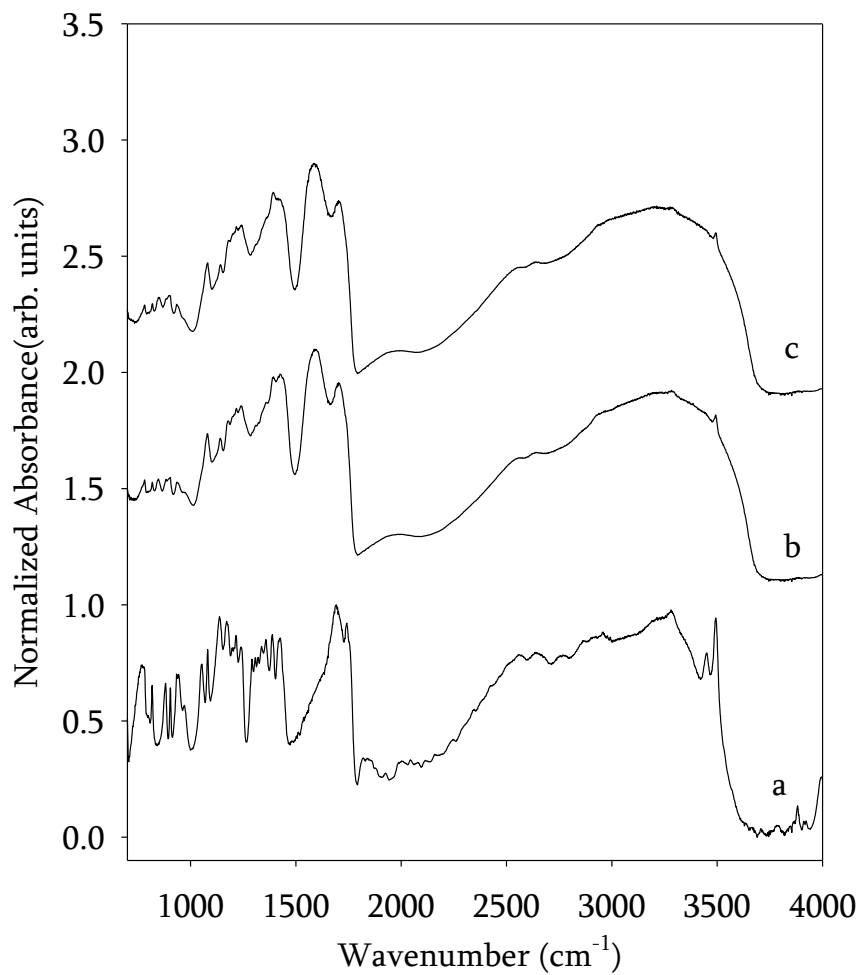


Fig. S4 – FTIR spectra of : a) citric acid; b) Lu-Hf acetate-citrate gel doped with 3 mol% Bi; c) Lu-Hf acetate-citrate gel doped with 1 mol% Eu. The spectra are shifted on the ordinate axis for better clarity.