Structural refinement, growth process, photoluminescence and photocatalytic properties of $(Ba_{1-x}Pr_{2x/3})WO_4$ crystals synthesized by the coprecipitation method

L.S. Cavalcante[a,b*], F.M.C. Batista[c], M.A.P. Almeida[d], A.C. Rabelo[d], I.C. Nogueira[d], N.C. Batista[b], J.A. Varela[a], M.R.M.C. Santos[c], E. Longo[b], M. Siu Li[e]

[a]*Universidade Estadual Paulista, P.O. Box 355, CEP. 14801-907 Araraquara, SP, Brazil*

[b]*UESPI, CCN, Departamento de Química, Rua João Cabral, P.O.Box 2231, 64002-150, Teresina-PI, Brazil*

[c]*LIMAV-CCN-Química, Universidade Federal do Piauí, 64049-550 Teresina, PI, Brazil*

[d]*Universidade Federal de São Carlos, P.O. Box 676, CEP. 13565-905, São Carlos, SP, Brazil*

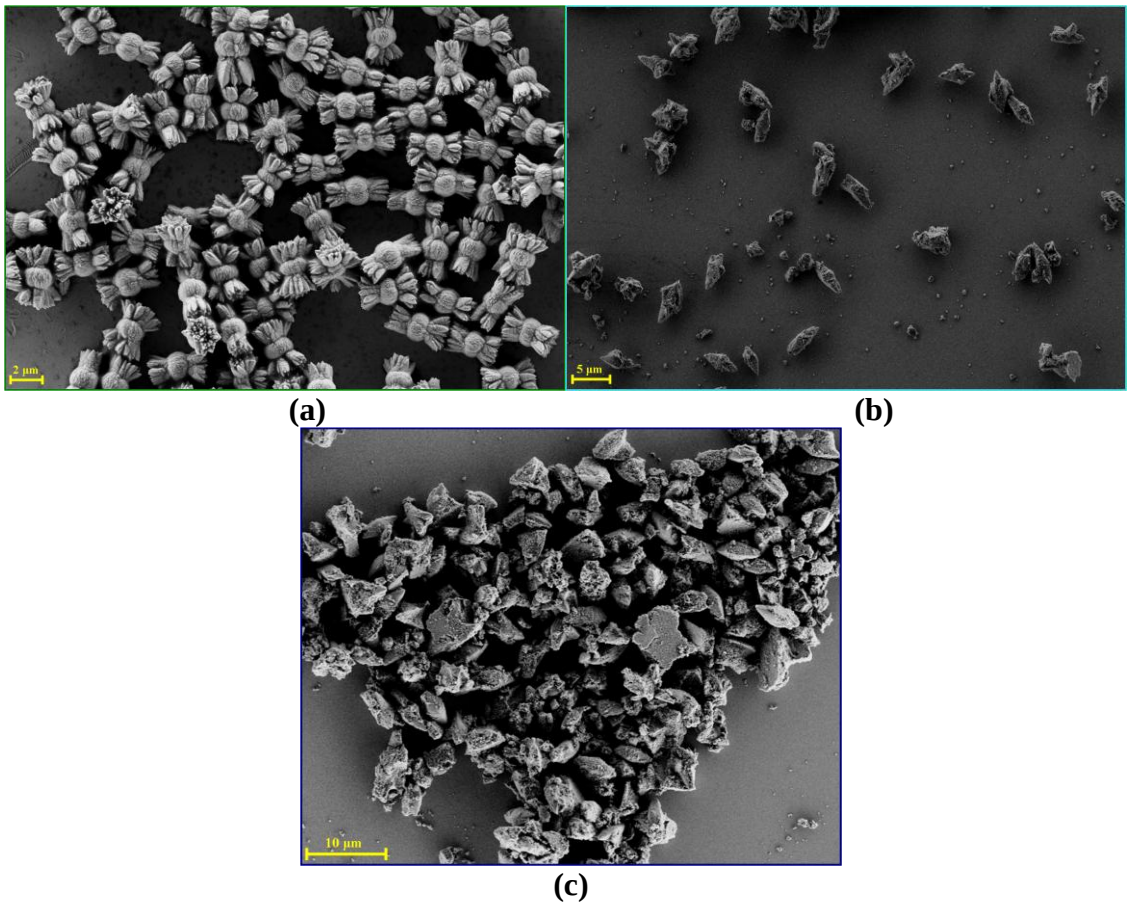
[e]*IFSC-Universidade de São Paulo, P.O. Box 369, 13560 970, São Carlos, SP, Brazil*

Supporting information:

Characterizations

X-ray powder diffraction (XRD) patterns using a D/Max-2500PC diffractometer (Rigaku, Japan) with Cu-Ka radiation (λ = 1.5406 Å) in the 2θ range from 10º to 70º with a scanning velocity of 2º/min in a normal routine scanning and in the 2θ range from 10º to 110º with 1º/min in the Rietveld routine (both with a step of 0.02º/s). FT-Raman spectroscopy was recorded with a Bruker-RFS 100 (Germany). Raman spectra were obtained using a 1064 nm line with a Nd:YAG laser; its maximum output power was kept at 100 mW with its performance in the range from 50 to 1000 cm^{-1}. FT-IR spectroscopy was recorded in the range from 200 to 1050 cm^{-1} using KBr pellets as a reference in a Bomem-Michelson spectrophotometer in the transmittance mode (Model MB-102). Morphologies of $(Ba_{1-x}Pr_{2x/3})WO_4$ crystals were observed by field emission scanning electron microscopy (FE-SEM) through a Carl Zeiss (Model Supra 35-VP, Germany) operated at 6 kV. Nitrogen adsorption/desorption isotherms and specific surface areas were recorded with an ASAP 2000 Phys/Chemisorption unit (Micromeritics, USA). In addition, the Brunauer-Emmett and Teller (BET method) was employed to estimate the specific surface area of the crystals. Ultraviolet visible (UV-vis) spectra were taken using a spectrophotometer of Varian (Model Cary 5G, USA) in diffuse reflectance mode. PL measurements were performed through a Monospec 27

monochromator (Thermal Jarrel Ash, USA) coupled to a R446 photomultiplier (Hamamatsu, Japan). A krypton ion laser (Coherent Innova 90K, USA) (l = 350 nm) was used as an excitation source its maximum output power was kept at 500 mW with a maximum power of 40 mW on the powders after the laser was passed through an optical chopper. PL measurements were performed at room temperature.



(a) **(b)**

(c)

Figure SI-1: FE-SEM micrographs of the (a) bonbon-like $BaWO_4$ microcrystals, (b) spindle-like $(Ba_{1-x}Pr_{2x/3})WO_4$ (x = 0.01) microcrystals, and (c) rice-like $(Ba_{1-x}Pr_{2x/3})WO_4$ (x = 0.02) microcrystals precipitate at room temperature.

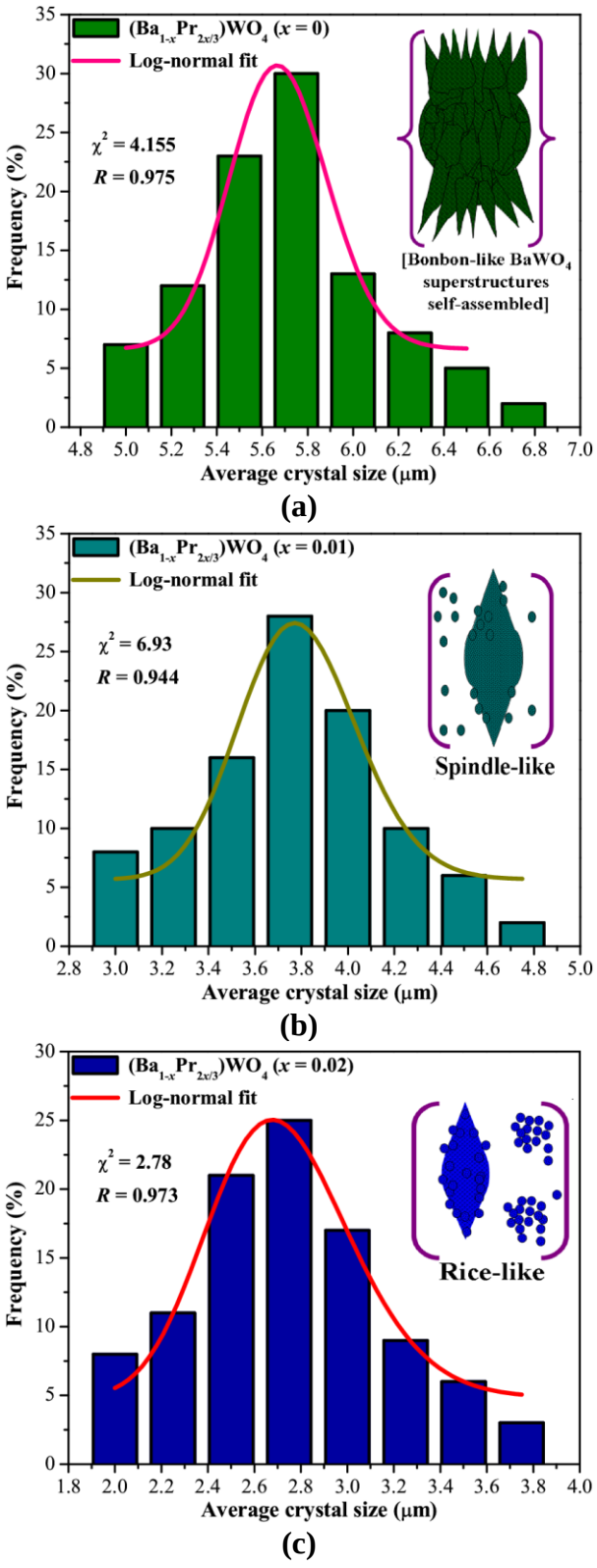


Figure SI-2: Average size distribution of the (a) bonbon-like $BaWO_4$ microcrystals, (b) spindle-like $(Ba_{1-x}Pr_{2x/3})WO_4$ (x = 0.01) microcrystals, and (c) rice-like $(Ba_{1-x}Pr_{2x/3})WO_4$ (x = 0.02) microcrystals precipitate at room temperature.

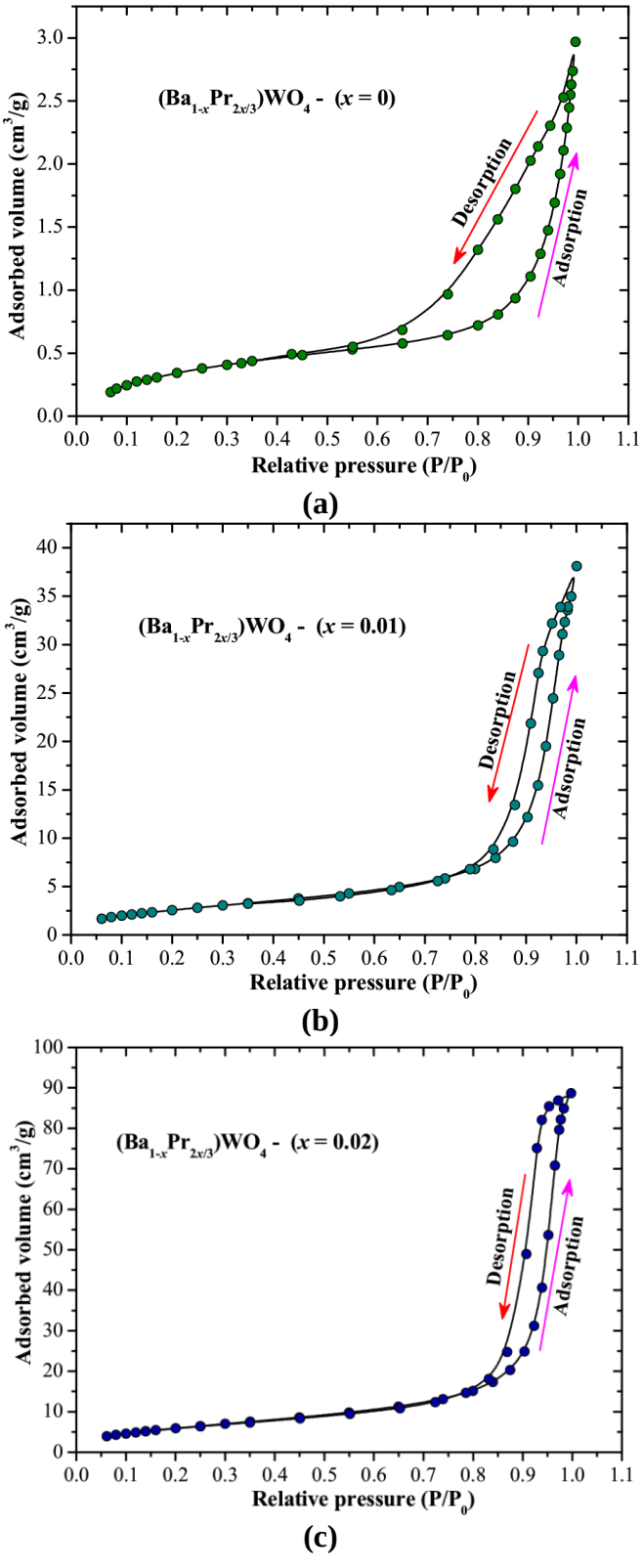


Figure SI-3: N2 adsorption-desorption isotherms of (a) bonbon-like $BaWO_4$ microcrystals, (b) spindle-like $(Ba_{1-x}Pr_{2x/3})WO_4$ (x = 0.01) microcrystals, and (c) rice-like $(Ba_{1-x}Pr_{2x/3})WO_4$ (x = 0.02) microcrystals precipitate at room temperature.

Table-S1(a). Crystal data and structure refinement for $BaWO_4$ crystals.

Identification code	*Barium tungstate*	
Empirical formula	$BaWO_4$	
Formula weight	385.165	
Temperature	298(5)K	
Wavelength	1.5405 nm	
Crystal system	Tetragonal	
Space group	$I4_1/a$	
Unit cell dimensions	a = 5.60433(1) Å	α = 90°.
	b = 5.60433(1) Å	β = 90°.
	c = 12.7338(4) Å	γ = 90°.
Volume	399.949(2) $Å^3$	
Z	4	
Density (calculated)	6.321 Mg/m^3	
Absorption coefficient	6.154 mm^{-1}	
F(000)	276	
Crystal size	powders	
Theta range for data collection	5.0 to 55.00°.	
Index ranges	-6<=h<=0, -6<=k<=0, -14<=0<=0	
Reflections collected	251	
Independent reflections	5001 [R(int) = 0.0325]	
Completeness to theta = 55.00°	94.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8863 and 0.99181	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5001 / 0 / 251	
Goodness-of-fit on F^2	2.032	
Final R indices [I>2sigma(I)]	R1 = 0.0280, wR2 = 0.1082	
R indices (all data)	R1 = 0.0812, wR2 = 0.5299	
Largest diff. peak and hole	2.105 and -1.2654 $e.Å^{-3}$	

Table-S1(b). Crystal data and structure refinement for $(Ba_{0.99}Pr_{0.01})WO_4$ crystals.

Identification code	*Barium praseodymium tungstate*	
Empirical formula	$Ba_{0.99}Pr_{0.01}WO_4$	
Formula weight	384.36	
Temperature	298(5)K	
Wavelength	1.5405 nm	
Crystal system	Tetragonal	
Space group	$I4_1/a$	
Unit cell dimensions	a = 5.61125(9) Å	α = 90°.
	b = 5.61125(9) Å	β = 90°.
	c = 12.73071(3) Å	γ = 90°.
Volume	400.841(1) $Å^3$	
Z	4	
Density (calculated)	6.346 Mg/m^3	
Absorption coefficient	6.128 mm^{-1}	
F(000)	276	
Crystal size	powders	
Theta range for data collection	10.0 to 110.00°.	
Index ranges	-6<=h<=0, -6<=k<=0, -14<=0<=0	
Reflections collected	251	
Independent reflections	5001 [R(int) = 0.0315]	
Completeness to theta = 55.00°	94.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.83063 and 0.99458	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5001 / 0 / 251	
Goodness-of-fit on F^2	2.095	
Final R indices [I>2sigma(I)]	R1 = 0.0346, wR2 = 0.1039	
R indices (all data)	R1 = 0.075, wR2 = 0.04388	
Largest diff. peak and hole	2.241 and -1.3224 $e.Å^{-3}$	

Table-S1(b). Crystal data and structure refinement for $(Ba_{0.98}Pr_{0.02})WO_4$ crystals.

Identification code	*Barium praseodymium tungstate*	
Empirical formula	$Ba_{0.98}Pr_{0.02}WO_4$	
Formula weight	385.336	
Temperature	298(5)K	
Wavelength	1.5405 nm	
Crystal system	Tetragonal	
Space group	$I4_1/a$	
Unit cell dimensions	a = 5.61140(7) Å	α = 90°.
	b = 5.61140(7) Å	β = 90°.
	c = 12.7288(4) Å	γ = 90°.
Volume	400.802(1) $Å^3$	
Z	4	
Density (calculated)	6.371 Mg/m^3	
Absorption coefficient	6.188 mm^{-1}	
F(000)	276	
Crystal size	powders	
Theta range for data collection	5.0 to 55.00°.	
Index ranges	-6<=h<=0, -6<=k<=0, -14<=0<=0	
Reflections collected	251	
Independent reflections	5001 [R(int) = 0.0574]	
Completeness to theta = 55.00°	92.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.77960 and 0.99290	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5001 / 0 / 251	
Goodness-of-fit on F^2	2.004	
Final R indices [I>2sigma(I)]	R1 = 0.0454, wR2 = 0.1064	
R indices (all data)	R1 = 0.0804, wR2 = 0.04018	
Largest diff. peak and hole	2.31574 and -1.5545 $e.Å^{-3}$	