Supporting Information

Electronic structure, growth mechanism and photoluminescence of $CaWO_4$ crystals

L.S. Cavalcante [a,*,†] V.M. Longo [a,†] J.C. Sczancoski [a,†] M.A.P. Almeida [b,‡] A.A. Batista [b,‡] J.A. Varela [a,†] M.O. Orlandi [a,†] E. Longo [a,†] and M. Siu Li [c§]

[a]*Universidade Estadual Paulista, P.O. Box 355, CEP. 14801-907 Araraquara, SP, Brazil.,*
[b]*Universidade Federal de São Carlos, P.O. Box 676, CEP. 13565-905, São Carlos, SP, Brazil.,*
[c]*IFSC-Universidade de São Paulo, P.O. Box 369, 13560-970, São Carlos, SP, Brazil.*

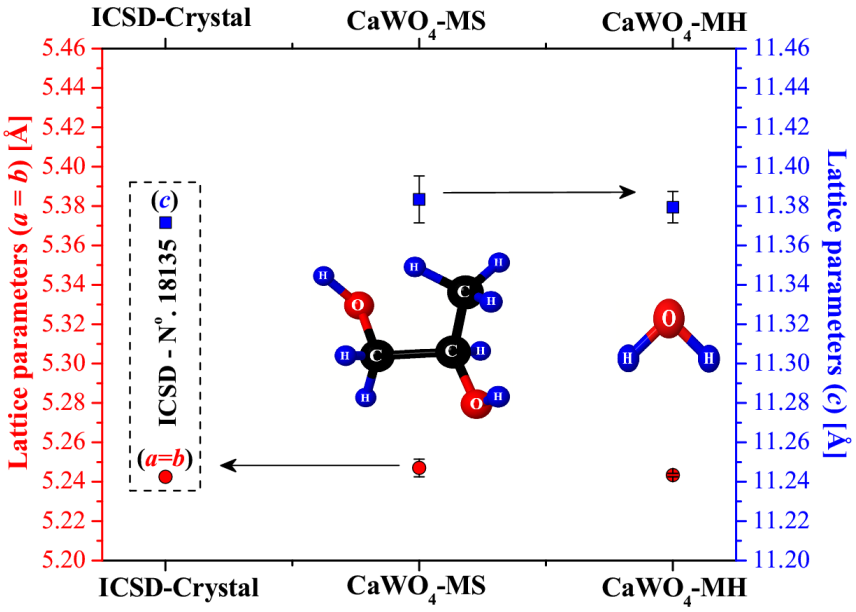

Fig. SI-1: Comparative between the lattice parameters of $CaWO_4$ micro- and nanocrystals with those reported in ICSD file Nº. 18135.

data_$CaWO_4$ microcrystals (110ºC/1h and 160ºC/30min)

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_chemical_formula_weight 1151.702

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loop_

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1 x,y,z

2 0.750-y,0.250+x,0.250+z

3 -x,0.500-y,z

4 0.250+y,0.250-x,0.250+z

5 -x,-y,-z

6 0.750+y,0.250-x,0.250-z

7 x,0.500+y,-z

8 0.250-y,0.250+x,0.250-z

9 0.500+x,0.500+y,0.500+z

10 1.250-y,0.750+x,0.750+z

11 0.500-x,1.000-y,0.500+z

12 0.750+y,0.750-x,0.750+z

13 0.500-x,0.500-y,0.500-z

14 1.250+y,0.750-x,0.750-z

15 0.500+x,1.000+y,0.500-z

16 0.750-y,0.750+x,0.750-z

loop_

_atom_type_symbol

_atom_type_oxidation_number

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Ca+2 2.000 0.990

W+6 6.000 0.410

O-2 -2.000 1.210

loop_

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_atom_site_occupancy

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_atom_site_Wyckoff_symbol

_atom_site_attached_hydrogens

_atom_site_calc_flag

_atom_site_thermal_displace_type

_atom_site_u_iso_or_equiv

Ca1 Ca+0 0.0000 0.2500 0.6250 1.000 4 b ? d ? ?

W1 W+0 0.0000 0.2500 0.1250 1.000 4 a ? d ? ?

O1 O+0 0.1497 0.0093 0.2097 1.000 16 f ? d ? ?

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data_$CaWO_4$ microcrystals (130ºC/6h and 160ºC/30min)

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loop_

_symmetry_equiv_pos_site_id

_symmetry_equiv_pos_as_xyz

1 x,y,z

2 0.750-y,0.250+x,0.250+z

3 -x,0.500-y,z

4 0.250+y,0.250-x,0.250+z

5 -x,-y,-z

6 0.750+y,0.250-x,0.250-z

7 x,0.500+y,-z

8 0.250-y,0.250+x,0.250-z

9 0.500+x,0.500+y,0.500+z

10 1.250-y,0.750+x,0.750+z

11 0.500-x,1.000-y,0.500+z

12 0.750+y,0.750-x,0.750+z

13 0.500-x,0.500-y,0.500-z

14 1.250+y,0.750-x,0.750-z

15 0.500+x,1.000+y,0.500-z

16 0.750-y,0.750+x,0.750-z

loop_

_atom_type_symbol

_atom_type_oxidation_number

_atom_type_radius_bond

Ca+2 2.000 0.990

W+6 6.000 0.410

O-2 -2.000 1.210

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

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_atom_site_fract_z

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_atom_site_symmetry_multiplicity

_atom_site_Wyckoff_symbol

_atom_site_attached_hydrogens

_atom_site_calc_flag

_atom_site_thermal_displace_type

_atom_site_u_iso_or_equiv

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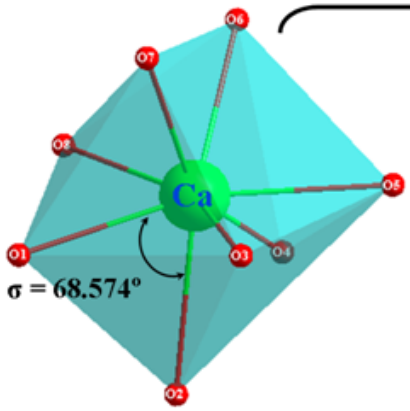
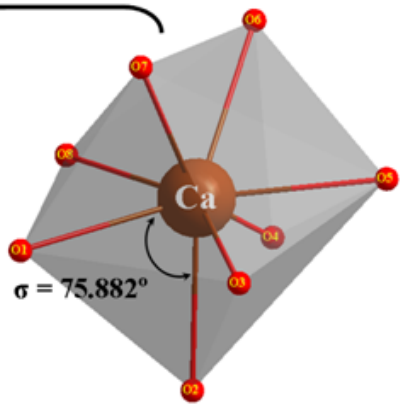
W1 W+0 0.0000 0.2500 0.1250 1.000 4 a ? d ? ?

O1 O+0 0.2510 0.1000 0.0476 1.000 16 f ? d ? ?

Table-SI-1: CIF generated from Rietveld refinements of $CaWO_4$ micro- and nanocrystals.

Deltahedral
[CaO_8] clusters





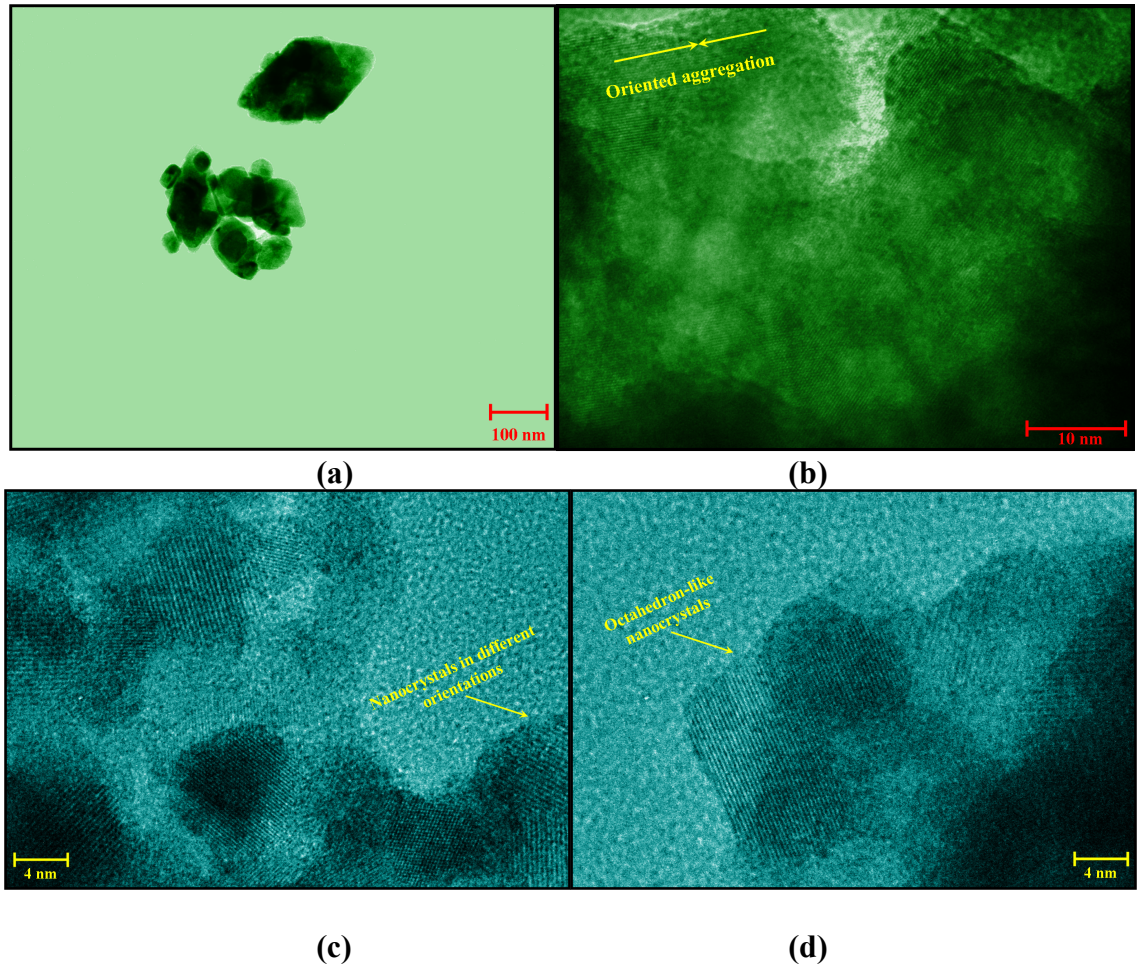
Bonds [O–Ca–O]	Bond angles (°)
O_1–Ca–O_2	σ = 68.57
O_1–Ca–O_3	φ = 79.7
O_1–Ca–O_4=O_1–Ca–O_6	ρ = 126.12
O_1–Ca–O_5	ε = 152.24
O_1–Ca–O_7	η = 76.62
O_1–Ca–O_8	δ = 73.25
O_2–Ca–O_5	γ = 98.68
O_2–Ca–O_7	μ = 134.26

(a)

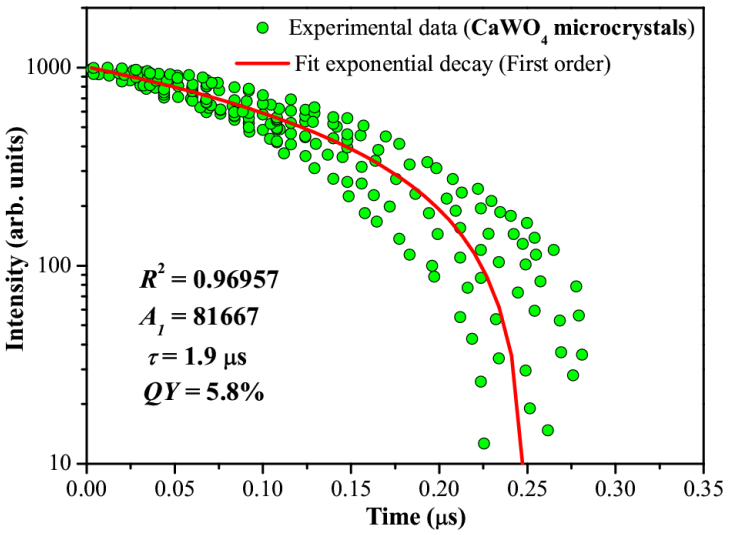
Bonds [O–Ca–O]	Bond angles (°)
O_1–Ca–O_2	σ = 75.88
O_1–Ca–O_3	φ = 75.64
O_1–Ca–O_4=O_1–Ca–O_6	ρ = 128.61
O_1–Ca–O_5	ε = 148.97
O_1–Ca–O_7	η = 70.66
O_1–Ca–O_8	δ = 73.62
O_2–Ca–O_5	γ = 97.61
O_2–Ca–O_7	μ = 137.32

(b)

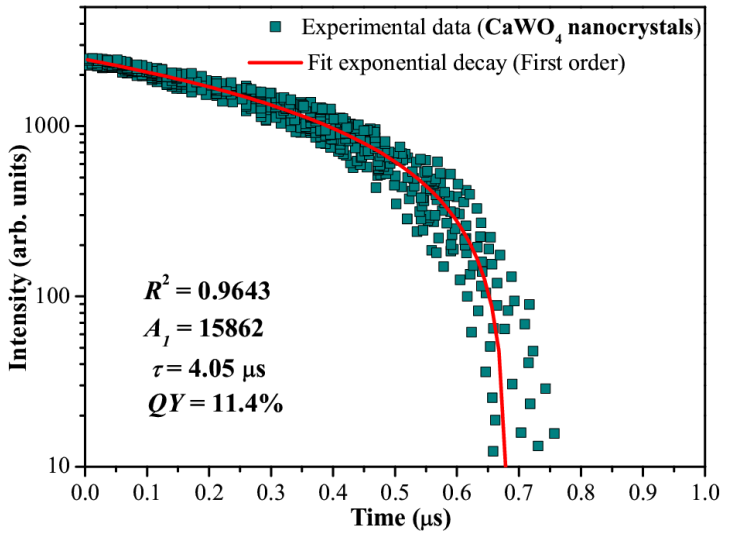
Figs. SI-2(a,b): O–Ca–O bond angles related to the deltahedral [CaO_8] clusters of $CaWO_4$ micro- and nanocrystals.



Figs. SI-3(a-d): TEM/HR-TEM images of $CaWO_4$ micro- and nanocrystals.



(a)



(b)

Figs. SI-4(a,b): Luminescence decay of $CaWO_4$ (b) micro- and (c) nanocrystals [excitation wavelength (λ_{exc} = 350 nm)] monitoring the maximum PL emissions at (491 and 487 nm), respectively.