Institute of Technical Sciences of the Serbian Academy of Sciences and Arts

DENSE SPHERICAL RARE EARTH OXIDE PARTICLES SYNTHESIS *VIA* SPRAY PYROLYSIS OF POLYMERIC PRECURSOR SOLUTION

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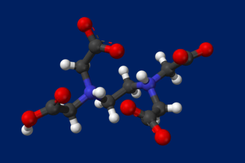
Abstract Cerium-doped yttrium aluminum garnet (YAG:Ce^{3+}) phosphor powder is synthesized *via* spray pyrolysis of corresponding aqueous nitrates solution either with or without polymer additive. Ultrasonically (0.8 and 1.3 MHz) generated aerosol droplets are decomposed in tubular flow reactor at designated temperature. Polymerization of nitrate solution is done by ethylenediaminetetraacetic acid (EDTA) and ethylene glycol (EG). The 0.1M true stable solution is obtained after pH correction with NH_4OH (final pH=0.15). Following the initial attempt for obtaining dense, nanostructured spherical particles of pure (YAG):Ce^{3+} phase, as-prepared powders from pure nitrate and polymer modified solutions are additionally thermally treated in air at 1000 ^oC. The particles morphology and their inner structure are analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM/HRTEM). Phase identification is performed by X-ray powder diffraction (XRPD) based on which the structural refinement through Rietveld method was done.

SPRAY PYROLYSIS ROUTE (SP)

Non-polymer route: H_2O

STARTING PRECUSOR NITRATES SOLUTION
$Y(NO_3)_3x6H_2O$,
$Al(NO_3)_3x9H_2O$
$Ce(NO_3)x6H_2O$

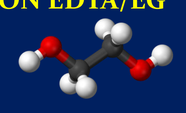
Polymer route: EDTA/EG



COMMON PRECUSOR AQUEOUS NITRATES SOLUTION

$Y(NO_3)_3x6H_2O : Al(NO_3)_3x\ 9H_2O = 3 : 5$

POLYMERIC PRECUSOR SOLUTION EDTA/EG
EDTA $C_{10}H_{16}N_2O_8$ / EG $C_2H_6O_2$
EDTA : Metal ions= 1:1
EDTA/EG=1:4



c [moldm^{-3}]	*pH*	*γ 10^3 [Pas]*	*ρ [gcm^{-3}]*	*μ [mNm^{-1}]*
0.06	0.15	1.043	1.064	112.29

c [moldm^{-3}]	*pH*	*γ 10^3 [Pas]*	*ρ [gcm^{-3}]*	*μ [mNm^{-1}]*
0.12	0.15	1.043	0.12485	64.2

Ultrasonic atomization
D_o, D_p

f 10^{-6}[s-1]	*D_o [μm]*	*$V_{drop.}$ 10^{11}[cm^3]*	*D_p [μm]*
0.8	5.5	8.53	1.1

f 10^{-6}[s-1]	*D_o [μm]*	*$V_{drop.}$ 10^{11}[cm^3]*	*D_p [μm]*
1.3	4.0	3.23	1.00

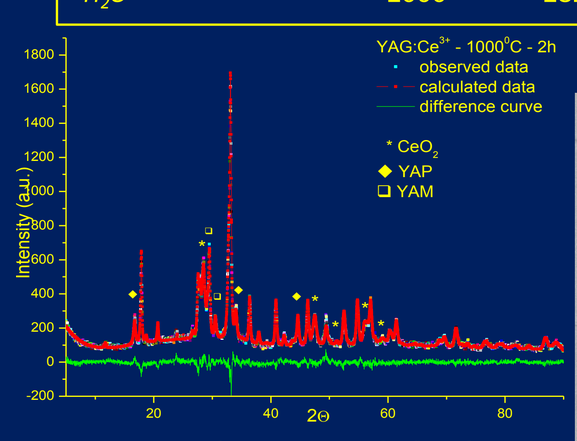
$$D_0 = 0.34\left(\frac{8\pi\gamma}{\rho f^2}\right)^{0.33} \qquad D_p = D_0\left(\frac{c^* M_p}{\rho_p M_s}\right)^{0.33}$$

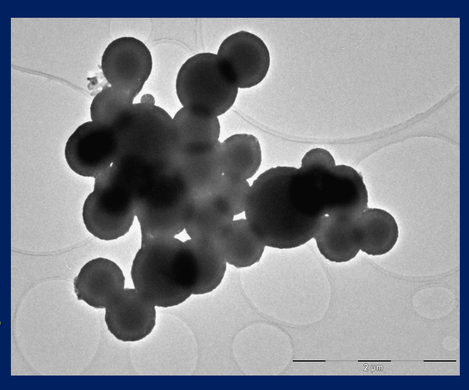
f 10^{-6}[s-1]	*D_o [μm]*	*$V_{drop.}$ 10^{11}[cm^3]*	*D_p [μm]*
1.3	6.7	15.3	1.77

Values of SP process parameters

$Y_3Al_5O_{12}$:Ce 2 at %	*F_G[cm^{3}min^{-1}]*	*v_G [cmmin^{-1}]*	*τ_G[min]*	*F_L [cm^{3}min^{-1}]*	*v_L [cmmin^{-1}]*	*τ_L 10^{-3}[min]*
H_2O	1000	132.5	1.434	0.133	0.0150	12.67

$Y_3Al_5O_{12}$:Ce 2 at %	*F_G[cm^{3}min^{-1}]*	*v_G [cmmin^{-1}]*	*τ_G[min]*	*F_L [cm^{3}min^{-1}]*	*v_L [cmmin^{-1}]*	*τ_L 10^{-3}[min]*
EDTA/EG	1000	132.5	1.434	0.722	0.0957	1.985





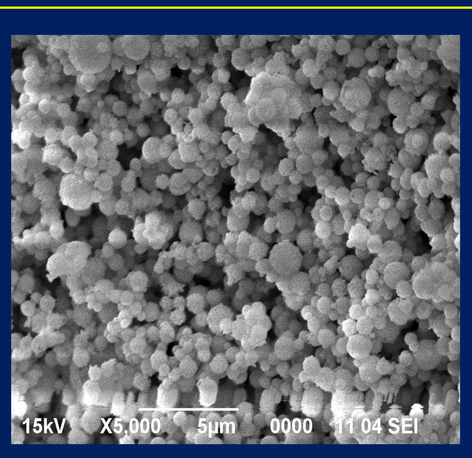
XRD pattern and TEM micrograph of powder obtained at 300^o C and heat treated at 1000 ^{o}C (non polymeric route)

$$n_0 = \frac{F_L}{V_D} \qquad \frac{N_0}{N_t} = \frac{1}{1+\frac{t}{\tau_C}} \qquad \tau_C = \frac{2}{\beta N_0}$$

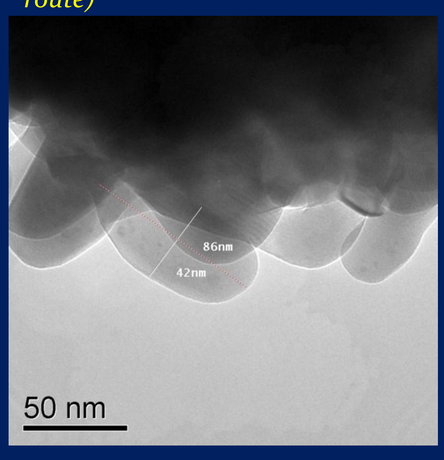
$$Nu = 1.56 + 0.616 Re^{0.5} Pr^{0.33}$$

$$Re = \frac{\rho\omega D_0}{\mu} \qquad Nu = \frac{\alpha D}{\lambda}$$

$$Bi = \frac{\alpha l}{\lambda}$$



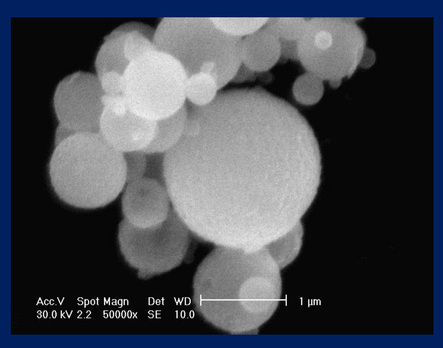
SEM and TEM micrographs of YAG:Ce^{3+} powder thermally treated at 1000 ^{o}C (polymeric route)



YAG	**CeO_2**	**YAP**
cubic	***cubic***	***hexagonal***
lp: 12.0579(1)	**lp: 5.4021(5)**	**lp=lp2: 3.678(1)**
		lp3: 10.499(1)
wt%: 47.5	**wt%: 8.1**	**wt%: 38.8**
CS: 76.4(2) nm	**CS: 20.5(1)**	**CS: 29.1(2)**
MS: 0.61(1)	**MS: 0.92(6)**	**MS: 0.07(3)**

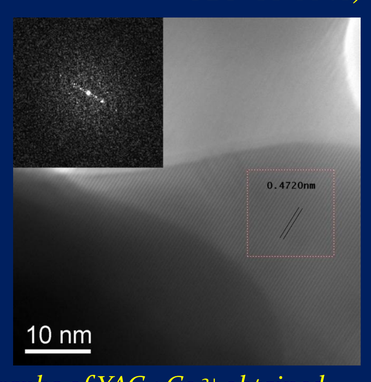
	f 10^{-6} [s^{-1}]	*T [K^{-1}]*	*Re 10^7*	*Pr*	*Nu*	*α 10^{-5}[Wm^{-2}K^{-1}]*	*Bi*
$Y_3Al_5O_{12}$:Ce 2 at % H_2O	1.3	150	3.307	0.680	1.560	2.712	0.260
		300	2.054	0.670	1.560	2.132	0.260
$Y_3Al_5O_{12}$:Ce 2 % atom. EDTA/EG	1.3	150	40.07	0.655	1.561	1.601	0.260
		300	24.05	0.674	1.561	1.258	0.260

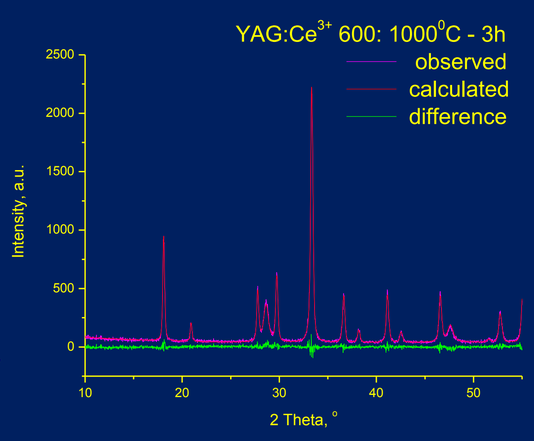
HRTEM micrograph of YAG : Ce $^{3+}$ powder thermally treated at 1000 ^{o}C (polymeric route) (211) plane PDF 33-0040)

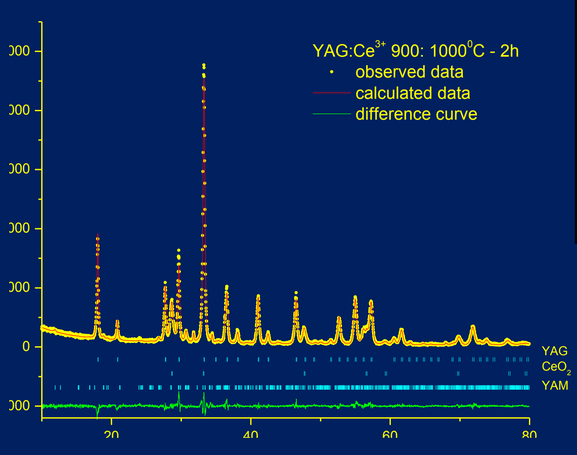


$$\varphi = \frac{cMW}{1000\rho}$$

$Y_3Al_5O_{12}$:Ce^{3+} H_2O	*$Y_3Al_5O_{12}$:Ce^{3+} EDTA/EG*
0.008	0.0156

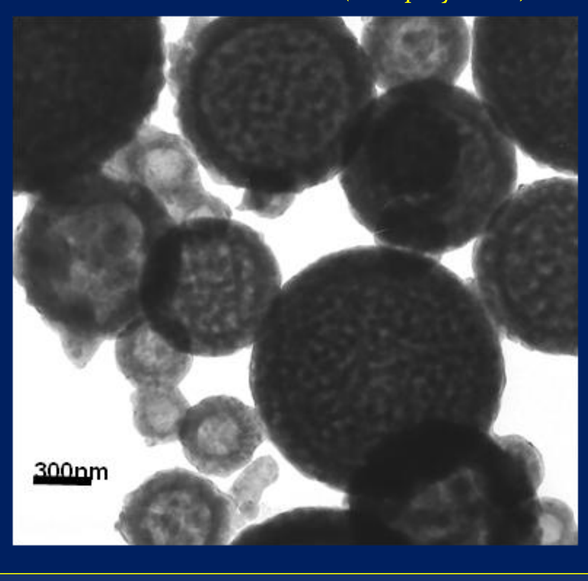




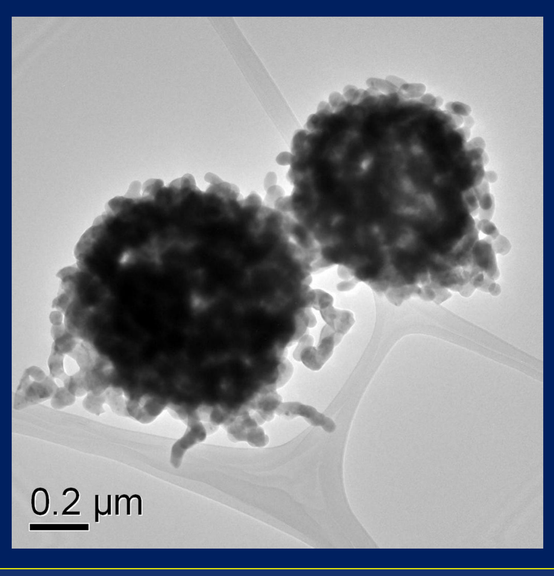


XRD micrographs of YAG : Ce $^{3+}$ powder obtained at 900 ^{o}C and heat treated at 1000 ^{o}C (non-polymeric route)

SEM and TEM micrographs of YAG : Ce $^{3+}$ obtained at 900 ^{o}C and heat treated at 1000 ^{o}C (non-polymeric)



TEM/HR TEM micrographs of YAG : Ce $^{3+}$ obtained from polymeric precursor and heat treated at 1000 ^{o}C



XRD pattern of YAG : Ce $^{3+}$ powder obtained at 600 ^{o}C and thermally treated at 1000 ^{o}C (polymeric)

YAG	**YAM**	**YAP**
Cubic	*Cubic*	*Monoclinic*
lp: 12.0412(1)	lp: 5.397(3)	lp1=11.023(1)
		lp2: 10.061(1)
		lp3: 7.149(1)
wt%: 84.5	wt%: 6.8	wt%: 8.7
CS: 40(2) nm	CS: 47(1)	CS: 23.1(2)
MS: 0.17(3)	MS: 0.25(4)	MS: 0.61(3)

YAG	**CeO_2**
cubic	*cubic*
lp: 12.0267(7)	lp: 5.4021(5)
wt%: 91	wt%: 9
CS: 52(2) nm	CS: 20.5(1)
MS: 0.27(1)	MS: 0.92(6)

Conclusion The processing of spherical, porous nanostructured YAG :Ce^{3+} particles *via* spray pyrolysis of pure and polymeric nitrates solutions at designated temperatures were done. Percolation criteria calculated for chosen precursors predicts hollow particles generation, while Biote number implies the presents of temperature/concentration gradient in them. TEM/HRTEM analysis prove formation of crust in case of particles obtained from pure nitrates solution as a consequence of surface precipitation. Polymerization of nitrate solution ensures volume precipitation in droplet and subsequently leads to dense particle generation. Beside it, more homogeneous phase composition is achieved without the formation of intermediate YAM and YAP phases. The better crystallinity of particles obtained from polymeric solution is also proved which together with other structural characteristics should result in improved optical properties.

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