Institute of Technical Sciences Serbian Academy of Sciences and Arts

UREA-ASSISTED SELF-COMBUSTION AEROSOL SYNTHESIS OF $Y_3Al_5O_{12}:Ce^{3+}$

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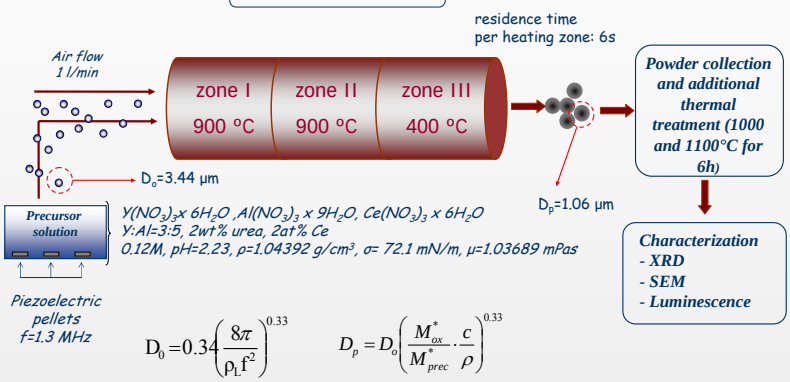
Abstract

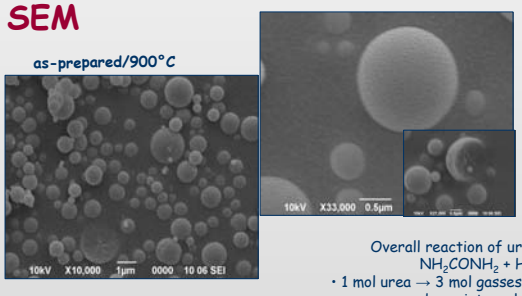
A simple route to pure garnet phase synthesis is difficult to achieve, due to the formation of other stable phases of Y_2O_3-Al_2O_3 system (monoclinic, perovskite and hexagonal). In this study, urea-assisted spray pyrolysis was employed, in the effort to synthesize a pure YAG phase with good structural and morphological characteristics. This route can be regarded as a self-combustion synthesis confined within a droplet where urea acts as an in-situ source of thermal energy due to its decomposition. The process involved ultrasonic aerosol formation (1.3 MHz) from the urea-modified nitrate precursor solution and consequent control over the aerosol decomposition united with self-combustion of droplets within a high-temperature tubular flow reactor (900°C). The as-prepared amorphous particles were additionally thermally treated in air at 1000 and 1100°C for 6h. Morphological features were investigated by means of SEM analysis while XRD analysis gave insight into the structural properties. Obtained data were refined by Rietveld method. Optical properties were investigated by photoluminescent measurements.

Spray pyrolysis

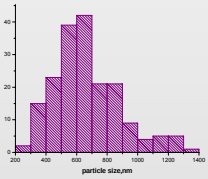


$$D_0 = 0.34\left(\frac{8\pi}{\rho_L f^2}\right)^{0.33} \qquad D_p = D_o\left(\frac{M^*_{ox}}{M^*_{prec}}\cdot\frac{c}{\rho}\right)^{0.33}$$

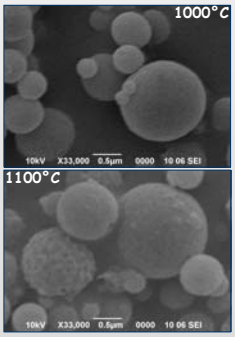
SEM



SEM JEOL JSM-6390-LV

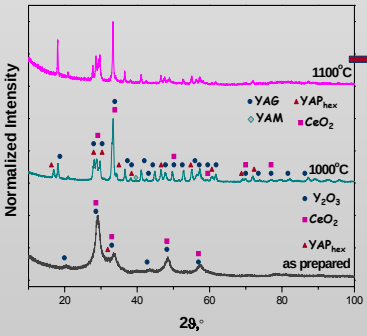


Overall reaction of urea under heat treatment:
$NH_2CONH_2 + H_2O \rightarrow 2NH_3 + CO_2$
• 1 mol urea → 3 mol gasses / large volume of decomposed gasses produces internal pressure inside the particles

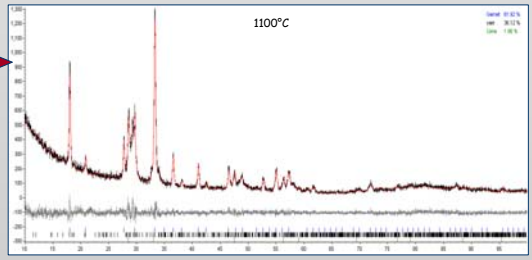


As-prepared particles are non-agglomerated with moderately broad size distribution. Smooth particle surface is in agreement with amorphous phase presence confirmed by XRD. Insight into a broken particle leads to the presumption that volume precipitation occurs.
Thermal treatment effect on particle morphology is obvious since there is an increase in particle surface roughness with temperature due to promoted crystallization.

XRD



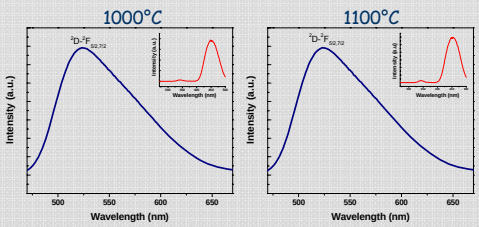
Philips X'Pert MPD



Temperature	1100°C		
Phase name	YAG	YAM	CeO_2
Phase content, wt%	61.92(9)	36,12(9)	1.96(2)
Space group	*Ia-3d*, cubic	*P2$_1$/c*, monoclinic	*Fm-3m*, cubic
Lattice parameters	a=12.035(7)	a=7.737(3) b=10.537(6) c=11.731(5) β=107.37(4)	a=5.412(1)
Crystallite size, nm	80.5 (9)	14.2(5)	57.0 (9)
Microstrain, Δa/a %	0.592(5)		
R_{Bragg},%	1.966	2.017	2.420
gof	1.134		

Thermal treatment leads not only to the segregation of targeted $Y_3Al_5O_{12}$ phase but also to the formation of other phases
as-prepared: amorphous phase present and the rising peaks are attributed to Y_2O_3 (PDF 89-5591), CeO_2 (PDF 65-5923) and hexagonal $YAlO_3$ phase space group *P63/mmc* (PDF 74-1334).
1000°C: beside YAG phase monoclinic YAM, space group *P2$_1$/c* (PDF 34-0368) and hexagonal YAP phases are present CeO_2 forms as well
1100°C: Rietveld refinement → the major phase content is attributed to YAG phase cubic structure, space group *Ia-3d* (PDF 33-0040)

Luminescence



Broad green-yellow emission band in the range of 470-670 nm peaking at 521nm is ascribed to the electron transition from the excited state of ^2D_J to the ground states of $^2F_{5/2,7/2}$ of Ce^{3+} ions in the $Y_3Al_5O_{12}$ host material.

Fluorolog-3 Model FL3-221/HORIBA JOBIN-Yvon
Xenon lamp 450W: λex=343 nm

Conclusion

Urea-assisted aerosol synthesis of YAG:Ce^{3+} led to the formation of fine powders with good morphological features i.e. spherical, non-agglomerated and submicron particles were synthesized. However, XRD analysis reviled that the phase segregation has occurred and that YAG phase is followed with the presence of hexagonal and monoclinic intermediate phases of Y_2O_3-Al_2O_3 system. Nevertheless, the luminescent measurements revile typical Ce^{3+} ion emission from the $Y_3Al_5O_{12}$ host lattice and prove Ce^{3+} incorporation into the host matrix.

Acknowledgments: This research is financially supported through the Project No. 142010 of the Ministry of Science and Technological Development of Serbia and COST 539 Action. Authors gratefully acknowledge MSc Luz Stella Gomez, Universidad Carlos III de Madrid, for kind assistance in XRD analysis.