Aerosol route in Processing of Nanostructured Functional Materials†

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Abstract

The diversity and potentials of the aerosol route for making functional materials at the nano size level are reviewed. Among the methods currently used for nanophase processing, synthesis through dispersion phase (aerosol) enables generation of ultrafine, either single or complex powders with controlled stoichiometry, chemical and phase content provided by high surface reaction, high heating and cooling rates and short residence time. It represents a "bottom-up" chemical approach and provides control over a variety of important parameters for particle processing. This may favor to the formation of either amorphous, nanocrystalline or metastable phases implying a huge impact in the search for advanced functional materials having novel and unique structures and properties. Particularly, the opportunities of the hot wall aerosol synthesis, i.e. spray pyrolysis, for the generation of ultrafine spherical particles with uniformly distributed components, phases and nano-clustered inner structure and luminescence properties is demonstrated with various analyzing techniques like XRPD, FE-SEM, HR-TEM, STEM and nanotomography. Following the initial attempts, a more detailed aspect of the several phosphor particles generation based on Gd₂O₂:Eu, Y₂O₃:Eu, (Yₓ,Gd₁₋ₓ)₂O₃:Eu and Y₃Al₅O₁₂:Ce is reviewed highlighting the research activities in the Institute of Technical Sciences of SASA, Serbia.

Keywords: aerosol, nanoparticles, synthesis, phosphors, luminescence

1. Introduction

Tremendous technological and scientific trend in material science for miniaturization and microstructure refinement is basically followed with the increasing interest for nanophase characterization and understanding. The field of nanoscience and nanotechnology has an exciting progress in recent years, particularly regarding the control synthesis of ultrafine particles or nanoparticles that might have a great potential for use in solid-state functional materials and devices, like phosphors, sensors, catalysts, drug delivery carriers etc. The key points important for the future research and development of nanophased materials represent the ability for further improvement of material properties through nanostructuring and fundamental research of structure-properties relationship, from one side, as well as development of assigned and controlled synthesis route with the ability to ensure nanophase synthesis in a controlled manner, from another. Synthesis of submicronic and nanosized powders and thin films represent an area of increasingly high interest and offers new opportunities in materials engineering whether one or multi component systems are considered.

The chemical synthesis routes, like liquid precipitation, sol-gel or hydrothermal methods, offer many advantages over conventional procedures for nanoscaled materials processing. Since the precursors are mixed at the molecular level in a solution, a high degree of structural homogeneity is achievable; doping is effective, surface area of powder produced is very high, leading to lower processing temperature. Moreover, the solution routes and low temperature processing minimize the potential for contamination, which is very important for the most applications in the electronic, optoelectronic, chemical industries etc. that are sensitive to some of the impurities.

Compared to other processing techniques, powder
Aerosol synthesis through aerosol routes enable the generation of fine, submicronic to nanoscale, either single or complex, powders from a variety of precursor solutions. It represents basically chemical route having a “bottom-up” approach for powder processing. The diversity of aerosol routes, depending mainly on the nature of aerosol and the manner how the aerosol decomposition energy is transferred to the system are presented on Fig. 1. Two cases are roughly evident in aerosol routes: gas-to-particle route, which relates to the particle formation from the gaseous precursors and droplet-to-particle route, that relates to the formation of discreet aerosol droplets and control of the aerosol decomposition into particles. Depending on how the thermal energy is provided to the precursors, affecting the most important particle formation parameters: residence time and temperature distribution, the main aerosol decomposition methods could be presented as is on Fig. 1. The advantages of aerosol synthesis are as follows: it represents a simple method for production of oxide, non-oxide, metal and composite powders of complex composition, either in amorphous, crystalline or nanocrystalline state. Solution chemistry approaches offer design of materials at the molecular level, spherical particle morphology with full or hollow spheres, with narrow particle size distribution and a very homogeneous composition can be achieved by properly adjustment of the process parameters. For the case of film processing, this method provides easy control of deposition rate and thickness, simple doping of films using any element in any proportion by addition of a suitable dopant into the starting solution, possible production of layered films and films with concentration gradient, vacuum not required in any step of the process and there are no limits concerning dimensions and shape of substrate.

In the case of hot-wall processing, energy source for reaction and particle formation is usually provided through tubular flow reactor, flame synthesis use combustion enthalpy of vapor flame, self sustaining flame reactors use combustion enthalpy of dispersed oil phase in the form of emulsion, self combustion aerosol synthesis use combustion enthalpy of entire solution being chemically modified. Tubular hot-wall flow reactor provide a well-controlled temperature profile over long residence times, while in the case of flame synthesis the decomposition temperatures are higher and the residence time is shorter. In aerosol assisted thin film preparation (Pyrosol process) there is precursor decomposition in the vicinity on the heated substrate. Under certain circumstances, Pyrosol could be assimilated to a chemical vapor deposition process, but it removes restrictions of CVD such as high vapor pressure of precursors and their good thermal stability. In comparison to the pneumatic atomizers, the aerosol produced by ultrasonic atomization enables better controlling of droplet size and size distribution.

2. Hot-Wall Aerosol Synthesis (Spray pyrolysis)

Hot-wall aerosol synthesis is based on the formation of aerosols of precursor solutions and control over the aerosol decomposition in a high temperature tubular flow reactor through the successive processes of droplet evaporation, drying, solute precipitation and decomposition. Since the heterogeneous gas/liquid-solid reaction occurs in a dispersed system-aerosol at the level of few micrometers sized droplets, compositional segregation is prevented and high heating rates (20-300°C/s), as well as high surface...
reaction could be achieved\(^2\). During decomposition, the aerosol droplets undergo evaporation/drying, precipitation and thermolysis in a single-step process. Consequently, spherical, solid, agglomerate-free, either submicronic, nanostructured or nanoscaled particles are obtained through the mechanisms of primary nano-particles coalescence, collision and sintering. Schematic of the hot-wall aerosol synthesis routes is presented in Fig. 2. The process involves formation of discreet droplets of precursor solution in the form of aerosol and control over their thermally induced decomposition and phase transformation.

*Synthesis I* refers to the chemical synthesis and solution preparation that could be in the form of true solutions, colloids or emulsions. In addition, the modification of the chemistry of the solution, i.e. additives like glycine, urea, suchrose etc. alters the morphology of the particles derived as well as the particle size, size distribution and agglomeration state. The precursors and precursors chemistry are usually characterized for their physico-chemical properties like determination of the solution surface tension, viscosity, density, concentration, pH, as well as the decomposition behavior of the precursors since there is a strong relationship between the mentioned solution properties and the droplet/particle size\(^21,22\).

Aerosol is most frequently formed ultrasonically, using high-frequency (100KHz - 10MHz) ultrasonic beam\(^17\) directed to the gas-liquid interface. Liquid atomization and aerosol formation occur for the certain values of the acoustic waves amplitude, where the average droplet size depends mostly on the solution properties (viscosity, surface tension, concentration, density etc.) as well as the ultrasound frequency. It was already shown that this technique is suitable for the aerosol formation with the narrow size of droplet distribution, thus affecting narrow particle size distribution. Depending on the atomization technique, either monodisperse or polydispersed particles could be obtained. The monodisperse nano particles are formed either through the evaporation-condensation mechanisms, using electrospray atomizer or differential mobility classifier\(^23,24\). Twin-fluid and ultrasonic atomization techniques usually led to the formation of polydispersed particles. The droplet size and size distribution depend on the type of atomization and the precursor properties, as presented in Table 1.

The particle size is then defined by the following equation for the case that one particle is derived from one droplet\(^22\):

\[
D_p = D_d \left( \frac{c^* M_s}{\rho_p M_p} \right)^{1/3}
\]

Where: \( D_p \) - particle diameter [\( \mu m \)], \( c^* \) - initial solution concentration [gcm\(^{-3}\)], \( M_s \) - molecular mass of resulting powder [gmol\(^{-1}\)], \( M_p \) - molecular mass of precursor [gmol-1], \( \rho_p \) - powder density [gcm\(^{-3}\)].

The aerosol is carried out by the flowing gas stream into high-temperature tubular flow reactor. Differential mobility analyzer (DMA) or Scanning Mobility Particle Sizer (SMPS) can be used for online determination of the aerosol-born particle’s size, size distribution and concentration\(^20\).

**Fig. 2** Schematic of the hot-wall aerosol synthesis route methodology\(^23\).
The flow rate of the carrier gas represents one of the most important process parameters enabling the supporting atmosphere as well as the aerosol flow rate and the droplets residence time to be controlled. During the main process, denoted as Synthesis II, aerosol droplets undergo evaporation, drying and solute precipitation in a single-step process caused by the mechanisms of heat and mass transfer inside the droplets and between the droplets and surrounding gas. Such mechanism enables high surface reaction, solution stoichiometric retention as well as segregation suppression to the droplet scale. As a result, spherical, solid, agglomerate-free, either nano scale or submicronic particles are obtained having composite inner nano structure.

After solvent evaporation/drying stage and consecutively solute precipitation and decomposition that occurs at the droplet level, the primary particles arise through the thermally induced processes of nuclei formation, collision and coalescence. Resulting particles then arise through the growth and aggregation of nano sized “primary particles” arranged in spherical so called “secondary particles”. The secondary particle size and size distribution are mainly influenced by the properties of aerosol generator and precursor solutions. Primary particles, that represent either crystallites or block-mosaic assemblies, sizing mainly below 50nm, could coalesced entirely or densified with existing nanoporosity and exhibiting high surface area. The Summary of the particle morphology hierarchy is presented at Fig. 3. The size of primary particles depends on the time-temperature history and materials properties. For low temperatures and short residence time particle coalescence proceeds slowly compared to collisions, producing weak agglomerates having a high specific surface area. On the contrary, at high temperatures and for small particles, particle coalescence is dominant process resulting in primary particle growth, hard agglomerates and small specific surface area.

Nanophase particles can be generated in accordance to this method by properly controlling over the initial aerosol droplet size, the mechanisms of the droplet collision and coalescence as well as by suppressing the excessive grain growth and grain coarsening. As a result, it is possible to obtain either nanoparticles directly from nano-sized droplets or to obtain submicronic sized particles, that offer a composite nanograin particle structure.

Table 1 The manner of the aerosol formation and droplet/particle size distribution

<table>
<thead>
<tr>
<th>Aerosol formation /Droplet size equations, $\mu m$</th>
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<tbody>
<tr>
<td><strong>Monodispersed droplets/particles</strong></td>
</tr>
<tr>
<td>Evaporation-Condensation <strong>23</strong></td>
</tr>
<tr>
<td>Electrospray aerosol route <strong>20</strong></td>
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<tr>
<td>Differential mobility classifier <strong>20</strong></td>
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<tr>
<td><strong>Polydispersed droplets/particles</strong></td>
</tr>
<tr>
<td>Twin-fluid atomizationEmpirical relationship S.Nukiyama, Y.Tanasawa <strong>21</strong> ***</td>
</tr>
<tr>
<td>[ D_d = \frac{585}{V} \left( \frac{r}{\rho} \right)^{0.5} + 597 \left( \frac{\mu}{(\gamma \rho)^{0.5}} \right)^{0.45} \left( \frac{1000 F_G}{F_G} \right)^{1.5} ]</td>
</tr>
<tr>
<td>Ultrasonic atomization Lang <strong>21</strong> ***</td>
</tr>
<tr>
<td>[ D_d = 0.34 \left( \frac{8 \pi \gamma}{\rho f} \right)^{1/3} ]</td>
</tr>
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</table>

** $D_d$: droplet diameter [ $\mu m$ ]; $V$: relative carrier gas- to -liquid velocity at the nozzle exit[ms$^{-1}$]; $\gamma$: solution surface tension [10$^3$ Nm$^{-1}$]; $r$: solution density [gcm$^{-3}$]; $\mu$: solution viscosity [Pas]; $F_G$: gas flow rate [cm$^3$s$^{-1}$]; $F_L$: liquid flow rate [cm$^3$s$^{-1}$]

*** $D_d$: droplet diameter [ $\mu m$ ]; $\gamma$: solution surface tension [dyncm$^{-1}$]; $r$: solution density [gcm$^{-3}$]; $f$: ultrasound frequency [10$^3$ s$^{-1}$]

Table 1 The manner of the aerosol formation and droplet/particle size distribution
species, that cause droplets/particles to be decomposed with additional heat and exploding during the process, leads to the direct synthesis of nanoparticles\textsuperscript{13,15}.

The choice of precursors, their thermal and decomposition behavior play an important role in nanoscaled particles synthesis, as well\textsuperscript{36,37}. The mechanisms of nucleation and growth of primary particles, ranging from few to several tens of nanometers, which gather together during decomposition process into spherical agglomerates, or so called “secondary particles” the mean size below 1000nm, play a crucial role in formation of particle size and morphology\textsuperscript{15,38}.

Salt assisted spray pyrolysis (SAD) enable releasing the nano-scaled primary particles by modification of the solution chemistry and preventing formation of hardly aggregated primary particles into the secondary particles\textsuperscript{36}.

From the viewpoint of the application of the as-generated particles for advanced materials synthesis, particle morphology is of great interest. Aerosol synthesis enables synthesis of various particle morphology, either as hollow or dense spheres. It is presumed that certain particle morphology is formed during the evaporation/drying stage that encountered processes of evaporation and diffusion of both the solvent, and

\textbf{Fig. 3} Summary of the particle morphology hierarchy.

\textbf{Fig. 4} Nanoscale particle synthesis through aerosol route.
solute, changing in droplet temperature and crust formation. They are governed by the basic laws of heat and mass transfer so several models describing the above mentioned phenomena are developed and can be applied in prediction of particle morphology\textsuperscript{39-41}. The problems regarding droplet collision and consequently droplet coalescence or agglomerated particles formation are often associated with ultrasonic spray pyrolysis, since reducing droplet size significantly increases the probability for collision\textsuperscript{2}.

Agglomerated particles are undesirable especially for afterwards sintering purposes, causing hard agglomerates formation and inducing local grain growth and inhomogeneity.

On the contrary of the reports on the mechanisms of particle formation from inorganic salts, solid particles are often generated from metal alkoxides or organic solutions if they undergo polymerization process\textsuperscript{29, 33, 42-43}. Another feature that strongly alters the particle morphology is transferring ions into gas phase in the case of volatile precursors\textsuperscript{44}. In this case the particles are formed both from gas as well as liquid (solid) phase, leading to the broad size of particle distribution and to the differences in particle morphology. From the viewpoint of difficulties for the stoichiometry retention in the case of multicomponent systems, this feature has to be controlled carefully.

Depending on the process parameters – temperature and residence time, either amorphous or crystalline particles can be obtained. It was shown that proper adjusting of the mentioned parameters enables synthesis of either nanophasre, polycrystalline or single-crystal particles by controlling over the mechanisms of grain growth and sintering\textsuperscript{2, 28}. Numerous materials, either in the form of thin films or nanostructured/nanoscaled particles as metal oxides, mixed metal oxides, nonoxides and metals have been obtained by this method and have reviewed in literature\textsuperscript{2,3,6,13,45,46,47}. The potentials of the aerosol routes for making solid-states structures at the nano size level are virtually unlimited, providing possibilities for new and unique applications in electronics, optoelectronics, catalysis, energy conversion systems, drug delivery etc. It has been reported synthesis of electrode material for solid oxide fuel cells\textsuperscript{48, 49}, phosphors\textsuperscript{47,50}, metal-ceramic and ceramic-ceramic nanocomposite particles synthesized in environmental conditions\textsuperscript{51, 52} and under microgravity\textsuperscript{53}. The examples of experimental set-up for the spray pyrolysis developed at the several research centers and universities are presented at Fig. 5.

The program of controlled and sophisticated powders and films synthesis has been realized in the Institute of Technical Sciences of the Serbian Academy of Sciences and Arts (ITS SASA) since past two decades. In the framework of this research, the method of aerosol synthesis of nanophased powders

![Fig. 5. Experimental set-up in Japan Fine Ceramic Centre, Nagoya (a,b,c), with 4 heating zones, $T_{max} = 1000^\circ C$\textsuperscript{48-50}, 4 separating heating zones, $T_{max} = 1000^\circ C$ for the synthesis of ceramic-metal nanocomposites; 5 heating zones, $T_{max} = 1200^\circ C$ for the synthesis of ceramic-ceramic nanocomposites\textsuperscript{51, 52}, respectively; Osaka University, JWRI (d) for the synthesis of ceramic nanoparticles under microgravity\textsuperscript{53} (with courtesy of Dr. Ohara, Osaka University, JWRI, Japan).]
and films is developed together with the experimental and pilot set-up [Fig. 6]: the experimental set-up is based both on electrospray (TDI) and ultrasonic (800 kHz, 1.3, 1.7 and 2.5 MHz, RBI) atomizing systems, while a pilot plant is based on twin-fluid atomization technique, equipped with a Scanning Mobility Particle Sizer (TDI) for in-situ determination of aerosol properties. It offers the opportunity for the synthesis of both monodisperse and polydisperse nanoscaled particles in different oxide and nonoxide systems. Moreover, a Pyrosol technique for thin film synthesis through aerosols is developed, too. Based on these techniques, the synthesis of fine, spherical, submicronic powders either in crystal or amorphous state based on oxides, metals and non-oxides have been processed as follows: ZnO\textsuperscript{38,41,54,55}, ZnO-Pt(IV)\textsuperscript{56}, ZnO-Ru(III)\textsuperscript{57}, BaTiO\textsubscript{3}\textsuperscript{42}, ZnO-Cr\textsubscript{2}O\textsubscript{3} spinel\textsuperscript{58}, Al\textsubscript{2}O\textsubscript{3} based materials\textsuperscript{59}, Ni, NiO\textsuperscript{60}, SiC\textsuperscript{61}, Q-TiO\textsubscript{2}\textsuperscript{62}, nano-composites Ag:(Bi,Pb)-2223\textsuperscript{15,63,64}, phosphors, Gd\textsubscript{2}O\textsubscript{3}: Eu\textsuperscript{10,65,66,67}, Y\textsubscript{2}O\textsubscript{3}: Eu, (GdY)\textsubscript{2}O\textsubscript{3}: Eu\textsuperscript{20,68,69}, Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}: Ce\textsuperscript{10,70-74}, LiFePO\textsubscript{4}\textsuperscript{75}. Those materials are applicable for electronics, optoelectronics, engineering ceramics, catalysts, biomaterials etc.

3. Opportunities of Hot Wall Aerosol Route (Spray Pyrolysis) for Phosphor Materials Processing

The opportunities for the synthesis of spherical, nonagglomerated particles with uniformly distributed components and phases are of special importance when phosphor materials having luminescence properties are considered. Phosphors represent inorganic crystal structures capable of emitting definite quantities of radiation within visible and/or ultraviolet spectrum as a result of excitation by an external energy source such as electron or a photon beam\textsuperscript{76,77,78}. Such properties of these materials are an outcome from the atomic state interactions that occur between luminescent centers and the host lattice material after the excitation. Rare earth ions (Eu\textsuperscript{3+}, Ce\textsuperscript{3+}, Tb\textsuperscript{3+}, Nd\textsuperscript{3+}) and transition metal ions (Cr\textsuperscript{3+}, Mn\textsuperscript{2+}) are commonly used as luminescent centers\textsuperscript{79,80}. Luminescent materials are normally utilized in cathode ray tubes for television screens and due to excellent characteristics of these materials their use has increased in the past years due to their application in modern emissive display industry such as flat screens, plasma and electroluminescence screens, etc. The most important properties that luminescent materials should pos-

![Fig. 6 Experimental set-up at ITS SASA having two (upper) and three (down) heating zones, equipped with an electrostatic precipitator for powder collecting and ultrasonic atomizers, 800 kHz, 2.1 MHz, RBI, Meylan, France (down).](image-url)
Luminescence properties are strongly affected by the phosphor crystallinity, phase purity, distribution of activator, surface area and particle morphology\(^{82-84}\), more efforts have been done in promoting the researches toward new methods for nanoparticles synthesis. Spray pyrolysis method has been recognized as a successful to obtain phosphor powders with high purity, homogeneous distributions of activator centers, narrow distribution of particle size and spherical morphology in nanometric scale\(^{47}\).

### 3.1. Gd\(_2\)O\(_3\):Eu\(^{3+}\)

Gadolinia doped with europium has been used in several applications for display devices as effective red phosphor material having improved stability in high vacuum and the absence of corrosive gas emissions under electron bombardment\(^{85}\). Since the luminescent behavior is greatly affected by the phosphor particle morphology and compositional homogeneity, the advantages of spray pyrolysis over conventional solid-state synthesis are huge, as already reported in literature\(^{47,82,85,86}\).

As part of a programme to develop high grade phosphor particles, spherical in shape, agglomerated-free and with a narrow size distribution, efforts have been made to prepare material using a hot wall spray pyrolysis approach\(^{10,50,65}\). With regards to that, nanostructured, spherical Gd\(_2\)O\(_3\):Eu\(^{3+}\) phosphor particles sizing bellow 800nm were synthesized from ultrasonically generated common nitrates solutions (Fig. 7). As seen, the particle inner structure clearly resolved by the low and high magnification TEM implies the typical particle morphology obtained by spray pyrolysis composed of nano sized primary particles assembled in a spherical secondary particle. Visual inspection of the particle morphology is done by means of STEM nanotomography corresponding to the particle annealed at low temperature (900°C/12h), as shown in Fig. 8\(^{86}\). The contrast obtained with HAADF-STEM implies bright and dark areas in a spherical shaped particle sized approx 500nm where dark contrast observed in the tilt series indicates the presence of voids and a rough particle surfaces. In the reconstructed images (Fig. 8, right), the better contrast than the original image allows confirming the porous and rough surfaces. It was supposed that the particle roughness is presumably a consequence of the primary particles crystallization, aggregation and growth in the secondary particles caused by the temperature increase.

In comparison to the particle morphology of conventionally obtained phosphor materials, here spherical particle morphology enables high packing.

**Fig. 7** Field emission scanning electron microscopy (FE-SEM) (upper), TEM, HR-TEM (400 KV JEOL JEM 4000 EX) of the as-prepared Gd\(_2\)O\(_3\):Eu\(^{3+}\) particles (down), respectively.
densities, higher brightness and resolution\(^{82}\). On the other side, hollow and porous particles have lower signal intensity in comparison with dense spherical particles\(^{86}\). Besides, particle roughness and the agglomeration state are very important factors that affect the luminescence signal, implying the necessity to follow the morphology features and correlate them with the process parameters, like temperature, residence time, precursor decomposition behavior etc. In addition, the sensitization of the as-prepared particles is a critical stage in phosphor preparation and sensitivity improves with increasing the crystallinity and homogenization of the Eu dopants within the particles. Success in this processing have been obtained with additional thermal treatments of the as-prepared particles above 800 °C, where the thermally induced interparticle sintering did not occur and initially obtained morphological features were preserved\(^{65}\).

Detailed phase and structural analysis proceeded in accordance to XRPD, TEM-HRTEM and EFTEM analysing methods, proved uniform compositional distribution of the constitutive elements along the particles obtained via spray pyrolysis as seen from the corresponding gadolinium and europium EFTEM spectra (Fig.9). EFTEM-EELS spectrum obtained for Gd:O\(_2\):Eu\(^{3+}\) particles additionally annealed at 900°C/12h (gray line) and 1000°C/12h (black line) in the ELNES region show the Gd M4 and Gd M5 signal for both samples (around 1185ev-1187ev) and the Eu M5 and Eu M4 signal around 1131ev-1186ev. The comparison between the spectrum indicates the incorporation of the Eu in the Gd matrix, while no changes in the energy and intensity M4/M5 ratio (0.83) indicates a (+3) oxidation state in the samples with different Eu content and thermal treatment (Fig. 10).

Host gadolinium oxide exhibits two polymorphic forms, low temperature (cubic) and high temperature (monoclinic), so several studies dealing with the investigation of Gd:O\(_2\) crystal phases development dur-

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**Fig. 8** STEM image of the tomographic tilt series. The vertical line indicates the rotation axis. A Tecnai TEM G² F20 X-TWIN with Fischione “single tilt” stage in HAADF mode operated at 200KV TEM was employed (left); reconstructed tomographic image: the inspect 3d v 2.5 X press Edition software and AMIRA software in cross correlation mode was employed (right).

**Fig. 9** The low magnification EFTEM images, Libra, 120kV, with a corrected 90° OMEGA energy filter.
ing aerosol synthesis and their relationship with luminescence properties were reported. XRPD revealed here the presence of two crystalline cubic phases in as-prepared powders: a bcc phase with \( Ia3 \) space group (\( a \approx 10.829(3) \) Å); and a fcc phase with \( Fm-3m \) space group (\( a \approx 5.6242(1) \) Å) for the Eu\(^{3+}\) doping concentration. After thermal treatment only the cubic \( Ia3 \) phase has been observed, with the cell parameters affected with Eu\(^{3+}\) doping concentration. HR-TEM implied the primary nanoparticles of the as-prepared powders are associated with the defect structure (Fig. 7). After annealing above 900°C, it is evident the better order related to the orientation in the atomic frames and a decreasing of defects content. In confirmation of the stated above, a HRTEM image of the cubic phase with \( Ia3 \) symmetry taken along the [100] zone axis is presented at Fig. 11 indicating high crystallinity and clearly resolved the (002) and (020) atomic planes. In addition, HRTEM analysis also proved the locally appearance of a monoclinic phase with \( C2/m \) symmetry taken along the [1-10] zone axis. The atomic distance (110) is resolved in the image (Fig. 11, right). The appearance of the higher density metastable monoclinic structure is probably a consequence of the extreme synthesis conditions during spray pyrolysis, i.e. high heating rates and short residence time and attributable to the Gibbs-Thomson effect, associated with increased surface tension with nanostructuring.

Luminescence studies carried out in Gd\(_2\)O\(_3\):Eu\(^{3+}\) phosphor system have demonstrated that annealing and crystalline phases control both the thermoluminescence and radioluminescence signals. Characteristic bands in the emission spectra are assigned to Eu\(^{3+}\) ion radiative \( ^{5}D_{0} \rightarrow ^{7}F_{i} \) (\( i = 0,1,2,3,4 \)) transitions. In all the samples maximum intensity peak is at 611 nm wavelength belonging to \( ^{5}D_{0} \rightarrow ^{7}F_{2} \) transition. All observed transitions are due to the Eu\(^{3+}\) in C\(_{2}\) crystallographic site except one line, at 581 nm (attributed to \( ^{5}D_{0} \rightarrow ^{7}F_{1} \) transition) that belongs to Eu\(^{3+}\) in S\(_{6}\) crystallographic site.

3.2. Y\(_2\)O\(_3\):Eu\(^{3+}\)

Y\(_2\)O\(_3\) doped with europium is a well known red phosphor material employed in modern high-resolution display devices such as plasma display panels (PDP) and field emission displays (FED). The incorporation of gadolinium in the yttria matrix may significantly contribute to the luminescent properties and x-ray absorption coefficient thus increasing the field of application in optoelectronic devices such as ceramic scintillators for computed tomography.

The interest of the Y\(_2\)O\(_3\) has been broadly known due to its particularly relevant physical and functional properties, including the crystallographic stability, a...
wide band-energy gap (5.5e.v.) and the ability to be a host material for rare earth ions. Yttrium oxide is a good phosphor material with different luminescent spectra depending on the luminescent center by which it is activated (for example Eu, Tb, Dy, Tm or Nd); doped with Eu$^{3+}$ is a well known red phosphor in flat panel displays$^{90-92}$. In particular, it has been shown that if in nanostructure form it possesses improved quantum efficiency while the mixed oxide with rare earth ions (RE), the RE$_x$Y$_{2-x}$O$_3$ type, represents a new group of superconducting materials.$^{93}$ Yttria represents one of the best host materials for rare earth ions due to the fact that its ionic radii and crystal structure are very similar to the ionic radii and crystal structure of the rare earth ions$^{82}$.

There are several crystal structures of Y$_2$O$_3$: cubic, type Mn$_2$O$_3$, which represents a stable equilibrium structure under stationary conditions and monoclinic structure with space group C$2/m$ that can be formed under extreme synthesis conditions$^{65,94}$. The nanostructured particles of Y$_2$O$_3$ doped with Eu$^{3+}$ were processed through the spray pyrolysis method from nitrate precursors$^{20}$. Synthesis was carried out with an ultrasonic aerosol device operating at 1.3 MHz in air atmosphere connected with a triple-zone tubular flow reactor (200-700-900 $^\circ$C) (Fig. 6). Particles were submitted to post-thermal treatments at temperatures among 1000 and 1200 $^\circ$C for 12hours in order to increase the crystallinity and uniform distribution of doped centers. The particles obtained were spherical, having narrow size distributions, high compositional homogeneity and were in unagglomerated state (Fig. 12). Exceptionally, sintering start point was noticed in the case of the samples thermally treated at 1200$^\circ$C. That is, TEM analysis revealed neck formation between secondary spherical particles$^{10,69}$.

The Ia$3$ phase has been identified by XRD and TEM-HRTEM/FFT in both as-prepared and thermally treated samples. No intermediate phase is observed along the particles. Rietveld refinement revealed that crystallite size of the as-prepared powders was around 20nm while sufficient energy supply during the thermal treatment led to crystallite growth (40-130nm for annealing temperatures 1000-1200$^\circ$C, respectively) and affected structural relaxation (lower values of microstrain in comparison to the values for ap samples) (Table 2).

Functional characterization done through the determination of photoluminescent characteristics showed typical emission spectra of Eu$^{3+}$ ion incorporated into yttrium oxide. Emission spectra were obtained at room temperature through excitation of Eu$^{3+}$ ion into $^5$£ energy level under 393nm wavelength (Fig. 13). The emission lines of Eu$^{3+}$ were ascribed to $^5$D$^0$调控 7F$^j$ (j = 1, 2, 3, 4) spin forbidden f-f transitions and the main emission peak corresponded to clear red emission at 611nm. Detailed analysis of the emission spectra showed that they consist out of sharp peaks, originating from Eu$^{3+}$ ion incorporated into C$_2$ site, while only one week line belonging to Eu$^{3+}$ ion incorporated into S$_6$ site was observed. Maximum Stark splitting ($\Delta E$) of the $^5$F$_1$ manifold, occurring under the influence of the crystal field, was in agreement with theoretical values Y$_2$O$_3$:Eu$^{3+}$ ($\Delta E$(Y$_2$O$_3$) = 355cm$^{-1}$)$^{95}$. Based on the fluorescence decay curves of the $^5$D$_0$ emitting level it was concluded that applied synthesis method (spray pyrolysis) leads to the formation of nanostructured powders having longer lifetimes in comparison to Y$_2$O$_3$:Eu$^{3+}$ in its bulk form ($\tau$ ($^5$D$_0$ $\rightarrow$ $^7$F$_2$)$_{\text{theor}}$=1.0ms (Y$_2$O$_3$)). Also, it was shown that samples with doping concentration of 10 at% Eu$^{3+}$ had lower $^5$D$_0$ lifetimes (around 1.2 ms) in comparison to 5 at% (around 1.4 ms) leading to a conclusion that in the case of higher doping level concentration quenching occurs (Table 2).

Through the analysis of lifetime values for Eu$^{3+}$ $^5$D$^1$ emitting level for Y$_2$O$_3$ with 5at% of Eu$^{3+}$ the influence of thermal treatment was monitored (Fig. 13).

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**Fig. 12** (Y$_{0.95}$Eu$_{0.05}$)$_2$O$_3$ (left) and (Y$_{0.90}$Eu$_{0.10}$)$_2$O$_3$ (right) thermally treated at 900$^\circ$C and 1000$^\circ$C, respectively.
Namely, as-prepared powders had a lower value of these parameter (around 11 μs) while the value for thermally treated was slightly higher (around 20 μs). Knowing that decrease of emission intensity from 5D1 emitting level is due to increased probability of cross-relaxation mechanism which occurs when there is an increase of Eu3+ concentration in the yttria host lattice it was concluded that cross-relaxation effect was stronger in the case of as-prepared samples. Above stated observations indirectly depicted more homogeneous distribution of Eu3+ ions in case of the annealed samples.

### 3.3. (Y,Gd)2O3:Eu3+

(Y1-xGdx)2O3:Eu3+ system, where the gadolinium content was varied (x = 0.25, 0.50, 0.75), has been synthesized throughout the same conditions as Y2O3:Eu3+. TEM investigations revealed that these systems poses the same morphological features as yttrium oxide system i.e. particles possess spherical filled morphology. Additionally SAED patterns revealed polycrystalline nature of the particles, while the ring width implied high defect content in as-prepared samples Fig. 14. Through XRD and TEM/SAED analysis it was also shown that gadolinium content had influence on the structural phase characteristics. To be exact, as-prepared samples with composition x = 0.25, 0.50 had solely Ia3 phase, but the sample compositionally closest to pure Gd2O3, with x = 0.75, showed the same characteristics as gadolinium oxide synthesized under similar conditions. Apart from primary, cubic bcc Ia3 phase a second cubic fcc...
phase with \( Fm-3m \) space group was confirmed in ap samples. All the as-prepared samples where ther- mally treated at 1100\(^\circ\)C for 12h and in this case only \( Ia3 \) phase prevailed.

Observing the optical properties, the same charac- teristic emission spectra of Eu\(^{3+} \) ion were seen as in the case of pure Y\(_2\)O\(_3\):Eu\(^{3+}\) system. Detailed analysis of the emission spectra showed that in the case of (Y\(_{1-x}\)Gd\(_x\))\(_2\)O\(_3\):Eu\(^{3+}\) system a linear increase of maximum Stark splitting (\( \Delta E \)) occurs with the increase of gadolinium content (Table 3), i.e. with the increase of lattice parameters. Since maximum splitting of the \( ^7F_1 \) manifold is affected by crystal field strength parameter in a proportional way, the increase of \( \Delta E \) value with the increase of gadolinium content could be treated as a clear indication of almost perfect mix- ing in solid solutions of (Y,Gd)\(_2\)O\(_3\):Eu\(^{3+}\) system.

When doped with 5at% mixed (Y\(_{1-x}\)Gd\(_x\))\(_2\)O\(_3\):Eu\(^{3+}\) ox-ides, thermally treated at 1100\(^\circ\)C, had similar lifetime values of \( ^5D_0 \) emitting level in comparison to yttria with same doping concentration (around 1.4 \( \mu \)s). In the case of \( x=0.50 \), doping was done with 5 and with 10at% of Eu\(^{3+}\) and in these case \( ^5D_0 \) lifetime of the sample with higher doping concentration was signifi- cantly smaller i.e. 0.86 \( \mu \) s. It indicated concentration quenching and that (Y\(_{1-x}\)Gd\(_x\))\(_2\)O\(_3\):Eu\(^{3+}\) with \( x=0.50 \) and 10 at% of Eu\(^{3+}\) had inferior properties than the material in bulk form. Relatively high values of \( ^5D_1 \) lifetimes for thermaaly treated (Y\(_{1-x}\)Gd\(_x\))\(_2\)O\(_3\):Eu\(^{3+}\) pow- ders with 5at% revealed, as in the case of Y\(_2\)O\(_3\):Eu\(^{3+}\), implied homogeneous distribution of the doping ion.

### 3.4. Y\(_3\)Al\(_5\)O\(_{12}\) (YAG): Ce\(^{3+}\)

The Y\(_3\)Al\(_5\)O\(_{12}\) (YAG) is optically isotropic mat-...
YAG:Ce 3+ with high thermal conductivity. Doped with rare earth ions it represents very useful phosphor material for variety of display applications including cathode ray tube, low voltage field emission display, and backlight source. Specially cerium doped YAG (YAG:Ce 3+), as a yellow-emitting component for the production of a white light, is a comprehensively studied previous years due to urgent demand for alternative light source in an illumination and display area. The broad Ce 3+ emission band originates from the 4f-5d electronic transition with intensive side bands due to vibronic coupling to the lattice and local vibration modes in the YAG lattice. Due to this YAG:Ce 3+ easily convert blue emission from blue light emitting diode (LED) into white LED. Even a lack of cerium emission toward the red region can be suppressed by a co-doping (Tb 3+ ) or cation substituting (Ga 3+ or Gd 3+ ) making presently this material to be the phosphor of choice in commercial white LEDs 100.

First publication related to luminescence investigation in YAG:Ce 3+ system dated from 1967 101. Compared with this traditionally produced garnet by solid-state reaction between the component oxides, today’s phosphor materials usually produced through soft-chemistry processes possess many advantages thanks to their certain structural and morphological characteristics. The field of aerosol processing was intensively developed in the last 10 years and many phosphorous materials have been produced up to now 102,103. Processing of YAG:Ce 3+ powder via spray pyrolysis (ultrasonic and FEAG) has been previously reported 102,103. Significant advance is shown due to the mixing of starting reactants at molecular scale, but obtaining of the pure garnet phase was hindered by retaining of amorphous phase in synthesized powders. Therefore, annealing process at high temperatures was applied for the crystallization and activation of cerium-doped YAG particles. In latter work 104, it was shown that the PL intensity of YAG:Ce 3+ particles was strongly affected by doping concentration of cerium, annealing temperature, mean particle size, and particle morphology. The non-aggregated spherical particles of YAG:Ce 3+ (1at% Ce 3+) annealed at 1300°C showed the maximum photoluminescence emission. Several papers devoted to the same topic were reported in the following years, highlighting the complexity of synthesis - structure relation towards achieving optimized phosphors properties. It was shown that concentration of nitrates solution and the flow rate of nitrogen used as a carrier gas have the major impact on the productivity of the spray pyrolysed particles 104. Significant morphological and functional enhancement through BaF 2 flux introduction in common nitrates solution during spray pyrolysis resulted in the intensification of the maximum peak intensity of the prepared YAG:Ce 3+ phosphor powders in comparison to that of the commercial phosphor powders 105. The addition of urea into nitrate precursor contributes to nanoparticles formation due to its combustion in the flame zone and improves their optical performance 106. Further enhancing of the YAG:Ce 3+ luminescence efficiency can be realized through Tb 3+ co-doping due to occurring of the effective energy transfer from Tb 3+ to Ce 3+ in YAG host lattice 107. But in all of above reports in situ generation of garnet phase during spray pyrolysis is omitted or associated with Y 3 Al 2 O 12 (YAM) or YAlO 3 (YAP) phases appearing so additional thermal treatment of processed powder is obligatory. The technique of spray pyrolysis was employed also to produce homogeneous solid solutions in the Al 2 O 3 –Y 3 O 5 system at temperatures as low as 150-300°C, owing to the prevention of segregation of the precursors prior to YAG phase crystallization 108. Another attempt has been made using “single-source” precursors (alkoxides and glycolates) instead of “multiplesource” precursor 109. The lack of formation of YAG in all the spray pyrolysis experiments was ascribed to the short heating times and fast heating rates, which resulted in the formation of kinetic products.

Rationalization of the sequence for nanocrystalline YAG:Ce 3+ phase evolution in the particles synthesized by ultrasonic spray pyrolysis method through variation of processing parameters or precursors composition was also the topic of our research 10,70-74. It was shown that particle morphological and structural characteristics are dependent on the applied synthesis methodology, especially regarding the precursors solution modification. Synthesis from common nitrates precursors was performed at 900°C in a tubular flow reactor using the air to carry the aerosol. Short residence time during synthesis resulted in multiphase powder generation. Beside garnet phase, YAM and Y 2 O 3 were also detected 71. Synthesized particles were submicronic in size, highly spherical and unagglomerated (Fig. 15). They exhibit rough surface implying that are built from primary nanoparticles 70. Their general morphology did not change significantly with annealing, but their roughness increase further due promoted crystallization affecting their specific surface 72. Incorporation of Ce 3+ ions at the host is confirmed with the broad emission having peak maximum at 533nm 70. The interpretation of the thermo- and radio- luminescence signals from
the YAG:Ce\textsuperscript{3+} powders implies that the cerium ions are not readily accommodated on the YAG lattice sites during synthesis\textsuperscript{65}. Even after annealing cerium ions do not offer a favourable excitation decay path; instead, there are broad emission bands typical of the host lattice defect sites and a very weak luminescence via the cerium on pathway near 300nm. The complexity of the temperature dependence of the TL as a function of wavelength also suggests that a variety of independent defect sites contributes to the TL. They also indicated numerous anomalies in the temperature dependence of their luminescence lifetime data.

To investigate the nature of the multiphase powder obtaining, an amorphous material with composition corresponding to yttrium aluminum garnet phase with same content of cerium has been synthesized at 320°C using a similar spray pyrolysis route. Precursor-derived amorphous phase crystallized at temperatures as high as 900 and 1000°C gave multi-phased powders with different compositions after 3h of annealing (YAG, YAP, YAM), while prolongation of treatment at higher temperature result in pure YAG phase formation (Fig. 16)\textsuperscript{73}.

In order to achieve additional heating during YAG:Ce\textsuperscript{3+} synthesis urea-assisted spray pyrolysis was employed\textsuperscript{111}. 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 as-prepared non-agglomerated amorphous powder has broad particle size distribution (200-1400nm) (Fig. 17). They were additionally thermally treated in air at 1000 and 1100°C for 6h preserving their morphological characteristics. Despite of precursor modification during synthesis, performed annealing did not yield pure YAG:Ce\textsuperscript{3+} product. While lower temperature is favorable for YAP and YAM phase segregation, increase of heating temperature enhanced YAG phase formation with YAM phase retention.

Having this in mind, preservation of the molecular homogeneity during precursor synthesis was done through polymerization with an organic complexing agent EDTA and ethylen glycol (EG)\textsuperscript{74}. Two reactions are involved, a complex formation between EDTA and metals (via four carboxylate and two amine groups) and esterification between EDTA and EG. Ultrasonically generated aerosol droplets were decomposed at 600°C in argon atmosphere. Following the initial attempt in providing pure YAG:
Ce$^{3+}$ phase generation the particles were additionally thermally treated for 3h in air at 1000°C and 1100°C. Comprehensive structural analysis implied that garnet phase was formed without contamination of other phase having different aluminum yttrium composition even at the lower annealing temperature and in a much shorter time. The spherical dense particles comprised grained-like structure, since they are composed of nanosized garnet monocrystals (Fig. 18). Although uncompleted, cerium incorporation in garnet matrix is confirmed by broad green-yellow emission spectra in the range of 470-670 nm peaking at 521nm. With this optimization of the spray pyrolysis reaction conditions towards synthesis of pure, un-agglomerated YAG:Ce$^{3+}$ particles with spherical shape and filled morphology were achieved.

4. Conclusions

Aerosol route represents a versatile synthesis method for processing novel functional materials. An insight into the diversity of this method and materials that could be produced was given within this paper with the highlight on hot-wall aerosol synthesis of phosphor particles based on Gd$_2$O$_3$:Eu, Y$_2$O$_3$:Eu, (Y$_{1-x}$Gd$_x$)$_2$O$_3$:Eu and Y$_3$Al$_5$O$_{12}$:Ce which are a part of the current research in the Institute of Technical Sciences of SASA, Serbia. As it was summarized, the syntheses from the aerosol are found to be of great value since they result in well defined phosphor powder characteristics essential for achieving higher brightness and resolution in displays. Particularly, it was shown that spray pyrolysis is one of the simplest among them and is capable in ensuring particle spherical morphology, good crystallinity and uniformity in size and shape. Those characteristics enhance uniform distribution of the luminescent centre in the host matrix influencing final luminescence properties.

Targeted cubic crystal structure of RE$_2$O$_3$:Eu oxide powders (RE=Gd,Eu) was obtained in all as-prepared samples and it persisted as the only phase through-
out the thermal treatment (1000-1200°C /12h) which led to the improvement of crystallinity. Appearance of secondary fcc Fm-3m phase in as-prepared samples of Gd2O3:Eu3+ and mixed oxide with highest content of gadolinium (Y0.25Gd0.75)2O3:Eu3+ was identified through XRD and TEM/SAED analysis. Additionally, in the case of Gd2O3:Eu system HRTEM analysis revealed local appearance of a metastable, monoclinic phase at temperatures above 1100°C associated with a high content of interfaces and high defect content. Generally, in the case of RE2O3:Eu oxides a good control over morphological features was accomplished. Controlled synthesis parameters led to the formation of powders consisted out of spherical, non-agglomerated particles with narrow size distribution (300-800nm). TEM/HRTEM analysis revealed their nanostructural nature (primary particles as low as 20 nm) and filled morphology. Functional characterization of RE2O3:Eu revealed typical emission spectra of Eu3+ ion incorporated into rare earth oxides with dominant red emission peak at 611nm. The development of local defect structure, depending on the time-temperature history of phosphor processing, may influence the emission spectra causing broader luminescent lines. For (Y,Gd)2O3:Eu oxides the increase of Gd content in the yttria matrix had an influence on the spectra and it was observed throughout the increase of maximum Stark splitting (ΔE) of the 7Fj manifold. Such behavior was treated as a clear indication of almost perfect mixing in solid solutions of (Y,Gd)2O3:Eu3+ system. Based on the fluorescence decay curves of the 5D0 emitting level of Y2O3:Eu3+ and (Y,Gd)2O3:Eu3+ systems it was concluded that applied synthesis method led to the formation of nanostructured powders having longer lifetimes in comparison to Y2O3:Eu3+ in its bulk form. Also, these analyses showed that concentration quenching occurs for the case of 10 at% doping concentration of Eu3+ in comparison to 5 at% due to lower values of 5D0 lifetimes.

In the case of YAG:Ce3+ the control over their morphological properties was not completely achieved due to the fact that fully dense particles were not generated from nitrate precursors. Additionally, applying the concept of low temperature aerosol decomposition resulted in preservation of the desired powder morphology but formation of YAG phase was still followed by YAM and Y2O3 phases. The drawback was in the fact that high heating rates and short residence time, inherent to spray pyrolysis process, led to the formation of kinetically stable phases rather than the thermodynamically stable target YAG phase. Since spray pyrolysis offers different approaches for controlling of the particle morphology and composition, obtaining of the YAG:Ce3+ particles with spherical and filled morphology was done through introduction of polymeric precursor solutions. The absence of intermediate phases implied that observed differences in solubility of yttrium and aluminum sources (liable for sequential precipitation and phase segregation) could be prevailed through homogeneous dispersion of Y3+ and Al3+ ions into polymeric organic network formed by esterification. Enhancement in PL intensity of synthesized particles indicated reduced dimensionality of their primary entities (crystallites) and homogeneity distribution of cerium ion in the YAG host lattice.

Acknowledgement

The authors are grateful to the Ministry of Science and Technology of the Republic of Serbia for financial support (Project #142010), NEDO International Joint Research Grant Program 01MB7 and COST 539 Action. The authors gratefully acknowledge Dr. Satoshi Ohara, JWRI, Osaka University, Japan for kind assistance as well as the contribution of Dr. M. Dramicanin, Institute “Vinca”, Japan, in the preparation of this article. FEI Holland is greatly acknowledged for nanotomography measurements.

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Author’s short biography

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