

## Synthesis and Properties of Multimetal Oxide Nanopowders via Nano-explosive Technique

Oleg Vasylykiv<sup>1a</sup>, Yoshio Sakka<sup>1b</sup>, Valeriy Skorokhod<sup>2c</sup>

<sup>1</sup>National Institute for Materials Science  
1-2-1, Sengen, 305-0047, Japan

<sup>2</sup>Institute for Materials Science NASU

<sup>3</sup>Krzhizhanivski Str., Kiev, 03680, Ukraine

<sup>a</sup>oleg.vasylykiv@nims.go.jp, <sup>b</sup>sakka.yoshio@nims.go.jp, <sup>c</sup>skorokh@materials.kiev.ua

### Abstract

*We demonstrate the methodology of engineering the multi-component ceramic nanopowder with precise morphology by nanoblast calcinations decomposition of preliminary engineered nanoreactors. Multiple explosions of just melted  $C_3H_6N_6O_6$  embedded into preliminary engineered nanoreactors break apart the agglomerates due to the highly energetic impacts of the blast waves. Also, the solid-solubility of one component into the other is enhanced by the extremely high local temperature generated during each nano-explosion in surrounding area. This methodology was applied for production of agglomerate-free nano-aggregates of  $Gd_{20}Ce_{80}O_{1.95}$  with an average size of 42 nm and  $LaSrGaMgO_{3-x}$  nanopowder with an average aggregate size of 83 nm.*

**Keywords :** oxides, sol-gel, nanopowders, synthesis, aggregates, agglomerates, explosive

### 1. Introduction

Agglomeration of nanosized particles refers to adhesion of particles to each other because of van der Waals forces of attraction, which is significant in case of nanoparticles. Strong forces due to dissolution-precipitation during synthesis and post-synthesis treatment at the contact regions, which form necks, and subsequent solid necking due to sintering (high-temperature calcination) result in aggregates or hard agglomerates. For these reasons, nano-sized powders readily agglomerate during processing. Once the nanopowder is agglomerated, the strength of the dried agglomerate is too high to realize the benefits of the nano-size primary crystallites. The critical parameter, which had been chosen for controlling and optimization in this study, was the mean secondary aggregate size of the powder after synthesis, post-synthesis treatment and after calcinations.

### 2. Engineering of micro-/nanoreactors

$CeCl_3 \cdot 7H_2O$ , and  $GdCl_3 \cdot 6H_2O$ ,  $LaCl_3 \cdot 7H_2O$ ,  $SrCl_2 \cdot 6H_2O$ ,  $Ga_2Cl_4$  and  $MgCl_2 \cdot 6H_2O$  (all 99.9% pure from Wako Pure Chemicals Co., Osaka, Japan) were weighted and separately dissolved in doubly distilled and deionized water at a concentration of 0.1 M. To produce complex bi- or four-component intermediate agglomerates, hexamethylene tetramine ( $C_6H_{12}N_4$ ) (Wako Pure Chemicals, Japan) was used as a precipitation agent, and as a source for cyclotrimethylene trinitramine (RDX).  $C_6H_{12}N_4$  was dissolved in deionized water at the concentration of 2M per 1-x M of precipitated compounds.

Nanoreactors comprised of the complex three-component in case of CGO and five-component in case of LSGM preparation intermediate agglomerates were synthesized as follows:

(1) To produce the matrix agglomerates for the three-component nanoreactors, nucleation of cerium oxide in the aqueous solution was conducted by spraying of hexamethylenetetramine aqueous solution into the cerium chloride solution under the stirring conditions.

Gadolinium complex was nucleated by spraying gadolinium chloride aqueous solution into a rapidly stirred suspension of the cerium oxide. Because of the existence of the residual non-reacted hexamethylenetetramine, decomposition began within the first minute from the start of the gadolinium chloride solution spraying.

(2) To produce the matrix agglomerates for the five-component nanoreactors (for LSGM synthesis), nucleation of strontium and lanthanum oxides in the aqueous solutions were conducted by spraying of hexamethylenetetramine solution into the respective solutions of chlorides.

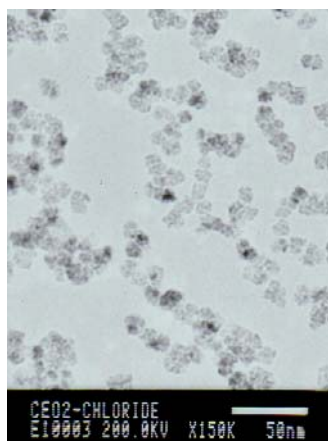
Gallium oxide was nucleated by spraying gallium chloride aqueous solution into a stirred solution of hexamethylenetetramine at 80 °C. Extremely diluted solution of magnesium chloride was sprayed into the suspension. Subsequent homogenization of both suspensions was conducted.

(3) To produce cyclotrimethylene trinitramine ( $C_3H_6N_6O_6$ ), hexamethylenetetramine was dissolved in deionized water at the concentration of 0.1 M. Concentrated (~93%) nitric acid (from Wako Pure Chemicals Co., Osaka, Japan) was added to urotropin solution. Mixing urotropin with nitric acid causes the formation and precipitation of cyclotrimethylene trinitramine ( $C_3H_6N_6O_6$ ). Mixing dissolved hexamethylene-

tetramine with diluted nitric acid causes the formation of well dispersed nanoparticles of the  $C_3H_6N_6O_6$  in the solvent. Dispersion of cyclotrimethylene trinitramine in ethanol leads to partial dissolution of  $C_3H_6N_6O_6$ .

(4) Nanoreactors were produced by saturation of the matrix agglomerates of intermediate complex of cerium and gadolinium compounds or lanthanum, strontium, gallium, magnesium, compounds with ethanol solution of the  $C_3H_6N_6O_6$ .

### 3. Nano-blast calcination of CGO and LSGM



**Fig. 1. TEM micrograph of CGO nano-aggregates produced the nanoblast synthesis from nano-reactors.**

A powder composed of the three-component and five-component intermediate agglomerates with embedded highly explosive component with relatively poor non-homogeneous morphology was filled into alumina containers for further thermal treatment. An important factor behind this methodology is to prevent the ignition of the impregnated particles of  $C_3H_6N_6O_6$  at  $\sim 180^\circ\text{C}$  by ultra-rapid heating of nano-reactors through thermal detonation temperature of  $\sim 233^\circ\text{C}$ . Extremely rapid detonation ( $10^{-8}$  sec/gram) forms gaseous products with a temperature of 2000 to 5000  $^\circ\text{C}$  compressed into a volume equaling the initial volume of each cyclotrimethylene trinitramine particle. The instantaneous power of each explosion is 500 MW/gram. The impacts of the blast waves lead to the fragmentation of the surrounding matter of matrix agglomerates. Multi-blast deagglomeration of the nanopowder occurred due to the highly energetic impact of the blast waves, while the short-term high temperature generated during the explosions enhanced the solid-solubility of one component into the other. Utilizing this technique, we produced cerium-gadolinium oxide (CGO) powder with an average size of clusters 7 ~ 9 nm, an aggregate size distribution of 34~ 73 nm (see Table 1) and uniform morphology.

The blast decomposition of the melted  $C_3H_6N_6O_6$  into the five-component nanoreactors-agglomerates of complex intermediate compounds of lanthanum, strontium, gallium, magnesium chlorides decomposition destroyed the solid agglomerates

and due to the high local temperature- enhance the solubility of the oxides. Table 1 shows the size distribution of the powders aggregate/agglomerate for the three-component intermediate agglomerates of cerium and gadolinium compounds embedded with  $C_3H_6N_6O_6$ , as synthesized, after multiple 'nano-blast' calcination/ deagglomeration; and, finally, after subsequent non-isothermal calcination up to  $450^\circ\text{C}$ . In addition the size distribution of the powders aggregate /agglomerate for the five-component intermediate agglomerates of complex intermediate compounds of lanthanum, strontium, gallium, magnesium chlorides decomposition embedded with  $C_3H_6N_6O_6$ , as engineered, after multiple 'nano-blast' calcination/ deagglomeration; and, finally, after subsequent two-hours calcination at  $1100^\circ\text{C}$  were analyzed.

As synthesized agglomerates of cerium and gadolinium intermediate compounds with a very wide size distribution of 30 - 1260 nm, impregnated with a separately synthesized particles of cyclotrimethylene trinitramine were washed and ultrasonically deagglomerated to reduce the size of the agglomerates to 27-475 nm. Multiple nano-blast calcination reduced the average aggregate size to 34 – 73 nm.

Nano-aggregates of clusters of gadolinia solid solution in ceria matrix synthesized by the multiple 'nano-blast' technique are shown in the TEM micrograph in Fig. 1. After the nano-blast treatment, the powder was calcined at  $450^\circ\text{C}$  for 30 min. to remove the products of explosive decomposition of cyclotrimethylene trinitramine. Thus, such treatment acts to preserve both the powder's compositional homogeneity and morphology.

Same treatment was conducted for the agglomerates of complex intermediate compounds of lanthanum, strontium, gallium, magnesium chlorides decomposition, which were preliminary ultrasonically deagglomerated to 45 – 837 nm. After the explosive treatment, the 22 – 89 nm powder of LSGM was calcined at  $1100^\circ\text{C}$  with 2 h. holds to remove the products of explosive decomposition of cyclotrimethylene trinitramine and mainly to homogenize the composition of four-metal oxide. After finalizing calcination the average particle size of LSGM powder was 83 nm.

### 4. Summary

The concept of *in situ* engineering of micro-/nanoreactors was suggested. Micro-/nanoreactors are agglomerates of complex intermediate metastable products of synthesis, impregnated with energetic particles. It allows localization of the solid and liquid phase reactions within the volume of a single nanoreactor, which provides the inherency of the final structure of the nanosize product. Introduction of nanoexplosive calcination technique expands the possibilities of selected chemical engineering method.

**Table 1. Powders aggregate/agglomerate size distribution after different steps of CGO and LSGM synthesis from engineered nanoreactors and, after subsequent calcination at  $450^\circ\text{C}$  with 30 min (CGO) and at  $1100^\circ\text{C}$  with 2 hours (LSGM) holds.**

Composition	Engineered nano-reactors (nm)	After multiple blast treatment (nm)	After calcination up to $450^\circ\text{C}$ (nm)
$Gd_{20}Ce_{80}O_{1.95}$	27 – 475	34 – 73	30 – 79
$LaSrGaMgO_{3-x}$	45 – 837	22 – 89	61 – 105