

## SHS Ceramics: History and Recent Advances

I.P. Borovinskaya<sup>a</sup>, K. Manukyan<sup>b</sup>, A.S. Mukasyan<sup>b\*</sup>

<sup>a</sup>Merzhanov Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka, Moscow Region, Russia; <sup>b</sup>University of Notre Dame, Notre Dame, Indiana, USA

In this paper, we focus on some historical aspects, as well as on recent achievements in the field of self-propagating high-temperature synthesis (SHS) of ceramics. While giving the tributes to the pioneers of the SHS, we overview the wide variety of recently established SHS-based routes for fabrication of advanced ceramics, including nanopowders and nanostructured bulk materials. Both, the conventional heterogeneous SHS and solution combustion synthesis (SCS) approaches are considered. Advantages and challenges for using of the self-sustained reactions for fabrication of ceramics are also discussed.

*Keywords: Ceramics, Self-propagating high-temperature synthesis, Solution combustion synthesis.*

### 1. Introduction

In the 1967, a group of researchers (Figure 1) from the Institute of Chemical Physics USSR Academy of Sciences, led by Prof. Alexander Merzhanov, searched for combustion systems, which would be burned without producing a gas flame [1]. This was necessary in order to understand the role of reactions in the condensed phase during combustion of gunpowder and solid rocket propellants. During this work the scientists discovered a new phenomenon of “wave localization for self-retarding solid state reactions” [2], or in modern terms the solid flame [3, 4]. The essence of the invention was formulated as follows [2]: “The previously unknown phenomenon of wave localization for self-retarded solid-state reaction, which involves the chemical interaction between the solid dispersed components and occurs without melting and gasification of the reactants and products has been experimentally discovered. After thermal initiation the reaction localized in a relatively thin zone which spontaneously moves along the reactive solid media in the form of a combustion wave”.

From the standpoint of conventional combustion, a solid flame is enigmatic, because it is hard to believe that solely solid-state diffusion may define the self-sustaining nature of the combustion process. It is a prevalent opinion that self-propagating combustion processes, such as metallothermic reactions, exist due to relatively fast mass transport in the liquid phase (diffusion and convection), therefore, melting of at least one component in the system is considered as a necessary condition for combustion. However, it was unequivocally shown that Mother Nature indeed “allows” the solid flame phenomenon [5, 6, and 7].

It is more important that based on this fundamental phenomenon a novel technological approach for fabrication of variety of materials, i.e. self-propagating high-temperature synthesis (SHS) or combustion synthesis (CS) has been developed [8,9]. History of



Figure 1. Inventors of Solid Flame Phenomenon from left to right: A.G. Merzhanov, I.P. Borovinskaya, V.M. Shkuro.

the using of the self-sustained reactions for material's preparation is discussed in variety of publications [1, 9-12]. No doubt that, while having predecessors including works by N.N. Beketov and H. Goldschmidt, only after thorough fundamental research initiated by A.G. Merzhanov and co-workers, SHS became the widely recognized technology for synthesis of almost any type of compounds, and ceramics were among the first materials fabricated by SHS method (Figure 2).

Statistical analysis of publications shows that the CS method for fabrication of materials attracts attention of more and more researchers and engineers, currently scientists in 117 countries are involved in the CS field and number of related publication increases exponentially (Figure 3).

New directions, where self-sustained reactions are used for fabrication of advanced materials and coatings, have been established. Among them solution combustion synthesis, originated by Indian scientists attracted most attention (see recent review [13]). Another currently popular field is combustion synthesis of ceramics [14, 15], especially by combination of SHS

\* Corresponding author  
E-mail address: amoukasi@nd.edu



Figure 2. Materials and net-shape articles produced by SHS.

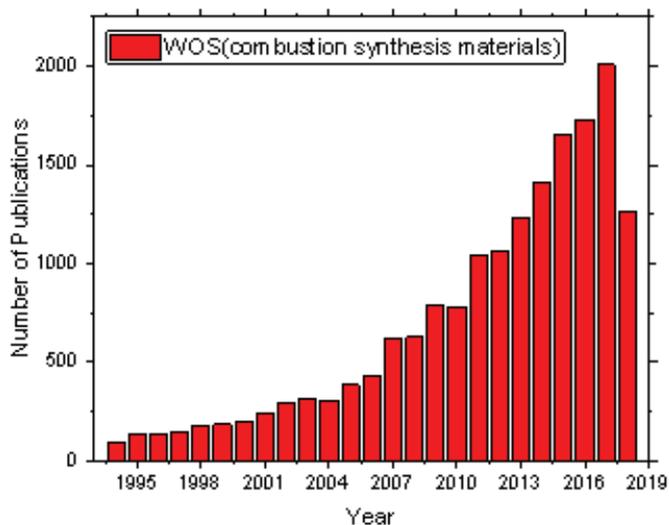


Figure 3. Dynamic of citation in the field of combustion synthesis of materials.

and spark plasma sintering [16], where contribution of scientists for US, Italy and Japan is difficult to overestimate. In addition, a variety of nano materials including zero, 1 and 2 dimensional structures were produced by different CS approaches (recent review [13, 17, and 18]). In this direction, one can find many exciting publications of the researchers specifically from China and South Korea. Combination of mechanical activation (MA) and SHS, so-called MASHS, initiated by scientists from Russia and France now found worldwide attention ([19, 20]). Among theoretical approaches, we want to outline a rapid development of molecular dynamic simulation (MDS) methods to analyze SHS processes [21, 22].

In this paper, we focus on some historical aspects, as well as on recent achievements in the field of CS of ceramic materials. The review is written based on our presentations on the XIV-th International Symposium on SHS, September, 25-29, 2017, Tbilisi, Georgia and on the 14th International Ceramics Congress of CIMTEC, June 4-12, 2018, Perugia, Italy.

## 2. Types of SHS Systems

The fundamental paradigm for combustion synthesis of ceramics consists of exothermic self-sustained reactions that, without any external heat sources, lead to formation of non-metallic inorganic solid materials comprising metal and non-metal atoms primarily held by ionic and covalent bonds. It is interesting that term "ceramics" comes from Greek word "Keramos", which is related to an old Sanskrit root meaning "to burn". Thus, SHS of ceramics is probably the most close to the root meaning of the term "ceramics", since it uses 'burning' both for synthesis and

consolidation of the material.

It is also worth noting that conventional reaction sintering (RS) method also involves synthesis and consolidation processes. However, in the latter case external heat source (e.g. furnace) is used to assist these processes. Moreover, during RS one has to avoid conditions (e.g. local overheating), which may lead to the "uncontrollable" events associated with self-sustained interactions. Thus, SHS can be considered as a limiting route of RS, when preheating conditions lead to local self-initiation of the reaction followed by its propagation along the media. Advantages and disadvantages of RS and SHS are straightforward. During RS, one may essentially independently change processing parameters, such as temperature, pressure and time, which, by probe and error method, allows optimizing conditions for fabrication of materials with desired microstructure and thus properties. Nevertheless, SR is long (hours) and energy consuming method, which also requires a complicated equipment. Rapid (seconds), energy saving SHS method needs simple equipment. However, all parameters of SHS process are strongly correlated with each other. Hence, it is not possible to change one of them keeping the others unchanged. Thus, the addressing the controllability issue is not so straightforward task for the SHS. However, it was proved by numerous works in the field of combustion synthesis that one may control the process based on the fundamental knowledge of the mechanism for self-sustained heterogeneous reactions [3,12,13]. It is important that many examples demonstrate the durability of such fundamental approach for controlling of the microstructure and properties of the materials produced by SHS-based technologies [3,9,12,15,18].

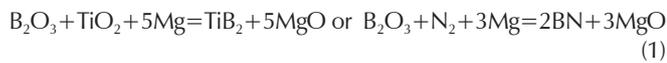
The necessary conditions for SHS of any compound is the sufficient exothermicity of the considered reactive system, which leads to formation of the desired material. The "exothermic" criteria was extensively discussed and it was, for example, suggested that corresponding adiabatic combustion temperature should exceed 1800 K [23]. However, recent works show that reaction front may propagate in the systems with much lower temperature and initiation temperature can be as low as 500K [7,24,25]. These parameters strongly depend on the specific amount ( $m^2/g$ ) and quality (e.g. clean, oxide free) of the contact surface area between the reactants and the characteristic diffusion scales and can be controlled by the initial mixing of the reagents [25,26,27].

From the fundamental standpoint, all systems, which lead to the SHS of ceramics can be subdivided into two main classes: (a) reactive solid powder mixtures in inert or reactive gaseous atmosphere – traditional heterogeneous SHS and (ii) reactive aqueous solutions in inert or reactive gaseous atmosphere – solution combustion synthesis. In turn, former class of systems can be sub-divided into several main groups. First group involves solid-solid systems in which compounds are produced from the elements. Examples of ceramics include, carbides (metal: TiC, ZrC, HfC, NbC, TaC and nonmetal: SiC, B<sub>4</sub>C) and borides (TiB, TiB<sub>2</sub>, ZrB, ZrB<sub>2</sub>, NbB, NbB<sub>2</sub>, TaB<sub>2</sub> etc.). Contribution of V. Shkuro, who is one of the co-author of the solid flame discovery, in investigation of the combustion mechanism in Ti-C system is difficult to overestimate [28,29]. It is important that SHS TiC-based pastes found wide commercial applications. Titanium boride was one of the first compound synthesized by combustion method [1,8]. Powder of TiB<sub>2</sub> also was produced on industrial level by SHS approach [9]. Currently, team headed by Dr. Yucel from Istanbul Technical University (Turkey) is world recognized leader in SHS of borides.

Second group consists of solid-gas systems and permits SHS of oxides, nitrides and hydride based ceramics. It is worth noting that, because of their extremely high exothermicity, the SHS of oxides by gas-solid reactions is probably not effective approach. Solution combustion synthesis is typically used to fabricate different nano-sized oxide powders. However, we want to outline works by M. Nersisyan and co-workers on SHS of high temperature superconductors [30,31], as well as effort led

by him and P. Avakyan on developing of continuous SHS-based technology for production of ferrites, which found industrial application [1,32,33]. In this group of systems we focus more on the SHS of nitride-based ceramics, including metallic nitride (TiN, ZrN, HfN, TaN, AlN etc), nonmetallic nitrides ( $\text{Si}_3\text{N}_4$ , h-BN, c-BN etc) and oxinitides (AlONs, SiAlONs etc) [14]. In regards of SHS in gas-solid systems, an important concept of infiltration combustion has been established based on pioneering experimental works on metal combustion in nitrogen by I. Borovinskaya, Yu. Volodin, A. Pityulin, V. Loryan [34-36] and theoretical studies by A. Aldushin [37,38]. SHS-based technology for nitrating of ferrovanadium alloy developed by M. Ziatdinov found wide industrial application [39]. Contributions of V. Martinenko and V. Prokudina in establishing of SHS technologies for production of silicon and aluminum nitrides should be also outlined (see in [40]). Industrial production of silicon nitride had history on the specially the SSH production plant in Spain [1].

Third group of SHS systems involves so-called thermite type of reaction systems that include stage during which one element (typically Mg, Al or C) reduce metal (e.g.  $\text{TiO}_2$ ) or nonmetal ( $\text{B}_2\text{O}_3$ ) oxides to produce elements (e.g. Ti and B), which may be followed by reaction between the elements to produced ceramics (e.g.  $\text{TiB}_2$  or BN):



In our opinion, this approach is preferable for fabrication of fine non-oxide ceramic powders by using combustion-based technology. The necessity of additional chemical leaching of MgO from combustion product does not make this method too complex. However, as it was shown in works by S. Mamyán [41], this method requires detailed optimization of the composition for the initial reactive powder mixture. The extremely high exothermicity of some thermite systems allows to produce large corundum crystals when using Al as a reducing element [42].

Fourth group of SHS systems includes so-called displacement reactions, in which one element displaces another from a compound. It is worth noting that thermite reactions represent a specific type of displacement reactions, but historically they made a separate class of combustion system. Metathesis self-sustained reactions that sometimes called double replacement or double decomposition reactions, which involves the exchange of bonds between two chemical compounds also belong to this group of SHS systems. On the best of our knowledge, metathesis systems were brought to SHS field by I. Parkin from University College London (England) [43] and, as it is shown below, currently such reactions are widely used to fabricate different type of bulk SHS ceramics, including borides, nitrides and carbides.

Solution combustion synthesis (SCS) involves propagation of self-sustained exothermic reactions along an aqueous or sol-gel homogeneous media. SCS allows for the synthesis of nanoscale materials and coatings (cf. [13]). It provides easy formation of high-quality multi-element compounds with complex crystal structures, such as perovskites, garnets, spinels, silicates, and phosphates. SCS also permits for efficient doping of materials, even with a trace amount of elements. The synthesis and processing of ceramic materials by solution combustion can be categorized into four major groups, including conventional oxide ceramic powders ( $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ , etc.), electro-ceramics, magnetic ceramics, and bioceramics. All these types of SCS ceramics are briefly overviewed in Section 5.

### 3. CS of Ceramic Powders

As mentioned above, CS of powders involves two different chemical schemes, i.e. classical self-propagating high-temperature synthesis (SHS), where heterogeneous powder mixtures are used and solution combustion synthesis by using homogeneous solution of precursors. Based on the above classification, let us briefly overview the recent advances in SHS of ceramic powders.

#### 3.1. SHS of ceramic powders

Titanium boride and carbide were among first powders produced by conventional SHS from elements [1]. Later, carbides and borides of metals for groups IV (Ti, Zr, Hf), V (V, Nb, Ta) and VI (Cr, Mo, W) of Periodic Table were synthesized by the SHS method [8]. These compounds have high heats of formation, which leads to extremely high reaction temperatures (typically above 3000 K). The latter allows synthesis of highly pure powders. For example, it was shown that SHS TiC powder contains only 2000 ppm of Al, 100 ppm of Si, 80 ppm of B, 100 ppm of Fe and 30 ppm of Ca [44]. It is important that with the exception of Fe, impurities in the product were two to seven times lower than in the initial mixture. Owing to the high combustion temperature, the material self-purifies by purging any volatile impurities from the reaction mixture.

Also many works were dedicated to SHS of non-metallic carbides, i.e. SiC and  $\text{B}_4\text{C}$  [40, 45]. Synthesis is carried out in vacuum or in a reactor filled with an inert gas (argon). The reaction is initiated by local preheating of the powder reactive mixture by a hot metal wire. CS takes place in a self-sustaining manner without any external power sources. After cooling, the product is recovered in the form of a porous weakly sintered cake and thus short-term additional milling followed by sieving are required to obtain powders of the desired grade. Some properties of SHS ceramic powders produced from elements or by using reduction reactions are presented in Table 1. In our opinion the latter approach, which uses metal and non-metal oxides (e.g.  $\text{TiO}_2$  and  $\text{B}_2\text{O}_3$ ) as the precursors, is the most promising routes to synthesized ceramic powders. Indeed in many systems, the cost of oxide powders is much less than that for pure elements (e.g. compare pure boron and boron oxide). In addition, reduction approach permits fabrication of much finer powders (see Table 1).

Currently attention is primarily paid to SHS of sub-micron ceramic powders. Several specific approaches were developed, which allow one to produce nano particles during high-temperature combustion reactions: (a) Salt-assisted SHS; (b) Teflon-assisted SHS; (c) Reduction of metal halides; (d) High-energy ball milling-assisted SHS. More specifically, TiC, WC,  $\text{TiB}_2$ ,  $\text{ZrB}_2$  powders

Table 1. Some properties of SHS ceramics data from ref [46].

| Compound                           | Main Phase wt. %                                   | Main Impurities wt. %                             | Average particle size or BET, specific surface area |
|------------------------------------|--|---|---|
| TiC from elements                  | Ti = 77.0-79.5<br>$C_{\text{bounded}} = 18.0-20$   | $C_{\text{unreacted}} < 0.2$                      | 3-5 $\mu\text{m}$                                   |
| NbC from elements                  | $C_{\text{total}} = 11$                            | $C_{\text{unreacted}} < 0.1$<br>Oxygen < 0.2      | 1-100 $\mu\text{m}$                                 |
| $\text{TiB}_2$ reduction           | Ti=66.7<br>$B_{\text{total}} = 30.5$               | $B_2O_3 < 0.2$<br>Mg < 0.3                        | 1-10 $\mu\text{m}$                                  |
| $\text{TiB}_2$ from elements       | Ti=69.6<br>$B_{\text{total}} = 29.2$               | Oxygen < 0.5                                      | 1-200 $\mu\text{m}$                                 |
| SiC( $\beta$ -phase) from elements | $C_{\text{total}} = 27-27.8$                       | $C_{\text{unreacted}} < 0.3$<br>O < 1.0; Fe < 0.2 | 8-10 $\text{m}^2/\text{g}$                          |
| $\text{B}_4\text{C}$ reduction     | $B_{\text{total}} = 74$<br>$C_{\text{total}} = 20$ | $B_2O_3 < 0.5$<br>Mg < 0.5; O < 0.5               | 3.9 $\text{m}^2/\text{g}$                           |

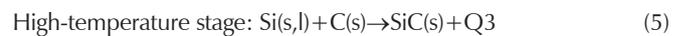
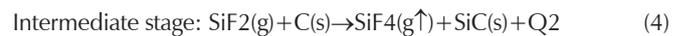
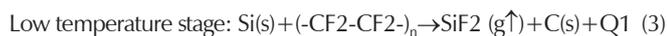
were synthesized by using salt-assisted method [47-51]. It was shown that using salt (NaCl, KCl, NaF) as diluent not only decreases combustion temperature, but also prevents growth of formed nuclei of carbide and boride compounds. Figure 4 shows the morphology of ZrB<sub>2</sub> nano powders produce by salt-assisted SHS and corresponding particle size distribution [52]. It can be seen the method allows synthesis of ZrB<sub>2</sub> rods with diameter around 100 nm and aspect ratio around 4.

However, more promising approach for synthesis of ceramic powders is combination of salt-assisted approach and reduction type reactions. The general scheme, for example, for SHS of carbides, is as follows:



A variety of carbides were synthesized by this approach with average particle size below 50 nm [53] and some of their characteristics are presented in Table 2.

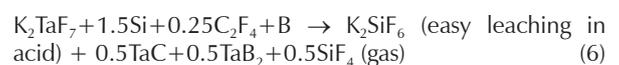
The other approach is so-called PTF ((-CF<sub>2</sub>-CF<sub>2</sub>-)<sub>n</sub>) - assisted SHS, which was initially proposed for synthesis of silicon carbide from elements [54]. The following set of equations represents the chemical reactions which occur in the combustion wave:



In this case, the main idea is chemically activated relatively low exothermic reaction (5) between silicon and carbon. Indeed, reaction (3) between silicon and PTF preheats the Si+C reaction media and forms the gaseous silicon containing species (SiF<sub>2</sub>, SiF<sub>4</sub>). On the next carbidization stage, SiC powder is formed through reactions (4) and (5). Reaction (5) may occur in self-sustain manner owing to preheating of the media by heat of reaction (3) and additional heat released in reaction (4). Note that gas phase reaction (4) and condensed phase reaction (5) should lead to different morphologies of the SiC product. Indeed, it was shown

that two different types of particles can be synthesized [54]. With the certain amount of PTF additive the cube-shape particles with size about 10 μm can be produced, while for the other composition the formation of the long ~1 mm thin (0.5 μm) fibers were formed. The other additives, such as KNO<sub>3</sub>, NaNO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub> and BaNO<sub>3</sub> also can be also used [55]. It is interesting that similar approach allows SHS fabrication of the graphene by combustion SiC + PTFE mixture [56].

Reduction of metal halides approach is close the Teflon-assisted SHS and involves the reduction of metal halides (K<sub>2</sub>TaF<sub>7</sub>, K<sub>2</sub>TiF<sub>6</sub>, TaCl<sub>4</sub>, etc.) in the presence of C and B [57, 58]. For example, let us consider formation of the tantalum carbide – tantalum boride powder mixture:



| Reaction system                                    | Average particle size, nm | BET, cm <sup>2</sup> /g | Phase composition          |
|--|---------------------------|-------------------------|----------------------------|
| TiO <sub>2</sub> + 2Mg + C + 1.3NaCl               | 48                        | 14                      | TiC, cubic                 |
| WO <sub>3</sub> + 3Mg + 0.5C + 7.0NaF              | 29                        | 10                      | W <sub>2</sub> C, hex      |
| MoO <sub>3</sub> + 3Mg + 0.5C + 7.0NaF             | 37                        | 13                      | Mo <sub>2</sub> C, orthor. |
| Ta <sub>2</sub> O <sub>5</sub> + 5Mg + 2C + 8.0NaF | 27                        | 11                      | TaC, cubic                 |
| Nb <sub>2</sub> O <sub>5</sub> + 5Mg + 2C + 8.0NaF | 42                        | 19                      | NbC, cubic                 |
| ZrO <sub>2</sub> + 2Mg + C + 1.3NaF                | 18                        | 46                      | ZrC, cubic                 |

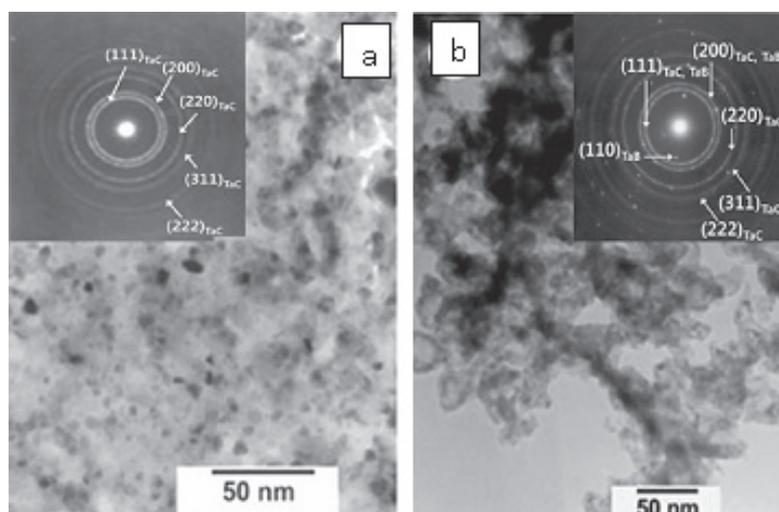


Figure 5. TEM images and SAD patterns for TaC (a) and TaC-TaB (b) nano particles.

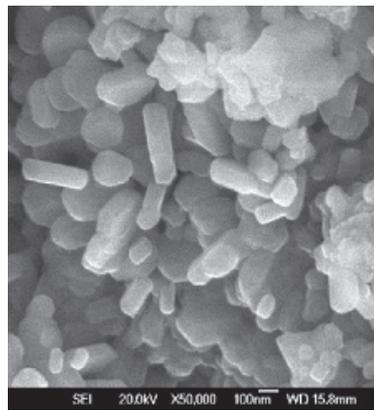
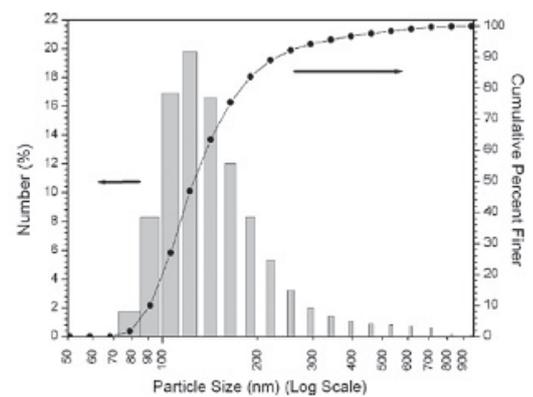


Figure 4. Morphology and particle size distribution of ZrB<sub>2</sub> produced by salt-assisted SHS from elements [52].



but also increases their contact surface area, which is typically oxygen-free from, since milling occurs in inert atmosphere. All these factors enhance the chemical activity of the reactive mixture and thus, are called mechanical activation (MA).

It was demonstrated that in pure Si-C system optimized MA processing permits synthesis of sub-micron SiC particles in SHS mode without any additives (Figure 6a) [62]. Also, several routes were developed to fabricate SiC powders by combination of chemical activation, i.e. adding the gasifying agents (Teflon,  $\text{NH}_4\text{Cl}$ , PVC etc) and HEBM. One of them involves first adding a small amount (1-3wt.%) of  $\text{NH}_4\text{Cl}$  and PVC into the Si-C powder mixture, followed by MA of the mixtures through HEBM (2-12 h). Thus obtained mixture is preheated to temperature (950-1200 °C) and keeping it at this temperature until self-initiates of the reaction. It was demonstrated, that MA allows one to initiate reaction at relatively low temperature 1050 °C and reach full conversion by using small amounts of additives. Fine  $\beta$ -SiC powders with specific surface area 4.4  $\text{m}^2/\text{g}$ , and the particle size < 5  $\mu\text{m}$  was synthesized (Figure 6b) [63]. Similar approach but with synthesis in SHS mode was also developed [64]. Slightly larger amount (~6wt.%) of PTFE was used as compared to VCS mode, however much finer particles (Figure 6c a) were obtained. Nitrides is another class of ceramic powders, which can be produced by combustion based approach [14]. SHS of nitrides can be subdivided into several chemical routes: (i) from elements (metals-nitrogen; nonmetal - nitrogen); (ii) reduction reaction of metal or/and nonmetal oxide with Mg (or Al) in presence of nitrogen sources (gas phase- $\text{N}_2$ ,  $\text{NH}_3$ ; or solid- $\text{NaN}_3$ ;  $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{F}$ ); (ii) metathesis reactions between metal chlorides (fluorides) and metal azides ( $\text{NaN}_3$ ;  $\text{Li}_3\text{N}$  etc); (iv) exchange reactions between metal or nonmetal nitride and metal or non metal.

For SHS of transition metal nitrides (e.g. TiN, ZrN) from elements it is important to outline the unique capability for fabrication of ceramics with small amounts of nitrogen ( $\text{MeN}_{0.13}$ - $\text{MeN}_{0.22}$ ) as well as synthesis of single phase oversaturated solid solutions ( $\text{MeN}_{0.34}$ - $\text{MeN}_{0.45}$ ), where concentration of nitrogen exceeds know values from equilibrium phase diagrams [65, 66]. In turn, metathesis reactions allows formation of metal nitrides nanopowders. For example, ZrN nanoparticels (10-30 nm) with high BET (up to 70  $\text{m}^2/\text{g}$ ) was synthesized by using self-sustained reaction between  $\text{ZnCl}_4$  and  $\text{NaN}_3$  in nitrogen atmosphere [67]. Tantalum nitride ( $\delta$ -TaN) nanoparticles (5-10 nm; BET~ 30  $\text{m}^2/\text{g}$ ) were synthesized in SHS mode other metathesis reaction system, i.e.  $\text{K}_2\text{TaF}_7 + (5+k) \text{NaN}_3 + k\text{NH}_4\text{F}$  [68].

Self-sustained reduction reactions are widely used to produce ceramic powders. Boron nitride was synthesized by reduction of  $\text{B}_2\text{O}_3$  by Mg in nitrogen atmosphere [69]:



Recently [70], AlN nanoparticles with size in the range 50-200nm; BET~20  $\text{m}^2/\text{g}$  were fabricated by SHS in  $\text{Al}_2\text{O}_3$ -Mg- $\text{NH}_4\text{Cl}$  system:

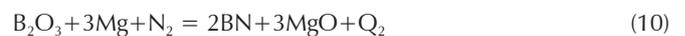


Ceramic powders with one-dimensional structures (e.g. whiskers type, rods etc.) also can be produced by the combustion-based methods. For example, SHS of fine uniform SiAlON whiskers (Figure 7a) obtained in the Si-Al- $\text{N}_2$  system were reported [71]. Thin (diameter ~100 nm) single-crystal  $\beta$ - $\text{Si}_3\text{N}_4$  fibers (Figure 7b) were fabricated by adding a tungsten as a catalyst to Si- $\text{N}_2$  system [72]. Although the SHS of  $\beta$ - $\text{Si}_3\text{N}_4$  whiskers has known since 1980 [73,74], it is an additional effective route to control the morphology of the synthesized powder.

There are two different chemical routes to produce h-BN powder by using the SHS-based approach. One is the CS from the elements:



The other one is CS by reduction reaction:



The comparison of some characteristics of BN powders produced by SHS and conventional powder metallurgical method are shown in Table 3. The boron nitride nanosheets with thickness below 100 nm and plate size on the order of several microns (Figure 7c) was produced by combustion in  $\text{B}_2\text{O}_3$ -Mg- $k\text{NH}_4\text{Cl}$  system [75, 76]. Recently cubic boron nitride was produced by self-sustained reaction in B-TiN system, when the reaction was initiated by shock wave [77].

Based on the above we can conclude that essentially all ceramic powders can be fabricated by using SHS methods. It is more

Table 3. Some characteristics and properties of BN powders [78].

| Content, wt.%                                | CS Product |                  | Furnace Product |               |
|--|------------|------------------|-----------------|---------------|
|  | Ultra-pure | Technically Pure | ORPAC Grade 99  | Denka (Japan) |
| Boron nitride, BN                            | >99.5      | 97.3             | 98-99           | >98           |
| Nitrogen, N                                  | >55.7      | 54.9             | 54-55           | 54.5          |
| Oxygen, O                                    | <0.5       | 1.5              | 1.5             | 1.5           |
| Carbon, C                                    | <0.01      | 0.3              | N/A             | N/A           |
| Metal impurities (Fe, Mg)                    | <0.2       | 0.3              | N/A             | N/A           |
| Specific surface area, $\text{m}^2/\text{g}$ | 11.0       | 8-14             | 10              | N/A           |

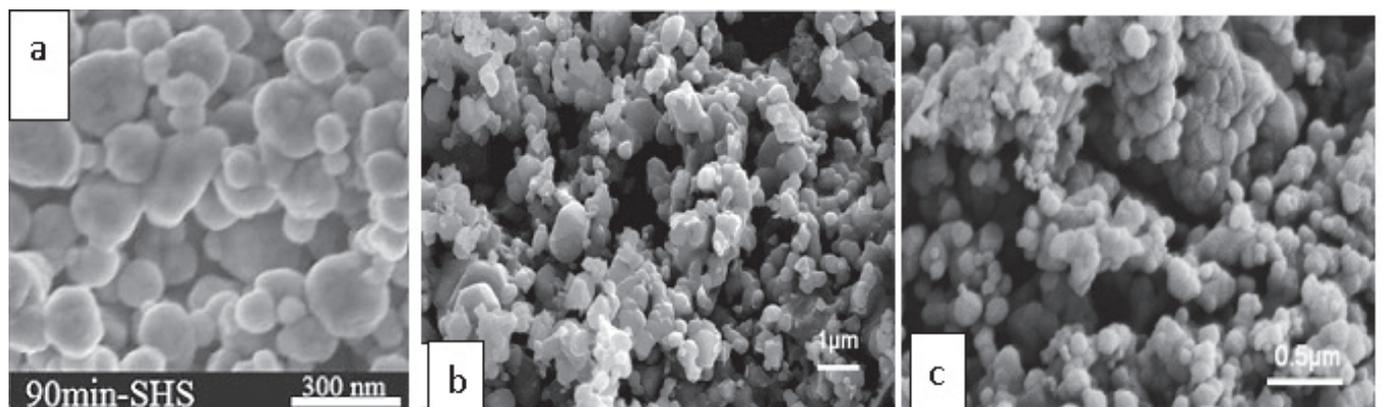


Figure 6. SEM images of SiC powders synthesized by different SHS routes.

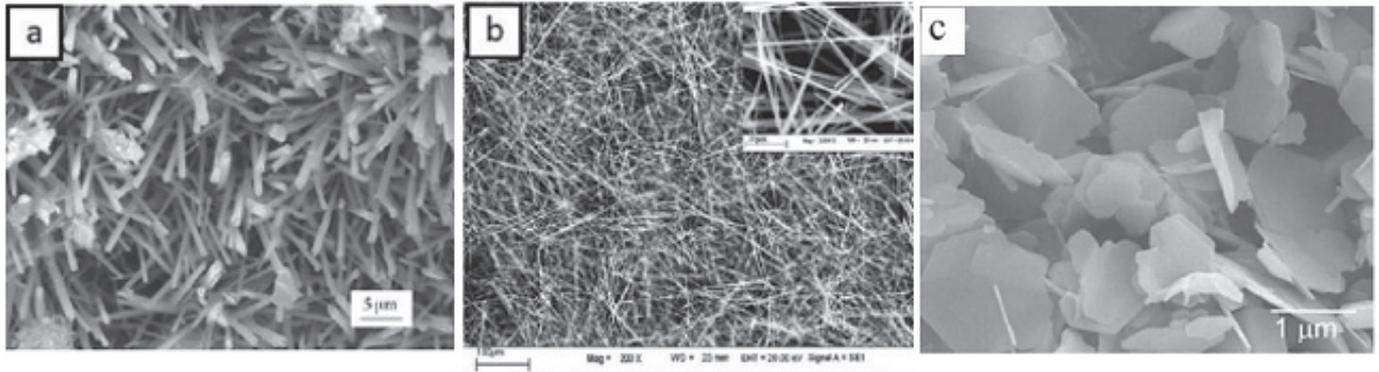


Figure 7. Microstructure of SIALON (a);  $\text{Si}_3\text{N}_4$  (b); BN (c).

important to outline that, while SHS was used for powders production for more than 50 years, a long list of novel routes have been recently developed, which permit synthesis of ceramic powders with controllable morphology

#### 4. SHS of Bulk Ceramics

There are two routes to make bulk ceramics by using SHS method [12, 4, 78]. First is a traditional powder metallurgy approach, which involves sintering of powders produced by combustion method. It was demonstrated that some SHS ceramic powders ( $\text{SiC}$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{AlN}$ ) possess better sinterability as compared to the those produced by conventional methods [79-84]. Such behavior is attributed to the specific morphological features and highly defected crystal structures of SHS powders.

However, it is more attractive to use extremely high temperatures of the combustion process not only for rapid synthesis of the powders, but also for their consolidation (sintering) to produce bulk, in many cases, pore-free ceramics. This one-step approach can be accomplished with or without using external loads to facilitate consolidation. Typically, combination of SHS and external densification (uniaxial loading, HP, HIP) is used for solid-solid systems to prepare cermet, i.e. materials, which consist of ceramic phase(s) and metallic matrix [1, 12]. Only recently, with advent of spark plasma sintering method (SPS), hybrid technology, i.e. SPS+SHS was developed to fabricate ceramics [85-87]. SPS provides more uniform heating of the media, because the extremely high DC (kA) current in pulsating manner passed not only through the pressing die, but also through the sintering media. Such Joule heating uniformly heats the whole volume of the material, which, under applied uniaxial loading, provides much rapid densification, as compared to conventional sintering approaches. It is interesting that, in the best of our knowledge, the pioneering works directed by Prof. Munir (Davis, USA), which led to development of SPS technology, were related to, so-called, field-assisted combustion synthesis [88, 89]. It was shown that by passing current through the reactive powder media one may enhance kinetics of chemical reactions in the considered system. For example, it is difficult to initiate self-sustained reaction in relatively low exothermic Si-C mixture to produce SiC ceramics [45]. However, when

optimized current is applied, SHS reaction occurred easily with full conversion [88].

Using reactive powder green mixture under SPS conditions leads to so-called reactive spark plasma sintering (RSPS) method. Many scientific reports were published in last five years on application of RSPS to produce variety of ceramic materials. It is important to compare properties of materials produced by SPS of SHS powders and by direct RSPS. Such comparison was accomplished for  $\text{HfB}_2$ ,  $\text{TaB}_2$ ,  $\text{ZrB}_2/\text{SiC}$ ,  $\text{HfB}_2/\text{SiC}$ ,  $\text{TaB}_2/\text{SiC}$  ceramics [90]. It was shown that RSPS leads to higher densification for the single-phase ceramics ( $\text{HfB}_2$ ,  $\text{TaB}_2$ ,  $\text{ZrB}_2$ ), while for the double-phase materials  $\text{ZrB}_2/\text{SiC}$ ,  $\text{HfB}_2/\text{SiC}$ ,  $\text{TaB}_2/\text{SiC}$ , full dense ceramics can be easily obtained starting from SHS powders. Such behavior was explained by complete different reaction mechanisms in single and double phase systems. In the former case, the self-sustained reactions rapidly occur in SPS mode, while for the latter case, a slow solid-state diffusion reactive sintering takes place. It is probably due to relatively low exothermicity of Si-C system, as compared to that for formation of borides. The importance for optimization of the heating rate and time for external force application was also outlined, i.e. higher heating rates favor RSPS and load should be applied after SHS reaction initiation.

Mechanical activation of the initial reaction mixture by high-energy ball milling is widely used before RSPS. First, it was shown that sub-micron SiC powders prepared by SHS of MA mixture can be completely densified without any additives by 1h of SPS processing at 2273 K and obtained ceramics possesses Vicker's hardness  $\sim 24$  GPa and fracture toughness in the range 3-5  $\text{MPa m}^{1/2}$  [91]. Next, pure SiC ceramics with density 3.1  $\text{g/cm}^3$  was fabricated in one-step using preliminary mechanically activated Si/C mixture directly by RSPS at 2273 K and 10 minutes sintering time, with even higher mechanical properties [92]. Similar approach was used for production of boron carbide ( $\text{B}_4\text{C}$ ) ceramics [93]. Optimization of HEBM + RSPS conditions

Table 4. Ceramics fabricated by different SHS methods and their properties.

| Ceramics composition  | Applies method | Properties  | Ref.   |
|---|----------------|---|--------|
| $\text{TaB}_2$  | RSPS           | TMD=95%; $H_v=17.5$ GPa; $K_{IC}=4.8$ $\text{MPam}^{1/2}$       | 90, 99 |
| $\text{HfB}_2$  | RSPS           | TMD=99%; $H_v=18.0$ GPa; $K_{IC}=3.5$ $\text{MPam}^{1/2}$       | 100    |
| $\text{HfB}_2\text{-SiC}$                                       | RSPS           | TMD=96%; $H_v=19.0$ GPa; $K_{IC}=3.9$ $\text{MPam}^{1/2}$       | 100    |
| $\text{ZrB}_2$  | RSPS           | TMD=96%; $H_v=10.8$ GPa; $K_{IC}=2.2$ $\text{MPam}^{1/2}$       | 101    |
| $\text{SiC}$  | MA+SPS; RSPS   | TMD=95-98%; $H_v=24$ GPa; $K_{IC}=3-5$ $\text{MPam}^{1/2}$      | 91, 92 |
| $\text{B}_4\text{C}$  | RSPS           | TMD=98.5%; $H_v=35$ GPa; $K_{IC}=4.5$ $\text{MPam}^{1/2}$       | 93     |
| $\text{B}_4\text{C-TiB}_2$                                      | MA+RSPS        | TMD=95.5%; $H_v=17.0$ GPa; $K_{IC}=4.8$ $\text{MPam}^{1/2}$     | 102    |
| $\beta\text{-Si}_6\text{-zAl}_2\text{O}_2\text{N}_{8\text{-z}}$ | SHS+SPS        | TMD=99.7%; $\lambda=9.5$ $\text{Wm}^{-1}\text{K}^{-1}$          | 103    |
| SIALON (Y, Ca)  | SHS+SPS        | TMD = 98-99%; $H_v=15-17$ GPa; $K_{IC}=3-4$ $\text{MPam}^{1/2}$ | 104    |

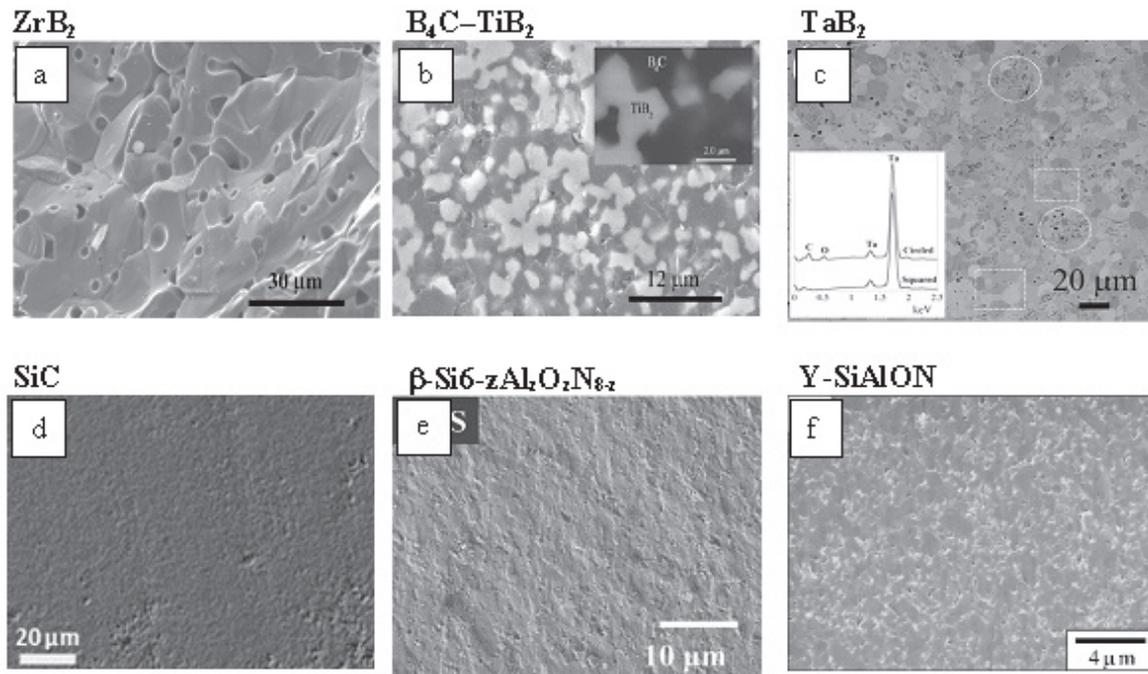
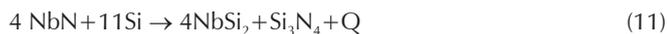


Figure 8. Typical microstructures of SHS ceramics.

allows rapid (less than 30 min of SPS) fabrication of  $B_4C$  ceramics with porosity less than 2%, hardness of  $\sim 35$  GPa and fracture toughness of  $\sim 4.5$  MPa  $m^{1/2}$ . Essentially pore-free titanium boride-boron carbide ( $TiB_2$ - $B_4C$ ) material was produced by RSPS under high heating rate conditions [94]. RSPS was also widely applied to fabricate ceramics through exchange reactions. For example, this method was applied for MA mixtures of silicon and different metal carbides (ZrC, NbC) to produce  $ZrSi_2$ -SiC,  $WSi_2$ -SiC materials [95-98]. The mechanical properties and typical microstructures of RSPS materials are shown in Table 4 and Figures 8 a-d.

The nitride-containing bulk materials also can be produced by exchange reactions, e.g. between metal nitrides and silicon or boron [76, 105, 106]:



However, the pure nitride bulk ceramics is typically produced by SHS in solid (metal: Al, Ti, Zr, Nb, Hf, Ta or nonmetal: Si, B) - nitrogen systems [4, 12, 14, 77]. We believe that the advantages of SHS method are most vividly manifest in the direct fabrication of nitrides based ceramics through gas-solid combustion. There are several reasons for such conclusion. First, is related to the processing temperature: the nitrides ceramics possess high melting points and thus difficult to sinter. Currently, there are no furnaces that allow sintering at temperatures above 2400 °C. Adiabatic combustion temperatures for these system are much higher being on the order of 3000 °C and higher [4,12]. It is more important that under equilibrium conditions many nitrides ( $Si_3N_4$ , AlN, BN) cannot be sintered at high temperatures, since they dissociate. Thus different additives are used to promote sinterability, which unfortunately deteriorates the physical and high-temperature properties of the ceramics. It was shown that under nonequilibrium conditions of the combustion wave the reaction/sintering temperatures may be equal to the dissociation temperature of the products. Thus, SHS allows sintering under temperatures, which in principle cannot be achieved for conventional powder metallurgical technologies. Second, in gas-solid systems, low-porosity (even pore free) ceramics may be produced in-one step directly by SHS without

the use of external loading [4, 12,78]. Indeed, at constant overall sample volume, the internal porosity decreases due to total mass increase through gas-solid reactions in the combustion front [65,78]. For example, in the case of boron-nitrogen system, such change of porosity can be as high as 60%. It is important that during steady-state combustion regime the reaction propagates uniformly along the whole volume of the sample. It is also shown that there exist wide post-combustion reaction zones, which significantly increase final degree of conversion. Duration of the post-combustion nitridation depends on the heat loss conditions, which are less for the larger volume of the synthesized ceramics. All above suggests that many optimization parameters exist allowing us to control synthesis/sintering conditions and thus obtained material with desired properties.

By using above optimization, the BN net shape articles (Figure 9a) were produced directly in combustion wave. It was shown that, on the one hand, material with low porosity (in the range 7-10%) and high mechanical properties ( $\sigma_b \sim 25$ MPa) with  $\sim 7$ wt% of unreacted boron can be produced. On the other hand, one may fabricate ceramics with high BN content ( $\sim 99$ wt%) and final porosity of 30% and corresponding bending strength of  $\sim 10$  MPa. Some properties of the CS BN-based ceramics are summarized in Table 5. Note that, for special applications (in MHD generator; erosion-residing sleeve in cutting torches for air-plasma cutting of metals and alloys and etc), which allow the present of  $SiO_2$  phase, one may significantly increase the mechanical strength of the ceramics without changing the material's thermal conductivity (see right column Table 5). Finally, it is known that sintered BN ceramic has semiconductor properties (with a band gap of about 3.7 eV) and is used as a high-temperature electrical insulator in directional solidification furnaces. Figure 9b shows high-temperature ceramic insulators after 30 days of work in a RAP-2 furnace. The product on the left was originally produced by the traditional method of sintering with additives, while the insulator on the right was made by direct synthesis in the SHS mode. It can be seen that sample, consolidated by the traditional technology, could not resist long-term (30 days) high-temperature (2400 °C) service in an environment of metal vapors, while the SHS-insulator retained all of its basic properties and may be subsequently used in the company producing single-crystal components.

The other fascinating example of nitride based bulk material produced directly by SHS method without application of the

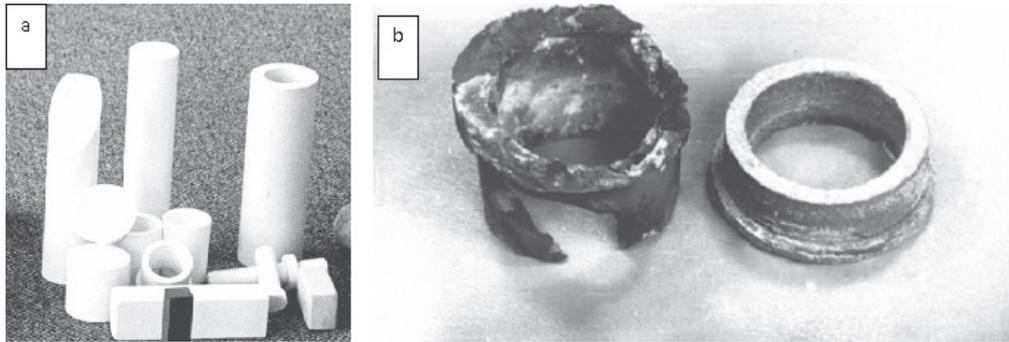


Figure 9. Boron nitride net shape articles.

Table 5. Some properties of BN-based ceramics (adopted [4]).

| Properties                          | BN                              | BN+SiO <sub>2</sub>           |
|-------------------------------------|---------------------------------|-------------------------------|
| Chemical composition, wt %          | N = 55; O<0.5; Bfree<0.5; C<0.5 | BN = 74; SiO <sub>2</sub> =26 |
| Density, g/cm <sup>3</sup>          | 1.5                             | 1.85                          |
| Dielectric strength, kV/mm          | 25                              | 19                            |
| Dielectric permeability             | 3.1                             | 6.0                           |
| Tangent of dielectric loss at 1MHz  | 0.0034                          | 0.036                         |
| Resistivity, Ω                      | 2·10 <sup>8</sup>               | 1.3·10 <sup>8</sup>           |
| Thermal conductivity, W/mK          |                                 |                               |
| T = 400 K                           | 20                              | N/A                           |
| T = 900 K                           | 8                               | 8                             |
| Bend strength, σ <sub>b</sub> , MPa | 25                              | 25                            |

Table 6. Properties of "black" ceramics produced by SHS.

| Property                            | Values    |
|-------------------------------------|-----------|
| Density, g/cm <sup>3</sup>          | 3.4       |
| Bending strength, MPa (1800 K)      | 650       |
| Elastic modulus, GPa                | 300       |
| Hardness, HRA                       | 93.5      |
| Micro hardness, Vickers             | 20        |
| Friction coefficient                |           |
| dry 273-117 K                       | 0.2-0.3   |
| hot lubrication                     | 0.02-0.03 |
| Heat conductivity, W/mK (400-900 K) | 18-20     |



Figure 10. Ceramic articles made of black ceramics, obtained by direct SHS-sintering.

external force is so-called "black ceramics". Black ceramics was obtained based on the fundamental discovery that silicon carbide powder can "burn" in nitrogen atmosphere at pressure ~100 MPa. The following exchange reaction occurs:



Why this reaction is so attractive for ceramic production? First, if one cannot reach the full degree of conversion to silicon nitride phase, the "unrecated" compound is SiC, which is also a refractory compound. Second, Si<sub>3</sub>N<sub>4</sub> has a lower theoretical density (2.34 g/cm<sup>3</sup>) as compared to that for SiC (3.2 g/cm<sup>3</sup>), thus the above reaction leads to the decrease of the theoretical density of the solid compound in the material. This effect results in an additional decrease of media porosity. All the above permits SHS fabrication of pore-free ceramics directly in the combustion wave without any external loads. It is also important that the formed carbon acts as a self-friction phase in the produced Si<sub>3</sub>N<sub>4</sub>-SiC-C ceramics, which favors its applications in refractory bearings. It is important that this ceramic retains

high mechanical properties up to temperatures of about 1600 °C. Pictures of net-shape articles produced by this technology, in particular corrosion-resistant chemical pump sleeves and spray for corrosive liquids, are shown in Figure 10. This method has been also used to produce cylinders and pistons for ceramic engines that were tested at NIKTID GSK Company (Vladimir, Russia) [12]. Some properties of such ceramics strengthened by TiN phase are presented in Table 6.

## 5. Solution Combustion Synthesis of Ceramic Materials

As mentioned above, the solution combustion synthesis (SCS) is a rapid method for the preparation of a large variety of ceramic materials [13, 18, 107-109]. A typical SCS process involves an exothermic chemical reaction between an oxidant (such as metal nitrates) and an organic compound (urea, glucose, etc.). These water-soluble organic compounds containing large quantities of carbon and hydrogen are being oxidized by gaseous products formed during the thermal decomposition of oxidants. The synthesis of powders by this method involves heating of homogeneous reactive solutions on a hot plate or in a preheated furnace. Rapid heating facilitates the evaporation of solvent and the formation of a viscous gel, which initiates a combustion reaction in the gels leading to the formation of solid products. The rapid increase in temperature leads to the precipitation of nuclei of metal oxides and their further growth into porous nanostructured solid products. Some fuels, such as glycine or citric acid, are capable of forming complexes with metal ions. These complex compounds help to achieve a more homogeneous mixing and avoid segregation processes during the water removal stage ([110-111]). These features make SCS invaluable for the preparation of complex and multicomponent materials such as perovskites, garnets, spinels, silicates, and phosphates [13, 18]. SCS also allows

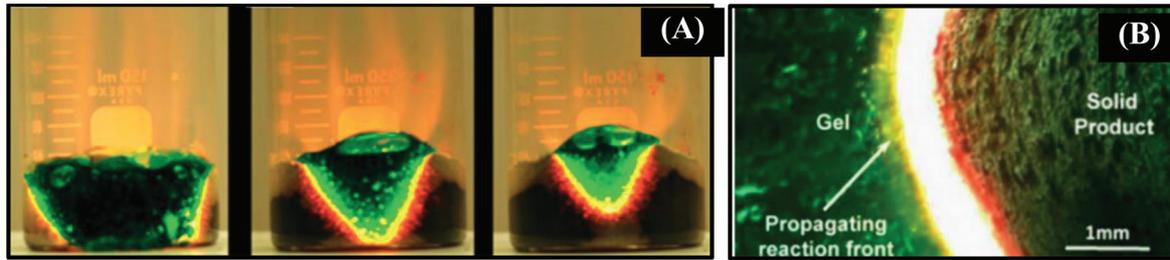
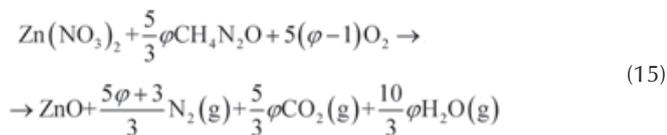


Figure 11. Regimes of SCS: volume combustion synthesis (A) or self-propagating combustion (B).

for uniform doping of materials with a small quantity of elements. Due to the mixing of reactants in molecular level SCS provides high distribution uniformity of dopant in the produced lattice.

Depending on the process organization SCS may occur by either volume combustion synthesis (VCS) or self-propagating combustion (SC) modes [13]. In the VCS case, the entire volume of the reactive solutions is preheated uniformly to the ignition point (Fig. 11A). In the SC case, the reaction is initiated locally, and combustion front propagates along the preliminarily prepared gel in the form of the glowing reaction wave (Fig. 11B). Recently several different modifications of SCS were also introduced. One of them is combustion of reactive gels impregnation in a porous matter such as cellulose or hard templates. Another variation is the spring of reactive solution into a preheated furnace or on a substrate. This process could result in the synthesis of hollow spherical nanoparticles or thin films. Spin coating of reactive solutions allows the formation of thin films on different substrates (silicon wafer, conductive glasses, faxable polymers etc.).

The reaction between a metal nitrate (for example zinc nitrate) and an organic fuel, such as urea ( $\text{CH}_4\text{N}_2\text{O}$ ) can be typically presented as follows:



where,  $\varphi$ , is the fuel-to-oxidizer ratio.  $\varphi = 1$  indicates that all oxygen required for complete oxidations of fuel derives from the oxidants, while  $\varphi > 1$  ( $< 1$ ) implies fuel-rich (or lean) combustion. The self-generated heat of synthesis provides a localized energy supply that eliminates or reduces the need for externally applied thermal processing. The evident advantages of the SCS method are time- and energy-efficiency. Once the reactive solution (gel) is ignited, the self-generated heat converts precursors into the corresponding ceramics without the requirement of additional external energy input. The reaction is completed within a short time (on the order of seconds) with maximum reaction temperatures ranging from 500 to 1500 °C. Such high temperatures facilitate the formation of crystalline materials. If organized properly, no calcination step is needed to obtain desired crystalline phases. The mixing of reactants on the molecular level and release of large quantities of gases result from nanoscale products. The phase composition, morphology, and surface area of SCS-derived products can be controlled by adjusting the fuel type, the fuel/oxidant ratio, the pH value of the solution and other factors. A higher combustion temperature usually results in well crystalline, larger grain sized, agglomerated, and low specific surface area products. The reaction temperature and gas release rate are two competing factors that determine the microstructure of the products.

#### • Energy conversion and storages applications

Solution combustion processes have been widely used to prepare nanostructured complex oxide-based ceramics for energy

applications such as electrode materials for rechargeable batteries, supercapacitors, and solid-oxide fuel cells [13,111-118]. SCS is a proven method for production of such ceramic materials with a high level of phase and structural uniformity.

Electrochemical performance of materials for battery applications is related to porosity, conductivity, the shape and size of the nanostructured ceramic. For example, Chen et al. synthesized  $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$  layered oxide layered complex oxides by the sucrose-assisted SCS [119]. The microstructure analysis suggested that combustion of gels containing metal acetates, sucrose fuel, and nitric acid produces non-agglomerated uniform nanoparticles with average particle sizes of  $\sim 200$  nm. The electrochemical characterization indicated that SCS-derived materials deliver a capacity of 253  $\text{mA}\cdot\text{h/g}$  at 0.1 C, corresponding to a specific energy density of 801  $\text{W}\cdot\text{h/kg}$ . These characteristics were shown to be significantly better than similar materials reported in the literature.

Xu et al. recently used combustion of solutions containing glucose and copper nitrate to produce  $\text{CuO-Cu}_2\text{O/C}$  composites with different carbon contents [120]. The as-prepared copper oxides exhibited uniform spherical morphology and, carbon was synthesized in situ with content ranging from 3 - 36 wt%. The electrochemical performance of the anodes made from the materials in Li-ion batteries demonstrated  $>400$   $\text{mAh/g}$  capacity at 20  $\text{mA/g}$  current density and highly stable cycling performance with capacity 260  $\text{mAh/g}$  after 600 cycles at current density of 0.2 A/g. The authors attribute this performance to the synergistic effect of porous structure, conducting carbon coating and two-component  $\text{CuO/Cu}_2\text{O}$  structure.

Abdollahifar et al. also prepared carbon-coated  $\text{ZnMn}_2\text{O}_4$  complex nanostructured ceramics via a novel SCS formulation using polyethylene glycol as a multifunctional microstructure-directing agent [121]. Controlling the molecular weight and the amount of the polymer in the reactive solutions enabled to tailor the mesoporous structures with increased specific surface areas. The resulting electrodes were exhibit ideal capacitor behaviors in an aqueous neutral electrolyte, possessing specific capacitances up to 150  $\text{F/g}$  and cycle stability showing no capacitance fade after 10,000 cycles at 60% of full capacity with  $>99\%$  Coulombic efficiency.

#### • Catalysts

SCS is an established method for the preparation of different types of catalysts such as bulk and supported heterogeneous catalysts and photocatalysts [122-133]. SCS uses elements of conventional catalysts preparation approaches along with its unique techniques. This includes impregnated active layer combustion [134] and template-assisted solutions combustion [135].

A unique type of ironically-dispersed catalysts was also developed by SCS-based approach [136]. SCS allows uniform distribution of metal (Pt, Pd, Fe, Cr) ions in ceramic compounds (e.g.,  $\text{CeO}_2$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{TiO}_2$ ). The combustion of ceric ammonium nitrate ( $\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ , chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ) and oxalyl dihydrazide ( $\text{C}_2\text{H}_6\text{N}_4\text{O}_2$ ) formed  $\text{Ce}_{1-x}\text{Pt}_x\text{O}_{2-8}$  solid-solutions [136]. Detailed analysis suggested that the Pt possesses both +2 and

+4 oxidation states. Pd, Rh, Ag and Au-substituted  $Ce_{1-x}M_xO_{2-\delta}$  and  $Ti_{1-x}M_xO_{2-\delta}$  catalysts were also prepared by this method [137]. Further investigations allowed to produce even more complex catalysts such as  $Ce_{1-x-y}Ti_xM_yO_{2-\delta}$  (M is Pt and Pd),  $Ce_{1-x-y}Sn_xPd_yO_{2-\delta}$ ,  $Ce_{1-x-y}Fe_xPd_yO_{2-\delta}$ ,  $Ce_{1-x-y}Zr_xPd_yO_{2-\delta}$  and  $Ce_{1-x-y}Hf_xPd_yO_{2-\delta}$  [138]. Similarly, homogeneous Fe- and Cr-doped  $Co_3O_4$  solid-solutions with spinel structure was also fabricated by SCS [139]. These catalysts showed high catalytic activity in CO oxidation reaction. For example, the Fe- and Cr-doped  $Co_3O_4$  catalysts showed high activity even at  $-85^\circ C$ .

SCS-based processes were also used in the preparation of structured catalysts. During the past two decades, a research group in Politecnico di Torino (Italy) developed new catalytic filter technologies for on-board collection and utilization of particulate matter and harmful gases emitting during fuel combustion in car engines and industrial boilers gases. Many complex oxide catalysts were deposited onto silicon carbide and cordierite honeycomb filters [140-1439]. These catalytic filters are capable of rapid simultaneous oxidation of soot and CO, as well as reduction of NO, and decomposition of  $N_2O$  a temperature window of  $300-450^\circ C$ . Moreover, regeneration of catalytic filters was three times faster than that of the non-catalytic filters. SCS-processed filters had high stability and showed no deactivation during soot combustion even after severe high-temperature ( $850^\circ C$ ) aging in humid air.

Recently, a novel SCS-based method was developed to produce metal-silica catalysts [107]. This method involves incorporation of metal nitrates and organic fuel (citric acid) in a stable silica gel through controlled hydrolysis of tetraethyl orthosilicate. Combustion of dried gels with  $NH_4NO_3$  in air or Ar atmospheres enabled synthesis of highly porous  $NiO/SiO_2$  or  $Ni/SiO_2$  nanomaterials with tunable metal content ( $\sim 5-30$  wt.%). The experiments suggested that the maximum combustion temperature and the front propagating velocity depends on the gas environment. High-speed infrared imaging indicates that local heating of a sample in air generates a sequence of two primary combustion waves that propagate along the sample (Fig. 12A). The temperature-time distribution for samples reacting in air revealed the maximum temperature within the first reactive zone is  $\sim 680^\circ C$ , whereas the temperature in this second wave could reach as high as  $\sim 1000^\circ C$ . In argon (Fig. 12B), however, the maximum temperature of a single stage-stage reaction is only  $600^\circ C$ . This

combustion-based approach allowed for independent tuning of the Ni (NiO) nanoparticle size from 2 to 50 nm. The surface area, average pore size, and pore volume of the materials can also be controlled in a wide range during the combustion. As prepared catalysts were tested for hydrogen formation from ethanol decomposition and exhibited high activity and stability.

#### • Inorganic phosphors

Inorganic phosphors are consisting of an inert host lattice, and an activator, typically a 3d or 4f metal and emit light upon excitation by an electron beam, X-rays or a photon. SCS is a traditional method for preparation of multicomponent complex phosphors, with a high degree of dopant structural uniformity [144-151]. The emission intensity is related to the synthesis temperature, and the crystallinity of phosphors. In many cases, one can avoid high-temperature post-combustion calcination. SCS is efficiently used for the preparation of complex doped compounds, such as silicates, titanates, aluminides, borates, phosphates, etc. [13]

Shi et al. were reported  $Eu^{3+}$ -doped  $Ce_2LaO_{5.5}$  phosphors were prepared by the SCS [150]. They showed that the  $Eu^{3+}$  substitutes either  $La^{3+}$  or  $Ce^{4+}$  sites in the crystal lattice due to their close ionic radii. It is interesting that for the series of  $Ce_2La_{1-x}O_{5.5}:xEu^{3+}$ , the lattice parameter was gradually decreased with increasing dopant concentration. For the series of  $Ce_{2-x}LaO_{5.5-x/2}:xEu^{3+}$ , the lattice parameter was enlarged with increasing Eu content. The authors pointed out that all doped materials samples produce characteristic red-light emission of  $Eu^{3+}$  when excavated by light with 466 nm wavelength light. However, when  $Eu^{3+}$  substituted the  $Ce^{4+}$  sites, the material exhibited significantly enhanced luminescence.

Zhang et al. proposed [152] citric acid as fuel for preparation of  $Ye_{3-x}Al_5O_{12}:Ce^{3+}$ . The results of structural studies indicated that combustion parameters phase pure cubic garnet is only reaction product. However, the luminescent intensity is depending on the fuel to oxidizer ratio. Emission characteristics can also be influenced by the concentration of cerium, pH of reactive solutions, as well as the post-combustion heat treatment temperature.

Qiu et al. reported on the synthesis of strontium, barium, and calcium aluminates co-doped with  $Eu^{2+}$  and other elements, such as Dy, Nd, and La, at  $600^\circ C$  without applying a post-combustion treatment [153]. The authors used that excessive amounts of urea

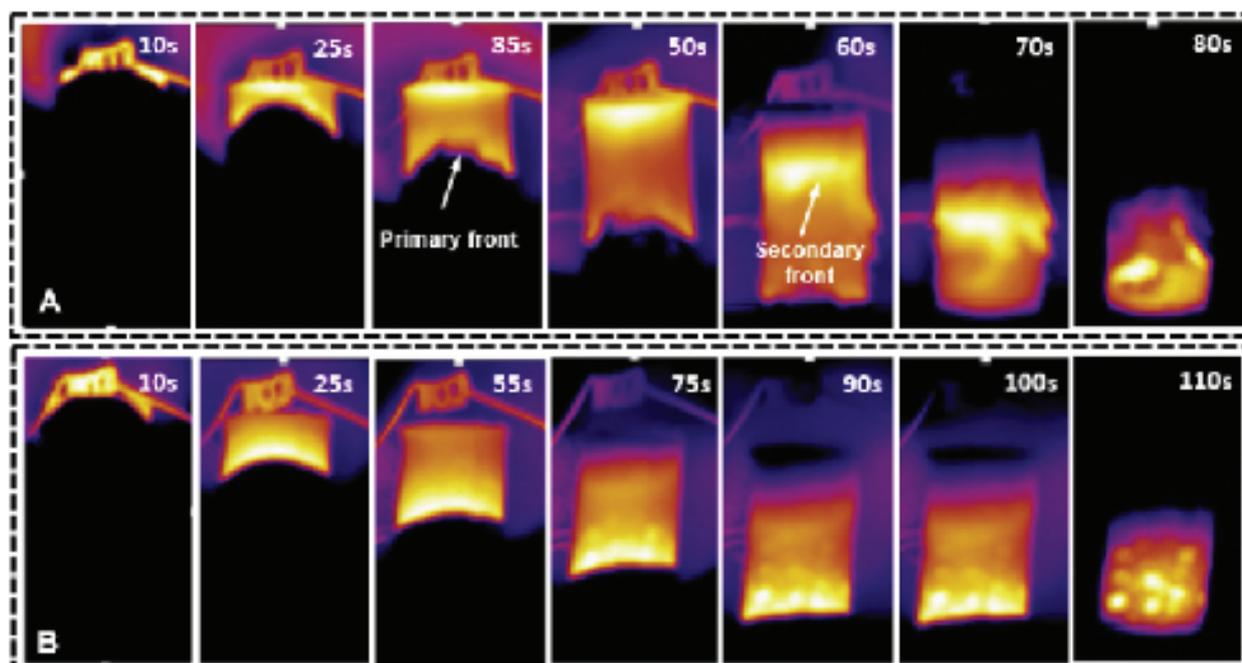


Figure 12. High-speed infrared images of  $Ni(NO_3)_2+citric\ acid+SiO_2+NH_4NO_3$  samples in air (A) and Ar (B).

fuel to form a reductive atmosphere and avoid the oxidation of  $\text{Eu}^{2+}$  to  $\text{Eu}^{3+}$ . It was shown that synthesized nanoscale phosphors have a perfect crystal structure, and the luminescence could be changed from yellow-green to blue-green and then to blue-purple in the visible range by changing the dopant type. Interestingly the nanomaterials exhibited a long afterglow time, sometimes lasting for over seven hours after the excited source was turned off.  $\beta\text{-Ca}_{1.95}\text{P}_2\text{O}_7\text{:Eu}^{2+}$  was also prepared by a SCS formulation using three times more urea than the stoichiometric quantity should be used to produce phosphors [154]. Excessive amounts of fuel during the combustion prevented the oxidation of the  $\text{Eu}^{2+}$  dopant. Depending on furnace temperature (igniting temperature) either  $\gamma\text{-Ca}(\text{PO}_3)_2$  or  $\beta\text{-Ca}_2\text{P}_2\text{O}_7$  host lattice can be formed.

#### • Functional ceramics

SCS was traditionally used over the past several decades to prepare functional ceramic (electro-ceramics, bio-ceramics, magnetic materials, etc.) materials. Hundreds of works have been reported on the synthesis of simple and complex oxides with controllable electrical and magnetic properties.

For example, two different SCS approaches were proposed for the preparation of lead-based niobates [155]. One of these approaches involved rapid ignition of solutions containing metal nitrates, ammonium nitrate, and niobium oxalate, and tetraformal trisazine in a preheated furnace. In the second method, various niobates and lead oxide were first prepared by solution combustion, which then mixed and then calcined to obtain ferroelectric ceramic powder. The materials prepared by both approaches have a fine microstructure, were sintered into compact samples with a relative density of 97-99%. The sintered samples made by the second route showed better dielectric properties than the materials produced by the first synthesis process. More recently, a series of doped lead-free complex titanate electroceramic materials were synthesized, where  $\text{TiO}_2$  or  $\text{TiO}(\text{NO}_3)_2$  was used as precursors and glycine or citric acid as fuels [156-158]. The authors showed that the materials exhibit the desired single-phase product and minimal grain growth during high-temperature sintering process.

SCS-based preparation of magnetic nanoscale materials (iron oxides and complex ferrites) were investigated for many years. For example, Deshpande et al. reported the synthesis of phase pure  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  fabrication with surface areas of 65, 120, and 45  $\text{m}^2/\text{g}$ , respectively [159]. They also applied mixed iron source (iron nitrate and oxalate) as well as glycine and hydrazine fuels to prepare mixtures of  $\alpha$  and  $\gamma$  phases for  $\text{Fe}_2\text{O}_3$  with surface areas changing from 75 to 175  $\text{m}^2/\text{g}$ .

Ianoş et al prepared  $\text{Fe}_3\text{O}_4$  nanomaterials using sucrose, citric acid, and glucose as fuels [160]. Depending on the fuel type, the specific surface area of the final product can be as high as 100  $\text{m}^2/\text{g}$  with a saturation magnetization of  $\sim 60$   $\text{emu/g}$ . A SCS-based approach for ultra-small superparamagnetic  $\alpha\text{-Fe}_2\text{O}_3$  nanoparticles with a specific surface area of  $\sim 130$   $\text{m}^2/\text{g}$  and high magnetization ( $\sim 21$   $\text{emu/g}$ ) was also reported using as silica-assisted template combustion approach [109].

Several recent examples of SCS-derived complex oxide magnetic ceramics include cobalt and nickel ferrites. Lazarova and coworkers reported on the synthesis of single phase nanoscale  $\text{NiFe}_2\text{O}_4$  powders prepared by SCS with using urea, glycine, sucrose or glycerol fuels [161]. The authors pointed out that the use of nitrogen-containing fuels leads to the fabrication of materials with a larger particle size ( $\sim 60$  nm) than materials prepared with nitrogen-free fuels ( $\sim 35$  nm). The magnetization for the materials with larger particle size was reported to be  $\sim 35$   $\text{emu/g}$ , while the products with smaller particles sizes showed  $\sim 25$   $\text{emu/g}$  magnetization value. Cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) nanoscale powders with the tunable surface area (35 - 285  $\text{m}^2/\text{g}$ ) were also reported by changing the fuel (glycine) to oxidant rations reactive solutions

[162]. The synthesized  $\text{CoFe}_2\text{O}_4$  powders exhibited the higher saturation magnetization and coercivity due to the high purity and crystallinity.

SCS has been also used in conjunction with a combination of microwave irradiation and molten salt (such as  $\text{NaNO}_3$ ) methods to produce bioceramics (pure and doped hydroxyapatite, tricalcium phosphate, biphasic calcium phosphate, fluorapatite, and chlorapatite) [163-167]. This approach was particularly successful for fabrication of 1-dimensional bioceramics. Microwave irradiation or reactive solutions ensures ignition and uniform heating of the solutions. High reaction temperatures cause the inert salt to melt, which dissolves the products precipitates during early stages of the process. These particles serve as nucleation centers in the molten phase as the product starts to solidify upon termination of microwave power. During solidification, the bioceramic phase rapidly crystallizes along the preferred growth axis forming nanorods or nanotubes.

#### • Thin films

During the last decade, new SCS formulations have been developed for the deposition of thin films to be used in electronics, solar cells, as well as light-emitting devices [168-172]. These SCS-based approaches involve deposition of thin reactive solutions (gels) layer on different types of substrates (silicon wafer, conductive glass, flexible polymer, etc.) using a spin coating or spraying techniques. Short heat treatment (10-30 min) of solution-coated substrates at temperatures 150-400  $^\circ\text{C}$  allows to produce amorphous and simple oxide ( $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{ZnO}$ ,  $\text{NiO}$ ,  $\text{CuO}$ , etc.) or complex (indium tin oxide, indium zinc oxide, indium gallium zinc oxide) films. These processes usually allow the formation of pore-free films with uniform thickness, which ensures high quality and reliable device fabrication.

Recently, Ban et al. reported the fabrication of indium tin oxide thin films by using photo-ignited combustion synthesis process under hydrogen atmosphere [173]. The authors noticed that the photochemically activated hydrogen on film surface could facilitate highly crystalline oxygen deficient structure, which significantly enhancing the carrier concentration and mobility. The authors also performed low-temperature functionalization of films, which increased the conductivity of  $>1607$   $\text{S/cm}$  under the process temperature of less than 300  $^\circ\text{C}$ . Transparent metal-oxide thin-film transistors and large-area integrated circuits with the indium tin oxide bus lines (Figure 13) were demonstrated showing good field-effect mobilities ( $>6.5$   $\text{cm}^2/\text{Vs}$ ) with relatively

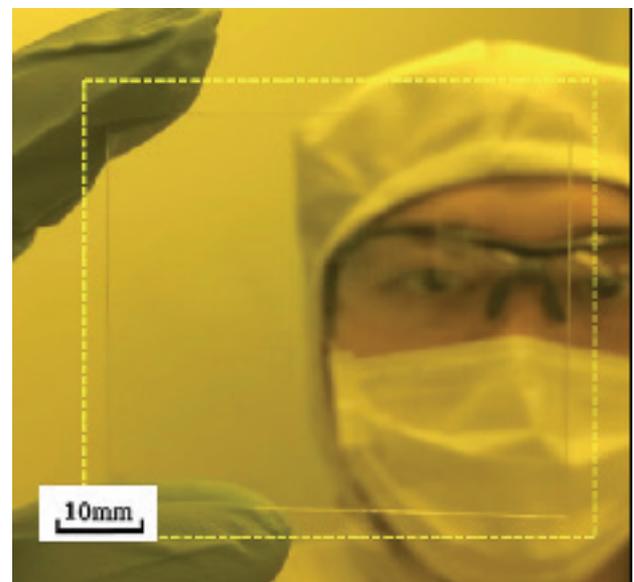


Figure 13. An optical image of SCS-processed thin film transistor.

good operational stability and the oscillation frequency of more than 1 MHz in 7-stage ring oscillators, respectively.

Pujar et al. reported the fabrication of high quality, transparent and conducting titanium-doped indium oxide films using SCS with acetylacetone as fuel [174]. The films exhibit high crystallinity and smooth surfaces. Hall effect measurements have revealed charge carrier densities of the order  $10^{19} \text{ cm}^{-3}$  irrespective of annealing temperature with maximum mobility ( $\sim 2 \text{ cm}^2/\text{Vs}$ ) and conductivity ( $20 \text{ S/cm}$ ) for the sample prepared at  $450 \text{ }^\circ\text{C}$ .

Combustion synthesis of thin oxide films can be organized continuously by spraying the reactive solutions intermittently on the substrates until the desired thickness (20 or 50 nm) [66]. This approach enables the production of films in a single-stage process. The combination of short pulses with combustion allows removal of gas trapped in the product, thus yielding pore-free and macroscopically continuous films. It was also shown that the characteristics of devices prepared by spray SCS are approaching those fabricated by magnetron sputtering protocols.

## 6. Concluding Remarks

It can be concluded from the above that combustion-based methods allow fabrication of a wide variety of ceramics: powders, bulk materials, coatings and net shape articles. Nanomaterials of any dimensions can be also produced through self-sustained reactions. Several advantages of the approach can be outlined. The SHS of ceramics do not need any external energy source, since they occur in a self-sustained synergetic manner. Thus, SHS is an energy saving process, which requires simple equipment without any heating elements. In addition, the unique conditions of the combustion approaches (e.g. high temperatures, rapid self-heating and cooling) facilitate formation of crystalline nanomaterials. Other advantages of SHS is its ability to produce multi element compounds with complex crystal structures. In addition, the SHS permits scale of materials production. Indeed increasing the amount of reactive mixture leads to more adiabatic conditions and thus more steady-state combustion regime. Finally, the SHS allows continuous schemes for processing of different ceramics.

However, several limitations of SHS should to be resolved, before this method can be widely implemented in large-scale production of advanced ceramics. The main issues are related to the uniformity of the morphology and microstructure for the produced materials and controllability of SHS process. In this regards it is important that many recent works showed that by investigating the mechanisms of the combustion reactions and structural transformations, which occur during SHS, one might establish effective ways to control the structure of the ceramics materials. Indeed, during the last decade, CS direction made several significant steps ahead in finding new routes of material synthesis. From completely not controlled thermal explosion by heating in furnace, to precisely controlled steady state self-propagating mode. From agglomerates with non-uniform microstructures, to super fine (less than 10 nm) nanoparticles. From powders to thin films and 1D and 2D crystals. From porous bulk materials to pore-free nanostructured net-shape articles.

We have to continue work on fundamentals of self-sustained reactions, based on which controllability issue can be resolved for synthesis of any kind of ceramics. We have also to analyze the market demands to find out the right niches for SHS technologies. Practice shows that SHS should not compete with traditional powder metallurgical technologies in production of conventional well-established materials. We have to consider the materials, which are difficult or impossible to produce by traditional methods. Direct fabrication of the net-shape pore-free ceramic articles, as well as synthesis of 1 and 2D nanopowders of refractory compounds, are may be among the promising for SHS directions.

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## References

- [1] A.G. Merzhanov, 40 years of SHS: A Lucky Star of Scientific Discovery (story-presentation with elements of a scientific paper), Bentham Science Publisher, Brussel, Belgium, 2012, pp. 1-104., doi: 10.2174/97816080512811120101.
- [2] A.G. Merzhanov, V.M. Shkiro, I.P. Borovinskaya, Phenomenon of wave localization for self-retarding solid state reactions, Diploma No. 287, filed 05.07.1967; Vestnik of USSR Academy of Science, No. 10, 1984 (in Russian).
- [3] A.G. Merzhanov, Solid flame: Discovery, concepts, and horizons of cognition, Comb. Sci. Technol. 98 (4-6) (1994) 307-336.
- [4] A.G. Merzhanov, A.S. Mukasyan, Solid-Flame Combustion (Tverdoplammenoe Gorenje), Moscow: Torus Press, 2007, pp. 336 (in Russian).
- [5] V.M. Shkiro, G.A. Nersisyan, I.P. Borovinskaya, Preparation of tantalum carbides by self-propagating high-temperature synthesis, Combust. Explos. Shock Waves, 14(4) (1978) 455-460.
- [6] C.E. Shuck, K.V. Manukyan, S. Rouvimov, A.S. Rogachev, A.S. Mukasyan, Comb. & Flame, Solid-flame: Experimental Validation, 163 (2016) 487-493.
- [7] A.S. Mukasyan, C.E. Shuck, J.M. Pauls, K.V. Manukyan, D.O. Moskovskikh, A.S. Rogachev, The Solid Flame Phenomenon: A Novel Perspective, Advanced Engineering Materials, 20 (8), (2018) Article Number 1701065.
- [8] A.G. Merzhanov, I.P. Borovinskaya, Self-spreading high-temperature synthesis of refractory compounds, Dokl. Chem., 204(2) (1972) 429-431.
- [9] A.G. Merzhanov, Self-propagating high-temperature synthesis: Twenty years of search and findings. In: Combustion and Plasma Synthesis of High-Temperature Materials, Munir Z., Holt J.B., Eds., New York: VCH, 1990, pp. 1-53.
- [10] V. Hlavacek, Combustion synthesis: A historical perspective, Amer. Ceram. Soc. Bull., 70(2) (1991) 240-243.
- [11] A.G. Merzhanov, History and Recent Development in SHS, Ceram. Inter., 21(5) (1995) 371-379.
- [12] A.S. Rogachev, A.S. Mukasyan, Combustion for Material Synthesis, CRC Press, Taylor and Francis, 2015, pp.1-398.
- [13] A. Varma, A.S. Mukasyan, A.S. Rogachev, K. Manukyan Chemical Review, 116 (2016) 14493-14586.
- [14] Nitride Ceramics: Combustion Synthesis and Applications, editors: AA. Gromov, L. Chukhlomina, Wiley, VCH, 2014, pp.1-234.
- [15] E.A. Levashov, A.S. Mukasyan, A.S. Rogachev and DV. Shtansky, International Materials Reviews 62(4) (2017) 203-239.
- [16] R. Orrù, G. Cao, Comparison of Reactive and Non-Reactive Spark Plasma Sintering Routes for the Fabrication of Monolithic and Composite Ultra High Temperature Ceramics (UHTC), Materials, 6 (2013) 1566-1583.
- [17] A.S. Mukasyan, K. Manukyan, Combustion/micropyretic synthesis of atomically thin two-dimensional materials for energy applications, Current Opin. in Chem. Eng., 7 (2015) 16-22.
- [18] H.H. Nersisyan, J.H. Lee, J.R. Ding, K.S. Kim, K. Manukyan, A.S. Mukasyan, Combustion synthesis of zero-, one-, two- and three-dimensional nanostructures: Current trends and

- future perspectives, *Progress in Energy and Combustion Science*, 63 (2017) 79-118.
- [19] E.L. Dreizin, *Metal-based reactive nanomaterials*, *Progress in Energy and Combustion Science*, 35 (2009) 141-167.
- [20] A.S. Rogachev, A.S. Mukasyan, *Comp. Combustion of Heterogeneous Nano-Structured Systems Expl. Shock Waves*, 46 (2010) 243-266.
- [21] V. Turlo, O. Politano, F. Baras *Acta Materialia*, Modeling self-sustaining waves of exothermic dissolution in nanometric Ni-Al multilayer 120 (2016) 189-204.
- [22] F. Baras, V. Turlo, O. Politano, S.G. Vadchenko, A.S. Rogachev, A.S. Mukasyan, SHS in Ni/Al nanofoils: a review of experiments and molecular dynamics simulations" *Adv. Engineering Materials*, 20 (8), (2018) Article Number: 1800091.
- [23] Z.A. Munir, and U. Anselmi-Tamburini, Self-propagating exothermic reactions: The synthesis of high-temperature materials by combustion. *Mater. Sci. Reports*, 3, (1989) 365-277.
- [24] K.V. Manukyan, W. Tan, R.J. deBoer, E.J. Stech, A. Aprahamian, M. Wiescher, S. Rouvimov, K.R. Overdeep, C.E. Shuck, T.P. Weihs, and A.S. Mukasyan, Irradiation-Enhanced Reactivity of Multilayer Al/Ni Nanomaterials, *ACS Appl. Mater. Interfaces*, 7 (21) (2015) 11272-11279.
- [25] K.V. Manukyan, Ya-C. Lin, S. Rouvimov, P.J. McGinn, A.S. Mukasyan, Microstructure-reactivity relationship of Ti-C reactive nanomaterials, *J. Appl. Phys.*, 113 (2) (2013) 024302-024302-10.
- [26] A.S. Mukasyan, S.T. Aruna and A.S. Rogachev, *Combustion Synthesis in Nanostructured Reactive Systems*, *Advanced Powder Technology*, 26(3) (2015) 954-976.
- [27] A.S. Rogachev, D.O. Moskovskikh, A.A. Nepapushev, T.A. Sviridova, S.G. Vadchenko, S.A. Rogachev, A.S. Mukasyan, Experimental investigation of milling regimes in planetary ball mill and their influence on structure and reactivity of gasless powder exothermic mixtures, *Powder Technology*, 274 (2015) 44-52.
- [28] V.M. Shkiro, I.P. Borovinskaya, Capillary flow of liquid metal during combustion of titanium mixtures with carbon, *Combust Explos. Shock Waves*, 12(6) (1976) 828-831.
- [29] V.M. Shkiro, G.A. Nersisyan, I.P. Borovinskaya, A.G. Merzhanov, V.S. Shekhtman, Preparation of tantalum carbides by self-propagating high-temperature synthesis, *Sov. Powd. Metall.*, 18(4) (1979) 227-230.
- [30] A.D. Kikin, A.G. Peresada, Y.S. Karimov Y.S, et al, Density of critical current of HTSC ceramics based on Yttrium and Thallium prepared by the self-propagation high-temperature synthesis method, *Z. Tekh. Fiz.*, 59(8) (1989) 29-31.
- [31] M.D. Nersisyan, J.T. Richardson, D. Luss, SHS of complex oxide ceramic materials, *International Symposium on Innovative Processing and Synthesis of Ceramics, Glasses, and Composites at the 102nd Annual Meeting of the American-Ceramic-Society*, St. Louis, MO, USA, in a book series: *Ceram Trans.* 15 (2000) 95-106.
- [32] P.B. Avakyan, M.D. Nersisyan, A.G. Merzhanov, New materials for electronic engineering *Amer. Ceram. Soc. Bul.*, 75(2) (1996) 50-55.
- [33] K.S. Martirosyan, P.B. Avakyan, M.D. Nersisyan, Phase formation during self-propagating high-temperature synthesis of ferrites, *Inorg. Materials*, 38(4) (2002) 400-03.
- [34] A.G. Merzhanov, I.P. Borovinskaya, Y.E. Volodin, Combustion of porous metallic samples in nitrogen, *Dokl. Phys. Chem.*, 206 (1972) 833-836.
- [35] I.P. Borovinskaya, V.E. Loryan, Self-propagating processes in the formation of solid solutions in the zirconium-nitrogen system, *Dokl. Phys. Chem.*, 231 (1976) 1230-1233.
- [36] I.P. Borovinskaya, A.N. Pityulin, Combustion of hafnium in nitrogen, *Combust. Explos. Shock Waves*, 14 (1978) 111-114.
- [37] A.P. Aldushin, New results in the theory of filtration combustion, *Combust. Flame*, 94 (1993) 308-320.
- [38] A.P. Aldushin, A.G. Merzhanov, Filtration combustion theory: General approaches and results, in a book *Thermal Wave Propagation in Heterogeneous Media*, Nauka, Novosibirsk, 1988, pp. 9-51.
- [39] M. Kh. Ziatdinov, Metallurgical SHS Processes as a Route to Industrial-Scale Implementation: An Autoreview, *Int. J. SHS*, 27(1) (2018) 1-13.
- [40] *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*, 1-st Edition, Editors: I. Borovinskaya, A. Gromov, E. Levashov, A.S. Mukasyan, A. Rogachev, Elsevier, Amsterdam, Netherlands, 2017.
- [41] S.S. Mamyán, V.I. Vershinnikov, Specific features of combustion of SHS systems containing magnesium as a reductant, *Int. J. SHS*, 1 (1992) 392-400.
- [42] V.I. Yukhvid, Technology of SHS casting, in the book *Self-Propagating High-Temperature Synthesis of Materials*, (A. Borisov, L. DeLuca and A. Merzhanov, Eds.), Taylor & Francis, New York, (2002) 238-268.
- [43] P.I. Parkin, Solid state metathesis reaction for metal borides, silicides, pnictides and chalcogenides: ionic or elemental pathways, *Chem. Soc. Rev.* 25, (1996) 199-207.
- [44] J.B. Holt, Z.A. Munir, Combustion synthesis of titanium carbide: Theory and experiment, *J. Mater. Sci.*, 21 (1986) 251-259.
- [45] A.S. Mukasyan AS, *Combustion Synthesis of Silicon Carbide*, in a book: *Properties and Applications of Silicon Carbide*, ed. by: Prof. R. Gerhardt, INTECH, Vienna, Austria, 2011, pp. 389-409.
- [46] A. Varma, A.S. Rogachev, A.S. Mukasyan, S. Hwang, *Combustion Synthesis of Advanced Materials: Principles and Applications*", *Advances in Chemical Engineering*, 24 (1998) 79-226.
- [47] S.L. Abovyan, H.H. Nersisyan S.L. Kharatyan, Activated combustion of the SiO<sub>2</sub>-Al-C system and synthesis of SiC/Al<sub>2</sub>O<sub>3</sub> composite powders, *Comb., Explos. & Sh. Waves* 36 (2000) 204-208.
- [48] A.V. Kostanyan, H.H. Nersisyan, S.L. Kharatyan, R. Orru, G. Cao, Chemically stimulated combustion in the Zr/SiO<sub>2</sub>/C system and synthesis of ZrO<sub>2</sub>/SiC composite ceramic powders containing SiC whiskers, *Int. J. SHS*, 9 (2000) 387-402.
- [49] S.L. Abovyan, H.H. Nersisyan, S.L. Kharatyan, R. Orru, R. Saiu, G. Cao, et al. Synthesis of alumina-silicon carbide composites by chemically activated self-propagation reactions, *Ceram Int.*, 27 (2001) 163-169.
- [50] J. Puzynski, S. Miao, Chemically-assisted combustion synthesis of silicon carbide from elemental powders, in: Sigh, J.P. (ed.) *Innovative Process/Synthesis; Ceramics, Glasses, composites II*, Amer. Cer. Soc, Westerville (1998) 13-28.
- [51] C.C. Wu, C.C. Chen, Direct combustion synthesis of SiC powders. *J Mat Sci.*, 34 (1999) 4357-4363.
- [52] H.E. Çamurlu, F. Maglia, Preparation of nano-size ZrB<sub>2</sub> powder by self-propagating high-temperature synthesis, *J. Eur. Ceramic Society* 29 (2009) 1501-1506.
- [53] H.I. Won, H. Nersisyan, C.W. Won, H.H. Lee, Simple synthesis of nanosized refractory metal carbides by combustion process, *J Mater Sci.*, 46 (2011) 6000-6006.
- [54] G.A. Nersisyan, V.N. Nikogosov, S.L. Kharatyan, A.G. Merzhanov, Chemical transformation mechanism and combustion regimes in the system silicon-carbonfluoroplast, *Combustion explosion and Shock Wave*, 27(6), (1991) 729-724.
- [55] S.L. Kharatyan, H.H. Nersisyan, Combustion synthesis of silicon carbide under oxidative activation conditions, *Int. J. SHS*, 3(1) (1995) 17-25.
- [56] K.V. Manukyan, S. Rouvimov, E.E. Wolf, A.S. Mukasyan, Combustion synthesis of graphene materials, *Carbon*, 62

- (2013) 3092-311.
- [57] Y.J. Lee, S.H.G. Kim, T.H. Lee, H.H. Nersisyan, K.H. Lee, M.H. Han, et al, Combustion synthesis and characterization of TaC, TaC/TaSi<sub>2</sub> and TaC/TaB nanoparticles, *Chem Eng Sci*, 107 (2014) 227-34.
- [58] D.Y. Kim, Y.J. Lee, T.H. Lee, K.H. Lee, H.H. Nersisyan, M.H. Han, et al, Aluminothermic reduction of K<sub>2</sub>TiF<sub>6</sub> to prepare TiC, TiB<sub>2</sub> and TiN nanopowders, *Combust Sci Technol* 186 (2014) 90-101.
- [59] T. Grigorieva, M. Korchagin, N. Lyakhov, Combination of SHS and mechanochemical synthesis for nanopowder technologies," *KONA Powder Particle*, 20 (2002) 144-158.
- [60] L. Takacs, Self-sustaining reactions induced by ball milling, *Prog. Mater. Sci.* 47 (2002) 355-414.
- [61] C. Suryanarayana, *Mechanical Alloying and Milling*, Marcel Dekker, New York, 2004.
- [62] A.S. Mukasyan, Y.C. Lin, A.S. Rogachev, D.O. Moskovskikh, Direct Combustion Synthesis of Silicon Carbide Nanopowder from the Elements, *J. Am. Ceram. Soc.*, 96 (2013) 111-117.
- [63] Y. Yang, K. Yang, Z-M. Lin, J-T. Li, Mechanical-activation-assisted combustion synthesis of SiC, *Mat. Lett.*, 61 (2007) 671-676.
- [64] Y. Yang, K. Yang, Z-M. Lin, J-T Li, Mechanical-activation-assisted combustion synthesis of SiC powders with polytetrafluoroethylene as promoter, *Mat. Res. Bull.*, 42 (2007) 1625-1632.
- [65] I.P. Borovinskaya, Formation of refractory compounds by combustion of heterogeneous condensed system, in the book: *Gorenie i Vzriv (Combustion and Explosion)*, papers of the IV National Symposium on Comb. and Explosion, Nauka, Moscow, (1977) 138-149.
- [66] I.P. Borovinskaya, V.E. Loryan, V. Zakorzhevsky, Combustion Synthesis of Nitrides for Development of Ceramic Materials of New Generation, in a book: *Nitride Ceramics: Combustion Synthesis and Applications*, Editors: AA. Gromov, L. Chukhlomina, Wiley, VCH, (2014) 1-48.
- [67] S.K. Lee, K.T. Park, H.Y. Ryu, H.H. Nersisyan, K.H. Lee, J.H. Lee, Size tailored nanoparticles of ZrN prepared by single-step exothermic chemical route, *Kor J Mater Res*, 5 (2012) 243-248.
- [68] Y.J. Lee, D.Y. Kim, K.H. Lee, M.H. Han, K.S. Kang, K.K. Bae KK, et al., Ammonium fluoride activated synthesis of cubic  $\delta$ -TaN nanoparticles at low temperatures, *Nanoscale Res Lett* 8 (2013) 1-9.
- [69] S.S. Mamyán, Magnesium – Thermal SHS of Inorganic Materials, in a book: *Self-Propagating High-Temperature Synthesis of Materials*, (A. Borisov, L. DeLuca and A. Merzhanov, Eds.), Taylor & Francis, New York, (2002) 202-237.
- [70] H.H. Nersisyan, B.U. Yoo, K.H. Lee, J.H. Lee, A thermochemical pathway for controlled synthesis of Al Nanoparticles in nonisothermal conditions, *Therm. Acta.*, 604 (2015) 77-82.
- [71] C.L. Yeh, F.S. Wu, YL. Chen, Effects of  $\alpha$  and  $\beta$ -Si<sub>3</sub>N<sub>4</sub> as precursors on combustion synthesis of ( $\alpha$ + $\beta$ )-SiAlON composites. *J Alloys Compd*, 604 (2014) 260-265.
- [72] M. Xia, C. Ge, H. Guo, Aligned single-crystalline  $\beta$ -Si<sub>3</sub>N<sub>4</sub> whiskers prepared with SHS process. *Adv Eng Mat.*, 14 (2012) 166-169.
- [73] B.V. Stepanov, A.S. Mukasyan, K.G. Shkadinskii, Macrokinetics of Si<sub>3</sub>N<sub>4</sub> formation with gas transport of silicon, *Dokl Phys Chem.*, 302 (1988) 814-818.
- [74] A.S. Mukasyan, B.V. Stepanov, Y.A. Gal'chenko, et al., Mechanism of Structure formation of silicon nitride with combustion of silicon in nitrogen, *Combust. Explos. Shock Waves*. 26 (1990) 39-45.
- [75] H.H. Nersisyan, T.H. Lee, K.H. Lee, Y.S. An, J.S. Lee, J.H. Lee, Few-atomic-layer boron nitride nanosheets synthesized in solid thermal waves, *RSC Adv.*, 5 (2015) 8579-8584.
- [76] H.H. Nersisyan, T.H. Lee, B.U. Yoo, S.C. Kwon, H. Suh, J.G. Kim, et al., B-containing nanomaterial synthesis when a combustion wave moves with in a packed bed of solid particles, *Combust Flame*, 172 (2016) 271-279.
- [77] M.T. Beason, J.M. Pauls, I.E. Gunduz, S. Rouvimov, K.V. Manukyan, K. Matous, S.F. Son, A.S. Mukasyan, Shock-induced reaction synthesis of cubic boron nitride, *APL*, 112(17) (2018) 171903.
- [78] A.S. Mukasyan, Combustion Synthesis of Boron Nitride Ceramics: Fundamental and Applications, in a book: *Nitride Ceramics: Combustion Synthesis and Applications*, Editors: A.A. Gromov, L. Chukhlomina, Wiley, VCH, (2014) 49-74.
- [79] J.A. Puszynski, A. Degraw, Past and current accomplishments in production of ceramic powders and structures by self-propagating high-temperature synthesis, *Adv. Sci. Technol.*, 63 (2010) 228-235.
- [80] Y. Miyamoto, M. Koizumi, O. Yamada, High-pressure self-combustion sintering for ceramics, *J Am Ceram Soc.*, 67 (1984) 224-225.
- [81] R. Pampuch, L. Stobierski, J. Liz, Synthesis of sinterable beta-SiC powders by a solid combustion method, *J Amer Ceram Soc.* 72(8) (1989)1434-1435.
- [82] L. Stobierski, E. Ermer, R. Pampucn R, et al., Supersaturated solid solutions of boron in SiC by SHS, *Ceram Int.*, 19 (1993) 231-234.
- [83] S.Y. Sharivker, I.P. Borovinskaya, G.A. Vishnyakova, et al., Morphological and technological characteristics of silicon nitride powder prepared by self-propagating high-temperature synthesis, *Soviet Powder Metallurgy and Metal Ceramics (Poroshkovaya Metallurgiya)*, 3(11) (1992) 915-920.
- [84] S.Y. Sharivker, S.S. Mamyán, V.A. Vlasov, et al., Activated sintering of silicon nitride powder made by SHS. *Soviet Powder Metallurgy and Metal Ceramics (Poroshkovaya Metallurgiya)*, 33(9) (1995) 541-544.
- [85] Z.A. Munir, D.V. Quach, M. Ohyanagi, Electric current activation of sintering: a review of the pulsed electric current sintering process, *J Am Ceram Soc*, 94 (2011) 1-19.
- [86] I.J. Shon, Synthesis of Ti<sub>5</sub>Si<sub>3</sub>-xNb Composites by the field-activated combustion method. *Metals Mater*, 3 (1997) 199-202.
- [87] E.A. Olevisky, W.L. Bradbury, C.D. Haines, et al., Fundamental aspects of spark plasma sintering: I. Experimental analysis of scalability. *J Am Ceram Soc.*, 95(8) (2012) 2406-2413.
- [88] A. Feng, and Z.A. Munir, Field-assisted self-propagating synthesis of SiC, *J. Appl. Phys.*, 76, (1994) 1927-1930.
- [89] S. Gedevisishvili, Z.A. Munir, An investigation of the combustion synthesis of MoSi<sub>2</sub> b-SiC composites through electric-field activation, *Mat. Sci. Eng. A*, 242 (1998) 1-6.
- [90] R. Orrù, G. Cao, Comparison of reactive and non-reactive spark plasma sintering routes for the fabrication of monolithic and composite ultra high temperature ceramics (UHTC) Materials. *Materials*, 6 (2013) 1566-1583.
- [91] D.O. Moskovskikh, Ya-C. Lin, PJ. McGinn, AS. Rogachev, AS. Mukasyan, Spark plasma sintering of SiC powders produced by different combustion synthesis routes, *J. Eur. Ceram. Soc.*, 35(2) (2015) 477-486.
- [92] D.O. Moskovskikh, Y. Song, S Rouvimov, A.S. Rogachev, A.S. Mukasyan, Silicon carbide ceramics: Mechanical activation and spark plasma sintering, *Ceramics International*, 42, (2016) 12686-12693.
- [93] D.O. Moskovskikh, K.A. Paramonov, A.A. Nepapushev, N.F. Shkodich, A.S. Mukasyan, Bulk Boron Carbide Nanostructured Ceramics by Reactive Spark Plasma Sintering, *Ceramic International*, 43 (11) (2017) 8190-8194.
- [94] L. Nikzad, R. Orrù, R. Licheri, et al., Fabrication and formation mechanism of B<sub>4</sub>C-TiB<sub>2</sub> composite by reactive spark plasma sintering using unmilled and mechanically

- activated reactants, *J Am Ceram Soc.*, 95(11) (2012) 3463-3471.
- [95] I.Y. Ko, J.H. Park, K.S. Nam, et al., Rapid consolidation of nanocrystalline NbSi<sub>2</sub>-Si<sub>3</sub>N<sub>4</sub> composites by pulsed current activated combustion synthesis, *Met Mater Int.* 16 (2010) 393-398.
- [96] I.Y. Ko, S.K. Bae, J.K. Yoon, et al., Rapid synthesis and consolidation of nanostructured TaSi<sub>2</sub>-SiC-Si<sub>3</sub>N<sub>4</sub> composite from mechanically activated powders by high-frequency induction-heated combustion, *J Alloy Compd.*, 504 (2010) 548-551.
- [97] I.K. Ko, J.H. Park, J.K. Yoon, et al. ZrSi<sub>2</sub>-SiC composite obtained from mechanically activated ZrC+3Si powders by pulsed current activated combustion synthesis, *Ceram Int.* 36 (2010) 817-820.
- [98] I.J. Shon, J.H. Park, I.Y. Ko, et al., Properties and consolidation of nanocrystalline WSi<sub>2</sub>-SiC composite from mechanically activated powders by pulsed current activated combustion synthesis, *Ceram Int.*, 37 (2011)1549-1555.
- [99] R. Licheri, C. Musa, R. Orrù, et al., Bulk monolithic zirconium and tantalum diborides by reactive and nonreactive spark plasma sintering, *J Alloys Compd.*, 663 (2016) 351-359.
- [100] C. Musa, R. Orrù, R. Licheri, et al., Spark plasma synthesis and densification of TaB<sub>2</sub> by pulsed electric current sintering, *Mater Lett.*, 65 (2011) 3080-3082.
- [101] R. Licheri, C. Musa, R. Orrù, et al., Influence of the heating rate on the in situ synthesis and consolidation by reactive spark plasma sintering, *J Europ Ceram Soc.*, 35 (2015) 1129-1137.
- [102] L. Nikzad, R. Orrù, R. Licheri, et al., Fabrication and formation mechanism of B<sub>4</sub>C-TiB<sub>2</sub> composite by reactive spark plasma sintering using unmilled and mechanically activated reactants. *J Am Ceram Soc.*, 95(11) (2012) 3463-3471.
- [103] X. Yi, W. Zhanga, T. Akiyama, Thermal conductivity of β-SiAlONs prepared by a combination of combustion synthesis and spark plasma sintering, *Thermochimica Acta.* 576 (2014) 56-59.
- [104] M. Koshiyama, H. Sako, M. Ohno, et al., Relationships between spark plasma sintering temperature and mechanical properties of combustion-synthesized α and β-SiAlON, *Japan Inst Met Mater*, 79(4) (2015) 191-194.
- [105] I.Y. Ko, J.H. Park, K.S. Nam, et al. Rapid consolidation of nanocrystalline NbSi<sub>2</sub>-Si<sub>3</sub>N<sub>4</sub> composites by pulsed current activated combustion synthesis. *Met Mater Int.*,16 (2010) 393-398.
- [106] I.Y. Ko, S.K. Bae, J.K. Yoon, et al. Rapid synthesis and consolidation of nanostructured TaSi<sub>2</sub>-SiC-Si<sub>3</sub>N<sub>4</sub> composite from mechanically activated powders by high-frequency induction-heated combustion. *J Alloy Compd.*, 504 (2010) 548-551.
- [107] K.V. Manukyan, A.V. Yeghishyan, C.E. Shuck, D.O. Moskovskikh, S. Rouvimov, E.E. Wolf, A.S. Mukasyan, Mesoporous metal - silica materials: Synthesis, catalytic and thermal properties, *Microporous Mesoporous Mater.* 257 (2018) 175-184. doi:10.1016/j.micromeso.2017.08.044.
- [108] K.V. Manukyan, Combustion and materials synthesis, *Int. J. Self-Propagating High-Temperature Synth.* 26 (2017). doi:10.3103/S1061386217030025.
- [109] K.V. Manukyan, Y.-S. Chen, S. Rouvimov, P. Li, X. Li, S. Dong, X. Liu, J.K. Furdyna, A. Orlov, G.H. Bernstein, W. Porod, S. Roslyakov, A.S. Mukasyan, Ultrasmall α-Fe<sub>2</sub>O<sub>3</sub> Superparamagnetic Nanoparticles with High Magnetization Prepared by Template-Assisted Combustion Process, *J. Phys. Chem. C.* 118 (2014) 16264-16271. doi:10.1021/jp504733r.
- [110] H. Birol, C. Renato Rambo, M. Guiotoku, D. Hotza, Preparation of ceramic nanoparticles via cellulose-assisted glycine nitrate process: A review, *RSC Adv.* 3 (2013) 2873-2884. doi:10.1039/c2ra21810k.
- [111] W. Wen, J.-M. Wu, Nanomaterials via solution combustion synthesis: a step nearer to controllability, *RSC Adv.* 4 (2014) 58090–58100. doi:10.1039/C4RA10145F.
- [112] W. Wen, J.-C. Yao, C.-C. Jiang, J.-M. Wu, Solution-combustion synthesis of nanomaterials for lithium storage, *Int. J. Self-Propagating High-Temperature Synth.* 26 (2017) 187-198. doi:10.3103/S1061386217030074.
- [113] A.S. Prakash, P. Manikandan, K. Ramesha, M. Sathiya, J.-M. Tarascon, A.K. Shukla, Solution-Combustion Synthesized Nanocrystalline Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> As High-Rate Performance Li-Ion Battery Anode, *Chem. Mater.* 22 (2010) 2857–2863. doi:10.1021/cm100071z.
- [114] F. Li, J. Ran, M. Jaroniec, S.Z. Qiao, Solution combustion synthesis of metal oxide nanomaterials for energy storage and conversion, *Nanoscale.* 7 (2015) 17590–17610. doi:10.1039/C5NR05299H.
- [115] A. Gupta, W.D. Chemelewski, C. Buddie Mullins, J.B. Goodenough, High-Rate Oxygen Evolution Reaction on Al-Doped LiNiO<sub>2</sub>, *Adv. Mater.* 27 (2015) 6063–6067. doi:10.1002/adma.201502256.
- [116] B. Shri Prakash, V.K. William Grips, S.T. Aruna, A single step solution combustion approach for preparing gadolinia doped ceria solid oxide fuel cell electrolyte material suitable for wet powder and plasma spraying processes, *J. Power Sources.* 214 (2012) 358–364. doi:10.1016/j.jpowsour.2012.04.049.
- [117] M. Vujković, M. Mitrić, S. Mentus, High-rate intercalation capability of NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C composite in aqueous lithium and sodium nitrate solutions, *J. Power Sources.* 288 (2015) 176-186. doi:10.1016/j.jpowsour.2015.04.132.
- [118] N.G. Prakash, M. Dhananjaya, A.L. Narayana, D.P. Shaik, P. Rosaiah, O.M. Hussain, High Performance One Dimensional α-MoO<sub>3</sub> Nanorods for Supercapacitor Applications, *Ceram. Int.* 44 (2018) 9967-9975. doi:10.1016/j.ceramint.2018.03.032.
- [119] M. Chen, D. Chen, Y. Liao, X. Zhong, W. Li, Y. Zhang, Layered Lithium-Rich Oxide Nanoparticles Doped with Spinel Phase: Acidic Sucrose-Assistant Synthesis and Excellent Performance as Cathode of Lithium Ion Battery, *ACS Appl. Mater. Interfaces.* 8 (2016) 4575-4584. doi:10.1021/acsami.5b10219.
- [120] C. Xu, K.V. Manukyan, R.A. Adams, V.G. Pol, P. Chen, A. Varma, One-step solution combustion synthesis of CuO/Cu<sub>2</sub>O/C anode for long cycle life Li-ion batteries, *Carbon.* 142 (2019) 51-59. doi:10.1016/j.carbon.2018.10.016.
- [121] M. Abdollahifar, S.S. Huang, Y.H. Lin, Y.C. Lin, B.Y. Shih, H.S. Sheu, Y.F. Liao, N.L. Wu, High-performance carbon-coated ZnMn<sub>2</sub>O<sub>4</sub> nanocrystallite supercapacitors with tailored microstructures enabled by a novel solution combustion method, *J. Power Sources.* 378 (2018) 90-97. doi:10.1016/j.jpowsour.2017.12.022.
- [122] S. Specchia, G. Ercolino, S. Karimi, C. Italiano, A. Vita, Solution combustion synthesis for preparation of structured catalysts: A mini-review on process intensification for energy applications and pollution control, *Int. J. Self-Propagating High-Temperature Synth.* 26 (2017) 166-186. doi:10.3103/S1061386217030062.
- [123] M.K. Hossain, E. Kecsenovity, A. Varga, M. Molnár, C. Janáky, K. Rajeshwar, Solution Combustion Synthesis of Complex Oxide Semiconductors, *Int. J. Self-Propagating High-Temperature Synth.* 27 (2018) 129-140. doi:10.3103/S1061386218030032.
- [124] T.S. Nguyen, G. Postole, S. Loidant, F. Bosselet, L. Burel, M. Aouine, L. Massin, P. Gélín, F. Morfin, L. Piccolo, Ultrastable iridium-ceria nanopowders synthesized in one step by solution combustion for catalytic hydrogen production, *J. Mater. Chem. A.* 2 (2014) 19822-19832. doi:10.1039/c4ta04820b.

- [125] M.Y. Nassar, E.I. Ali, E.S. Zakaria, Tunable auto-combustion preparation of TiO<sub>2</sub> nanostructures as efficient adsorbents for the removal of an anionic textile dye, *RSC Adv.* 7 (2017) 8034-8050. doi:10.1039/c6ra27924d.
- [126] M.G. Chourashiya, A. Urakawa, Solution combustion synthesis of highly dispersible and dispersed iridium oxide as an anode catalyst in PEM water electrolysis, *J. Mater. Chem. A.* 5 (2017) 4774-4778. doi:10.1039/c6ta11047a.
- [127] X. Zou, X. Yan, G. Li, Y. Tian, M. Zhang, L. Liang, Solution combustion synthesis and enhanced gas sensing properties of porous In<sub>2</sub>O<sub>3</sub>/ZnO heterostructures, *RSC Adv.* 7 (2017) 34482-34487. doi:10.1039/c7ra04852a.
- [128] P. Samoila, C. Cojocar, L. Sacaescu, P.P. Dorneanu, A.A. Domocos, A. Rotaru, Remarkable catalytic properties of rare-earth doped nickel ferrites synthesized by sol-gel auto-combustion with maleic acid as fuel for CWPO of dyes, *Appl. Catal. B Environ.* 202 (2017) 21-32. doi:10.1016/j.apcatb.2016.09.012.
- [129] M. Piumetti, S. Bensaid, T. Andana, N. Russo, R. Pirone, D. Fino, Cerium-copper oxides prepared by solution combustion synthesis for total oxidation reactions: From powder catalysts to structured reactors, *Appl. Catal. B Environ.* 205 (2017) 455-468. doi:10.1016/j.apcatb.2016.12.054.
- [130] G. Ercolino, P. Stelmachowski, G. Grzybek, A. Kotarba, S. Specchia, Optimization of Pd catalysts supported on Co<sub>3</sub>O<sub>4</sub> for low-temperature lean combustion of residual methane, *Appl. Catal. B Environ.* 206 (2017) 712-725. doi:10.1016/j.apcatb.2017.01.055.
- [131] G.F. Samu, Á. Veres, B. Endrodi, E. Varga, K. Rajeshwar, C. Janáky, Bandgap-engineered quaternary M<sub>2</sub>Bi<sub>2-x</sub>Ti<sub>2</sub>O<sub>7</sub> (M: Fe, Mn) semiconductor nanoparticles: Solution combustion synthesis, characterization, and photocatalysis, *Appl. Catal. B Environ.* 208 (2017) 148-160. doi:10.1016/j.apcatb.2017.02.036.
- [132] L. Renuka, K.S. Anantharaju, Y.S. Vidya, H.P. Nagaswarupa, S.C. Prashantha, S.C. Sharma, H. Nagabhushana, G.P. Darshan, A simple combustion method for the synthesis of multi-functional ZrO<sub>2</sub>/CuO nanocomposites: Excellent performance as Sunlight photocatalysts and enhanced latent fingerprint detection, *Appl. Catal. B Environ.* 210 (2017) 97-115. doi:10.1016/j.apcatb.2017.03.055.
- [133] B. Babu, A.N. Kadam, R.V.S.S.N. Ravikumar, C. Byon, Enhanced visible light photocatalytic activity of Cu-doped SnO<sub>2</sub> quantum dots by solution combustion synthesis, *J. Alloys Compd.* 703 (2017) 330-336. doi:10.1016/j.jallcom.2017.01.311.
- [134] A. Ashok, A. Kumar, F. Tarlochan, Preparation of Nanoparticles via Cellulose-Assisted Combustion Synthesis, *Int. J. Self-Propagating High-Temperature Synth.* 27 (2018) 141-153. doi:10.3103/S1061386218030020.
- [135] A.A. Voskanyan, K.Y. Chan, Scalable Synthesis of Three-Dimensional Meso/Macroporous NiO with Uniform Ultra-large Randomly Packed Mesopores and High Catalytic Activity for Soot Oxidation, *ACS Appl. Nano Mater.* 1 (2018) 556-563. doi:10.1021/acsnm.7b00064.
- [136] P. Bera, K.R. Priolkar, A. Gayen, P.R. Sarode, M.S. Hegde, S. Emura, R. Kumashiro, V. Jayaram, G.N. Subbanna, Ionic dispersion of Pt over CeO<sub>2</sub> by the combustion method: Structural investigation by XRD, TEM, XPS, and EXAFS, *Chem. Mater.* 15 (2003) 2049-2060. doi:10.1021/cm0204775.
- [137] M.S. Hegde, G. Madras, K.C. Patil, Noble metal ionic catalysts, *Acc. Chem. Res.* 42 (2009) 704-712. doi:10.1021/ar800209s.
- [138] P. Bera, M.S. Hegde, Noble metal ions in CeO<sub>2</sub> and TiO<sub>2</sub>: Synthesis, structure and catalytic properties, *RSC Adv.* 5 (2015) 94949-94979. doi:10.1039/c5ra16474e.
- [139] T. Baidya, T. Murayama, P. Bera, O. V. Safonova, P. Steiger, N.K. Katiyar, K. Biswas, M. Haruta, Low-Temperature CO Oxidation over Combustion Made Fe- and Cr-Doped Co<sub>3</sub>O<sub>4</sub> Catalysts: Role of Dopant's Nature toward Achieving Superior Catalytic Activity and Stability, *J. Phys. Chem. C.* 121 (2017) 15256-15265. doi:10.1021/acs.jpcc.7b04348.
- [140] D. Mescia, J.C. Caroca, N. Russo, N. Labhsetwar, D. Fino, G. Saracco, V. Specchia, Towards a single brick solution for the abatement of NO<sub>x</sub> and soot from diesel engine exhausts, *Catal. Today.* 137 (2008) 300-305. doi:10.1016/j.cattod.2007.11.010.
- [141] A. Vita, G. Cristiano, C. Italiano, L. Pino, S. Specchia, Syngas production by methane oxy-steam reforming on Me/CeO<sub>2</sub> (Me=Rh, Pt, Ni) catalyst lined on cordierite monoliths, *Appl. Catal. B.* 162 (2015) 551-563. doi:10.1016/j.apcatb.2014.07.028.
- [142] A. Civera, G. Negro, S. Specchia, G. Saracco, V. Specchia, Optimal compositional and structural design of a LaMnO<sub>3</sub>/ZrO<sub>2</sub>/Pd-based catalyst for methane combustion, *Catal. Today.* 100 (2005) 275-281. doi:10.1016/j.cattod.2004.09.062.
- [143] N. Russo, S. Furfori, D. Fino, G. Saracco, V. Specchia, Lanthanum cobaltite catalysts for diesel soot combustion, *Appl. Catal. B.* 83 (2008) 85-95. doi:10.1016/j.apcatb.2008.02.006.
- [144] A. Vlastic, D. Sevic, M.S. Rabasovic, J. Krizan, S. Savic-Sevic, M.D. Rabasovic, M. Mitric, B.P. Marinkovic, M.G. Nikolic, Effects of temperature and pressure on luminescent properties of Sr<sub>2</sub>CeO<sub>4</sub>:Eu<sup>3+</sup>+nanophosphor, *J. Lumin.* 199 (2018) 285-292. doi:10.1016/j.jlumin.2018.03.061.
- [145] M.A. Lephoto, K.G. Tshabalala, S.J. Motloung, G.H. Mhlongo, O.M. Ntwaeaborwa, Photoluminescence studies of green emitting BaB<sub>8</sub>O<sub>13</sub>: Bi<sup>3+</sup>+phosphors prepared by solution combustion method, *J. Lumin.* 200 (2018) 94-102. doi:10.1016/j.jlumin.2018.04.014.
- [146] A.K. Soni, V.K. Rai, M.K. Mahata, Yb<sup>3+</sup> sensitized Na<sub>2</sub>Y<sub>2</sub>B<sub>2</sub>O<sub>7</sub>:Er<sup>3+</sup> phosphors in enhanced frequency upconversion, temperature sensing and field emission display, *Mater. Res. Bull.* 89 (2017) 116-124. doi:10.1016/j.materresbull.2017.01.009.
- [147] V. Kumar, S. Som, V. Kumar, V. Kumar, O.M. Ntwaeaborwa, E. Coetsee, H.C. Swart, Tunable and white emission from ZnO: Tb<sup>3+</sup>+nanophosphors for solid state lighting applications, *Chem. Eng. J.* 255 (2014) 541-552. doi:10.1016/j.cej.2014.06.027.
- [148] M. Dalal, S. Chahar, J. Dalal, R. Devi, D. Kumar, S. Devi, V.B. Taxak, A. Khatkar, M. Kumar, S.P. Khatkar, Energy transfer and photoluminescent analysis of a novel color-tunable Ba<sub>2</sub>Y<sub>1-x</sub>V<sub>3</sub>O<sub>11</sub>:xSm<sup>3+</sup>+nanophosphor for single-phased phosphor-converted white LEDs, *Ceram. Int.* 44 (2018) 10531-10538. doi:10.1016/j.ceramint.2018.03.073.
- [149] K.N. Venkatachalaiah, H. Nagabhushana, G.P. Darshan, R.B. Basavaraj, B.D. Prasad, Novel and highly efficient red luminescent sensor based SiO<sub>2</sub>@Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>, M<sup>+</sup> (M<sup>+</sup> = Li, Na, K) composite core-shell fluorescent markers for latent fingerprint recognition, security ink and solid state lighting applications, *Sensors Actuators, B Chem.* 251 (2017) 310-325. doi:10.1016/j.snb.2017.05.022.
- [150] S. Shi, K. Li, S. Wang, R. Zong, G. Zhang, Structural characterization and enhanced luminescence of Eu-doped 2CeO<sub>2</sub>-0.5La<sub>2</sub>O<sub>3</sub> composite phosphor powders by a facile solution combustion synthesis, *J. Mater. Chem. C.* 5 (2017) 4302-4309. doi:10.1039/c7tc00727b.
- [151] N. Rakov, G.S. Maciel, Near-infrared emission and optical temperature sensing performance of Nd<sup>3+</sup>:SrF<sub>2</sub> crystal powder prepared by combustion synthesis, *J. Appl. Phys.* 121 (2017) 1-7. doi:10.1063/1.4978380.
- [152] L. Zhang, Z. Lu, J. Zhu, H. Yang, P. Han, Y. Chen, Q. Zhang, Citrate sol-gel combustion preparation and photoluminescence properties of YAG:Ce phosphors, *J. Rare Earths.* 30 (2012) 289-296. doi:10.1016/S1002-

- 0721(12)60040-4.
- [153] Z. Qiu, Y. Zhou, M. Lü, A. Zhang, Q. Ma, Combustion synthesis of long-persistent luminescent  $\text{MAl}_2\text{O}_4$ :  $\text{Eu}^{2+}$ ,  $\text{R}^{3+}$  ( $\text{M}=\text{Sr}$ ,  $\text{Ba}$ ,  $\text{Ca}$ ,  $\text{R}=\text{Dy}$ ,  $\text{Nd}$  and  $\text{La}$ ) nanoparticles and luminescence mechanism research, *Acta Mater.* 55 (2007) 2615–2620. doi:10.1016/j.actamat.2006.12.018.
- [154] N. Ta, D. Chen, Combustion synthesis of  $\beta\text{-Ca}_{1.95}\text{P}_2\text{O}_7:0.05\text{Eu}^{2+}$  blue phosphor for near ultraviolet excitation, *J. Alloys Compd.* 484 (2009) 514–518. doi:10.1016/j.jallcom.2009.04.150.
- [155] M.M.A. Sekar, A. Halliyal, Low-Temperature Synthesis, Characterization, and Properties of, *J. Am. Ceram. Soc.* 81 (1998) 380–388.
- [156] L. Singh, U.S. Rai, K.D. Mandal, Dielectric properties of zinc doped nanocrystalline calcium copper titanate synthesized by different approach, *Mater. Res. Bull.* 48 (2013) 2117–2122. doi:10.1016/j.materresbull.2013.02.005.
- [157] L. Singh, I.W. Kim, B.C. Sin, S.K. Woo, S.H. Hyun, K.D. Mandal, Y. Lee, Combustion synthesis of nano-crystalline  $\text{Bi}_2/3\text{Cu}_3\text{Ti}_2.90\text{Fe}_0.10\text{O}_{12}$  using inexpensive  $\text{TiO}_2$  raw material and its dielectric characterization, *Powder Technol.* 280 (2015) 256–265. doi:10.1016/j.powtec.2015.04.025.
- [158] L. Singh, I.W. Kim, B.C. Sin, K.D. Mandal, U.S. Rai, A. Ullah, H. Chung, Y. Lee, Dielectric studies of a nano-crystalline  $\text{CaCu}_2.90\text{Zn}_0.10\text{Ti}_4\text{O}_{12}$  electro-ceramic by one pot glycine assisted synthesis from inexpensive  $\text{TiO}_2$  for energy storage capacitors, *RSC Adv.* 4 (2014) 52770–52784. doi:10.1039/c4ra08915d.
- [159] K. Deshpande, A. Mukasyan, A. Varma, Direct synthesis of iron oxide nanopowders by the combustion approach: Reaction mechanism and properties, *Chem. Mater.* 16 (2004) 4896–4904. doi:10.1021/cm040061m.
- [160] R. Ianoş, A. Taculescu, C. Pacurariu, I. Lazau, Solution Combustion Synthesis and Characterization of Magnetite,  $\text{Fe}_3\text{O}_4$ , Nanopowders, *J. Am. Ceram. Soc.* 95 (2012) 2236–2240. doi:10.1111/j.1551-2916.2012.05159.x.
- [161] T. Lazarova, M. Georgieva, D. Tzankov, D. Voykova, L. Aleksandrov, Z. Cherkezova-Zheleva, D. Kovacheva, Influence of the type of fuel used for the solution combustion synthesis on the structure, morphology and magnetic properties of nanosized  $\text{NiFe}_2\text{O}_4$ , *J. Alloys Compd.* 700 (2017) 272–283. doi:10.1016/j.jallcom.2017.01.055.
- [162] B. Pourgolmohammad, S.M. Masoudpanah, M.R. Aboutalebi, Synthesis of  $\text{CoFe}_2\text{O}_4$  powders with high surface area by solution combustion method: Effect of fuel content and cobalt precursor, *Ceram. Int.* 43 (2017) 3797–3803. doi:10.1016/j.ceramint.2016.12.027.
- [163] A.A. Lopera, E.A. Chavarriaga, B. Zuluaga, S. Marin, G.O. Giraldo, H.A. Estupiñan, V. Zapata, C.P. Garcia, Effect of salt concentration on the electrical and morphological properties of calcium phosphates obtained via microwave-induced combustion synthesis, *Adv. Powder Technol.* 28 (2017) 2787–2795. doi:10.1016/j.apt.2017.08.007.
- [164] D.E. Wagner, J. Lawrence, S.B. Bhaduri, Microwave-assisted solution combustion synthesis of high aspect ratio calcium phosphate nanoparticles, *J. Mater. Res.* 28 (2013) 3119–3129. doi:10.1557/jmr.2013.314.
- [165] D.E. Wagner, K.M. Eisenmann, A.L. Nestor-Kalinoski, S.B. Bhaduri, A microwave-assisted solution combustion synthesis to produce europium-doped calcium phosphate nanowhiskers for bioimaging applications., *Acta Biomater.* 9 (2013) 8422–8432. doi:10.1016/j.actbio.2013.05.033.
- [166] M. Nabyouni, H. Zhou, S.B. Bhaduri, Microwave assisted solution combustion synthesis (MASCS) of europium (Eu) doped chlorapatite nanowhiskers, *Mater. Lett.* 108 (2013) 54–57. doi:10.1016/j.matlet.2013.06.089.
- [167] S. Jalota, A.C. Tas, S.B. Bhaduri, Microwave-assisted synthesis of calcium phosphate nanowhiskers, *J. Mater. Res.* 19 (2004) 1876–1881. doi:10.1557/JMR.2004.0230.
- [168] M.-G. Kim, M.G. Kanatzidis, A. Facchetti, T.J. Marks, Low-temperature fabrication of high-performance metal oxide thin-film electronics via combustion processing, *Nat. Mater.* 10 (2011) 382–388. doi:10.1038/nmat3011.
- [169] B. Wang, X. Yu, P. Guo, W. Huang, L. Zeng, N. Zhou, L. Chi, M.J. Bedzyk, R.P.H. Chang, T.J. Marks, A. Facchetti, Solution-Processed All-Oxide Transparent High-Performance Transistors Fabricated by Spray-Combustion Synthesis, *Adv. Electron. Mater.* (2016) 1500427. doi:10.1002/aelm.201500427.
- [170] X. Yu, J. Smith, N. Zhou, L. Zeng, P. Guo, Y. Xia, A. Alvarez, S. Aghion, H. Lin, J. Yu, R.P.H. Chang, M.J. Bedzyk, R. Ferragut, T.J. Marks, A. Facchetti, Spray-combustion synthesis: Efficient solution route to high-performance oxide transistors, *Proc. Natl. Acad. Sci.* 112 (2015) 3217–3222. doi:10.1073/pnas.1501548112.
- [171] E. Carlos, R. Branquinho, A. Kiazadeh, J. Martins, P. Barquinha, R. Martins, E. Fortunato, Boosting Electrical Performance of High- $\kappa$  Nanomultilayer Dielectrics and Electronic Devices by Combining Solution Combustion Synthesis and UV Irradiation, *ACS Appl. Mater. Interfaces.* 9 (2017) 40428–40437. doi:10.1021/acsami.7b11752.
- [172] J. Wang, T.B. Daunis, L. Cheng, B. Zhang, J. Kim, J.W.P. Hsu, Combustion Synthesis of p-Type Transparent Conducting  $\text{CuCrO}_2+x$  and  $\text{Cu:CrO}_x$  Thin Films at 180 °C, *ACS Appl. Mater. Interfaces.* 10 (2018) 3732–3738. doi:10.1021/acsami.7b13680.
- [173] S.G. Ban, K.T. Kim, B.D. Choi, J.W. Jo, Y.H. Kim, A. Facchetti, M.G. Kim, S.K. Park, Low-Temperature Postfunctionalization of Highly Conductive Oxide Thin-Films toward Solution-Based Large-Scale Electronics, *ACS Appl. Mater. Interfaces.* 9 (2017) 26191–26200. doi:10.1021/acsami.7b07528.
- [174] P. Pujar, R.V. Vardhan, D. Gupta, S. Mandal, A balancing between super transparency and conductivity of solution combustion derived titanium doped indium oxide: Effect of charge carrier density and mobility, *Thin Solid Films.* 660 (2018) 267–275. doi:10.1016/j.tsf.2018.06.031.