

SH-synthesis of ceramic powders in the fusion salts of alkali metal

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The formation of some ceramic powders (BaTiO₃, PZT, BaMgAl₁₀O₁₇, WC) under a self-propagating high-temperature synthesis (SHS) mode in the fusion salts of alkali metals (NaCl, KCl, Na₂WO₄, NaBO₂, etc.) were investigated. The effects of molten salts on the combustion parameters, product morphology and composition were evaluated using a thermocouple technique, transmission and scanning electron microscopy and X-ray diffraction analysis. It was shown that the fusion of alkali metal salts in the combustion wave leads to the formation of unagglomerated powder with a desired shape and size (including nanodimension) and also positively effects the electro-physical properties (dielectric constant, emission intensity) of oxide ceramics. These results are discussed in the context of the features of molten salts.

Key words: fusion salt, ceramic powder, complex oxide, combustion synthesis, transition metal carbide.

Introduction

The performance of ceramic materials depends on their properties. The properties in turn depend on the composition, microstructure, agglomeration degree, shape and size of powder which are controlled by synthesis conditions and method. The preparation of ceramic powder can be carried out in the solid, liquid, or gaseous state by different syntheses methods: solid-state synthesis, ball milling, combustion synthesis, sol-gel method, sonochemistry, laser ablation, microwave plasma, ion sputtering, etc [1-5]. The combustion synthesis method which is famous for self-propagating high-temperature synthesis (SHS) is one of the progressive and modern processes which has allowed one to carry out the synthesis of a large number of ceramic materials [6-10]. The SHS synthetic approach is to bring the solid precursors (such as metal oxides, peroxides, inorganic and organic solid fuel) into close contact by grinding and mixing, and to subsequently burn at room temperature. The diffusion of atoms during the combustion depends on the temperature of the reaction and grain boundary contacts. Usually the combustion reaction at elevated temperature leads to agglomerated solid with large grain size. This is why a significant part of SHS ceramic powders have unsatisfactory physical-chemical characteristics (large size, high aggregation degree, etc.) and remain outside the interest of modern engineering. Many scientific investigations have been performed to obtain optimization of

the above mentioned parameters. However, these studies were directed toward solving individual tasks and have not resulted in an improvement of a situation in SHS on the whole.

The importance of the problem have required the using of a non-standard approaches which take into account the above-mentioned problems. Our recent investigations have shown that grain growth and aggregation of particles can be inhibited by means of fusion salts of alkali metals [11-13]. These compounds can be introduced specially to the green mixture or they must be formed during the combustion. SHS syntheses with fusion salts have many interesting aspects:

- a fusion salt can successfully lower the combustion temperature thus remaining chemically inert to the reaction mixture;
- they can improve the heat - kinetic characteristics of the reaction medium, thus providing a higher level of reaction completion.
- the presence of the melt in the combustion wave can result in the formation of passivated ultra-fine powders, due to the protective shells formed around the particles.

This approach has been tested on several SHS systems and rather interesting results were obtained. In this paper we will attempt to demonstrate the advantages of ceramic powders synthesized under the SHS mode with fusion salts of the alkali metals.

Experiment

The combustion of the reaction mixtures was carried out in a constant pressure reactor under an argon atmosphere of 0.5-2.5 MPa. The initial mixture was

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preliminary compacted into a cylindrical, stainless steel mould with a 2 mm thickness, 30 mm diameter and height of 40 mm. The green density of the pellets was 1.5-2.0 g/cm³. Next, chemical compounds were used as raw materials: tungsten oxide-WO₃ with a particle size of less than 10 µm (98% purity, Korea); sodium azide-NaN₃, sodium chloride-NaCl (Samchun Pure Chemical, Co. LTD, Korea), granulated black carbon (<0.1 µm), sulfur (Aldrich Chemical Company, USA), barium peroxide powder with a particle size of less than 45 µm (95% purity, Aldrich Chemical Co., USA); titanium dioxide with a particle size of 1-2 µm -TiO₂ (98% purity, Hankook Titanium Co., Korea); titanium hydride (prepared by the SHS method); barium nitrate (99% purity, Aldrich Chemical Company, USA), aluminium powder (99.5% purity); magnesium oxide (99.5% prepared by hydrothermal synthesis); aluminium oxide (99% purity, Wako Pure Chemical Industries, Ltd., Korea) were all used in the experiments. The experiments were conducted according to the method described in [11] in detail. During a typical experiment the pellet was placed into the reactor and the reaction was initiated by means of a nickel-chromium wire located at the upper portion of the pellet and heated from power supply.

The maximum combustion temperatures (T_c) were measured utilizing tungsten - rhenium thermocouples (W/Re-5 vs W/Re-20) 100 µm in diameter previously covered with a thin layer of alumina and placed along the pellet a distance of 1cm from each other. The input signals of the thermocouples were transformed by a data logger (DASTC) at the rate of 10 Hz, and were recorded by a computer. The average values of the combustion velocity were as follows: $U_c = l/t$, where U_c is combustion velocity; l - is distance between thermocouples; t - is time interval between signals of thermocouples. The standard errors of measurement for T_c and U_c were 10 and 5% respectively.

The phase composition of the combustion products was determined by an X-ray diffractometer (XRD; Siemens 5000). The morphology of the products was observed using a Scanning Electron Microscope (SEM; JSM 5410) equipped with Energy Dispersive X-ray Spectroscopy (EDS; Oxford ISIS 300). A transmission electron microscope (TEM) was used to examine the grain size of a tungsten carbide nanopowder.

Experimental Results

Synthesis of the complex oxide ceramics

Generally a considerable part of the complex oxides represent a special interest for modern electronic engineering. Among these BaTiO₃, PZT and BaMgAl₁₀O₁₇: Eu⁺² are of special interest. The first two are widely used as material for capacitors and piezoelectric ignitors, the third is used as a photoluminescent material for three-color lamps [14, 15].

– The synthesis of tetragonal BaTiO₃

The BaTiO₃ structure is based on the ideal perovskite structure and has small distortions leading to its interesting ferroelectric properties. Ceramics made from BaTiO₃ have high dielectric constants, which strongly depend on powder characteristics (purity, particle size, degree of agglomeration). Barium titanate powders have been synthesized by a variety of methods including SHS. SH-synthesis was made from a BaO₂-xTiO₂-(1-x)Ti green mixture, the exothermicity of which is regulated by Ti concentration [16, 17]. The basic reaction that takes place can be represented through the following:



Reaction (1) performs in a solid medium and produces BaTiO₃ which has a lower degree of tetragonality and unsatisfactory microstructural characteristics.

To overcome this shortcoming a BaO₂-TiO₂-αC-0.5KCl multi-component mixture (here α is mole-number of carbon) was selected to be an optimum for ultrafine and unagglomerated BaTiO₃ powder synthesis. Here, carbon is the solid fuel and KCl is the as grain growth inhibitor and dispersant. The burning character of this mixture and composition of final products are shown in Fig. 1. Here T_c is the combustion temperature, and U_c is the combustion speed. As one can see the change of combustion parameters has a linear character in the investigated interval of α. At α < 0.15 α total attenuation of the combustion wave take place, because of the low combustion heat. At α < 0.25 the combustion process leads to multiphase reaction product formation: BaTiO₃, Ba₂TiO₄, BaCO₃, KCl. From α ≥ 0.25 the formation of monophasic BaTiO₃ becomes possible. It is noteworthy that monophasic tetragonal BaTiO₃ can be generated at low temperature (800-1000 °C) over several seconds (Fig. 2), whereas conventional synthesis methods require long time heating at 1150-1200°C. It is at once apparent that the formation of the tetragonal structure at such low temperatures can be

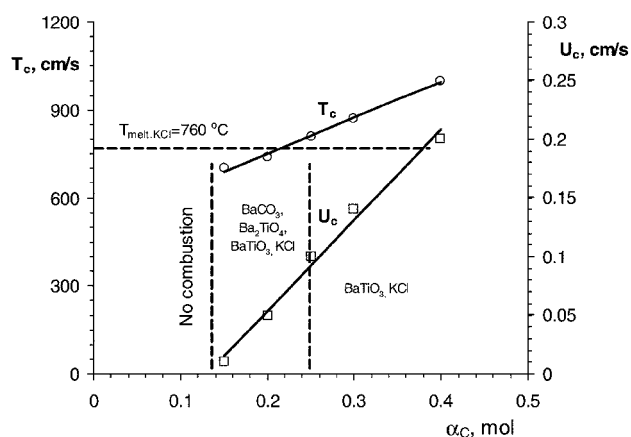


Fig. 1. Dependences T_c and U_c upon α at combustion of BaO₂-TiO₂-αC-0.5KCl mixture.

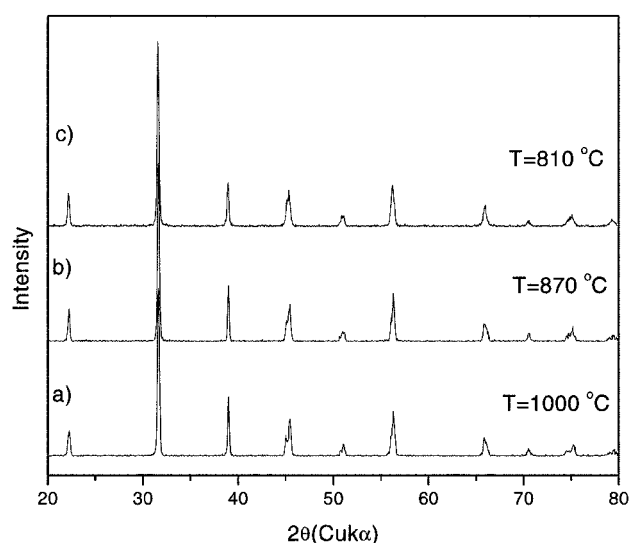


Fig. 2. XRD diffraction patterns of BaTiO₃ powders synthesized from BaO₂-TiO₂-αC-0.5KCl mixture at different α: a) 0.4; b) 0.3; c) 0.25.

explained by the high heating rate of the combustion product (10^3 - 10^5 K/s) and fusion of salts that improve contact between the particles and accordingly diffusion of atoms.

Figure 3 shows scanning electron micrographs of BaTiO₃ powder prepared at different α. As α decreases grain size also decreases. The average size of a grain estimated from the micrographs is: at α=0.4, 1 μm; α=0.3, 0.4 μm; and α=0.25, 0.2 μm. The particles have good crystallinity and are well separated from each other. The same reaction without fusion salts resulted in hard agglomerated particles with a size 1-5 μm. From the given data it is rather obvious that a key feature is the KCl which has a multifunctional role during the synthesis. First, as an inert diluent it does not participate in chemical reaction, warms up and melts due to the reaction heat thus lowers the combustion temperature. Second, the melting of KCl creates a protective media around of BaTiO₃ particles thus preventing them away from merging and growing. This salt protection mechanism was described in our recent papers [11-13] in detail.

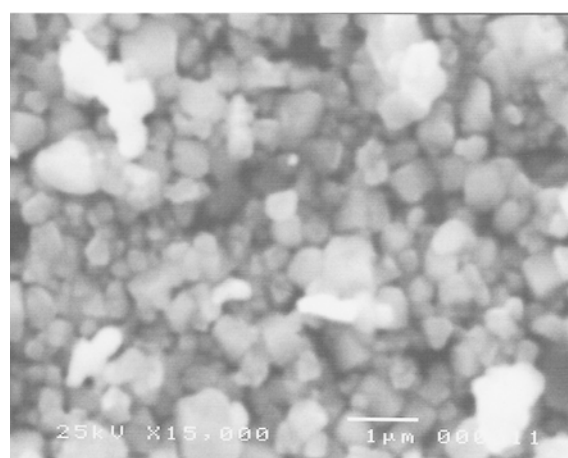
The BaTiO₃ compact prepared from as-prepared powder (at α=0.3) and sintered at 1300 °C shows similar behavior to a commercial one (Sakai-03, Japan) dielectric constant (ε=15600) in the Curie point (Fig. 4). However the room temperature dielectric constant of Sakai-03 twice that of BaTiO₃-SHS. Probably this difference comes from the abnormal grain growth which is more typical for BaTiO₃-SHS. The values of dielectric loss are in the range of 1-1.5%.

– Combustion synthesis and characterization of PZT

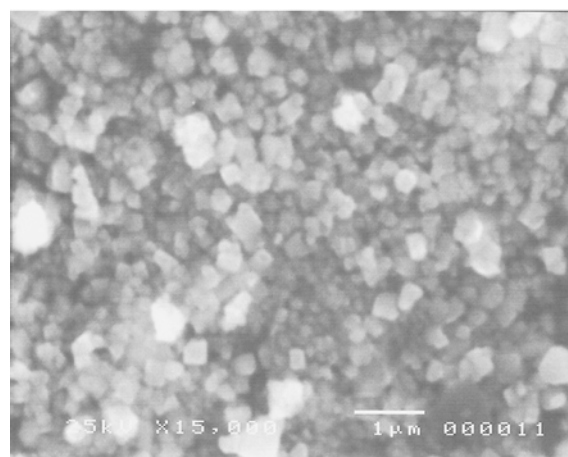
The synthesis of PZT powder of PbTi_{0.48}Zr_{0.52}O₃ composition was done by combustion of a 0.35Pb₃O₄-0.48TiO₂-0.52ZrO₂-0.35 (KClO₃-1.5C) mixture under an argon atmosphere to suppress the evaporation of



(a)



(b)



(c)

Fig. 3. SEM micrographs of BaTiO₃ powders synthesized at different α: (a) 0.4; (b) 0.3; (c) 0.25.

Pb₃O₄. Besides the raw oxides an appropriate amount of an exothermal mixture of KClO₃-1.5C also were used to create favorable thermal conditions for steady combustion. As distinct from the previous case in the synthesis of PZT the formation of an alkali metal salt (KCl) occurs at the expense of the chemical reaction

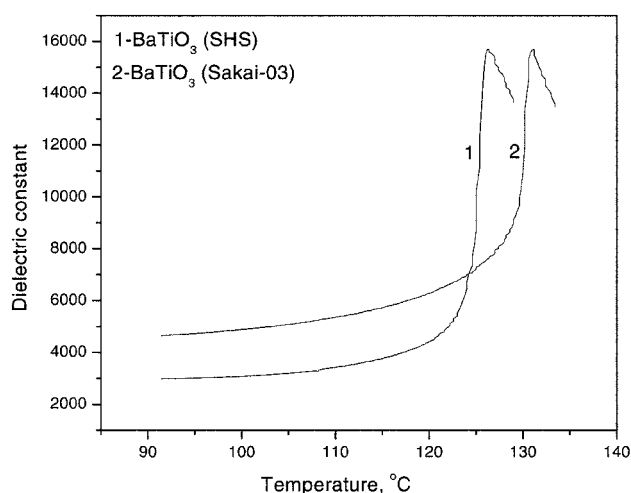
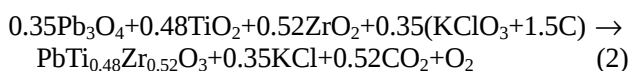


Fig. 4. Dielectric constant of BaTiO₃ as a function of temperature: 1-SHS, 2-Sakai-03.

the scheme of which is given below:



In the course of reaction combustion a wave develops with 0.2-0.3 cm/s speed and within 20-30 seconds the green mixture completely transforms to the final product. With this the combustion temperature increases rapidly to 900°C. A typical XRD pattern of PbTi_{0.48}Zr_{0.52}O₃ is presented in Fig. 5. It can be seen that XRD pattern matches the one of PbTi_{0.48}Zr_{0.52}O₃ indicating that the composition of the powder is close to what would be expected for a stoichiometric Zr/Ti ratio of 52/48. Neither PbTiO₃ nor PbZrO₃ was detected as a separate phase. However noticeable trace of PbO can be seen on Fig. 5a. After enrichment of the final product by acetic acid single phase PZT was found (Fig. 5b). Tetragonal splitting is clearly seen on

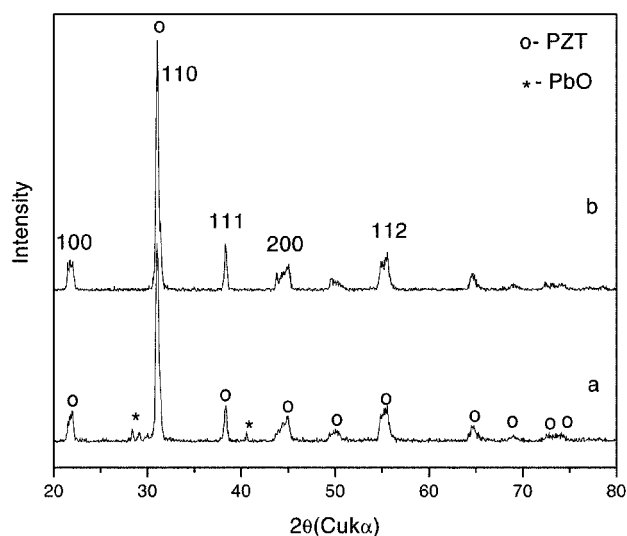
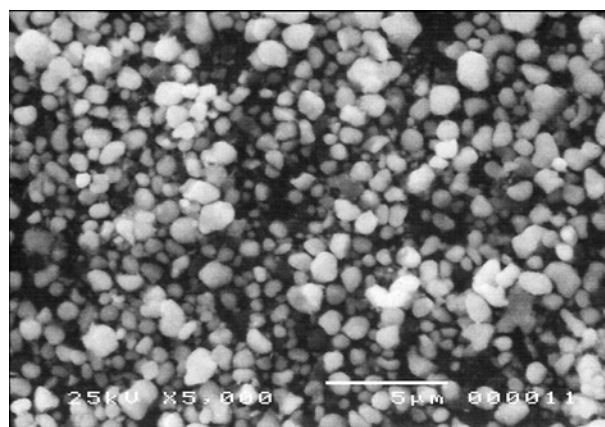
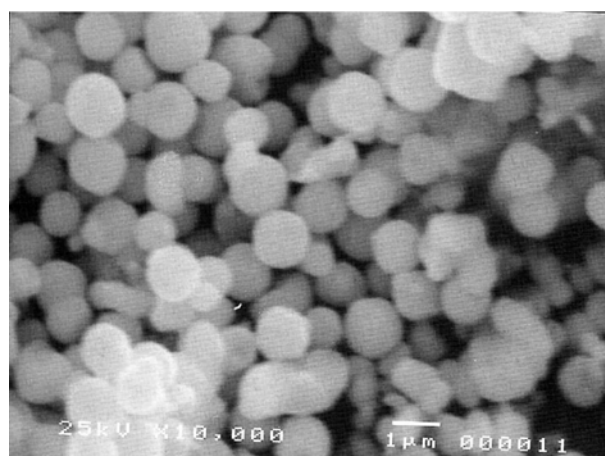


Fig. 5. XRD patterns of as prepared PZT powder: a- after combustion; b- after acid enrichment.



(a)



(b)

Fig. 6. Typical microstructure of PZT powder, prepared from the 0.35 Pb₃O₄-0.48TiO₂-0.52ZrO₂-0.35(KClO₃+1.5C) mixture: a) P = 0.5 MPa; b) P = 5 MPa.

Fig. 3b (100, 200 and 112 peaks).

The particle size and morphology of PZT were analyzed by SEM. It can be easily seen from Fig. 6a that PZT powder prepared by the combustion synthesis method is well dispersed and contains nearly spherical shape particles the size of which is about 0.5-1.0 μm. Moreover the size and morphology of the PZT powder can be developed by varying the combustion parameters. Finally the condition for formation of absolutely spherical particles was achieved by increasing the external pressure (Fig. 6b). This result probably arisen from orientated external pressure gas realise during the synthesis. According to the equation (2) CO₂ and O₂ are the main gaseous components which can be responsible for the formation of PZT spherical particles. However, as mentioned above the protection effect of molten KCl is the main cause of well-dispersed PZT powder formation. Of particular interest when the synthesis of PZT was performed from the mixture which does not generate fusion salts (for example 0.35Pb₃O₄+0.2TiO₂+0.28Ti+0.52ZrO₂) the PZT powder obtained was completely agglomerated and had a size around 5-

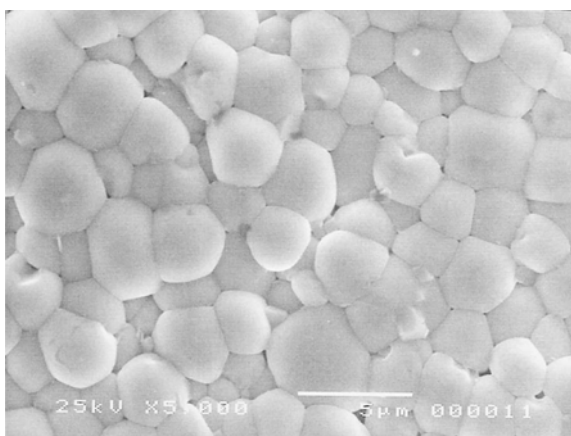


Fig. 7. SEM micrographs of PZT compact sintered at the 1200 °C.

10 µm. It is necessary to note that without the probability of the formation of molten salt, secondary phase formation increases rapidly.

For electrical characteristic measurements $\text{PbTi}_{0.48}\text{Zr}_{0.52}\text{O}_3$ powder was molded to a cylindrical shape, normally at room temperature, by the application of 500 kg/cm² pressure. No binder or lubricant material was used in this operation. The densification behavior of PZT compacts was further studied under isothermal conditions at the different temperatures. Figure 7 shows the grain size and morphology of a compact sintered at 1200 °C for 2 hours. The final grain size in the PZT matrix is about 1-5 µm and a density of 7.6 g/cm³ was recorded at this temperature. The measurement of electrical characteristics (dielectric constant- ϵ , dissipation factor-D) was carried out on PZT sintered pellets with dimensions of 10 mm in diameter and 1 mm in thickness. As in normal ferroelectric materials, the dielectric constant of PZT increases gradually with temperature and attains a maxima ($\epsilon_{\text{max}}=8000$) at the Curie point (370 °C) (Fig. 8). According to the phase diagram, only compositions of PZT close to $\text{PbTi}_{0.48}\text{Zr}_{0.52}\text{O}_3$ can display a Curie temperature around of 360-370 °C. Thus, it can be suggested that the composition of the PZT powder

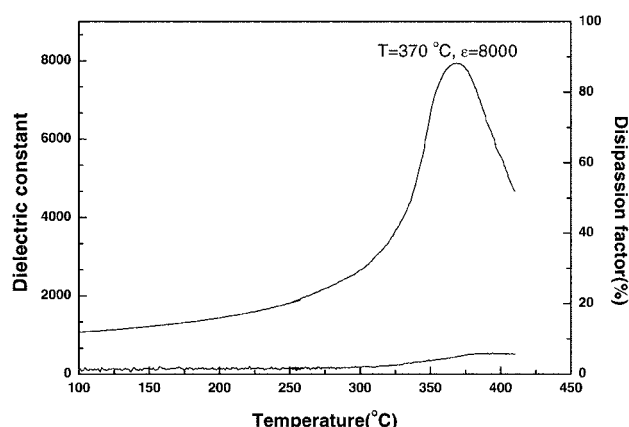


Fig. 8. Dielectric constant (ϵ) and dissipation factor (D) of PZT compact sintered at 1200 °C.

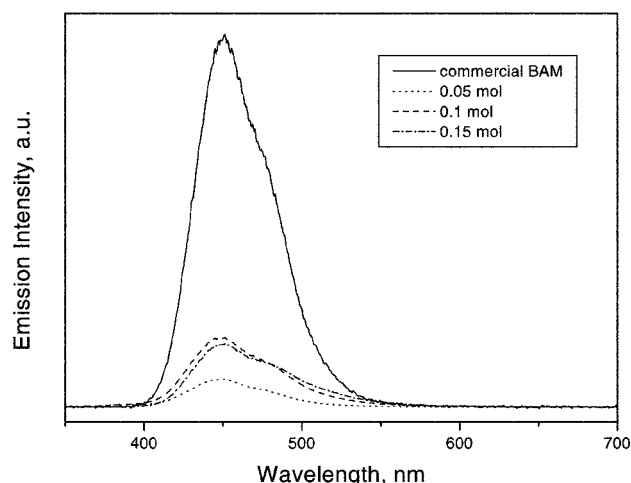
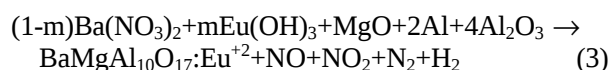


Fig. 9. Emission spectra of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{+2}$ according to $\text{Eu}(\text{OH})_3$ quantity.

prepared by combustion reaction contains both rhombohedral and tetragonal structures which is called the “morphotropic phase boundary” (MPB) [18].

– Preparation of Eu^{+2} doped $\text{BaMgAl}_{10}\text{O}_{17}$

Eu^{+2} doped $\text{BaMgAl}_{10}\text{O}_{17}$ phosphor was prepared by the combustion of a $(1-m)\text{Ba}(\text{NO}_3)_2+m\text{Eu}(\text{OH})_3+\text{MgO}+2\text{Al}+4\text{Al}_2\text{O}_3$ mixture (here m is the mol-number of $\text{Eu}(\text{OH})_3$) according to the reaction scheme given below:



The quantity of $\text{Eu}(\text{OH})_3$ was altered in the interval 0.05-0.15 mol.

All final products when exposed to UV light showed a blue color, indicating phosphorus formation. Emission spectra of Eu^{+2} doped $\text{BaMgAl}_{10}\text{O}_{17}$ are shown in Fig. 9. The emission spectrum excited by 310 nm UV consists of a wide band with the peak at about 450 nm, which corresponds to the 4f-5d transition of the Eu^{+2} ion. For comparison, the intensity of commercial Eu^{+2} doped $\text{BaMgAl}_{10}\text{O}_{17}$ (Kasei Optonix., Japan) is also given in Fig. 9. As one can see, the intensity of the emission spectra of the samples prepared under a combustion mode is several times lower than that the commercial one. Maximum intensity was recorded from the samples containing 0.1 mol $\text{Eu}(\text{OH})_3$ which corresponds to 2 wt.% metallic Eu^{+2} .

Different chemical additives, such as KCl, NaCl, Na_2SiO_3 , SiO_2 and B_2O_3 were used during the combustion reaction to improve the emission properties of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{+2}$. The amount of additives was changed in the interval 1-10 wt.%. It was shown that effect of KCl on the emission characteristics of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{+2}$ among the additives was the highest. As can be seen from Fig. 10 (curve 1) the emission intensity of BAM sample which was synthesized from the mixture containing 5 wt.% KCl corresponds to 90-95% of the commercial one (Fig. 10, curve 2).

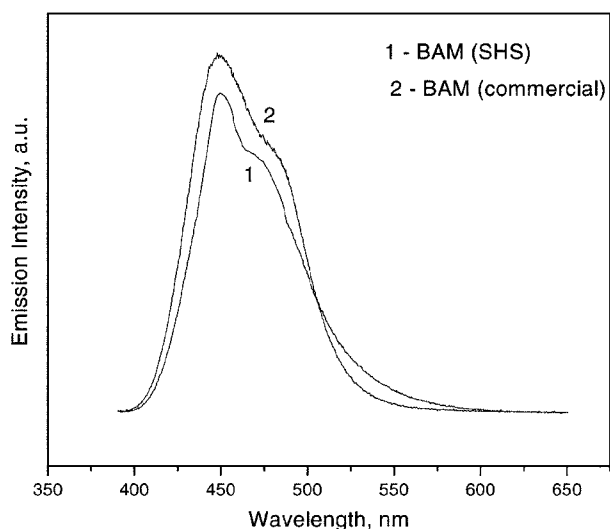


Fig. 10. Emission spectra of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{+2}$: 1-SHS; 2-commercial.



Fig. 11. SEM microstructure of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{+2}$ phosphor.

The morphology of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{+2}$ phosphor obtained in the presence of the fusion salt is displayed in Fig. 11. It can be seen that the particles of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{+2}$ display the form of perfect hexagonal flakes with well-developed faces and a size between 2-5 μm . The microstructural improvements are mainly due to the homogeneous doping of $\text{BaMgAl}_{10}\text{O}_{17}$ by Eu^{+2} obtained in the melting of alkali metal salt in the combustion wave.

– Preparation of nanoscale WC powder

Among the non-oxide ceramic materials tungsten carbide is the more highly valued because of its high hardness and low thermal expansion coefficient. As with other ceramic materials nanostructured tungsten carbide (WC) is also wanted because WC is an important carbide for WC-Co hard metals. Nanostructured WC powder has been fabricated by various methods such as using the spray drying process [19], mechanical milling [20], chemical vapor condensation (CVC) [21, 22] etc. The preparation of WC nanopowder by the SHS method

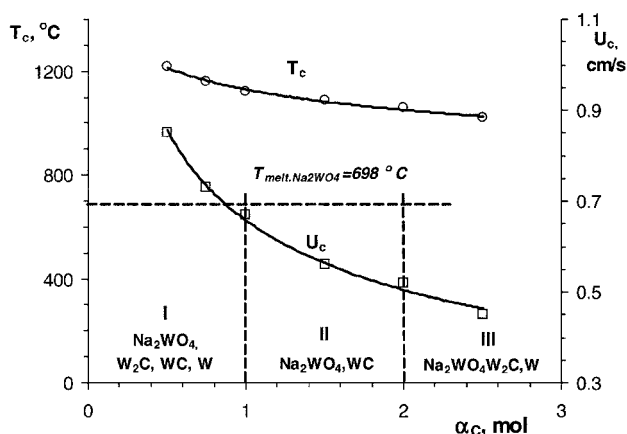


Fig. 12. Effect of the carbon concentration on the combustion parameters (T_c , U_c) and phase composition of the products obtained from the $\text{WO}_3 + 2\text{NaN}_3 + \alpha\text{C}$ mixture.

is very attractive because of the potential opportunity of this method. In this study WC nanopowder was prepared from WO_3 using sodium azide (NaN_3) as the reducing agent. The chemical reaction which is expected to take place, are as follows:



According to this reaction only part of the WO_3 can transforms to WC. More than 50% of the WO_3 forms water soluble sodium tungstate (Na_2WO_4). A priori it can be noted that the synthesis of nanostructured WC became possible due to Na_2WO_4 salt formation.

The combustion characteristics of $\text{WO}_3 + \text{NaN}_3 + \alpha\text{C}$ mixture (here α is mole-number of carbon) are shown in Fig. 12. As one can see the concentration of carbon gradually effects the phase composition. At $\alpha < 1$ the combustion product is multiphase and consists of Na_2WO_4 , WC, W_2C and elemental W. At $1.0 \leq \alpha \leq 2.0$

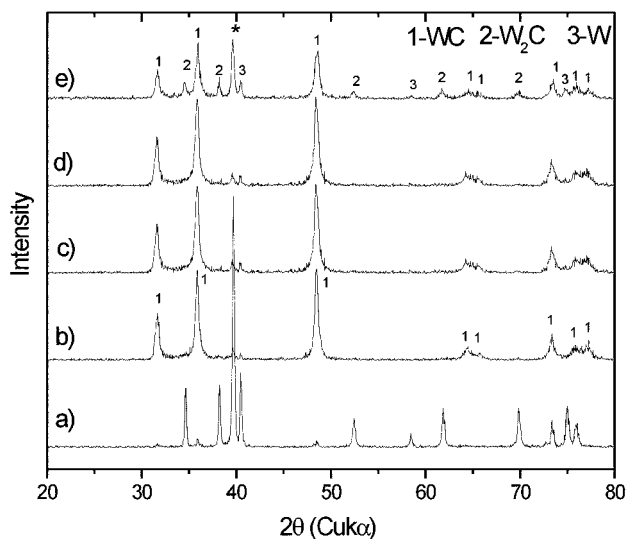


Fig. 13. XRD patterns of products synthesized from the $\text{WO}_3 + 2\text{NaN}_3 + \alpha\text{C}$ mixture at the different α : a) 0.5; b) 1.0; c) 1.5; d) 2.0; e) 2.5.

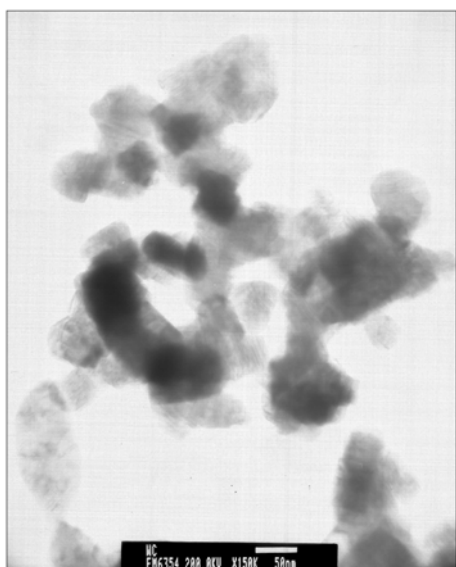


Fig. 14. Typical TEM microstructure of WC powder.

there are two main phases: WC and water soluble Na_2WO_4 (the concentration of W_2C is about 5%). A future increasing of carbon ($\alpha > 2.0$) negatively effects the phase composition and again leads to multiphase product formation. It is noteworthy that monophasic WC was formed at a relatively low combustion temperature (1000–1200 °C) and this can be explained only by the formation and melting of Na_2WO_4 . The appropriate XRD patterns of reaction products after washing are given in Fig. 13. It can be seen that in addition to successful synthesis of single-phase WC powder the XRD pattern yields an estimation of normal particle size from the Scherrer equation. The simple comparison of XRD peaks of WC powders (Fig. 13b) shows that the tungsten carbide powder obtained using NaN_3 has broad peaks, which indicates nanodimensions. The particle size calculated from these peaks corresponds to 50 nm.

The TEM analysis of WC powder shows very fine structure (Fig. 14). As synthesized WC powder has nearly spherical shape and a size less than 100 nm estimated from this micrograph.

Summary and Conclusions

The results of our experiments clearly specify the basic role of molten salts during the combustion reaction, in spite of their inertness to the initial mixture. Henceforth, molten salts may be considered as an ideal reaction medium to perform combustion synthesis of many ceramic compounds. Generally, ionic salts lower the combustion temperature which is due to the expenditure of reaction heat in their warming up and melting. In turn the molten salt can create auspicious conditions for shaped and small size powder formation.

At high temperature molten salts are also capable of

a microstructural effect on the physical properties of the products. This is particularly visible in the examples of BaTiO_3 and $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{+2}$. In particular, the high dielectric constant of BaTiO_3 and increasing of photoluminescent characteristics of $\text{BaMgAl}_{10}\text{O}_{17}$ can be related to certain rearrangements in the crystalline structure due to the molten salt.

The above-stated examples are not exceptional, and only form part of the results obtained by using of molten salts as a reaction medium for SHS synthesis. Even now it can be said that this methodology has a large potential opportunity for practical realization.

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