Fabrication of Bismuth Trioxide Nanoparticles for Gas-Generators Application

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ABSTRACT

Nanoenergetic materials release significant amount of energy at a higher rate and have a potential for various military applications. These systems lead to a fast propagation of a reaction front through the solid reactant mixtures. Most previous research in this area was focused on the impact of the particle size on the amplitude and velocity of the moving temperature front and ignition features. Recently, we proposed Nanoenergetic Gas Generators (NGG) systems that may release a significant amount of gas and can be used as next generation explosives. A nano-particle mixture of Bi_2O_3 and Al generates the highest pressure pulse among all the mixtures studied so far. We have shown that use of highly crystalline Bi_2O_3 nanoparticles increases the amplitude of the gas release. The goal of this study was to develop a highly efficient combustion synthesis process that can produce pure crystalline bismuth trioxide nanoparticles in the range of 20-40 nm with lattice parameter a=7.736(7)Å and c=5.628(9)Å. The use of these synthesized Bi_2O_3 nanoparticles in the reaction $Bi_2O_3+2Al=Al_2O_3+2Bi$ generates a peak pressure of ~10MPa at m=0.5g and V=0.342L.

Keywords: combustion synthesis, bismuth oxide nanoparticles, nanoenergetic materials, gas-generators, high pressure release.

1 INTRODUCTION

Bismuth oxides are widely used for various applications such as electronics and catalytic materials due to their high oxygen-ion conductivity and temperature stability [1, 2]. Recently, bismuth oxide has found extensive application as a reducing component in Nanoenergetic Materials (NM) or Metastable Intermolecular Composites (MIC) [3-7]. NM mainly consist a mixture of Al and metal oxides and currently are of a great interest for military applications as primers, explosives and pyrotechnics composites [8, 9].
These reacting mixtures release energy up to 3 orders of magnitude faster than similar mixtures consisting of micron-size reactants. The main distinguishing features of these materials are their significant enthalpy release and tunable rate of energy discharge, which gives rise to a wide range of reaction rates, energy release and ignition sensitivity. Most previous research in this area focused on studying the impact of the particle size on the corresponding amplitude and velocity of the temperature front and the ignition features of binary reacting systems.

Recently, we have shown that Al/Bi_2O_3 mixture generated the highest pressure pulse among common thermite reactions and potentially can be used as Nanoenergetic Gas Generators having the potential of being used in next generation of weapons and explosives [10, 11]. The goal of this study is to develop a modified solution combustion synthesis of nanostructured highly crystalline bismuth trioxide that can be used for nanoenergetic gas generators application. The solution combustion method [12, 13] produces powders with narrow particle size distribution. Other synthesis techniques, i.e., sol–gel, hydrothermal and colloid emulsion, are more time-consuming due to the existence of complex, steps in those techniques. In addition, all these wet-chemical methods require, in general, calcination at a high temperature to obtain a product with the desired composition and structure. Other advantages of the combustion synthesis are the possibility of creating very pure and crystalline materials and the flexibility of the process with respect to final product quality.

2 EXPERIMENTAL

2.1 Synthesis of Bi_2O_3 Nanoparticles

Bismuth trioxide nanoparticles were prepared by a modified solution (nitrate-glycine) combustion technique. The nitrate-glycine combustion synthesis of multicomponent oxides produced amorphous and crystalline powders with nano particle sizes. High purity bismuth nitrate $Bi(NO_3)_3\ 5H_2O_2$, was used as the oxidizer and organic compound-amino acid (glycine, NH_2CH_2COOH) was used as the fuel. Several types of bismuth trioxide nanoparticles were produced using a modified nitrate-glycine combustion synthesis by the reactions:

$$Bi(NO_3)_3\cdot 5H_2O+\frac{5}{3}\phi[CH_2NH_2CO_2H]+\frac{15}{4}(\phi-1)O_2 \Rightarrow$$
$$\frac{1}{2}Bi_2O_3(s)+\frac{10}{3}\phi CO_2(g)+\frac{25}{6}(\phi+\frac{6}{5})H_2O(g)+\frac{(\frac{5}{3}\phi+3)}{2}N_2(g) \quad (1)$$

where ϕ is the stoichiometric coefficient that shows if the mixture is fuel rich ($\phi>1$) or fuel lean ($\phi<1$). At $\phi=1$

atmospheric oxygen is not needed to completely oxidize the fuel.

To avoid formation of hydrated bismuth nitrate in water we dissolved molten bismuth nitrate (T_m=71 °C) into molten glycine (T_m=172 °C) in a Pyrex dish. The bismuth nitrate and glycine formed a clear homogeneous solution that was vigorously stirred for 1 hr and introduced into a muffle furnace preheated up to 250 °C at the rate 1 °C/s. The mixture boiled, followed by frothing. It then ignited releasing a large amount of gases, and producing white-yellow nano particles. Using less than 10 g of metal nitrate/glycine mixture, the reactions were highly controlled and safe. The local combustion temperature was measured by inserting in the center of sample an S-type (Pt-Rh) thermocouple of about 0.1 mm diameter. The thermocouple readings were recorded and processed using an Omega data acquisition board connected to a PC. An IR high speed camera (Merlin Mid InSb MWI8, Indigo Systems) was also used to determine the maximum combustion temperature and reaction time during the nanoparticles synthesis.

2.2 Nanopowder characterization

The composition and crystal structure of the powder was determined by X-ray diffraction using a Siemens D5000 diffractometer with Cu Kα radiation (λ=1.54056 Å). The scans were taken at room temperature over a wide range of 2θ=(20-80°) at 0.05 degrees intervals. High-Resolution Transmittal electronic microscopy (HRTEM, JEOL JEM-2000 CX2) was used to determine the particles size and electron diffraction pattern of the nanoparticles.

2.3 Testing of Bi_2O_3 nanoparticles for NGG Application

We conducted experiments to determine the impact of the properties of the Bi_2O_3 particles on the peak pressure. The reactions were conducted inside a commercial stainless steel, high pressure, cylindrical reactor, 30.7 mm ID and 115 mm long (Parr, V=0.342L). High-frequency pressure transducers (PCB Piezotronics Inc. Model S101A02) on top of the reactor measured the pressure up to 30 MPa.

A loose reactants mixture (0.1-0.5 g) was loaded into a ceramic boat, placed in the reactor. Due to the high energetic nature of the reactions they were conducted with a small sample, i.e, 0.5 g reactant mixture. The reactants mixture was ignited by an electrically heated coil, inserted into the sample. The pressure transducer and thermocouple readings were recorded and processed by an Omega Data Acquisition Board (Omega Eng Inc.) connected to a PC with a resolution of 1 μs.

3 RESULTS AND DISCUSSION

The ratio between the oxidizer (bismuth nitrate) and fuel (glycine) in the molten solution has a strong impact on the temperature rise, reaction period and particle size. A reaction was not attained when ϕ was less than 0.05. At ϕ=0.05 the reaction was self-sustained and propagated at the maximum temperature ~280 °C. Figure 1 shows the evolution of the product during a combustion synthesis of bismuth trioxide at stoichiometric coefficient ϕ=0.05.

The impact of the ϕ (stoichiometric coefficient) on the maximum reaction temperature during fabrication of bismuth trioxide nanoparticles by combustion synthesis is shown in Figure 2.

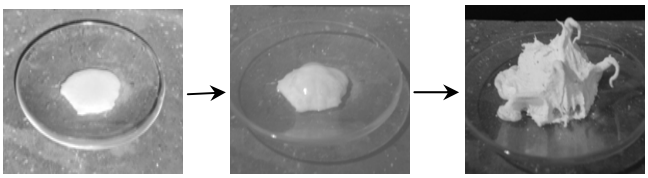

Figure 1: Evolution of the bismuth trioxide nanoparticles nucleation during combustion synthesis.

Increasing the value of ϕ to 0.4 is raised the maximum temperature to 1200 °C. At ϕ> 0.4 the reaction proceeded very fast in an explosive way.

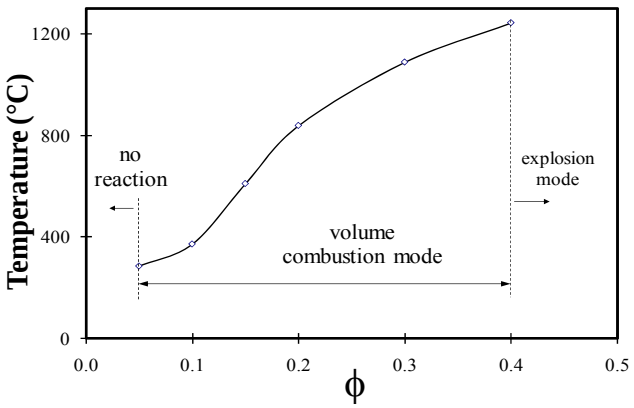

Figure 2: Dependence of the peak temperature on the stoichiometric coefficient ϕ during fabrication of bismuth trioxide nanoparticles by combustion synthesis.

Figure 3 shows a typical temporal temperature at the center of a sample during the synthesis of bismuth oxide for ϕ=0.1. The maximum reaction temperature was 370°C. The process can be divided into different stages with different characteristic temperature gradient. Stage (I) of preheating the precursors is longer (~3.5 min) than the other stages. During the second stage (II) melting of the bismuth nitrate and glycine occurs at ~190°C (relatively flat line on the temporal temperature profile). This stage ended a with rapid temperature rise, which is defined as the ignition temperature ~210 °C. The third stage (III) is a combustion stage in which volume combustion occurs with a temperature rise rate of $\Delta T/\Delta t$~25°C/s. The duration of this stage was 6s. After cooling (stage IV), the products are fine solid bismuth oxide powders.

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Figure 4 shows the X-ray diffraction pattern of as-synthesized bismuth oxide obtained at different ϕ. The powder patterns correspond to bismuth trioxide and did not require further calcination to complete the reactants conversion. Low angle XRD patterns of the powder synthesized with ϕ=0.05 (combustion temperature of 280 °C) contains an "amorphous hump" indicating that some amorphous phase of Bi_2O_3 formed.

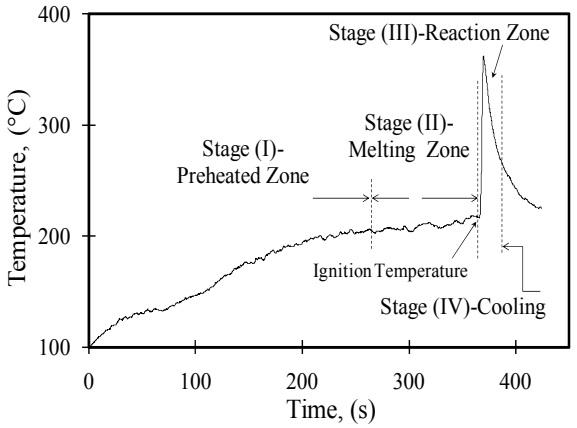

Figure 3: Temporal temperatures during the synthesis of bismuth oxide at stoichiometric coefficient ϕ=0.1.

A pure crystalline Bi_2O_3 with lattice parameter a=7.736(7) Å; c=5.628(9) Å formed from a mixture with ϕ=0.1 at a combustion temperature of 370 °C.

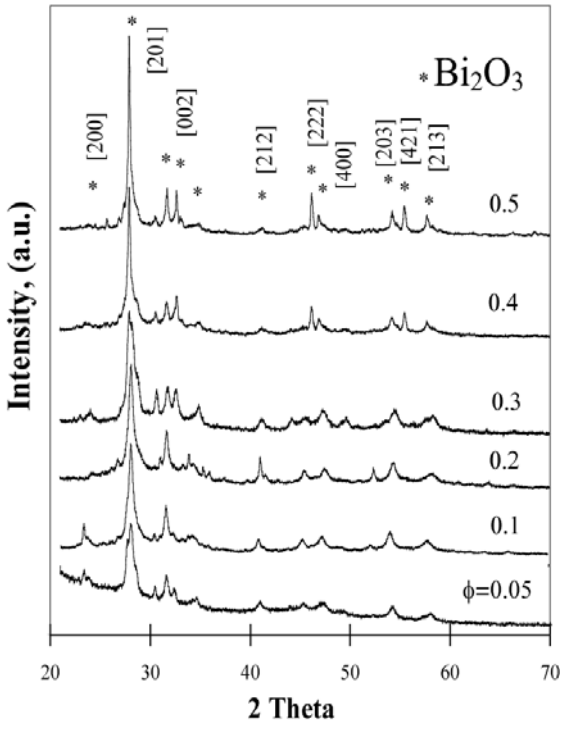

Figure 4: X-ray diffraction patterns of fabricated bismuth oxides obtained at stoichiometric coefficient ϕ=0.05; 0.1; 0.2; 0.3; 0.4; 0.5 and 0.6.

The minimum size of coherent scattering regions (the apparent crystallite size) of the bismuth oxide nanoparticles was estimated by the Scherrer equation $D = 0.9\lambda/(B\cos\theta_B)$. The D is the crystallite diameter, λ=1.54Å the wavelength of the Cu filament in the XRD machine, B the width of a peak at half of its intensity and θ_B the angle of the same peak. The computed crystallite sizes of the bismuth oxides samples obtained at ϕ=0.05; 0.1; 0.2; 0.3; 0.4 and 0.5 were 18, 36.7, 45.6, 54.6, 67.8, and 95.8 nm, respectively. Thus, the crystallite size of the bismuth trioxides was larger at elevated ϕ and consequently at higher combustion temperatures.

TEM analysis was performed for verification of particle size and crystallite structure of bismuth oxides powders at ϕ=0.1. The morphology of these powders is shown in Figure 5. The figure shows that the powders are agglomerates of fine particles. The powder consists of high crystalline particles (with lattice spacing ~ 0.7 nm) mostly in the range 30-40 nm in size, consistent with the particle diameter (D) of 36.7 nm determined from the XRD.

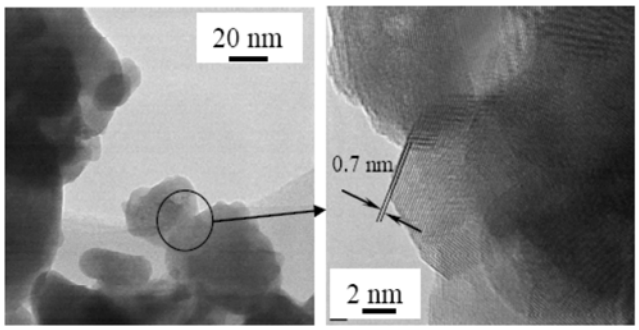

Figure 5: TEM morphology of fabricated bismuth oxides obtained at stoichiometric coefficient ϕ=0.1.

3.1 Performance of as-synthesized bismuth oxides

We tested the performance in NGG systems of as-synthesized bismuth oxides amorphous like synthesized at stoichiometric coefficient ϕ=0.05 and high crystalline at ϕ≥0.1. Stoichiometric mixtures of the bismuth oxide powders were mixed with Al nanoparticles (100 nm) in a closed cylinder containing hexane and nitrogen for 6 hrs by a rotary mixing machine. This environment avoids the partial oxidation of the fine Al particles. The hexane prevents electrostatic charge build up that may lead to ignition and/or explosion of the powders during the mixing and handling.

Experiments confirmed that the pressure peak depended the on bismuth oxide concentration in the mixture. The largest pressure peak of ~10 MPa was obtained for 80 % weight percentage of highly crystalline Bi_2O_3. The dynamic features of the pressure discharge during the combustion of different mixtures of Al and Bi_2O_3 are shown in Figure 6. The data shows that the pressure release for the crystalline

bismuth oxides powder at ϕ=0.1 were higher than for either the amorphous like powder at ϕ=0.05 or the highly crystalline bismuth trioxide at ϕ=0.5. For all these reactions, the pressure in the vessel rose very rapidly to the peak with a duration of ~ 0.05 ms and a $\Delta P/\Delta t$ of up to 650 GPa/s.

Figure 7 shows dependence of the peak pressure during the reaction of Bi_2O_3+2Al by using as-synthesized bismuth trioxide nanoparticles with different values of stoichiometric coefficient (ϕ). The maximum peak pressure of ~10 MPa was generated at ϕ=0.1-0.2.

The pressure release of NGG systems using commercial Bi_2O_3 nanoparticles (100 nm) is about one third of those using the nanopowders we synthesized.

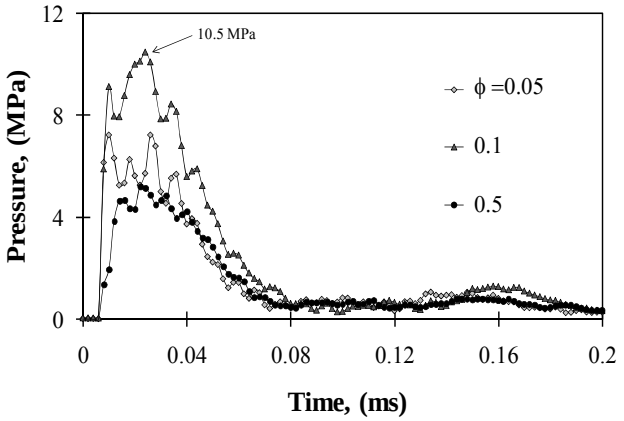

Figure 6: Temporal pressure rise during reaction of Bi_2O_3+2Al at stoichiometric coefficient ϕ=0.05; 0.1; and 0.5, at V=0.342L and m=0.5g.

To estimate the energy release (E) we used the adiabatic ideal gas relation $E=PV/(\gamma-1)$, where γ-is the ratio of specific heat in the system. For complex polyatomic gases γ=1.2 and for diatomic gases γ=1.4. We used in our estimation γ=1.3. P is the pressure, and V is the reactor volume (V=0.342L). Based on the peak pressure the energy released for by Bi_2O_3/Al reaction was calculated to be ~20 MJ/kg.

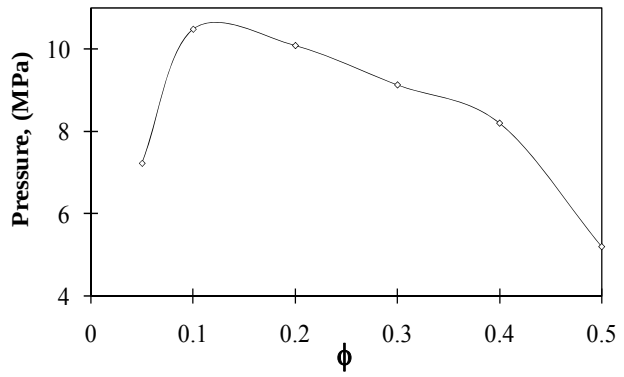

Figure 7: Peak pressure rise during the reaction Bi_2O_3+2Al using as-synthesized bismuth trioxide nanoparticles at different values of stoichiometric coefficient (ϕ).

CONCLUSIONS

A highly efficient, one step process for synthesis of crystalline Bi_2O_3 nanostructured particles has been developed. The maximum synthesis temperature can be varied from 1200 to 360 °C by changing the nitrate/glycine ratio. Highest peak pressure were generated using particles that were synthesized at stoichiometric coefficient ϕ=0.1-0.2.

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