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Synthesis, Characterization and Analysis of Thermal Properties and Burning rate of the Zr/$BaCrO_4$ Mixture

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ABSTRACT

In this work, nanoparticles of the metal fuel Zirconium (Zr) and nanoscale oxidizer $BaCrO_4$ are synthesized considering their unique nanoparticle characteristics like mixing homogeneity and high surface/volume ratio. Using the synthesized fuel and oxidizer, the pyrotechnic mixture of Zr/$BaCrO_4$ was developed under 4 different conditions and analyzed in terms of the thermal behavior and burning rate. In the synthesis stage, the oxidizer nanopowder $BaCrO_4$ was developed through precipitating Barium Nitrate and Chromate Potassium in the vicinity of Dodecyl benzene sulfonate sodium (DBSS) stabilizer. Also, Zr nanopowder was prepared using direct reduction of Zr $(NO_3)_2$ by N_2H_2 and was coated by a 4% Collodion. Then, the pyrotechnic mixture Zr/$BaCrO_4$ was charged and pressed in the constructed combustion chamber. The burning rate of the mixture was captured by the direct footage of the combustion process using digital cameras with 60 frame-per-second capabilities. The fastest burning occurs when both the fuel and the oxidizer are nano-scaled. The thermal behavior of the mixture was studied using the simultaneous thermal analysis (STA) machine within the temperature range of 25 to 1000 °C. Results of the thermal analysis show that the thermal decomposition temperature of the Zr/$BaCrO_4$ mixture in the micron size is higher than in the nano size and the amount of destruction is lower. Increasing the concentration of zirconium in the nano-size from 10 to 50% leads to a decrease in the decomposition temperature from 565 to 437 °C, while the pyrotechnic mixture destruction rate increases from 39% to over 63%.

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1. Introduction

High-energy materials are developed through spontaneous and highly exothermic processes. The energy released by these materials excites electron transition leading to glowing effects like flashovers, flames etc. As a general rule, high-energy materials are classified into three groups namely, explosives, propellants and pyrotechnics. Pyrotechnics are very similar to explosives and propellants only differ in reaction and burning rates. Explosive materials have the highest burning rates (in the order of km/s) while propellants produce gases and have lower burning rates (in m/s order). With burning rates in the order of cm/sec, pyrotechnics produce solid wastes[1]. Pyrotechnics comprise different constituents such as fuel, oxidizer, connector (for increased mechanical strength), fuel accelerator, additives (to reduce pyrotechnic sensitivity) and process enhancers[2]. The characteristics of an excellent pyrotechnic material include high homogeneity, high purity, high burning speed, and low thermal decomposition temperature.Based on their usage as well as their ingredients and impacts, pyrotechnics are divided into numerous subcategories such as smoke-generating, sound-generating, light-generating materials and so on[3-5].The delayed pyrotechnic mixture Zr/$BaCrO_4$ with a moderate burning rate is utilized in two-stage rockets and the strip fuses of thermal batteries[6-8]. Barium Chromate as a bimetal mixture combined with oxygen as the oxidizer, provides the required oxygen to burn Zr. In previous researches, $BaCrO_4$ nanoparticles have been mainly prepared using egg shells or through precipitation. Jinku Liu et al. [9] used an eggshell washed by deionized water as a membrane to separate precipitated $BaCrO_4$ nanoparticles. This resulted in production of Barium Chromate with branched structure of 125 nanometers. In a study done by Lycas et al.[10], $NaNO_3$ and Na_2CrO_4 were used along with oleic acid and olelamin to synthesize $BaCrO_4$ particles. The authors used an autoclave with Teflon coating in a temperature range of 100-140 °C and achieved similar results. As an intermediate metal, Zr is used as a fuel in pyrotechnic materials. It has a hexagonal structure and commercially is produced mainly by the Kroll process. In the work of Kroll et al. [11, 12] flexible Zirconium was produced from zirconium sand as the primary material. Zirconia reduction by liquid calcium and liquid calcium chloride was investigated in [13]. The authors produced Zirconium with 800 ppm oxygen content with the theoretical calcium content of 200 %. Following that, Park et al [14] synthesized porous Zr microspheres using an initial mixture of ZrO_2+2Mg as the reducing agent through combustion techniques. In 2011, the synthesis and characterization of Zr nanoparticles were performed by Michel Eshed et al [15] using the RAPET method on commercial Zirconium oxide with magnesium powder in an autoclave cell at 750°C. In another research[16], the combustion properties of the micro-scale Zr/$BaCrO_4$ were examined. By varying the concentration of Zr, the authors measured the combustion time. Results showed that by increasing the Zr content, the chemical burning time decreased as a result of the easier reaction between the fuel and oxidizer agent. The same authors also examined the micro powder mixture of the delayed Zr/$BaCrO_4$ pyrotechnic in separate research in which the mixture elements were coated by a Viton with formula $C_5H_{3.5}F_{6.5}$. They also determined the impact of the static electrical energy and the concentration of Zr on burning delay. The mean sizes of Zr and $BaCrO_4$ particles were measured as 8.4 and 0.4 µm respectively[17].

As predicted, research results so far indicate that the uniform distribution of particles and their reduced size lead to enhanced burning rates and improved thermal behaviors. On the other hand, the reduced size of particles leads to an accelerated burning process. Therefore, the final product can be developed with a lower amount of ingredients. Currently, pyrotechnics are produced using conventional materials and without any control on the synthesis process of initial elements. Also, the impact of the particle size as a critical property on the burning rate and thermal behavior has not been examined. A technique to overcome this problem can be a controlled production of the highly pure initial mixture of Zr/$BaCrO_4$. Thus, in the current research, Zr nano powder is produced by a novel approach using the direct reduction process applied to Zr $(NO_3)_2$. Both Zr and $BaCrO_4$ are synthesized in micro and nano scales. In order to assess the size impact, four different cases for the fuel and oxidizer mixing are considered. In the first case, both Zr and $BaCrO_4$ are micro-scaled. In the second scenario, Zr is considered as nano-scaled and in the 3rd scenario, only the oxidizer is considered in nano-scale. In the fourth case, both elements are considered as nano-scaled. Further, in order to evaluate the effect of the concentration of Zirconium in the mixture, the Zirconium content in all cases is varied from 10 to 50 %.

2. Materials and Methods

2.1. Raw Materials

Ba $(NO_3)_4$ powder of (98% purity, and particle size of $2-10\ \mu m$), K_2CrO_4 powder (98% purity and particle size of $10\ \mu m$), N_2H_4 reducer (99.7% pure), $Na_3C_6H_5O_7.2H_2O$ powder (99% pure, particle size of $5\ \mu m$) were supplied from Merck, Germany. $CH_3(CH_2)_{11}C_6H_4SO_3Na$ powder (99% pure, particle size $\leq 50\ \mu m$) was supplied by Sigma Aldrich, and Zr $(NO_3)_4$ powder (99% pure, particle size of $2-10\ \mu m$) was supplied by Haihang industrial company in China.

2.2. Experimental approach

2.2.1. Barium Chromate nano particles

$BaCrO_4$ was synthesized as in the previous research [18] by adding the Ba $(NO_3)_4$ solution to the K_2CrO_4 solution in the presence of DBSS with different concentrations at room temperature. The solution was stirred for 20 hours to develop $BaCrO_4$ nano crystals. The product was rinsed by ethanol and dried for 4 hours at 120 °C in a thermal furnace.

2.2.2. Zr Nanoparticles

Zirconium nanoparticles were synthesized using Zirconium Tetranitrate along with hydrazine reducers at the presence of sodium Citrate stabilizers. The experiment conditions are given in **Table 1**.

Table 1

Different experiment parameters for the Zirconium nanoparticle synthesis

Synthesis method	Basic material	Solvent	Stabilizer	Amount of stabilizer	T (°C)	Time (h)	pH
Direct reduction	Zr $(NO_3)_4$ N_2H_4	aqueous	$Na_3C_6H_5O_7.2H_2O$	0.034 M	50	7	**6**

Zr $(NO_3)_4$ is finely solved in water. To produce the Zr $(OH)_4$ solution, the pH value should be precisely controlled according to the pH-Eh diagram of Zirconium, as shown in **Fig. 1.** The pH value after adding Zr $(NO_3)_4$ and stabilizer should reach 5 to create the

mentioned ion. No other additive is required to regulate the pH. Finally, by adding hydrazine reducers, the unstable Zr $(OH)_4$ is reduced into Zr.

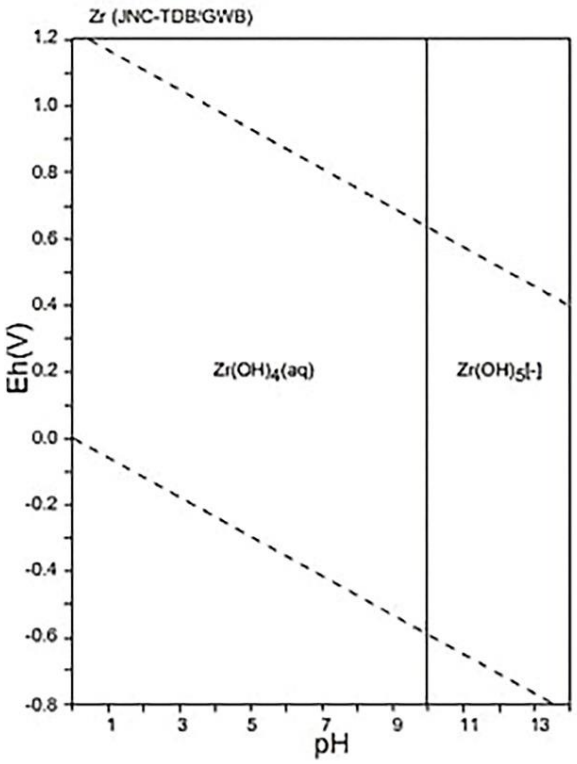


Figure 1. pH-Eh diagram of the Zr $(NO_3)_4$ ion development [19].

The synthesized solution was separated using the centrifugal force. The obtained light brown-colored powder was washed in several steps by distilled water and ethanol so that the stabilizer and other impurities would be removed from the powder. In order to coat the synthesized powder using Collodion, the wet powder was placed in Acetone and the Collodion solution for 20 minutes. The product was finally put in an oven for 3 hours at 50 °C to be completely dried.

The pyrotechnic compound of $Zr/BaCrO_4$ is well-known as a fast and non-gaseous delay compound in which Zirconium metal fuel reacts with $BaCrO_4$ with an initiation energy of 50 to 100 kJ per mole depending on the concentration of Zr. After assembling the initial substances, the powders are sieved to remove agglomerated particles. Then, the fuel and oxidizer are dry-mixed together with given proportions using a set of sieve and shaker for 5 successive iterations. The obtained mixture then goes through the wet mixing process. For this purpose, each 100 gr of the dry mixture is mixed with 15ml of Acetone and 12.ml of the Collodion solution and stirred to get homogenous texture. The mixture is then placed at ambient temperature for 15 minutes to agglomerate and is passed through a 420 μm sieve in order to obtain fine granules. In the end, the obtained granules are dried for two hours inside an oven at the temperature 80 °C. **Figure 2** shows the charging element for the $Zr/BaCrO_4$ delay compound in order to evaluate its burning rate. Given the low amount of the sample material in the experiments, the charging action was done manually. However, use of filler machines in the industrial and semi-industrial charging can improve the speed and accuracy of the test. During the burning rate test, the used chamber was charged by 360 mg of the prepared material. After charging, the upper pressing tool is placed on the chamber and a pressure of 35 bar is applied by a hydraulic press on the delay pyrotechnic powder.

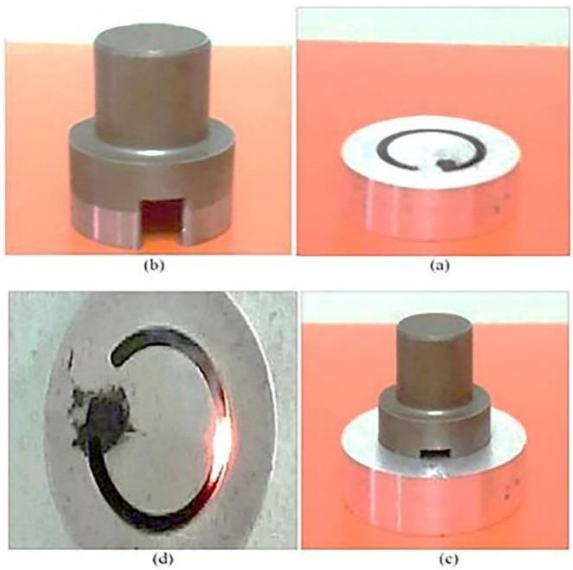


Figure 2. (a) Charging element for Zr/$BaCrO_4$, (b) upper pressing element, (c) placement of pressing element, (d) combusted sample

3. Results and discussion

3.1. Characterization of $BaCrO_4$ nanoparticles

In order to observe the composition and crystal structure of barium chromate nanoparticles, the XRD[1] analysis (Xpert-Philips) was performed on the synthesized sample. The peaks of the synthesized samples, as shown in **Fig. 3**, comply with standard barium chromate card no. 00-078-1401 verifying the development of the $BaCrO_4$ crystal compound with orthorhombic network. The size and shape of these nanoparticles are shown in **Fig. 4.** $BaCrO_4$ nanoparticles have spherical morphology with the average size of 20 nm.

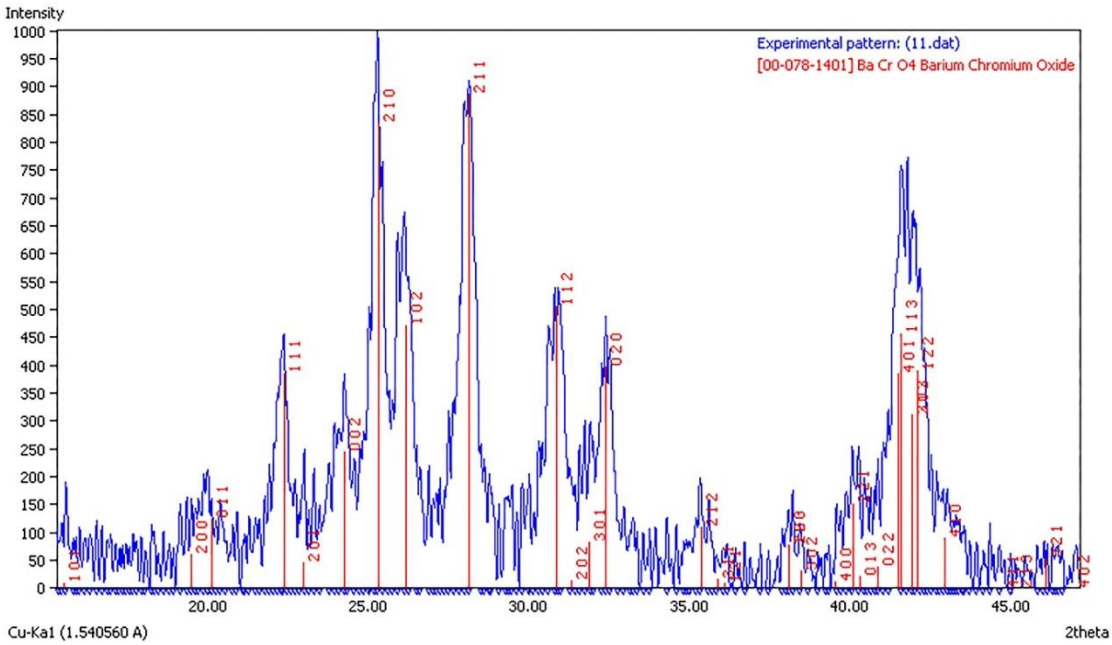
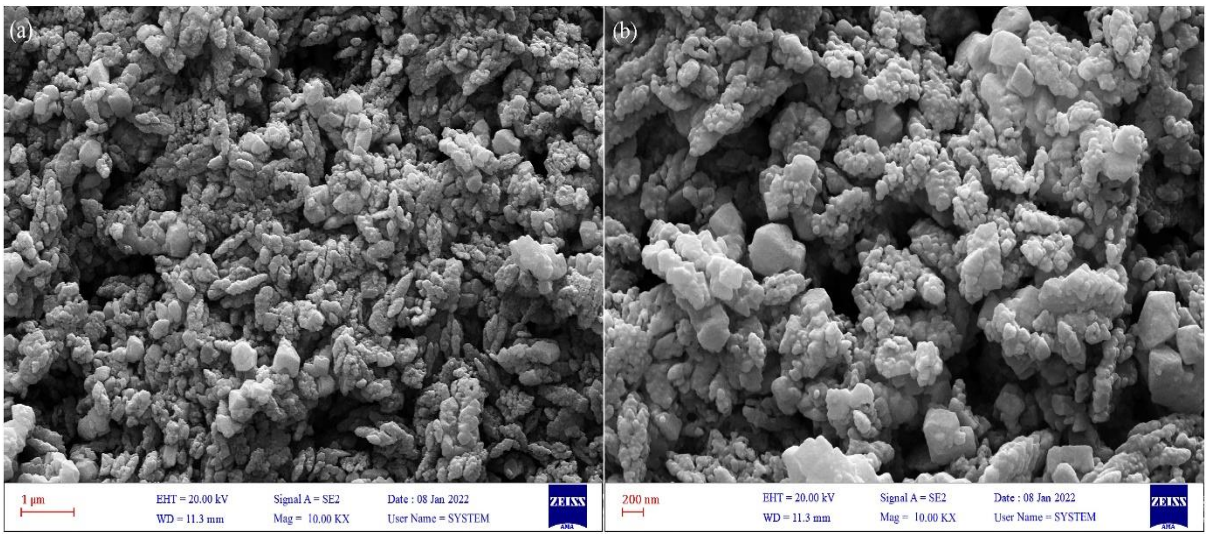


Figure 3. Image of the XRD analysis on synthesized $BaCrO_4$ nano particles.



[1]. X-ray diffraction

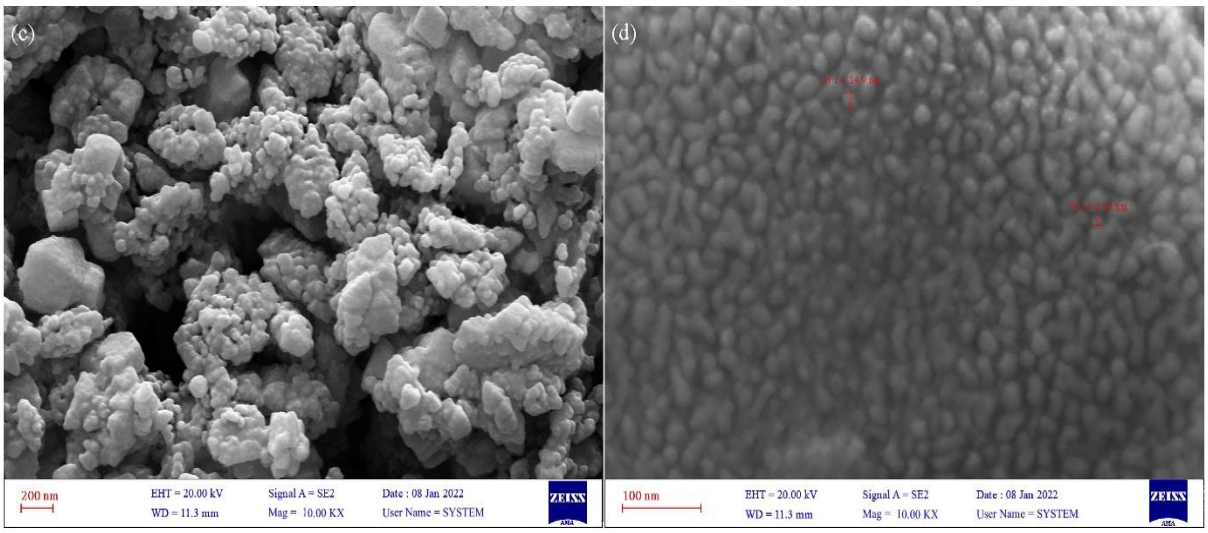
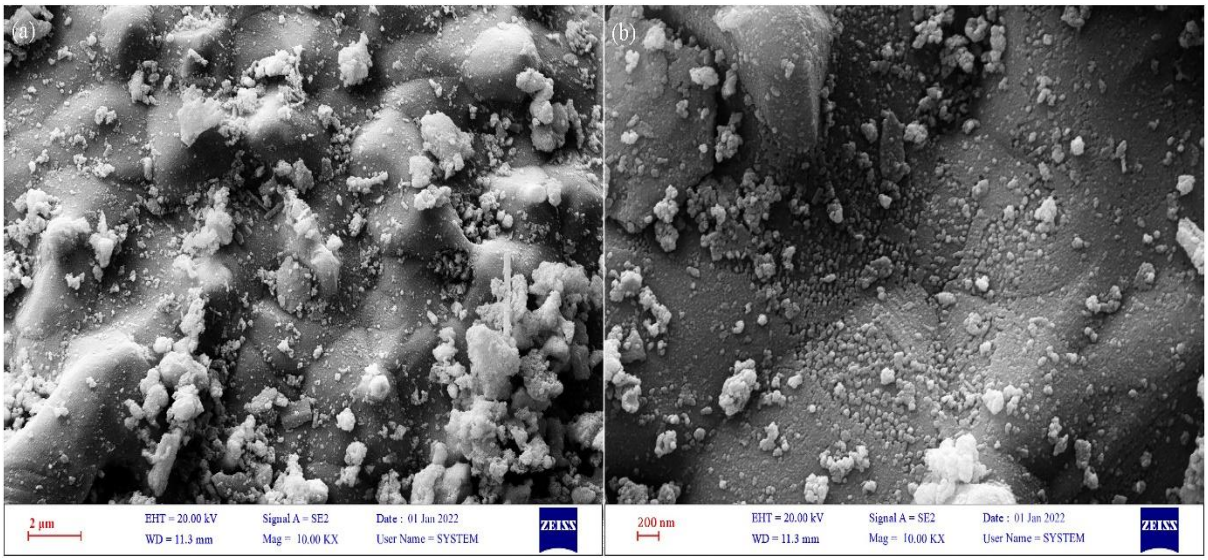


Figure 4. FE-SEM image of synthesized $BaCrO_4$ nanoparticles.

3.2. Characterization of Zirconium nanoparticles

Figure 5 illustrates the FE-SEM (Zeiss Sigma-Philips) image of the chemically synthesized Zirconium powder. The produced Zr particles are uniformly spherical with a size of less than 20 nm. However, most of particles are accumulated and form bigger sizes. In order to verify the development of the Zr crystal structure, the X-ray diffraction (XRD) analysis is performed for the angles between 0 and 115 degrees. Based on **Fig. 6**, the spikes (peaks) conform to those of the standard pattern of Zirconium metal with hexagonal structure, file no. 005-00-0665. Also, the Miller index analysis revealed that the crystal planes were mainly developed in the direction of the peak (101).



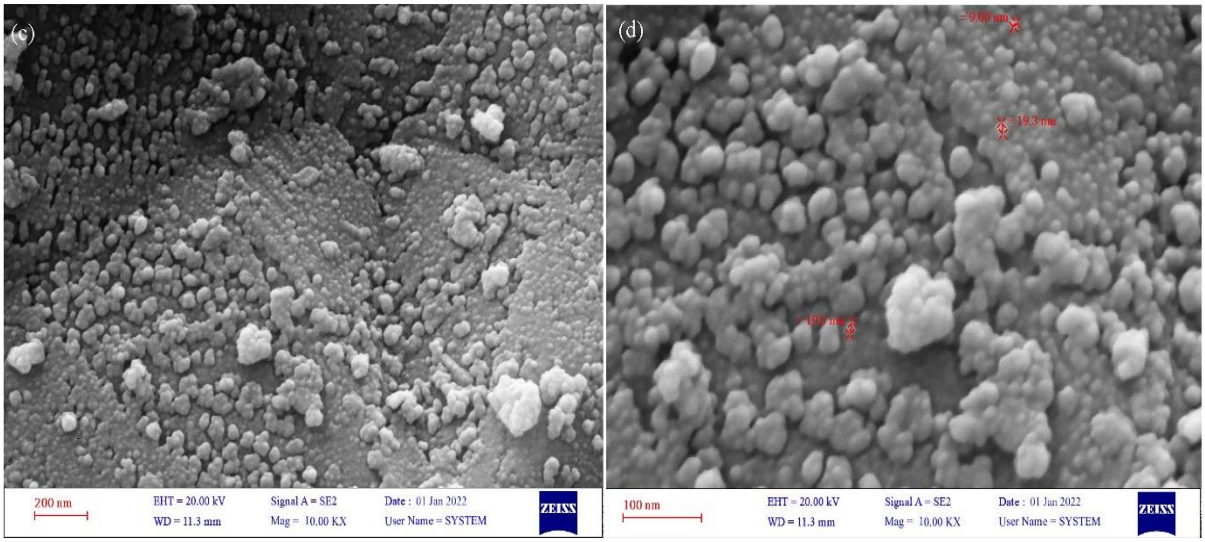


Figure 5. FE-SEM image of synthesized Zr nanoparticles.

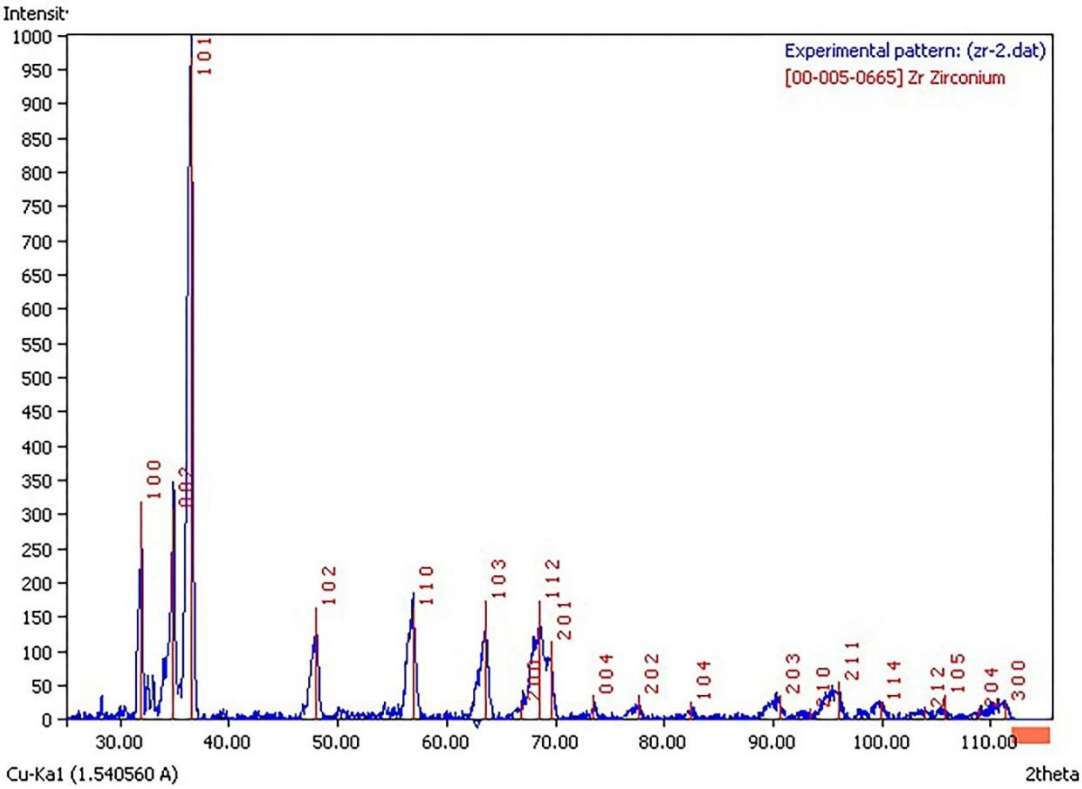


Figure 6. Image of the X-ray diffraction in synthesized Zr nano particles.

3.3. Zr/$BaCrO_4$ mixed burning rates

This study is focused on the effect of fuel and oxidizer particle sizes as well as the fuel-to-oxidizer ratio on the mixed burning rate of Zr/$BaCrO_4$. For all tests, the column length of the mixture charge is taken constant at 60 mm. In this test, first the burning duration of the delay column is measured and then the burning rate is obtained by dividing the delay column length by the burning duration. Also, the effect of press on the burning rate is analyzed. The burning rate of compounds is usually measured using standard methods such as strand burner or other protocols [20]. In this research, the burning rate is in the order of mm-per-second. Therefore, for accurate

measurements, the burning process is captured using a D-810 Nikon Body camera with 60 frame-per-second **recording** capability.

The Zr and $BaCrO_4$ oxidizer mixture was prepared in 5 different weight ratios and in two sizes of nano and micro scales. Four different cases of synthesized mixtures were developed. For the first case, both Zr and $BaCrO_4$ of micro scale, as typical to the industry, were used. In the second case, nano-scale Zr and micron-sized $BaCrO_4$ were used. The third case, contrary to the second case, micro-scale Zr and nano-sized $BaCrO_4$ were utilized and in the final case, both initial substances were in nano scale.

The trends of the burning rate for each of the mentioned cases are shown in **Fig. 7.** For each case, 6 tests were carried out. Three out of all the tests failed due to incomplete burning processes and the flame extinguishment during the flame progress. Two inactions were witnessed in the burning of the micron-sized fuel and oxidizer. Also, one inefficiency was recorded for the case with only the micron-sized fuel. The results indicate that the use of nano-scaled substances eliminates inaction probability though the nano-sized oxidizer has a greater effect in reducing the dispersion.

Figure 8 shows the effect of pressing on the burning rate of Zr/BaCrO4 pyrotechnic mixtures. Five samples of the mixture, prepared using nano-scale materials with a fuel-to-oxidizer ratio of 1:4, were charged into the combustion chamber. The samples were subjected to a pressure of 10-50 bar using a hydraulic press, and their burning speed was measured. According to **Fig. 8**, as pressure increases, density increases and the contact surface decreases, resulting in a decrease in theburning speed, which is clearly visible at a pressure range of 10-20 bar [21]. Given the mentioned fuel-to-oxidizer ratio, the pressure value of 30 to 40 bar had the least fluctuation.

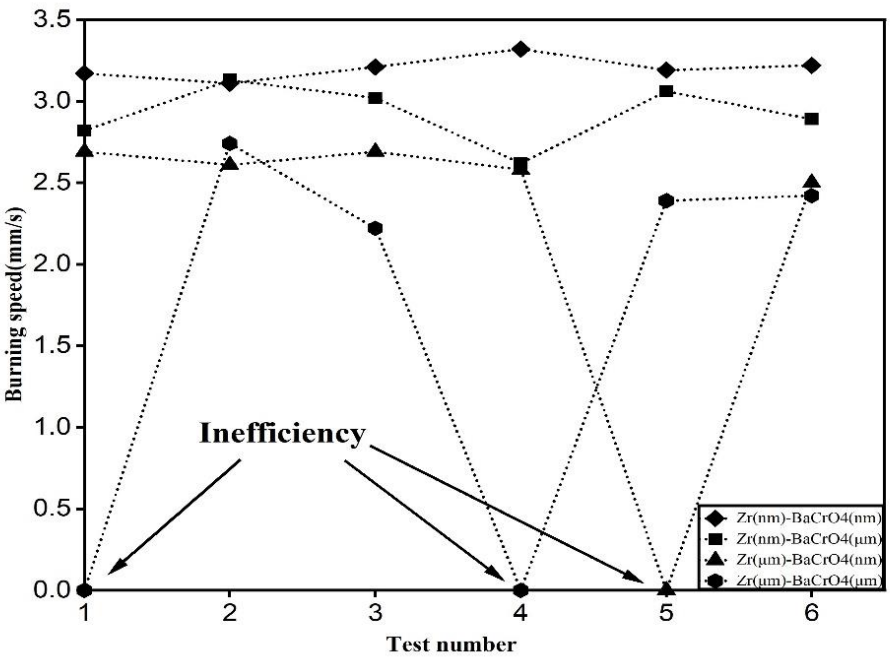


Figure 7. Zr/$BaCrO_4$ burning rates distribution.

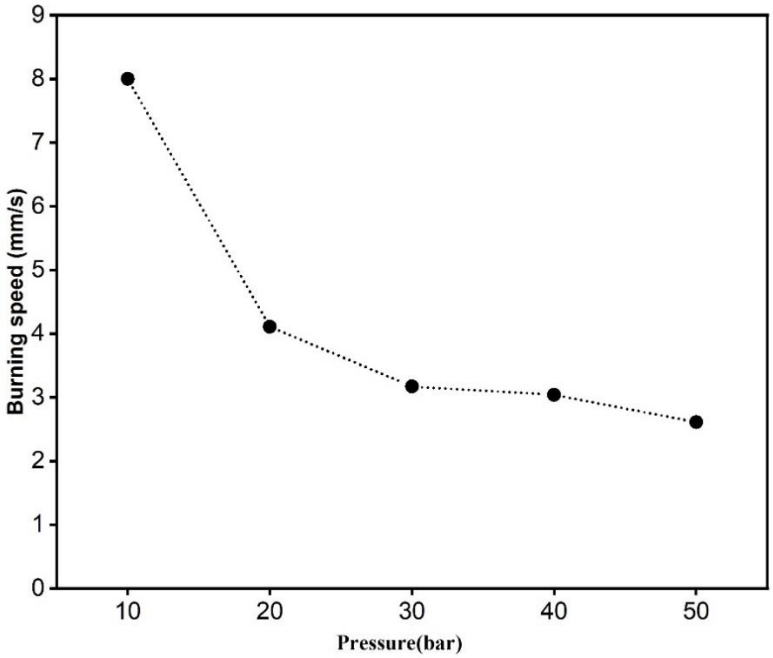


Figure 8. Effect of pressing on burning rates.

3.4. DSC[1] and TGA[2] analysis of the Zr/$BaCrO_4$ mixture

Similar to section 3.3, samples with five different weight ratios and four different cases representing different particle scales for fuel and oxidizer were used for the thermal behavior analysis. DSC is a thermal decomposition method in which the changes in the heat capacity of the Zr/BaCro4 pyrotechnic composition as a function of temperature are continuously measured. The DSC analysis is carried out using data from decomposition with the heating rate of 10 °C/min on an alumina crucible with the temperature range of 25-1000 °C in a STA device model 6000 PerkinElmer. In order to eliminate ambient effects on sample decomposition, the tests were performed under the neutral gas of nitrogen. DSC analysis results for the Zr/$BaCrO_4$ mixture with 20 percent of Zr and 80 percent of $BaCrO_4$ are shown in **Fig. 9**. In the case where both the fuel and oxidizer are nano-sized, the heat generation spike is witnessed at 582.36 °C. This spike corresponds to the main reaction between the fuel and oxidizer. The heat spikes occur at higher temperatures for the higher sizes of fuels and oxidizers such that when both substances are micro-sized, the spike occurs at 635.85 °C.

[1]. Differential Scanning Calorimetry

[2]. Thermal gravimetric analysis

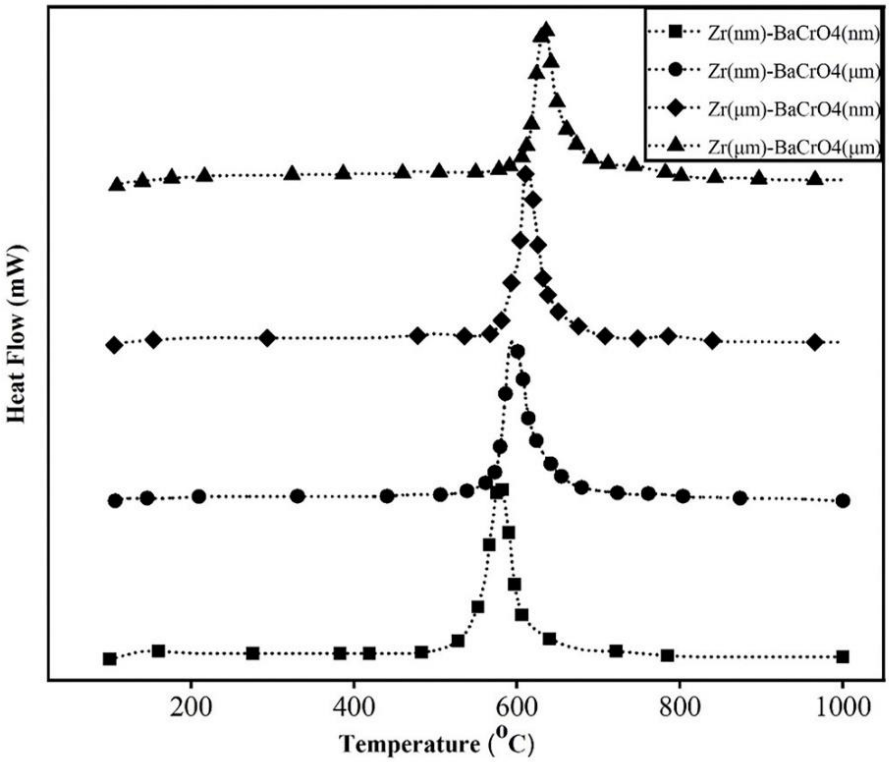


Figure 9. DSC analysis of Zr/$BaCrO_4$.

The TGA[2] analysis has been used to investigate and discover the behavior of Zr/$BaCro_4$ against heat. The method of use is that a small amount of Zr/BaCro4 is placed in the device and the device is gradually heated from 25 to 1000 degrees Celsius. The amount of the substance placed in the device is usually a few milligrams. **Table 2** shows the TGA analysis results. As shown, when both the fuel and oxidizers are nano-sized, the lower reaction (decomposition) temperature is lower and also the amount of degradation is higher than in those of micron-sized. The increased concentration of Zirconium in Zr/BaCrO4 leads to the increased destruction of the Zr/BaCrO4 mixture and the lower reaction temperature.

Table 2
Effect of different concentrations of zirconium on the thermal behavior of Zr/$BaCrO_4$ in nano and micron sizes.

Zr-$BaCrO_4$	Zr(μm)- $BaCrO_4$(μm)			Zr(nm)- $BaCrO_4$(nm)		
	T_{Onset}	T_{End}	% (Destr)	T_{Onset}	T_{End}	% (Destr)
۱۰-۹۰	۶۴۹	۷۵۵	۱۵,۷۶	۵۶۵	۷۱۵	۳۹,۵۵
۸۰-۲۰	۵۹۶	۶۹۲	۱۸,۹۲	۵۲۰	۶۷۰	۴۳,۷۶
۷۰-۳۰	۵۷۶	۶۴۱	۲۲,۱۲	۴۹۵	۶۰۵	۴۷,۲۸
۶۰-۴۰	۵۳۸	۶۰۴	۲۵,۸	۴۸۲	۵۷۰	۵۶,۶۴
۵۰-۵۰	۴۹۶	۵۸۷	۳۲,۶	۴۳۷	۵۴۸	۶۳,۰۵

4. Conclusion

In this manuscript, the burning rate and thermal behavior of Zr/$BaCrO_4$ were studied. To avoid the use of commercial materials and control the initial material synthesis, Zr and $BaCrO_4$ were separately supplied as the fuel and oxidizer elements. Initially Zr nanoparticles were produced by direct reduction of the Zr $(NO_3)_4$ salt and lightly coated (10% coating) by Collodion for stability. XRD analysis results indicate the pure Zr product with no other elements. Also, FE-SEM images verify a size of about 20 nanometers for Zr and $BaCrO_4$. The burning test results indicate that the synthesized mixture of the nano-scale fuel and oxidizer has an enhanced and more stable burning rate of 23% due to the homogeneity and the related surface effects. Also, according to the TGA analysis, increasing the concentration of zirconium leads to an increase in surface effects and a decrease in the decomposition temperature from 496°C in the micron sample to 435°C in the nano sample and an increase in the degradation of the Zr/BaCrO4 mixture by 63%. Also, the DSC analysis shows that the exothermic peak occurs at higher temperatures with the increase in the size of the fuel and oxidant particles.

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