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ORIGINAL ARTICLE

Synthesis of micro porous barium nitrate with improved ignition reliability as a reliable pyrotechnic oxidant

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KEYWORDS

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Abstract Pure barium nitrate is one of the most widely used oxidizing materials in the field of pyrotechnics. The ignition reliability of compositions based on this material is not very high and needs to be improved. In the present work, modified barium nitrate with micro porous structure has been synthesized using three different vesicants to make it more reliable as a pyrotechnic oxidant. Two pyrotechnic compositions were formulated by using pure and modified barium nitrate as oxidant and micro sized aluminum powder was used as a fuel. The ignition temperature of both the compositions was determined using differential thermal analysis. The composition formulated with the modified oxidizer ignited at lower temperatures as compared to the one formulated with pure barium nitrate depicting an improvement in the ignition behavior. SEM results show that the modified barium nitrate has obvious pores of the order of few micrometers. Bulk density of the modified oxidizer decreased due to the development of micro pores. Crystallite size of the barium nitrate also decreased after the modification.

1. Introduction

Pyrotechnic compositions generally comprise of a physical mixture of solid fuel and an oxidizer. The oxidizer plays an important role and provides oxygen for the combustion of the fuel. The pyrotechnic compositions produce special effects when they are suitably initiated and the effects include heat, light sound and smoke. These effects are used in fireworks as well as in certain military applications [4]. Various compounds are being used as oxidizers in pyrotechnic and propellant compositions. These oxidizers include potassium chlorate, potassium per chlorate, barium nitrate, strontium nitrate and ammonium per chlorate to name a few [14,18,8,13,12]. Potassium chlorate had been one of the most widely used oxidizers in the field of pyrotechnics for quite some time due to ease and reliability of ignition and cost economics [3,7,12]. However, the use of potassium chlorate as a pyrotechnic oxidizer has caused many accidents in the past due to which its use has been limited and even banned in many parts of the world due to safety considerations. Barium nitrate on the other hand is relatively much safe oxidizer than potassium chlorate; however

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there are some inherent drawbacks in the ignition behavior of barium nitrate [19]. Pyrotechnic compositions based on this oxidizer are difficult to ignite and they can easily flame out. These two factors seriously affect the reliability of pyrotechnic composition in which this oxidizer is used. The choice of an oxidizer for pyrotechnic compositions depends on different factors including safety, reliability and the oxygen content of the oxidizer [6]. The oxygen balance of this oxidizer is fairly good and suitable for its use as a pyrotechnic oxidant [11]. Although, barium nitrate is very safe as a pyrotechnic oxidizer but its reliability of ignition needs to be improved. There are different methods by which the reliability of ignition of barium nitrate can be increased. One of the methods is to use some thermal decomposition catalysts which may sensitize the oxidant and make it more reliable and easy to ignite [9,2,17]. However, the method employed in the present work is based on the use of inorganic vesicants to modify the performance of oxidizers in terms of its sensitivity and reliability of ignition [10,20]. The vesicants used for the modification of barium nitrate include sodium bicarbonate, ammonium per chlorate and potassium carbonate. Micro porous barium nitrate has been produced by this method which was characterized using scanning electron microscope (SEM) and X-ray diffraction (XRD). The ignition behavior of the vesicant modified barium nitrate in the pyrotechnic mixture formulated with aluminum powder is being reported for the first time in this work. Thermal analysis has been used to monitor the ignition behavior of the pyrotechnic compositions.

2. Experimental

Analytical grade barium nitrate by Scharlau (Barcelona, Spain), potassium carbonate by Merck (Darmstadt, F.R Germany), sodium bi-carbonate by Sigma Aldrich (Seezle, Germany) and defense grade ammonium per chlorate by National Development Complex (Islamabad, Pakistan) have been used to prepare the modified barium nitrate. The modification has been carried out by adding approximately five per cent of the inorganic vesicant in each case to the thermally saturated solution of barium nitrate. The contents of the mixed solution were then evaporated by careful heating and allowed to crystallize. The crystals were then heated in the furnace to decompose the vesicant. The product was ground finely and sieved through 100 mesh sieve. The characterization of the pure and the modified barium nitrate was carried out using different analytical techniques. The XRD instrument by STOE

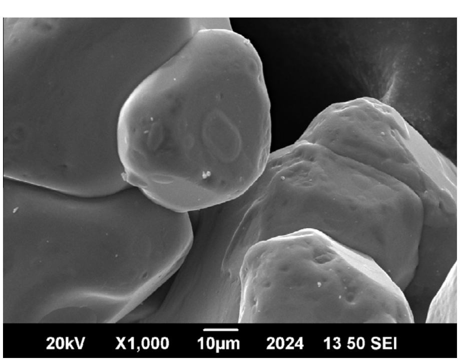

Figure 1a SEM micrographs of pure barium nitrate.

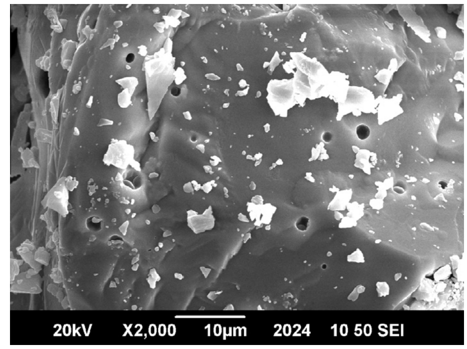

Figure 1b SEM micrographs of barium nitrate modified with potassium carbonate.

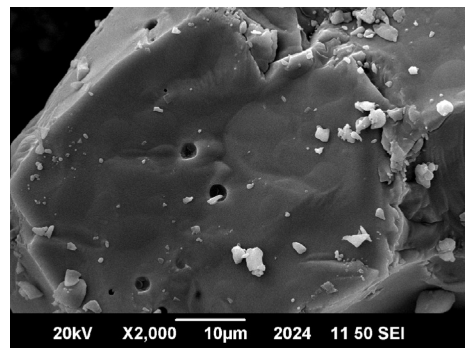

Figure 1c SEM micrographs of barium nitrate modified with sodium bicarbonate.

Germany has been used for analysis and the scan range was from 10° to 70°. Scanning electron microscope JSM-6490 has been used and the micrographs were taken at 500, 1000 and 2000 magnifications. The thermal and ignition behavior of the pyrotechnic compositions made of pure and modified barium nitrate has been carried out using Diamond TG/DTA instrument of Perkin Elmer. The heating rate of 10 °C/min was used for the analysis of pyrotechnic mixtures. The nitrogen gas was used as inert medium and the flow rate was kept close to 100 ml/min. Alumina pans were used to hold the sample and as a reference. The sample mass in both the cases was kept close to 5 mg.

3. Results and discussion

3.1. SEM analysis

The SEM micrographs of the pure and the vesicant modified barium nitrate are shown in Fig. 1a–d. Three different vesicants including potassium carbonate, ammonium per chlorate and sodium bi-carbonate have been used. The morphology and surface feature of modified barium nitrate are seen to be different with different types of vesicants. Pure barium nitrate is solid in shape and surface feature is very smooth and plain as shown in Fig. 1a. On the other hand, modified barium nitrate is porous and fluffy with relatively uneven surface. It can be seen from Fig. 1b–d that barium nitrate modified with different vesicants is porous and the number and size of pores are different in all the cases. Also, surface features of barium

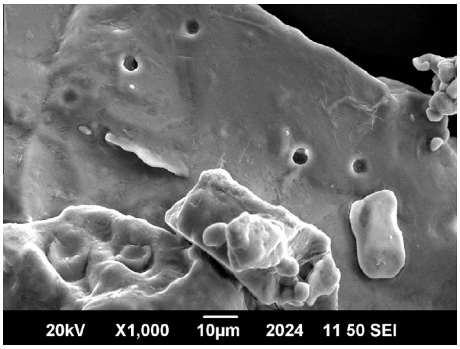

Figure 1d SEM micrographs of barium nitrate modified with ammonium per chlorate.

nitrate modified with different vesicants are different in all the three cases.

Fig. 1b shows that barium nitrate modified with potassium carbonate has the highest number of pores but the pore size is relatively small. The surface feature is relatively rough and uneven. Barium nitrate modified with sodium carbonate also shows pronounced pores and its surface feature has been least effected during the modification and is somewhat smooth. Barium nitrate modified with ammonium per chlorate has relatively less number of pores but the size of the pore is large as compared to other vesicants.

The measurement of the pore size shows that all the pores are of the order of the micrometers and modified barium nitrate is in fact a micro porous structure. The porous material is in general more reactive than the solid material because of its larger exposed area, so the modified barium nitrate is expected to be more reactive. Moreover, physical and chemical properties of the barium nitrate modified with different vesicants are different.

3.2. Bulk density

Bulk density of pure and the modified barium nitrate has been calculated using graduated cylinder method. It can be seen from Table 1 that the bulk density of the barium nitrate decreases after the modification in all the cases, however to a different extent. Various factors can have an influence on the bulk density of material. One of the most important factors is the entrapped air and the interstitial air. The bulk density is found to decrease in all the modified versions of barium nitrate. The development of pores in the modified barium nitrate is one of the main reasons for the decrease in the bulk density. Barium nitrate modified with potassium carbonate has the lowest bulk density and the percentage decrease in this case is close to 12%. The bulk density of barium nitrate modified with ammonium per chlorate and sodium bi carbonate decreased by 4% and 10% respectively.

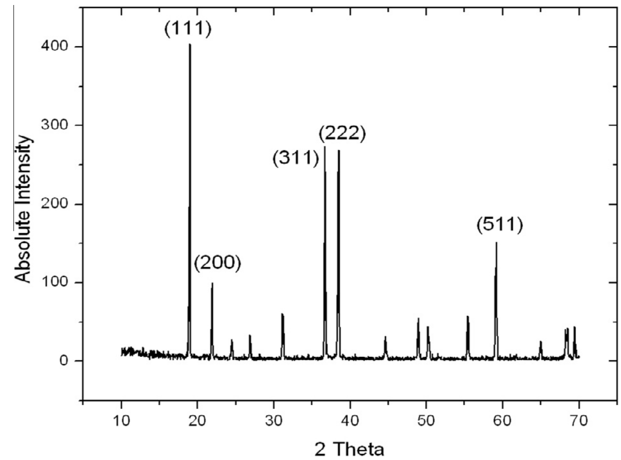

Figure 2 XRD spectra of pure barium nitrate.

3.3. XRD analysis

XRD analysis of pure barium nitrate and the modified samples has been carried out to see different types of structural changes that result due to the modification. It is observed that the crystal structure of the barium nitrate before and after the modification was cubic and it did not change in any of the modified samples. The XRD spectra of pure and the modified barium nitrate have been shown in Figs. 2 and 3 respectively (Miller indices marked). A total of fifteen distinct peaks were observed in the XRD spectra of pure barium nitrate out of which five

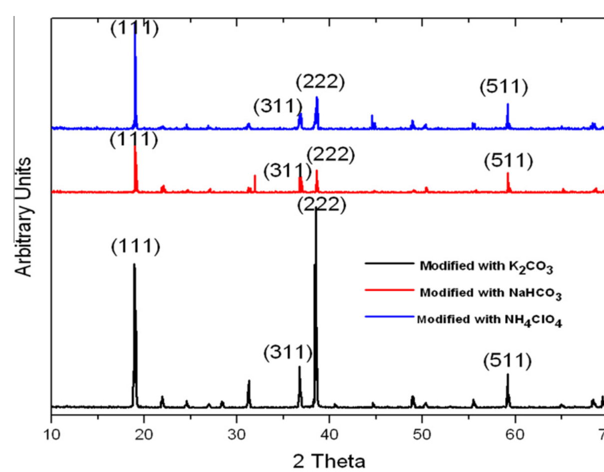

Figure 3 XRD spectra of modified barium nitrate.

Table 1 Bulk density of pure and modified barium nitrate.

Inorganic vesicant	Mass of the sample (g)	Volume of the sample (cm^3)	Bulk density (g/cm^3)	Percent decrease in bulk density
Pure barium nitrate	9.947	5	1.98	Nil
Potassium carbonate	9.561	5	1.74	12.12
Ammonium per chlorate	8.715	5	1.91	3.66
Sodium bi-carbonate	8.951	5	1.79	9.59

Table 2 Lattice parameters of pure and modified barium nitrate.

Composition	Cell parameters			Volume of the cell (10^6 pm^3)	Crystallite size (nm)
	a (nm)	b (nm)	c (nm)		
Pure barium nitrate	81.184	81.184	81.184	535.07	79
Potassium carbonate modified	81.260	81.260	81.260	536.58	53.6
Ammonium per chlorate modified	81.190	81.190	81.190	535.19	73.2
Sodium bi-carbonate modified	81.100	81.100	81.100	533.41	35.3

main diffraction peaks were observed at 2θ position of 18.96°, 21.93°, 36.6°, 38.5° and 59.15°.

It is seen from Fig. 3 that the total number of diffraction peaks decreased in barium nitrate modified with the ammonium per chlorate however, the peak position of the main diffraction peaks did not change much. The intensity of main diffraction peaks decreased which meant that the barium nitrate after modification with ammonium per chlorate became less crystalline. The crystallite size of the modified barium nitrate also decreased significantly (Table 2). In case of barium nitrate modified with the potassium carbonate, the number of peaks and the peak positions did not change much. However, in this case the absolute intensity of the main diffraction peaks increased significantly and the modified barium nitrate became more crystalline as opposed to the one modified with ammonium per chlorate. The crystallite size however, decreased in this case as well. The XRD spectra of barium nitrate modified with sodium bi carbonate showed that the relative intensity of the main diffraction peaks decreased greatly which meant that the modification decreased the crystallinity of the barium nitrate as in case of ammonium per chlorate.

The crystal structure of the modified versions of barium nitrate remained the same in all cases showing that the modification did not affect the purity of barium nitrate. The crystallite size has reduced greatly in all the modified versions of barium nitrate and therefore, it is expected that the modification has increased the reactivity of the barium nitrate. The information regarding different cell parameters as well as the values of crystallite size have been presented in Table 2. The data show that no significant variation has occurred in the value of the different cell parameters due to the modification of barium nitrate. The parameters a, b and c have not changed much and the volume of the cell also remains the same.

The reduction in the crystallite size of the grain exposes more surface area and therefore makes it more reactive. The most significant variation has been seen for barium nitrate modified with sodium bi carbonate where the crystallite size has reduced from 79 nm to 35.3 nm.

3.4. Thermal analysis of binary pyrotechnic mixtures

Thermal analysis is the most widely used technique to investigate the ignition behavior of pyrotechnic mixtures [1,15,16,5]. DTA curve of pyrotechnic mixture made up of micro sized aluminum powder and pure barium nitrate is shown in Fig. 4. The DTA curve of the pyrotechnic mixture made with modified barium nitrate is also presented in Fig. 4. The heat flow curve of the pyrotechnic mixture consisting of aluminum powder and pure barium nitrate shows an endothermic peak near 583 °C close to the melting point of the barium nitrate showing that the barium nitrate in the pyrotechnic mixture melts near this temperature. Just after melting, the pyrotechnic mixture decomposes exothermically near a temperature of 635 °C. This temperature is regarded as the ignition temperature of the pyrotechnic composition based on pure barium nitrate. On the other hand, it is clearly seen from Fig. 4 that pyrotechnic composition formulated with modified barium nitrate shows only a single exothermic peak and ignites at a temperature of 606 °C. Since this temperature is much lower than the ignition temperature of pure barium nitrate based composition therefore, it can be concluded that the ignition behavior of modified barium nitrate has improved.

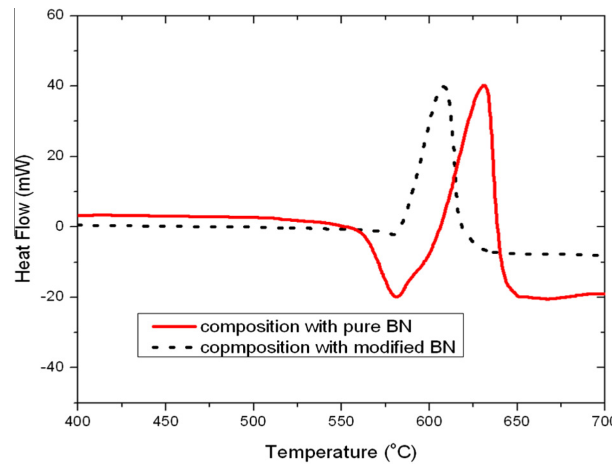

Figure 4 Heat Flow curves of aluminum with pure and modified barium.

4. Conclusions

Barium nitrate has been modified using three different inorganic vesicants to increase its ignition reliability as a safe and reliable pyrotechnic oxidant. The morphology of the barium nitrate has been found to change after the modification. The modified version of barium nitrate has a porous structure with a number of micro sized pores. Barium nitrate modified with potassium carbonate shows the highest number of pores. The exposed area of barium nitrate increases due to the production of pores and increases the reaction activity of the pyrotechnic mixture. The bulk density of barium nitrate has been found to reduce in all the cases. This reduction in the bulk density is attributed to the production of pores which lower the density. The crystal structure of barium nitrate did not change after the modification. The crystallite size of barium nitrate reduces after modification with vesicants showing that its reactivity has increased. The pyrotechnic composition based on aluminum powder and modified barium nitrate ignited at a lower temperature as compared to the one formulated with pure barium nitrate showing that the sensitivity of modified barium nitrate has increased as a pyrotechnic oxidant. The research work encourages the use of modified barium nitrate as a safe and reliable oxidant for the pyrotechnic applications.

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