Energetic Materials

DOI: 10.1002/ange.201007827

Boron Carbide as a Barium-Free Green Light Emitter and Burn-Rate Modifier in Pyrotechnics**

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Although there has been significant interest in the development of environmentally friendly pyrotechnics,[1] the development of cost-effective barium-free green-light-emitting pyrotechnic formulations has remained elusive. Many barium compounds are human health hazards,[2] and recent work by Steinhauser has shown that barium ores as raw materials may contain radioactive radium.[3] Recent papers by Klapötke have shown that copper(II)-based high-nitrogen-content compounds can contribute to green light emission,[1,4] but not all of these compounds combust to yield bright green light in pyrotechnic formulations. Many of these copper salts are difficult and expensive to synthesize, and they can be sensitive to impact, friction, and electrostatic discharge.

The use of amorphous boron and potassium nitrate ($BKNO_3$) is known to have green-light-emitting qualities owing to its formation of metastable boron oxide (BO_2), but these mixtures often burn too rapidly to find practical use in long-burning pyrotechnic applications. The Armament Research, Development, and Engineering Center (ARDEC) recently disclosed a series of formulations in which crystalline boron was used as an inert additive to extend the burn time of amorphous boron-containing green-light-emitting pyrotechnics.[5] However, the use of crystalline boron in pyrotechnics is an expensive solution toward the development of barium-free green-light-emitting pyrotechnics, and a cheaper alternative was desired.

A program was initiated by ARDEC to develop a cost-effective barium-free alternative to a US Army green-light-emitting pyrotechnic item, namely the M125A1 hand-held signal (Table 1). As summarized in Table 1, barium nitrate served as the oxidizer, magnesium 30/50 (mesh size) was the main fuel source, and Laminac 4116/Lupersol was the binder system. The unique role of poly(vinyl chloride) (PVC) was its liberation of chlorine during the combustion process, which reacts with barium to yield metastable barium(I) chloride (BaCl), the species directly responsible for green light emission. Chlorine also reacted with incandescent magnesium oxide to produce the more volatile magnesium chloride species, further aiding in boosting the observed color purity of the pyrotechnic flame.[1,6]

Table 1: M125A1 control formulation.

Components	Wt%
barium nitrate	46
magnesium 30/50	33
poly(vinyl chloride)	16
Laminac 4116/Lupersol	5

To establish a relevant data point toward developing a cost-effective barium-free pyrotechnic, $BKNO_3$ was chosen as the initial fuel/oxidizer system, with Epon 828/Epikure 3140 serving as the binder system (Table 2). Owing to the absence of barium nitrate, PVC would no longer be needed to produce green-light-emitting BaCl. Therefore, PVC was eliminated in all future boron-containing formulations because BO_2 formation would be the species responsible for green light emission. The elimination of PVC from green-light-emitting formulations provided additional benefits, as PVC is known to produce toxic polychlorinated biphenyls (PCBs) during the combustion process.[7]

Table 2: Formulation A.

Components	Wt%
potassium nitrate	83
amorphous boron	10
Epon 828/Epikure 3140	7

The performance of formulation **A** compared to the barium-containing control is summarized in Table 3. Although the dominant wavelength and spectral purity values were acceptable, the $BKNO_3$ formulation, as expected, burned rapidly compared to the control. The luminous intensity of formulation **A** compared to the control was expected as faster burning formulations are known to have larger luminous intensities.[8] In future iterations, the burn time needed to be extended without a significant loss in luminous intensity.

Table 3: Performance of formulation A and the barium-containing control.

Formulation	Burn time [s]	Luminous intensity [cd]	Dominant wave-length [nm]	Spectral purity [%]
control	8.15	1357.40	562.29	61.50
A	2.29	1706.50	559.30	55.00

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[**] We thank the US Army and Picatinny Arsenal, NJ for funding this work.

To extend the burn time of the barium-free formulations, it was decided to explore the use of boron carbide (B_4C) in pyrotechnics (Table 4). Although unreactive at low temperatures, B_4C has been shown to react with oxygen at elevated temperatures.[9] Because of its thermal behavior, it was believed that B_4C would serve as a burn-rate retardant, while forming metastable BO_2 at elevated temperatures to provide green light emission. Although used as an abrasive in ceramics, the use of B_4C in pyrotechnics had never been explored. A series of formulations were prepared in which the percentages of KNO_3 and epoxy binder system remained constant, while the percentage of amorphous boron was reduced at the expense of B_4C.

Table 4: Barium-free formulations.

Components	Wt%
potassium nitrate	83
amorphous boron/boron carbide	10
Epon 828/Epikure 3140	7

The effect of using B_4C in pyrotechnics is detailed in Table 5. Introducing B_4C resulted in prolonged burn times, especially at higher quantities. As is common in pyrotechnics, longer-burning formulations are associated with lower luminous intensities, thus accounting for the lower visible light output spanning from formulations **B**–**G**. Presumably, the lower reactivity of B_4C compared to amorphous boron was responsible for this phenomenon. It is noteworthy that formulations **D**–**G** all exhibited a brilliant green flame, and exceeded the M125A1 barium-containing control in burn time and luminous intensity.

Table 5: Effect of boron carbide in pyrotechnics.

Formulation[a]	Burn time [s]	Luminous intensity [cd]	Dominant wavelength [nm]	Spectral purity [%]
control	8.15	1357.40	562.29	61.50
A	2.29	1706.50	559.30	55.00
B	5.89	2545.30	562.96	53.75
C	6.45	2168.60	562.57	53.54
D	8.67	1914.10	562.42	52.69
E	8.10	1818.50	562.53	53.07
F	8.92	1458.20	561.66	51.99
G	9.69	1403.30	561.85	51.96

[a] Amorphous boron/boron carbide ratio: A 100:0, B 50:50, C 40:60, D 30:70, E 20:80, F 10:90, G 0:100.

Particularly striking in Table 5 is formulation **G**, because the sole boron source in this formulation is B_4C. The performance of formulation **G** confirms that the B_4C/KNO_3 fuel/oxidizer system served as a green light emitter. The ability of B_4C to serve as a colorant and engage in green light emission was never considered previously, though combustion analysis of formulation **G** by the NASA-CEA code[10] did indicate that B_4C/KNO_3/binder would undergo the necessary reactions to produce metastable BO_2. The green-light-emitting nature of formulation **G** the M125 A1 control are provided in Figure 1.

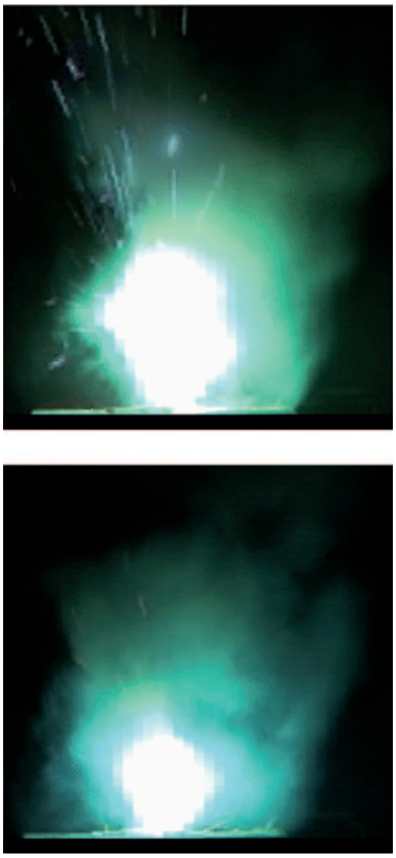

Figure 1. Photographs showing green-light emission of the M125 A1 control (top) and formulation G (bottom).

Despite the abrasive nature of B_4C, formulation **G** was determined to be very insensitive toward a variety of ignition stimuli. Table 6 summarizes the impact, friction, and electrostatic discharge (ESD) sensitivities, and the thermal stability of formulation **G** as determined by TGA analysis. Apart from using B_4C for military illumination applications, the material, when combined with a suitable oxidizer, may serve as an alternative in replacing barium in commercial green-light-emitting fireworks.

Table 6: Behavior of formulation G toward various ignition stimuli.

Formulation	Impact	Friction	ESD[a]	Thermal onset
G	>63.7 J	>360 N	>9.4 J	403.5 °C

[a] ESD = electrostatic discharge.

In summary, the use of B_4C as a replacement for both amorphous boron and barium compounds in green-light-emitting pyrotechnic applications is a cost-effective approach in solving the long-standing problem of developing an environmentally benign green light emitter with acceptable performance.

Experimental Section

Mg 30/50 was purchased from Reade. $Ba(NO_3)_2$, poly(vinyl chloride) (PVC), and KNO_3 (mean particle size of 38.34 μm) were purchased from Hummel Croton. Boron carbide (mean particle size of 7.80 μm) was purchased from Sigma–Aldrich. Amorphous boron (mean particle size 16.82 μm) was purchased from Alfa Aesar. Laminac 4116 was purchased from Ashland Chemical Company. Lupersol was purchased from Norac. Epon 828 and Epikure 3140 were purchased from Hexion Specialty Chemicals.

Twenty-gram formulations of M125A1 were prepared by weighing out the chemicals according to their respective weight percentages in the formulations. After drying the chemicals overnight at 60 °C, they were introduced to a binder system (95 % Laminac 4116/5 % Lupersol or 80 % Epon 828/20 % Epikure 3140), and the mixture was hand-blended for 20 min. After hand-mixing, Laminac 4116/Lupersol-based formulations were dried in the oven overnight at 60 °C, and Epon828/Epikure 140-based formulations were dried in air for 2–3 h at ambient temperature before consolidation.

Formulations were weighed out in two 2 g increments, and with the aid of a tooling die and manual press, were pressed into pellets 1.27 cm in diameter and 2.50 cm high, at a consolidation deadload of 893 kg. After consolidation, the top of each pellet was coated with A1A igniter slurry, and the pellets were then dried in the oven overnight at 60 °C. Between 3.99–4.02 g of energetic material was used per pellet, 5 pellets were tested per formulation, and their average performances were determined and reported. Pellets were ignited using an electric match with an energy of two volts.

Optical emissive properties of these formulations were characterized using both a single-element photopic light detector and a 2048 element optical spectrometer. The light detector used was manufactured by International Light and is composed of a SED 033 silicon detector (33 mm^2 area silicon detector with quartz window) coupled to a photopic filter (Y-filter) and a field-of-view limited hood (H-hood). The current output of the detector was converted into voltage using a DL Instruments 1211 transimpediance amplifier. Voltage output was collected and analyzed from the amplifier using a NI-6115 National Instruments datacard and in-house developed Labview-based data acquisition and analysis software.

Impact sensitivity tests were carried out according to STANAG 4489[11] using a BAM drophammer. Friction sensitivity tests were carried out according to STANAG 4487[12] using the BAM friction tester. Electrostatic discharge sensitivity tests were carried out using an electric spark tester (Albany Ballistic Laboratories). Thermal stability was determined using a Perkin–Elmer DTA/TGA instrument.

Received: December 13, 2010

Keywords: boron carbide · energetic materials · green light emitters · sustainable chemistry

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