Superior reactivity of ferroelectric Bi$_2$WO$_6$/aluminum metastable intermolecular composite

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Abstract

Recent developments in energetic materials have shown that tuning the sensitivity or reactivity by the piezoelectric response to an external electric field can be achieved. Various classes of oxidizers, including ferroelectric materials, have been explored for these applications. Herein, ferroelectric bismuth tungstate (Bi$_2$WO$_6$) was studied as an oxidizer for aluminum-based micrometeorites. The reactivity of Al/Bi$_2$WO$_6$, Al/Bi$_2$O$_3$, Al/WO$_3$, and Al/(Bi$_2$O$_3$ + WO$_3$) composites was measured using combustion cell and high-speed imaging. Al/Bi$_2$WO$_6$ shows a pressurization rate almost ten times higher than that of Al/Bi$_2$O$_3$, with a reaction that initiates in the condensed phase at a relatively low ignition temperature (920 K). The volatility of bismuth leads to vigorous release of gaseous species, which can promote heat convection and reduce reactive sintering leading to a highly reactive system.

1. Introduction

Metastable intermolecular composites (MICs), also known as nanothermites, are a class of energetic materials composed of intimately mixed nanoparticles of a fuel and an oxidizer and offer higher energy density than monomolecular energetic materials (Dreizin, 2009; Khasainov et al., 2017). The choice of nanoscale components is to decrease mass transfer resistances to enhance the energy release rate (Comet et al., 2019; Dlott, 2013; Martirosyan, 2011).

The formulation of MICs is a rather complicated topic as it involves many aspects of the fuel and oxidizer: physical properties, redox thermodynamics, particle morphology and size distribution, etc. Aluminum is the most commonly used fuel in MICs due to its high energy density and availability. A wide range of oxidizers...
have been explored, including common metal oxides (e.g., CuO, Fe_{2}O_{3}, MoO_{3}, WO_{3}, Bi_{2}O_{3}, etc.) (Sanders et al., 2007; Wang et al., 2011; Son et al., 2007). Among this class of MICs, Al/Bi_{2}O_{3} is particularly reactive, featuring a large pressure output and high propagation velocity (Martirosyan et al., 2009). On the other hand, Al/WO_{3} produces minimal gas but has a high flame temperature. Previous research on the Al/Fe_{2}O_{3}/WO_{3} system shows that the higher flame temperature sustained by WO_{3} enhances the gasification of Fe_{2}O_{3} and promotes the reactivity (Jacob et al., 2018). The result suggests that by integrating oxidizers that possess different attributes, enhanced reactivity can be achieved compared with the use of a single oxidizer. Thus, it is reasonable to speculate that complex metal oxides might outperform simple metal oxides in MIC formulations.

Recently, in addition to improving the performance of energetic materials by various strategies (Lyu et al., 2019; He et al., 2020a, 2020b; Wang et al., 2014; Ghildiyal et al., 2021), there are increasing interests in tuning the ignition and combustion behavior of energetic materials via external stimuli. For example, it was demonstrated that nanoaluminum/fluoropolymer reactive composites can be sensitized with the application of a DC voltage, due to the piezoelectric nature of fluoropolymers (Janesheski et al., 2012; Row and Groven, 2018). In order to explore the effect of an external electric field on MICs, the development of an electroactive energetic system is a prerequisite. Herein, a ferroelectric complex bismuth oxide – bismuth tungstate (Bi_{2}WO_{6}) – is studied as an oxidizer in the aluminum-based MIC system. The reactivity was evaluated in a combustion cell and compared with its simple metal oxide counterparts. The reaction mechanism was investigated by a fast-heating method coupled with mass spectrometry, high-speed imaging and color pyrometry, highlighting the interaction of gas generation, flame temperature and energy transfer in the course of the reaction.

2. Experimental section

2.1. Materials

Aluminum nanopowders (nAl, average size ~80 nm, 81% active by mass) were purchased from Novacentrix, bismuth nitrate (Bi(NO_{3})_{3}), sodium tungstate (Na_{2}WO_{4}), bismuth oxide (Bi_{2}O_{3}, 90–210 nm), and tungsten oxide (WO_{3}, <100 nm) were purchase from Sigma Aldrich.

2.2. Synthesis of Bi_{2}WO_{6}

Bi_{2}WO_{6} was synthesized by a hydrothermal method described elsewhere (Zhang and Zhu, 2005). Briefly, Bi(NO_{3})_{3} and Na_{2}WO_{4} (1:2 M ratio) were added into DI water sequentially while stirring. White precipitate was formed, followed by sonication and washing. Then, the precipitate was placed in a Teflon lined stainless steel hydrothermal reactor (50 ml). The reactor was filled with DI water to 80% of its total volume and kept in an oven at 160 °C for 12 h. After the reaction, the product was washed with DI water and air-dried before being collected. For a typical synthesis process, 1.25 mmol Na_{2}WO_{4} (412.31 mg) and 2.5 mmol Bi(NO_{3})_{3} (1212.68 mg) were used, and a final yield of ~50% was achieved.

2.3. Preparation of MIC samples

MICs of nAl and Bi_{2}O_{3}, WO_{3}, equimolar mixture of Bi_{2}O_{3} and WO_{3} (denoted as Bi_{2}O_{3} + WO_{3}), and Bi_{2}WO_{6} powders were prepared according to chemical Eqs. (1)–(4), respectively. The nAl and metal oxide powders (total amount < 50 mg) were dispersed in hexane and sonicated for 30 min to ensure sufficient mixing, followed by the evaporation of the solvent. The as-prepared Al/Bi_{2}WO_{6} MIC was characterized by SEM (Figure S1) to ensure the homogeneous mixing of fuel and oxidizer particles. The as-prepared MIC samples are highly sensitive and reactive, thus should be handled with extreme caution!

2.4. Characterizations

Powder X-Ray Diffraction (XRD) analysis was performed on a Bruker D8 diffractometer using CuKα target (λ = 1.5418 Å). Morphology of samples was characterized by SEM (Hitachi SU-70) and TEM (JEOL JEM 2100 FEG). Energy dispersive X-ray spectrometry was coupled with SEM to map the elemental distribution. Size distribution of samples was obtained from statistical analysis of SEM images using Nano Measurer 1.2. Simultaneous thermogravimetric (TG) and differential scanning calorimetry (DSC) was performed on a Netzsch STA 449 F3 Jupiter thermal analyzer.

2.5. Pressure cell measurements

Pressure cell tests were used to obtain the peak pressure, pressurization rate and burn time of the MICs. 25 mg of the MIC sample was put into a bowl-shaped sample holder inside a constant volume combustion cell (~20 cm³), and was ignited by a Joule-heated nichrome coil in contact with the top of the sample (Xu et al., 2021). The combustion cell is equipped with two ports for simultaneous pressure and optical signal collection. The pressure signal is obtained by a high frequency pressure transducer (PCB Piezoelectronics). The optical emission is focused by a convex lens and transferred to a photomultiplier tube (Hamamatsu) through a fiber optic cable. Both signals are recorded by an oscilloscope.

2.6. Temperature-jump (T-Jump) time-of-flight mass spectrometry (TOFMS)

Rapid heating experiments on Al/Bi_{2}WO_{6}, Al/(Bi_{2}O_{3} + WO_{3}) and Bi_{2}WO_{6} powders were performed using the T-Jump TOFMS to gain insights into the reaction mechanism. The details of the T-Jump TOFMS setup is described elsewhere (Zhou et al., 2009, Zhou et al., 2010). The samples for each of the experiments were prepared by dispersing the respective powders of Al/Bi_{2}WO_{6}, Al/(Bi_{2}O_{3} + WO_{3}) and Bi_{2}WO_{6} in hexane by sonication for 30 min. The dispersion obtained after sonication (~0.1 mg sample) was uniformly coated on the center part of a platinum wire (~1 cm, d = 76 µm, OMEGA Engineering Inc.) soldered to the copper leads of the sample holder, with a micro-pipette. The prepared sample holder was then loaded into the TOFMS chamber (maintained at ~10⁻⁶ Torr) and the platinum wire was resistively heated with a pulsed square wave signal of ~3 ms. The current across the wire was measured by a Teledyne LeCroy CP030A 30 A 50 MHz current probe. The Callender-Van Dusen equations were used to calculate the temperature of the wire from their respective current–voltage relationship, which showed that the temperature of the wire ranges in between 1273 and 1473 K with an approximate heating rate of 10⁵ K/s. The evolved reaction products upon rapid heating of the sample are ionized by a 70 eV electron gun. The positive ions produced are accelerated through the time-of-flight chamber towards the detector by an accelerator plate maintained at ~1500 V. The raw signal from the detector is collected by a Teledyne LeCroy 600 MHz oscilloscope. All of the above events consisting of rapid wire heating, ionization, and collection of spectra by the oscilloscope are synchronized with each other to obtain accurate current, voltage and time resolved spectra.
2.7. T-jump ignition characterization

The ignition behavior of the MIC samples was characterized by T-jump coupled with a high-speed camera (Vision Research Phantom V12.1). The samples were prepared the same way as described above in the T-jump TOFMS section. Then, the sample holder was inserted into a six-way cross followed by evacuation using a vacuum pump. To probe the ignition temperature, the samples were heated by a -3 ms pulse to ~1400 K at a heating rate of ~10^3 K/s. Meanwhile, the ignition process was recorded by the synchronized high-speed camera at 67,000 fps through an observation window. The ignition time was determined visually from optical emission of the samples and the ignition temperature was obtained correspondingly from the temperature profile of the wire.

2.8. Color camera pyrometry

The flame temperature of the MICs was measured in vacuum by a color camera pyrometry method, using the RGB filter in the camera to enable ratio pyrometry. The aforementioned rapid wire ignition of the samples was captured by a Vision Research Phantom Miro M110 color camera. To obtain an optimized result, f/11, frame rate of 140,000 fps, exposure time of 6 μs were selected by trial-and-error. The video was then processed by a custom MATLAB script to give spatiotemporal temperature map of the reaction. Temperature estimation by color ratio pyrometry is based on calibration of the spectral response of the camera and other camera-specific calibration factors to estimate the ratios in different color channels (assuming graybody emission). This method is largely based on the work described by Densmore et al (Densmore et al., 2011). Using Planck’s Law, one can estimate the intensity of light at a given wavelength and temperature for a radiating blackbody. By integrating over the entire light spectrum to which the camera’s CMOS sensor is sensitive and incorporating the Red, Green, and Blue filter transmission from the camera’s Bayer filter, we can get an expected value for Red, Green, and Blue pixels for a given temperature. To simplify this calculation and minimize error, ratios in different channels are taken to remove dependency on image capture parameters and only a calibration factor is used to correct for non-ideal responses in the sensor and camera lens. The estimated values of the different ratios and their corresponding temperature are placed in a lookup table. The video processing algorithm simply computes these ratios at each pixel location in the image and estimates the temperature based on the measured color ratios and those in the lookup table. More details regarding this method can be found in our previous work (Jacob et al., 2018).

3. Results and discussion

3.1. Characterizations of Bi2WO6

Bi2WO6 is the simplest member of the Aurivillius phase family, comprising alternating Bi2O22+ layers and pseudo-perovskite WO4 layers (Figure S2) (Zhang et al., 2011). Aurivillius phases have been studied as lead-free piezoelectric materials and oxide ion conductors (Moure, 2018; Kendall et al., 1996; Saiful Islam et al., 1998). Bi2WO6 used in this study was synthesized via a hydrothermal method (Zhang and Zhu, 2005). As shown in Fig. 1a, XRD of the as-synthesized Bi2WO6 can be indexed to an orthorhombic Bi2WO6 phase without any impurity phase. Because of the particular layered crystal structure, the lateral crystal growth of Bi2WO6 is favored, and results in an anisotropic morphology. SEM (Fig. 1b) and TEM (Fig. 1c) characterizations show square-like Bi2WO6 platelets. The SEM image was further analyzed statistically using Nano Measurer to obtain the size distribution of nanoparticles, as shown in Fig. 1d. The edge length of the platelets ranges from 40 to 240 nm, with an average of 90 nm.

As one of the motivating factors in using Bi2WO6 was to introduce piezoelectric powders into the combusting system, we verified the piezoelectricity of the material on pellets processed by conventional sintering using the parameters described elsewhere (Zeng et al., 2015). The bulk samples were polished and electroded with air-dry silver paint. Poling was performed in a silicone oil bath and poled with DC current at 120 kV/cm at 80 °C with a 5-minute voltage ramp up and 15-minute hold. Piezoelectric properties (d33) were characterized by TF2000 ferroelectric analyzer (aixACCT, Aachen, Germany) coupled with a laser-doppler vibrometer (Polytec OPV-5000, Waldbronn, Germany). While piezoelectric coefficients (d33) were measured for polycrystalline (9.2–14 pC/N after conventional sintering (Zeng et al., 2015; Liao et al., 2016); 15 pC/N after spark plasma sintering (Zeng et al., 2009) and single crystalline (27 pC/N) (Takeda et al., 2010) Bi2WO6, it was either through the use of a quasi-static d33-meter (polycrystalline) or resonance measurements (single crystalline). The converse high field piezoelectric properties have never been reported to our knowledge. One reason for this is the high leakage current and relatively low breakdown of these materials at electric fields close to the poling and measurement fields (Yanovskii and Voronkova, 1986). While we are reporting the piezoelectric behavior here, it should be noted that many samples experienced electric breakdown around 130 kV/cm during the measurements.

The flame temperature of the MICs was measured in vacuum by a color camera pyrometry method, using the RGB filter in the camera to enable ratio pyrometry. The aforementioned rapid wire ignition of the samples was captured by a Vision Research Phantom Miro M110 color camera. To obtain an optimized result, f/11, frame rate of 140,000 fps, exposure time of 6 μs were selected by trial-and-error. The video was then processed by a custom MATLAB script to give spatiotemporal temperature map of the reaction. Temperature estimation by color ratio pyrometry is based on calibration of the spectral response of the camera and other camera-specific calibration factors to estimate the ratios in different color channels (assuming graybody emission). This method is largely based on the work described by Densmore et al (Densmore et al., 2011). Using Planck’s Law, one can estimate the intensity of light at a given wavelength and temperature for a radiating blackbody. By integrating over the entire light spectrum to which the camera’s CMOS sensor is sensitive and incorporating the Red, Green, and Blue filter transmission from the camera’s Bayer filter, we can get an expected value for Red, Green, and Blue pixels for a given temperature. To simplify this calculation and minimize error, ratios in different channels are taken to remove dependency on image capture parameters and only a calibration factor is used to correct for non-ideal responses in the sensor and camera lens. The estimated values of the different ratios and their corresponding temperature are placed in a lookup table. The video processing algorithm simply computes these ratios at each pixel location in the image and estimates the temperature based on the measured color ratios and those in the lookup table. More details regarding this method can be found in our previous work (Jacob et al., 2018).

3.2. Reactivity of Al/Bi2WO6 composite

The reactivity of the MICs was tested in a constant volume combustion cell (Sullivan and Zachariah, 2010). In a typical measurement, the composite is ignited in the combustion cell and the pressure and optical signals are recorded simultaneously. The pressure signal indicates gas release and temperature increase, and the optical emission is a reasonable measure of the duration of the reaction. Stoichiometric Al/Bi2WO6 composite was prepared according to chemical equation (1):

\[
4\text{Al} + \text{Bi}_2\text{WO}_6 \rightarrow 2\text{Al}_2\text{O}_3 + 2\text{Bi} + \text{W}
\]  

(1)

A fixed amount of loosely-packed powder of Al/Bi2WO6 sample was used in each test. Fig. 3a shows a typical pressure rise profile and optical emission profile of Al/Bi2WO6 samples versus time. The slope of the pressure rise is defined as pressurization rate and the full width at half maximum (FWHM) of optical emission intensity is taken as burn time. In Fig. 3a, the pressure increases dramatically to over 1000 kPa within about 0.01 ms, indicating vigorous and rapid gas generation after initiation of the reaction. The burn time is determined to be 0.17 ms.

The particle size of the oxidizer plays an important role in the propagation of nanothermite reaction. Weisimiller et al. (Weisimiller et al., 2011) showed that reducing the size decreases the timescale of heating associated with the decomposition and vaporization of oxide particles, and the length scale is also shorter for gas to diffuse away from particles, both leading to a higher local pressurization rate and an enhancement of overall convective propagation. This implies that the reaction may benefit from the nanoscale size of Bi2WO6 particles.

For comparison purposes, other oxidizers were also selected and tested with nano-Al in the combustion cell, including Bi2O3,
WO$_3$ and equimolar physical mixture of Bi$_2$O$_3$ + WO$_3$. The first two are simple oxide components of Bi$_2$WO$_6$, while the last one has the same chemical composition as Bi$_2$WO$_6$. The corresponding MICs were prepared according to Eqs. (2)–(4), respectively.

\[
\begin{align*}
2\text{Al} + \text{Bi}_2\text{O}_3 & \rightarrow \text{Al}_2\text{O}_3 + 2\text{Bi} \\
2\text{Al} + \text{WO}_3 & \rightarrow \text{Al}_2\text{O}_3 + \text{W} \\
4\text{Al} + \text{Bi}_2\text{O}_3 + \text{WO}_3 & \rightarrow 2\text{Al}_2\text{O}_3 + 2\text{Bi} + \text{W}
\end{align*}
\]

The pressure profiles of Al/Bi$_2$O$_3$, Al/Bi$_2$O$_3$ + WO$_3$, Al/Bi$_2$WO$_6$ are plotted in Fig. 3b, with the inset showing the zoomed-in plot of the initial rise and total pressure rise time. Since Al/WO$_3$ is known to generate minimal gas, it is not shown. The pressure rise time of Al/Bi$_2$O$_3$ is 0.12 ms, while the pressurization time of Al/Bi$_2$O$_3$ + WO$_3$ is only half of that. The peak pressure of Al/Bi$_2$O$_3$ + WO$_3$ is also slightly higher than that of Al/Bi$_2$O$_3$, suggesting that more gas is generated within a shorter time after the addition of WO$_3$. This result is in accordance with previous study of Al/Fe$_2$O$_3$/WO$_3$ system that shows the higher flame temperature sustained by WO$_3$ enhances the gasification of Fe$_2$O$_3$ (Jacob et al., 2018). Noticeably, the peak pressure of Al/Bi$_2$WO$_6$ is almost three times as high as that of Al/Bi$_2$O$_3$, and the pressurization rate is more than ten times higher. This demonstrates that Al/Bi$_2$WO$_6$ is a superior gas generator and the gasification of reactants and products is highly efficient.

A complete comparison of peak pressure, pressurization peak and burn time of the abovementioned samples is shown in Fig. 3c. Al/WO$_3$ shows significantly lower peak pressure and pressurization rate as well as longer burn time, compared to the other three systems. This is expected due to lack of gaseous products (Jacob et al., 2018). In contrast, Al/Bi$_2$O$_3$ is one of the most reactive MICs known and can be used a reference (Wang et al., 2011). As shown in Fig. 3c, Al/Bi$_2$WO$_6$ exhibits considerably better reactivity than Al/Bi$_2$O$_3$: the peak pressure is 3 times as high as Al/Bi$_2$O$_3$, the pressurization rate is 10 times higher and the burn time is about 20% shorter. The fact that Al/Bi$_2$WO$_6$ outperforms Al/Bi$_2$O$_3$ indicates that Bi$_2$WO$_6$ is a superior oxidizer for Al-based nanothermite system.

Stoichiometry can also significantly affect the reactivity of MICs (Dutro et al., 2009). The peak pressure, pressurization rate and burn time of Al/Bi$_2$WO$_6$ composite with different stoichiometry are shown in Fig. 3d. The stoichiometric mixture shows the highest peak pressure, pressurization rate and the shortest burn time. Shifting the stoichiometry to either fuel lean or rich decreases the overall reactivity as expected.
3.3. Reaction mechanism

3.3.1. Rapid heating measurements

Temperature-Jump Time-of-Flight Mass Spectrometry (T-Jump TOFMS) was used to probe the initiation of the reaction between Al and Bi₂WO₆. The temporal nature of this method enables the measurement of time and temperature of different species produced throughout the duration of the reaction. The time-resolved release of reaction intermediates and products reveals important information about the initiation of a reaction (Zhou et al., 2009; Zhou et al., 2010).

The summary plot of the mass spectrum of Al/Bi₂WO₆ reaction is shown in Figure S3. Peaks of species from background (H₂O⁺, N₂⁺), reaction intermediates (Al⁺, AlO⁺) and products (Bi⁺, Bi₂⁺) can be observed. In order to gain more insights into the reaction kinetics of Al/Bi₂WO₆, the time-resolved release of reaction intermediates and products reveals important information about the initiation of a reaction (Zhou et al., 2009; Zhou et al., 2010).

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The ignition behavior of Al/Bi₂WO₆ composite was studied by T-jump coupled with a high-speed camera. The experiment was conducted in vacuum with a very small amount of sample (~0.1 mg)
coated on the platinum wire. The temperature profile and high-speed video are recorded simultaneously upon triggering the heating of the wire. The time of ignition can be determined from the video and the corresponding temperature can be obtained from the temperature profile. In this case, the ignition temperature of Al/Bi2WO6 was determined to be 923 ± 10 K, which is significantly lower than the oxygen release temperature of Bi2WO6 (~1298 K). Furthermore, the Bi signal of Al/Bi2WO6 reaction (~1.2 ms) also appears much earlier than Bi2WO6 decomposition (~2.7 ms). Therefore, it is evident that the reaction initiates prior to the release of molecular oxygen and is thus in the condensed phase. Some studies have shown that for nanothermite composites, oxygen ion conductivity is vital to the condensed phase initiation of reaction (Wang et al., 2017; Wang et al., 2016). The unique oxygen ion transport behavior was also suggested to assist in the violent reaction of Al/Bi2O3 nanothermite (Piekiel et al., 2014). In this regard, Bi2WO6 has been recognized as a good oxide ion conductor (Kendall et al., 1996; Takahashi and Iwahara, 1973), which might contribute to the rapid initiation of the reaction.

The snapshots of Al/Bi2WO6 reaction captured by high-speed camera are shown in Fig. 4c. Upon ignition, the size of the reaction area starts to increase dramatically in a short duration of time. The reaction propagates radially as well as along the wire before it dies. For aluminum-based thermites, aggregates of particles caused by reactive sintering is a common issue and negatively affects the reactivity (Sullivan et al., 2012). However, the reaction of Al/Bi2O3 propagates homogeneously and no spark was observed, indicating that the extent of sintering is not significant.

3.3.2. Reaction temperature

Flame temperature was obtained by a high-speed color camera pyrometry (Jacob et al., 2018). The snapshots of the color camera video and spatiotemporal temperature map of Al/Bi2WO6 and Al/(Bi2O3 + WO3) are shown in Fig. 5a and 5b, respectively. Within 0.04 ms, Al/Bi2WO6 produced a large cloud of reacted material compared with Al/(Bi2O3 + WO3), indicating vigorous reaction and the presence of a large amount of gaseous species. In the temperature map, a transition of colors (i.e., from yellow to green to blue) from the center to the periphery of the reaction area suggests a decreasing temperature gradient. This could be a sign of enhanced convective heat transfer, as Al/(Bi2O3 + WO3) shows no distinguishable temperature gradient. This result is in agreement with the higher reactivity of Al/Bi2WO6 shown by the pressure cell results.

The measured flame temperature for Al/Bi2WO6 is ~2960 K as shown in Figure S5, and the corresponding calculated adiabatic flame temperature by CHEETAH code is shown in Table 1. Previous work by Jacob et al. showed that a higher flame temperature enhances the gasification of unreacted materials and increases the reactivity of nanothermite composites (Jacob et al., 2018). In this case, Al/Bi2WO6 has a higher flame temperature compared to Al/Bi2O3, presumably because Al/WO3 also has a high flame temperature (~3360 K). Higher temperatures will also nominally result in a higher pressurization rate. It is often found that, although nanothermites are intimately mixed and highly reactive, some nanothermite reactions may not reach completion due to severe sintering of reactants (Jacob et al., 2017), and the flame temperature is an important indicator of the extent of completion. The high measured temperature relative to the adiabatic temperature implies that the reaction is approaching the thermodynamic limit of completion. This is likely because the condensed phase dominated reaction is more efficient compared with gas phase reactions, especially for such a short timescale (Jacob et al., 2017), and the high oxygen ion conductivity would seem to promote rapid reaction (Piekiel et al., 2014; Wang et al., 2017).

In nanothermite reactions, propagation is largely determined by the ignition threshold and heat transfer properties. A low ignition temperature and efficient heat transfer will greatly benefit propagation (Wang et al., 2019). As demonstrated by the T-jump experiments, the reaction between Al and Bi2WO6 initiates in the condensed phase, further facilitated by the high oxygen ion conductivity of Bi2WO6, leading to a low ignition temperature. During the reaction, bismuth is produced and vaporized rapidly due to its low boiling point (1837 K) relative to the flame temperature.
The convection and condensation of substantial gaseous bismuth can play an important role in heat transfer (Egan and Zachariah, 2015). In addition, the gas generation disaggregate the unreacted material, thus reducing the reactive sintering effect. As a result, the ignition and heat transfer of the reaction are both enhanced and create a positive feedback leading to high reactivity.

3.3.3. Combustion products analysis

In order to verify the proposed reaction mechanism, the combustion products of Al/Bi₂WO₆ composite were collected from the combustion cell. SEM images (Fig. 6a and S6) of the products show two populations of particles with distinct size distribution. The majority of the particles have a size smaller than 100 nm, with only a few micro-sized particles. To investigate the nature of two different particles populations, elemental mapping of the combustion products was obtained by EDS. As shown in Fig. 6a and b, the large micro-sized particles are rich in Al and O and thus should be aluminum oxide, indicative of reactive sintering. It also shows

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slightly higher W signal, possibly because W cannot be vaporized (b.p. = 5555 K) and stays in the condensed phase, becoming part of the large particle upon quenching. The small particles are mainly composed of Bi as evidenced by the elemental mapping. From the zoomed-in image (Fig. 6c and d), it can be observed that the surface of the large particle is partially covered by some small particles. No platelet-shaped particles can be observed in the combustion product, implying that Bi$_2$WO$_6$ was fully reacted, or at least underwent phase change that destroyed the original morphology. Further examination shows that the particles are all highly regular spheres, suggesting that they are likely formed by solidification of molten state or vapor condensation (Jacob et al., 2015). The fine spherical shape and uniform particle size distribution validates the vigorous gasification during the reaction.

4. Conclusions

The formulation of a powerful MIC, Al/Bi$_2$WO$_6$, was developed by incorporating a ferroelectric material as an oxidizer. Al/Bi$_2$WO$_6$ is highly reactive as evidenced by a pressurization rate almost ten times higher than that of Al/Bi$_2$O$_3$. T-jump mass spectrometry and high-speed imaging results show that the reaction initiates in the condensed phase followed by rapid generation of gaseous products, which is enhanced by the high flame temperature. The vigorous gas release can improve heat transfer and mitigate the reactive sintering effect, thus increasing the overall reactivity. Al/Bi$_2$WO$_6$ can serve as a promising candidate for coupled piezoelectric and nanoenergetic composites.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2021.116898.

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