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Sulfates-Based Nanothermites: An Expanding Horizon for Metastable Interstitial Composites**

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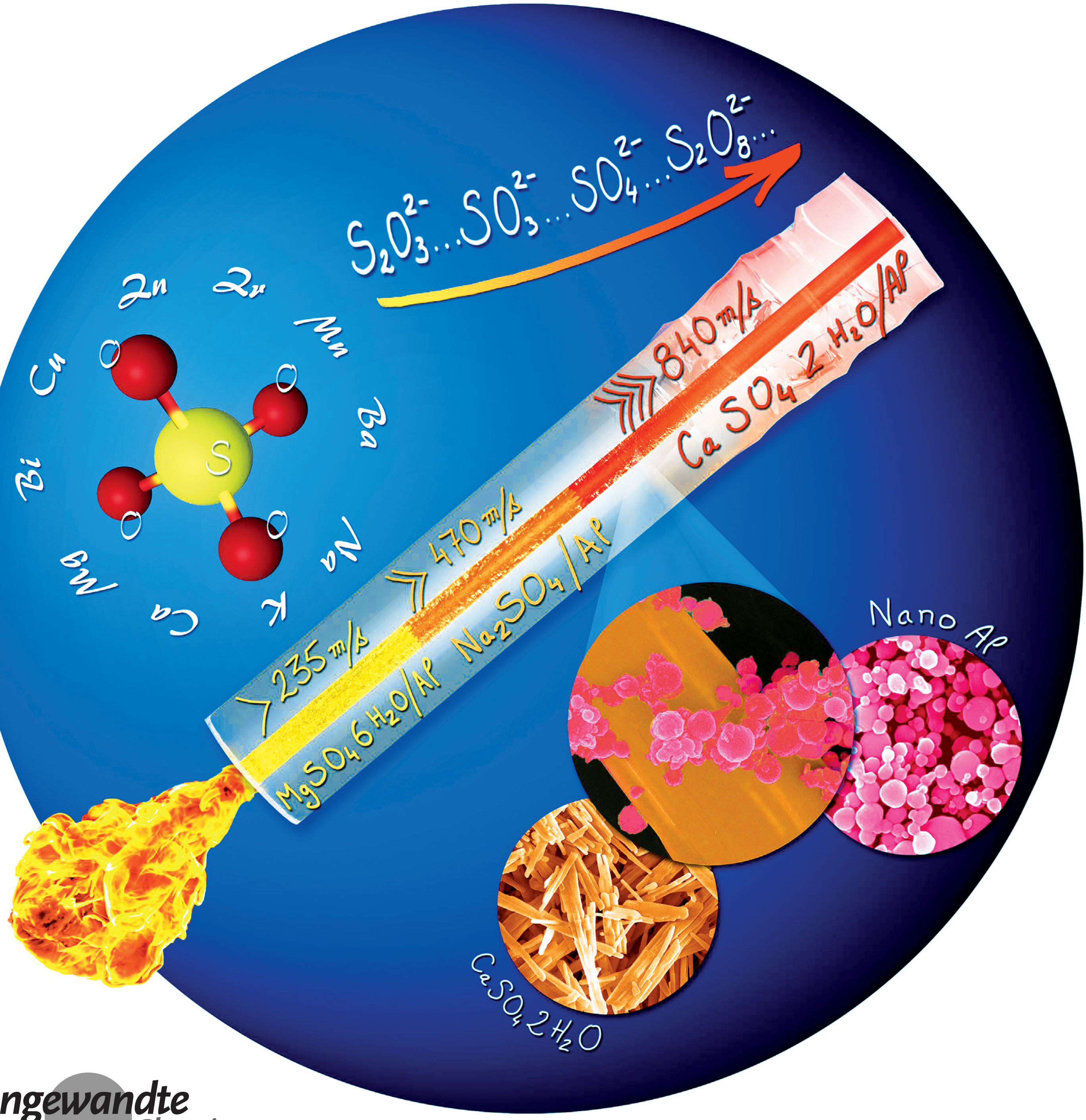

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Abstract: *Metal sulfates (Ba, Bi, Ca, Cu, Mg, Mn, Na, Zn, Zr) were used as oxidizers in reactive compositions with Al nanopowder. These new kinds of nanothermites have outstandingly high reaction heats (4–6 kJ* g^{-1}*) compared to conventional Al/metal oxides (1.5–4.8 kJ* g^{-1}*) and also have good combustion velocities (200–840 m* s^{-1} *vs 100–2500 m* s^{-1}*). These compositions are extremely insensitive to friction making their preparation and handling easy and safe. The sulfate hydration water increases the reaction heats and has a significant effect on the sensitivity to impact and to electrostatic discharge. The reaction of Al with water is easier to initiate than the one with sulfate which leads to two possible decomposition modes for samples exposed to an open flame. The pyrotechnical properties observed with sulfates have also been found for other sulfur oxygenates (*SO_3^{2-}*,* $S_2O_3^{2-}$*,* $S_2O_8^{2-}$*) which opens up new horizons in the domain of metastable interstitial composites.*

By the end of the nineteenth century, the German chemist Goldschmidt had prepared the first “thermit” compositions, by mixing reducing metal powders with metallic oxides and sulfides.[1] The classical meaning of the word “thermite”, can be extended to pyrotechnic mixtures containing significant amounts of metal-based compounds as reactive species. Interestingly, it can be noticed that the discovery of thermites was contemporary to the coming to maturity of industrial electrolytic processes used for synthesizing strongly reducing metals, such as, aluminium, calcium or magnesium. For one century, thermites have been almost exclusively used for welding or incendiary purposes.

In the mid 1990s, cutting-edge research in this domain was carried out in the Los Alamos National Laboratories, leading to the first metastable interstitial composites (MICs) made of aluminium and oxide nanoparticles.[2] Since then, an ever-increasing number of publications have highlighted the outstanding properties of nanothermites, which offer a wide range of new applications and lead to the concept of smart functional pyrotechnics. The main features of nanothermites are: 1) a higher sensitivity to ignition; 2) lower sensitivity thresholds, especially to friction and electrostatic discharge; 3) small apparent densities of loose powders; 4) high propagation rates driven by convection mechanisms, and 5) high reactive power. Up to now, the most studied fuel has been aluminium nanopowders (n-Al) with typical size distribution from 20 to 200 nm.[3] The strong reactivity of aluminium nanoparticles comes from the abrupt breaking of their core–shell structure, in accordance with the theory of the melt dispersion of aluminium proposed by Levitas.[4] The use of fuels, such as red phosphorus or boron leads to nanothermites with good, albeit lower reactivity owing, respectively, to heterogeneous gas/solid and surface reactions.[5]

MICs have outstanding reactive properties, which make them ideal candidate materials for many pyrotechnic applications. For instance, their short ignition delay times and their fast propagating combustion can be used in pyrotechnic actuators for projectile guidance.[6] Furthermore, the combustion of MICs provides large amounts of hot particles and droplets, which are of particular interest for the compositions used in lead-free ammunition primers.[7] Last but not least, the shock waves produced by the most reactive MICs, like pure or hybrid n-CuO/n-Al nanocompositions can probably be used to detonate secondary explosives, as a replacement of universally used (but highly toxic) lead azide.[8] Despite their wide range of applications, the use of MICs is limited by their excessively low sensitivity thresholds to friction and electrostatic discharge (ESD), which are often below 5 N and 0.14 mJ.

The main metallic oxides which can be used in nanothermite formulations have been identified by Fischer and Grubelich[9] and listed according to the calculated thermochemical properties of the thermite compositions in which they are used as oxidizers. Amongst numerous potential compositions, most research has focused on the aluminothermy reactions with Fe_2O_3, MoO_3, CuO, and Bi_2O_3.[10] More recently, in an attempt to further increase the reactivity of nanothermites, the use of unconventional oxidizing substances, such as $AgIO_3$, I_2O_5, and $KMnO_4$ has also been reported.[11]

The standard Gibbs energy of formation, determined in solution, of oxygen-containing anions used in energetic compositions is slightly negative and sometimes even positive. For instance, the Gibbs energy of ClO_3^-, ClO_4^-, and BrO_3^- anions is −8.0, −8.5, and +18.6 kJ mol^{-1}, respectively.[12] Conversely, oxygenated anions with low Gibbs energy, such as PO_4^{3-} (−1018.7 kJ mol^{-1}) or SO_4^{2-} (−744.5 kJ mol^{-1}), are considered as being of limited use for preparing energetic compositions. Furthermore, the mixing of ammonium sulfate with ammonium nitrate in a proportion higher than 40% by weight inhibits its detonation properties. The tragic Oppau explosion in 1921 has been attributed to a $(NH_4)_2SO_4$-lean zone in the fertilizer, leading to the nitrate mass detonation by unclogging operations.

Despite these theoretical unfavorable thermodynamic properties, sulfates can be used in pyrotechnics. For instance, Olander and Petersen have patented the preparation of combustible compositions from Ca and Mg sulfates mixtures with aluminium powder.[13] The use of highly hydrated salts—including sulfates—as sources of “solid water” for metal/water reaction was proposed by Fitzpatrick and more recently by Schroder and Dass who have used for this purpose nano-Al as fuel.[14] The combustion of aluminium/plaster ($CaSO_4 \cdot 2H_2O$) compositions made of coarse micron-sized particles typically spreads at some cm s^{-1}.

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Kosanke, Kosanke and Jennings-White mention that some metal sulfates can be used as color agents in pyrotechnic compositions.[15] For instance, barium, calcium, sodium, and strontium sulfates give respectively: green, reddish orange, yellow and red flame colors when they are enclosed into appropriate pyrotechnic compositions. Interestingly, these authors add that, “sulfates and oxides often act as high-temperature oxidizers in the presence of reactive metal fuels”. Further, these authors report that the flash reaction responsible for the twinkling of glitter compositions is produced by the flash reaction of aluminium with potassium and barium sulfates previously formed by the consecutive “on board” and “spritzel” reaction steps.

Herein, the reactive properties of a new family of nanothermites made of Al nanoparticles (ca. 100 nm) and metallic sulfates (Ba, Bi, Ca, Cu, Mg, Mn, Na, Zn, Zr) micro- and nanoparticles have been investigated. These materials possess high reaction heats (4–6 kJ g^{-1}) compared to most of Al/oxide based nanothermite compositions (1.5–4.8 kJ g^{-1}) and fast reaction rates (200–840 m s^{-1} vs 100–2500 m s^{-1}). Unlike conventional oxide-based MICs, sulfate-based nanothermites are insensitive to friction, with thresholds above 360 N for most of them. They are also less sensitive to electrostatic discharge, even though their sensitivity levels to ESD are globally low. Sulfate-based nanothermites are therefore safer to handle than traditional MICs, while having comparable levels of performance. One-off tests carried out on other oxygenated sulfur anions (SO_3^{2-}, $S_2O_3^{2-}$, $S_2O_8^{2-}$) have shown that the results obtained with sulfates can be probably extrapolated to most of SO_x^{y}-based salts.

To establish the ideal stoichiometry for each n-Al/sulfate mixture, the evolution of the reaction heat (Q_R) was determined by systematic calorimetric measuring, according to the aluminium content (X_{Al}). In the composition range close to stoichiometry (± 20 wt %), Q_{exp} varies according to a parabolic law $A_iX_{Al}^2 + B_iX_{Al} + Ci$ whose coefficients are given in Table 1. The highest reaction heat (Q_{Max}) and the corresponding optimized aluminium content ($X_{Al/Max}$) have been calculated by differentiating these experimental equations. The Q_R value is higher for compositions prepared from hydrated sulfates, as well as for metals which can be reduced to elemental state (Bi, Cu).

The analysis of the combustion residues by X-ray diffraction has shown that their composition depends on the sulfate nature and the Al content of the composition. For Na and Mg sulfates, the formation of aluminates is systematically observed. In the case of Ca sulfate, an increasing Al content leads first to the dehydration, then to the formation of an aluminate, and finally to calcium sulfide. The behavior of $BaSO_4$ is similar, with the exception of the dehydration step. For Bi, Cu, Mn the metallic sulfide is systematically formed. An Al excess reduces the sulfide into the corresponding metal (for Bi) or an Al alloy (for Cu).

The steady combustion rates of the optimized compositions (Table 2) measured at the extremity of confining tubes are typically in the same order of magnitude as those observed for thermites made of oxide nanoparticles (300–2500 m s^{-1}). To highlight the reactive performances of sulfate-based nanothermites, an experiment was carried out in the same operating conditions with the Swiss black powder No. 1. This conventional energetic material undergoes a slow combustion (0.056 m s^{-1}) which further evolves to an accelerated propagation, reaching only 100 m s^{-1} at the tube end.

Table 1: Coefficients of the experimental equation of reaction heats and optimized reaction parameters.

Sulfate	*A*	*B*	*C*	Q_{Max} [kJ g^{-1}]	$X_{Al/Max}$ [wt %]
$Ba(SO_4)$	−1.5673	150.74	−279.71	3.34	48.1
$Bi_2(SO_4)_3$	−3.2917	294.56	−1662.7	4.93	44.7
$Ca(SO_4)\cdot 2H_2O$	−3.3616	347.54	−3816	5.17	51.7
$Cu(SO_4)\cdot 5H_2O$	−3.5182	360.75	−3349.2	5.90	51.3
$Mg(SO_4)\cdot 6H_2O$	−4.1926	456.27	−6813.4	5.60	54.4
$Na_2(SO_4)$	−1.4617	145.59	467.42	4.09	49.8
$Zn(SO_4)\cdot 7H_2O$	−3.0188	309.71	−2700.7	5.24	51.3

Table 2: Combustion rates [m s^{-1}] of the optimized compositions in tubes, with the corresponding percentage of porosity.[a]

Preparation/ Powder state	PM/LP	PP on n-Al/LP	PP on n-Al/CP
$Ba(SO_4)$	321 ± 56 (82.5)	n.d.	n.d.
$Bi_2(SO_4)_3$	424 ± 52 (81.9)	n.d.	n.d.
$Ca(SO_4)\cdot 2H_2O$	724 ± 52 (86.0)	843 ± 83 (90.8)	746 ± 45 (80.1)
$Cu(SO_4)\cdot 5H_2O$	512 ± 69 (77.2)	831 ± 110 (82.0)	244 ± 44 (67.2)
$Mg(SO_4)\cdot 6H_2O$	n.d.	236 ± 41 (79.7)	n.d.
$Na_2(SO_4)$	351 ± 45 (81.4)	470 ± 62 (87.7)	202 ± 34 (78.2)

[a] PM = physical mixing, PP = precipitation; loose and compressed powders (LP, CP); n.d. = not determined.

It can be noticed that the combustion front velocities of sulfate-based nanothermites vary in a similar way to their reaction heats and increase with their porosity, which is consistent with a convective propagation mechanism.[16] The highest velocities seem to be with sulfates having an intermediate number of hydration water molecules (Table 2). The porosity of $Ca(SO_4)\cdot 2H_2O$ based composite materials are less influenced by being compacted than the porosity of the other materials, a result of the acicular (needle-like) shape of $Ca(SO_4)\cdot 2H_2O$ particles (Figure 1, A1) which are covered by n-Al particles (Figure 1, A2–A3).

Pure sulfates prepared by precipitation, are made of fine micron-sized particles with needle (Ca, Figure 1, A1), platelet (Cu, Figure 1, B1) and tile (Mg, Figure 1, C1) morphologies. In the composite materials prepared by the antisolvent precipitation in the presence of n-Al particles, the sulfate phases are more homogeneously distributed in the bulk than in the case of Ca-based material. Cu sulfate forms in the interparticle porosity of n-Al powder (Figure 1, B2–B3), while Mg sulfate rather solidifies both in the form of nanoparticles on the n-Al surface (Figure 1, B2–B3) and of larger micron-sized particles (Figure 1, B2). These morphologies account for the lower porosities obtained by compaction and for the related combustion speed reduction.

The decomposition of the n-Al/$CaSO_4\cdot 2H_2O$ upon progressive heating is representative of the behavior of sulfate-based nanothermites. The first weight loss (85–120 °C) is attributed to the removal of hydration water molecules

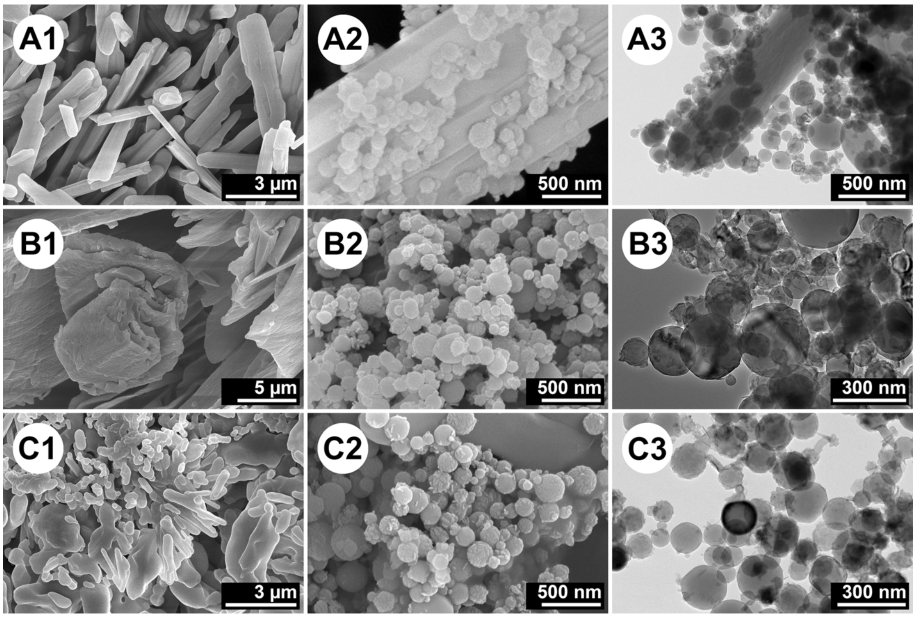

Figure 1. Electron micrographs of pure Ca (A1), Cu (B1), Na (C1) sulfates submicron-sized particles (SEM) and of their composites prepared by the precipitation of sulfates in the presence of Al nanoparticles (SEM: A2, B2, C2; TEM: A3, B3, C3).

(Figure 2). Al nanoparticles oxidize in two steps, corresponding to: 1) the solid-state oxidation of aluminium (480–660 °C) by the diffusion of oxygen through the Al_2O_3 shell to the Al core, and 2) the oxidation of liquid Al exuding from the cracks produced in the shell by the molten Al expansion (660–870 °C). The sulfate decomposition occurs at a higher temperature, depending on the nature of the metal. The temperature domain of sulfate decomposition (1150–1330 °C) is lowered in the composite material (1010–1190 °C). This effect is attributed to the intermediate formation of Al sulfate, whose melting and thermal decomposition occur above 770 °C.

The decomposition mechanism revealed by thermogravimetric analysis (TGA) accounts for the two dissimilar reactive behaviors which can be observed when a n-Al/$CaSO_4{\cdot}2H_2O$ composition is put in an open flame: A quick ignition followed by a slow, sparkling combustion. This reaction mode is attributed to the immediate reaction of Al with water, which initiates the whole combustion of the material. The slow reaction rate of n-Al/water mixtures (some $cm\,s^{-1}$) was recently reported by Tappan et al. who assumed that the oxidation of Al was actually governed by the kinetic of proton abstraction from H_2O molecule.[17] The analysis by XRD of the residues of Al-lean n-Al/$CaSO_4{\cdot}2H_2O$ compositions, has confirmed that the reaction of Al with water is the first to take place. Other times, the reaction does not instantaneously happen and the composition heats until it is red hot before reacting abruptly. The explosion of some milligrams can blow out the flame of a Bunsen burner. This second reaction mode occurs when hydration water is removed from the sample without inducing the decomposition. The sulfate reaction, which is more difficult to activate, requires a strong pre-heating of the material.

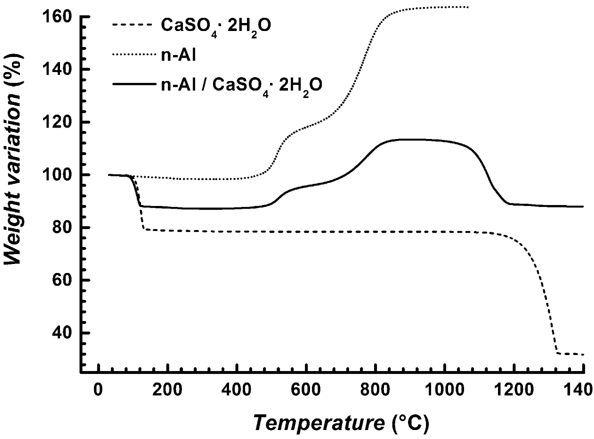

Figure 2. Thermogravimetric analysis of the slow decomposition of the n-Al/$CaSO_4{\cdot}2H_2O$ composite material.

One of the most interesting features of sulfate-based nanothermites is their outstanding insensitivity to friction, which makes their preparation by crushing safe (Table 3). The $Bi_2(SO_4)_3$ based thermite is the only composition that was found to be moderately sensitive to this kind of stress.[18] In contrast, classical oxide based nanothermites are extremely sensitive to friction and most of them have sensitivity thresholds below 5 N.

Table 3: Sensitivity thresholds of the optimized compositions.

Preparation	Stimulus Impact [J] PM/PP on n-Al	 Friction [N] PM/PP on n-Al	 ESD [mJ] PM/PP on n-Al
$Bi_2(SO_4)_3$	> 49.6/n.d.	168/n.d.	6.1/n.d.
$Ca(SO_4){\cdot}2H_2O$	25.1/5.0	> 360/ > 360	20.4/8.3
$Cu(SO_4){\cdot}5H_2O$	7.5/3.5	> 360/ > 360	61.6/47.3
$Mg(SO_4){\cdot}6H_2O$	6.5/6.5	> 360/ > 360	186.6/61.6
$Na_2(SO_4)$	> 49.6/ > 49.6	> 360/ > 360	1.0/0.1
$Na_2(SO_4){\cdot}10H_2O$	> 49.6/n.d.	> 360/n.d.	78.2/n.d.
$Zn(SO_4){\cdot}7H_2O$	10.4/6.5	> 360/ > 360	88.7/61.8

The thermites prepared from fine micron-sized sulfates have higher impact-sensitivity thresholds than their nano-sized counterparts. The relationship between the impact-sensitivity threshold and the number of hydration water molecules follows a parabolic law. It reaches a minimum value for five water molecules, irrespective of the nature of the sulfate counterions. This means that the hot spots produced by the impact, lead to the reaction of Al with water. Increasing the number of water molecules from none to five sensitizes the composition. The oxidation of Al by water, which occurs more easier than the oxidation of Al by sulfate, is the driving force of reaction initiation. In the presence of a greater amount of water ($n > 5$), the propagation of the reaction is made more difficult by the heat-sink effect of water.

The sensitivity levels to electrostatic discharge of sulfate-based thermites are significantly higher than those of most of oxide-based nanothermites. There is a general trend towards an increase of the ESD thresholds with the number of hydration water molecules. The presence of water is assumed to increase the electrical conductivity of the composition and to absorb a part of the heat dissipated by the spark in the material.

The reactivity of Al nanopowder with sulfur oxygenates was finally tested on 50–50 wt% compositions with Na_2SO_3, NaS_2O_3, and $Na_2S_2O_8$. The measured combustion rates were 183 ± 45, 211 ± 40, and 510 ± 59 m s^{-1}, respectively. The sulfur atom, in its +IV oxidation state, logically shows weaker oxidizing properties than S^{VI}. The reaction heat of $Na_2S_2O_8$ with n-Al is exceptionally high (6.16 kJ g^{-1}) and approximates with that of the I_2O_5/Al mixture (6.22 kJ g^{-1}), which is considered to be one of the most reactive thermite compositions.[9,11]

Experimental Section

Aluminium nanopowder (n-Al) purchased from Intrinsiq Materials has an Al^0 content of 74.5 wt% and a mean particle diameter of 100 nm. Metal sulfates were purchased from Sigma–Aldrich (Ba, Cu, Na, Mn, Zn), Alfa Aesar (Bi, Zr), and Fluka Analytical (Mg). The $Ca(NO_3)_2, 4H_2O$ and the $(NH_4)_2S_2O_8$ used to prepare calcium sulfate were from Sigma–Aldrich and Prolabo, respectively.

The first preparation method was the physical mixing (PM) of n-Al with fine micron-sized sulfate powders. The phases are first mixed by gentle crushing with the back of a spatula, before being homogenized with a Vortex mixer operating at 2500 rpm, for 2 min. Fine micron-sized sulfates were prepared by grinding in a mortar except for Cu, Na, and Mg sulfates which were obtained by antisolvent precipitation from aqueous solutions by acetone. The $CaSO_4 \cdot 2H_2O$ was synthesized from aqueous solutions of $Ca(NO_3)_2 \cdot 4H_2O$ to which $(NH_4)_2S_2O_8$, was added dropwise under vigorous stirring. The composite materials were prepared according to the same precipitation protocols (PP), with Al nanopowder dispersed into acetone (for Cu, Na, Mg) and calcium nitrate solution (for Ca).

SAFETY WARNING: All experiments involving energetic materials were performed in NS3E laboratory, which is a research unit, specialized in the preparation and the characterization of energetic nanomaterials. Any experiments described herein, may be carried out by scientists who are fully aware of specific hazards in pyrotechnic research and in accordance with local laws, safety regulations, and rules concerning the preparation and the testing of such substances. The authors are not responsible for any inappropriate use of these results.

Keywords: aluminum · metastable compounds · nanoparticles · reactivity · sulfur

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[1] H. Goldschmidt, DE 96317, **1895**.
[2] G. P. Dixon, J. A. Martin, D. Thompson, US 5717159, **1998**.
[3] J. J. Granier, M. L. Pantoya, *Combust. Flame* **2004**, *138*, 373–383.
[4] V. I. Levitas, B. W. Asay, S. F. Son, M. Pantoya, *Appl. Phys. Lett.* **2006**, *89*, 071909.
[5] M. Comet, V. Pichot, B. Siegert, F. Schnell, F. Ciszek, D. Spitzer, *J. Phys. Chem. Solids* **2010**, *71*, 64–68; M. Comet, F. Schnell, V. Pichot, J. Mory, B. Risse, D. Spitzer, *Energy Fuels* **2014**, *28*, 4139–4148.
[6] C. Baras, D. Spitzer, M. Comet, F. Ciszek, F. Sourgen, US 8716640, **2014**.
[7] J. Hirlinger, M. Bichay, Demonstration of Metastable Intermolecular Composites (MIC) on Small Caliber Cartridges and CAD/PAD Percussion Primers, ESTCP Project WP-200205, **2009**.
[8] R. Shende, S. Subramanian, S. Hasan, S. Apperson, R. Thiruvengadathan, K. Gangopadhyay, P. Redner, D. Kapoor, S. Nicolich, W. Balas, *Propellants Explos. Pyrotech.* **2008**, *33*, 122–130; S. Apperson, R. V. Shende, S. Subramanian, D. Tappmeyer, S. Gangopadhyay, Z. Chen, K. Gangopadhyay, P. Redner, S. Nicolich, D. Kapoor, *Appl. Phys. Lett.* **2007**, *91*, 243109; R. Thiruvengadathan, A. Bezmelnit *syn*, S. Apperson, C. Staley, P. Redner, W. Balas, S. Nicolich, D. Kapoor, K. Gangopadhyay, S. Gangopadhyay, *Combust. Flame* **2011**, 158, 964–978.
[9] S. H. Fischer, M. C. Grubelich, Proceedings of the 24th International Pyrotechnics Seminar, Monterey (USA), **1998**.
[10] T. M. Tillotson, A. E. Gash, R. L. Simpson, L. W. Hrubesh, J. H. Satcher, Jr., J. F. Poco, *J. Non-Cryst. Solids* **2001**, *285*, 338–345; K. Moore, M. Pantoya, S. F. Son, *J. Propul. Power* **2007**, *23*, 181–185; J. A. Puszynski, *J. Therm. Anal. Calorim.* **2009**, *96*, 677–685; K. S. Martirosyan, L. Wang, A. Vicent, D. Luss, *Nanotechnology* **2009**, *20*, 405609.
[11] K. T. Sullivan, N. W. Piekel, S. Chowdhury, C. Wu, M. R. Zachariah, C. E. Johnson, *Combust. Sci. Technol.* **2011**, *183*, 285–302; K. S. Martirosyan, L. Wang, D. Luss, *Chem. Phys. Lett.* **2009**, *483*, 107–110; A. Prakash, A. V. McCormick, M. R. Zachariah, *Nano Lett.* **2005**, *5*, 1357–1360.
[12] J. Barrett, *Inorganic Chemistry in Aqueous Solution*, Royal Society of Chemistry, Cambridge, **2003**, p. 20.
[13] D. E. Olander, D. W. Petersen, US 4381207, **1983**.
[14] J. A. Fitzpatrick, US 2885277, **1959**; K. A. Schroder, R. I. Dass, US 2012/0216926, **2012**.
[15] K. L. Kosanke, B. J. Kosanke, C. Jennings-White, *Lecture Notes for Pyrotechnic Chemistry*, Journal of Pyrotechnics, Inc., Whitewater, CO 81527, USA, **2004**, p. 1–34; 8–33.
[16] D. Prentice, M. L. Pantoya, A. E. Gash, *Energy Fuels* **2006**, *20*, 2370–2376.
[17] B. C. Tappan, M. R. Dirmyer, G. A. Risha, *Angew. Chem. Int. Ed.* **2014**, *53*, 9218–9221; *Angew. Chem.* **2014**, *126*, 9372–9375.
[18] D. G. Piercey, T. Klapötke, *Cent. Eur. J. Energ. Mater.* **2010**, *7*, 115–129.

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