

ON THE SYNTHESIS OF SULPHIDES IN COMBUSTION REGIME

V. V. Boldyrev^{1}, R. K. Tukhtaev¹, A. I. Gavrilov¹ and S. V. Larionov²*

¹Institute of Solid State Chemistry, Russian Academy of Sciences, Siberian Branch, Kutateladze 18, Novosibirsk 128, 630128, Russia

²Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Branch, Lavrentjeva 3, Novosibirsk 90, 630090, Russia

Abstract

The present investigation deals with combustion (in inert atmosphere) of mixtures based on metal nitrates and sulphur-containing compounds possessing reductive properties, such as ammonium thiocyanate, thiosemicarbazide, thiocarbamide. It is demonstrated that at definite component ratios these mixtures burn forming sulphides of the corresponding metals. Morphology and disperse state of the resulting sulphides can be controlled by changing combustion conditions and ratios between components.

Keywords: combustion, disperse state, mixtures, morphology, particles, sulphides

Introduction

Heat released in chemical reactions can be used not only to detect separate processes and phases as it is involved in thermal analysis but also to conduct reactions themselves, for example to obtain inorganic compounds by means of combustion. This synthesis method has become widespread within the recent years.

However, the investigations into the processes of sulphide synthesis in the combustion regime receive much less attention in comparison with other classes of compounds [1]. One of the possible reasons of such situation is likely to be relatively low heat of formation for many sulphides. Low heat of formation hinders direct synthesis from elements; because of this, other ways are to be searched for, in order to carry out the process in the combustion regime.

Earlier we proposed to use for this purpose the complex compounds of metal nitrates with sulphur-containing hydrazine and ammonia derivatives, in particular with thiosemicarbazide and thiocarbamide [2–4]. Combustion of the complexes of nickel, copper, cobalt, iron, cadmium and zinc with thiosemicarbazide as well as of the complexes of zinc, cadmium, lead, bismuth and indium with thiocarbamide was investigated. It was found that all of them burn giving the sulphides of the corresponding

* Author for correspondence: E-mail: boldyrev@solid.nsk.su

metals. A specific feature of the combustion of these compounds is the fact that the evolution of energy needed to sustain the combustion process is provided not by the reaction of sulphide formation which is in fact the target of the process, but by the interaction of nitrate ions with hydrazine and amine groups of ligands. So, the formation of sulphides in combustion regime becomes possible due to the accompanying reaction between the oxidizer (nitrate ion) and the fuel (ligand).

The use of such complexes has at least two advantages. The first one is connected with the structure of the complexes. Their structure is so that each thiosemicarbazide molecule is coordinated to metal atom through the nitrogen atom of the amine group and sulphur atom [5, 6]. Thiocarbamide molecules are also coordinated to metal through the sulphur [7]. So, metal atom initially has got a coordination bond with sulphur atoms; its bonding to the oxygen atom of the nitrate group is weakened substantially, which simplifies the formation of sulphide during combustion. The second advantage is that these systems are homogeneous in the chemical aspect, which provides high purity and uniformity of the resulting products [4].

However, not all the metals form complex compounds of this type; the list of possible ligands is also limited. There are also some metals that do not form nitrates. These features provide limitations for the method. Because of this, the next step was to investigate the possibilities to obtain sulphides in the combustion of mechanical mixtures composed of separately taken metal nitrates as oxidizers and sulphur-containing ammonia and hydrazine derivatives as a fuel.

Experimental

Experimental procedure was as follows. The initial components were mixed in a mortar or ball mill, and pressed as cylindrical tablets; they were then burnt in a constant-pressure bomb, in the atmosphere of nitrogen. Gas pressure (P) being varied within 101.3–3039 kPa. Since most nitrates contain the crystallization water, the mixtures were dried at a temperature of 60°C before pressing. The linear burning rate (U) and combustion temperature (T_p) were measured using tungsten-rhenium micro-thermocouples as it was described in [3, 4]. The final products were analyzed by means of XPA and electron microscopy.

Results and discussion

The results on the synthesis of different sulphides are shown in Table 1. Nickel, cobalt, copper, manganese, zinc and cadmium nitrates were used as oxidizers; reducing agents were thiosemicarbazide (TSC), thiocarbamide (Thio) and ammonium thiocyanate. Components ratio was the same as in the complex compounds mentioned above [2–4]: one fuel molecule per one nitrate group. This provides generally reductive atmosphere in combustion and two-fold excess of sulphur with respect to metal. One can see that this component ratio creates the conditions favourable for the synthesis: all the compositions

Table 1 Combustion of mixtures based on metal nitrates

No.	Composition of mixtures	P/kPa	$T_f/^\circ\text{C}$	$U/\text{mm s}^{-1}$	Combustion products
1.	Ni(NO ₃) ₂ +2TSC	1013	700	0.46	NiS; NiS ₂ admixture
		2026	790	1.0	NiS
2.	Ni(NO ₃) ₂ +2Thio	1013	400	0.34	NiS ₂
		2026	460	0.65	NiS ₂ ; NiS admixture
3.	Ni(NO ₃) ₂ +2NH ₄ NCS	1013	660	0.50	NiS; NiS ₂ admixture
		2026	740	1.1	NiS; NiS ₂ admixture
4.	Co(NO ₃) ₂ +2TSC	1013	720	0.45	Co _{1-x} S; Co ₄ S ₃ admixture
		2026	910	0.98	Co _{1-x} S; Co ₄ S ₃ admixture
5.	Co(NO ₃) ₂ +2Thio	1013	910	0.57	Co _{1-x} S; Co ₄ S ₃ admixture
		2026	990	1.9	Co _{1-x} S; Co ₄ S ₃ admixture
6.	Co(NO ₃) ₂ +2NH ₄ NCS	101.3	710	1.4	Co _{1-x} S; Co ₄ S ₃ admixture
		1013	930	1.9	Co _{1-x} S; Co ₄ S ₃ admixture
		2026	950	2.5	Co _{1-x} S; Co ₄ S ₃ admixture
7.	Cu(NO ₃) ₂ +2TSC	101.3	380	0.29	CuS; Cu _{1.8} S admixture
		2026	520	1.6	Cu _{1.8} S
8.	Cu(NO ₃) ₂ +2Thio	101.3	310	0.26	CuS
		2026	350	1.0	CuS
9.	Cu(NO ₃) ₂ +2NH ₄ NCS	1013	420	0.61	Cu _{1.8} S
		2026	460	0.89	Cu _{1.8} S
10.	Mn(NO ₃) ₂ +2TSC	101.3	1120	0.52	MnS
		1013	1380	2.7	MnS
		2026	1440	3.6	MnS
11.	Mn(NO ₃) ₂ +2Thio	2026	480	0.24	MnS
12.	Mn(NO ₃) ₂ +2NH ₄ NCS	101.3	700	3.1	MnS
		1013	1180	6.2	MnS
13.	Zn(NO ₃) ₂ +2TSC	1013	1390	3.4	α -ZnS
		2026	1440	6.2	α -ZnS
14.	Zn(NO ₃) ₂ +2Thio	101.3	700	2.7	β -ZnS; α -ZnS
		2026	1190	6.3	α -ZnS
15.	Zn(NO ₃) ₂ +2NH ₄ NCS	101.3	1160	1.4	α -ZnS
		1013	1320	9.3	α -ZnS
16.	Cd(NO ₃) ₂ +2TSC	1013	1210	4.6	α -CdS
		2026	1330	4.3	α -CdS
17.	Cd(NO ₃) ₂ +2Thio	101.3	340	0.24	β -CdS
		1013	920	4.5	α -CdS; β -CdS
18.	Cd(NO ₃) ₂ +2NH ₄ NCS	101.3	730	3.7	α -CdS; β -CdS
		1013	1190	4.1	α -CdS
		2026	1300	4.3	α -CdS

investigated burn with the formation of sulphides. The phase composition of products depends on the nature of metal and combustion temperature.

In the case of nickel nitrate the main product for the mixtures based on thiosemicarbazide and ammonium thiocyanate, having relatively high combustion temperature, is nickel monosulphide. A mixture with thiocarbamide, having the lowest combustion temperature, burns with the formation of nickel disulphide which is thermally less stable.

Some other situation is realized in the combustion of mixtures based on cobalt nitrate. The qualitative composition of the products in this case is similar for all the three mixtures; it includes two sulphides. The main phase is non-stoichiometric cobalt monosulphide, the relative intensity of diffraction lines of the second phase does not exceed 10%.

The most thermally stable compound among copper sulphides is dihenite $\text{Cu}_{1.8}\text{S}$. Dihenite is the only product in combustion of complex compound of copper nitrate with thiosemicarbazide [4], and it also forms in combustion of copper nitrate mixtures with thiosemicarbazide and ammonium thiocyanate. In the case of mixture with thiocarbamide, due to very low combustion temperature it is possible to obtain the copper monosulphide CuS .

All the mixtures based on manganese nitrate burn with the formation of only cubic manganese monosulphide. This is quite clear because other phases existing in the system manganese-sulphur are not stable at temperatures achieved during the combustion of the mixtures under investigation.

The results on the combustion of zinc-containing compositions show that zinc sulphide is formed in all the cases; at high temperatures we obtain the sulphide of hexagonal structure while at low temperatures mainly cubic phase is formed.

Similar results are obtained in the combustion of mixtures based on cadmium nitrate. In this case sulphide is formed, too; however, its structure is determined by the combustion temperature.

So, we observe that the combustion of mechanical mixtures, as well as the combustion of complex compounds, leads to the formation of sulphides. The formation of sulphides occurs both in the systems in which the formation of complexes is possible, and in the systems where no complex compounds exist. For example, ammonium thiocyanate turned out to be a promising reactant for the synthesis of sulphides, though it does not form complex compounds. As a rule, combustion temperature for mixtures is lower than that for the corresponding complexes; in some cases, this allows obtaining less stable low-temperature phases of sulphides.

It is evident that the possibility of the formation of sulphides in the combustion of mechanical mixtures should be dependent on fuel to oxidizer ratio. This dependence was investigated for some compositions. Table 2 shows the results obtained for the system: cadmium nitrate–ammonium thiocyanate. One can see that the formation of sulphides occurs within a broad range of fuel to oxidizer ratio from 1.1 to 4 moles of thiocyanate per 1 mole of cadmium nitrate. Depending on combustion temperature, the sulphide is obtained either in hexagonal form or as a mixture of hexagonal and cubic modifications. The most reactive mixtures are those containing 1.5 and 1.3 moles of thiocyanate. These compositions selfignite after pressing. It should be

noted, that mixtures containing 1.3 and 1.1 moles of thiocyanate contain oxygen in excess; nevertheless, a noticeable formation of cadmium oxide is observed only when the thiocyanate content is less than 1 mole per 1 mole of nitrate.

Table 2 Influence of component ratio on combustion of cadmium nitrate–ammonium thiocyanate mixtures

No.	Composition of mixtures	P/kPa	$T_f/^\circ\text{C}$	$U/\text{mm s}^{-1}$	Combustion products
1.	$\text{Cd}(\text{NO}_3)_2+1.1\text{NH}_4\text{NCS}$	3039	1350	3.6	$\alpha\text{-CdS}$
2.	$\text{Cd}(\text{NO}_3)_2+1.3\text{NH}_4\text{NCS}$		self-ignited		
3.	$\text{Cd}(\text{NO}_3)_2+1.5\text{NH}_4\text{NCS}$		self-ignited		
4.	$\text{Cd}(\text{NO}_3)_2+1.8\text{NH}_4\text{NCS}$	3039	1400	4.7	$\alpha\text{-CdS}$
5.	$\text{Cd}(\text{NO}_3)_2+2.5\text{NH}_4\text{NCS}$	3039	980	2.5	$\alpha\text{-CdS}$
6.	$\text{Cd}(\text{NO}_3)_2+3.0\text{NH}_4\text{NCS}$	3039	600	1.3	$\alpha\text{-CdS}$; $\beta\text{-CdS}$
7.	$\text{Cd}(\text{NO}_3)_2+4.0\text{NH}_4\text{NCS}$	3039	420	0.39	$\beta\text{-CdS}$; $\alpha\text{-CdS}$

Unlike classical SHS systems our compositions burn giving rise to a large amount of gaseous products. This results in the formation of solid combustion products as a porous mass which is easily dispersed into separate particles. On the other hand, this provides the possibility to vary combustion temperature and burning rate within a broad range by changing pressure; variations of these parameters leads to the changes in the conditions under which final product is formed in the combustion wave, and, as a sequence, to the changes in their morphology and disperse state. This effect is most vividly exhibited in the synthesis of cadmium and zinc sulphides that are volatile at the combustion temperature of the mixtures. Figure 1 shows how the disperse state and morphology of cadmium sulphide particles obtained in the combustion of a mixture of cadmium ni-

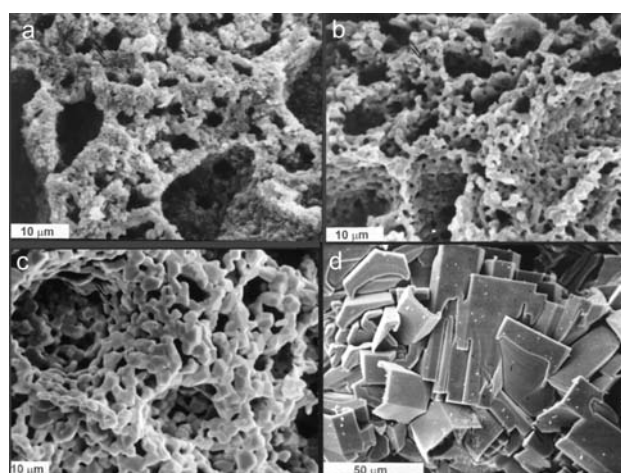


Fig. 1 Micrographs of CdS crystals, obtained at different pressure values: a – $P=101.3$ kPa; b – $P=506.5$ kPa; c – $P=1013$ kPa; d – $P=3039$ kPa

trate with ammonium thiocyanate change with changing pressure. Nanosize material is formed at atmospheric pressure, at 506.5 kPa the product consist of prismatic crystals of about 2 micron in size, more large prismatic crystals were obtained at 1013 kPa and sharp changes in morphology and particle size were observed at 3039 kPa. Figure 2 shows the results for zinc sulphide, obtained in the combustion of the similar mixture. Particle size

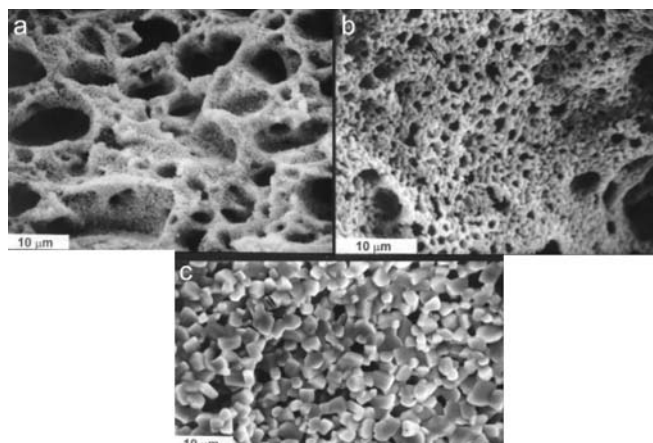


Fig. 2 Micrographs of ZnS crystals, obtained at different pressure values:
a – P=101.3 kPa; b – P=1013 kPa; c – P=2026 kPa

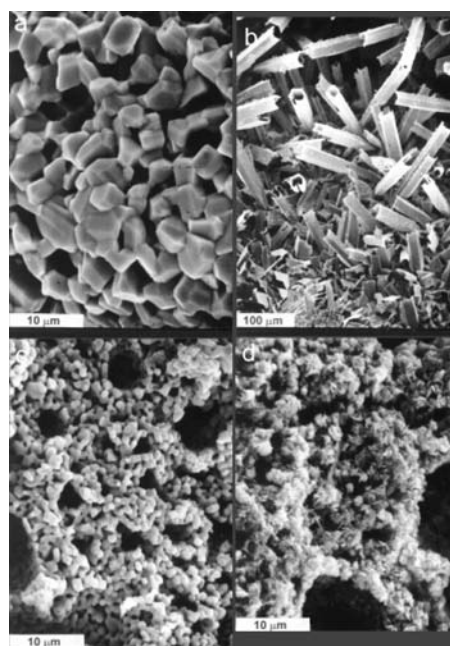


Fig. 3 Micrographs of CdS crystals, obtained at different component ratios
(P=3039 kPa): a – $\text{Cd}(\text{NO}_3)_2 + 1.1\text{NH}_4\text{NCS}$; b – $\text{Cd}(\text{NO}_3)_2 + 1.8\text{NH}_4\text{NCS}$;
c – $\text{Cd}(\text{NO}_3)_2 + 2.5\text{NH}_4\text{NCS}$; d – $\text{Cd}(\text{NO}_3)_2 + 3.0\text{NH}_4\text{NCS}$

substantially increases with increase of pressure and combustion temperature. The change of fuel to oxidizer ratio affects the morphology and disperse state of particles, too, because combustion temperature and burning rate change in this case, too. Figure 3 demonstrates the changes of the appearance and disperse state of cadmium sulphide crystals with changing mixture composition.

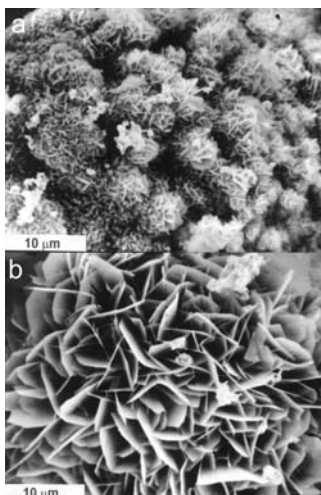


Fig. 4 Micrographs of a – MoS₂ and b – WS₂ crystals

The use of mechanical mixtures of metal nitrates with sulphur-containing derivatives of ammonia and hydrazine allows substantially expand the range of metals giving sulphides in the combustion regime. However, there are metals that do not form nitrates. It was found that in many cases a nitrate can be replaced by a mixture of oxide with ammonium nitrate or ammonium perchlorate. For example, disulphides of molybdenum and tungsten were obtained according to this method. Figure 4 shows micrographs of the resulting crystals. The mixtures used for their synthesis were composed of metal trioxide, ammonium perchlorate and thiosemicarbazide. By the similar method but with using of ammonium nitrate as an oxidizer were obtained the sulphides of zinc, copper, manganese, lead and some other metals.

Conclusions

A new method of sulphide synthesis is proposed. It is based on the combustion of mixed compositions containing an oxidizer and fuel. Metal nitrates (as well as mixtures of oxides with ammonium nitrate or perchlorate) can be used as oxidizers; sulphur-containing derivatives of ammonium and hydrazine can be used as fuel. The method allows substantial broadening of the range of metals, whose sulphides can be obtained by combustion. Due to relatively low temperature and substantial gas evolution during combustion, the sulphides are obtained in the dispersed state; their mor-

phology and particle size can be varied depending on pressure in reaction bomb and the composition of the mixture.

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