Synthesis and characterization of new inorganic-organic composite

$ZnS(1,3\text{-}DAP)_{1/2}$

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Unusual properties (optical, magnetic and electrical) [1] of nanomaterials make them so interesting that they are in the center of attention of researchers for many years. Number of new synthesized compounds is enormous, however among them, special attention deserve hybrid inorganic-organic layered materials. These are precursors of nano-semiconductors of groups II and VI, formed of alternating inorganic and organic layers, connected by chemical bonds. The applicability of such materials are very board, ranging from electronic devices [2,3] and ending to photocatalysts [4].

The main goal of our work was synthesis and characterization of new hybrid inorganic-organic layered materials $MQ(L)_{1/2}$ type, where M.- Zn, Cd, Mn , Q- S, Te, Se and L-amine. Among obtained results, we were able to synthesize, characterize, and solve by powder diffraction methods the structure of $ZnS(1,3\text{-}DAP)_{1/2}$ (DAP denotes diaminopropane).

$ZnS(1,3\text{-}DAP)_{1/2}$

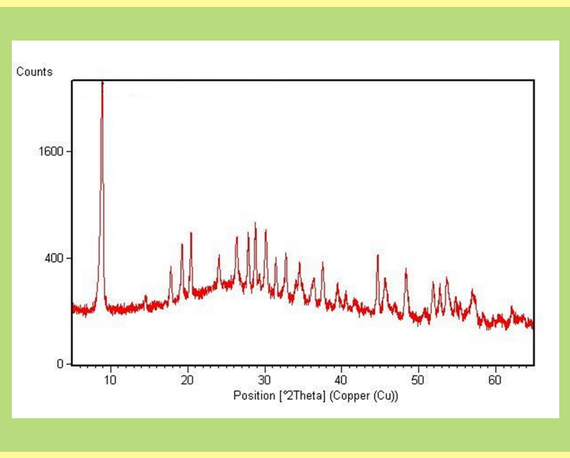


Fig. 1 An XRD pattern of $ZnS(1,3\text{-}DAP)_{1/2}$

Table 1. Crystallographic data for the $ZnS(1,3\text{-}DAP)_{1/2}$

Empirical formula	**Zn1S1C1.5N1H5**
Formula weight	**134.5 g/mol**
System	**Orthorombic**
Space group	**C m c 2_1 (36)**
A	**19.89(2) Å**
B	**6.397(7) Å**
C	**6.194(7) Å**
V	**788.6(1) Å^3**
R_p	**8.03 %**
R_{wp}	**11.36 %**

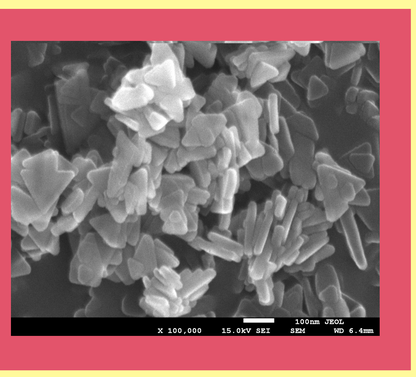
Table 2. Atomic coordinates.

Atom	x	y	z	B_{iso}
Zn1	0.2889(2)	0.1532(7)	0.876(2)	1.03512
S1	0.3096(4)	0.189(1)	1.242(2)	1.03512
N1	0.388(1)	0.328(4)	0.735(4)	1.50000
C3	0.435(1)	0.201(4)	0.844(6)	1.50000
C4	0.50000	0.294(7)	0.742(7)	1.50000

Table 3. Selected interatomic distances

Atom1	Atom2	d(Å)
Zn1	S1	2.317(9)
Zn1	S1	2.342(9)
Zn1	S1	2.381(9)
Zn1	N1	2.44(2)
N1	C3	1.42(4)
C3	C4	1.55(4)

In our case, the hybrid material was made up of infinite layers of ZnS separated by organic linkers- 1,3-DAP molecules. The inorganic layers are built of six-membered rings, in which sulphur and zinc are arranged alternately. The organic and inorganic layers are connected by the atoms: Zn1-N1-C3-C4-C3-N1-Zn1.



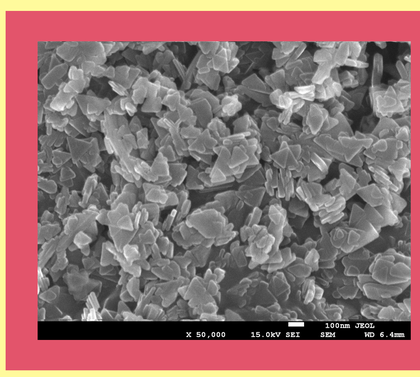
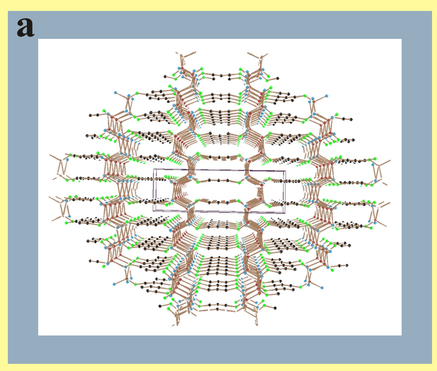


Fig. 2 SEM images of $ZnS(1,3\text{-}DAP)_{1/2}$

SEM images of $ZnS(1,3\text{-}DAP)_{1/2}$

- Crystals have the shape of prisms, which are based on triangles.

- Height of triangles is in the range of 50-100nm and the prism thickness is about 10nm.



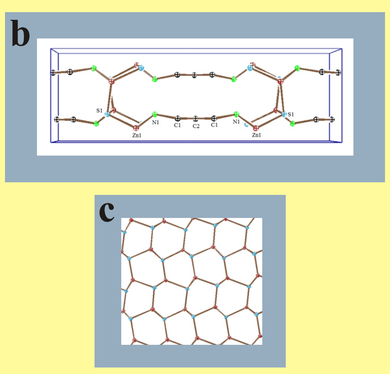


*Fig. 3 View of $ZnS(1,3DAP)_{1/2}$ (Zn-brown, S-blue, N-green, C-black), **a** projection along z-axis, **b** unit cell content, view along z-axis, **c** single layers of ZnS*

At the 300^{0}C the investigated material decomposed to ZnS and at temperature of 600^{0}C, the ZnO phase is observed. The appearance of ZnO is related to the oxidation of fine-crystalline ZnS. With the temperature increase, the proportion of ZnO phase grows.

The analysis of diffraction patterns for differet temperatures shows, that in low temperatures, small agreggates of ZnS dominated. Then, in higher temperatures they become larger.

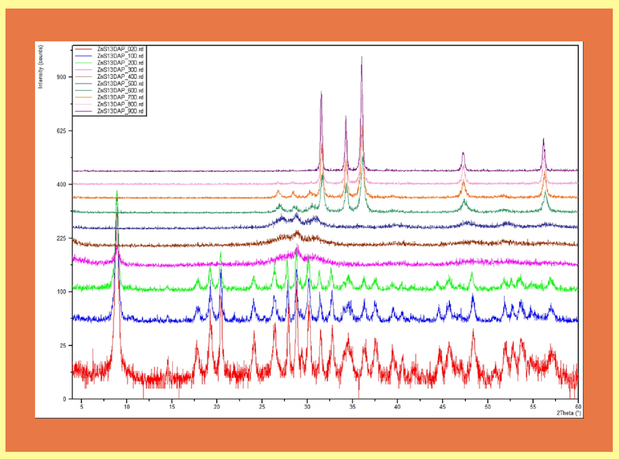


Fig. 4 XRD patterns obtained during heat treatment $ZnS(1,3\text{-}DAP)_{1/2}$

ZnS(1,2-DAP)

We have performed a series of syntheses using 1-aminopropane and 1,2-diaminopropane. In both cases, the quality of diffraction patterns makes it impossible to carry out a full structural surveys.

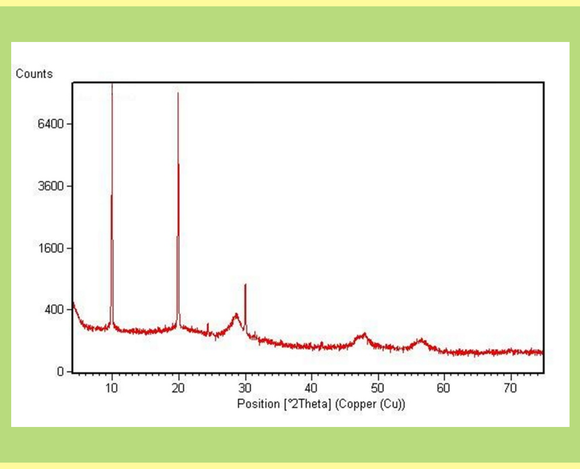
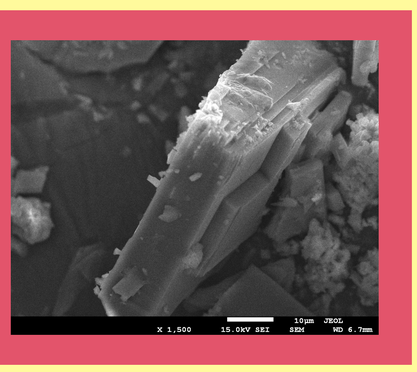


Fig. 5 An XRD pattern of ZnS(1,2-DAP)

Sem images show that obtained compounds have also lamellar structure.



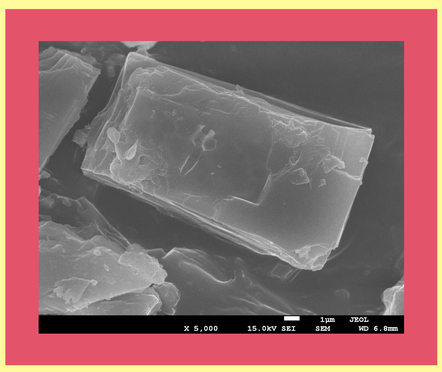


Fig. 6 SEM images of ZnS(1,2-DAP).

CONCLUSIONS

We have performed a series of syntheses using different types of amines: 1-aminopropane, 1,2-diaminopropane and 1,3-diaminopropane. Only in the case of 1,3-DAP, hybrid layered compounds were obtained, which suggests that there is a strong correlation between the type of used amines and the probability of hybrid lamellar materials obtained.

Compounds have been examined with the use of different techniques, including: X-ray diffraction, chemical analysis, UV-vis spectroscopy, scanning electron microscopy and thermal analysis. These methods allowed the full characterization of the obtained structures.

ZnS(1-AP)

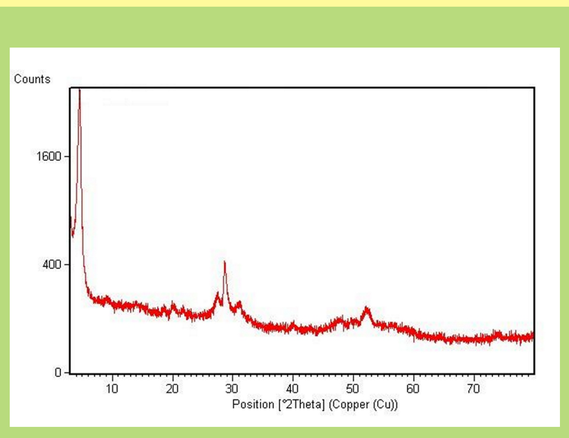
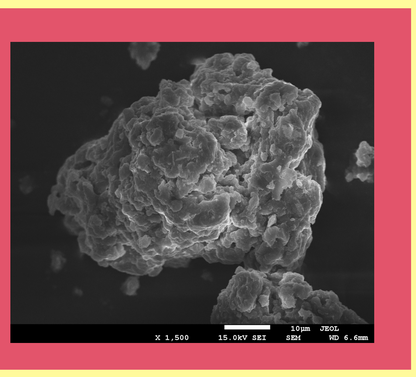


Fig. 7 An XRD pattern of ZnS(1-AP)



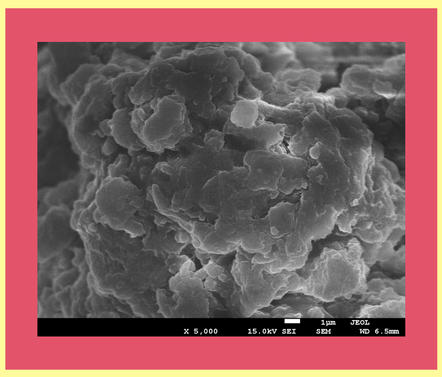


Fig. 8 SEM images of ZnS(1-AP)

References
[1] Juping Li, Yao Xu, Dong Wu and Yuhan Sun,Solid State Communications 130 (2004) 619-622.
[2] P. Calandra, M. Goffredi and Liveri V. Turco. Colloids Surf. A 160 (1999).
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[4] Juping Li, Yao Xu, Yong Liu, Dong Wu and Yuhan Sun, China Particuology Vol. 2, No. 6, 266-269, 2004.

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