Recent achievements in sonochemical synthesis of binary chalcogenides

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Syllabus

- Introduction:
  - Applications of metal chalcogenides
  - Fundamentals of the sonochemical method
  - Overview of the work done up to now

- Experimental: synthesis and characterization
- Results:
  - ✓ Ag_2S, Ag_2Se, Ag_2Te
- Summary

Introduction

Nanocrystalline transition metal chalcogenides:

- Receiving growing attention due to their unique physical, chemical, semiconducting and optical properties
- Applications: photodiodes, thermoelectrical devices, semiconducting materials, solar cells, optical devices
- Classical methods: high T, long reaction times, poor control, use of highly toxic precursors (H_2S, H_2Se)

Use of silver chalcogenides, Ag_2E (E = S, Se, Te)

- Ag_2S: interesting semiconducting material for production of photocells, photoconductors / photoresistors, IR detectors
- Ag_2Se: solar cells, optical filters, superionic conductors
- Ag_2Te: material with great magnetic resistance (magnetic reluctance, MR)

Some classical methods of synthesis

- Solid – state synthesis from elements
  - high T (500 – 600 ^{0}C), long reaction times, vacuum or inert atmosphere
  - difficult to obtain nanosized products, especially in the case of Ag_2S (tends to form agglomerates)

- Reaction between aqueous solutions of metal ions and gaseous H_2E (E = S, Se, Te)
  - Working with gaseous, highly poisonous reagents!

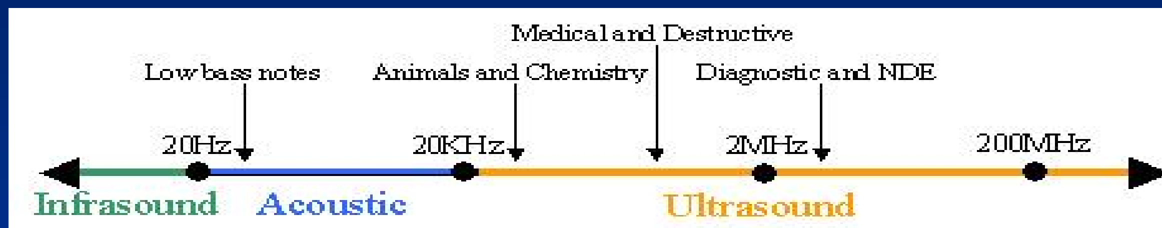
Modern methods for the synthesis of transition metal chalcogenides

- Safer, avoiding toxic reactants
- Milder reaction conditions → easier to control!

- Inverse (revers) micelles
- Sol – gel method
- Synthesis in liquid ammonia
- Hydrothermal syntheses
- Solvothermal syntheses in aqueous NH_3 and ethylenediamine

Basic principles of sonochemical reactions

- Ultrasound: cyclic sound pressure with fequencies between 20 kHz and 10 MHz



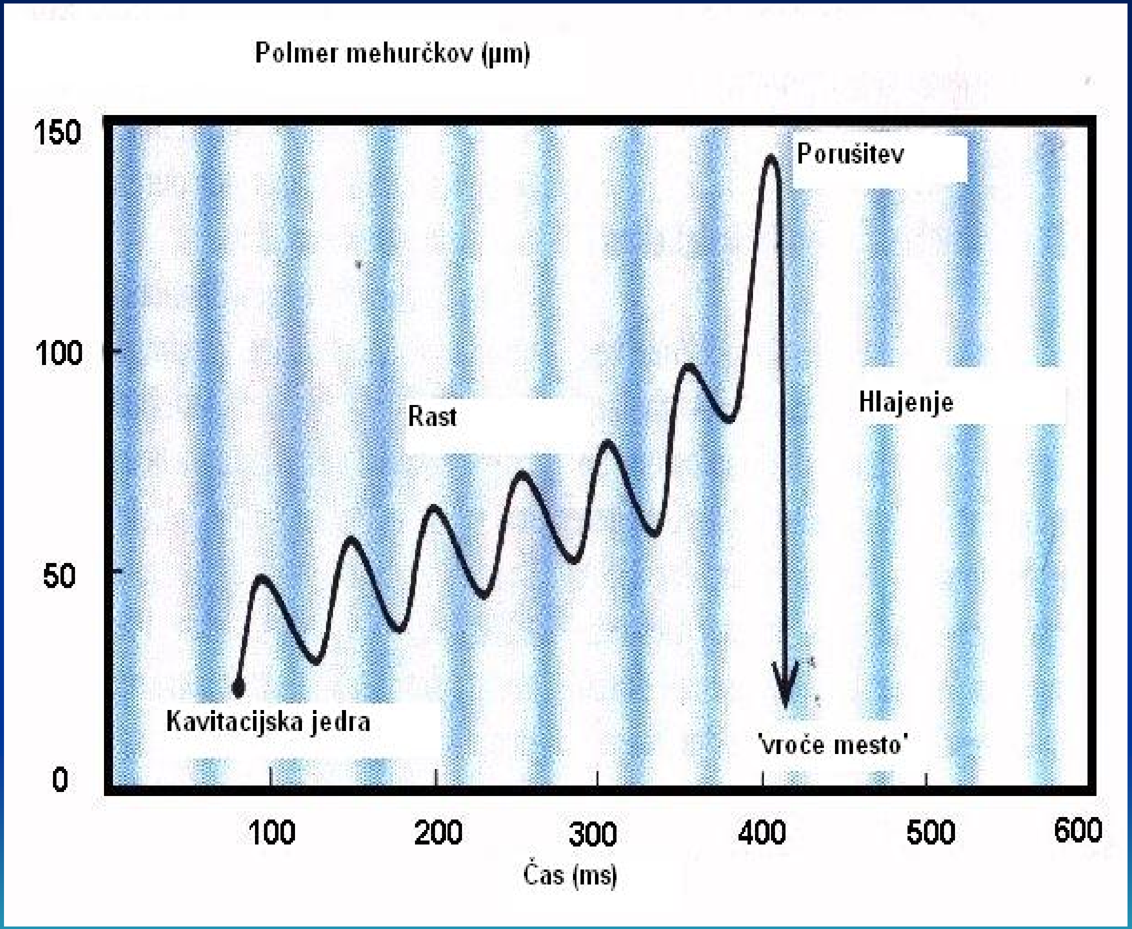
- Effect of ultrasound to molecules: indirect, most probable through the mechanism called **acoustic cavitation**: formation, growth and implosive collapse of gas/vapour bubbles inside the liquid
- Extreme conditions at the collapse[1] ('hot – spot') :

  $T > 5000^0C$, $P > 2000$ bar, $\Delta T / \Delta t \approx 10^9$ K/s

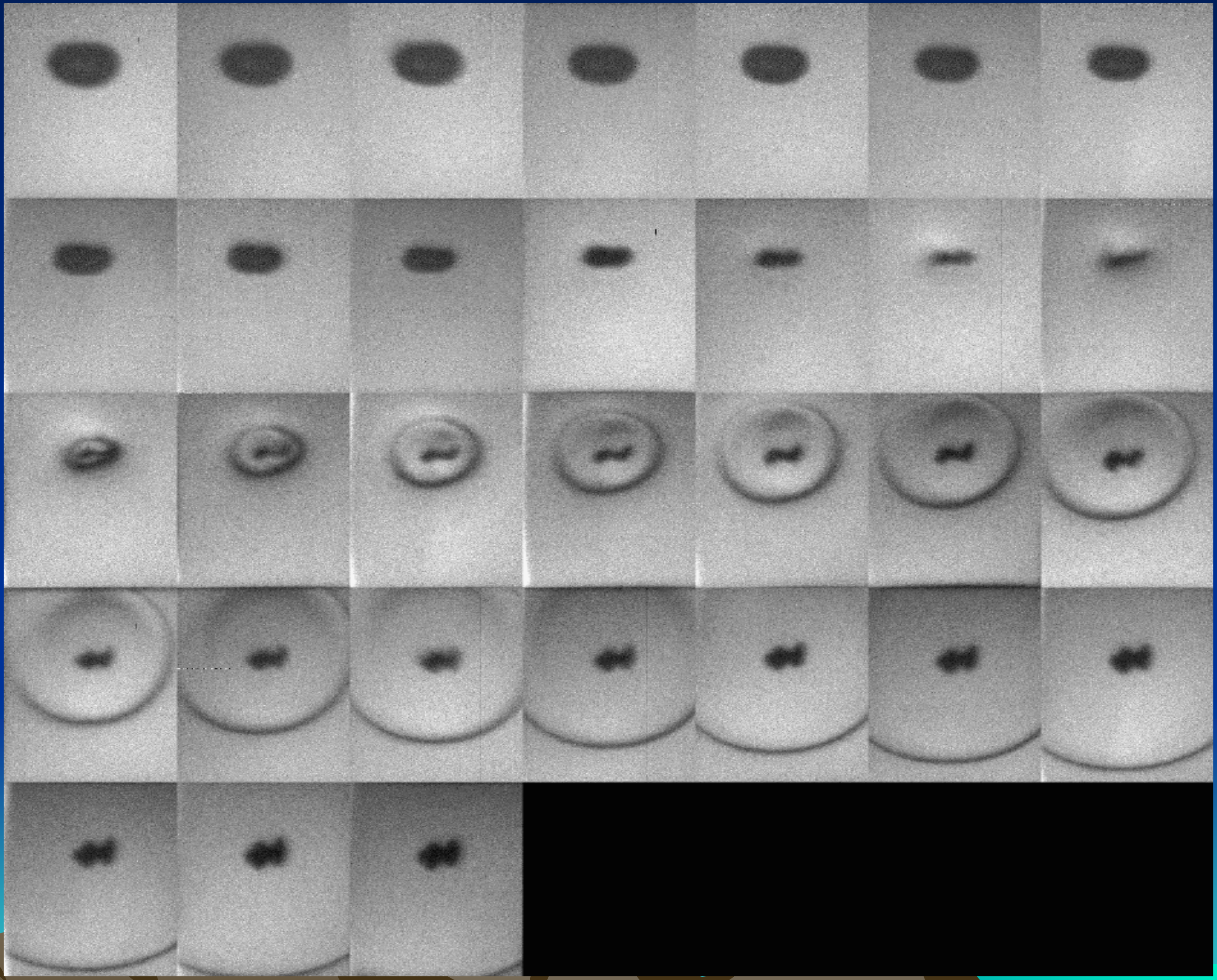
1: K. S. Suslick, Science 247 (1990) 1439

Bubble dynamics inside a liquid

- Formation, growth and implosive collapse of gas bubbles inside a liquid



Photograph of a collapsing bubble during acoustic cavitation, 20 million frames / s



Some new theories of theoretical sonochemistry:

There are **two** reaction sites during the bubble collapse:

- **Gaseous / volatile reagents**: the reaction takes place inside the collapsing bubble in the gaseous phase, T > 25000^{0}C, $\Delta T / \Delta t \approx 10^{11}$ K/s → products are always **amorphous**
- **Non volatile reagents:** the reaction takes place in the liquid phase (≈ 200 nm) just outside the collapsing bubble, T ≈ 1900^{0}C → products are either **amorphous or nanocrystalline**[2]

2: A. Gedanken, Ultrason. Sonochem. 11 (2004), 47.

Sonochemical syntheses of transition metal **sulfides**: literature review

Compound	*Year*	*Reactants*	*Solvent*	*Atm.*
MoS_2	1998	$Mo(CO)_6$ + S	tetramethyl-benzene	Ar
ZnS	1999	$Zn(Ac)_2$ + thioacetamide	water	air
HgS PbS	2000	$Hg(Ac)_2$ + S $Pb(Ac)_2$ + S	ethylenediamine 1 - decanethiol	air
$RuS_{1.7}$	2000	$RuCl_3$ + thiourea	water	Ar
WS_2	2002	$W(CO)_6$ + S	diphenylmethane	Ar

Compound	*Year*	*Reactants*	*Solvent*	*Atm.*
Au_2S_3 [3]	2003	$Au(Ac)_3$ + S	decaline	N_2
α - HgS β - HgS	2004	$Hg(Ac)_2 + Na_2S_2O_3$ $Hg(Ac)_2$ + thiourea	water + TEA water	air
ZnS	2005	$Zn(Ac)_2$ + S	ethylenediamine 1-decanethiol	air
CdS	2006	$Cd(Ac)_2$ + S	ethylenediamine 1-decanethiol	air
HgS [4]	2008	$Hg(NO_3)_2$ + S	water / EDTA	air

3: M. Kristl, M. Drofenik, Inorg. Chem. Commun. 6 (2003), 1419.
4: M. Kristl, M. Drofenik, Ultrason. Sonochem. 15 (2008), 695.

Sonochemical syntheses of transition metal **selenides** and **tellurides**: literature review

Compound	*Year*	*Reactants*	*Solvent*	*Atm.*
Ag_2Se CuSe PbSe	1999	$AgNO_3$ + Se CuI + Se $PbCl_2$ + Se	ethylenediamine	air
Cu_4Te_3 Cu_7Te_4	2000	$CuCl_2$ + Te	ethylenediamine en + N_2H_4	air
ZnSe	2000	$Zn(Ac)_2$ + selenourea	water	Ar

Compound	*Year*	*Reactants*	*Solvent*	*Atm.*
$Cu_{2-x}Se$ β – CuSe Cu_3Se_2	2001	CuI + Na_2SeSO_3	water + EtOH water + hexanole	N_2
Ag_2Te Ag_7Te_4	2001	$AgNO_3$ + Te	ethylenediamine EtOH	air
α - CuSe	2002	$Cu(Ac)_2$ + Se	DMSO	H_2/Ar 5:95
HgSe	2002	$Hg(Ac)_2$ + Na_2SeSO_3	water + NH_3 / en / triethanolamine	air

Compound	*Year*	*Reactants*	*Solvent*	*Atm.*
CdSe	2003	$CdCl_2$ + Na_2SeSO_3	water + NH_3	air
HgSe	2003	$Hg(Ac)_2$ + Se	PEG	air
$MoSe_2$ [5]	2003	$Mo(CO)_6$ + Se	decaline	N_2
Bi_2Se_3	2004	$Bi(NO_3)_3$ + Na_2SeSO_3	water + EDTA	air
HgTe	2004	$Hg(ClO_4)_2$ + Te	ethylenediamine	air

5: M. Kristl, M. Drofenik, Inorg. Chem. Commun. 6 (2003), 68.

Compound	*Year*	*Reactants*	*Solvent*	*Atm.*
CdSe	2007	$Cd(Ac)_2$ + Na_2SeSO_3	water + tartaric acid	air
HgSe [4]	2008	$Hg(NO_3)_2$ + Se	EDTA (0.1 M) + NaOH (2.5 M)	air
HgTe [4]	2008	$Hg(NO_3)_2$ + Te	EDTA (0.1 M) + NaOH (5M)	air

4: M. Kristl, M. Drofenik, Ultrason. Sonochem. 15 (2008), 695.

Experimental: Synthesis of Ag_2E (E = S, Se, Te)

Used chemicals:

- $AgCH_3COO$, 99%, Sigma - Aldrich
- ethylenediamine, p.a., Aldrich
- elemental S, Merck
- Se, 99.5%, 100 MESH, Aldrich
- Te, 99.8%, 200 MESH, Aldrich

Synthesis of Ag_2S:

- 0.005 mol (= 0.8345g) $AgCH_3COO$ + 25 mL en
- dissolving on a magnetic stirrer
- + 0.0025 mol (= 0.080g) S
- stirring 10 – 15 min
- sonication with high – intensity ultrasound (15 – 120 min)
- separation with a centrifuge 5 min (5000 min^{-1}), washing 2x with water + 1x EtOH (absolute)
- air drying, 24 – 48 h

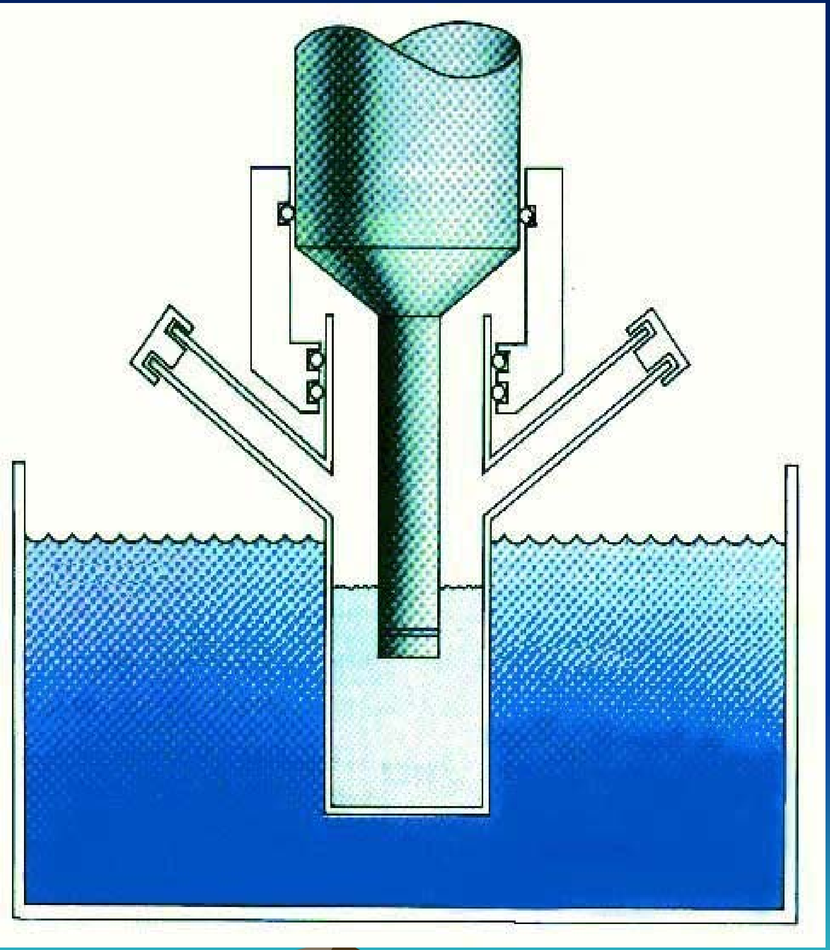
Synthesis of Ag_2Se in Ag_2Te:

Identical procedure as described before, except for:

- m (Se) = 0.1975 g (n = 0.0025 mol)
- m (Te) = 0.3190 g (n = 0.0025 mol)
- at some experiments cooling of the reaction mixture
- at some experiments 10% or 20% excess of Te
- replacing $AgCH_3COO$ with $AgNO_3$: m = 0.849 g (n = 0.005 mol)

Used ultrasonisc system:

- Sonics & Materials VCX 750
- 1.25 cm^2 Ti – probe
- 20 KHz
- 100 W/cm^2
- 50 mL beaker

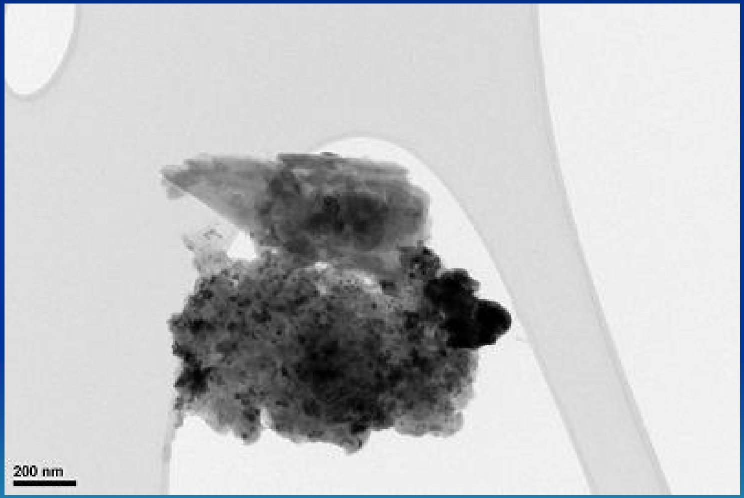


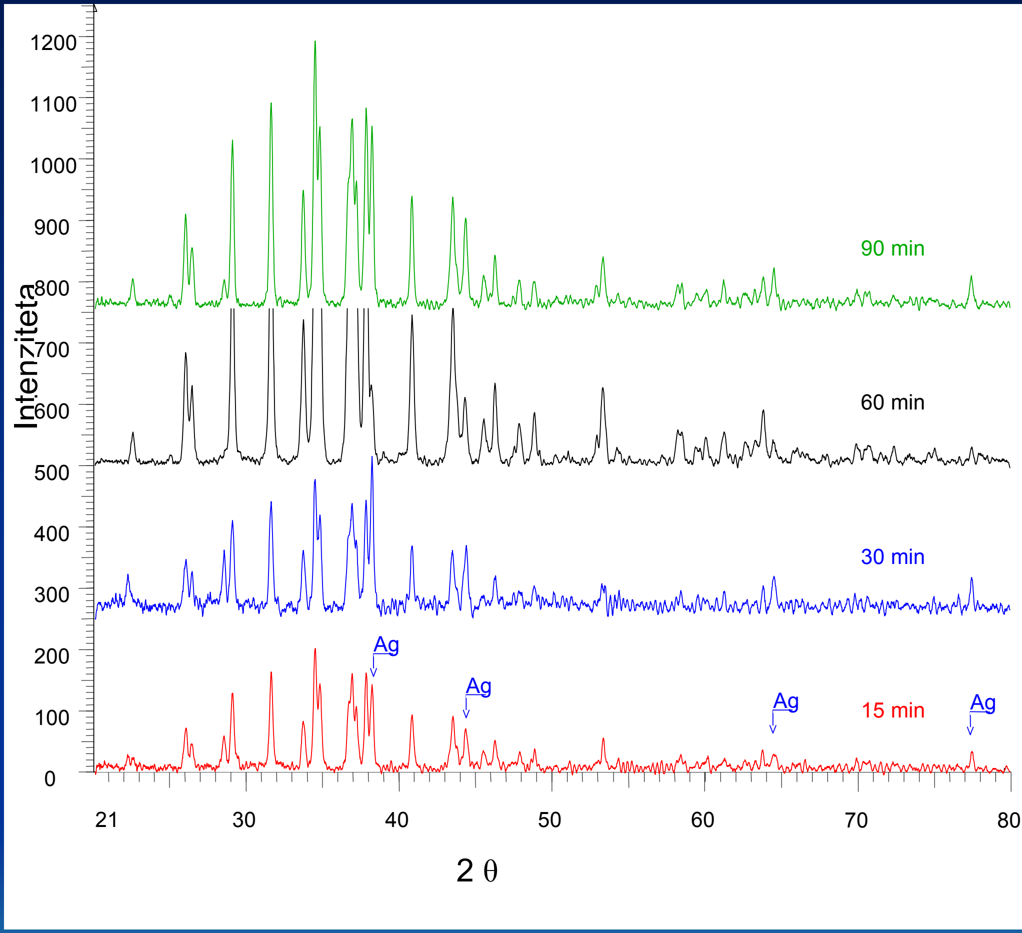
Characterization:

- X – ray powder diffractometer (XRD): *AXS-Bruker/Siemens D5005*, CuK_{α} radiation, graphite monochromator (λ = 1.54178 Å)
- Transmission electron microscope (TEM): *JEOL JEM-2100*, working voltage 200 kV, Cu - grid
- Energy dispersive X-ray spectroscopy (EDS)

Results – Ag_2S

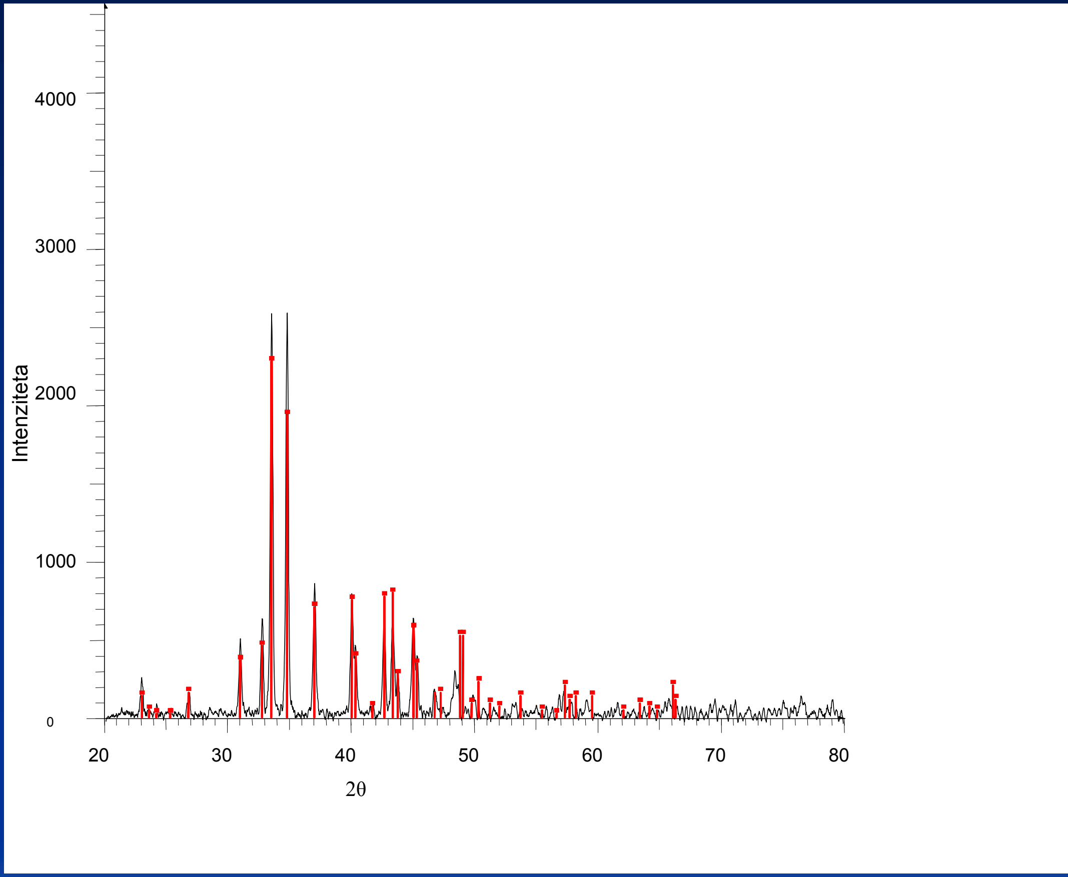
- Different reaction times
- Main product: Ag_2S, PDF No. 00-014-0072
- EDS: Ag_2S + Ag

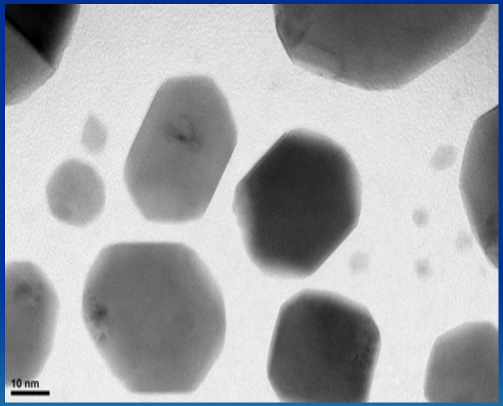




Results – Ag_2Se

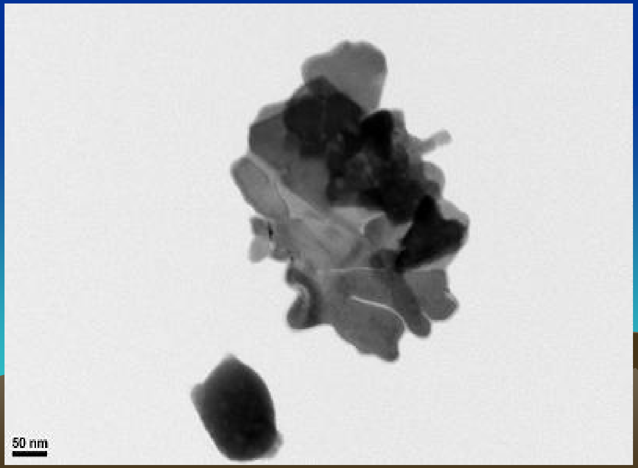
- Reaction time: 1h
- pure Ag_2Se, PDF No. 00-024-1041
- EDS: 65 at % Ag + 35 at % Se

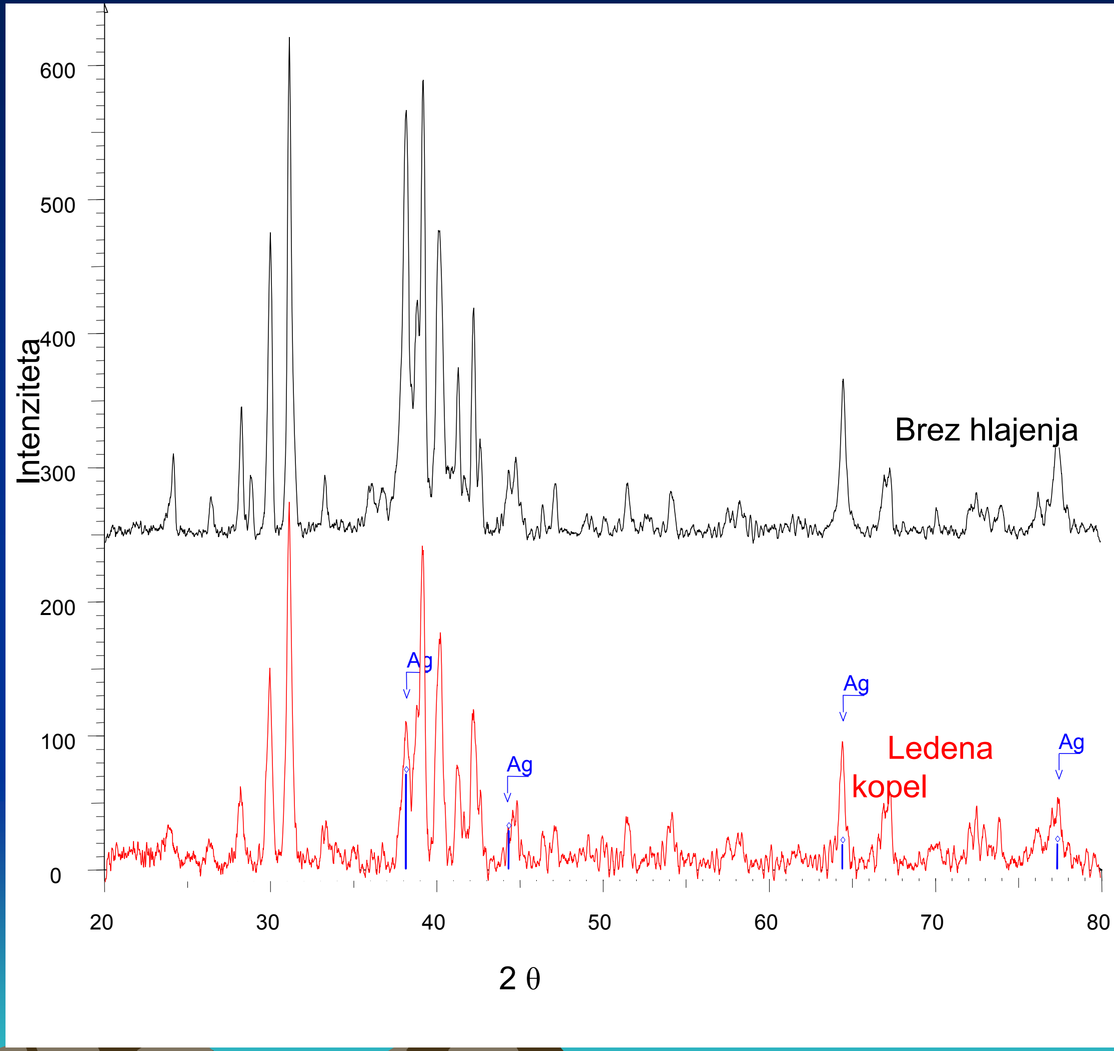




Results – Ag_2Te

- Reaction time: 1h
- Ag_2Te, PDF No. 00-034-0142
- EDS: 64 at % Ag + 36 at % Te
- cooling reduces the presence of Ag!





Conclusion

- Overview of recent achievements in the area of sonochemical syntheses of transition metal chalcogenides
- Rapid growth of publishing: *sono** + *nanop** =
  - 2 hits (1994 + 1995),
  - 59 hits (2002),
  - 124 hits (2007)

- comparatively simple method for the synthesis of silver sulphide, -selenide and -telluride.
- establishing optimal reaction conditions
- further investigations underway!

Acknowledgment

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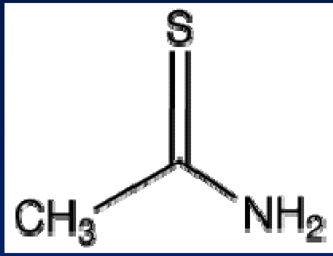
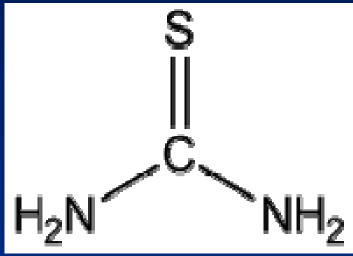
- Tina Kelc, *prof. ke - bio*, for helping in laboratory work

Supplement: formulae of some reagents

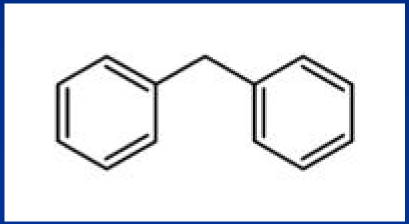
- Thioacetamide: CH_3CSNH_2



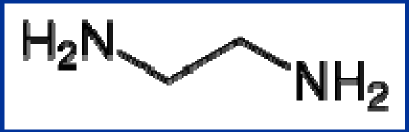
- Thiourea: $(NH_2)_2CS$



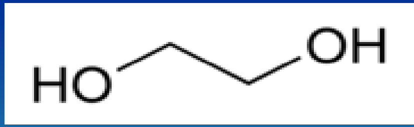
- 1 –decanethiole: $CH_3(CH_2)_9SH$
- Diphenylmethane: $(C_6H_5)_2CH_2$



- Ethylenediamine: $C_2H_4(NH_2)_2$



- Ethylene glycol: $C_2H_4(OH)_2$



- Triethanolamine: $N(C_6H_{12})(OH)_3$