

CHARACTERIZATION OF THE NATURAL MINERAL FORM FROM THE PbS–Sb₂S₃ SYSTEM

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Abstract

This paper presents the results of experimental investigations of natural mineral form from the PbS – Sb₂S₃ system. Investigated sulfosalt appears in nature in the form of nanowires with diameters ranging from 200 to 500 nm and its length can reach up to 150 μm. In most cases these nanowires are arranged like bundles, which were inspected with scanning electron microscopy (SEM). The chemical composition of this material was analyzed and its stoichiometry responded to “plumosite”. Crystal structure was analyzed using XRD analyses and compared to available literature data. Investigated samples were subjected to thermal analyses and resulting mechanism of oxidation was concluded. Also, kinetic parameters were calculated for the process of oxidation.

Keywords: Sulfide materials; Oxidation; Reaction kinetics.

1. Introduction

It is well known that semiconductor nanowires have attracted great research interest in materials science for several years due to their potential use in microelectronic, electronic, optical, magnetic and sensor

devices [1, 2, 3]. For making semiconductor nanowire devices, the contacting is one of the most important procedures. The metallic contacts have to be stable and the contact resistance has to be low. Furthermore, for low-temperature measurements the contacts should remain of good quality at milli-

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Kelvin temperatures. Thus, the design of nanostructures of the commonly-used semiconductor materials such as Si and ZnO could be appreciably improved using new materials [4]. According to this, attempts were made to find alternative materials, which are promising for applications in the nanotechnology [5, 6]. It is known that the properties of the semiconductors are strongly influenced by the type of elements presented in the structure mainly because of the role that *d* electrons play in their chemical bonding [7]. Recently, it was reported that it is possible to synthesize nanowires and nanotubes of binary sulfides like MoS₂, [8] PbS [9, 10] and Sb₂S₃ [11] which are natural existing minerals as well. Synthesizing enables introduction of an element with unoccupied *d* orbitals that favors low energy electronic movements which influence the optical and physical properties of those materials.

As known from the literature the bulk materials of PbS–Sb₂S₃ sulfosalts are semiconductors having band gaps between 1.2 and 1.7 eV including boulangerite with a band gap of 1.34 eV.[12] Sulfosalts are complex sulfides of similar structures, consisting of long layers or chains of M–S-polyhedra (M=Pb and Sb) on the basis of the archetype structures of SbS and PbS [13]. Because of relatively strong bonds in chain direction, PbS–Sb₂S₃ sulfosalts tend to grow as thin needles parallel to the chain direction. Furthermore, the formation of closed microrings was reported for PbS–Sb₂S₃ natural minerals, [14] which have not been completely understood so far.

Based on the extremely rare occurrence of nanowires of natural boulangerite

(Pb₅Sb₄S₁₁) and jamesonite (FePb₆Sb₄S₁₄), [14] synthesis of nanowires of boulangerite and other mineral forms in the PbS–Sb₂S₃ system obtained scientific significance lately. Results of characterization of those sulfosalts are presented in literature references.[13, 14, 15]

If having in mind growing interest for those compounds from the PbS–Sb₂S₃ system, it should be noted that basic information concerning physicochemical and mineralogical characteristics of this system are not completely investigated yet. Fortunately, natural minerals from the PbS–Sb₂S₃ system could be found in mineral deposits in our country, which gave us the opportunity to study this system using natural mineral forms instead of sensitized ones. Accordingly, in this paper we investigated characteristics of natural sulfosalt from the PbS–Sb₂S₃ system obtained from Trepča mine locality (Serbia). According to the expert's evaluations this mine has reserves of 60 millions tons of ore containing 5 millions tons of lead and zinc metal. Sulfosalts from the PbS–Sb₂S₃ system are largely contained at this locality.

Natural occurrence of sulfosalts from the PbS–Sb₂S₃ system is reported in following localities worldwide: Tuscany (Italy); Trepča (Serbia); Baja Mare (Romania); Nova Litica (Bosnia and Herzegovina); Příbram (Czech Republic); Molières (France); Sala (Sweden); Nerchinsk (Russia); Nevada (USA); Tasmania (Australia) and in some localities in Chile, Peru, Bolivia and Mexico.

Most common natural mineral form from the PbS–Sb₂S₃ system is boulangerite. It is usually situated in ore deposits of antimony and lead ores and often contains Fe, Ni, Cu,

Zn and Ag as minor constituents. Other known mineral forms from this system are fulopit ($\text{Pb}_3\text{Sb}_8\text{S}_{15}$); zinkenite (PbSb_2S_4); plagionite ($\text{Pb}_5\text{Sb}_8\text{S}_{17}$); semseyite ($\text{Pb}_9\text{Sb}_8\text{S}_{21}$); yenerite ($\text{Pb}_{11}\text{Sb}_8\text{S}_{22}$) and meneghinit ($\text{Pb}_{13}\text{Sb}_7\text{S}_{23}$).

Maybe the most interesting mineral form from the $\text{PbS-Sb}_2\text{S}_3$ system is “plumosite” ($\text{Pb}_2\text{Sb}_2\text{S}_5$). This mineral form is occurring in Trepča mine, in many of ore mines in the vicinity of Baia Mare and in other Miocene vein type deposits elsewhere in northern Romania [16]. There are lots of discrepancies concerning “plumosite” as mineral form. Many authors don't approve existence of “plumosite” as separate mineral form. It is often referred as iron free jamesonite [16, 17] or even synonym of boulangerite [18]. Although Mumme [18] noted the apparent structural identity of “plumosite” and suggested that it may in fact be a discrete phase within the meneghinite ($\text{Pb}_{13}\text{CuSb}_7\text{S}_{24}$) homologous series. In this manner, the term “plumosite” has been used to describe fibrous varieties of a number of Pb sulfosalts over the past 150 years. In the literature reference Cook and Damian, [19] the authors suggest usage of the term “plumosite” in the sense of Oudins [20] description: “as a descriptive term which may be applied to jamesonite, boulangerite, zinkenite, any other lead sulfosalt, or as mixture thereof, that has a plumosite texture or that occurs in a fibrous aggregate”. On the other hand, on the basis of analysis of composition and structural investigations of falkmanite ($\text{Pb}_5\text{Sb}_4\text{S}_{11}$) and boulangerite, Mozgova [21] et al suggested that the name “plumosite” should be applied for Pb-poor boulangerite ($\text{Pb}_{<4.7}\text{Sb}_{>4.2}\text{S}_{11}$).

The aim of this paper is to present first hand results concerning the structure and physicochemical characteristics of natural $\text{PbS-Sb}_2\text{S}_3$ sulfosalt from Trepča mine. Also, this paper presents the results of thermal analysis and kinetic parameters of the investigated sample oxidation process.

2. Experimental procedure

Starting sample for investigations presented in this paper was natural mineral form from the $\text{PbS-Sb}_2\text{S}_3$ system obtained from Trepča mine, which appears in nature as wool of microscopic needles or nanowires with diameter range from 200 to 500 nm. Those wires are highly flexible. When crushed to powder, they become very adhesive.

Mineralogical investigations were conducted using X-ray diffraction (XRD) with the atomic powder diffractometer “PHILIPS” APD SYSTEM PW 1710, under the following conditions: 2θ range (5-90°), velocity 0,05°/s, Cu anti-cathode with 40A current and voltage of 35 V.

Characterizations of investigated samples were done using scanning electron microscopy (SEM) with EDEX-9100 analyses and PAX software package, with resolution of 1 nm (30kV), excitation voltage of 0,2-30kV, maximum magnification of 500000 times and with the secondary electron detector. Energy Dispersion X-ray Fluorescence analysis was done on Canberra equipment with the radioisotopes: Cd-109 (22.1 keV) and Am-241 (59.5 keV).

The non-isothermal oxidation process was investigated using the results of DTA analysis. A thermal analysis Derivatograph

1500 (MOM Budapest) was used, operating under the following conditions: air atmosphere, heating rate of 20°C/min and $T_{\max} = 1273$ K.

3. Results and discussions

Results of X-ray analysis of the starting sample were compared with results reported for the mineral forms of the PbS–Sb₂S₃ system present in the literature (Table 1). This was the only way possible for discussing X-ray results, since mineralogical databases rarely contains enough data concerning this system. Diffraction study presented in this paper was compared to diffraction patterns from Herja (Romania) “plumosite” [19] and jamesonite; [22] jamesonite from Bolivia [23] and of benavidesite from Uchucchacua (Peru) [20], which had a Mn/(Fe+Mn) ratio of 0.61.

Results of X-Ray analysis for “plumosite” from Herja (Romania) [19] showed the phase to correspond to jamesonite with a slight peak shift toward the Mn-analogue of jamesonite, benavidesite, Pb₄(Mn,Fe)-Sb₆S₁₄. It was concluded that the relatively high Mn content of the Herja “plumosite” caused this shift [20, 24]. Udubasa et al., [16] interpret “plumosite” to have been one of the latest minerals to have crystallized from hydrothermal solution and from this reason, collected the relatively incompatible elements such are Mn or Ti.

Presence of Mn is confirmed in investigated sample from Trepča, as well, using EDXRF analysis. Nevertheless, amount of Mn in sample was too small to have significant influence on RDA results. If compare peaks in table1, it is obvious that

“plumosite” from Trepča has largest phase correspondence to jamesonite. This proved statement published in book of Tučan, [17] where “plumosite” from Trepča was described as iron free jamesonite.

Both natural (this work) and synthetic [14] PbS-Sb₂S₃ sulfosalts with boulangerite as main mineral form were found to grow as microscopical needles consisting of parallel intergrown nanowires (Figure 1), where the diameter of each individual wire ranges between 200 and 500 nm and its length can reach up to 150 μm.

EDX spot analysis, presented in Figure 1 (as spectrum 1), revealed following composition: Pb = 51.57%, Sb = 29.56% and S = 18,87%. This composition is almost equal to stoichiometry of pure “plumosite” (Pb₂Sb₂S₅), which is: Pb 50.65%, Sb 29.76% and S 19.59%.

Further EDXRF analysis upon fluorescence excitation with the 241Am radioisotope discovered small amount of Mn and Fe impurities, Figure 2.

The results of the differential thermal analysis (DTA), of the investigated sample are presented in Figure 3. The DTA results show the existence of a first exothermal peak in the temperature range 97.33-146.89°C and the second one at 146.89-181.59°C, followed by endothermal peak at 237.87-527.86°C and then again two exothermal peaks at 527.86-591.17°C and 591.17-632.82°C.

According to the DTA analysis, XRD characterization of the samples heated at 500° and 700°C, Gibbs free energies change versus temperature calculated for potential reactions (Figure 4) and previous investigations of Sb₂S₃ and PbS oxidation processes,[24, 25] mechanism of PbS-Sb₂S₃

Table 1. X-Ray diffraction spectra of investigated sample compared to literature results, [19, 21, 22, 23]

Plumosite Trepča (present study)		Plumosite [19]		Jamesonite [20]		Jamesonite [21]		Benavidesite [20]	
d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I
		9.552	1	9.47	8			9.57	5
		8.161	9	8.09	14			8.17	10
		6.065	6	6.01	12	6.05	5	6.08	5
		5.901	1	5.87	8			5.91	
		5.048	1	5.03	6	5.05	5	5.06	5
		4.08	28	4.06	25	4.07	30	4.09	30
		3.926	2	3.9	16	3.92	40	3.93	5
3.825	28	3.845	7	3.82	30			3.85	20
3.705	40	3.712	2	3.7	35	3.7	20	3.72	10
		3.587	4			3.59	30		
		3.528	10	3.51	12			3.53	5
3.42	100	3.436	100	3.43	100	3.43	100	3.44	100
3.296	10	3.342	3	3.33	10	3.34	10	3.35	10
3.198	40	3.196		3.2	12				
		3.184				3.17	50		
		3.153	6	3.14	12			3.166	20
		3.12	2	3.11	14				
		3.099	3			3.1	50	3.103	
		3.086	13					3.091	20
		3.078		3.08	30				
		3.035		3.01	10				
2.962	30	2.951	12	2.94	16	2.93	20	2.956	40
		2.825	6			2.83	90	2.831	
2.804	40	2.819	7	2.813	35			2.821	30
		2.658	3	2.656	12			2.742	
		2.72	30	2.714	35			2.725	
2.682	15	2.682	2	2.675	16				
		2.658		2.656	12			2.677	5
2.364	10	2.367	1	2.361	8	2.36	10	2.356	5
2.298	12	2.295	8	2.29	12	2.29	30		
		2.285	2					2.289	5
2.245	5	2.242	5	2.236	12	2.23	40	2.249	

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		2.241	5					2.245	20
		2.236	3						
		2.184						2.187	5
2.17	5	2.173	2						
		2.116	1	2.109	6				
								2.185	
								2.127	10
		2.126	1					2.13	
								2.104	
								2.104	
								2.06	5
		2.061	2						
		2.054	2	2.047	12			2.061	
		2.032	1	2.026	12				
		2.03	3					2.034	
		2.022	3						
		2.013	1					20.03	
		1.943	3						
				1.942	8				
1.915	25	1.91	4	1.909	25				
				1.894	10				
		1.867							
1.859	26			1.857	10				
				1.826	12				
1.758	25			1.756	8				
				1.716	10				
				1.516	6				
1.455	10			1.452	6				

sulfosalt sample oxidation could be concluded. In narrow temperature interval from the beginning of oxidation to 130°C (peak at 116.6°C) Sb_2S_3 is oxidized to $\text{Sb}_2(\text{SO}_4)_3$. After this temperature Sb_2S_3 is oxidized to Sb_2O_3 (130 – 200°C with peak at 159.9°C), with parallel reaction of Sb_2O_3 to SbO_2 and further to $\text{Sb}_2(\text{SO}_4)_3$ until 490°C

and only to SbO_2 above this temperature. This reaction mechanism was to some extent similar to those of pure Sb_2S_3 oxidation, reported in previous investigations [25]. Only difference was that $\text{Sb}_2(\text{SO}_4)_3$ wasn't recorded in the previous study. $\text{Sb}_2(\text{SO}_4)_3$ starts to dissociate at the temperatures above 690°C back to Sb_2O_3 . RDA analyses

discovered Sb_2O_3 and $\text{Sb}_2(\text{SO}_4)_3$ at 500°C , while at 700°C only Sb_2O_3 and SbO_2 remained in the sample. Peak at 159.9°C also covers oxidation of PbS to PbO_2 . This compound is stable until 350°C where it starts to decompose endothermally to XRD (peak at 405.8°C). Small amount of PbO_2 was determined with X-ray analysis even at

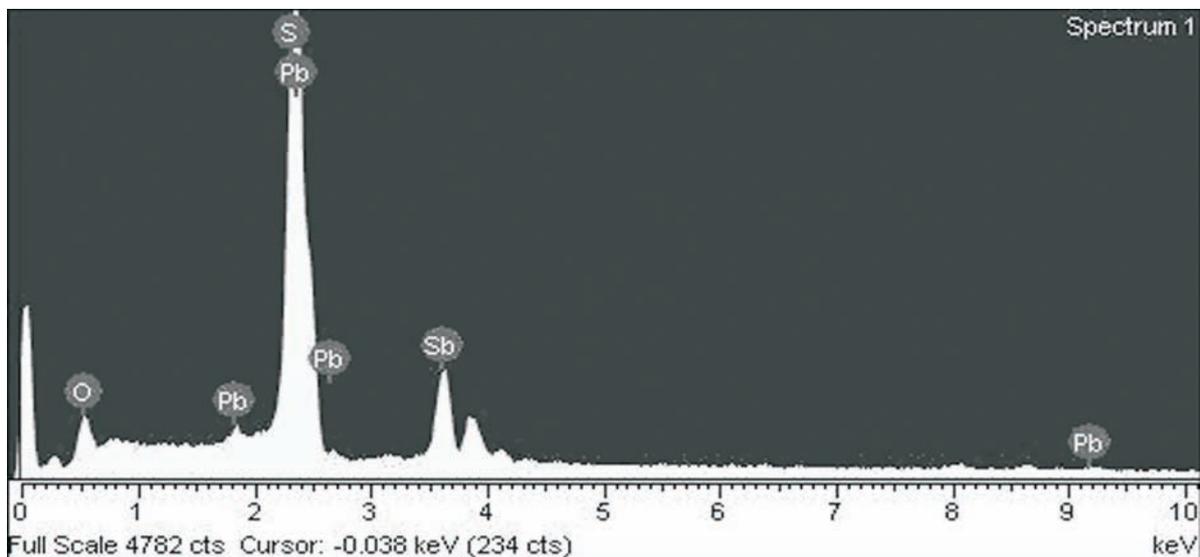
500°C , while on 700°C this compound wasn't recorded in the sample. Remaining PbS is oxidized to PbSO_4 (peak at 554.4°C) and consequently to PbO (peak at 602.7°C), similar mechanism responded for pure PbS investigated earlier [26]. PbSO_4 was determined using XRD both on 500 and 700°C .

3.1. Kinetics

According to the nature of the investigated oxidation process in the $\text{PbS-Sb}_2\text{S}_3$ system, which results in the corresponding shape of DTA curve, Figure 3, it is possible, using non-isothermal model of Borchardt and Daniels [27], to determine the activation energy of oxidation, in the temperature ranges: $97,33 - 146,89^\circ\text{C}$; $146,89 - 181,59^\circ\text{C}$; $237,87 - 527,86^\circ\text{C}$; $527,86 - 591,17^\circ\text{C}$ and $591,17 - 632,82^\circ\text{C}$, respectively.



a)



b)

Fig.1. $\text{PbS-Sb}_2\text{S}_3$ sulfosalt from Trepča. (a) SEM image of some bundles. Each bundle consists of few individual single-crystalline wires (b) EDX spectra (spot analysis) of investigated sample

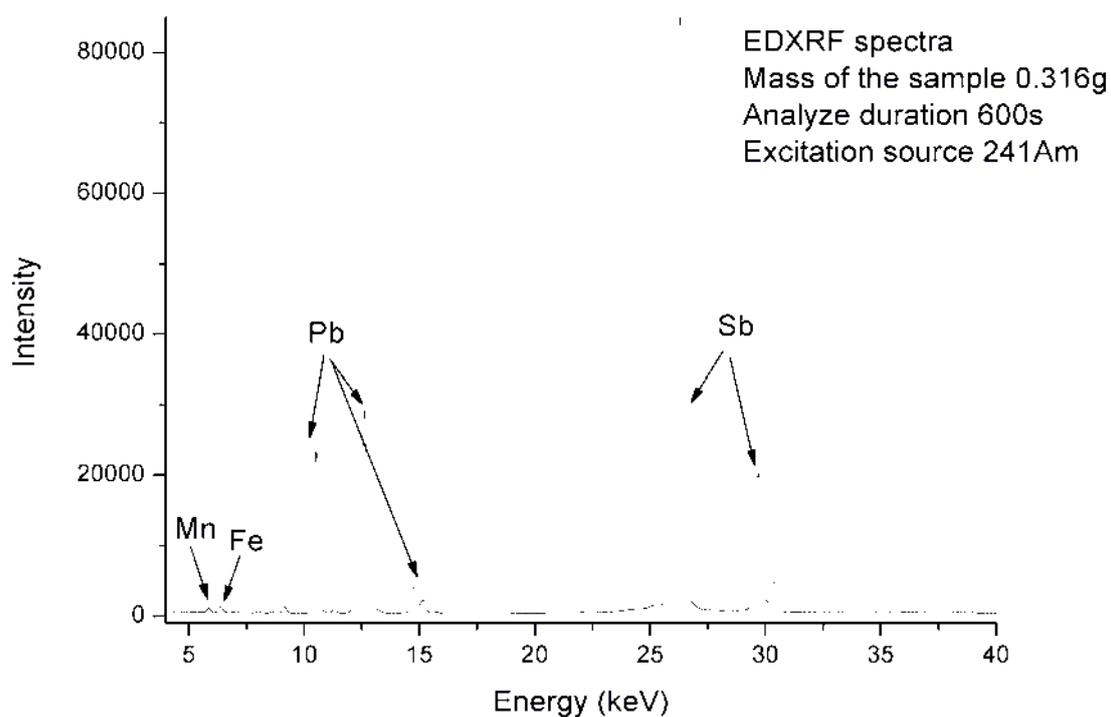


Fig.2. EDX spectra (whole sample area) of investigated sample

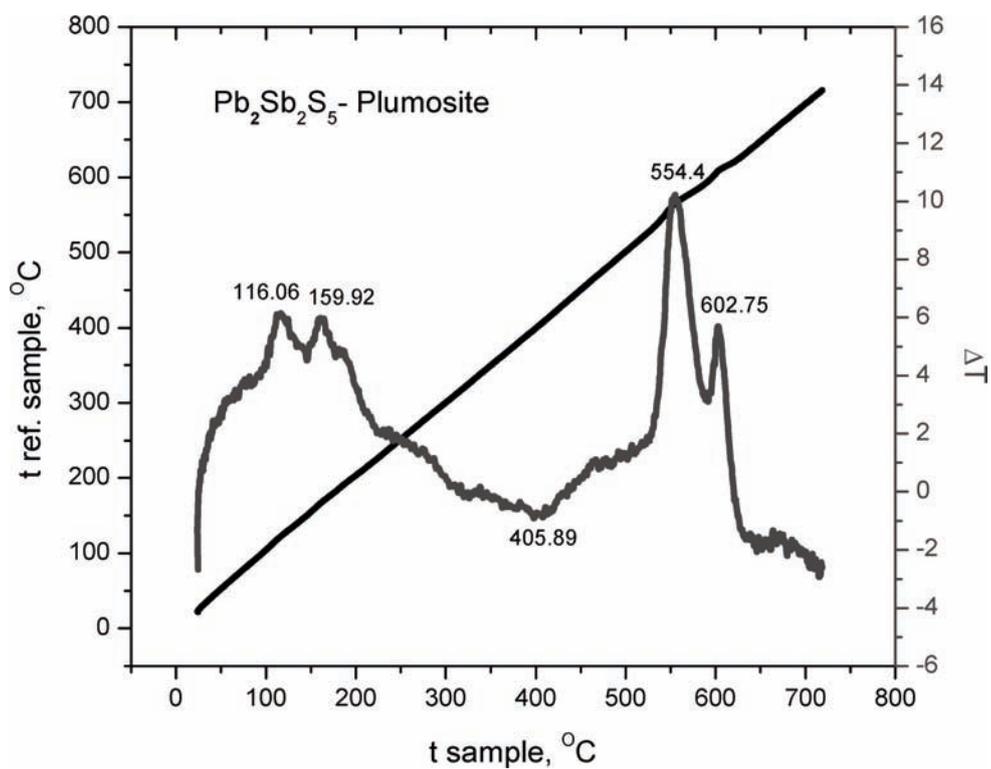


Fig. 3. Results of DTA analysis of the investigated sample

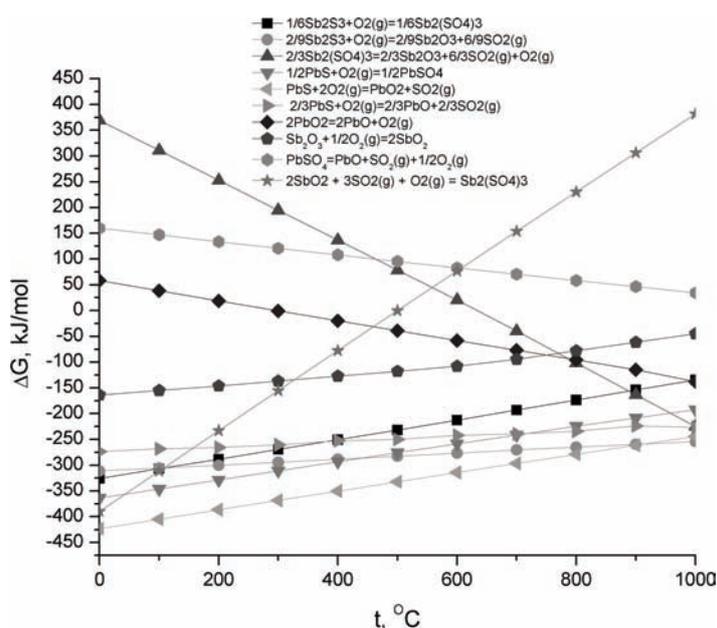


Fig.4. Graphic presentation of Gibbs free energy change vs. temperature for the potential reactions in the PbS-Sb₂S₃ system (HSC software)

Using equation:

$$k_i = \Delta T_i / A - a_i \quad \dots(1)$$

which is the essence of the Borchardt and Daniels model (where *A* is the area of the

peak present on the DTA curve, *a_i* – the areas of the peaks segments and ΔT_i – the temperature interval of the segments), the rate constants *k_i* were determined for different temperature intervals. Based on

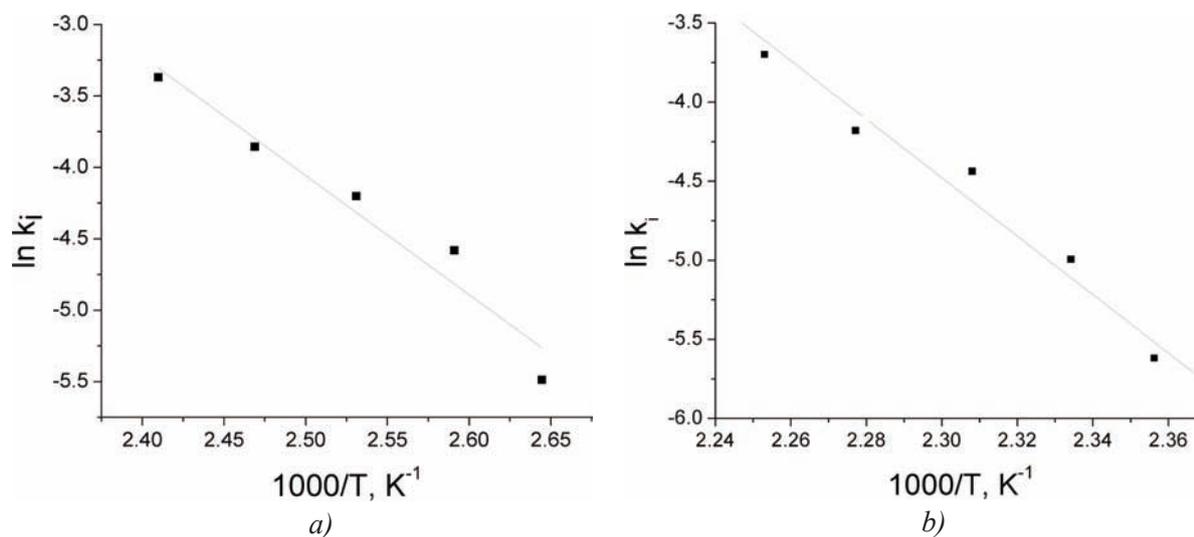


Fig. 5. Arrhenius diagrams for the process of PbS-Sb₂S₃ sulfosalt oxidation obtained under non-isothermal conditions in the temperature interval: a) 97.33-146.89°C; b) 146.89-181.59°C;

these results, the corresponding Arrhenius diagrams were constructed and presented in Figure 5.

Based on the diagrams in Fig. 5, the corresponding values for activation energy have been calculated for the process. Activation energies for characteristic

segments on DTA curves, are found to be 69, 154, 15; 175 and 90 kJ/mol, respectively, which means that oxidation process starts in the kinetic domain, according to classical kinetic theory [28, 29, 30]. Endothermal dissociation is happening under diffusion domain and followed with exothermal

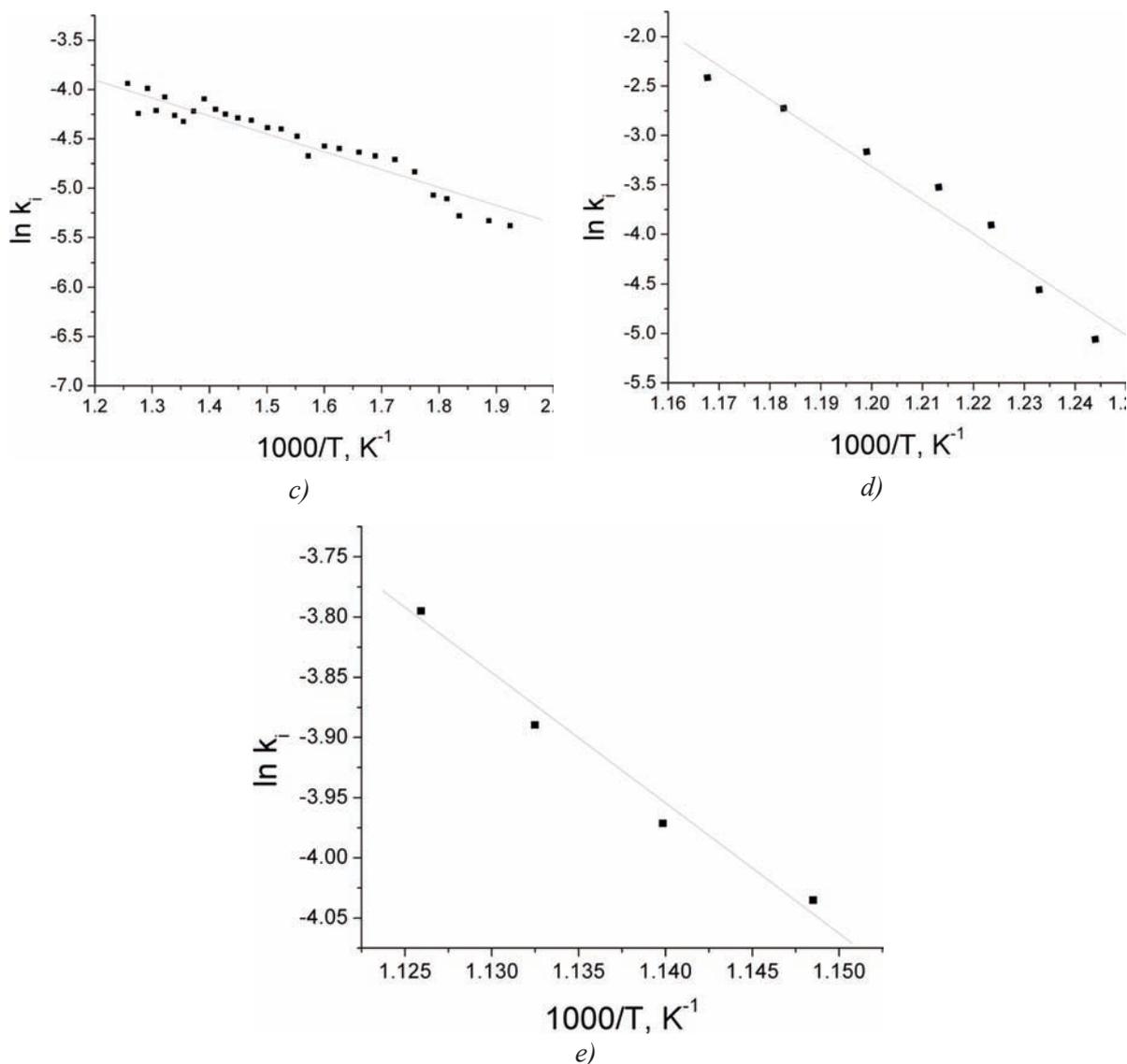


Fig. 5. Arrhenius diagrams for the process of $PbS-Sb_2S_3$ sulfosalt oxidation obtained under non-isothermal conditions in the temperature interval:
c) 237.87-527.86°C; d) 527.86-591.17°C; e) 591.17-632.82°C

oxidation in the kinetic domain, again.

4. Conclusions

Natural mineral form from the PbS-Sb₂S₃ system has been experimentally investigated by DTA, RDA, SEM and EDX analysis. According to the chemical analysis it was found that its composition is close to the “plumosite” (Pb₂Sb₂S₅) stoichiometry, with small content of Mn and Fe discovered using EDX. The RDA analysis positioned this mineral form in the range of “iron free” jamesonite. According to the SEM analysis it was concluded that this natural mineral form is composed of numerous nanowires with diameters ranging from 200 to 500 nm and the length up to 150 μm.

The results including kinetic parameters and mechanism of the investigated process have been determined and presented in the paper. The mechanism of oxidation was determined using DTA and RDA analysis coupled with calculation of Gibbs free energies for potential reactions. It was found that first two exotherms, on DTA curve, respond to two stadiums in Sb₂S₃ oxidation process: Sb₂S₃ → Sb₂(SO₄)₃ and Sb₂S₃ → Sb₂O₃. Second peak is also representing oxidation of PbS to PbO₂. Endothermal peak is representing decomposition of PbO₂ to PbO. Next two exotherms cover oxidation of remaining PbS to PbSO₄ and PbO. This mechanism was in partial accordance with mechanism of separate Sb₂S₃ and PbS samples oxidation [25, 26]. Kinetic analysis, carried out according to Borchardt and Daniels [27], showed that the values of activation energy are consistent with oxidation taking place in kinetic region for

all exotherms, which implies that reaction surface and temperature have the limiting influence on reaction rate. It is also determined that endothermal dissociation is taking place in diffusion region. This means that diffusion of gaseous reactants, through formed oxide layer covering each particle of the starting sample, have the limiting influence on overall reaction rate.

As the next step in further investigation of PbS-Sb₂S₃ system, research of synthesized samples with different stoichiometry could be done, since there is a lack of references dealing with the mentioned system. Also, this kind of new materials investigation is in line with recent trends in extractive metallurgy [31], which could be interpreted as matching strategies to situations [32, 33, 34].

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References:

- [1] J. Hu, T.W.Odom, C.M. Lieber: *Acc. Chem. Res.*, 32 (5) (1999) 435.
- [2] C. Dekker: *Phys. Today*, 1999, 52, 22-28.
- [3] Y. Cui, Q. Wei, H. Park, C.M. Lieber: *Science*, 293 (5533) (2001) 1289 .
- [4] L.X. Yi, J. Heitmann, R. Scholz, M. Zacharias: *Appl. Phys. Lett.*, 81 (22) (2002) 4248.
- [5] H. Hu , B. Yang, Q. Li, X. Liu, W. Yu, Y. Qian: *J. Crystal Growth*, 261 (2004) 485.
- [6] E. Leontidis, M. Orphanou, T. Kyprianidou-

- Leodidou, F. Krumeich, W. Caseri: *Nano Lett.*, 3 (4) (2003) 569.
- [7] M. J. Correia, J. Carvalho, J. Monhemius: *Minerals Engineering*, 14 (2) (2001) 185.
- [8] W. Li, E. Shi, J. Ko, Z. Chen, H. Ogino, T. Fukuda: *J. Crystal Growth*, 250 (3–4) (2003) 418.
- [9] D. Yu, D. Wang, Z. Meng, J. Lu, Y. Qian: *J. Mater. Chem.*, 12 (2002) 403.
- [10] M. Afzaal, P. O'Brien: *J. Mater. Chem.*, 16 (2006) 1113.
- [11] H. Hu, M. Mo, B. Yang, X. Zhang, Q. Li, W. Yu, Y. Qian: *J. Crystal Growth*, 258 (2003) 106.
- [12] H. Ditttrich, K. Herz: *Institute of Physics Conference Series 152 (Ternary and Multinary Compounds)*, 1998, 293.
- [13] A. Skowron, I.D. Brown: *Acta Crystallogr.*, (B) 50 (1994) 524.
- [14] M. Heuer, G. Wagner, T. Doringa, K. Bente, G. Kryukova: *Journal of Crystal Growth*, 267 (2004) 745.
- [15] T. Lager, K. S. E. Forssberg: *Minerals Engineering*, 2 (3) (1989) 321.
- [16] G. Udubasa, G. Ilinca, S. Marincea, G. Sabau, S. Radin: *Romanian Journal of Mineralogy*, 75 (1992) 1.
- [17] F. Tućan, *Special Mineralogy*, Second edition, Zagreb, 1957, p.111. (in Croatian)
- [18] W. Mumme: *Neues Jahrbuch Mineral. Monatsh*, 1989, p.498.
- [19] N.J. Cook, G.S. Damian: *Geologica Carpathica*, 48 (6) (1997) 387.
- [20] E. Oudin, P. Picot, E. Pillard, Y. Monlo, E.A.J. Burke, M.A. Zakrzewski: *Bulletin de Mineralogie*, 105 (1982) 166.
- [21] N.N. Mozgova, N.S. Bortnikov, A.I. Tsepin, Yu.S. Borodaev, S.V. Vrublevskaia, L.N. Vyalsov, O.V. Kuzmina, A.V. Sivtsov: *Neues Jahrb. Mineral. Abh.*, 147 (1983) 80.
- [22] C. Garavelli: *Periodico di Mineralogia*, 27 (1958) 207.
- [23] L.G. Berry: *Mineralogical Magazine*, 40 (1940) 597.
- [24] L.L.Y. Chang, Li Xilin, Z. Chusheng: *Canadian Mineralogist*, 25 (1987) 667.
- [25] Z. Zivkovic, N. Štrbac, D. Zivkovic, D. Grujčić, B. Boyanov: *Thermochimica Acta*, 383 (2002) 137.
- [26] D. Zivkovic, N. Štrbac, I. Mihajlovic, Z. Zivkovic, V. Andric: *Kinetics and mechanism of natural mineral galena oxidation process. In proceedings of VII scientific symposium: „Metallic and nonmetallic materials“*, Zenica, Bosnia and Herzegovina, 2008, p.399.
- [27] H.J. Borchardt, F. Daniels: *J. Am. Ceram. Soc.*, 79 (1957) 41.
- [28] A.W. D. Hills: *Heat and Mass Transfer in Process Metallurgy*, London, 1967 p.39.
- [29] Ž. Živković: *Theory of Metallurgical Processes*, Technical Faculty in Bor., Bor, 1991, p.234. (in Serbian)
- [30] N. Štrbac, I. Mihajlović, D. Minić, D. Živković, Ž. Živković, *Journal of Mining and Metallurgy Section B-Metallurgy*, 45 (1) B (2009) 59.
- [31] F. Habashi, *Journal of Mining and Metallurgy Section B-Metallurgy*, 45 (1) B (2009) 1.
- [32] F.G. Umukoro, O.L. Kuye and A.A. Sulaimon., *Serbian Journal of Management*, 4 (2) (2009) 259.
- [33] I. Stefanovića, P. Damnjanović, O. Jaško, *Serbian Journal of Management* 5 (1) (2010) 97.
- [34] S. Radosavljević, M. Radosavljević, *Serbian Journal of Management*, 4 (1) (2009) 91.