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Use of XPS method in determination of chemical environment and oxidation state of sulfur and silver atoms in $Ag_6S_3O_4$ and $Ag_8S_4O_4$ compounds

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Metal chalcogenide semiconductors such as sulfides (Ag_2S, CdS, ZnS), selenides ($CuGaSe_2$, $CuInSe_2$, ZnSe) and tellurides (Ag_2Te, CdTe, ZnTe) have been studied because of their optoelectronic applications [1, 2]. In particular, silver sulfide (α-Ag_2S, acanthite) is a n-type semiconductor [3, 4] which has been commonly used in photoconductors, photovoltaic and solar cells as well as in infra-red detectors.

Our studies on the reactivity, in air, in the solid state between Ag_2S and Ag_2SO_4 showed that both reagents were not mutually inert and reacted to give two phases: β-$Ag_6S_3O_4$ and β-$Ag_8S_4O_4$ [5–7]. We found that these phases showed polymorphism [8]. Low-temperature polymorphic forms of $Ag_6S_3O_4$ and $Ag_8S_4O_4$ compounds (α-phases) can be obtained, as precipitates, only in the reaction occurring between aqueous solutions of $AgNO_3$ and $Na_2S_2O_3$ [8, 9]. High-temperature polymorphic modification of $Ag_6S_3O_4$ is formed by heating Ag_2S/Ag_2SO_4 mixture according to the following reaction [5, 7]:

$$2Ag_2S_{(s)} + Ag_2SO_{4(s)} = \beta\text{-}Ag_6S_3O_{4(s)} \qquad (1)$$

High-temperature polymorphic form of $Ag_8S_4O_4$, β-$Ag_8S_4O_4$, can be obtained by heating an initial mixture comprising 75.00 mol% of Ag_2S and 25.00 mol% of Ag_2SO_4 according to Equation 2 [6, 7]:

$$3Ag_2S_{(s)} + Ag_2SO_{4(s)} = \beta\text{-}Ag_8S_4O_{4(s)} \qquad (2)$$

α-$Ag_6S_3O_4$ undergoes irreversible, endothermic polymorphic transition to β-phase at 221 °C [9]. β-$Ag_6S_3O_4$ melts at 390 °C [10]. Low-temperature polymorphic form of $Ag_8S_4O_4$ undergoes irreversible, endothermic polymorphic transition to β-$Ag_8S_4O_4$ at 223 °C [9]. The latter phase melts at 400 °C [6]. α-, β-$Ag_6S_3O_4$ and β-$Ag_8S_4O_4$ crystallize in the monoclinic system while α-$Ag_8S_4O_4$ is tetragonal [5, 6, 8, 9]. Thermopower measurements at room temperature showed that α-modifications are p-type semiconductors while β-modifications are of n-type [11].

α- and β-forms of $Ag_6S_3O_4$ and $Ag_8S_4O_4$ compounds were prepared as described previously [5, 6, 9]. X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCA 100 VSW (Manchester, UK) spectrometer with a Mg K_α X-ray source ($h\nu = 1253.6$ eV). The residual pressure inside the analysis chamber was in the 2×10^{-8} mbar range. X-ray photoelectron spectra were calibrated using the $Ag3d_{5/2}$ signal from an Ag-foil (BE = 368.2 eV). The samples were sputtered with an Ar ion beam before the spectra were recorded (energy of Ar^+ ions—2.5 keV, time of sputtering—10 min.).

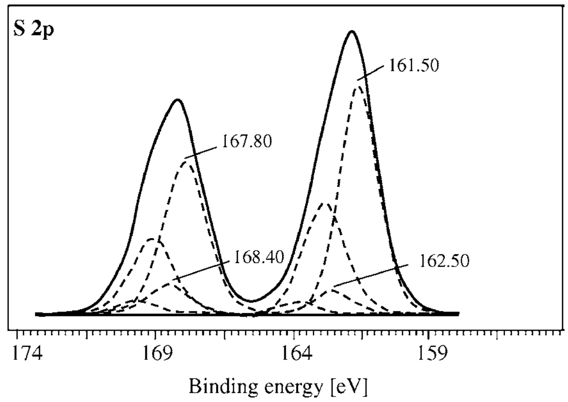

Figure 1 XPS spectrum of S2p for α-$Ag_8S_4O_4$.

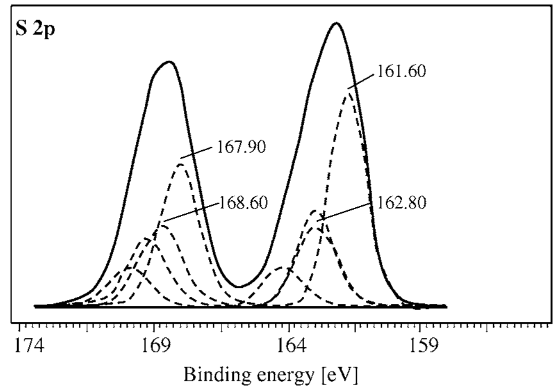

Figure 2 XPS spectrum of S2p for β-$Ag_8S_4O_4$.

Figs 1 and 2 show the spectra of $S2p_{3/2-1/2}$ for α- and β-$Ag_8S_4O_4$, respectively. The BE values of S2p for Ag_2S, a mixture of Ag_2S/Ag_2SO_4, both polymorphic forms of $Ag_6S_3O_4$ and $Ag_8S_4O_4$ and for some reference sulfur compounds are listed in Table I. As summarized in the 4th column of Table I, the BE values of the $S2p_{3/2}$ peaks, recorded for Ag_2S and Ag_2S/Ag_2SO_4 mixture (S(−II): 161.20 eV, 161.50 eV and S(+VI): 168.30 eV),

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TABLE I Comparison of S2p BEs (eV) found in literature along with our values for Ag_2S, Ag_2S/Ag_2SO_4 mixture, and for both polymorphic forms of $Ag_6S_3O_4$ and $Ag_8S_4O_4$

Compound	Oxidation degree	$S2p_{1/2}$ (eV)	$S2p_{3/2}$ (eV)	Reference
1	2	3	4	5
α-$Ag_6S_3O_4$	–	162.50	161.80	This study
		168.40	168.00	
β-$Ag_6S_3O_4$	–	162.80	161.50	This study
		168.50	168.00	
α-$Ag_8S_4O_4$	–	162.50	161.50	This study
		168.40	167.80	
β-$Ag_8S_4O_4$	–	162.80	161.60	This study
		168.60	167.90	
Ag_2S and Ag_2SO_4 mixed at the molar ratio 2:1	−II	162.50	161.50	This study
	+VI	–	168.30	
Ag_2S	−II	162.90	161.20	This study
		–	160.70	12
FeS_2	−I	–	162.30	13
			162.70	14
$Na_2S_2O_3$	−II	–	161.80	13
$Na_2S_2O_3$	+VI	–	162.00	14
			167.80	13
			168.10	14
Na_2SO_3	+IV	–	166.50	13,14
$FeSO_4$	+VI	–	168.80	15

TABLE II Comparison of Ag3d BEs (eV) found in literature along with our values for Ag_2S, Ag_2S/Ag_2SO_4 mixture, and for both polymorphic forms of $Ag_6S_3O_4$ and $Ag_8S_4O_4$

Compound	Oxidation degree	$Ag3d_{3/2}$ (eV)	$Ag3d_{5/2}$ (eV)	Reference
1	2	3	4	5
α-$Ag_6S_3O_4$	–	373.80	367.90	This study
β-$Ag_6S_3O_4$	–	373.90	367.90	This study
α-$Ag_8S_4O_4$	–	374.00	368.00	This study
β-$Ag_8S_4O_4$	–	373.90	367.90	This study
Ag_2S and Ag_2SO_4 mixed at the molar ratio 2:1	+I	373.90	367.90	This study
Ag_2S	+I	373.70	367.70	This study
		–	367.80	12
Ag_2O	+I	373.70	367.70	16,17
		–	367.80	18
			367.90	19
AgO	+II	373.20	367.30	16,17
		–	367.60	19
Ag metallic	0	–	368.10	19

remain in good agreement with the literature values [12, 15]. Results of XPS studies, performed for low- and high-temperature polymorphic forms of $Ag_6S_3O_4$ and $Ag_8S_4O_4$, show a presence of only two different types of sulfur atoms. One of them ($S2p_{3/2}$ BE: $161.50 \div 161.80$ eV) could be attributed to S(−II) sulfur. The other one ($S2p_{3/2}$ BE: $167.80 \div 168.00$ eV) could be assigned to S(+VI) sulfur in SO_3S tetrahedron analogous to S(+VI) sulfur in $Na_2S_2O_3$ [13, 14]. From a comparison of the measured $S2p_{3/2}$ BE values for $Ag_6S_3O_4$ and $Ag_8S_4O_4$ compounds with the published values [12–15] it follows that neither S(+VI) in SO_4^{2-} nor S(+IV) in SO_3^{2-} as well as nor S(−I) in S_2^{2-} sulfur atoms can be seen in the analyzed phases.

The $Ag3d_{5/2-3/2}$ spectra for α- and β-$Ag_6S_3O_4$ are showed in Figs 3 and 4,respectively. In Table II, the BE values of Ag3d electron doublet, measured for Ag_2S, Ag_2S/Ag_2SO_4 mixture, α- and β-forms of $Ag_6S_3O_4$ and $Ag_8S_4O_4$, are given together with analogous, published values for some silver(I) compounds [16–19]. The BE values of $Ag3d_{5/2-3/2}$ for AgO ($Ag^{I}Ag^{III}O_2$—two kinds of silver atoms [20]) are given in Table II, too. In this work, the BEs of the $Ag3d_{5/2}$ peak were recorded at 367.70 eV and at 367.90 eV for Ag_2S and Ag_2S/Ag_2SO_4 mixture, respectively. These values are very similar to those reported by other authors (Table II) [12, 16–19] and they are assigned to Ag(+I) silver atoms. XPS investigations show that the BE values of $Ag3d_{5/2}$ for both forms of $Ag_6S_3O_4$ and $Ag_8S_4O_4$ were shifted, in comparison to analogous BE value for AgO, to higher BE values. Likewise, the BEs of $Ag3d_{5/2}$ measured for analyzed phases are in very good agreement with those observed in Ag_2S, Ag_2S/Ag_2SO_4 mixture and Ag_2O [16–19]. These facts

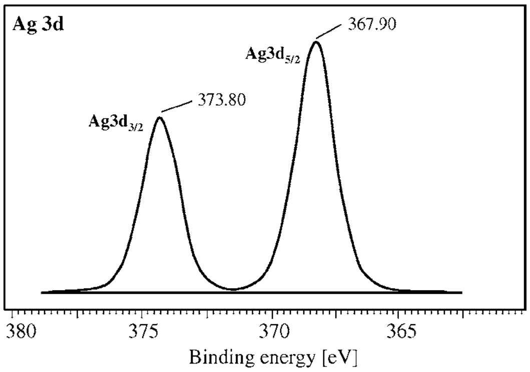

Figure 3 XPS spectrum of Ag3d for α-$Ag_6S_3O_4$.

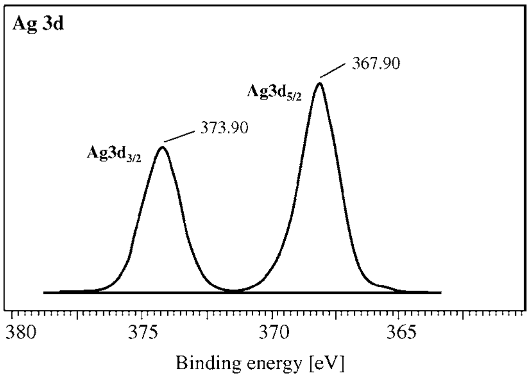

Figure 4 XPS spectrum of Ag3d for β-$Ag_6S_3O_4$.

point to the presence of Ag(+I) silver in analyzed compounds.

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