

Spectroscopic investigation of fluorinated monophosphate tungsten bronzes

N.V.Stus, V.V.Lisnyak, M.S.Slobodyanyk

Department of Chemistry, T.Shevchenko Kyiv National University,
64 Volodymyrska St., 01033 Kyiv, Ukraine

Novel materials, silver-containing type of monophosphate tungsten bronzes with hexagonal channels (MBTB_h), Ag₄(WO₃)₈(PO₂)₄, and fluorinated analogues (FMBTB_h), Ag₄(WO_{3-x}F_x)₈(PO₂)₄, where $0 \leq x \leq 0.05$, containing silver atoms in different valence states have been synthesized and studied using X-ray photoelectron spectroscopy, photoemission electron microscopy, and resistivity measurements. The resistivity anomalies observed for FMBTB_h may testify to the electron instability state realization at temperatures about 150 to 250 K.

Новые материалы — серебросодержащие представители монофосфатных вольфрамовых бронз с гексагональными каналами (MBTB_h) состава Ag₄(WO₃)₈(PO₂)₄, и их фторированные аналоги (FMBTB_h) Ag₄(WO_{3-x}F_x)₈(PO₂)₄, где $0 \leq x \leq 0,05$, содержащие атомы серебра в различных валентных состояниях, были синтезированы и изучены посредством рентгеновской фотоэлектронной спектроскопии и фотоэмиссионной электронной микроскопии; проведены также измерения удельного сопротивления. Аномалии удельного сопротивления, наблюдаемые для FMBTB_h, могут свидетельствовать о реализации состояния электронной неустойчивости при температурах порядка $T = 150-250$ К.

Nowadays, the interest in macroscopic quantum phenomena, such as charge density waves (CDW) or spin density ones in solids is grown. Tungsten oxide bronzes are low-dimensional semimetallic conductors, which are studied extensively as model objects. An extremely small variation of thermodynamic conditions as chemical potential, temperature and pressure can cause an extremely large change in physical properties of these inorganic materials [1]. The purpose of this work was to synthesize a novel kind of monophosphate tungsten bronzes with hexagonal channels [2] containing silver (AgMPTB_h) and its fluorinated analogue (FMPTB_h). The determination of interrelations between composition and properties for such complex substances may provide a base for creation of specialized sensor materials having high selectivity to small molecules and ions with excellent analytical sensitivity.

The high reactivity of silver compounds makes it necessary to develop a convenient single crystal growth technique for the

bronzes. The Ag₄(WO₃)₈(PO₂)₄ and Ag₄(WO_{3-x}F_x)₈(PO₂)₄ single crystals were grown by gas-transport technique in sealed quartz ampoules. The starting compositions were prepared in several stages: (1) first mixture of NH₄H₂PO₄ and WO₃ with 1:2 molar ratio was heated at 875 K; (2) appropriate amount of W metal powder was added to resulting mass followed by heating at 1280 K; (3) after metal dissolution in the melt was quenched; (4) the resulting glass was crushed and mixed with powders of AgPO₃ and/or AgF. An equimolar mixture of P₂O₅:J₂ was applied as the medium for gas-transport reaction.

The starting compositions were ground in an s-shaped two-zone ampoule, ends thereof were placed in a thermostatically controlled two-zone furnace at 890–930 K and 725–807 K, respectively. After cooling and rapid depressurization of system, the plate-like brown-reddish single crystals (1×1×0.1 mm³) with metallic shine were leached with hot water and selected for ex-

amination. The single crystals were studied by X-ray powder diffraction (DRON-4a diffractometer, CuK_α radiation). The preliminary elemental analyses using plasma emission spectroscopy (Beckman, ICP-6000) have determined Ag and W ratio in the crystals to be (1:2). All further studies were performed on selected single crystals. The precise content of Ag, W, F, and O in the crystals was determined by X-ray energy dispersion analysis (EDX) using a microprobe (Si:Li detector) mounted on JEOL electron microscope (EM/SEM). The stoichiometries proposed for $\text{Ag}_4(\text{WO}_{3-x}\text{F}_x)_8(\text{PO}_2)_4$ ($x = 0.01, 0.022, 0.05$) are based on analysis of the characteristic lines in the EDX spectra. AgMPTB_h and FMPTB_h samples were studied by X-ray photoelectron spectroscopy (XPS) on AESIS ESCA LAB-5 (surface layer of 10 to 20 Å in depth) and EDX to elucidate the structure features of the compounds. The investigation of silver clustering was carried out by photoemission electron microscopy (PEEM). Resistivity temperature dependence was measured using four-microprobe technique at ^1He cryostat along the *ab* crystal plane.

Due to high reactivity of silver compounds, especially at high temperatures, interaction $\text{W}^{n+} + \text{Ag}^+ = \text{Ag}^0 + \text{W}(n+1)^+$ is possible in a melt containing low-valence tungsten ions and Ag^+ . Moreover, the silver reduction in crystals may be caused by a radiation (UV, gamma, or X-ray) or electron beam effects according to the scheme $\text{Ag}^+ h\nu \rightarrow \text{Ag}^0$. The size of generated clusters correlates with the radiation beam diameter and depends on silver content in the crystal. The crystals obtained are found to be representatives of the MPTB_h series [3] with lattice parameters close to sodium-containing compounds.

The MBTB_h structures contain large cavities formed by 18 oxygen atoms, where mono- or divalent atoms are located. According to single crystal data, the potassium and lead atoms occupy the eight-fold coordinated position, than for smaller silver atoms six-fold coordination should be realized similar to sodium ones [2]. The addition of fluoride ions to the system breaks part of W–O–W-bonds in the melt and shifts the redox equilibrium, therefore, formation of silver (+3) becomes possible. So, it has been determined unambiguously by XPS that the crystals may contain up to three form of silver (Ag^0 , Ag^+ and Ag^{+3}). According to XPS results, in fluoride-free compounds photoelectron transfer $\text{Ag}3d_{5/2}$

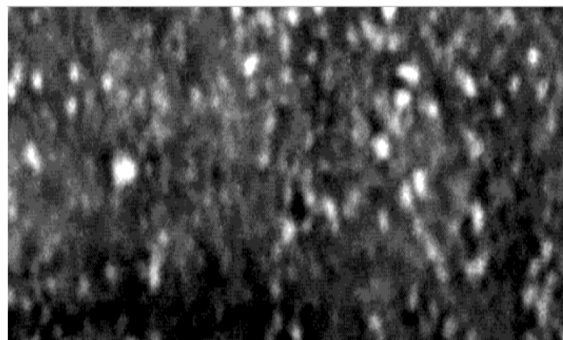


Fig. 1. The PEEM/EDX image (3 μm high and 10 μm long) of silver clusters embedded in an $\text{Ag}_4(\text{WO}_3)_8(\text{PO}_2)_4$ single crystal.

should be referred to two type of silver atoms Ag^0 and Ag^+ , which was confirmed by qualitative comparison of the bonding energy values with literature ones.

For FMBTB_h , three types of lines are observed in the spectrum; one of those belongs to Ag^+ , whereas the second type corresponds to insignificant admixture of Ag^{3+} ($E_b = 371.1$ eV). The embedded silver presence is confirmed by spectral lines with bonding energy characteristic for Ag^0 ($E_b \text{ Ag}3d_{5/2} = 367.9$ eV). A typical image of $\text{Ag}_4(\text{WO}_{3-x}\text{F}_x)_8(\text{PO}_2)_4$ surface (see Fig. 1) was generated from AgK lines analysis in the PEEM/EDX spectra for *ab*-oriented plate, the depth of refined surface is 20 ± 5 Å. The black field corresponds to stoichiometric surface distributions of Ag, which is commensurable with predicted for negligible small crystal area, the white areas are those of excess Ag concentration, i.e., atomic clustering. As is seen from Fig. 1, the surface layer containing a significant amount of embedded silver clusters of different sizes about 0.06 μm .

The $\text{Ag}3d_{5/2}$ spectrum lines of Ag^+ correspond to 368.2 and 368.1 eV. It is to note that those lines are split into two doublets. The split value (up to 0.05 eV) for Ag^+ signal in XPS spectra depends from F concentration (see for example Fig. 2). The complex material prepared in proposed way is a CDW system, due to matrix electrophysical properties. Thus, modification by Ag^0 (centers for catalysis) and F (defects in perovskite layer [3]) result in an instability, which is sensitive to changes on the surface such as small gaseous molecules adsorption on metallic centers. Therefore, XPS Ag line analysis in combination with resistivity determination can be used to determine those changes. As it is seen from Fig. 3, the temperature-composition drift of resistivity anomalies (found to be at $T = 187$ K for

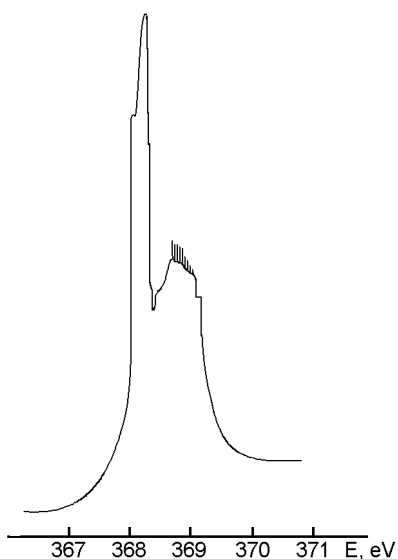


Fig. 2. XPS spectra of $\text{Ag}_4(\text{WO}_{3-x}\text{F})_8(\text{PO}_2)_4$ $x = 0.01$ recorded at 100 K.

pure $\text{Ag}_4(\text{WO}_3)_8(\text{PO}_2)_4$ can be considered to be caused by effects of F^- and embedded silver atoms.

Thus, the quantitatively analyzed phenomena in FMPTB_h are related with resistivity changing in the crystal surface layer due to electron density transfer according to scheme: adsorbed gas molecule: $\text{Ag}^{\delta+} \rightarrow (\text{W} \rightarrow \text{O})_m$. So, it has been shown that it is possible to make use of X-ray photoelectron technique for gas detection using quasi-low-dimensional compounds.

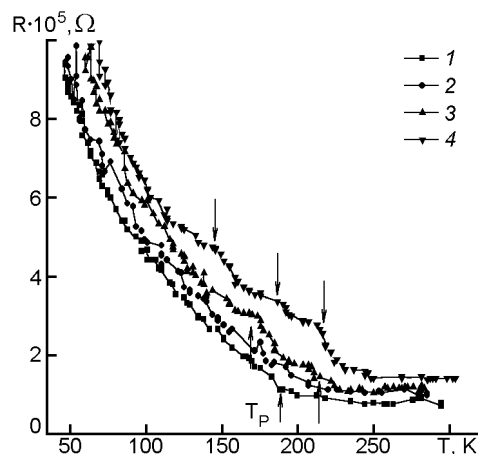


Fig. 3. The resistivity vs T plot for $\text{Ag}_4(\text{WO}_{3-x}\text{F})_8(\text{PO}_2)_4$ measured for single crystals $1 \times 1 \times 1 \text{ mm}^3$: (1) pure $\text{Ag}_4(\text{WO}_3)_8(\text{PO}_2)_4$ sample, (2) $x = 0.01$, (3) $x = 0.022$, (4) $x = 0.05$. The temperature of possible Peierls transition is shown by arrows.

Acknowledgement. Authors are thankful to National Budget Common Foundation (National Program for Fundamental Study No.40101, Program 5: Materials and Substances) for grant-in-aid (Grant No.0101U002160).

References

1. A.Ottolenghi, J.P.Pouget, *J. Phys. (I) France*, **6**, 1059 (1996).
2. N.V.Stus, V.V.Lisnyak, N.S.Slobodyanik, *J. Alloys Comp.*, **325**, 73 (2001).
3. P.Roussel, O.Perez, Ph.Labbe, *Acta Crystallogr. Sect. B. Struct. Crystallogr.*, **57**, 603 (2001).

Спектроскопічне дослідження фторованих монофосфатних вольфрамових бронз

Н.В.Стусь, В.В.Лісняк, М.С.Слободяник

Нові матеріали: срібловмісні представники монофосфатних вольфрамових бронз з гексагональними каналами (надалі MBTB_h) складу $\text{Ag}_4(\text{WO}_3)_8(\text{PO}_2)_4$ та їх фторовані аналоги (FMBTB_h) $\text{Ag}_4(\text{WO}_{3-x}\text{F}_x)_8(\text{PO}_2)_4$ де $0 \leq x \leq 0,05$, що містять атоми срібла в різних валентних станах були синтезовані і вивчені за допомогою рентгенівської фотоелектронної спектроскопії, фотоемісійної електронної мікроскопії, також проведено виміри питомого опору. Аномалії питомого опору, що спостерігаються для FMBTB_h можуть свідчити на користь реалізації стану електронної нестійкості при температурах порядку $T = 150\text{--}250$ К.