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Investigation of Polyvinyl Alcohol-CuS Compound with Metal-Like Conductivity

© I.Yu. Prosanov¹, A.I. Romanenko², G.E. Chebanova²¹ Institute of Solid State Chemistry and Mechanochemistry SB RAS, Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia² Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia

E-mail: prosanov@mail.ru

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PVA-CuS compound produced from hybrid interpolymeric polyvinyl alcohol (PVA)-CuCl₂ complex through solid state sulfurization was investigated by means of X-ray diffraction, UV-Vis and Raman spectroscopy, and direct current measurements. It is claimed that CuS in this compound has one-dimensional structure. This result is achieved by using a precursor technique based on diffusion limitation at solid state synthesis, so that the structure of initial reagents is inherited by reaction products. The produced material is determined to possess metal-type conductivity and thermopower in the vicinity of room temperature.

Keywords: hybrid interpolymeric complexes, polyvinyl alcohol, CuS, inorganic polymers, one-dimensional structures, electrical properties.

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1. Introduction

One-dimensional structures attract significant attention due to their expected valuable properties due to quantum-size effects. Ballistic conductivity is an example of such behavior [1]. Unfortunately, there is a lack of true one-dimensional systems like polymers suitable for some applications. For example, it is not easy to produce highly conductive or (electro)luminescent polymers. The number of known inorganic polymers is not high, and it is desirable to increase it. One of the routes to the production of inorganic polymers was suggested by us previously [2]. It is based on the synthesis of hybrid interpolymeric complexes of complexing organic polymers like polyvinyl alcohol (PVA –(CH₂–CHOH)_n–). The well-known representative of such compounds is PVA-iodine complex [3] where iodine has a structure of linear –(I₃)_n– or –(I₅)_n– polymeric chains complexed with PVA chains like the components of DNA (deoxyribonucleic acid) double helix. Hybrid interpolymeric PVA-Cu(OH)₂ complex has also been reported [4,5]. It has been suggested that other similar hybrid interpolymeric complexes can also be synthesized [2], including PVA-CuS compound [6] (Fig. 1).

The problem is in confirming the polymeric structure, in view of the absence of three-dimensional periodicity. Raman spectroscopy can help in this case. Raman scattering is stipulated by the influence of molecular oscillations on molecular polarizability. This means that the features of a Raman spectrum are determined by the electrical properties of the material under investigation, and we can use it not only for structure determination but also for other research purposes. The method of inorganic polymeric

structure identification using Raman spectroscopy has been suggested [7]. In our research, we use this method to investigate the structure of PVA-CuS compound, while previously we have used it to study PVA-CdS compound [7]. Bulk CuS is known for its metal-like conductivity and superconducting transition at 1.6 K [8]. It would be worth to produce polymeric CuS-based compound with a similar electric behavior. On the other hand, CdS is known as a direct-band semiconductor [9], and PVA-CdS compound indicates some unexpected Raman behavior [7]. Therefore, the comparison of both compounds' properties can help to understand them better. It can also be mentioned that the expected PVA-CuS hybrid interpolymeric complex has a structure of Little's superconductors [10], which makes it an interesting object for investigation. The results of many studies of CuS particles, layers, and microstructures [11–24] and (organic)polymer-CuS composites [25] including PVA-CuS composites [26,27] can be used for comparison with our results for the claimed new material — hybrid interpolymeric PVA-CuS complex. Through our research, we initially want to understand whether our PVA-CuS compound has metal-like conductivity similar to bulk CuS. Then we should determine some properties of this compound in comparison with other CuS-based materials.

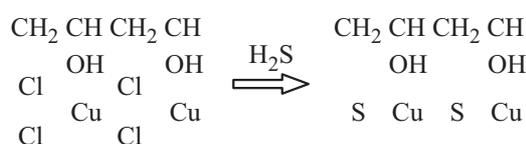


Figure 1. Scheme of polymeric CuS synthesis with PVA mediation.

2. Experimental

2.1. Samples preparation

PVA of 6-98 grade, produced by BDH Chemicals Ltd., and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ of analytically pure reagent grade were used for samples preparation. Sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) of analytically pure grade and HCl of pure grade were used for sulfurization.

PVA-CuS samples were prepared from PVA-CuCl₂ complex through solid state synthesis. We suppose that PVA and CuCl₂ form hybrid interpolymeric complex consisting of two linear chains, like a DNA double helix. Solid state synthesis allows this structure to be inherited by the resulting PVA-CuS compound due to diffusion restriction. Initially, we prepared a compound with components ratio 1 PVA unit ($-\text{CH}_2-\text{CHOH}-$) to 1 CuCl₂ unit, which we regard as having CuCl₂ in excess. Saturated aqueous CuCl₂ solution was mixed with a 10 wt% aqueous solution of PVA in the proper ratio. This compound was cast onto the fluoroplastic plate and dried for ~ 24 hours at room temperature. Then the prepared films were peeled off and washed in ethanol to remove excessive CuCl₂.

Sulfurization of PVA-CuCl₂ films was carried out by exposing to gaseous H₂S formed in the interaction of sodium sulfide with HCl. Exposure time was ~ 50 hours. Sulfurized films are quite fragile and corrugated. Therefore, they were ground and pressed into tablets. The measured averaged density of the tablets was 1.7 g/cm^3 . Then a bar was cut from the tablet for conductivity measurements or the tablet was used immediately. For optical transmittance measurement, a thin transparent PVA-CuS layer was formed on a celluloid film.

The reference CuS powder was prepared by mixing $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ solutions, and then the precipitate was washed.

2.2. Sample characterization

XRD analysis was carried out with a Bruker D8 Advance diffractometer using $\text{CuK}\alpha$ radiation.

Raman measurements were carried out with a Bruker RFS-100/S spectrometer equipped with a 1064-nm excitation source. The resolution was 4 cm^{-1} . All spectra were measured at room temperature, registration conditions were chosen to avoid local heating of the films by laser radiation.

The temperature dependences of electrical resistivity $\rho(T)$ from 4.2 to 300 K and the thermopower $S(T)$ from 77 to 300 K were measured on original installations. We used a standard four-probe method with a change in the direction of current for measuring the electrical conductivity, and a differential method for measuring the thermopower.

3. Results and discussion

According to our expectations, the stoichiometric ratio of PVA-CuCl₂ complex is 3 PVA units ($-\text{CH}_2-\text{CHOH}-$) to

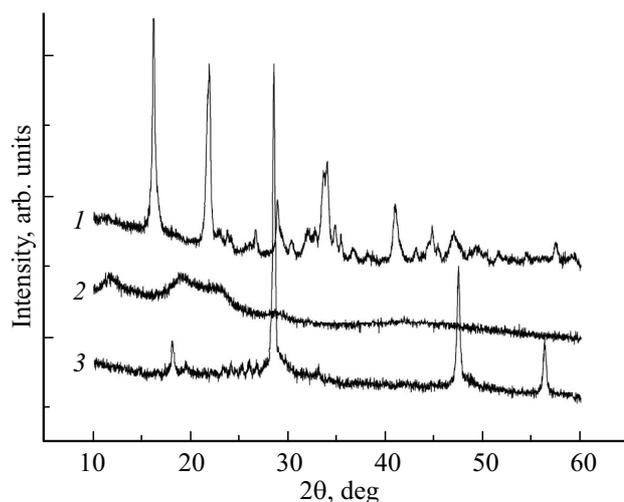


Figure 2. X-ray patterns: curve 1 — 1:1 (molar ratio) PVA-CuCl₂ compound, 2 — this compound after washing in ethanol, and 3 — after sulfurization.

1 CuCl₂ unit ($\sim 50 \text{ wt}\%$). At higher CuCl₂ content, it drops as a separate crystalline phase in dried samples. At lower CuCl₂ content, a non-stoichiometric amorphous complex is formed. Correspondingly, XRD analysis indicates the presence of a crystalline phase at CuCl₂ ratio higher than the stoichiometric one (Fig. 2). This result is in accordance with other reported data [28]. The XRD pattern of the washed sample does not indicate narrow peaks of a crystalline phase but reveals broad bands of a semi-crystalline complex. After sulfurization, PVA-CuCl₂ films contain CuCl phase according to X-ray diffraction data. This means that the formation of polymeric Cu_{1-x}S ($0 < x < 1$) can be expected as a component of PVA-CuS compound.

The Raman spectrum of PVA-CuS compound is to some extent similar to the Raman spectra of polyacetylenes (cis- and trans-), dehydrated PVA (which is a kind of polyacetylene), and PVA-CdS compound [7]. They all have a prominent background and two bands at 1110 and 1490 cm^{-1} (Fig. 3) like carbonaceous G and D bands. Pristine PVA bands are not observed in such spectra. There is a suggestion that such a spectrum is a result of SERS-like (surface enhanced Raman scattering) effect for PVA oscillations near an inorganic linear (conjugated) polymer like $-(\text{CdS})_n-$ [7]. However, there is a difference between the above-mentioned spectra. There are bands at 480 and 373 cm^{-1} in the case of PVA-CuS. Both these bands were observed in the reference CuS spectrum (Fig. 4). The band at 480 cm^{-1} can be attributed to S-S stretching vibrations, as it was reported for the 475 cm^{-1} band of CuS films and nanoparticles [22,23]. The band at 373 cm^{-1} was not reported among the Raman bands of CuCl [29,30] and CuS. We suppose that the Raman data generally verify the formation of polymeric one-dimensional CuS as a part of the hybrid interpolymeric PVA-CuS compound.

UV-Vis transmittance spectrum of PVA-CuS compound is presented in Fig. 5. It indicates a monotonous dependence

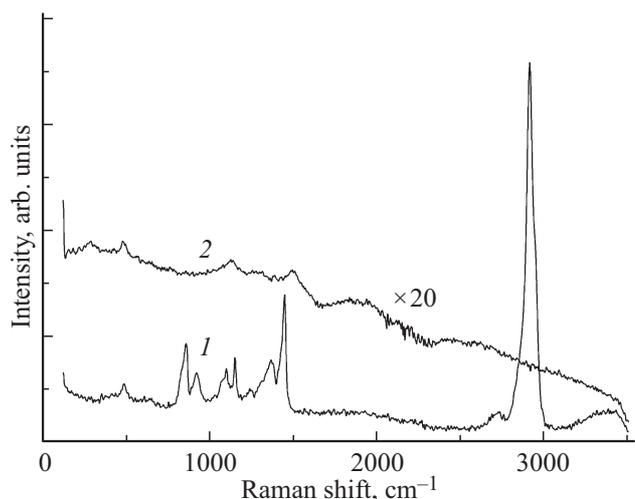


Figure 3. Raman spectra: curve 1 — pristine PVA, 2 — PVA-CuS compound.

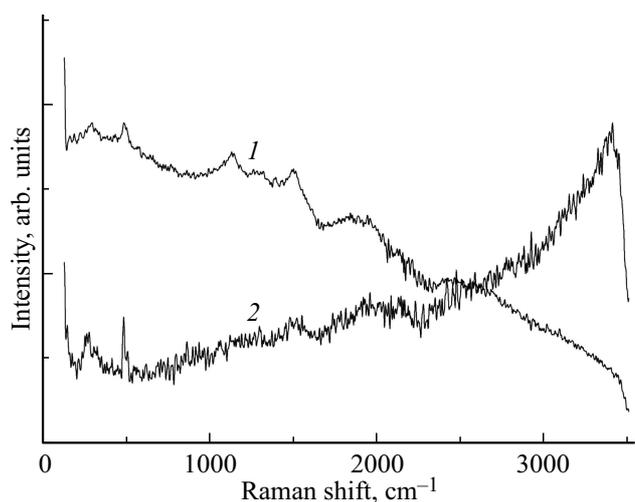


Figure 4. Raman spectra: curve 1 — PVA-CuS compound, 2 — CuS reference sample.

of optical transmittance on the wavelength within the 300–1100 nm range, in contrast to the behavior of other CuS-based materials reported in [15,16,19,21,24]. We regard this difference as one more verification of new CuS structure formation in our material.

The electrical properties of PVA-CuS compound are the most interesting issue for applications. It is a polymeric material convenient for the production of films, layers, and coatings. The temperature dependence of the resistivity of PVA-CuS compound within the range of 4.2–296 K is presented in Fig. 6. The data were obtained through a decrease and following increase of the temperature, to check repeatability. They indicate metal-type conductivity at a temperature higher than ~ 120 K. Earlier, a thermally activated type of conductivity was observed for PVA-CdS composition [27]. Fig. 7 shows that the cubic dependence provides a satisfactory approximation of the relationship

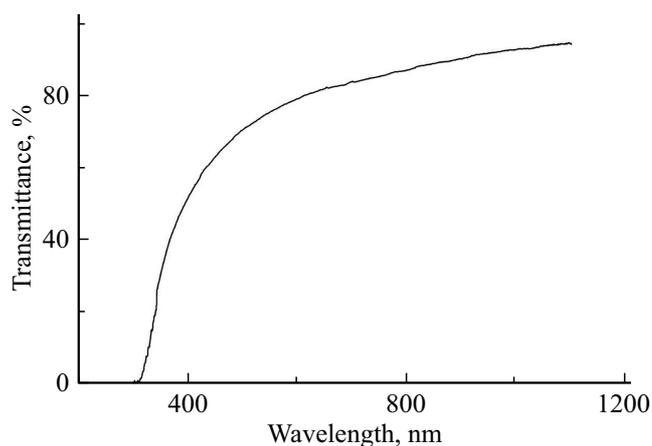


Figure 5. UV-Vis transmittance spectrum of PVA-CuS compound.

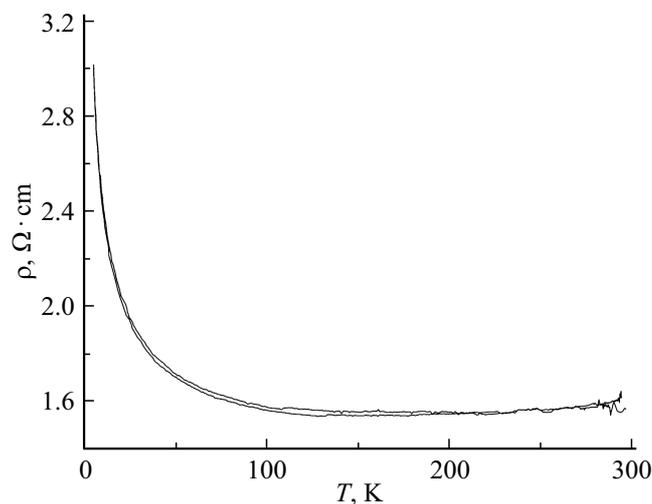


Figure 6. Temperature dependence of PVA-CuS compound resistivity $\rho(T)$.

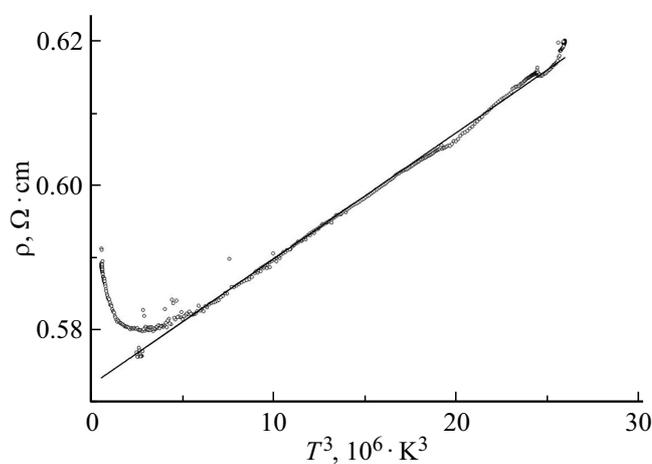


Figure 7. Cubic approximation of PVA-CuS compound's temperature dependence of resistivity.

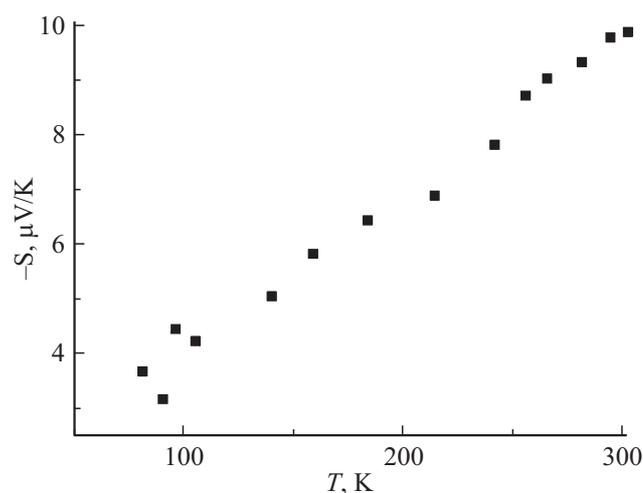


Figure 8. Temperature dependence of PVA-CuS compound thermopower $S(T)$.

between metal-like resistivity and temperature. Such dependence has been observed earlier for quasi-one-dimensional conductors [31,32]. Therefore, it is one more evidence of CuS chain polymeric structure in the PVA-CuS compound. Unlike bulk CuS [14], our material indicates thermoactivated conductivity below ~ 120 K. The temperature dependence of PVA-CuS compound thermopower S within 80–300 K range is presented in Fig. 8. It is linear, similarly to the behavior of organic conjugated polymers [33]. Their negativity indicates domination of electron-type carriers. We also observed linear current–voltage dependence at room temperature up to 15 mA/cm^2 current density and the absence of photoconductivity.

4. Conclusion

The discovered PVA-CuS compound possesses interesting properties that are valuable for applications. We regard it as a kind of coordinative polymer and as a representative of the new class of one-dimensional materials — hybrid interpolymeric complexes. The suggested way of solid state synthesis using precursor approach can be expanded on other analogous compounds. The Raman spectrum of this compound has a distinctive shape similar to that of polyacetylenes. This shape can be used for identification of other similar compounds based on PVA.

Conflicts of interests

The authors declare that they have no conflict of interest.

References

- [1] S. Frank, P. Poncharal, Z.L. Wang, W.A. de Heer. *Sci.* **280**, 5370, 1744 (1998).
- [2] I.Yu. Prosanov, N.V. Bulina, K.B. Gerasimov. *Phys. Solid State* **55**, 10, 2132 (2013).
- [3] C.A. Finch. Some properties of polyvinyl alcohol and their possible applications. In: *Chemistry and technology of water-soluble polymers* / Ed. C.A. Finch. Springer Science+Business Media, N. Y. (1983). P. 287-306.
- [4] H. Yokoi, S. Kawata, M. Iwaizumi. *J. Am. Chem. Soc.* **108**, 12, 3358 (1986).
- [5] Ch.-L. Ku, J.-H. Chen, L.-P. Hwang. *Polymer* **32**, 17, 3177 (1991).
- [6] I.Yu. Prosanov, N.V. Bulina. *Phys. Solid State* **56**, 6, 1270 (2014).
- [7] I.Yu. Prosanov, A.A. Sidelnikov, S.A. Hanna. *Semiconductors* **56**, 3, 349 (2022).
- [8] S.H. Chaki, J.P. Tailor, M.P. Deshpande. *Mater. Sci. Semicond. Proc.* **27**, 1, 577 (2014).
- [9] *Physics and chemistry of II-VI compounds* / Eds M. Aven, J.S. Prener. Wiley (1967). 862 p.
- [10] W.A. Little. *Phys. Rev.* **134**, 6A, A1416 (1964).
- [11] A.K. Sahoo, S.K. Srivastava. *J. Nanopart. Res.* **15**, 4, 1591 (2013).
- [12] Sh. He, G.-S. Wang, C. Lu, X. Luo, B. Wen, L. Guo, M.-S. Cao. *Chem. Plus. Chem.* **78**, 3, 250 (2013).
- [13] S.K. Majia, N. Mukherjee, A.K. Dutta, D.N. Srivastava, P. Paul, B. Karmakar, A. Mondal, B. Adhikary. *Mater. Chem. Phys.* **130**, 1–2, 392 (2011).
- [14] B. Raveau, T. Sarkar. *Solid State Sci.* **13**, 10, 1874 (2011).
- [15] I. Grozdanov, M. Najdoski. *J. Solid State Chem.* **114**, 2, 469 (1995).
- [16] S.H. Chaki, M.P. Deshpande, J.P. Tailor. *Thin Solid Films* **550**, 291 (2014).
- [17] S.S. Dhasade, J.S. Patil, S.H. Han, M.C. Rath, V.J. Fulari. *Mater. Lett.* **90**, 138 (2013).
- [18] P.A. Ajibade, N.L. Botha. *Res. Phys.* **6**, 581 (2016).
- [19] S. Riyaz, A. Parveen, A. Azam. *Perspectiv. Sci.* **8**, 632 (2016).
- [20] U. Shamraiz, R.A. Hussain, A. Badshah. *J. Solid State Chem.* **238**, 25 (2016).
- [21] M. Baláš, E. Dutková, Z. Bujňáková, E. Tóthová, N.G. Kostova, Y. Karakirova, J. Briančin, M. Kaňuchová. *J. Alloys. Compounds* **746**, 576 (2018).
- [22] D.E. Ortiz-Ramos, A.I. Martínez-Enríquez, L.A. González. *Mater. Sci. Semicond. Proc.* **89**, 18 (2019).
- [23] X. Li, K. Zhou, J. Zhou, J. Shen, M. Ye. *J. Mater. Sci. Technol.* **34**, 12, 2342 (2018).
- [24] H. Qi, J.-F. Huang, L.-Y. Cao, J.-P. Wu, D.-Q. Wang. *Ceram.Int.* **38**, 3, 2195 (2012).
- [25] X.-L. Zheng, J.-B. Weng, B.-H. Hu, X.-Z. Lv, D.-L. Meng, A.S.C. Chan. *Mater. Chem. Phys.* **130**, 3, 1054 (2011).
- [26] J. Xu, X. Cui, J. Zhang, H. Liang, H. Wang, J. Li. *Bull. Mater. Sci.* **31**, 2, 189 (2008).
- [27] M.B. Muradov, A.Sh. Abdinov, R.H. Hajimamedov, G.M. Eiyavazova. *Surf. Eng. Appl. Electrochem.* **45**, 2, 167 (2009).
- [28] B.M. Abo El-Khair, S.M. Mokhtar, A.Z. Dakroury, M.B.S. Osman. *J. Macromol. Sci. Phys.* **B33**, 3–4, 387 (1994).
- [29] R.L. Frost. *Spectrochimica Acta A* **59**, 6, 1195 (2003).
- [30] C. Ulrich, A. Göbel, K. Syassen, M. Cardona, A. Cros, A. Cantarero. *Phys. Status Solidi B* **211**, 1, 287 (1999).
- [31] M.H. Rashid, D.J. Sellmyer. *Phys. Rev. B* **29**, 4, 2359 (1984).
- [32] A.I. Romanenko, F.S. Rakhmenkulov, V.N. Ikotsky, P.S. Nikitin. *JETP Lett.* **42**, 9, 464 (1985).
- [33] A.B. Kaiser. *Rep. Prog. Phys.* **64**, 1, 1 (2001).