

Chalcogenide glass - carbon nanotube composite

Stepan Stehlik^a, Jiri Orava^b, Tomas Kohoutek^b, Tomas Wagner^{b,c}, Miloslav Frumar^c, Vitezslav Zima^d,
Toru Hara^e, Yoshio Matsui^e, Kazuyuki Ueda^f, Martin Pumera^g,

^a Institute of Physics AS CR, Cukrovarnická 10, 162 53 Prague, Czech Republic

^b Center for Materials Science, University of Pardubice, Studentská 95, 53210 Pardubice, Czech Republic;

^c Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice,
Legion's sq. 565, 53210 Pardubice, Czech Republic; tomas.wagner@upce.cz

^d Joint Laboratory of Solid State Chemistry of the Institute of Macromolecular Chemistry Academy of Sciences,
University of Pardubice, Studentska 84, 52310 Pardubice, Czech Republic

^e High-Voltage Electron Microscopy Station, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki
305-0044, Japan

^f Nano High Tech Research Center, Toyota Technological Institute, Nagoya 468-8511, Japan

^g Division of Chemistry & Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang
Technological University, SPMS-CBC-04-07, 21 Nanyang Link, Singapore 637371

ABSTRACT

This paper describes the preparation of multi-walled carbon nanotube—chalcogenide glass composite by direct synthesis and the melt-quenching method. The carbon nanotubes—chalcogenide glass composite was characterized by high-resolution transmission electron microscopy (HRTEM), TEM/energy-dispersive X-ray spectroscopy, low energy electron excited X-ray spectroscopy, Raman spectroscopy, spectroscopic ellipsometry, microhardness, and impedance spectroscopy. CNTs–AgAsS₂ glass composite possess highly increased ionic conductivity, from $\sigma_{25^\circ\text{C}} = 4.38 \pm 0.0438 \times 10^{-6}$ to $\sigma_{25^\circ\text{C}} = 6.57 \pm 0.0657 \times 10^{-6}$ S.cm⁻¹ and decreased refractive index from $n = 2.652$ to 2.631 at the wavelength $\lambda = 1.55$ μm .

Key words: carbon nanotubes, chalcogenide glasses, ionic conductivity, composites.

1. INTRODUCTION

Chalcogenide glasses have been widely studied due to their interesting and unique electrical and optical properties [1–4]. If undoped, chalcogenide glasses belong to a large family of vitreous semiconductors usually having p-type conductivity [5]. Chalcogenide glasses doped with metals (such as Ag, Cu, Li) [6–8] or their compounds (i.e., AgI, CuS, Li₂S) behave like ionic conductors or even fast ionic conductors (FIC) [9,10] having $\sigma > 10^{-7}$ S cm⁻¹.

The study of the ion conductivity of such glasses is extremely important since these glasses are widely used in many existing applications, in particular as parts of solid state batteries [11] and highly selective and sensitive electrochemical electrodes (i.e., Ag⁺, S²⁻, Se²⁻, etc.) [12,13], PMC (*Programmable Metallization Cell*) memory is one type of RRAM devices that shows a large promise as a future low energy non-volatile solid state memory [14].

Chalcogenide ionic glass conductors usually consist of: (i) a network former (sulfides or selenides, e.g., As₂S₃, GeS₂, Ga₂S₃, GeSe₂), which are covalent compounds that generally form glass easily, (ii) a network modifier (e.g., Ag₂S, Li₂S, Cu₂S), which are usually compounds with significant ionic features that do not form glass by themselves but can easily react with a glass former and become incorporated in its network, and (iii) a doping element or salt (e.g., Ag, AgI, LiI), which can be introduced into a vitreous network only if the network already contains a former and a modifier [1].

Carbon nanotube (CNT)-doped materials have an enormous potential in a wide variety of applications [15]. CNTs can dramatically alter the mechanical, optical, thermal, electrical, and electrochemical properties of composite materials at surprisingly low levels of doping [15–17]. This has an enormous impact on a wide variety of potential applications, such as reinforced materials, energy storage devices, sensors, and actuators, just to name a few [15–17]. CNTs are incorporated in polymer matrixes [16] or inorganic matrixes, such as silicates or metals [18,19].

Surprisingly, there has been no report on the CNTs–AgAsS₂ glass composite. Including of CNTs in to ion-conductive chalcogenide glasses is expected to change their physicochemical properties due to the incorporation into the glass network by the introduction of: (i) a lighter element (lower atomic weight of carbon vs. Ag, As, and S) leading to a

change in the optical properties and a consequent decrease in the refractive index; (ii) highly oriented and covalently bonded structures of CNTs resulting in increased hardness, which is expected to improve the mechanical properties of AgAsS₂ glass; (iii) crystalline, highly conducting structures, which are expected to increase electron conductivity; and (iv) one-dimensional structures such as CNTs, which are expected to increase ion conductivity. In this article, we show that CNTs–AgAsS₂ glass composite showed a significant increase in its ion conductivity and a simultaneous decrease of the activation energy of the Ag⁺ ion conductivity.

2. CONCLUSION

We have successfully prepared ion-conductive CNTs–AgAsS₂ glass composite at relatively low temperature. To the best of our knowledge, this paper represents the first example of conductivity study of CNT–chalcogenide glass composite. Despite a low level of CNTs concentration and a slight change in the CNTs morphology in the glass network, the presence of CNTs brought about rapid improvement of silver ion transport and conductivity, which is expected to offer significant benefits for future battery applications. A likely prospect seems to be the adding of single-walled CNTs in to ion-conductive glasses, which is expected to further enhance ion transport due to the possibility of tailoring the diameter of single-walled CNTs. Further systems Ag–Ge–Se and Ag–Ge–S are under current studies.

Authors acknowledge financial support from projects MSM0021627501, Research Centre LC523 P204/11/0832 and P106/11/0506.

REFERENCES

- [1] M. Frumar, B. Frumarova, T. Wagner, Amorphous and Glassy Semiconducting Chalcogenides. In: Bhattacharya P, Fornari R, and Kamimura H, (eds.), Comprehensive Semiconductor Science and Technology, vol. 4, (2011) pp. 206–261 Amsterdam: Elsevier.
- [2] M. Frumar, T. Wagner, Curr. Opin. Sol. State Mater. Sci. 7 (2003) 117.
- [3] T. Wagner, S.O. Kasap, Phil. Mag. B: Phys. Cond. Matter 74 (1991) 667.
- [4] M. Frumar, A.P. Firth, A.E. Owen, Phil. Mag. B: Phys. Cond. Matter 50 (1984) 463.
- [5] S.R. Elliott, Adv. Phys. 36 (1987) 135.
- [6] P. Boolchand, W.J. Bresser, Nature 410 (2001) 1070.
- [7] A.V. Kolobov, S.R. Elliott, Adv. Phys. 40 (1991) 625.
- [8] M. Ohto, M. Itoh, K. Tanaka, J. Appl. Phys. 77 (1995) 1034.
- [9] M. Mitkova, Y. Wang, P. Boolchand, Phys. Rev. Lett. 83 (1999) 3848.
- [10] W. Yao, S.W. Martin, Solid State Ionics 178 (2008) 1777.
- [11] M.D. Ingram, in: M. Cable, J.M. Parker (Eds.), High-Performance Glasses, Chapman and Hall, New York, 1992 (Chapter 7).
- [12] M.N. Kozicki, M. Mitkova, M. Park, M. Balakrishnan, C. Gopalan, Superlattice. Microst. 34 (2003) 459.
- [13] C. Cali, D. Foix, G. Taillades, E. Siebert, D. Gonbeau, A. Pradel, M. Ribes, Mater. Sci. Eng. 21 (2002) 3.
- [14] M.N. Kozicki, M. Mitkova: Journal of Non-Crystalline Solids 352 (2006) 567–577.
- [15] P.M. Ajayan, J.M. Tour, Nature 447 (2007) 1066.
- [16] K. Kobashi, T. Villmow, T. Andres, L. Haubler, P. Potschke, Smart Mater. Struct. 18 (2009) 035008.
- [17] M. Pumera, S. Sanchez, I. Ichinose, J. Tang, Sensor. Actuator. B 123 (2007) 1195.
- [18] T. Seeger, Th. Kohler, Th. Frauenheim, N. Grobert, N. Ruhle, M. Terrones, G. Seifert, Chem. Comm. 34 (2002).
- [19] M. Reibold, P. Paufler, A.A. Levin, W. Kochmann, N. Patzke, D.C. Meyer, Nature 444 (2006) 286.

Biography

Prof. Tomas Wágner, CSc.

He has been studying photoinduced reactions of the metals (mainly Ag) with amorphous chalcogenides for more than ten years. He is an author or co-author more than 140 refereed journal papers; more than 220 lectures and posters on international and national conferences. In the most of the papers he studied chalcogenide glasses (mainly dealing with photodoping phenomena, optical and thermal properties, structure and their application in optics and optical recording, phase-change phenomena, ionic conductive glasses, memories).