JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **9** No 4, 04028(3pp) (2017)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **9** № 4, 04028(3cc) (2017)

Short Communication

Thermoelectric Properties of the Colloidal Bi_2S_3-Based Nanocomposites

O.A. Dobrozhan[1,*], A.S. Opanasyuk[1,†], D.I. Kurbatov[1], U.B. Trivedi[2], C.J. Panchal[3], Priya Suryavanshi[3], V.A. Kheraj[4]

[1] *Sumy State University, 2, Rymsky Korsakov Str., 40007 Sumy, Ukraine*
[2] *Sardar Patel University, Vallabh Vidyanagar 388120 Gujarat, India*
[3] *The M.S. University of Baroda Vadodara 390001 India*
[4] *S. V. National Institute of Technology, Surat 395007 India*

(Received 15 April 2017; revised manuscript received 25 July 2017; published online 27 July 2017)

In this work we present the proof of the concept of the novel strategy to improve the thermoelectric properties of Bi_2S_3 based nanostructured bulk materials by blending the metallic nanoinclusions with the semiconductor nanoparticles forming the nanocomposites (NCts). The obtained NCts were composed of Bi_2S_3 nanorods (length – 100 nm and width – 10 nm) and Ag nanoparticles (diameter – 2-3 nm) synthesized by the colloidal method. The morphology, phase and chemical composition, electrical conductivity and Seebeck coefficient of NCts were investigated by using transmission electron microscopy (TEM), *X*-ray diffraction, energy dispersive *X*-ray analysis (EDAX), 4-point probes method and static *dc*-method. This strategy is the perspective way to improve the conversion efficiency of others thermoelectric materials.

Keywords: Colloidal nanocomposite, Bismuth sulfide, Silver, Thermoelectric properties.

DOI: 10.21272/jnep.9(4).04028 PACS numbers: 84.60.Rb, 81.16.Be

1. INTRODUCTION

Bismuth telluride (Bi_2Te_3) is one of the most popular thermoelectric (TE) materials for refrigeration near the room temperature [1]. But, due to the high production cost of tellurium is necessary to synthesize the alternative materials for TE cooling applications with low-cost and abundant chemical elements. Therefore, Bi_2S_3 with a direct optical band gap ($E_g = 1.3$ eV), *n*-type conductivity has a great potential in TE refrigeration applications because of the relatively low thermal conductivity (k) and high Seebeck coefficient (S) [2]. However, TE efficiency of Bi_2S_3 based devices is hindered by low electrical conductivity (σ) due to the low carrier concentrations (n) and mobilities (μ). It was proven that the improvements in the thermoelectric performance could be gained from the nanostructuring of materials that allows to control the electrical and thermal charge transport separately. Moreover, combining metal and semiconductor nanoparticles into NCts is the effective strategy to regulate the charge carrier concentrations without the deterioration of mobilities [3].

The chemical colloidal synthesis is a potential method to synthesize nanocrystals because of the excellent ability to control over size and shape, crystallographic structure, elemental composition of crystals as well as to obtain a broad gamut of materials. The choice of silver nanoinclusions is explained by the possibility to form an Ohmic contact with bismuth sulfide host matrix as the conduction band minimum of bismuth sulfide (~ 4.4 eV) matches with silver work function (~ 4.26-4.74 eV). On the one hand, silver nanodomains open the route of electrons injection into Bi_2S_3 host semiconductor, thus, increase the carrier concentration in NCt and, therefore, improve the electrical conductivity. On the other hand, Ag nanodomains ensure the locking of phonon dissemination, thus, allowing the decrease of thermal conductivities inside the material. All specified above determined the main goal of this work, that is, to investigate the thermoelectric performance by exploring the electrical conductivity (σ) and Seebeck coefficient (S) of Bi_2S_3 and Bi_2S_3-Ag NCts produced by the blending of chemically produced colloidal nanocrystals.

2. EXPERIMENTAL DETAILS

In this work it was used the experimental procedures to synthesize Bi_2S_3 nanorods [4] and Ag nanoparticles additives [5]. The NCt was produced by the blending Bi_2S_3 nanocrystals with 5 mol. % of Ag nanoinclusions. It is well known, that colloidal synthesis involves the applying of organic molecules (ligands) which are insulators. In turn, it inhibits the charge transfer between nanocrystals. To minimize the impact of ligands on the charge transport, the blended nanocrystals were annealed at 723 K for 60 min in Argon atmosphere. Further, the consolidation of the annealed NCts into nanostructured bulk form was performed by using a hot press procedure at the temperature of 723 K and pressure of 50 MPa during 5 min.

X-ray diffraction (XRD) analysis was used to study the phase composition of Bi_2S_3 and Bi_2S_3-Ag NCts. XRD patterns were recorded on a Bruker AXS D8 ADVANCE *X*-ray diffractometer with Cu_α-K radiation ($\lambda = 0.15406$ nm). The phase analysis was carried out by comparing the relative intensities at specified degrees of

* dobrozhan.a@gmail.com
† opanasyuk_sumdu@ukr.net

the sample with those of the etalons for Bi_2S_3, Bi and Ag.

The morphological properties were investigated by transmission electron microscopy (ZEISS LIBRA 120 microscope, operation voltage – 120 kV). Elemental composition was determined by EDAX technique using the energy dispersive X-ray spectroscopy detector attached to Carl ZEISS Auriga microscope.

Both, the electrical conductivity (σ) and Seebeck coefficient (S) was measured simultaneously by using LSR-3 LINSEIS system under Helium atmosphere.

3. RESULTS

Figure 1 represents TEM micrographs of Bi_2S_3 (Fig. 1a) and Ag (Fig. 1b) nanocrystals. The study of morphological properties showed that Bi_2S_3 had a form of nanorods with the length of 100 nm and width of 10 nm. Ag nanoparticles had a spherical form with the average diameter of 2-3 nm.

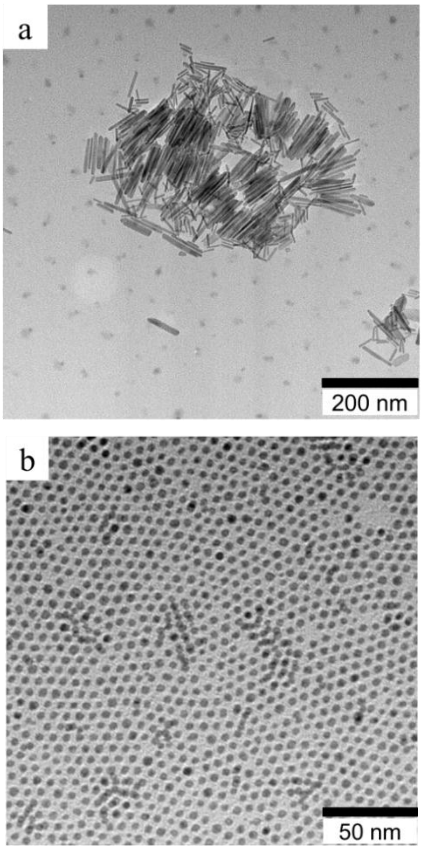

Fig. 1 – TEM images of Bi_2S_3 nanorods (a) and Ag nanoparticles (b) obtained by the colloidal synthesis

Figure 2 shows *XRD* patterns of Bi_2S_3 and Bi_2S_3-Ag NCts. Both Bi_2S_3 and Bi_2S_3-Ag NCts had an orthorhombic crystal structure. The results of phase analysis for the most intense and no-Bi_2S_3 peaks are presented in Table 1. As can be seen from Fig. 2 and Table 1, several peaks are not belonging to Bi_2S_3 (37.95-38.00°, 55.98-56.20°). In the case of pure Bi_2S_3 NCt the peak at 38.00° could be assigned to Bi phase. The peak at 37.95° on the pattern from Bi_2S_3-Ag is either belongs to Ag or Bi phases. The peak at 55.98-56.20° is dedicated to Bi phase.

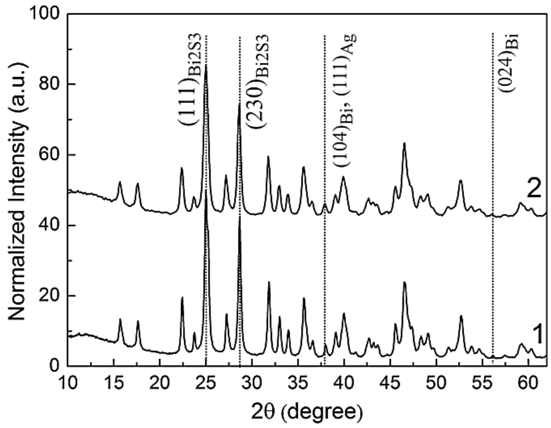

Fig. 2 – XRD patterns of Bi_2S_3 (1) and Bi_2S_3-Ag (2) NCts

EDAX measurements are presented in Table 2 and showed that Bi_2S_3 nanorods had near stoichiometric values.

Figure 3 shows the electrical conductivity (σ) and Seebeck coefficient (S) of Bi_2S_3 and Bi_2S_3-Ag NCts. The total electrical conductivity of both NCts lied in the range of ($4.0 \cdot 10^{2}$-$1.4 \cdot 10^{3}$) $S \cdot m^{-1}$, Seebeck coefficients – (190-210) $\mu V \cdot K^{-1}$ at the measured temperatures of (325-625) K.

The Bi_2S_3 with Ag additives showed the higher σ compared to the pristine sample in the temperature range of (450-625) K as well as higher S for all measured temperature range.

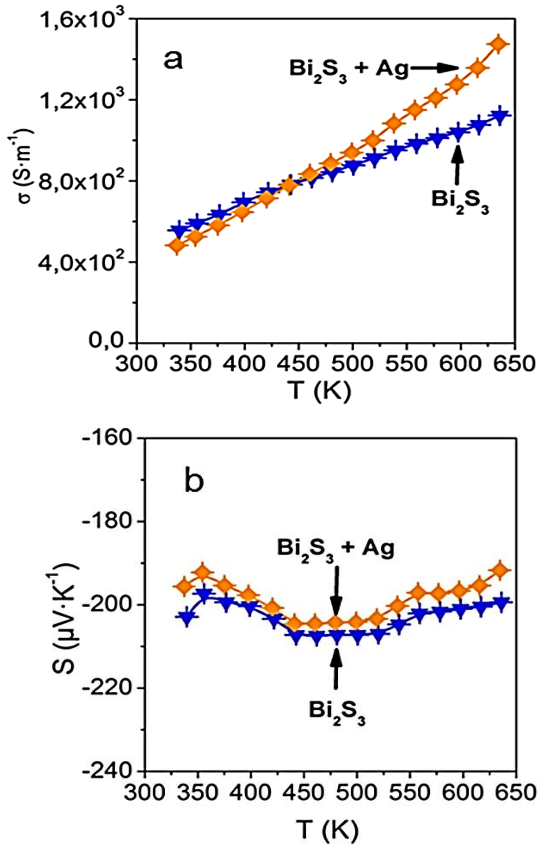

Fig. 3 – Temperature dependence of electrical conductivity (σ) (a) and Seebeck coefficient (S) (b) of Bi_2S_3 and Bi_2S_3+Ag NCts

Table 1 – The results of the phase analysis for Bi_2S_3 and Bi_2S_3-Ag NCts (showed peaks with $I > 50$ % and ones do not belong to Bi_2S_3)

Experimental results				**Literature data**								
Bi_2S_3		Bi_2S_3-Ag		Bi_2S_3 (JCPDS card No. 00-006-0333)			Bi (JCPDS card No. 01-085-1330)			Ag (JCPDS card No. 01-087-0717)		
2θ	I (%)	2θ	I (%)	(hkl)	2θ	I (%)	(hkl)	2θ	I (%)	(hkl)	2θ	I (%)
25.00	100.0	25.00	100.0	(111)	24.99	95	-	-	-	-	-	-
28.65	84.2	28.63	75.4	(230)	28.61	100	-	-	-	-	-	-
38.00	12.2	37.95	26.9	-	-	-	(104)	38.09	33.9	(111)	38.12	100.0
56.20	5.9	55.98	13.7	-	-	-	(024)	56.2	9.8	-	-	-

Table 2 – The results of EDAX analysis of Bi_2S_3 nanorods

Element	**Measured at. %**	**Stoichiometry at. %**
Bi	38.17	40.00
S	61.83	60.00
Total	100.00	100.00

4. CONCLUSIONS

We demonstrate an enhancement strategy to improve the electrical conductivity of the thermoelectric nanocomposite produced by the blending of Bi_2S_3 nanorods with Ag nanoparticles, which is promising for designing the novel TE materials for cooling applications.

The study of morphological properties showed that Bi_2S_3 had a form of nanorods with the length of 100 nm and width of 10 nm. Ag nanoparticles had a spherical form with the average diameter of 2-3 nm.

XRD analysis showed that Bi_2S_3 and Bi_2S_3-Ag NCts had an orthorhombic crystal structure. Secondary phases, like Bi and Ag, were identified. EDAX measurements showed that Bi_2S_3 nanorods had near stoichiometric values.

The total electrical conductivity of both NCts was placed in the range of ($4.0\cdot10^{2}$-$1.4\cdot10^{3}$) $S\cdot m^{-1}$, and Seebeck coefficients – (– 190-210) $\mu V\cdot K^{-1}$ at the measured temperatures in the range of (325-625) K.

Bi_2S_3 with Ag additives showed the higher electrical conductivities compared to the pristine sample in the temperature range of (450-625) K as well as higher Seebeck coefficients for whole measured temperature range.

Thereby, this strategy is the perspective way to enhance the conversion efficiency of others thermoelectric materials.

ACKNOWLEDGEMENTS

O.D. thanks AGAUR, IREC, Dr. Maria Ibáñez and Prof. Andreu Cabot for the opportunity to perform the experimental part of this work, valuable ideas, and seminal discussions. This work was supported by the Ministry of Education and Science of Ukraine (Grants No. 0116U002619, No. 0115U000665c, No. 0116U006813). Partially, the work was performed with the financial support of Sumy State University (internal grant “HTCA-2017“).

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