

## Impact of Graphene Addition on the Microstructure and Thermoelectric Properties of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ Ceramics

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The present paper reports on the impact of graphene (Gr) addition on the microstructure and thermoelectric properties of  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  ceramics. Reference and graphene added to  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_{y+x}$  wt. % Gr thermoelectric (TE) materials ( $x=0, 0.15, 0.35, 0.70,$  and  $1.15$ ) were prepared by using the solid-state reaction method. The phase purity and microstructure of the samples were examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. XRD analysis revealed that the addition of graphene did not alter the structure of  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  and this compound remained as a single-phase. SEM analysis showed slight increase of the amount of grains with smaller sizes for 0.35-0.70 wt. % Gr and deterioration of texturing degree for 1.15 wt. % graphene additive. Electrical transport characteristics of prepared materials were studied and values of their power factor (PF) were calculated. It was found that the incorporation of graphene into the  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  ceramics resulted in a monotonic decrease of electrical resistivity for 0.15-0.70 wt. % Gr while the Seebeck coefficient of all synthesized samples remained practically unaffected. Graphene addition leads to 1.4-fold enhancement of the power factor from  $37.0 \mu\text{W}/(\text{m}\cdot\text{K}^2)$  at 973 K for the reference sample to  $50.7 \mu\text{W}/(\text{m}\cdot\text{K}^2)$  for the sample with 0.70 wt. % Gr additive. © 2022 Bull. Georg. Natl. Acad. Sci.

$\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  thermoelectric, graphene additive, microstructure, power factor

Renewable energy sources and green technologies are becoming increasingly important with the world's growing energy need, environmental degradation and depletion of natural resources. In

this respect, thermoelectric materials that can convert waste heat directly into usable electric power are the objects of intensive studies. The development of efficient TE materials is expected

to provide a breakthrough in the widespread application of thermoelectric generators (TEGs) for electrical power generation from waste heat discharged from various systems (industrial furnaces, incinerators, automotive exhaust, etc.) and heat emanating from renewable energy sources (e.g., solar and geothermal) [1].

Applicability of conventional thermoelectrics, such as the layered chalcogenides of heavy metals is not feasible due to their toxicity, high cost and thermal degradation at elevated temperatures. Therefore, the current niche applications of these materials include the production of electrical energy in radioisotope thermoelectric generators installed on spacecrafts, or in navigation beacons in remote locations [2]. The above-mentioned restrictions have been overcome by the discovery of promising thermoelectric properties of layered cobaltites such as  $\text{Na}_x\text{CoO}_2$  [3],  $\text{Ca}_3\text{Co}_4\text{O}_9$  [4, 5],  $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$  and  $\text{Bi}_2\text{Ca}_2\text{Co}_2\text{O}_y$  [6, 7]. The  $p$ -type layered cobaltites have a great potential for use in thermoelectric devices due to their environmentally friendliness, easy processing, high thermal and chemical stability in air at elevated temperatures, abundance and relatively low cost of raw materials, suggesting their practical usage and possible commercialization with development of TEGs [1, 8]. Thermoelectric characteristics of layered cobaltites such as the power factor  $PF$  ( $PF=S^2/\rho$ ) and thermoelectric figure-of-merit  $ZT$  ( $ZT=S^2T/(\rho\lambda)$ , where  $S$ ,  $\rho$ ,  $\lambda$  and  $T$  are the Seebeck coefficient, resistivity, thermal conductivity and absolute temperature, respectively, are inferior to the traditional thermoelectrics. However, the potential of cobaltites for use in thermoelectric generators can be greatly enhanced by improving their TE properties through doping and introducing additives [9–15] or using of advanced fabrication techniques [8, 16–18].

Over the past decade, the graphene/ceramic composites have stimulated worldwide scientific and technological interest, because graphene with its ultrahigh electrical conductivity of above

$10^6$  S/m and large contact area for building the conductive paths can dramatically alter the electrical performance of the composites and broaden applications of ceramic materials, including energy conversion devices [19, 20]. Several studies have been conducted since 2015 to examine the impact of graphene (Gr) or reduced graphene oxide (RGrO) additives on the thermoelectric properties of  $p$ -type  $\text{CuAlO}_2$ ,  $n$ -type  $\text{SrTiO}_3$  and ZnO-based materials,  $\text{WO}_3$ ,  $\text{TiO}_2$  or  $\text{BaTiO}_3$  [21–27]. These studies have confirmed that the optimal amount of Gr/RGrO additive could lead to the markedly increased electrical conductivity while effectively lowering the lattice thermal conductivity by phonon scattering. As a result, the thermoelectric conversion efficiency of prepared materials will be dramatically enhanced. The effect of reduced graphene oxide on the power factor of  $\text{Na}_x\text{Co}_2\text{O}_4$  layered cobaltite was reported in [28]. It was found that the RGrO incorporation into the  $\text{Na}_x\text{Co}_2\text{O}_4$  matrix led to significant enhancement of power factor due to increase in electrical conductivity and Seebeck coefficient.

To the best of the authors' knowledge, the impact of graphene additive on thermoelectric properties of the layered  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  cobaltite has not been reported elsewhere. In this work, the graphene-added  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  thermoelectric materials were prepared and their structural, morphological and electrical transport properties were studied. Based on the measured temperature dependences of resistivity and Seebeck coefficient, the power factors of prepared materials were calculated.

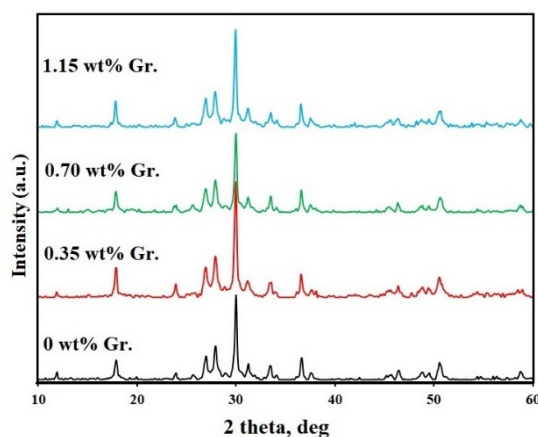
## Materials and Methods

Reference and graphene-added  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_{y+x}$  wt. % Gr ceramic samples ( $x=0, 0.15, 0.35, 0.70$  and  $1.15$ ) were prepared by means of solid-state reaction method from reagent-grade powders of bismuth oxide ( $\text{Bi}_2\text{O}_3$ ), strontium carbonate ( $\text{SrCO}_3$ ), cobalt (II, III) oxide ( $\text{Co}_3\text{O}_4$ ) and graphene nanopowder ([www.graphene-supermarket.com](http://www.graphene-supermarket.com),

purity: 99.2%, average flake thickness: 12 nm (30–50 monolayers), average particle (lateral) size:  $\sim 4.5 \mu\text{m}$ ). The mixtures of these powders were homogenized in a planetary mill (Fritsch Pulverisette 7 Premium line) for 1 h at a rotating speed of 120 rpm. After homogenization, the powders were calcined at 1043–1088 K for 18 hours with intermediate grindings in an agate mortar, then pressed into pellets at a hydrostatic pressure of 220 MPa. Finally, the pellets were sintered at 1103–1108 K in air for 20 h, then cooled to room temperature in the furnace. The phase purity and microstructure of the prepared materials were examined using X-ray diffraction (XRD, Dron-3M diffractometer,  $\text{CuK}\alpha$ -radiation) and scanning electron microscopy (SEM, VEGA TS5130MM) techniques. The resistivity of the samples as a function of temperature  $\rho(T)$  in the temperature range from 293 to 923 K was measured by the standard four-probe method. The temperature dependence of the Seebeck coefficient was determined with a homemade setup using a KEITHLEY DMM6500 multimeter. Electrical transport measurements were performed on bar-shaped samples with dimensions of  $\sim 13 \times 7 \times 2.5 \text{ mm}^3$ .

## Results and Discussion

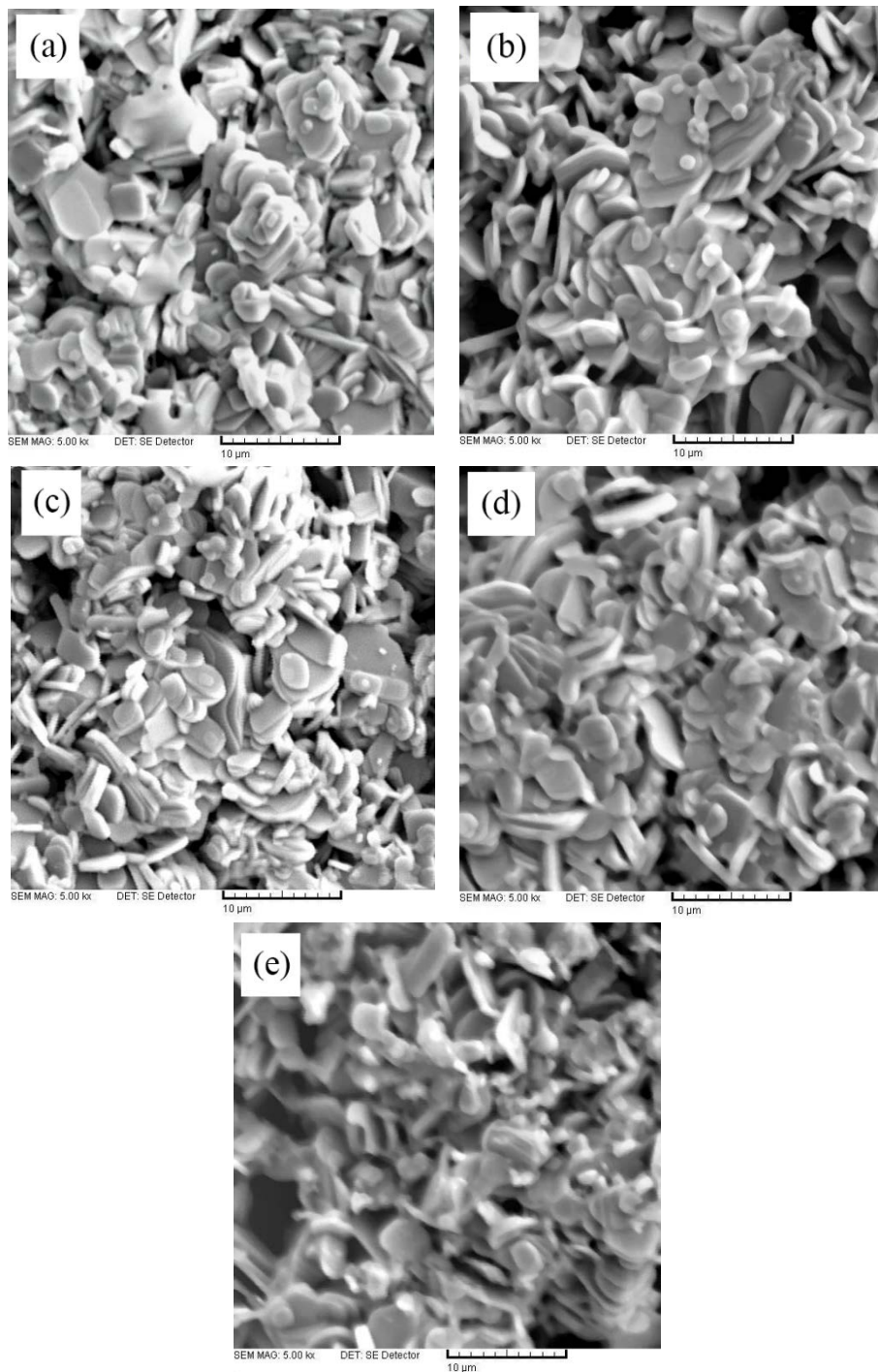
XRD patterns of the reference and graphene-added  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  samples are presented in Fig. 1. No diffraction peaks of graphene were identified due to its extremely low contents. XRD analysis showed that the addition of graphene did not alter the structure of  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  and this compound remained as a single-phase with lattice constants of  $a=4.837\text{--}4.892 \text{ \AA}$ ,  $b=5.348\text{--}5.351 \text{ \AA}$ ,  $c=14.90\text{--}14.94 \text{ \AA}$ ,  $\beta=92.2\text{--}93.1^\circ$ ,  $V=385.6\text{--}390.0 \text{ \AA}^3$ , which was close to the data obtained for layered bismuth–strontium cobaltite in [13]. Thus, XRD patterns indicate that graphene particles were dispersed along the grain boundaries in the  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  matrix, resulting in the formation of graphene/ceramic composite.



**Fig. 1.** X-ray diffraction patterns of  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y + x \text{ wt} \% \text{ Gr}$  samples.

SEM images of the surface morphology of prepared samples are displayed in Fig. 2. The grains of partially textured  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  ceramics had plate-like shape which is typical for layered bismuth–strontium cobaltite and their size varied within  $1\text{--}6 \mu\text{m}$  (Fig. 2, a). The grain size interval of graphene-added samples was similar to the reference one, although a number of grains with relatively smaller sizes got larger for 0.35 to 0.70 wt. % Gr addition (Fig. 2, c, d). The second effect of introduction of graphene into the  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  ceramics is the lowering of texturing degree observed for the 1.15 wt. % graphene-added sample which mostly consists of disoriented plate-like grains (Fig. 2, e).

Apparent density of reference sample,  $4.06 \text{ g/cm}^3$ , was 59.6% of theoretical value ( $6.81 \text{ g/cm}^3$  [2]). Graphene addition increases the density of  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y/\text{Gr}$  composites up to  $4.15 \text{ g/cm}^3$  and  $4.25 \text{ g/cm}^3$  for 0.35 wt. % Gr and 0.70 wt. % Gr, respectively. This implies, that the addition of graphene enhances the sinterability of  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  ceramics, which results in increasing of its apparent density for 0.35–0.70 wt. % Gr. Marked decrease of density to  $3.80 \text{ g/cm}^3$  (55.8% of theoretical value) was observed in the 1.15 wt. % graphene-added sample due to the formation of loose matrix with relatively high porosity and deteriorated texture.



**Fig. 2.** Surface SEM images of the  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_{y+x}$  wt. % Gr samples with a magnification of 5000 $\times$ . (a):  $x = 0$ , (b):  $x = 0.15$ , (c):  $x = 0.35$ , (d):  $x = 0.70$ , (e):  $x = 1.15$ .

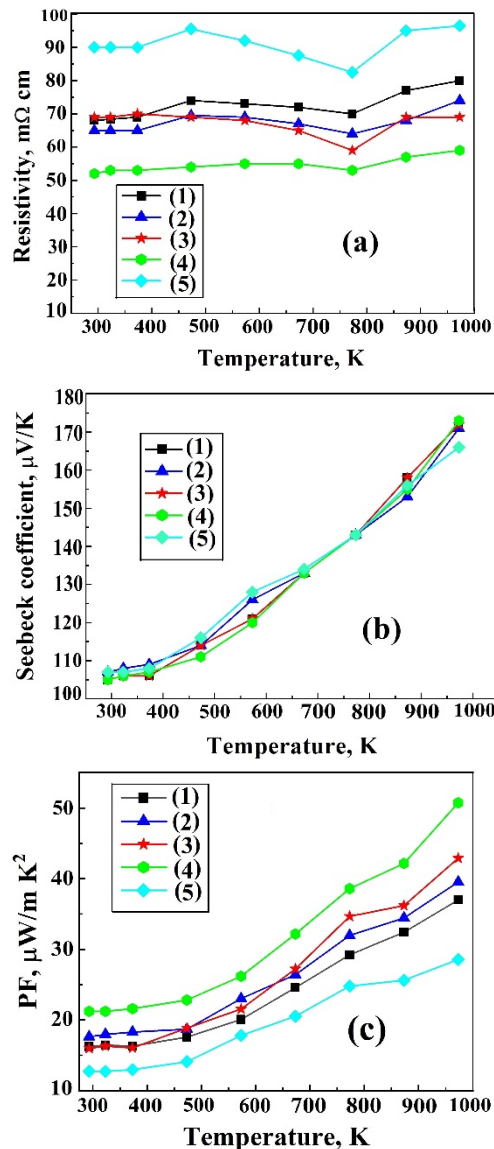
Fig. 3 illustrates the temperature dependences of electrical resistivity, Seebeck coefficient, and power factor of prepared materials. Temperature dependence of electrical resistivity of reference and

graphene-added ceramics showed, in the whole, slightly pronounced metallic character ( $\partial\rho/\partial T > 0$ ) (Fig. 3, a). This observation is consistent with the results of [11], where similar trend of  $\rho(T)$

dependence was found for layered bismuth–strontium cobaltite and its derivatives. Addition of 0.15–0.70 wt. % Gr graphene into the  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  resulted in decreasing of electrical resistivity, while  $\rho$  values of  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y+1.15$  wt. % Gr were 1.3 and 1.2 times larger (at 293 and 973 K, respectively) than for reference sample. The trend in dependence of electrical resistivity of  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y+x$  wt. % Gr composites on graphene content is similar to that observed for apparent density. Hence, the variation of resistivity with increasing graphene content can be well explained by the variation in ceramics porosity. The lowest values of electrical resistivity (52 and 59  $\text{m}\Omega\cdot\text{cm}$  at 293 and 973 K, respectively) were observed for relatively dense  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y+0.70$  wt. % Gr ceramics, which were 1.3 and 1.4 times smaller than for reference sample.

Seebeck coefficients of  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y/\text{Gr}$  composites increased with temperature (almost linearly above 450 K) and were close to each other. In our previous study of  $\text{Sr}(\text{BO}_2)_2$ -doped  $\text{Bi}_{2-x}[\text{Sr}(\text{BO}_2)_2]_x\text{Co}_{1.8}\text{O}_y$  system we observed similar behavior: the values of Seebeck coefficient of single-phase ceramics practically did not depend on doping level [14]. In contrary, formation of phase inhomogeneity in layered calcium cobaltite ceramics resulted in essential increasing of Seebeck coefficient [29, 30]. Hence, the results of Seebeck coefficient measurements prove that the  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  in the herein prepared ceramics is a single-phase. Noteworthy, the values of Seebeck coefficient for  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y/\text{Gr}$  composites are close to those reported for  $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ -based materials in [9–11, 14].

As can be seen from Fig. 3, c, the *PF* of ceramics increased from  $37.0 \mu\text{W}/(\text{m}\cdot\text{K}^2)$  at 973 K to  $50.7 \mu\text{W}/(\text{m}\cdot\text{K}^2)$  with increasing graphene content up to  $x = 0.70$  wt. %, which demonstrates the positive impact of graphene additive on power factor of  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  thermoelectrics. Further increase of graphene content to 1.15 wt. % resulted in the decrease of power factor.



**Fig. 3.** Temperature dependences of electrical resistivity (a), Seebeck coefficient (b), and power factor (c) of the  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y+x$  wt.% Gr samples, (1):  $x = 0$ , (2):  $x = 0.15$ , (3):  $x = 0.35$ , (4):  $x = 0.70$ , (5):  $x = 1.15$ .

## Conclusions

In this paper, the impact of graphene addition on the thermoelectric properties of  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  ceramics has been investigated. The structure and microstructure of prepared materials were examined using XRD and SEM techniques. The XRD analysis confirmed the phase purity of synthesized thermoelectrics. Based on the measurements of resistivity and Seebeck coefficient, the power factors for prepared samples

were calculated. The addition of graphene resulted in about 40% enhancement of the power factor of  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  thermoelectric ceramics.

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## ფიზიკა

# გრაფენის დანამატის ზეგავლენა $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ კერამიკის მიკროსტრუქტურასა და თერმოელექტრულ თვისებებზე

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§სომხეთის მეცნიერებათა ეროვნული აკადემიის ფიზიკურ კვლევათა ინსტიტუტი, ამტარაკი, სომხეთი

(წარმოდგენილია აკადემიის წევრის ა. ხელაშვილის მიერ)

წარმოდგენილ ნაშრომში შესწავლილია გრაფენის დანამატის ზეგავლენა  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  კერამიკის თერმოელექტრულ თვისებებზე. მიღებული მასალების სტრუქტურა და მიკროსტრუქტურა გამოკვლეულ იქნა რენტგენოდიფრაქციული ანალიზისა და მასკანირებელი ელექტრონული მიკროსკოპიის მეთოდების გამოყენებით. რენტგენოდიფრაქციულმა ანალიზმა დაადასტურა სინთეზირებული თერმოელექტრიკების ფაზური სისუფთავე. კუთრი წინაღობისა და ზეებევის კოეფიციენტის გაზომვითა საფუძველზე გამოთვლილ იქნა მიღებული ნიმუშების სიმძლავრის ფაქტორი. გრაფენის დანამატმა განაპირობა  $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$  თერმოელექტრიკის სიმძლავრის ფაქტორის დაახლოებით 40%-ით გაუმჯობესება.



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