

Effect of $\text{Pb}(\text{BO}_2)_2$ Doping on Power Factor of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ Thermoelectric Ceramics

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In this work, $\text{Pb}(\text{BO}_2)_2$ -doped $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ thermoelectric materials with composition $\text{Bi}_{2-x}[\text{Pb}(\text{BO}_2)_2]_x\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ ($x = 0, 0.075, 0.15, 0.25$) were prepared through the solid-state reaction method. Electron transport and microstructural characteristics of prepared materials were studied, and values of their power factor were calculated. It was found that the slight doping of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ with lead borate leads to the decrease in electrical resistivity at 923 K from 126 to 76.5 m Ω cm for $x = 0.15$. The resistivity increases upon further $\text{Pb}(\text{BO}_2)_2$ doping for $x = 0.25$. The increase in the Seebeck coefficient was observed with an increase in dopant content from $x = 0.15$ up to 0.25. The $\text{Pb}(\text{BO}_2)_2$ doping resulted in a 1.8-fold enhancement of the power factor from 21.7 $\mu\text{W}/(\text{m K}^2)$ at 923 K in the reference sample to 38.2 $\mu\text{W}/(\text{m K}^2)$ in the doped sample with $x = 0.15$. Partial substitution of Bi_2O_3 by $\text{Pb}(\text{BO}_2)_2$ also promotes both grain growth and densification of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ thermoelectric ceramics.

topics: $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ thermoelectric, doping, resistivity, Seebeck coefficient

1. Introduction

The heat evolved into the environment during the operation of enterprises and autos can be directly converted into electrical energy in thermoelectric generators (TEGs). To produce TEGs, one needs so-called thermoelectric materials, which must possess low electrical resistivity (ρ), thermal conductivity (λ), and high Seebeck coefficient (S).

Layered bismuth–strontium cobaltite $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ crystallizes in monoclinic syngony, and its crystal structure consists of alternating $[\text{CoO}_2]$ and $[\text{Bi}_2\text{Sr}_2\text{O}_4]$ layers, in which a , c , and β lattice constants are identical, but b parameters mismatch each other, so this complex oxide belongs to so-called misfit-layered phases [1–3]. $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ is the possible candidate for p-branches of high-temperature TEGs because it possesses high Seebeck coefficient S , low resistivity ρ , and thermal conductivity λ values. Moreover, $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ cobaltite is stable in air at elevated temperatures [1, 3]. Thermoelectric characteristics, such as power factor $PF = S^2/\rho$ and thermoelectric figure-of-merit $ZT = S^2T/(\rho\lambda)$, where T

is the absolute temperature of layered bismuth–strontium cobaltite, are inferior to the traditional thermoelectrics based on the layered chalcogenides of heavy metals but can be improved through optimization of its chemical composition [4–6] or using advanced preparation methods [7, 8].

Cobaltite thermoelectrics show a resemblance in structure to the high-temperature cuprate superconductors, such as the 2D character of CoO_2 and CuO_2 conducting layers and the mixed valence ($\text{Cu}^{2+}/\text{Cu}^{3+}$, $\text{Co}^{3+}/\text{Co}^{4+}$), suggesting that these two systems have similar underlying physics [9, 10]. Our previous reports indicate that the introduction of $\text{Pb}(\text{BO}_2)_2$ into the Bi-2223 superconductor promotes the formation of the Bi-2223 phase and leads to the increase in the intergranular critical current density compared to the reference sample [11, 12].

Recently, we found that the power factor of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ may be essentially improved through doping by $\text{Sr}(\text{BO}_2)_2$ [13]. The aim of this work is to check the possibility of improving the thermoelectric properties of layered bismuth–strontium cobaltite through its doping by $\text{Pb}(\text{BO}_2)_2$.

2. Experimental technique

Reference (undoped) and $\text{Pb}(\text{BO}_2)_2$ -doped samples of nominal composition $\text{Bi}_{2-x}[\text{Pb}(\text{BO}_2)_2]_x\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ ($x = 0, 0.075, 0.15,$ and 0.25) were prepared by the solid-state reaction method from Bi_2O_3 , $\text{Pb}(\text{BO}_2)_2$, SrCO_3 and Co_3O_4 raw materials (purity 98–99%). The mixtures of the initial powders were thoroughly mixed and calcined at 1023–1073 K for 23 h, with intermediate grinding in an agate mortar. Then the powders were pressed into pellets with a diameter of 15 mm at a hydrostatic pressure of 165 MPa. The pellets were sintered at 1093 K in air for 25 h, then cooled to room temperature in the furnace. The resistivity $\rho(T)$ of the samples in the temperature range from room temperature to 923 K was measured by the standard four-probe method. The temperature dependence of the Seebeck coefficient was determined by the differential method on a setup designed in the laboratory using a KEITHLEY DMM6500 multimeter at $T = 300$ –923 K on bar-shaped samples with dimensions of $13 \times 7 \times 3 \text{ mm}^3$. The microstructure and elemental composition of prepared materials were analysed by the scanning electron microscope (SEM) VEGA TS5130MM coupled with energy dispersive X-ray (EDX) microanalysis system INCA Energy 300.

3. Results and discussion

The prepared reference sample was single-phase, within XRD accuracy, and consisted of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$, with lattice constants equal to $a = 4.816 \text{ \AA}$, $b = 5.378 \text{ \AA}$, $c = 14.90 \text{ \AA}$ and $\beta = 91.84^\circ$, that was close to data given in [1, 3]. $\text{Pb}(\text{BO}_2)_2$ -doped samples, on the contrary, were multi-phase and, besides the main $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ phase, contained small amounts of impurity phases (probably bismuth, strontium, and cobalt oxides [14]), quantities of which increased with increasing doping level. The apparent density of reference sample 3.98 g/cm^3 was 58% of the theoretical value (6.81 g/cm^3 [2]). $\text{Pb}(\text{BO}_2)_2$ -doping leads to the monotonic increase in density in $\text{Bi}_{2-x}[\text{Pb}(\text{BO}_2)_2]_x\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ materials up to 5.02 g/cm^3 (about 74% of the theoretical density) for $x = 0.25$. So the introduction of lead borate into layered bismuth–strontium cobaltite enhances its sinterability. Surface SEM micrographs of the $\text{Bi}_{2-x}[\text{Pb}(\text{BO}_2)_2]_x\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ samples are shown in Fig. 1. The grains of ceramics had a plate-like shape, which is typical for layered bismuth–strontium cobaltite [2, 4, 7]. The thickness of grains varied within the range of 200–700 nm, and their size increased from 3–4 μm for the reference $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ sample to 6–17 μm for ceramics with the composition of $\text{Bi}_{1.75}[\text{Pb}(\text{BO}_2)_2]_{0.25}\text{Sr}_2\text{Co}_{1.8}\text{O}_y$.

According to EDX results, the calculated composition of the reference sample $\text{Bi}_{2.02}\text{Sr}_2\text{Co}_{1.84}\text{O}_y$

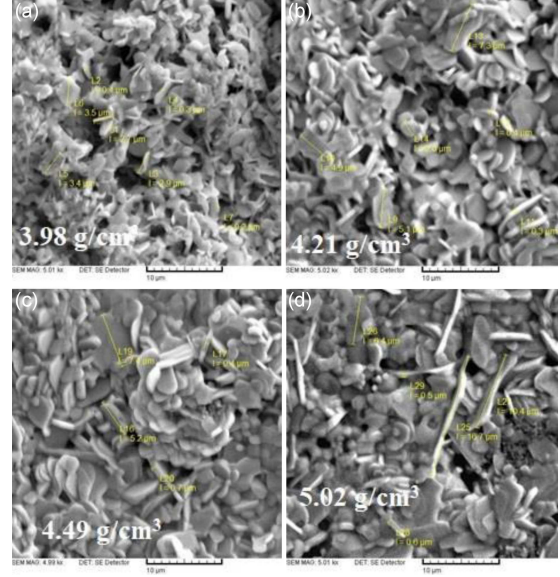


Fig. 1. Surface SEM micrographs of the $\text{Bi}_{2-x}[\text{Pb}(\text{BO}_2)_2]_x\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ samples with a magnification of $\times 5000$, where $x = 0$ (a), 0.075 (b), 0.15 (c), and 0.25 (d).

strongly corresponds to its nominal composition of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ within the accuracy of this method. The composition of main phase grains in $\text{Pb}(\text{BO}_2)_2$ -doped samples slightly varied and was, as a whole, close to their nominal compositions. Grains of impurities in these samples consisted of bismuth, strontium, and cobalt oxides (in many cases, with small additions of other oxides). This result agrees with the XRD data and proves them.

Temperature dependences of electrical resistivity, Seebeck coefficient, and power factor of prepared $\text{Bi}_{2-x}[\text{Pb}(\text{BO}_2)_2]_x\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ materials are presented in Fig. 2. Temperature dependence of electrical resistivity of reference $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ cobaltite showed a semiconducting character ($\partial\rho/\partial T < 0$) (Fig. 2a), which is typical for the $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ ceramics prepared by conventional sintering [13, 15]. The same but less pronounced character of resistivity was observed for $\text{Bi}_{1.75}[\text{Pb}(\text{BO}_2)_2]_{0.25}\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ sample. At the same time, the electrical resistivity of $\text{Bi}_{1.925}[\text{Pb}(\text{BO}_2)_2]_{0.075}\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ and $\text{Bi}_{1.85}[\text{Pb}(\text{BO}_2)_2]_{0.15}\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ cobaltites remained almost unchanged within the temperature interval studied. The large enough values of resistivity of reference sample (180 $\text{m}\Omega \text{ cm}$ and 125 $\text{m}\Omega \text{ cm}$ at 290 and 923 K, respectively) agree with the literature data for $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ cobaltite prepared using solid-state reactions method [3, 15]. Doping with lead borate leads to a sharp decrease in resistivity for the samples with $x = 0.075$ and 0.15 . The lowest value of electrical resistivity, equal to 77 $\text{m}\Omega \text{ cm}$ at 923 K, was found for the $\text{Bi}_{1.85}[\text{Pb}(\text{BO}_2)_2]_{0.15}\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ sample, which is 1.6-fold smaller than for reference material.

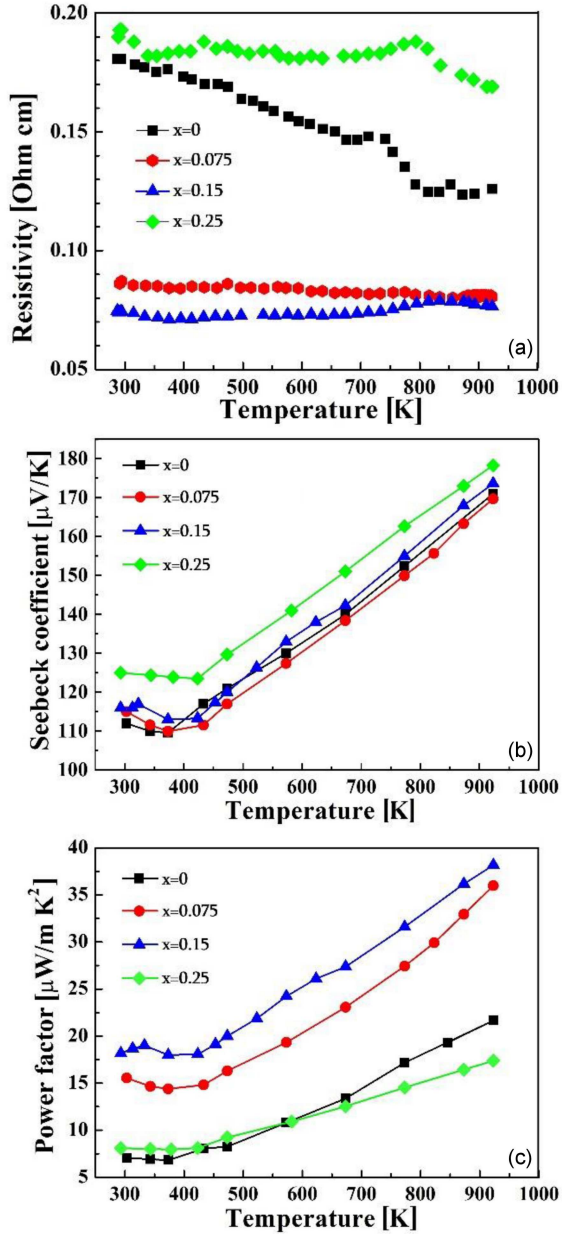


Fig. 2. Temperature dependences of electrical resistivity (a), Seebeck coefficient (b), and power factor (c) of $\text{Bi}_{2-x}[\text{Pb}(\text{BO}_2)_2]_x\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ samples.

We assume that due to the very low melting point of $\text{Pb}(\text{BO}_2)_2$, $T_m = 500^\circ\text{C}$, lead borate promotes an extra liquid phase formation, thus increasing the mobility of the elements required to form the $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ phase and enhancing the sintering process [11, 12]. Results of resistivity measurements agree fairly well with clearly visible enlargement of crystallite sizes due to the introduction of $\text{Pb}(\text{BO}_2)_2$ into the matrix estimated from SEM micrographs (Fig. 1) and the increased density of samples. It is also possible that the partial substitution of Bi_2O_3 with $\text{Pb}(\text{BO}_2)_2$ leads to an increased charge carrier concentration due to hole-doping, which in turn provides improved

electrical conductivity. The conductivity decreases sharply for higher $\text{Pb}(\text{BO}_2)_2$ content, $x = 0.25$ (Fig. 2a), probably because of the elevated concentrations of high-resistivity impurities (bismuth, strontium, and cobalt oxides) in the ceramics.

It is known that porosity can affect the thermoelectric performance of ceramics in various ways. Gostkowska-Lekner et al. [16] successfully fabricated highly porous, in-filled CoSb_3 skutterudite materials with an attractive thermoelectric figure of merit ($ZT \approx 1$). It was shown that in-filled CoSb_3 samples with higher porosities exhibit lower values of electrical conductivity, but the benefit of lower thermal conductivity outweighs losses in electrical conductivity, resulting in higher ZT values. The ZT of 1.18 was obtained in the highly porous BiTeSe thermoelectric chalcogenide nanocomposite [17]. It has been reported that a dense $\text{Ca}_3\text{Co}_4\text{O}_9$ thermoelectric possesses a higher electrical conductivity and thus a higher power factor, but also a higher heat conductivity and thus a lower ZT value compared with a porous one [18]. On the other hand, it was found that Cs substitution for Sr in $\text{Bi}_2\text{Sr}_{2-x}\text{Cs}_x\text{Co}_2\text{O}_y$ materials led to the formation of a liquid phase during the sintering procedure, drastically enhancing grain growth and decreasing porosity [19]. Moreover, electrical resistivity decreases with Cs doping, which results in the enhancement of power factor values. Accurate consideration of a high power factor (dense sample) and low heat conductivity (porous sample) can be beneficial, and help to discover an ideal proportion [18].

Seebeck coefficient values of prepared $\text{Bi}_{2-x}[\text{Pb}(\text{BO}_2)_2]_x\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ samples increased with increasing temperature (almost linearly above 423 K) and doping level and reached the maximum value of $178.3 \mu\text{V}/\text{K}$ at 933 K for $x = 0.25$ (Fig. 2b). In our previous study of the $\text{Sr}(\text{BO}_2)_2$ -doped $\text{Bi}_{2-x}[\text{Sr}(\text{BO}_2)_2]_x\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ ($x = 0-0.15$) system, we found that values of the Seebeck coefficient of the single-phase ceramics practically did not depend on doping level [13]. An increase in Seebeck coefficient in multiphase $\text{Pb}(\text{BO}_2)_2$ -doped $\text{Bi}_{2-x}[\text{Pb}(\text{BO}_2)_2]_x\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ materials with increasing content of dopant (and impurity phases) agrees fairly well with the essential increase in Seebeck coefficient due to creation of phase inhomogeneity in calcium cobaltite $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ [20]. Note that values of Seebeck coefficient of $\text{Bi}_{2-x}[\text{Pb}(\text{BO}_2)_2]_x\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ samples were close to those obtained for $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ -based ceramics prepared by the solid-state reaction method in [2, 4-6, 9].

As can be seen in Fig. 2c, values of the power factor of materials studied increased with temperature increasing above 400 K. $\text{Pb}(\text{BO}_2)_2$ -doping leads to the marked enhancement of PF values in $\text{Bi}_{2-x}[\text{Pb}(\text{BO}_2)_2]_x\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ samples with $x = 0.075-0.15$ and a sharp decrease upon further doping with $x = 0.25$. A maximum PF value of $38.2 \mu\text{W}/(\text{m K}^2)$ at 923 K was found

for the $\text{Bi}_{1.85}[\text{Pb}(\text{BO}_2)_2]_{0.15}\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ ceramics, which possessed both low resistivity and high Seebeck coefficient values. This value is significantly smaller than for $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ -based ceramics [20] but essentially larger than for $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ -based solid solutions obtained in [3] ($1\text{--}15 \mu\text{W}/(\text{m K}^2)$) and 1.8 times higher than for reference bismuth–strontium cobaltite. That indicates that $\text{Pb}(\text{BO}_2)_2$ doping is an effective way to improve the thermoelectric properties of layered bismuth–strontium cobaltite. It should be pointed out that PF values for the samples prepared in this work are not so large as to recommend them for use in TEGs but can be improved in the future by means of tuning their composition and variation of sintering method. However, it should be noted that, as a whole, the p-type misfit layered cobaltites are not yet commercially viable and their thermoelectric performance needs to be improved substantially to address technological and commercial challenges.

4. Conclusion

In this paper, for the first time we studied the impact of partial substitution of Bi_2O_3 by $\text{Pb}(\text{BO}_2)_2$ on the power factor of $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ thermoelectric ceramics. $\text{Bi}_{2-x}[\text{Pb}(\text{BO}_2)_2]_x\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ ($x = 0, 0.075, 0.15, \text{ and } 0.25$) samples were prepared by the solid-state reaction method. Resistivity and Seebeck coefficient were measured from room temperature to 923 K, and microstructure of prepared materials was analysed. Doping with $\text{Pb}(\text{BO}_2)_2$ resulted in a decrease in the resistivity for $x = 0.075\text{--}0.15$ and increase in Seebeck coefficient for $x = 0.15\text{--}0.25$. SEM images revealed the significant increase in crystallite sizes in the $\text{Pb}(\text{BO}_2)_2$ doped $\text{Bi}_{2-x}[\text{Pb}(\text{BO}_2)_2]_x\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ samples. Improvement of the electrical conductivity, Seebeck coefficient and density of the doped materials with increased grain growth and modulated microstructure upon $\text{Pb}(\text{BO}_2)_2$ doping leads to the 1.8-fold enhancement of thermoelectric power factor in doped $\text{Bi}_{2-x}[\text{Pb}(\text{BO}_2)_2]_x\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ sample, $x = 0.15$, compared with the reference $\text{Bi}_2\text{Sr}_2\text{Co}_{1.8}\text{O}_y$ ceramics.

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