Thermoelectric Ceramics Based on the Layered Cobaltates of Bismuth and Alkaline-Earth Metals

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Abstract Using solid-state reactions method the ceramic samples of 
\((Bi,Pb)_{2}Ba_{2}(Co_{M})_{2}O_{y}\), 
\((Bi,Pb)_{2}Sr_{2}(Co_{M})_{2}O_{y}\), and \((Bi,Pb)_{2}Ca_{2}(Co_{M})_{2}O_{y}\) \((M = \text{Mn, Zn})\) solid solutions had been prepared, their lattice constants had been determined and their thermal expansion, electrical conductivity and thermo-EMF had been measured, and their power factor had been calculated. Effect of the bismuth substitution by lead and cobalt substitution by manganese and zinc in the layered cobaltates of bismuth and alkaline-earth metals (AEM) on the crystal structure and physicochemical and functional properties of their derivatives was analyzed. It was found that cobaltates studied are \(p\)-type conductors, which linear thermal expansion coefficient (LTEC) values varied within \((9.68–13.2)\cdot10^{-6} \text{ K}^{-1}\). Power factor values for the samples studied unmonotonously changed when temperature increased and at 1000 K were maximal for \(\text{Bi}_{2}\text{Ba}_2\text{Co}_2\text{O}_y\), \(\text{Bi}_{2}\text{Sr}_2\text{Co}_{1.7}\text{Mn}_{0.3}\text{O}_y\), and \(\text{Bi}_{2}\text{Ca}_{2}\text{Co}_{1.7}\text{O}_y\) compounds – 12.1, 10.1, and 10.6\(\mu\text{W}/(\text{m} \cdot \text{K})\) respectively.

Keywords Layered Bismuth and Alkaline-Earth Metals Cobaltates, Thermoelectrics, Thermal Expansion, Electrical Conductivity, Thermo-EMF, Power Factor

1. Introduction

Heat evolved into environment during working of factories and transport can be effectively and directly converted into electrical energy in devices called thermoelectric generators (TEGs) [1]. To produce TEGs one needs both \(n\)-type and \(p\)-type thermoelectric materials. Manganites \((\text{CaMnO}_3)\) [2, 5], titanates \((\text{TiO}_2, \text{SrTiO}_3)\) [2, 6], or plumbates \((\text{Ba,Sr, PbO})\) [2, 7, 8] are prospective \(n\)-type thermoelectrics, but layered cobaltates \((\text{Na,Co,Co})\) [2, 9, 10], \(\text{Ca}_3\text{Co}_4\text{O}_{4+}\delta\) [2, 11, 12], \(\text{Bi}_2\text{Ba}_2\text{Co}_2\text{O}_y\) [13], \(\text{Bi}_3\text{Sr}_2\text{Co}_{1.8}\text{O}_y\) [14], \(\text{Bi}_2\text{Ca}_2\text{Co}_{1.5}\text{O}_y\) [15–17] are prospective \(p\)-type thermoelectrics.

Layered cobaltates of bismuth and alkaline-earth metal \((\text{Bi}_2\text{Ba}_2\text{Co}_2\text{O}_y, \text{Bi}_3\text{Sr}_2\text{Co}_{1.8}\text{O}_y, \text{Bi}_2\text{Ca}_2\text{Co}_{1.5}\text{O}_y)\) belong to the so-called misfit-layered phases, which structure consists of stacked \([\text{CoO}_2]_a\) layers (structure type of \(\text{CdI}_2\)) and \([\text{Bi}_2\text{M}_2\text{O}_4]\) \((M = \text{Ca, Sr, Ba})\) (structure type of \(\text{NaCl}\)), where \(a, c, \) and \(\beta\) of both of layers are identical, but \(b\) parameters differ [13–15]. These complex oxides possess high electrical conductivity due to high concentration of charge carriers (“holes”) in conducting \([\text{CoO}_2]_a\) layers, high values Seebeck’s coefficient because cobalt ions in their structure are in different charge \((\text{Co}^{3+}, \text{and Co}^{4+})\) and spin states (high-spin state, intermediate-spin state, and low-spin state), and have low thermal conductivity due to strong anisotropy and mismatch of their crystal structure in \(b\) direction.

To improve functional (thermoelectric) properties of ceramic materials based on these layered compounds one can use solution method synthesis instead of traditional solid-state reactions method [15, 17], special methods of thermal treatment and sintering of ceramics [17], as well as chemical substitution of different ions in their structure [6, 11, 12, 14].

The aim of this work is to study the effect of partial substitution of bismuth by lead and of cobalt by manganese or zinc on the crystal structure and physicochemical properties of solid solutions based on the layered cobaltates of bismuth and alkaline-earth metals \((\text{Bi}_2\text{Ba}_2\text{Co}_2\text{O}_y, \text{Bi}_3\text{Sr}_2\text{Co}_{1.8}\text{O}_y, \text{Bi}_2\text{Ca}_2\text{Co}_{1.5}\text{O}_y)\).

2. Materials and Methods

The ceramic samples of the layered cobaltates of bismuth and alkaline-earth metals were prepared using solid-state reactions method from \(\text{Bi}_2\text{O}_3\) (pure grade), \(\text{BaCO}_3\) (pure grade), \(\text{SrCO}_3\) (pure grade), \(\text{PbO}\) (pure for analysis grade),
Mn₂O₃ (super pure grade), Co₃O₄ (pure grade), and ZnO (pure grade) taken in appropriate stoichiometric compositions in air at different conditions (see Table 1).

| Compound | Synthesis | Sintering |
|----------|-----------|-----------|
| Bi₂Ca₂Co₁,₇O₉ | 1073 K / 12 h | 1133 K / 12 h |
| Bi₁,₆Pb₀,₄Ca₂Co₁,₇O₉ | 1073 K / 12 h | 1073 K / 12 h |
| Bi₂Ca₂Co₁,₆Mn₀,₁O₉ | 1073 K / 12 h | 1133 K / 12 h |
| Bi₂Ca₂Co₁,₆Zn₀,₁O₉ | 1073 K / 12 h | 1133 K / 12 h |
| Bi₂Sr₂Co₁,₈O₉ | 1073 K / 12 h | 1113 K / 12 h |
| Bi₁,₆Pb₀,₄Sr₂Co₁,₈O₉ | 1073 K / 12 h | 1073 K / 12 h |
| Bi₂Sr₂Co₁,₇Mn₀,₁O₉ | 1073 K / 12 h | 1113 K / 12 h |
| Bi₂Sr₂Co₁,₇Zn₀,₁O₉ | 1073 K / 12 h | 1113 K / 12 h |
| Bi₂Ba₂Co₂O₉ | 1073 K / 12 h | 1073 K / 12 h |
| Bi₁,₆Pb₀,₄Ba₂Co₂O₉ | 1073 K / 12 h | 1073 K / 12 h |
| Bi₂Ba₂Co₁,₉Mn₀,₁O₉ | 1073 K / 12 h | 1073 K / 12 h |
| Bi₂Ba₂Co₁,₉Zn₀,₁O₉ | 1073 K / 12 h | 1073 K / 12 h |

The values of the sintering temperatures of the ceramics were chosen in such a way as to avoid its melting and were based on the results of our preliminary experiments. Identification of the samples and determination of their lattice constants was performed using X-ray diffraction analysis (XRD) (Bruker D8 XRD Advance diffractometer, CuKα-radiation, Ni filter). The apparent density (ρ) of the samples was calculated using their mass and geometrical dimensions.

Thermal expansion, electrical conductivity and thermo-EMF coefficient of the samples were investigated in air within 300–1100 K temperature interval by methods described in [8, 10, 12]. Linear thermal expansion coefficient (LTEC, α) values of the oxides studied were calculated from the linear parts of the Δl/l₀ = f(T) dependences. Values of power factor of the ceramics were calculated using formula

\[ P = S^2 \sigma. \]

3. Results and Their Discussion

As can be seen from the Figure 1, all the samples prepared, were, within XRD accuracy, monophase (excluding Bi₂Sr₂Co₁,₇Zn₀,₁O₉, Bi₁,₆Pb₀,₄Sr₂Co₁,₈O₉ compounds, on which diffractograms, in addition to the reflexes of main phase – layered bismuth–strontium cobaltate – the reflexes of impurity phase were observed), and their structure corresponded to the structure of layered cobaltate of bismuth and AEM [13–15]. Partial substitution of bismuth by lead and of cobalt by manganese or zinc in Bi₂M₂CoₓO₉ (M = Ca, Sr, Ba) cobaltates did not affect the form of diffractograms and had only led to the small shifts of the peaks positions to the smaller or larger angles (Figure 1), so such substitution does not affect the crystal structure of the samples but only changed their lattice constants. On the diffractograms of all samples the 00l peaks were most pronounced, so we can conclude that ceramics were partially textured (its grains were aligned mainly in direction of c axis).

![Figure 1](image-url)
The lattice constants of the samples studied are given in Table 2. One can see that partial substitution in the Bi$_2$Sr$_2$Co$_1.7$O$_y$ of bismuth by lead and of cobalt by manganese or zinc results in the increasing of lattice constants of Bi$_1.6$Pb$_0.4$Co$_x$O$_y$ and Bi$_2$Sr$_2$Co$_1.8$O$_y$ (Figure 2); so, we can conclude that within temperature interval studied these compounds do not undergo any structural phase transitions. LTEC values of the Bi$_1.6$Pb$_0.4$Co$_x$O$_y$ and Bi$_2$Sr$_2$Co$_1.8$O$_y$ deteriorates, in the whole, at partial substitution in it of Bi or Co by other metals, but sinterability of Bi$_2$Ba$_2$Co$_2$O$_y$ in contrary, is improved at such substitution.

Temperature dependences of the relative elongation ($\Delta l/l_0$) of the sintered ceramics of bismuth and AEM layered cobaltates: 1 – Bi$_2$Ca$_2$Co$_1.9$O$_y$, 2 – Bi$_2$Ca$_2$Co$_1.9$Mn$_{0.1}$O$_y$, 3 – Bi$_2$Ca$_2$Co$_1.9$Zn$_{0.1}$O$_y$, 4 – Bi$_2$Pb$_{0.4}$Ca$_2$Co$_1.7$O$_y$, 5 – Bi$_2$Sr$_2$Co$_1.8$O$_y$, 6 – Bi$_2$Sr$_2$Co$_1.8$Mn$_{0.1}$O$_y$, 7 – Bi$_2$Sr$_2$Co$_1.8$Zn$_{0.1}$O$_y$, 8 – Bi$_1.6$Pb$_0.4$Sr$_2$Co$_1.8$O$_y$, 9 – Bi$_1.6$Pb$_0.4$Ba$_2$Co$_2$O$_y$, 10 – Bi$_2$Ba$_2$Co$_1.9$Mn$_{0.1}$O$_y$, 11 – Bi$_2$Ba$_2$Co$_1.9$Zn$_{0.1}$O$_y$, 12 – Bi$_1.6$Pb$_0.4$Ca$_2$Co$_1.7$O$_y$ solid solutions. So results of this work show that sinterability of Bi$_2$Ca$_2$Co$_1.9$O$_y$ and Bi$_2$Sr$_2$Co$_1.8$O$_y$ deteriorates, in the whole, at partial substitution in it of Bi or Co by other metals, but sinterability of Bi$_2$Ba$_2$Co$_2$O$_y$ is improved at such substitution.

Temperature dependences of the relative elongation of all ceramic samples investigated were close to the linear (Figure 2); so, we can conclude that within temperature interval studied these compounds do not undergo any structural phase transitions. LTEC values of the Bi$_1.6$Pb$_0.4$Co$_x$O$_y$ and Bi$_2$Sr$_2$Co$_1.8$O$_y$ solid solutions varied within (11.7–13.2)·10$^{-5}$ K$^{-1}$ and were essentially larger than for unsubstituted cobaltates Bi$_2$M$_x$Co$_{1-y}$O$_y$ ((11.7–13.2)·10$^{-5}$ K$^{-1}$) (Table 2).

Obtained increasing of LTEC values of Bi$_2$M$_x$Co$_{1-y}$O$_y$ derivatives in comparison to the Bi$_2$M$_x$Co$_{1-y}$O$_y$ base phases, by our opinion, is due to the increasing of anharmonicity degree of metal–oxygen vibrations in their structure at partial substitution of bismuth by lead or cobalt by manganese or zinc.

### Table 2. Syngony, lattice constants (a, b, c, $\beta$, V), apparent density ($\rho$), and linear thermal expansion coefficient ($\alpha$) of the bismuth and AEM layered cobaltates

| Compound                        | Syngony | a, Å   | b, Å   | c, Å   | $\beta$, $^\circ$ | V, Å$^3$ | $\rho$, g/cm$^3$ | $\alpha$·10$^-6$, K$^{-1}$ |
|---------------------------------|---------|--------|--------|--------|-------------------|----------|-----------------|-----------------------------|
| Bi$_2$Ca$_2$Co$_1.9$O$_y$       | M       | 4.894  | 4.765  | 14.69  | 93.74             | 341.8    | 5.00            | 9.68                        |
| Bi$_2$Pb$_{0.4}$Ca$_2$Co$_1.7$O$_y$ | M       | 4.910  | 4.779  | 14.74  | 93.59             | 345.3    | 4.78            | 11.7                        |
| Bi$_2$Ca$_2$Co$_1.9$Mn$_{0.1}$O$_y$ | M       | 4.912  | 4.812  | 14.74  | 93.96             | 347.5    | 4.98            | 10.6                        |
| Bi$_2$Ca$_2$Co$_1.9$Zn$_{0.1}$O$_y$ | M       | 4.915  | 4.774  | 14.71  | 93.37             | 344.5    | 4.19            | 11.4                        |
| Bi$_2$Sr$_2$Co$_1.8$O$_y$        | M       | 4.824  | 5.367  | 14.98  | 91.29             | 387.8    | 4.54            | 11.5                        |
| Bi$_2$Pb$_{0.4}$Sr$_2$Co$_1.8$O$_y$ | M       | 4.877  | 5.275  | 15.04  | 93.10             | 386.4    | 4.49            | 12.4                        |
| Bi$_2$Sr$_2$Co$_1.8$Mn$_{0.1}$O$_y$ | M       | 4.811  | 5.354  | 14.96  | 91.24             | 385.3    | 4.32            | 12.2                        |
| Bi$_2$Sr$_2$Co$_1.8$Zn$_{0.1}$O$_y$ | M       | 4.821  | 5.347  | 14.95  | 91.76             | 385.2    | 4.80            | 12.6                        |
| Bi$_2$Ba$_2$Co$_1.9$O$_y$        | O       | 4.886  | 5.799  | 15.43  | –                 | 437.3    | 5.14            | 11.3                        |
| Bi$_2$Pb$_{0.4}$Ba$_2$Co$_2$O$_y$ | O       | 4.874  | 5.820  | 15.17  | –                 | 430.5    | 5.66            | 13.2                        |
| Bi$_2$Ba$_2$Co$_1.9$Mn$_{0.1}$O$_y$ | O       | 4.887  | 5.776  | 15.45  | –                 | 436.1    | 5.28            | 12.4                        |
| Bi$_2$Ba$_2$Co$_1.9$Zn$_{0.1}$O$_y$ | O       | 4.866  | 5.773  | 15.32  | –                 | 430.5    | 5.18            | 12.3                        |
Figure 3. Temperature dependences of electrical conductivity ($\sigma$), thermo-EMF coefficient ($S$), and power factor ($P$) of bismuth and AEM layered cobaltates: 1 – Bi$_2$Ca$_2$Co$_{1.7}$O$_y$, 2 – Bi$_2$Ca$_2$Co$_{1.6}$Mn$_{0.1}$O$_y$, 3 – Bi$_2$Ca$_2$Co$_{1.6}$Zn$_{0.1}$O$_y$, 4 – Bi$_1.6$Pb$_{0.4}$Ca$_2$Co$_{1.7}$O$_y$, 5 – Bi$_2$Sr$_2$Co$_{1.8}$O$_y$, 6 – Bi$_2$Sr$_2$Co$_{1.7}$Mn$_{0.1}$O$_y$, 7 – Bi$_2$Sr$_2$Co$_{1.7}$Zn$_{0.1}$O$_y$, 8 – Bi$_1.6$Pb$_{0.4}$Sr$_2$Co$_{1.8}$O$_y$, 9 – Bi$_2$Ba$_2$Co$_{2}$O$_y$, 10 – Bi$_2$Ba$_2$Co$_{1.9}$Mn$_{0.1}$O$_y$, 11 – Bi$_2$Ba$_2$Co$_{1.9}$Zn$_{0.1}$O$_y$, 12 – Bi$_1.6$Pb$_{0.4}$Ba$_2$Co$_{2}$O$_y$. 
All the samples studied were p-type conductors, which conductivity character changed from semiconducting to metallic near 800–900 K (for Bi$_2$Pb$_0$Ba$_2$Co$_2$O$_y$ near 750 K), except Bi$_2$Ca$_2$Co$_{1.9}$Mn$_{0.1}$O$_y$ (M = Mn, Zn) solid solutions possessing semiconducting character of electrical conductivity within all temperature interval studied (Figure 3). Note that for the several samples (Bi$_{1+\delta}$Pb$_{1-\delta}$Ca$_2$Co$_{1.7}$O$_y$, Bi$_2$Sr$_2$Co$_{1.8}$O$_y$, Bi$_2$Sr$_2$Co$_{1.7}$Mn$_{0.1}$O$_y$, Bi$_2$Ba$_2$Co$_{1.8}$O$_y$, Bi$_2$Ba$_2$Co$_{1.9}$Zn$_{0.1}$O$_y$, Bi$_2$Ba$_2$Co$_{1.8}$Mn$_{0.1}$O$_y$ (M = Mn, Zn)) conductivity character changed again from metallic to semiconducting near 950–1000 K. Observed on the $\sigma=f(T)$ dependences anomalies were, probably, due to the evolution of so-called weakly-bonded oxygen from the samples to environment as well as due to the spin state transition of the cobalt ions in their crystal structure [10, 12].

Values of electrical conductivity of ceramics studied in this work (Figure 3, Table 3) were close to the literature data, according to them $\sigma$ of layered cobaltates of bismuth and AEE obtained using ceramic method varied within 2-20 S/cm [14, 16–19]. So, for example electrical conductivity of Bi$_{1+\delta}$Pb$_{1-\delta}$Sr$_2$Co$_{1.8}$O$_y$ within 323–923 K temperature interval varied within 6–12 S/cm [18] and $\sigma$ values of Bi$_{1+\delta}$Pb$_{\delta}$Sr$_{3-\delta}$M$_{\delta}$O$_{2-\delta}$ ($M=\text{Sc}^{3+}, \text{Y}^{3+}, \text{or} \text{La}^{3+}$) ceramics at room temperature were less than 10 S/cm [19]. Such values of electrical conductivity of ceramics are insufficiently large to use it in TEGs, but they can be improved using special methods of synthesis [15, 17] or sintering of ceramics [17] as well as by means of addition of noble metals powders (in particular, Ag) to the ceramics [18].

As can be seen from the Figure 3 and Table 3, electrical conductivity values of Bi$_2$Ca$_2$Co$_{1.8}$O$_y$ sharply decreased at substitution of Bi by Pb and of Co by Mn or Zn in its structure, for Bi$_2$Sr$_2$Co$_{1.8}$O$_y$ at such substitution the values of electrical conductivity at low temperatures decreased but at high temperatures increased, and, finally, electrical conductivity values of Bi$_2$Ba$_2$Co$_{1.8}$O$_y$ derivatives were smaller than for the parent phase, except Bi$_{1+\delta}$Pb$_{\delta}$Ba$_2$Co$_{2}$O$_y$ solid solution which $\sigma$ values within temperature intervals 500–800 and 1000–1100 K were larger than for Bi$_2$Ba$_2$Co$_{2}$O$_y$ (Figure 3). Decreasing of electrical conductivity of derivatives of bismuth and AEE layered cobaltates in comparison to the parent complex oxides may be connected to the decreasing of mobilities of charge carriers ("holes") in them due to the creation of chemical inhomogeneity in the samples. Our data are in a good accordance with the results of [19] where had been found that partial substitution of calcium by lanthanum in Bi$_{1+\delta}$Pb$_{\delta}$Ca$_2$Co$_{2}$O$_{2.5}$ lead to the increasing of electrical resistivity of ceramics formed.

Maximal values of electrical conductivity Bi$_2$Ba$_2$Co$_{2}$O$_y$ and Bi$_{1+\delta}$Pb$_{\delta}$Ba$_2$Co$_{2}$O$_y$ cobaltates possessed (more than 10 S/cm within temperature interval 500–900 K) (Figure 3).

Thermo-EMF coefficient values of the ceramic samples studied increased (for Bi$_2$Ca$_2$Co$_{1.8}$O$_y$, in contrast, decreased) at temperature increasing, hereby and for the almost all samples at relatively high temperatures (for example, above 600 K for Bi$_2$Ca$_2$Co$_{1.8}$Mn$_{0.1}$O$_y$, and above 900 K for Bi$_2$Sr$_2$Co$_{2}$O$_y$) values of thermo-EMF coefficient decreased at temperature increasing (Figure 3). Observed anomalies of thermo-EMF of the layered cobaltates as anomalies of their electrical conductivity are, obviously, due to change of their oxygen stoichiometry and spin state of cobalt ions in their crystal structure.

Values of the thermo-EMF coefficient of the samples studied in this work varied, in the whole, within 100–150 $\mu$V/K and were typical for the layered cobaltates of the bismuth and AEE and their derivatives [12–14, 16–18]. Maximal values of Seebeck’s coefficient were found for Bi$_2$Sr$_2$Co$_{2}$Mn$_{0.1}$O$_y$ solid solution (about 160 $\mu$V/K within temperature interval 900–100 K) (Table 3).

Power factor values of Bi$_2$Ca$_2$Co$_{1.8}$O$_y$ decreased at temperature increasing, and for all other samples nonmonotonously changed when temperature increased and had passed through maximum near 800–900 K depending on composition (Figure 3). Such maxima on the $P=f(T)$ dependences for the cobaltates studied is connected with the maxima on their $\sigma=f(T)$ and $S=f(T)$ dependences (see above) (Figure 3). At 1000 K power factor reaches maximal

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**Table 3. Values of electrical conductivity ($\sigma$), thermo-EMF coefficient ($S$), and power factor ($P$) of sintered ceramics based on of the bismuth and AEM layered cobaltates**

| Compound | $\sigma_{300}$, S/cm | $S_{300}$, $\mu$V/K | $P_{300}$, $\mu$W/($m^2$K$^2$) | $\sigma_{1000}$, S/cm | $S_{1000}$, $\mu$V/K | $P_{1000}$, $\mu$W/($m^2$K$^2$) |
|----------|---------------------|---------------------|-----------------------------|---------------------|---------------------|-----------------------------|
| Bi$_2$Ca$_2$Co$_{1.8}$O$_y$ | 8.21 | 150 | 18.5 | 7.32 | 120 | 10.6 |
| Bi$_{1+\delta}$Pb$_{\delta}$Ca$_2$Co$_{1.7}$O$_y$ | 1.66 | 114 | 2.15 | 3.72 | 126 | 5.94 |
| Bi$_2$Ca$_2$Co$_{1.8}$Mn$_{0.1}$O$_y$ | 2.14 | 133 | 3.78 | 3.65 | 101 | 3.73 |
| Bi$_2$Ca$_2$Co$_{1.7}$Zn$_{0.1}$O$_y$ | 2.66 | 127 | 4.27 | 4.07 | 100 | 4.07 |
| Bi$_2$Sr$_2$Co$_{1.8}$O$_y$ | 2.31 | 95.7 | 2.12 | 3.33 | 117 | 4.55 |
| Bi$_{1+\delta}$Pb$_{\delta}$Sr$_2$Co$_{1.8}$O$_y$ | 1.54 | 103 | 1.63 | 5.38 | 127 | 8.73 |
| Bi$_2$Sr$_2$Co$_{1.7}$Mn$_{0.1}$O$_y$ | 1.19 | 80.0 | 0.76 | 3.92 | 161 | 10.1 |
| Bi$_2$Sr$_2$Co$_{1.7}$Zn$_{0.1}$O$_y$ | 1.20 | 73.2 | 0.64 | 5.55 | 121 | 8.09 |
| Bi$_2$Ba$_2$Co$_{2}$O$_y$ | 10.9 | 68.6 | 5.13 | 9.46 | 113 | 12.1 |
| Bi$_{1+\delta}$Pb$_{\delta}$Ba$_2$Co$_{2}$O$_y$ | 8.55 | 67.2 | 3.86 | 9.80 | 51.5 | 2.60 |
| Bi$_2$Ba$_2$Co$_{1.9}$Mn$_{0.1}$O$_y$ | 4.01 | 64.0 | 1.64 | 4.28 | 112 | 5.37 |
| Bi$_2$Ba$_2$Co$_{1.9}$Zn$_{0.1}$O$_y$ | 5.67 | 50.0 | 1.42 | 6.99 | 96.3 | 6.48 |
values for Bi$_2$Ba$_2$Co$_2$O$_y$, Bi$_2$Sr$_2$Co$_{1.8}$Mn$_0.1$O$_y$, and Bi$_2$Ca$_2$Co$_{1.7}$O$_y$ compounds – 12.1, 10.1, and 10.6 μW/(m·K$^2$) respectively (Table 3), but within all the temperature interval studied the maximal values power factor are found for Bi$_2$Ca$_2$Co$_{1.7}$O, Bi$_2$Sr$_2$Co$_{1.7}$Mn$_0.1$O$_y$, and Bi$_2$Ba$_2$Co$_2$O$_y$ cobaltates – 18.5, 13.5, and 14.7 μW/(m·K$^2$) at temperatures 300, 900, and 900 K respectively.

Values of power factor of ceramics based on the layered cobaltates of bismuth and AEE obtained in this work are less than ones for ceramics based on the layered cobaltates of sodium and calcium [5, 9–12] but they can be improved by means of enlarging of electrical conductivity of ceramics using different ways (see above).

It is note two features of ceramics based on the layered cobaltates of bismuth and AEE which distinguish them from ceramics based on the layered cobaltates of sodium (Na$_2$CoO$_2$) or calcium (Ca$_2$CoO$_{2.9}$): relatively large values of power factor near the room temperature and weak dependence of power factor on temperature. The first feature indicates the possibility of usage of this ceramics in TEGs operating near the room temperature, the second demonstrates its good self-compatibility within wide interval of temperatures.

4. Conclusions

By means of solid-state reactions method the ceramic samples of (Bi,Pb)$_2$Ba$_2$(Co,M)$_y$O$_x$, (Bi,Pb)$_2$Sr$_2$(Co,M)$_y$O$_x$, and (Bi,Pb)$_2$Ca$_2$(Co,M)$_y$O$_x$ (M = Mn, Zn) solid solutions had been prepared, their crystal structure, thermal expansion, electrical conductivity, thermo-EMF, and power factor were investigated. The effect of the bismuth substitution by lead and cobalt substitution by manganese in the Bi$_2$Ba$_2$Co$_2$O$_y$, Bi$_2$Sr$_2$Co$_{1.8}$O$_y$, and Bi$_2$Ca$_2$Co$_{1.7}$O$_y$ layered cobaltates on the crystal structure, physicochemical, and functional properties of their derivatives was discussed. It was determined that cobaltates studied are the p-type conductors, which linear thermal expansion coefficient (LTEC) values varied within (9.68–13.2)·10$^{-6}$ K$^{-1}$.

It was found that at 1000 K power factor reached maximal values for Bi$_2$Ba$_2$Co$_2$O$_y$, Bi$_2$Sr$_2$Co$_{1.8}$Mn$_0.1$O$_y$, and Bi$_2$Ca$_2$Co$_{1.7}$O$_y$ compounds – 12.1, 10.1, and 10.6 μW/(m·K$^2$) respectively, but within all the temperature interval studied the maximal values power factor were observed for Bi$_2$Ca$_2$Co$_{1.7}$O, Bi$_2$Sr$_2$Co$_{1.7}$Mn$_0.1$O$_y$, and Bi$_2$Ba$_2$Co$_2$O$_y$ cobaltates – 18.5, 13.5, and 14.7 μW/(m·K$^2$) at temperatures 300, 900, and 900 K respectively.

It was also detected that partial substitution of bismuth by lead and of cobalt by manganese or zinc in Bi$_2$Sr$_2$Co$_{1.7}$O$_y$ layered cobaltate let us essentially increase the functional (thermoelectric) properties of its derivatives. So power factor values of Bi$_2$Sr$_2$Co$_{1.7}$Mn$_0.1$O$_y$, Bi$_2$Sr$_2$Co$_{1.7}$Zn$_0.1$O$_y$, and Bi$_2$Pb$_0.1$Sr$_{1.9}$Co$_{1.7}$O$_y$ solid solutions at 900 K are 2.3, 1.4, and 1.9 times higher than for Bi$_2$Sr$_2$Co$_{1.7}$O$_y$ parent phase.

Abbreviations

EMF electromotive force
AEM alkaline-earth metals
XRD x-ray diffraction
LTEC linear thermal expansion coefficient
TEG thermoelectrogenerator

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