Effect of a powder compaction process on the thermoelectric properties of Bi$_2$Sr$_2$Co$_{1.8}$O$_x$ ceramics

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Abstract

Bi–Sr–Co–O ceramics, as members of a thermoelectric cobaltite family, do not reach the quality of thermoelectric compounds used at low temperatures. Their thermoelectric performance can be, however, boosted by the microstructure tailoring or by the variation of cobalt valence. In this work, we compare Bi$_2$Sr$_2$Co$_{1.8}$O$_x$ polycrystalline samples that were compacted using different procedures. The precursor powder was prepared by a chelating sol–gel method. Three compaction methods were subsequently tested: (i) cold uniaxial pressing, (ii) hot uniaxial pressing on BELT equipment and (iii) spark plasma sintering, all three followed by additional annealing in air. The thermoelectric ceramics were characterized by XRD, SEM and electric temperature measurement up to 950 K. The temperature dependence of the power factor and the figure of merit were also calculated. The spark plasma sintering process yielded a material with an improved value of Seebeck coefficient – 190 $\mu$V/K at 300 °C – the highest value reported for the polycrystalline Bi-222 material so far.
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1. Introduction

The reported promising thermoelectric (TE) properties of Na$_2$CoO$_2$ layered cobalt oxide$^1$ initiated the intensive research of cobalt oxides with mixed cobalt valance. Many of them were first prepared as the analogues of superconducting Bi- or Tl-based layered cuprates.$^2$–$^4$ Later on, a misfit Ca$_3$Co$_4$O$_7$ material was synthesised as another layered equivalent to the “parent” cobalt phase.$^5$ The above described cobalt oxides possess a layered structure composed of two crystal subsystems—the CdI$_2$-type electrically conducting layers of CoO$_2$ octahedra and the insulating rock-salt-type blocks composed of stacked MO and AO planes (M = Bi, Tl, Co; A = Sr, Ca;…).$^6$ The benefit of the layered cobaltites can be seen in their chemical stability in air up to high temperatures and low toxicity in comparison with the “low temperature” thermoelectrics.$^7$ On the other hand, the cobalt oxides have not reached the performances comparable with the practical state-of-art materials (alloys and intermetallic compounds) so far.

The thermoelectric performance of cobalt oxides (represented by the figure of merit $ZT = S^2T/\rho\lambda$, where $S$ stands for the thermoelectric power, $\rho$ for the electrical resistivity and $\lambda$ for the thermal conductivity) can be influenced either by the chemical composition of the system (the change of cobalt valence—the modification of carriers concentration reflected in $S$ and $\rho$; modified phonon conductivity due to point defect scattering etc.) or by the improved microstructure (the enhanced electric conductivity and/or suppressed thermal conductivity due to controlled phonon scattering). Concerning the [Bi$_{0.87}$Sr$_{0.13}$][CoO$_2$]$_{1.82}$ phase (hereafter abbreviated Bi-222 phase), the cation doping has been largely investigated: the doping of Pb for Bi,$^8$–$^9$ the replacement of Sr for Ca, Ba$^{10}$–$^{12}$ or the intergrowth of additional layers in the rock-salt-block.$^{12}$ However, the published impact of doping on TE properties is not consistent and do not e.g. confirm the described interesting trend in the Ca/Sr/Ba substitution within the rock-salt-type block.$^{13}$ In another work, the significant decrease of electrical resistivity was achieved by combining the metallic silver addition and the laser floating zone growth.$^{14}$

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However, the influence of silver on thermal conductivity was not reported. Also, the use of sol–gel prepared powder precursor can promote the favourable microstructure of the final Bi-222 sintered samples.\textsuperscript{15}

In this work, with the aim to improve TE performance of resulting ceramics, we describe the study of Bi$_2$Sr$_2$Co$_{1.82}$O$_x$ polycrystalline samples compacted and annealed using different procedures. For all samples, the same powder precursor was used—i.e. the powders prepared by a chelating sol–gel method based on EDTA and TEA mixture. Three different approaches to obtain a ceramic material from this green ceramic powder were subsequently tested: one sample was pressed uniaxially at 300 K (labelled CP), another sample was compacted by hot uniaxial pressing on BELT equipment (labelled HP) and, finally, the third sample was prepared by spark plasma sintering (labelled SPS). The influence of cooling process after sintering was also examined.

2. Experimental

The precursor powder of Bi$_2$Sr$_2$Co$_{1.82}$O$_x$ stoichiometry was prepared by the chelating EDTA/TEA sol–gel route, the details of which are described in Ref. [15]. The gel was decomposed at 250 °C in air and then gradually calcined at 500 °C and 800 °C, both for 2 h in air. Three different compaction methods were used:

(i) Cold uniaxial pressing (CP)—the precursor powder (approx. 1.3 g) was pressed into a pellet (12 mm in diameter) using the pressure of 500 MPa for 1 min.

(ii) Hot uniaxial pressing (HP)—the precursor powder (approx. 10 g) was pressed into a pellet (20 mm in diameter) by the pressure of 6 GPa for 1 min at 850 °C using the BELT apparatus.

(iii) Spark plasma sintering (SPS)—the precursor powder (approx. 10 g) was poured in a cylindrical graphite die (20 mm in diameter) and sintered for 5 min under pressure of 80 MPa at 840 °C using an SPS furnace.

The samples were cut into pieces, which were additionally annealed in air at 870 °C for 96 h. At the end, the samples were either slowly cooled in a furnace or quenched on a copper block.

The bulk density of the prepared ceramics was determined by the volume and weight measurement. The theoretical value of bulk density 6.81 g/cm$^3$ was considered for the Bi$_2$Sr$_2$Co$_{1.82}$O$_x$ phase.

X-ray powder diffraction (XRD) data were collected at room temperature with Bruker AXS D8 θ–2θ powder diffractometer with parafocusing Bragg–Brentano geometry using CoK$\alpha$ radiation ($\lambda = 1.79021$ Å, $U = 34$ kV, $I = 20$ mA). Data evaluation was performed in the HighScore Plus software package. Scanning electron microscopy (SEM) was carried out using TESCAN Vega3 equipped with EDS analyzator (Oxford Instruments INCA 350). All presented micrographs were taken in a secondary electrons regime. Transport properties (electrical resistivity, thermal conductivity and the thermoelectric power) were measured using a four-probe method (self-designed equipment). The measurement was carried out in a vacuum cell integrated into a closed-cycle helium cryostat.

3. Results and discussion

All prepared samples were synthesized using a sol–gel prepared powder precursor. Once the second calcination step (800 °C) was completed, the precursor was mainly composed of the desired Bi-222 phase. Bi$_{0.75}$Sr$_{0.25}$O$_3$, Bi$_2$Sr$_2$CoO$_3$ and cobalt oxides (Co$_3$O$_4$, CoO) are present as minor phases up to the concentration of several percent. Most importantly, the powder was carbonate free (confirmed by XRD—not presented). A uniaxial pressed sample (named as CP) was then sintered on air. Other samples were processed either by hot pressing (HP) or spark plasma sintering (SPS). In Fig. 1 we present the XRD patterns of SPS and HP samples and of the sol–gel precursor powder. We note that the HP sample lost the favourable phase composition and possessed poor compactness. On the other hand, the SPS sample exhibited a dense microstructure and the phase composition was only slightly changed in comparison with the precursor powder.

Two samples from each method (HP and SPS) were then annealed in air at 870 °C for 96 h to promote the growth between the individual grains, i.e. to improve the microstructure and to adjust the proper phase composition and oxygen stoichiometry. Subsequently one sample of each pair was then cooled slowly in a furnace, the second one was quickly removed from the furnace and quenched on a copper plate. The labelling of samples is summarized in Table 1.

Let us to note that the applied cooling rate had no influence on the phase composition of the final samples. The XRD pattern of the sample CP and the XRD pattern of the pair of samples SPS-C and SPS-Q are shown in Fig. 2. The patterns of the pair HP-C and HP-Q are not presented; however, the trends described hereafter are the same. The application of the advanced compaction methods brings apparently a significant improvement of material quality as the phase composition and microstructure concerns. The volume fraction of phase impurities (Bi$_{0.75}$Sr$_{0.25}$O$_3$ and CoO) is lower than in the cold pressed sample (CP). It is probably due to higher reactivity during the additional annealing caused by the spark plasma sintering (or at the hot pressing). The samples HP-Q and SPS-Q reveal a slightly stronger c-axis orientation. This fact is represented by the decreasing intensity of peaks others than 0 0 l (1 1 1, 1 1 2, 1 1 3, 0 2 0 and 1 2 1). The SEM images of CP, HP-Q, SPS-Q, HP-C and SPS-C samples are shown in Fig. 3. The difference in microstructure is visible when comparing the individual compaction methods used—the hot pressing produces ceramics with smaller grains, on the other hand, the samples treated by the spark plasma sintering contain more developed and larger grains. As in the case of the phase composition, the microstructure was not influenced by the cooling rate after the additional annealing. In general, the samples prepared by the SPS method were the most compact and mechanically resistant. On the other hand, the HP samples (whether slowly cooled or quenched) were not as dense and mechanically compact. These facts are represented by the bulk density given in Fig. 3 and
The cold–gel precursor powder

Fig. 1. XRD patterns of samples processed by hot pressing (HP) and spark plasma sintering (SPS) in comparison with the sol–gel precursor powder. The simulated patterns of the Bi-222 (as the main phase) and of the Bi$_{0.75}$Sr$_{0.25}$O$_x$ (as the most abundant minor phase) are added.

Further corroborated by the thermoelectric properties described later.

The thermoelectric power of slowly cooled and quenched samples behaves differently and, moreover, the properties of the quenched samples measured on increasing temperature from 300 K up to 950 K in air are different from those obtained on cooling. After such thermal cycle, the characteristics of the quenched samples are almost identical with those achieved for the slowly-cooled samples. In Fig. 4, we show the example of such behaviour for the HP-Q sample. It confirms that the quenched samples HP-Q and SPS-Q are not equilibrated (mainly concerning the oxygen stoichiometry) and their properties just after quenching are irrelevant for possible applications at elevated temperatures in air. Therefore, in the next discussion of the transport properties only the slowly-cooled samples are predominantly taken into account.

The next graph in Fig. 5 presents the thermoelectric power measurement of the cold pressed sample (CP) in comparison to a sample just after the SPS process and, further, the samples HP-C and SPS-C that were annealed in air after the hot pressing process or the spark plasma sintering, respectively. The as hot-pressed sample (the sample HP) was not characterized because the phase composition was distinctly multi-phase (presented in Fig. 1). The sign and the increasing trend of the thermoelectric power with temperature indicate the hole mechanism of conduction in the entire temperature range applied. Presumably slowly decreasing concentration of charge carriers with increasing temperature (corresponding to the reversible sample reduction) is also evidenced by utmost linear increase of the thermopower at high temperature. As concerns the thermoelectric power, the samples CP and SPS reveal a similar trend. Interestingly, the samples SPS-C and HP-C exhibit quite different thermoelectric power even though both samples were annealed at the same conditions at the end of their preparation (870 °C, 96 h, in air). This fact points to a different influence of the spark plasma sintering and the hot pressing process on the

The names of prepared samples (in italics) depending on the method of pressing and on cooling rate.

<table>
<thead>
<tr>
<th>Method</th>
<th>Sol–gel precursor powder</th>
<th>Spark plasma sintering</th>
<th>Hot pressing</th>
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<tbody>
<tr>
<td>Cold pressing</td>
<td>SPS CP</td>
<td>SPS CP</td>
<td>HP CP</td>
</tr>
<tr>
<td>Annealing at 870 °C for 96 h in air</td>
<td>SPS CP</td>
<td>SPS CP</td>
<td>HP CP</td>
</tr>
<tr>
<td>Furnace cooling</td>
<td>SPS CP</td>
<td>SPS CP</td>
<td>HP CP</td>
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<td>HP C</td>
<td>SPS Q</td>
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<td>Quenching</td>
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Fig. 3. SEM images of CP (a), HP-Q (b), SPS-Q (c), HP-C (d) and SPS-C (e) samples (magnification 1000×). Relative bulk density (related to the theoretical value 6.81 g/cm³) is also presented in each picture. The inserted scheme demonstrates the fracture face from which the images were taken.
thermoelectric properties—the thermoelectric power of the SPS-C sample was increased in comparison to the cold pressed sample (CP). On the other hand, the hot pressing did not result in a suitable oxygen stoichiometry that would enhance the values of Seebeck coefficient. The best achieved value of $S$ at 300 K was 165 $\mu$V/K for the SPS-C sample (and 190 $\mu$V/K at 300 °C). This value is the best reported for the polycrystalline Bi-222 material so far.

The measurement of electrical resistivity (not presented) showed a similar behaviour for all samples; at low temperatures the resistivity decreases with increasing temperature up to $\sim$150 K and then the metallic-like character of the resistivity is recovered up to 950 K. In every case, the resistivity differed only slightly for various samples reaching the typical values of 17 m$\Omega$cm at 300 K. As a consequence, the power factor (PF) is mostly influenced by the thermoelectric power—see Fig. 6. The highest values of PF in our sample series were achieved for the SPS-C sample (with additional annealing in air and slowly cooled): $\text{PF} = 0.165 \text{mW/K}^2/\text{m}$ at 300 K ($\text{PF} = 0.198 \text{mW/K}^2/\text{m}$ at 300 °C).

On Fig. 7, we present the temperature dependence of the thermal conductivity between 3.5 and 300 K. Based on the Wiedemann–Franz law, we can estimate the electronic part of thermal conductivity $\lambda_e = L \sigma$ where $L = 2.44 \times 10^{-8} \text{V}^2/\text{K}^2$ denotes the Lorenz number and $\sigma$ is the electrical conductivity. Considering the fact that in the metallic region of electrical resistivity behaviour, i.e. above $\sim 150$ K, the maximum contribution of the electronic part amounts to $\sim 0.05 \text{W/mK}$, we can associate the total thermal conductivity with the lattice component $\lambda_p$ (a phonon part).

Most interestingly, no typical low temperature enhancement of lattice thermal conductivity is observed in any sample. This thermal conductivity enhancement is mandatory observed in crystalline materials, where the phonon mean free path increases and promotes the heat transport due to gradually vanishing umklapp phonon scattering below the Debye temperature. The absence of such an enhancement together with the very low
absolute values of thermal conductivity (at 300 K between 2.75 and 2.0 W/m/K) can be thus associated with so called “glass”-like behaviour, where the mean free path of lattice vibrations is limited by the inter-atomic distance. Such behaviour is typical for highly disordered materials, very complex phases with large unit cells or polymers. Indeed, the studied misfit cobaltite naturally belongs to this family and the recently published thermal conductivity data of Bi$_2$Sr$_2$Co$_{1.82}$O$_x$ (both single crystals and ceramics)\textsuperscript{16,17} corroborate our results.

Unfortunately, those authors did not perform any detailed analysis of the observed thermal conductivity. In this respect, the straightforward and simple assessment can be made, attempting to estimate the minimum high temperature limit of thermal conductivity of Bi$_2$Sr$_2$Co$_{1.82}$O$_x$ phases. The comparison with the observed experimental data can then insinuate whether further decrease of thermal conductivity is possible leading thus to the additional possible improvement of the figure of merit.

The estimation of the high temperature limit of thermal conductivity can be made using the approach of Slack\textsuperscript{18} considering the contributions of both acoustical and optical phonons to the minimum thermal conductivity $\lambda_{\text{min}}$. Using our recently published thermodynamic data,\textsuperscript{19} we can simply characterize the experimentally observed specific heat by an average Debye temperature $\Theta_D$ of 510 K which yields the average sound velocity $v \sim 4$ km/s. Employing further the crystallographic parameters of the studied Bi$_2$Sr$_2$Co$_{1.82}$O$_x$ phases, we obtain, using the Slack analysis mentioned above, the value of $\lambda_{\text{min}} = 0.83$ W/m/K. This value, compared with our data, leads us to a conclusion that an additional suppression of the thermal conductivity, either via microscopic nanostructuration or via point defect scattering due to suitable substitution, can be further anticipated.

On the other hand, we can exclude any substantial effect of the phonon scattering on grain boundaries of our micro-crystalline ceramic material. As mentioned, the small absolute value and glass-like temperature dependence of the lattice thermal conductivity implies very short phonon mean free path, orders of magnitude shorter than that characterizing the sample microstructure (see Fig. 3 documenting a typical micrometer size of the crystallites). These facts point to a dominant role of nanoscopic defects (point defects, structure misfit) in the phonon scattering process, which largely overwhelms the grain-boundary scattering. The link between the sample microstructure and thermal conductivity can be thus eventually traced in terms of sample relative bulk density. Indeed, denser samples should exhibit a higher absolute thermal conductivity due to lower porosity, possessing however the similar temperature dependence. As shown in Fig. 7, this trend is roughly followed by our experimental data, where samples with density largely exceeding 80% exhibit higher thermal conductivity in contrast to HP-C sample with the density of only $\sim$60%.

The final thermoelectric efficiency is decisively influenced by thermal conductivity. Therefore, the values of ZT are the most important for the assessment of the material for potential applications. As due to small size of the bar-shaped samples, we succeeded to measure the thermal conductivity only up to 300 K; in Fig. 8 we present the calculated temperature dependence of ZT only at low temperatures. Nonetheless, it is clearly visible that the SPS method enhances the thermoelectric efficiency and, simultaneously, that the final annealing is important for the ZT values (that was also visible at the thermoelectric power behaviour). On the other hand, the hot pressing method yielded a sample with inferior quality even when compared to the conventional cold pressing procedure. The highest achieved ZT value (at 300 K) at the presented series of samples is ZT = 0.024 for the sample prepared by the SPS method and subsequently annealed in air (SPS-C). The ZT characteristic for this sample reveals a promising slope; however, it is questionable how the ZT values are influenced by the thermal conductivity at higher temperatures.

4. Conclusions

We prepared thermoelectric samples of composition [Bi$_0.87$Sr$_2$O$_{2.2}$]Co$_{1.82}$ using different compaction process of precursor powder. The powder was prepared by the EDTA/TEA sol–gel method. The prepared intermediate was mainly composed of the desired Bi-222 phase after the calcination at 800 °C. The precursor powder was processed using three different techniques: cold uniaxial pressing (CP), hot uniaxial pressing on BELT equipment (HP) and spark plasma sintering (SPS). For all samples, the final sintering at 870 °C in air was applied. The advanced compaction methods (SPS and HP) brought apparently a significant improvement of material quality as the phase composition and microstructure concerns. The thermoelectric power of the spark plasma sintered sample was improved in comparison to the cold pressed sample, on the other hand, the hot pressing did not lead to suitable oxygen stoichiometry promoting the high values of thermoelectric power. The best achieved value of $S$ at 300 K was 165 $\mu$V/K for the spark plasma sintered sample (190 $\mu$V/K at 300 °C). The values of electrical resistivity were not influenced by the synthesis method used. The calculated power factor, evaluated up to 960 K, reaches the value of 0.165 mW/K$^2$/m at 300 K (0.198 mW/K$^2$/m at 300°C). We also measured thermal conductivity at low temperatures (up to 300 K) and the temperature dependence of ZT is also presented. The ZT characteristic for the spark plasma sintered sample exhibits
a promising tendency towards high temperatures and, therefore, the measurement of high-temperature thermal conductivity will be the aim of our future work. Simultaneously, we aim to repeat the hot pressing experiments with modified method parameters since we still believe that we could yield a material with comparable quality to the SPS method upon optimization using this technique.

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