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Direct synthesis of \( p \)-type bulk BiCuSeO oxyselenides by reactive spark plasma sintering and related thermoelectric properties†

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Abstract

Herein, we demonstrate that BiCuSeO compound can be formed in bulk directly from the raw materials through reactive spark plasma sintering (RSPS) followed by ball milling and a second short spark plasma sintering step. Compared to BiCuSeO samples obtained by a conventional solid-state reaction, the electrical transport properties of the RSPS bulk were moderately affected by the sintering technique, while the lattice thermal conductivity was almost unaffected, and the figure of merit \( zT \) attained a modest enhancement of \(~20\%\) at 773 K. The synthesis time was reduced from a few days to less than 10 hours.

**Keywords:** BiCuSeO; oxyselenides; thermoelectric materials; reactive spark plasma sintering
Due to the ability of thermoelectric materials to directly interconvert temperature gradient and electrical power, thermoelectric devices have been recognised as promising candidates for many applications such as waste heat recovery from different energy sources, power generation in deep space or solid-state cooling [1–4]. Performance of the thermoelectric materials can be characterised by the dimensionless figure of merit $\varrho T = a' T \kappa T^{-1}$, where $a$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature, and $\kappa$ is the total thermal conductivity [5]. To achieve a high $\varrho T$, materials are required to have high $\alpha$ and $\sigma$ and low $\kappa$, which are intertwined properties related to the charge carriers and phonons transport. Considering Wiedemann-Franz law and Pisarenko relation [6], the inverse coupling strongly hinders the achievement of high thermoelectric performance [5,7]. Thus, significant attention was received by materials with intrinsically low thermal conductivity, such as Bi-Sb-Te alloys [8], copper sulfides [9,10], borides [11], BiCuChO (Ch = S, Se, Te) oxychalcogenides [12–14] or SnSe [15]. As an emerging layered oxygen-containing thermoelectric material, BiCuSeO was found to exhibit high efficiency in the wide temperature range ($\varrho T$ > 1.0 at 923 K for Ba doped BiCuSeO) [16,17]. The extremely low thermal conductivity of BiCuSeO (~1 W m$^{-1}$ K$^{-1}$ at room temperature) is believed to originate from large anharmonicity, low Young's modulus, layered crystal structure and large atomic weight of constituents [12,18]. Moreover, the electrical transport properties may be improved by optimizing the charge carrier concentration, tuning the band structure or defect engineering [19–24].

From an industrial point of view, a large $\varrho T$ value observed at a given temperature is not the only important parameter. The development of a straightforward scalable synthesis route appropriate for industrial mass production becomes a critical issue for thermoelectric device fabrication. Typically, synthesising polycrystalline BiCuSeO samples is a two-step solid-state reaction route (SSR) involving preparation of feedstock (typically it is already BiCuSeO single-phase) in the form of powder followed by consolidation into a dense sample suitable for transport measurements. SSR technique is cumbersome, energy-intensive, and even more, it is hard to control the stoichiometry of the final product. Nevertheless, it was widely reported that BiCuSeO oxyselenides might be synthesised by various types of powder metallurgy methods, such as mechanical alloying (MA) [25–27] or self-propagating high-temperature synthesis (SHS) [28–30]. However, all techniques include powder fabrication and consolidation steps, while it is favourable to reduce powder handling steps in order to avoid contaminations, partial oxidation etc. In an effort to drive oxyselenides towards another step closer to industrial application, we report on synthesis of BiCuSeO oxyselenides in a bulk form using two-step reactive spark plasma sintering (RSPS).

The “BiCuSeO” stoichiometric mixture of precursors, Bi, Cu and Bi$_2$O$_3$ powders (> 99.95%) and Se (99.997%), was mixed and ball-milled using a Pulversette 7 planetary micro mill (Fritsch, Germany) with zirconium oxide balls (Ø = 5 mm, powder-to-ball ratio of 1:5) and bowls (45 ml) in air at 850 rpm for 5 min. The samples were sintered from the powder using a Dr.Sinter-1080 SPS system (Fuji-SPS, Japan) at different temperatures (see Table 1) for 5 minutes under a uniaxial pressure of 50 MPa with heating and cooling rates of 50 K min$^{-1}$ and 20 K min$^{-1}$ respectively. All densified disk-shaped specimens had a dimension of 10 mm diameter × 10 mm height. Noteworthy, the pellets obtained using this synthesis route are generally poorly densified (less than 90% of the theoretical density, see Table 1); to prepare a well-densified sample, a further densification step is necessary; obtained bulk sample were thus ball milled and densified once again at 973 K for 5 min and 50 MPa (labelled as RS7, see Table 1). For comparison, two more samples were synthesised using a two-step solid-state reaction similar to a previous report [31]. More details on the experimental procedure can be found in the electronic supporting information file (ESI).

X-ray diffraction data were collected by a SmartLab diffractometer (Rigaku, Japan) using CuKα radiation ($\lambda = 1.5419$ Å) at room temperature. The microstructure of as-synthesised specimens was examined by scanning electron microscopy (SEM; Vega 3 SB, Tescan, Czech Republic). The chemical compositions were analysed by energy-dispersive X-ray spectroscopy (EDS; x-act, Oxford Instruments, UK). Transport properties characterisation was carried out in a direction perpendicular to the pressing direction. The electrical conductivity and Seebeck coefficient were measured simultaneously on bars 1 × 3 × 10 mm$^3$ by the four-probe and differential methods using laboratory-made system (Cryotel Ltd., Russia) under He atmosphere. The thermal diffusivity was measured using a laser flash method (LFA 457, Netzsch, Germany) under continuous Ar flow; the pellets were covered by a thin layer of graphite. The total thermal conductivity was calculated by using $\kappa = \chi C_p \rho$, where $\chi$ is the thermal diffusivity, the
density, ρ, was measured by the Archimedes method and shown in Table 1, and the specific heat capacity, C_p, was calculated by the Debye model [32]. The uncertainty of the Seebeck coefficient and the electrical conductivity measurements was within 8 %, and that of thermal conductivity was estimated to be within 5 %, considering the uncertainties for χ and ρ. The combined uncertainty for all measurements involved in zT determination was expected to be ~20 %.

In order to determine a suitable sintering temperature, the SPS profiles of BiCuSeO powder fabricated by SSR and sintered at 903 K, 973 K and 1023 K were analysed. According to the obtained data, the densification process is finished at T ~900K (see Fig. 1a), and any higher temperature should be enough for the fabrication of dense BiCuSeO sample. However, sintering at 1023 K induced a local liquid phase formation and thereby led to high internal stresses that broke the samples. Thus, for RSPS, the sintering temperatures of 903 K and 973 K were used. SPS profiles for the powders of BiCuSeO phase (Fig. 1a) and the stoichiometric mixture of precursors (Fig. 1b) were completely different. For SSR BiCuSeO powder the SPS profile looked similar to typical sintering process profile for single-phase powders with gradual densification at moderate temperature. On the other hand, for RSPS process the densification rapidly started at T ~350 K and already reached ~50% at 473 K, where the additional holding step was added; with further temperature increasing the densification process was fast and finished at ~660 K. Such densification behaviour for raw mixture can be related to the formation of phases occurring along with densification. It can be speculated that the BiCuSeO phase formation path during RSPS was the same as one observed during the SHS process due to their similar mechanisms [29]. However, further comprehensive investigations on this system are necessary in order to understand the phase formation mechanism during RSPS in more details. Considering that the relative density of the RSPS specimens was lower than 90% of theoretical one (see Table 1), the numerous attempts to synthesise dense bulk BiCuSeO samples by one-step RSPS technique using different heating rates, applied pressure and sintering temperature were performed (see ESI). These attempts were unsuccessful, and the origin of this anomaly is not clear. It can be suggested that induced porosity of the samples may be related to inhomogeneous phase formation or the evaporation of volatile elements during RSPS process.

Table 1. Code, method, sintering temperature, T_s, relative volume density, ρ, elemental ratios obtained by EDS and lattice constants of the BiCuSeO samples prepared by various methods

Fig. 1. The SPS profiles for (a) single-phase BiCuSeO powder during SPS and (b) a stoichiometric mixture of precursors Bi2O3, Bi, Cu and Se during RSPS: relative pistol displacement (shrinkage; blue line), temperature (red line) and displacement ratio (dark yellow line). (c) XRD patterns for BiCuSeO samples after sintering.

After RSPS, all samples contain mainly one phase, which can be indexed as BiCuSeO (PDF#45-0296) adopting layered tetragonal ZrSiCuAs-type structure with P4/mmm space group (Fig. 1c). However, negligible traces of Bi2O3 and Cu1.8Se impurity phases were detected in all the specimens except for the S7 sample (see labels in Table 1) which is consistent with EDS measurements. The observation of such impurity phases in the composition may be a sign of the presence of copper or bismuth vacancies, which undoubtedly affect the electronic transport of BiCuSeO, as previously reported [33–35]. The unit cell parameters for all the samples are similar and in good agreement with those reported in the literature [29,36]. The EDS measurements indicated that the specimens of the series are homogeneous and the relative elemental proportion of Bi:Cu:Se found from the EDS were close to nominal one within the uncertainty of EDS analysis (see Table 1).

All samples exhibited the same lath-like microstructure with randomly arranged platelet grains, which is typical for oxychalcogenide compounds (Fig. 2). SEM images also displayed the formation of pores with submicron scale sprouting on the surface of the larger particles for R7 sample (indicated by white arrows and dashed ellipse in Fig. 2d), which can be caused by the evaporation of volatile elements as discussed above. However, such pores were observed only for R7 sample and were not the case for R0 sample likely due to its lower sintering temperature.
Fig. 2. SEM images of the fracture surfaces for bulk BiCuSeO fabricated by SPS at (a) 903 K and (b) 973 K, and by RSPS at (c) 903 K and (d) 973 K.

The electrical conductivity ranged from 20 to 50 Ω⁻¹ cm⁻¹ and decreased with temperature up to an upturn temperature, \( T \), (depending on the sample), indicating degenerate behaviour below \( T \) (Fig. 3). For degenerate semiconductors the temperature dependence of the electrical conductivity can be described by a power-law \( \sigma \propto T^m \), where \( m \) is the scattering factor [37]. According to \( \sigma(T) \) plotted in the log-log scale, \( m \) for all the samples close to \(-1\) corresponding to acoustic phonon scattering of the charge carriers in a strongly degenerate model (see ESI) [7,37].

It should be noted that the electrical conductivity of RSPS specimens was lower than that for SPS samples at room temperature, which was most likely caused by induced porosity of RSPS bulks (see Fig. 3a). However, at high temperature, the values obtained for R0 and R7 specimens were quite close to ones obtained for S0 and S7 bulks. Moreover, the electrical conductivity of the RS7 sample was close to those of S7 specimen at \( T < 500 \) K and even higher at \( T > 500 \) K. The presence of porosity may be accounted for by the Maxwell–Eucken expression [38]:

\[
\sigma_{\text{eff}} = \sigma_{\text{porous}} \left(1 - \frac{\varphi}{1 + \beta \varphi}\right),
\]

where \( \sigma_{\text{eff}} \) is the corrected value of the electrical conductivity for a bulk medium with theoretical density, \( \sigma_{\text{porous}} \) is the electrical conductivity measured for porous bulk medium, \( \varphi \) is the degree of porosity described by a fraction between 0 and 1, and \( \beta \) is the correction factor typically with the value of 2 assuming a nearly spherical pore shape. After porosity correction, the room temperature values of the \( \sigma \) exhibited \( (33 \pm 3) \times 10^2 \) cm⁻¹ for S0, R0 and R7 samples, and \( (55 \pm 4) \times 10^2 \) cm⁻¹ for S7 and RS7 bulks, respectively. Such difference may be attributed to the sensitivity of the BiCuSeO electrical transport properties to various type of defects (vacancies, relevant charge state, anti-sites etc.) as was widely reported by other groups [22,35,39–41]. However, further studies should be carried out for a deep understanding of the effect of synthesis technique on both \( p \) and \( \mu \).

Positive Seebeck values indicated \( p \)-type conduction with the absolute values of the \( \alpha \) increased with increasing temperature (Fig. 3b). Considering almost linear behaviour of the \( \alpha \) below \( T \), the charge carrier density can be estimated using Pisarenko formula [7] assuming the simplified case of the effective mass similar for all the samples and \( m^* = 1.1 m_e \) as reported by L.-D. Zhao et al. for pristine BiCuSeO [12]:

\[
\alpha = \frac{8\pi^2 k_B^2 m^* T}{3e \hbar^2} \left(\frac{\pi}{3 p}\right)^{2/3},
\]

where \( m_e \) is the electron mass, \( k_B \) is the Boltzmann constant, \( \hbar \) is the reduced Planck’s constant. Thus, the charge carrier mobility may also be evaluated. This is only an estimation but compared to measured values were quite reliable [31]. All values of \( p \) were in the range of \( 2 \times 10^{19} \) cm⁻³ < \( p \) < \( 3 \times 10^{19} \) cm⁻³ with the highest \( p \) value for RS7 sample with the lowest Seebeck coefficient, while the mobility ranged from \( 6 \) cm² V⁻¹ s⁻¹ for R0 to \( 14 \) cm² V⁻¹ s⁻¹ for S7 at room temperature. According to this data, it can be speculated that the synthesis technique mainly affected the charge carrier mobility, while the charge carrier density only slightly changed.

Fig. 3. Temperature dependence of the (a) electrical conductivity, (b) Seebeck coefficient and (c) power factor for pristine BiCuSeO samples prepared by various methods.

The power factor (Fig. 3c) of RSPS samples, due to an induced porosity, was the lowest almost over the whole temperature range. However, mainly due to increase in the electrical conductivity, the power factor of RS7 specimen was the highest at \( T > 573 \) K with a remarkably high value of \( (3.57 \pm 0.57) \) μW cm⁻¹ K⁻² at 773 K for pure BiCuSeO.
The total thermal conductivity data were close to each other for all the samples (Fig. 4a). However, the presence of porosity typically lowers $\kappa$ due to the additional scattering at the pore sites [38,42,43]. Thus, the equation Error! Reference source not found. was used to calculate the effective thermal conductivity by replacing the terms $\sigma_{\text{eff}}$ and $\kappa_{\text{porous}}$ with $\kappa_{\text{eff}}$ and $\kappa_{\text{porous}}$, respectively [44]. Corrected values of the thermal conductivity exhibited $(1.3 \pm 0.1) \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature for all the bulks suggesting that $\kappa$ was not significantly affected by the synthesis technique. The lattice thermal conductivity, $\kappa_{\text{lat}}$, was estimated by subtracting the electronic contribution, $\kappa_{\text{el}}$, from the total thermal conductivity. $\kappa_{\text{el}}$ was calculated according to the Wiedemann–Franz law, $\kappa_{\text{el}} = \sigma L T$, where $L$ is the Lorenz constant, estimated from the experimental $\alpha$ values within SPB-APS model (see ESI). $\kappa_{\text{lat}}$ of all the specimens reduced with temperature as $\kappa_{\text{lat}} \propto T^{-1}$, indicating the dominance of the phonon-phonon scattering, while no obvious bipolar contribution was observed (Fig. 4b). The experimental $\kappa_{\text{lat}}$ values of all the studied samples were close to each other over the entire temperature range, reaching $(0.70 \pm 0.06) \text{ W m}^{-1} \text{ K}^{-1}$ at 773 K. Based on this data, the porosity did not significantly affect the lattice thermal conductivity as it can be expected.

![Fig. 4. Temperature dependence of (a) the total thermal conductivity, (b) the lattice and electronic contribution to the thermal conductivity and (c) the figure of merit $zT$ for pristine BiCuSeO samples prepared by various methods. The minimum lattice thermal conductivity, $\kappa_{\text{min}}$, is calculated by Cahill’s model [45].](https://ssrn.com/abstract=3603424)

Combining the results of the electrical and the thermal transport properties, the thermoelectric figure of merit $zT$ was calculated and shown in Fig. 4c. The $zT$ values of the BiCuSeO samples followed an increasing trend with temperature (Fig. 4c). A maximum $zT$ was obtained for the RS7 sample, which is ~20% higher than those for the pristine BiCuSeO fabricated by conventional technique.

In summary, BiCuSeO bulks were successfully synthesised by a one-step RSPS process. However, the density of the obtained bulks was less than 90%, and the origin of such a low density may be attributed to evaporation of volatile elements during sintering. Nevertheless, it was also shown that the use of additional ball milling followed by SPS for RSPS bulks allows one to fabricate dense polycrystalline BiCuSeO bulk specimens with 20% higher $zT$ than that for BiCuSeO prepared by traditional SSR route. Compared to SSR, the RSPS route can be considered as easily scaled, time and energy-efficient process that allows producing bulks with comparable to state-of-the-art BiCuSeO $zT$ value. Therefore, further studies aimed at optimisation of RSPS process, as well as the efforts on enhancing thermoelectric performance of the RSPS BiCuSeO based ceramics may be expected in the future.

Conflicts of interest

There are no conflicts to declare.

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Table 1. Code, method, sintering temperature, $T_s$, relative volume density, $\rho$, elemental ratios obtained by EDS and lattice constants of the BiCuSeO samples prepared by various methods

| Code | Method       | $T_s$ (K) | $\rho$ ± 1% (%) | Elemental ratios Bi:Cu:Se | Lattice constants (Å) |
|------|--------------|-----------|-----------------|---------------------------|-----------------------|
| R0   | RSPS         | 903       | 89              | 1.02:1.03:0.99            | 3.93004(5) 8.9301(2)  |
| R7   | RSPS         | 973       | 87              | 1.03:0.96:1.01            | 3.93166(9) 8.9339(9)  |
| S0   | SSR + SPS    | 903       | 94              | 1.02:0.99:0.98            | 3.93176(9) 8.9308(9)  |
| S7   | SSR + SPS    | 973       | 94              | 1.04:1.00:0.96            | 3.93007(9) 8.9314(3)  |
| RS7  | RSPS + SPS   | 973       | 94              | 1.04:0.99:0.97            | 3.92967(9) 8.9270(4)  |
Figure 4

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Graphical Abstract

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two-step RSPS route
< 10 hours
~20% enhancement
two-step SSR route
48 - 72 hours
