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ARTICLE TYPE

A copper-containing oxytelluride as a promising thermoelectric material for waste heat recovery

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The new thermoelectric material BiOCuTe exhibits an electrical conductivity of 224 S cm^{-1} and a Seebeck coefficient of +186 μV K^{-1} at 373 K, together with an extremely low lattice thermal conductivity of ~ 0.5 W m^{-1} K^{-1}. This results in a ZT of 0.42 at 373 K, which increases to 0.66 at the maximum temperature investigated, 673 K.

Thermoelectric power generation is a promising technology to convert waste heat into electricity. This has led to a tremendous growth in research into new materials with high thermoelectric performance. This performance is normally expressed in terms of a figure of merit, ZT, related to the Seebeck coefficient (S), electrical conductivity (σ) and thermal conductivity (κ) of the material by $ZT = S^2\sigma T/\kappa$.[1] Given that vast quantities of low-grade waste heat (T < 623 K) are discharged into the earth's environment every year, it is highly desirable to develop thermoelectric generators suited for these temperatures.[2] There is however a paucity of candidate thermoelectric materials suitable for operation over the temperature range 273 ≤ T/ K ≤ 623.[3] Currently, power generation at near ambient temperatures is carried out using heavily-doped Bi_2Te_3, with a maximum value of ZT ≈ 1 at 380 K.

A promising approach to improve thermoelectric performance is to design materials containing "natural superlattices",[4] in which layers with excellent electronic transport properties are combined with a second type of layer which serves as a phonon scatterer. Evidence for the success of this approach can be found in the outstanding thermoelectric properties of layered cobalt oxides,[5] the misfit layered compounds $(SnS)_{1+x}(TiS_2)$ (ZT = 0.37 at 773 K),4 and the oxyselenide $BiOCu_{1-x}Se$ (ZT = 0.81 at 923 K).[6] However, whilst these results demonstrate the potential of the "natural superlattice" concept, ZT values over the temperature range required for low-grade waste heat recovery (T < 623 K) are significantly lower than that of Bi_2Te_3. In seeking to identify materials suitable for thermoelectric generation below 623 K, we have taken into account the relationship between maximum ZT and band gap,[7] and thus focused our work on naturally layered phases with band gaps close to those of Bi_2Te_3 (0.13 eV)[8] and PbTe (0.33 eV).7 Within the family of oxychalcogenides AOBQ (A = La, Ce, Nd, Pr, Bi; B = Cu, Ag and Q = S, Se, Te)[9] bismuth-containing phases are particularly interesting, because they have significantly lower band gaps than those containing rare earths, due to the contribution of Bi 6*p* states to the bottom of the conduction band.[10] The lowest band gap, estimated as 0.2-0.5 eV, occurs for BiOCuTe.9[(e)] This led us to study, for the first time, the thermoelectric properties of BiOCuTe. We also investigated the effect of Pb^{2+} as a dopant on ZT. We demonstrate here that, in accord with our reasoning above, BiOCuTe has a remarkable thermoelectric performance at temperatures suitable for waste heat recovery, with values of ZT of 0.42-0.60 over the temperature range 373 ≤ T/ K ≤ 623. For BiOCuTe, ZT at 673 K (ZT = 0.66) is significantly higher than that for $BiOCu_{1-x}Se$ (ZT ~ 0.3)6 or $(SnS)_{1+x}(TiS_2)$ (ZT ~ 0.32)4 at the same temperature.

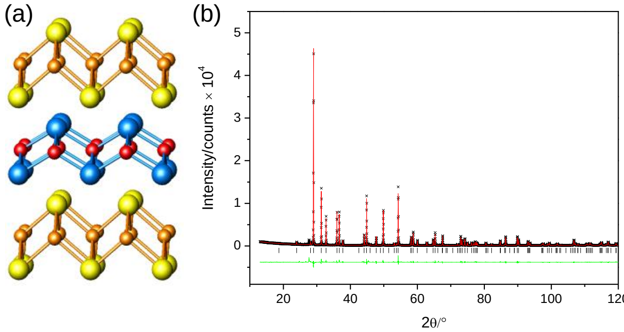

Figure 1. (a) View of the crystal structure of BiOCuTe along the [010] direction. Key: copper, orange; tellurium, yellow; bismuth, blue; oxygen, red; (b) Rietveld refinement using powder X-ray diffraction data for BiOCuTe (R_{wp}= 12.4%).

Samples with composition $Bi_{1-x}Pb_xOCuTe$ (0 ≤ x ≤ 0.08) were prepared by solid-state synthesis at temperatures in the range 623 ≤ T/K ≤ 773. For transport measurements, the as-prepared powders were hot pressed into well-densified pellets (Supporting Information). Analysis of powder X-ray diffraction data indicates that BiOCuTe and all doped samples crystallize in the ZrSiCuAs structure (space group *P4/nmm*), which can be described as composed of alternating fluorite- and antifluorite-type layers, stacked along [001] (Figure 1(a)). These layers consist of edge-sharing OBi_4 and $CuTe_4$ tetrahedra respectively. Rietveld refinements (Figure 1(b) and Supplementary Information) indicate that the *a* axis decreases slightly with increasing lead content, whilst there is a relatively large expansion of the unit cell along the *c* axis. This results in an increase of the Bi-Te distances, which may indicate a weakening of the bonding between the oxide and chalcogenide layers with increasing lead content. The thermal parameter of the copper site is significantly larger than those of the other crystallographic sites. Attempts to refine the occupancy of the copper site led to values below 1, but with large standard deviations. This may be indicative of copper deficiency, an observation which would be consistent with previous work on the related phases MCuFQ (M = Sr, Eu), which show copper deficiency.[11] Thermogravimetric analysis of BiOCuTe shows that, under an inert N_2 atmosphere, this material is thermally stable up to at least 873 K. By contrast, under a pure O_2 atmosphere, the onset of oxidation occurs at 543 K, a temperature comparable to those at which some high-temperature thermoelectric materials such as skutterudites oxidize (e.g. $CeFe_4Sb_{12}$ begins to oxidize at 573 K).[12]

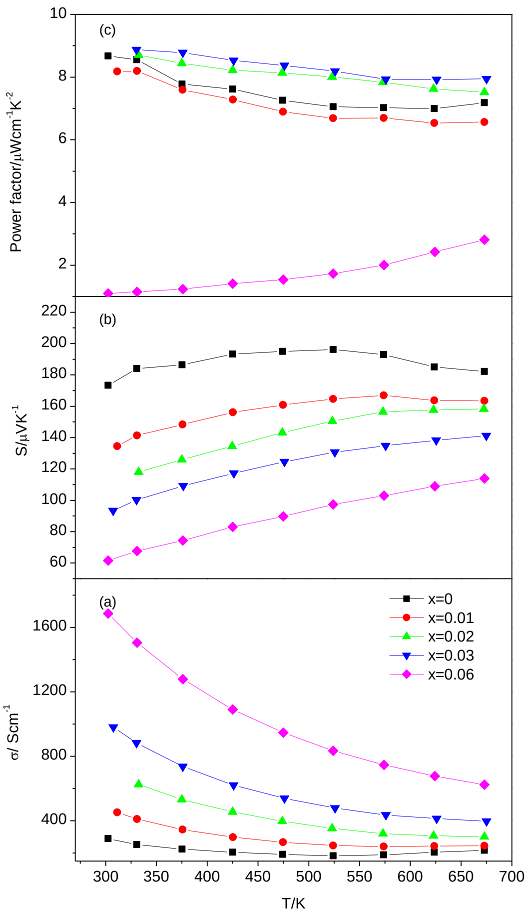

Figure 2. Temperature dependence, over the temperature range 298 < T/K ≤ 673, of the (a) electrical conductivity, (b) Seebeck coefficient and (c) power factor for $Bi_{1-x}Pb_xOCuTe$.

The electrical conductivity of as-prepared BiOCuTe has a reasonably high value of 289 Scm^{-1} at 300 K. The conductivity decreases with increasing temperature (Figure 2(a) and Supplementary Information), reaching a minimum value of 181 Scm^{-1} at 523 K. The Seebeck coefficient exhibits an almost linear temperature dependence up to 523 K, and reaches a maximum value of 196 μVK^{-1} at this temperature (Figure 2(b)). The Seebeck coefficient indicates that the majority charge carriers in BiOCuTe are holes, and is consistent with p-type semiconducting behaviour. The origin of this p-type behaviour may be related to copper deficiency, which generates mobile holes and leads to the p-type conduction normally observed for this family of oxychalcogenides.9 The metal-like temperature dependence of the electrical conductivity may be related to copper defficiency or to a a shallower valence band maximum.9[(e)]
The temperature dependence of the electrical conductivity and the Seebeck coefficient up to 523 K are characteristic of conduction by extrinsic charge carriers, and indicate that BiOCuTe is a degenerate semiconductor. The reduction in the Seebeck coefficient above 523 K can be attributed to the increase in minority charge carriers which occurs in the intrinsic region. The band gap of BiOCuTe can be estimated from the maximum value of the Seebeck coefficient (S_{max}), using the expression, $S_{max} = E_g/(2eT_{max})$ where E_g is the band gap energy, e is the electron charge and T_{max} is the absolute temperature at which the maximum occurs.[13] This leads to an estimated value of 0.21 eV for the band gap of BiOCuTe, which is in reasonable agreement with those previously determined by optical measurements (0.4-0.5 eV) and DFT calculations (0.2 eV).9[(e)] Data on doped samples (Figure 2 and Supplementary Information) indicate that lead doping results in a progressive increase of the electrical conductivity, and a simultaneous reduction of the Seebeck coefficient. This results in a small enhancement of the power factor for samples with a lead content x ≤ 0.03 (Figure 2(c)).
The thermal conductivity of BiOCuTe (Figure 3(a)) is remarkably low when compared to Bi_2Te_3 (~ 2 W m^{-1} K^{-1}).8 The electronic and lattice contributions were estimated using the electrical conductivity data in conjunction with the Wiedemann-Franz law, with a Lorenz constant of 2.45×10^{-8} W Ω K^{-2}. This results in a lattice thermal conductivity of only 0.47 W m^{-1} K^{-1} for BiOCuTe at 373 K, indicating that the phonon mean free path in this material is rather small. The total thermal conductivity increases with increasing lead content, because the electronic contribution rises with x, whilst the lattice thermal conductivity remains almost constant. For BiOCuTe, the electronic thermal conductivity is *ca.* 30% of the total, while at the maximum doping level investigated (x = 0.08), the electronic thermal conductivity reaches *ca.* 65% of the total. The low thermal conductivity of BiOCuTe may arise from the two-dimensional nature of the structure of this material. Band structure calculations on AOBQ phases indicate that the bonding is highly anisotropic,[14] with the charge carriers confined in the $[B_2Q_2]$ layers, and that the nature of the bonding between the $[A_2O_2]$ and $[B_2Q_2]$ layers is mainly electrostatic and weaker than the intralayer bonding.[15] Scattering of phonons at the interfaces between these layers may be the origin of the low thermal conductivity.4 In addition, we can draw some parallels between BiOCuTe and the recently discovered thermoelectric material $Cu_{2-x}Se$,[16] that may explain the low thermal conductivity of the former. $Cu_{2-x}Se$, a superionic conductor with the antifluorite structure, has an extremely low thermal conductivity, attributed to the presence of a highly disordered copper ion sublattice. In the AOBQ family to which BiOCuTe belongs, ionic mobility of the transition metal ions within the antifluorite $[B_2Q_2]$ layers

has also been reported.[17] Fast-ion conduction has been shown in LaOAgS,[17(b)] whilst copper can be readily extracted and inserted from CeOCuS under mild conditions.[17(c)] By contrast, the ionic conductivity of BiOCuSe is reported to be negligible.[18] To the best of our knowledge the ionic conductivity of BiOCuTe has not been investigated, but the large magnitude of copper thermal parameter arising from Rietveld refinements suggest copper deficiency, disorder in the copper sublattice and/or mobility. This may be a contributory factor to the low thermal conductivity of this material, and should be investigated further, as ionic conductivity may cause degradation of the thermoelectric device.[19]

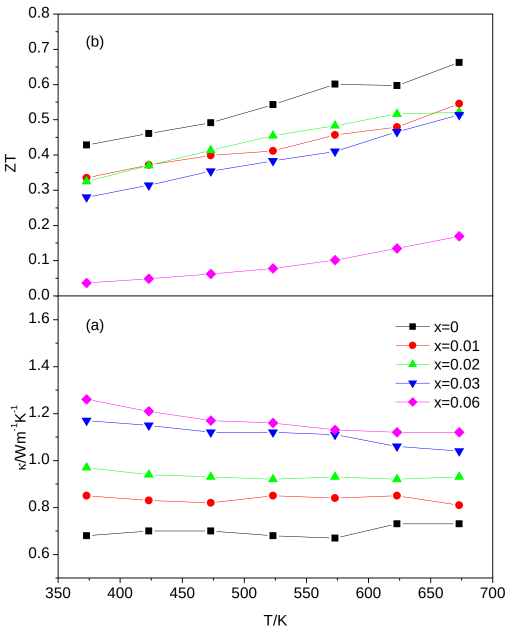

Figure 3. Temperature dependence of the (a) thermal conductivity and (b) ZT, for $Bi_{1-x}Pb_xOCuTe$.

The power factor of BiOCuTe (8.7 μW cm^{-1} K^{-2} at 298 K) is moderate in comparison to that of Bi_2Te_3 (~ 40 μW cm^{-1} K^{-2}),8 but similar to those of other thermoelectric materials such as Zn_4Sb_3 (~ 13 μW cm^{-1} K^{-2} at 673 K)[20] or $BiOCu_{1-x}Se$ (~ 4 μW cm^{-1} K^{-2} at 923 K).6 Because of its low thermal conductivity, BiOCuTe exhibits remarkable values of the thermoelectric figure of merit, ZT, (Figure 3(b)) at temperatures suitable for waste heat recovery. As ZT continues to increase with increasing temperature, this material may exhibit even higher ZT values at higher temperatures. Our preliminary work on doping indicates that, although low levels of lead doping result in an enhancement of the power factor, ZT is reduced due to the simultaneous increase in electronic thermal conductivity. This suggests that further efforts on BiOCuTe are required to optimise the charge carrier concentration, and in particular, to investigate samples with smaller charge carrier concentrations. Given the promising thermoelectric performance found for as-prepared BiOCuTe, we believe that there is considerable scope for the improvement of ZT through careful control of the stoichiometry and doping. The outstanding thermoelectric properties of $BiOCu_{1-x}Se$6 and those reported here for BiOCuTe suggest that the antifluorite $[Cu_2Q_2]^{2-}$ slabs have remarkable electronic and thermal transport properties. This opens up a new direction for research in thermoelectrics, as other phases containing $[Cu_2Q_2]^{2-}$ slabs should also be screened as prospective thermoelectric materials.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, powder X-ray diffraction data and Rietveld refinements, low-temperature electrical conductivity and Seebeck coefficient, thermogravimetric analysis, lattice and electronic thermal conductivity data. See DOI: 10.1039/b000000x/

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