

# *Layered oxychalcogenides: structural chemistry and thermoelectric properties*

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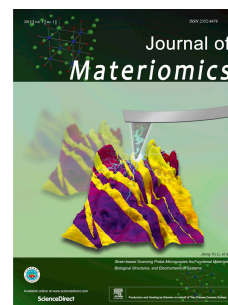
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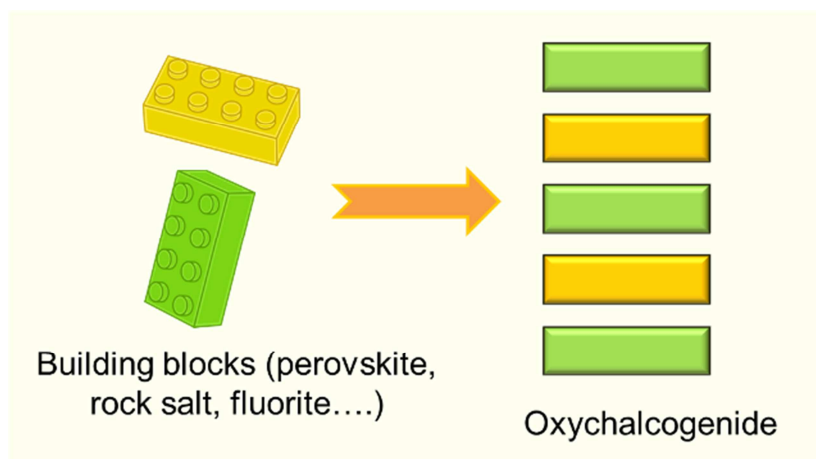
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**Graphical Abstract****Layered oxychalcogenides: structural chemistry and thermoelectric properties**

Son D N Luu and Paz Vaqueiro\*



This review provides an overview of the structural chemistry of layered oxychalcogenides, which are described using a building block approach, and on the potential of these materials for thermoelectric applications.

# Layered oxychalcogenides: structural chemistry and thermoelectric properties

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## Abstract

Layered oxychalcogenides have recently emerged as promising thermoelectric materials. The alternation of ionic oxide and covalent chalcogenide layers found in these materials often results in interesting electronic properties, and also facilitates the tuning of their properties via chemical substitution at both types of layers. This review highlights some common structure types found for layered oxychalcogenides and their interrelationships. This review pays special attention to the potential of these materials for thermoelectric applications, and provides an overview of the thermoelectric properties of materials of current interest, including BiCuSeO.

**Keywords:** Oxychalcogenides; Layered structures; Thermoelectric; BiCuSeO

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## 1. Introduction

Layered oxychalcogenides are mixed-anion compounds, in which oxide and chalcogenide anions (Group 16) indirectly bound via one or more cations, creating a stack of alternating oxide and chalcogenide layers. The coexistence of ionic oxide anions and more covalent chalcogenide anions leads to a highly distinctive structural chemistry. Owing to the preference of “hard” non-polarisable cations to coordinate to smaller oxide anions, while “soft” more polarisable cations preferentially coordinate to larger chalcogenide anions, quaternary oxychalcogenides tend to adopt structures in which oxide and chalcogenide anions are segregated, with each coordinating preferentially to one type of cation, as early noted by Guittard *et al* [1]. This often results in structures with low-dimensional characteristics, and structural low dimensionality may lead to highly anisotropic electronic band structures, together with interesting electronic properties. In addition, the covalent character of the chalcogenide layers promotes high-mobility semiconduction, whereas low thermal conductivity is favoured by the more ionic interactions of the oxide blocks. The alternation of distinct layers found in oxychalcogenides also facilitates the tuning of their properties via chemical substitution at both the oxide and chalcogenide layers. The coexistence of low-dimensionality together with covalent and ionic bonding offers great for potential for thermoelectric applications, and can also result in a wide range of unexpected and fascinating properties. For instance,  $\text{Ce}_2\text{O}_2\text{S}$  nanoparticles anchored on graphitised carbon has been recently found to be a promising anode material for Li-ion batteries, with a stable specific capacity up to  $627 \text{ mA h g}^{-1}$  after 180 charge-recharge cycles [2].  $\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$  has attracted considerable attention as a photocatalyst for water splitting [3], and  $\text{LaOCuS}$  is considered a promising *p*-type transparent semiconductor for optoelectronic applications [4]. Superconductivity has been recently reported in bismuth oxysulfides, although the  $T_c$  is rather low  $\sim 4.5 \text{ K}$  [5,6,7]. An improvement of the superconducting properties of compounds containing  $[\text{BiS}_2]^{2-}$  layers has been found in electron doped  $\text{NdO}_{0.5}\text{F}_{0.5}\text{BiS}_2$  ( $T_c \sim 5 \text{ K}$ ) [8] or  $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$  ( $T_c \sim 10.6 \text{ K}$ ) [9].

Although oxychalcogenides can also adopt structures without low-dimensional characteristics, as exemplified by  $\text{Eu}_5\text{V}_3\text{S}_6\text{O}_7$  and  $\text{La}_{10}\text{Se}_{14}\text{O}$  [10], throughout this review we restrict our scope to layered oxychalcogenides, with a particular focus on their potential for thermoelectric applications. The structures of some families of layered oxychalcogenides have been previously reviewed [1, 11, 12].

## 2. Structural Chemistry of Layered Oxychalcogenides

### 2.1. Common Building Blocks

Structures of layered oxychalcogenides can be described as a combination of two (or more) types of building blocks. Certain inorganic slabs, such as perovskite, fluorite, or rock-salt blocks, which are encountered in many structures, can be considered as two-dimensional building blocks, and layered structures in which two or more types of such building blocks are stacked along a given direction, can be generated. **Table 1** presents four common building blocks found in layered oxychalcogenides. In each case, the parent structure is shown, as well as a two-dimensional slab derived from each parent structure. Representative compounds containing these building blocks are discussed in the following sections. Chalcogenide anions are denoted as Q.

### 2.2. Materials containing sheets of $Q^{2-}$ and $(Q_2)^{2-}$ anions

Three related families of materials containing sheets of  $Q^{2-}$  and/or  $(Q_2)^{2-}$  anions, which alternate with oxide slabs, are known. Planar sheets of  $Q^{2-}$  anions are found in  $[A_2O_2]Q$ , while  $[A_4O_4](Q_2)(Q)$  contains both  $Q^{2-}$  and  $(Q_2)^{2-}$ , and in  $[A_2O_2]Q_2$  only  $(Q_2)^{2-}$  anions are present.

The crystal structures of materials with stoichiometry  $[A_2O_2]Q$ , where A is rare earth element (La-Yb, Y, Lu) or Bi, and Q is S, Se or Te, consist of alternating  $[A_2O_2]^{2+}$  and  $Q^{2-}$  layers. The oxygen anions are tetrahedrally coordinated by  $A^{3+}$  cations, forming  $A_4O$  tetrahedra, while the  $Q^{2-}$  anions form a planar chalcogenide array. Two distinct structure types are found, which differ markedly on the nature of the  $[A_2O_2]^{2+}$  layers. Materials containing the heavier chalcogen Te, including  $[A_2O_2]Te$  (A = La-Nd, Sm-Ho Bi) [13,14] as well as the oxyselenide  $Bi_2O_2Se$  [15], crystallise in the tetragonal (space group  $I4/mmm$ ) *anti*- $ThCr_2Si_2$  structure type (**Figure 1a**), while most of the remaining compounds ( $[A_2O_2]Q$  with A = La-Yb, Y, Lu; Q = S, Se) [16,17,18,19] crystallise in the trigonal (space group  $P\bar{3}m1$ ) structure (**Figure 1b**) of  $La_2O_3$ . The structure of  $Bi_2O_2S$ , which is closely related to the *anti*- $ThCr_2Si_2$  type, has been described by Koyama *et al.* in an orthorhombic space group ( $Pnmm$ ). This structure appears to be a slightly distorted form of the tetragonal structure of  $Bi_2O_2Se$  [20]. The *anti*- $ThCr_2Si_2$  structure is also adopted by the oxypnictides  $[A_2O_2]X$  (A = rare-earth element, X= Sb, Bi) [21,22]. A commensurately modulated structure, arising from the distortion of the square nets of the pnictide ions, results in a lowering of the symmetry for  $Pr_2O_2Sb$  [23], but the single

crystal study of  $\text{Bi}_2\text{O}_2\text{S}$  provides no evidence for a modulated structure [20].

In the tetragonal *anti*- $\text{ThCr}_2\text{Si}_2$  structure, the  $\text{A}_4\text{O}$  tetrahedra share four edges, forming fluorite-like two-dimensional slabs. The  $\text{Q}^{2-}$  ion adopts an 8-fold square prismatic coordination and the A site is in a (4O+4Q) distorted square anti-prism. By contrast, in the trigonal structure, the  $\text{A}_4\text{O}$  tetrahedra share three edges, forming 6 membered rings of tetrahedra (**Figure 1c**). Each chalcogenide ion is octahedrally coordination by  $\text{A}^{3+}$  cations, and each  $\text{A}^{3+}$  cation is seven coordinate with four short bonds to O and three longer bonds to Q.

In the  $[\text{A}_4\text{O}_4](\text{Q}_2)(\text{Q})$  structure ( $\text{A} = \text{La-Yb}$ , Y and Q = Se), fluorite-like  $[\text{A}_2\text{O}_2]^{2+}$  slabs alternate with chalcogen sheets, formed by chains of  $\text{Se}^{2-}$  and  $(\text{Se}_2)^{2-}$  anions [24,25]. Depending on the size of the A atom, four closely-related structure types, labelled as the  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ - $\text{A}_4\text{O}_4\text{Se}_3$  structures, exist [23]. The structure of  $\alpha$ - $\text{A}_4\text{O}_4\text{Se}_3$  phase is illustrated in **Figure 2a**. Whilst ordered chains of alternating  $\text{Se}^{2-}$  and  $(\text{Se}_2)^{2-}$  anions are found in the  $\alpha$  and  $\beta$  phases, in the  $\gamma$  and  $\delta$  types the Se atoms form “wave like” chains, which cannot be interpreted as a simple ordered array of  $\text{Se}^{2-}$  and  $(\text{Se}_2)^{2-}$ . More details have been presented elsewhere [23]. Neither sulfur nor tellurium analogues of  $\text{A}_4\text{O}_4\text{Se}_3$  have been reported to date.

The structure of  $[\text{A}_2\text{O}_2](\text{Q}_2)$  (**Figure 2b**) was first described by Wichelhaus, who reported compounds where A is La, Pr, Nd and Q is S [26], and is composed of alternating fluorite-type  $[\text{A}_2\text{O}_2]^{2+}$  layers and  $(\text{S}_2)^{2-}$  planar sheets. Although this crystal structure was initially described in the *Pcam* space group [24], J. Ostoréro *et al.* have shown that  $\text{La}_2\text{O}_2\text{S}_2$  crystallises in the *Cmca* space group [27]. Selenium or tellurium analogues have not been described.

### 2.3. Materials containing fluorite-like oxide blocks and transition-metal chalcogenide blocks

Two distinct structural types, both of which contain fluorite-like  $[\text{A}_2\text{O}_2]^{2+}$  slabs, are known:  $[\text{AO}][\text{BQ}]$  and  $[\text{AO}][\text{BQ}_2]$ , depending on the oxidation state of the transition metal. The monovalent transition metals Cu and Ag adopt the former, whilst divalent transition metals adopt the later structure.

Materials with the general formula  $[\text{AO}][\text{BQ}]$  (where A is Bi, Y, La-Yb; B is a monovalent cation such as Cu, Ag and Q is S, Se, Te) [28,29,30,31,32], crystallise in the tetragonal  $\text{ZrCuSiAs}$  structure [33]. The  $\text{A}^{3+}$  ions had been limited to  $\text{Y}^{3+}$  and lanthanides until 1993



when Kholodkovskaya *et al.* [27] reported the substitution of  $\text{Bi}^{3+}$  into the A site. The  $[\text{AO}][\text{BQ}]$  crystal structure consists of fluorite-type  $[\text{A}_2\text{O}_2]^{2+}$  and antifluorite-type  $[\text{B}_2\text{Q}_2]^{2-}$  slabs stacked alternately along the  $c$ -axis (Figure 3). This structure type has been reported for approximately 150 compounds, containing the anions oxide, fluoride, silicide, germanide, chalcogenide, pnictide, and hydride [34], and in particular, is also adopted by the superconducting oxypnictides  $\text{LnOFePn}$  ( $\text{Ln} = \text{La, Pr, Ce, Sm}$ ;  $\text{Pn} = \text{P and As}$ ) [35]. In 1980, Palazzi *et al.* reported ionic conductivity for  $\text{LaOAgS}$  [28], while in  $\text{CeOCuS}$  copper can be readily extracted from the  $[\text{Cu}_2\text{S}_2]^{2-}$  layers, to produce highly deficient copper phases [36]. The rare-earth containing oxychalcogenides have been primarily investigated for their optoelectronic properties, as many of them are transparent  $p$ -type semiconductors [37].

The structure of  $[\text{A}_2\text{O}_2][\text{BQ}_2]$  is composed of  $[\text{BQ}_2]^{2-}$  ( $\text{B} = \text{Fe, Zn, Mn, Cd}$ ;  $\text{Q} = \text{Se}$ ) slabs separated by  $[\text{A}_2\text{O}_2]^{2+}$  layers ( $\text{A} = \text{La, Ce}$ ). In the chalcogenide layers, the  $\text{B}^{2+}$  cations occupy half of the available B sites of the antifluorite-type  $[\text{B}_2\text{Q}_2]$  slab in an ordered fashion. In the case of  $\text{La}_2\text{O}_2\text{CdSe}_2$ , a checkerboard arrangement of corner-sharing  $\text{CdSe}_4$  tetrahedra is found, instead of the edge-sharing tetrahedra found in  $[\text{AO}][\text{BQ}]$  (Figure 4) [38]. It has been shown that different ordering patterns are possible depending on the composition, and in particular on the nature of the transition metal. The  $[\text{BSe}_2]^{2-}$  layers can contain  $\text{BSe}_4$  tetrahedra that are exclusively edge-sharing (stripe-like), exclusively corner-sharing (checkerboard-like arrangement), or mixtures of both. Details of the different ordering patterns in  $[\text{A}_2\text{O}_2][\text{BSe}_2]$  phases have been discussed in detail elsewhere [39, 40]. The investigation of the electronic properties of  $\text{La}_2\text{O}_2\text{CdSe}_2$  indicate that this material is insulating, with electrical resistivities  $>10^{10} \Omega\text{cm}$ , and a band gap of 3.3 eV [36].

#### 2.4. Materials adopting the $[\text{AO}][\text{BQ}_2]$ structure and related structures

The repetition of fluorite-type  $[\text{A}_2\text{O}_2]^{2+}$  blocks and rock-salt  $[\text{B}_2\text{Q}_4]^{2-}$  blocks, stacked in an alternating fashion along the  $c$ -axis, creates the layered structure of  $[\text{AO}][\text{BQ}_2]$  (where  $\text{A} = \text{La, Ce, Pr, Nd, Sm, Yb, Bi}$ ;  $\text{B} = \text{Bi}$ ;  $\text{Q} = \text{S, Se}$ ), [41] which is exemplified by  $\text{LaOBiS}_2$  (Figure 5a). These materials are currently attracting considerable attention due to their superconducting behavior and have been recently reviewed, [11] hence they will not be discussed here in further detail.  $[\text{A}_2\text{O}_2][\text{SnS}_3]$  ( $\text{A} = \text{La-Nd}$ ) can be considered to be closely related to the  $[\text{AO}][\text{BQ}_2]$  structure, as it contains fluorite  $[\text{A}_2\text{O}_2]^{2+}$  blocks alternating with thinner and distorted rock-salt  $[\text{SnS}_3]^{2-}$  blocks [1, 42] (Figure 5b).

## 2.5. Materials adopting the $[A_2MO_2][B_2Q_2]$ structure and anti-type variants

A representative compound of the  $[A_2MO_2][B_2Q_2]$  structure ( $A = \text{Ba, Sr}$ ;  $M = \text{Mn, Co, Ni, Zn}$ ;  $B = \text{Cu, Ag}$ ;  $Q = \text{S, Se}$ ) [43,44,45] is  $\text{Sr}_2\text{ZnO}_2\text{Cu}_2\text{S}_2$  [46], which crystallises in the  $\text{Sr}_2\text{Mn}_3\text{Sb}_2\text{O}_2$  (or  $\text{Sr}_2\text{MnO}_2\text{Mn}_2\text{Sb}_2$ ) structure type [47]. This structure contains antifluorite  $[B_2Q_2]^{2-}$  chalcogenide layers and oxide  $[MO_2]^{2-}$  planar sheets, which are separated from the  $[B_2Q_2]^{2-}$  blocks by  $A^{2+}$  ions (**Figure 6**). The  $[A_2MO_2]^{2+}$  blocks can be considered to be derived from the perovskite structure, through removal of the apical oxide anions in a perovskite block (**Table 1**), leading to the square planar coordination found for the  $M^{2+}$  cations.

The  $[A_2M_2O][B_2Q_2]$  structure is a half anti-type of  $[A_2MO_2][B_2Q_2]$  in which  $A$  and  $M$  are monovalent cations. It comprises the same antifluorite chalcogenide layers  $[B_2Q_2]^{2-}$  and oxide  $M_2O$  planar sheets, which are separated from the  $[B_2Q_2]^{2-}$  slabs by  $A^+$  ions. A representative compound is  $\text{Na}_2\text{Cu}_4\text{OSe}_2$  or  $[\text{Na}_2\text{OCu}_2][\text{Cu}_2\text{Se}_2]$ , which exhibits  $p$ -type metallic behaviour due to a small sodium deficiency [48].  $[A_2O_2][B_2OQ_2]$  is an anti-structure of  $[A_2M_2O][B_2Q_2]$ . The representative compound of this structure type is  $\text{La}_2\text{Fe}_2\text{O}_3\text{Se}_2$  or  $[\text{La}_2\text{O}_2][\text{Fe}_2\text{OSe}_2]$  [49]. It consists of oxide fluorite-type slabs  $[A_2O_2]^{2+}$ , while the oxide  $M_2O$  planar sheet is separated from the  $[A_2O_2]^{2+}$  layers by chalcogenide anions.

## 2.6. Materials containing Thicker Oxide Layers

Examples of materials containing thicker oxide layers include the following homologous series:  $[A_{n+1}M_nO_{3n-1}][B_2Q_2]$  and  $[A_{n+1}O_{2n}][B_2Q_2]$  ( $n \geq 1$ ), in which  $B$  is Cu or Ag and  $Q$  is a chalcogen.

The structure of  $[A_{n+1}M_nO_{3n-1}][B_2Q_2]$  ( $A = \text{divalent cation}$ ;  $M = \text{di- or trivalent}$ ;  $Q = \text{S, Se}$ ) consists of antifluorite  $[B_2Q_2]^{2-}$  layers alternating with perovskite-like  $[A_{n+1}M_nO_{3n-1}]^{2+}$  slabs of different thicknesses (**Figure 7**). The structure for  $n = 1$ ,  $[A_2MO_2][B_2Q_2]$  (**Figure 6**), has been already described in section 2.5, and is exemplified by  $\text{Sr}_2\text{ZnO}_2\text{Cu}_2\text{S}_2$ . For  $n = 2$ ,  $[\text{Sr}_3\text{M}_2\text{O}_5][\text{Cu}_2\text{S}_2]$  with  $M = \text{Fe}$  and  $\text{Sc}$  have been reported [43,50], while for  $n = 3$   $[\text{Sr}_4\text{Mn}_3\text{O}_{7.5}][\text{Cu}_2\text{Q}_2]$  is known [51].

In the homologous series  $[A_{n+1}O_{2n}][B_2Q_2]$ , antifluorite-type  $[Cu_2Q_2]$  layers are separated by fluorite-like  $[A_{n+1}O_{2n}]$  oxide layers, in which  $A$  are trivalent cations (Bi, Y, La-Yb). The  $n = 1$  member of this series, for which a representative example is  $[\text{Bi}_2\text{O}_2][\text{Cu}_2\text{Se}_2]$  (or  $\text{BiOCuSe}$ ),

has already been described in section 2.3. The  $n=2$  members  $[\text{Bi}_2\text{LnO}_4][\text{Cu}_2\text{Se}_2]$  ( $\text{Ln} = \text{Y, Gd, Sm, Nd, La}$ ) are known [52], but members with higher values of  $n$  have not been reported to date.

## 2.7. Materials containing Thicker Chalcogenide Layers

Homologous series containing thicker chalcogenide layers have been primarily investigated for transition metals, and are exemplified by the  $[\text{A}_2\text{MO}_2][\text{B}_{2n-\delta}\text{Q}_{n+1}]$  series ( $\text{A} = \text{Ba, Sr; M} = \text{Mn, Co, Ni, Zn; B} = \text{Cu, Ag; Q} = \text{S, Se}$ ) [53]. The  $n=1$  member of this series was already described in section 2.5, while  $n=2$  and 3 members have been found, for instance, in  $\text{Sr}_2\text{MnO}_2\text{Cu}_{2n-\delta}\text{S}_{n+1}$  [52]. As illustrated in **Figure 8**, members of this homologous series consist of perovskite-like  $[\text{A}_2\text{MO}_2]$  blocks alternating with antifluorite-like  $[\text{B}_{2n-\delta}\text{Q}_{n+1}]$  layers of increasing thickness depending on the value of  $n$ . Intergrowth structures in which antifluorite-like  $[\text{B}_{2n-\delta}\text{Q}_{n+1}]$  blocks with different values of  $n$  coexist have also been found, as illustrated by  $\text{Sr}_4\text{Mn}_2\text{Cu}_5\text{O}_4\text{S}_5$ , which contains  $[\text{Cu}_4\text{S}_3]$  and  $[\text{Cu}_2\text{S}_2]$  layers [54]. It has been shown that in  $\text{Sr}_2\text{MnO}_2\text{Cu}_{2n-\delta}\text{S}_{n+1}$  the copper ions can be replaced by lithium ions through topotactic ion exchange reactions [55].

## 3. Thermoelectric Properties of Oxychalcogenides

Despite the numerous families of oxychalcogenides that have been discovered, many of the published reports are concerned with their optical and magnetic properties [12, 36]. Little effort has been devoted to the study of their thermoelectric properties, the exception being the copper-containing oxyselenide  $\text{BiOCuSe}$ , which has been extensively investigated as a promising thermoelectric material since 2010 [56]. Some representative examples of thermoelectric oxychalcogenides are given in **Table 2**, and their properties are discussed below. As evidenced by data in **Table 2**, a common characteristic of these materials is a rather low thermal conductivity.

The first report of the thermoelectric performance of oxychalcogenides adopting the  $[\text{AO}][\text{BQ}]$  structure focused on  $\text{La}_{1-x}\text{Sr}_x\text{OCuSe}$  [57], but interest in these materials grew considerably after the report of  $ZT = 0.76$  at 873 K for the bismuth analogue,  $\text{Bi}_{1-x}\text{Sr}_x\text{OCuSe}$  [58]. Since then, the number of publications on this family of oxychalcogenides has been increasing steadily. Higher  $ZT$  values are found for oxychalcogenides with smaller band gaps. Usually, the temperature at which  $ZT$  reaches a maximum value is related to the band gap [59]. This is because for a given band gap energy, there is a temperature at which the onset of intrinsic

conduction will occur, and the simultaneous excitation of intrinsic electrons and holes will reduce the Seebeck coefficient ( $S = S_p + S_n$ ) and hence  $ZT$ . It has been shown that, for a given operating temperature  $T$ , the optimal thermoelectric performance will be found for semiconductors with a band gap of approximately  $10k_B T$  [60]. Bismuth-containing [AO][BQ] phases have significantly lower band gaps than those containing rare earth elements, due to the contribution of Bi  $6p$  states to the bottom of the conduction band [61]. Although the lowest band gap is found for the oxytelluride for which  $ZT = 0.66$  at 673 K, there is a very limited number of doping studies [62,63], and most of the effort in optimising the thermoelectric performance has centred on the bismuth oxyselenide. For instance, high values of the thermoelectric figure of merit,  $ZT$ , have been obtained by doping with divalent ( $Sr^{2+}$ ,  $Ca^{2+}$ ,  $Pb^{2+}$ ,  $Mg^{2+}$ ) [58,64,65,66] or monovalent cations ( $Na^+$ ,  $K^+$ ) [67,68]. Alternatively,  $p$ -type doping can be achieved by introducing vacancies at the copper site, which leads to a  $ZT$  value of 0.81 at 923 K for  $BiOCu_{0.975}Se$  [69]. In addition, the thermal conductivity of  $Ba^{2+}$  doped  $BiOCuSe$  could be decreased by approximately 40% when reducing the grain sizes down to 200 - 400 nm, resulting in an even higher  $ZT$  value of 1.1 at 923 K [70]. Similar reductions in thermal conductivity have been found for ball milled  $BiOCuSe$  [71], suggesting that nanostructuring may be an effective approach to enhance the thermoelectric response of these materials. The highest figure of merit,  $ZT \sim 1.4$  (at 923 K), seems to have been achieved through the introduction of texture in  $Bi_{0.875}Ba_{0.125}CuSeO$  by hot forging [72]. More recently, dual vacancies at the bismuth and the copper site have been exploited to reduce the thermal conductivity and control the charge carrier concentration, leading to a  $ZT$  value of 0.84 at only 750 K [73]. In general, the most common approach to achieve a high  $ZT$  in these oxychalcogenides is to tune the electrical conductivity via doping, given their naturally low thermal conductivity. Due to the high Grüneisen parameter of  $BiOCuSe$  [74], it has been suggested that the low thermal conductivity in  $BiOCuQ$  is related to the presence of the  $Bi^{3+}$  lone pair, which can reduce the lattice thermal conductivity due to bond anharmonicity [75]. Saha calculated the phonon band structure of the oxyselenide, and attributed the low thermal conductivity of  $BiOCuSe$  when compared to  $LaOCuSe$  to a stronger hybridization of acoustic and optical phonons in the former than in the later [76]. The origin of the unusual thermal transport properties of  $BiOCuQ$  has also been investigated using a combination of neutron diffraction and computational calculations [77]. This study has shown that the main contributors to the unusually large Grüneisen parameter of these phases are copper and the chalcogen, and that despite the presence of the lone pair, the bismuth contribution is relatively small, with the change in thermal conductivity associated with the Bi/La substitution related to

the variation in atomic mass. Vaqueiro *et al.* concluded that weak bonding of the copper atoms leads to an unexpected rattling vibrational mode of copper at low frequencies, which is likely to be a major contributor to the low thermal conductivity found for BiOCuQ [76]. Recent calculations of phonon transport and lifetimes in BiOCuSe indicate that there is a significant contribution of optical phonons, arising primarily from O vibrations, to the overall lattice thermal conductivity [78]. Calculations of the electronic band structure of BiOCuQ indicate that the top of the valence band consist of a mixture of light- and heavy-mass bands [79]. This is considered a desirable feature for good thermoelectric performance [80], given that a light-mass band promotes good electrical conduction, whilst a heavy-mass band can result in a high Seebeck coefficient. However, it should be noted that the hole mobility in BiOCuSe is small,  $\sim 20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [81]. This is detrimental for the thermoelectric performance, because  $ZT$  is proportional to the mobility, according to the expression  $Z \propto (m^*)^{3/2} \mu$  (where  $m^*$  is the effective mass and  $\mu$  the mobility)[59].

Other materials containing antifluorite-like  $[\text{Cu}_2\text{Q}_2]$  layers have also been considered as potential thermoelectric materials. This includes  $\text{Bi}_2\text{YO}_4\text{Cu}_2\text{Se}_2$ , which was described in section 2.6. In  $\text{Bi}_2\text{YO}_4\text{Cu}_2\text{Se}_2$ , copper has a nominal oxidation state of +1.5 instead of +1.0, as confirmed by X-ray absorption spectroscopy [82], and this results in metallic behaviour. The large charge carrier density associated with metallic conduction leads to a significantly reduced Seebeck coefficient ( $\sim 25 \text{ } \mu\text{VK}^{-1}$  at room temperature), and a  $ZT$  value of only 0.03 at 673 K [83]. A small number of materials consisting of antifluorite  $[\text{Cu}_2\text{Se}_2]^{2-}$  layers alternating with perovskite-type oxide layers have also been assessed as potential thermoelectric materials. This includes  $\text{A}_2\text{FeO}_3\text{CuQ}$  ( $\text{A} = \text{Sr}, \text{Ca}$ ,  $\text{Q} = \text{S}, \text{Se}$ ) [84] and  $\text{Sr}_{2-x}\text{Ba}_x\text{CoO}_2\text{Cu}_2\text{Se}_2$  [85]. The  $\text{A}_2\text{FeO}_3\text{CuQ}$  phases were found to be *p*-type semiconductors with high resistivity values of 1-10  $\text{k}\Omega \text{ cm}$  at room temperature [76], while for  $\text{Sr}_{2-x}\text{Ba}_x\text{CoO}_2\text{Cu}_2\text{Se}_2$  a power factor of  $1.5 \text{ } \mu\text{W cm}^{-1}\text{K}^{-2}$  at room temperature has been reported [77]. The thermal conductivity of  $\text{Sr}_{2-x}\text{Ba}_x\text{CoO}_2\text{Cu}_2\text{Se}_2$  has not been measured, but given that their hole mobility of  $\sim 33.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [42] is similar to that of BiOCuSe, doping studies of  $\text{Sr}_2\text{CoO}_2\text{Cu}_2\text{Se}_2$ , together with measurements of the thermoelectric properties as a function of temperature would be of interest, as these materials may exhibit good thermoelectric performance. There are also some preliminary studies of oxychalcogenides containing rock-salt blocks, including  $\text{LaOBiS}_{2-x}\text{Se}_x$ , for which a  $ZT = 0.17$  is reached at 743 K [86]. More effort has been devoted to the thermoelectric properties of  $\text{Bi}_2\text{O}_2\text{Q}$  ( $\text{Q} = \text{Se}, \text{Te}$ ), which crystallise in the *anti*- $\text{ThCr}_2\text{Si}_2$  structure type described in section 2.2. The thermoelectric performance of  $\text{Bi}_2\text{O}_2\text{Se}$ , which is

an *n*-type semiconductor with a  $ZT = 0.007$  at 300 K, was first reported by Ruleova *et al* [87]. Bismuth deficiency has been shown to improve  $ZT$  [88], whilst doping with Sn at the bismuth site in  $\text{Bi}_{2-x}\text{Sn}_x\text{O}_2\text{Se}$  leads to a  $ZT$  value of 0.20 at 773 K [89]. The oxytelluride  $\text{Bi}_2\text{O}_2\text{Te}$ , which is a narrow gap semiconductor with a band gap of  $\sim 0.23$  eV, reaches a value of 0.13 at 573 K [90]. As evidenced by the values of  $ZT$  presented in **Table 2**, the performance of *n*-type oxychalcogenides to date is significantly lower than those of *p*-type phases, and the best performing material is still  $\text{BiOCuSe}$ .

#### 4. Concluding remarks

While in the past research on layered oxychalcogenides has centered on their magnetic properties, these materials are rapidly emerging as promising thermoelectric materials. A common feature to all materials investigated to date seems to be a relatively low thermal conductivity, and further studies to clarify the origin of this behavior are needed.

Band structure calculations suggest that the electronic structures of layered oxychalcogenides, which have a clear two-dimensional character, may be considered as the superposition of the electronic structures of each type of layer, stabilised by charge transfer. For the *p*-type phases containing  $[\text{Cu}_2\text{Q}_2]$  blocks, the electrical transport properties will be primarily determined by the electronic structure of the  $[\text{Cu}_2\text{Q}_2]$  layer, as the top of the valence band is formed by states arising from the hybridisation of Cu 3*d* and chalcogen *p* orbitals [30], while the oxide block acts as a charge reservoir to control the Fermi level. For the *n*-type oxychalcogenides, which have been far less investigated as thermoelectric materials, the electrical transport properties will be dependent on the nature of the bottom of the conduction band. For instance, in  $\text{LaOBiS}_2$ , the bottom of the conduction band is formed by unoccupied Bi 6*p* states hybridized with S 3*p* states, and has a clear two-dimensional character, with conduction electrons located in the  $[\text{BiS}_2]$  blocks [91].

From a thermoelectric perspective, the best performing oxychalcogenide to date is  $\text{BiOCuSe}$ , but given the variety of already known oxychalcogenides, there is a large field of unexplored materials that offer real prospects to improve  $ZT$ . The building block approach described here also offers ample opportunities to design and discover entirely new families of oxychalcogenides.

#### Acknowledgment

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## List of Figure Captions

**Fig. 1.** Crystal structures with stoichiometry  $[A_2O_2]Q$ : (a) *anti*- $ThCr_2Si_2$  type along  $[010]$ ; (b)  $La_2O_3$  type along  $[100]$ ; (c) polyhedral view of the  $[A_2O_2]^{2+}$  layer in the  $La_2O_3$  type structure, with the  $OA_4$  tetrahedra shown in blue. Unit cells are shown. Key: A, blue circles; O, red circles; Q, yellow circles.

**Fig. 2.** View of (a) the  $\alpha$ - $A_4O_4Se_3$  crystal structure; (b) the  $La_2O_2S_2$  structure. Key as for Figure 1.

**Fig. 3.** View of the crystal structure of  $[AO][BQ]$  along  $[010]$ . Key: A, blue circles; B, green circles; O, red circles; Q, yellow circles.

**Fig. 4.** View of the crystal structure of  $[AO][BQ_2]$  along  $[010]$ . Key as for Figure 2.

**Fig. 5.** View of the crystal structures of (a)  $[AO][BQ_2]$  and (b)  $[A_2O_2][SnS_3]$ . Key as for Figure 2.

**Fig. 6.** The  $[A_2MO_2][B_2Q_2]$  structure-type. Key: A, blue circles; B, green circles; M, pink circles; O, red circles; Q, yellow circles.

**Fig. 7.** The  $n=2$  and  $n=3$  members of the homologous series  $[A_{n+1}M_nO_{3n-1}][B_2Q_2]$ . Key as for Figure 6.

**Fig. 8.** The  $n=2$  and  $n=3$  members of the homologous series  $[A_2MO_2][B_{2n-6}Q_{n+1}]$ . Key as for Figure 6.



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**Table 1.** Common building blocks found in oxychalcogenides.

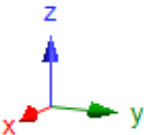
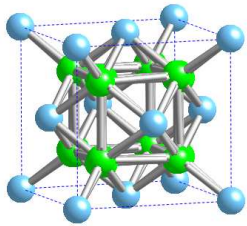
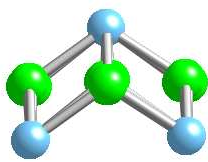
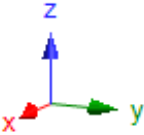
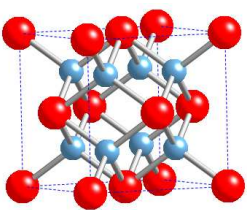
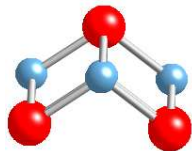
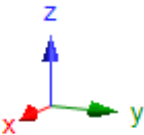
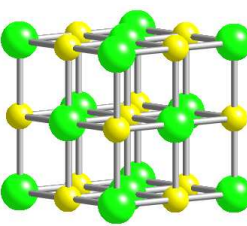
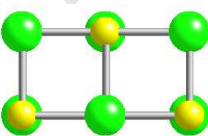
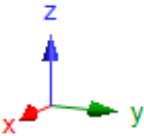
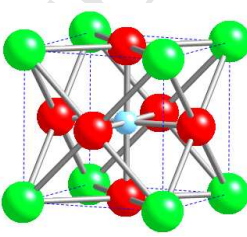
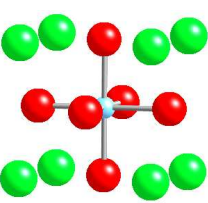
Structure	Unit cell	Building block slab	Key
Fluorite ( $\text{CaF}_2$ ) 			$\text{Ca}^{2+}$ (blue) $\text{F}^-$ (green)
Antifluorite ( $\text{Na}_2\text{O}$ ) 			$\text{Na}^+$ (blue) $\text{O}^{2-}$ (red)
Rock-salt ( $\text{NaCl}$ ) 			$\text{Na}^+$ (yellow) $\text{Cl}^-$ (green)
Perovskite ( $\text{SrTiO}_3$ ) 			$\text{Sr}^{2+}$ (green) $\text{Ti}^{4+}$ (blue) $\text{O}^{2-}$ (red)

Table 2. Total thermal conductivity (at room temperature), together with maximum ZT values at a temperature T, for selected oxychalcogenides.

Material	<i>p/n</i> -type	$\kappa/\text{Wm}^{-1}\text{K}^{-1}$	ZT	T/K	Ref.
$\text{Bi}_{1-x}\text{Sr}_x\text{OCuSe}$	<i>p</i> -type	0.9	0.76	873	58
$\text{BiOCuTe}$	<i>p</i> -type	0.8	0.66	673	62
$\text{Bi}_{0.875}\text{Ba}_{0.125}\text{CuSeO}$	<i>p</i> -type	0.9	1.4	923	72
$\text{Bi}_2\text{YO}_4\text{Cu}_2\text{Se}_2$	<i>p</i> -type	1.5	0.03	673	83
$\text{LaOBiS}_{2-x}\text{Se}_x$	<i>n</i> -type	2.0	0.17	743	86
$\text{Bi}_{2-x}\text{Sn}_x\text{O}_2\text{Se}$	<i>n</i> -type	1.0	0.20	773	89
$\text{Bi}_2\text{O}_2\text{Te}$	<i>n</i> -type	0.9	0.13	573	90

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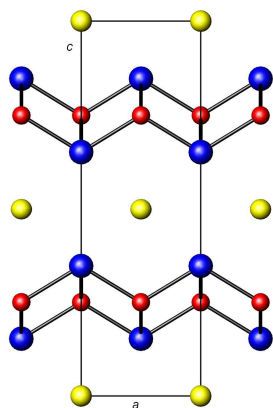
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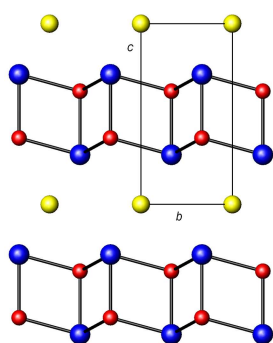
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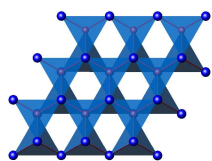
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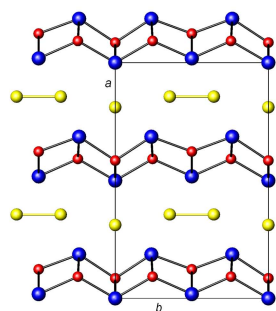
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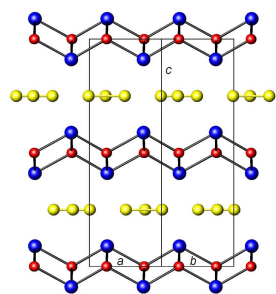
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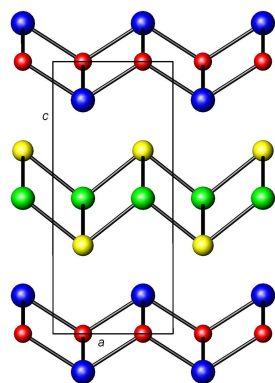


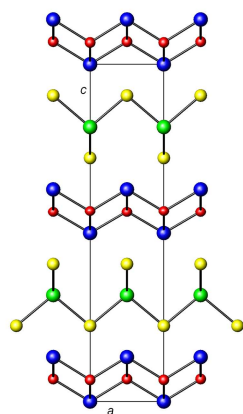


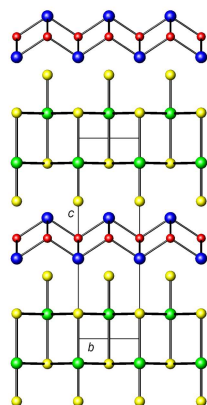


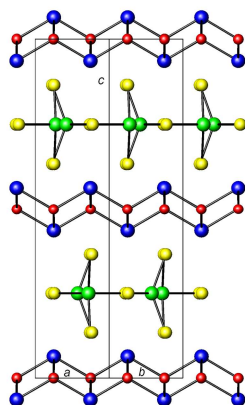


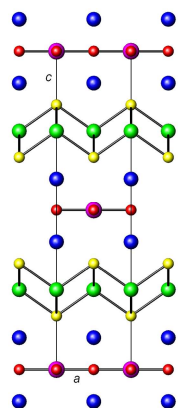


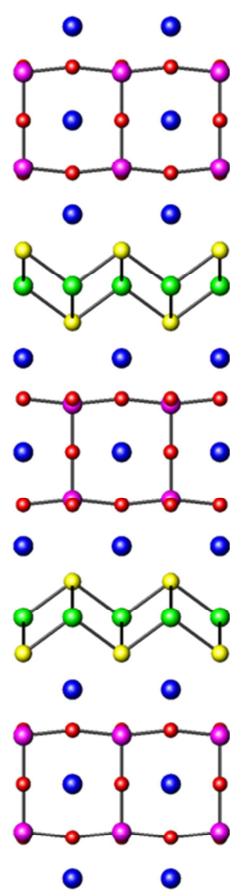
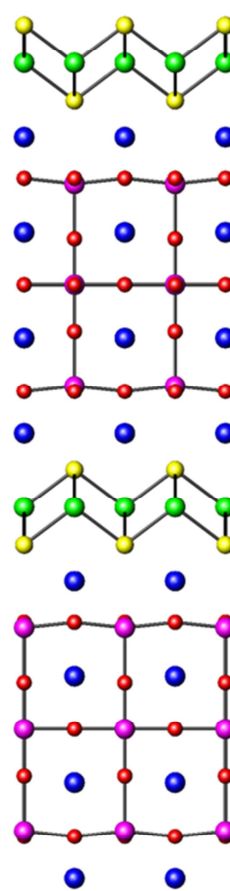










 $n = 2$  $n = 3$

