1. Introduction

Renewable energy sources are globally researched but maximizing their energy efficiency is challenging. Moreover, energy waste as thermal energy cannot be avoided in energy conversion processes. This condition leads to an increase in energy consumption. For the utilization of the energy waste, the thermal energy can be recovered and provide clean energy using the thermoelectric effect, which generates electric power from temperature ($T$, in K) gradient.\(^1\)\(^-\)\(^3\) The thermoelectric effect is measured by the figure of merit ($ZT$) formulated by

$$ZT = \frac{S^2\sigma T}{\kappa} \quad \text{(dimensionless)}$$

(1)

where $S$ is the Seebeck coefficient (in V K\(^{-1}\)), $\sigma$ is the electrical conductivity (in S m\(^{-1}\)), and $\kappa$ is the thermal conductivity (in W m\(^{-1}\) K\(^{-1}\))\(^{-4}\)\(^-\)\(^8\). $S$ can be expressed by the Mott formula\(^7\)\(^-\)\(^8\) which is formulated by

$$S = \frac{\pi^2 k_B^2 T}{3q} \left[ \frac{1}{D(E)} \frac{dD(E)}{dE} + \frac{1}{\mu(E)} \frac{d\mu(E)}{dE} \right] e^{-\epsilon_F} \quad \text{(in V K\(^{-1}\))}$$

(2)

where $q$ is the elementary charge ($q = 1.602 \times 10^{-19}$ C), $k_B$ is the Boltzmann constant ($k_B = 1.381 \times 10^{-23}$ J K\(^{-1}\)) and $\mu(E)$ is the mobility (in m\(^2\) V\(^{-1}\) s\(^{-1}\)). Furthermore, $S$, $\sigma$, and $\kappa$ are dependent on each other as the functions of the carrier concentration ($n$, in m\(^{-3}\)) and the electronic properties. Notably, $\kappa$ is a function of $\sigma$, and phonons passing through crystal lattices ($k_B$), which is a function of $\sigma$, and phonons.\(^1\)\(^9\) The superlattice structures are promising in generating the high cooling fluxes, which is potentially useful for modern device applications.\(^10\) The superlattice structure, accompanied by n-type $\delta$-doped Bi\(_2\)Te\(_3\)–Se\(_2\) x in the superlattice thermoelectric modules, show the high cooling fluxes, which is potentially useful for modern device applications.\(^11\) Furthermore, the hybrid inorganic–organic superlattice is promising for the flexible thin-film thermoelectric material.\(^12\) Moreover, the natural superlattice ($SnS_2$) has its thermoelectric performance improved in the in-plane direction. Moreover, $\sigma$ along the in-plane is higher than that of the cross-plane directions, showing the anisotropic behavior. On the other hand, the lattice $\kappa$ of this system is low because of the phonon scattering in the modulating periodic layers.\(^13\)
The layered oxycalloysides (RO)TmCh (R = La, Ce, Nd, Pr, Bi; Tm = Cu, Ag; and Ch = S, Se, Te) are the p-type semiconductors. The systems provide potential applications in thermoelectrics and optoelectronics and are considered as the natural superlattice systems consisting of the insulating oxide and conducting chalcogenide layers. The systems have (LaO)AgS-type crystal structure with the space group of P4/nmm (no. 129), in which Ag (O) is tetrahedrally surrounded by S (La) atoms. For example, the layered oxycalloysides (LaO)CuCh show the wide bandgap ($E_g$) of 2.3 to 3.1 eV by substituting Ch from Te to S, providing potential applications in optoelectronics. Also, the excitonic emission at RT has been observed. Our previous report has shown that the dielectric constant ($\varepsilon_0$), the optical dichroism, and the plasmonic states of (LaO)CuCh systems can be tuned by the Ch substitution. However, despite possessing the natural superlattice structure, (LaO)CuCh systems exhibit the low $\sigma$, indicating that these systems are not suitable for the thermoelectric application.

Regarding the layered oxycalloysides, (BiO)CuCh (Ch = Se, Te) are more suitable for the thermoelectric application. (BiO)CuSe show ZT of 0.50 at 923 K, while (BiO)CuTe show ZT of 0.42 and 0.66 at 373 and 673 K, respectively. From the experimental and first-principles perspectives, our previous report shows that, in spite of having the lower $\varepsilon_0$ than that of (BiO)CuSe system, (BiO)CuTe system provides the larger thermoelectric power due to the high $\sigma$ and the metallic behavior. Intriguingly, Sr$^{2+}$ and Ca$^{2+}$ doping at Bi site and Ba doping modulation can enhance ZT of (BiO)CuSe system. The previous report shows that La doping in (BiO)CuSe increases both $\sigma$ and $\kappa$ but decreases $\varepsilon_0$ as the La doping concentration (x) increases, leading to the maximum ZT of 0.74 at 923 K for x = 0.08. The increase of $\sigma$ is induced by the significant increase of $\mu$. It has also been shown that the increasing x from 0.02 to 0.06 enhances $\sigma$ and $n$ but reduces $\mu$ at high T. It is suggested that the increase of $n$ is induced by the presence of Bi vacancies due to the doping. On the other hand, the other report shows the increment of $\mu$ due to the increasing $x$. However, doping (BiO)CuTe system for tuning the thermoelectric performance is still a few. For example, the enhancement of the thermoelectric power factor of 16% by Bi addition in (BiO)CuTe system at 723 K has previously been reported. Moreover, structural properties and contributions of orbital states toward the thermoelectric properties of doped (BiO)CuCh are still yet to be explored.

In this paper, we investigate structural, electronic, and thermoelectric properties of layered oxycalloysides (La$_{0.5}$Bi$_{0.5}$O)CuCh (Ch = S, Se, Te) systems calculated by first principles. As the small $x$ tunes the thermoelectricity of La-doped (BiO)CuSe, we are interested in the possible role of the same portion of La and Bi elements in inducing new structural, electronic, and thermoelectric properties of (La$_{0.5}$Bi$_{0.5}$O)CuCh. The results are comprehensively discussed to investigate the effect of Ch substitution on the properties, which are compared to that of (LaO)CuCh and (BiO)CuCh systems. The structural properties were fully optimized to obtain their most stable condition, followed by calculations of band structure, total density of states (TDOS), and projected density of states (PDOS). This study reveals the local-symmetry distortion (LSD) at CuCh$_4$ and OLa$_2$Bi$_2$ tetrahedra, as well as the effect of Ch substitution on both electronic and thermoelectric properties.

### 2. Computational methodology

The structural and electronic properties of (La$_{0.5}$Bi$_{0.5}$O)CuCh (Ch = S, Se, Te) systems were calculated using Quantum-ESPRESSO package code. Fig. 1 shows the crystal structure model of (La$_{0.5}$Bi$_{0.5}$O)CuCh unit cell. In the unit cell, the system consists of [LaBiOlO$_2$] and [Cu1Cu2Ch1Ch2] layers showing CuCh$_1$Ch$_2$ tetrahedra ($i = 1, 2$) and OLa$_2$Bi$_2$ ($k = 1, 2$) tetrahedra. Ch1 and Ch2 element are also denoted by Ch$_i$ ($j = 1, 2$). Table 1 summarizes the initial structural parameters based on that of (LaO)CuCh. The use of $i$, $j$, and $k$ is due to the structural symmetry distortion with the presence of two different layers, that are La and Bi layers. The term ‘distortion’ refers to the fact that the top and the bottom sides of [Cu1Cu2Ch1Ch2] layers are located between different La and Bi layers, leading to the decrease of the structural symmetry degree. The structural symmetry distortion will be later discussed in Results and discussions.

The calculation employs the plane-wave method within the generalized gradient approximation (GGA), which includes the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functionals. The previous reports have successfully carried out this method for various systems. The norm-conserving pseudopotential methods are used to approach all-electron potentials. For Cu, Ch$_i$, and O$_k$ atoms, the Troullier– Martins (TM) method or the Goedecker–Hartwigsen–Hutter–Teter (GHHHT) method are used. Note that we use the different pseudopotential methods since this technique can minimize deviations between experimental and calculated structural properties. This technique has been used in our previous report in investigating the structural and electronic properties of (LaO)ZnPn (Pn = P, As, Sb) systems. The
calculation is initiated by the full structural optimization by means of the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method\textsuperscript{41–51} with threshold force of \(\sim 0.03\) eV Å\(^{-1}\). The corresponding command is variable-cell relaxation (vc-relax). Notably, the BFGS method is suitable for large molecular systems.\textsuperscript{52} Using this method, the optimized lattice parameters of several systems\textsuperscript{53–56} are comparable with that of the corresponding experimental results. Hence, this method is also suitable for small systems. The Broyden mixing method\textsuperscript{57} was used for the corresponding self-consistent field (SCF) calculation. The SCF calculation employed threshold and cut-off kinetic energies of \(\sim 3.0\) and \(\sim 1088\) eV, respectively, as well as \(k\)-point mesh of and \(9 \times 9 \times 4\). The SCF calculation was followed by the band structure calculation. A \(k\)-point path of \(\Gamma–X–R–Z–\Gamma–M–A–Z\) is used in the corresponding Brillouin zone. In the whole paper, visualizations of all crystal structures and calculations of LSD parameters are performed using VESTA.\textsuperscript{58} Any term of ‘Ch substitution’ refers to the Ch substitution from S to Te.

### 3. Results and discussion

#### 3.1. Structural properties

Table 1 presents the calculated structural parameters of (La\(_{0.5}\)Bi\(_{0.5}\)O)CuCh (Ch = S, Se, Te) systems compared with that of the previous experimental reports of (LaO)CuCh and (BiO)CuCh systems.\textsuperscript{38} The structural parameters include the lattice parameters \(a\) and \(c\). We use a general term \(\Delta \eta\) to represent \(\Delta a\) and \(\Delta c\), which is the difference percentage between calculated data (\(\eta_{\text{calc}}\)) and experimental results (\(\eta_{\exp}\)). This term is expressed as

\[
\Delta \eta = \left(\frac{\eta_{\text{calc}}}{\eta_{\exp}} - 1\right) \times 100\% \text{ (dimensionless)}.
\]

The terms \(\Delta a\) and \(\Delta c\) represent the percentages of the differences between the calculated and experimental \(a\) and \(c\), respectively. The calculated \(a\) and \(c\) are increased by the Ch substitution, as also observed in the experimental for both (LaO)CuCh and (BiO)CuCh systems. This increase is due to the different effective ionic radii of S\(^2\)\(^-\), Se\(^2\)\(^-\), and Te\(^2\)\(^-\), i.e., 1.84, 1.98, and 2.21 Å.\textsuperscript{29} Furthermore, the previous experimental results show that both \(a\) and \(c\) are dependent on La and Bi, summarized in Fig. 2. The calculated results show that \(a\) is smaller than that of (LaO)CuCh and larger than that of (BiO)CuCh systems. On the other hand, the calculated \(c\) is larger than that of (LaO)CuCh and larger than that of (BiO)CuCh systems. However, (La\(_{0.5}\)Bi\(_{0.5}\)O)CuS shows that both \(a\) and \(c\) are larger than that of the experiments. This result indicates that the co-existence of La and Bi significantly influences both \(a\) and \(c\). Moreover, in each (La\(_{0.5}\)Bi\(_{0.5}\)O)CuS and (La\(_{0.5}\)Bi\(_{0.5}\)O)CuSe systems, the calculated cell volumes (\(V_{\text{cell}}\)) are between those of both (LaO)CuCh and (BiO)CuCh (Ch = S, Te) systems, while \(V_{\text{cell}}\) of (La\(_{0.5}\)Bi\(_{0.5}\)O)CuTe system is larger than those of both systems.

Each system reveals the structural symmetry distortion, indicated by the fact that the change of atomic positions is no longer only possessed by both \(z_{\text{La}}\) and \(z_{\text{Ch}}\). Instead, all the atoms shift their coordinate components \((x, y, z)\) from the experimental coordinates. The atomic positions of O\(_i\) and Cu slightly shift from 2a and 2b sites, respectively, within the \(P4/nmm\) space group. In (La\(_{0.5}\)Bi\(_{0.5}\)O)CuS and (La\(_{0.5}\)Bi\(_{0.5}\)O)CuSe systems, both \(x_{\text{Cu}}\) and \(y_{\text{Cu}}\) are lower than 1/4, while (La\(_{0.5}\)Bi\(_{0.5}\)O)CuS system shows the opposite result. Moreover, (La\(_{0.5}\)Bi\(_{0.5}\)O)CuS system shows that \(z_{\text{Cu}}\) is higher than 1/2, which is in contrast with that of the other systems. Regarding O\(_i\) atom, for all the systems, \(x_{\text{O}}\) and \(y_{\text{O}}\) are slightly higher than 1/4. (La\(_{0.5}\)Bi\(_{0.5}\)O)CuS shows that \(z_{\text{O}}\) is slightly higher (lower) than 1/2, while (La\(_{0.5}\)Bi\(_{0.5}\)O)CuTe system shows that \(z_{\text{O}}\) is slightly lower than 1/2. On the other hand, (La\(_{0.5}\)Bi\(_{0.5}\)O)CuSe system does not show any \(z_{\text{O}}\) shift.

The calculation shows that the atomic positions La, Bi, and Ch\(_1\) shift from their 2c sites. \(x_{\text{La}}\) and \(x_{\text{Bi}}\) are lower than 1/4, except \(x_{\text{Bi}}\) for (La\(_{0.5}\)Bi\(_{0.5}\)O)CuS and (La\(_{0.5}\)Bi\(_{0.5}\)O)CuTe systems. On the other hand, \(x_{\text{Ch1}}\) and \(x_{\text{Ch2}}\) are higher than 1/4, except \(x_{\text{Ch2}}\). Furthermore, \(z_{\text{La}}\) is higher than that of (LaO)CuCh, while \(z_{\text{Bi}}\) is lower than that of (BiO)CuCh systems. For (La\(_{0.5}\)Bi\(_{0.5}\)O)CuS and (La\(_{0.5}\)Bi\(_{0.5}\)O)CuSe systems, \(z_{\text{Ch1}}\) is lower than that of both (LaO)CuCh and (BiO)CuCh systems, while \(z_{\text{Ch2}}\) shows the opposite result. These results provide LSD in Cu\(_1\)Ch\(_2\)2 and O\(_2\)La\(_2\)Bi\(_2\) tetrahedra.

The LSD parameters\textsuperscript{60,61} are to describe the LSD in Cu\(_1\)Ch\(_2\)2 and O\(_2\)La\(_2\)Bi\(_2\) tetrahedra. First, the mean quadratic elongation (\(\lambda_{\text{tet}}\)) is expressed as

\[
\lambda_{\text{tet}} = 0.25 \sum_{i=1}^{4} \left(\frac{l_i}{l_{\text{tet}}}\right)^2 \text{ (dimensionless)}
\]

where \(l_i\) is \(A–X\) bond length for an ideal AX\(_4\) tetrahedron with the same volume with that of the distorted tetrahedron and \(l_{\text{tet}}\) is \(A–X\) bond lengths. The bond-angle variance (\(\theta_{\text{tet}}^2\)) as the second parameter is expressed as

| Initial lattice parameter (Å) | (La\(_{0.5}\)Bi\(_{0.5}\)O)CuS | (La\(_{0.5}\)Bi\(_{0.5}\)O)CuSe | (La\(_{0.5}\)Bi\(_{0.5}\)O)CuTe |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| \(a\)                       | 3.9938                      | 4.0670                      | 4.1808                      |
| \(c\)                       | 8.5215                      | 8.8006                      | 9.3441                      |

**Table 1** Initial structural parameters of (La\(_{0.5}\)Bi\(_{0.5}\)O)CuCh (Ch = S, Se, Te) systems

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RSC Adv., 2020, 10, 27481–27491 | 27483
LSD of both tetrahedra is induced by the aspiration of the insulating and conducting layers to fit each other on the interface between them. Furthermore, the LSD of CuICh1Ch2 tetrahedra cannot be provoked by the Jahn–Teller (JT) effect which the fully-occupied Cu 3d orbital cannot possess. We suggest that this LSD is induced by the pseudo-JT effect (PJTE) in CuICh1Ch2 tetrahedra, which will be discussed later.

3.2. Band structures

The left panels of Fig. 4 present the band structures of \((\text{La}_{0.5}\text{Bi}_{0.5}\text{O})\text{Cu}\) (Ch = S, Se, Te) systems (range: \(-2.8 \leq E - E_F \leq 2.8\) eV), zoomed in the right panels (range: \(-1.0 \leq E - E_F \leq 1.0\) eV). \(E_F\) is the Fermi energy level. We find that all the systems are semiconductors, indicated by the presence of \(E_F\). The Ch substitution decreases \(E_F\). The band structures pattern is also modified by the Ch substitution. Fig. 4(d) and (e) show

\[
\theta_{\text{tet}}^2 = 0.2 \sum_{i=1}^{6} \left( \theta_{i} - 109.4712^\circ \right)^2 \quad \text{(in °)}
\]

where \(\theta_i\) is the X–A–X bond angles.\(^{60}\) The value of 109.4712° is the bond angle in the ideal tetrahedron.\(^{62}\)

Table 3 summarizes the average bond length \((l_{av})\) and the LSD parameters of \((\text{La}_{0.5}\text{Bi}_{0.5}\text{O})\text{Cu}\) systems, except \(l_{av}\) of \((\text{La}_{0.5}\text{Bi}_{0.5}\text{O})\text{Cu}\) and \((\text{Bi}_{0.5}\text{O})\text{Cu}\) systems, which is lower than that of \((\text{La}_{0.5}\text{Bi}_{0.5}\text{O})\text{Cu}\) system. Furthermore, both \(\theta_{\text{tet}}\) and \(\theta_{\text{tet}}^2\) of CuICh1Ch2 tetrahedra are higher than that of \((\text{La}_{0.5}\text{Bi}_{0.5}\text{O})\text{Cu}\) but lower than that of \((\text{Bi}_{0.5}\text{O})\text{Cu}\) systems. In contrast, both \(\theta_{\text{tet}}\) and \(\theta_{\text{tet}}^2\) of \((\text{La}_{0.5}\text{Bi}_{0.5}\text{O})\text{Cu}\) systems are lower than that of \((\text{La}_{0.5}\text{Bi}_{0.5}\text{O})\text{Cu}\) but higher than that of \((\text{Bi}_{0.5}\text{O})\text{Cu}\) systems. This result shows the co-existence of La and Bi ions significantly influences the local-symmetry distortion, compared to those of both \((\text{La}_{0.5}\text{Bi}_{0.5}\text{O})\text{Cu}\) and \((\text{Bi}_{0.5}\text{O})\text{Cu}\) systems. For comparing the LSD among the systems, we summarize the LSD parameters from the calculation in Fig. 3. We find that \(l_{av}\) of CuICh1Ch2 tetrahedra are higher than that of \((\text{La}_{0.5}\text{Bi}_{0.5}\text{O})\text{Cu}\) tetrahedra. Intriguingly, the increases of \(l_{av}\) of both CuICh1Ch2 and \((\text{La}_{0.5}\text{Bi}_{0.5}\text{O})\text{Cu}\) tetrahedra are almost linear with respect to the Ch substitution, where CuICh1Ch2 tetrahedra show the larger \(l_{av}\) gradient. On the other hand, \(\theta_{\text{tet}}\) and \(\theta_{\text{tet}}^2\) of \((\text{La}_{0.5}\text{Bi}_{0.5}\text{O})\text{Cu}\) are higher than that of CuICh1Ch2 tetrahedra. Concerning the Ch substitution, \(\theta_{\text{tet}}\) and \(\theta_{\text{tet}}^2\) increments of \((\text{La}_{0.5}\text{Bi}_{0.5}\text{O})\text{Cu}\) are also higher than that of CuICh1Ch2 tetrahedra. This result indicates that the LSD of \((\text{La}_{0.5}\text{Bi}_{0.5}\text{O})\text{Cu}\) is more sensitive to the Ch substitution than that of CuICh1Ch2 tetrahedra. Notably, the

**Table 2** Calculated structural parameters of \((\text{La}_{0.5}\text{Bi}_{0.5}\text{O})\text{Cu}\) (Ch = S, Se, Te) systems (Calc) compared with the previous experimental results denoted by Exp1 and Exp2 for \((\text{La}_{0.5}\text{Bi}_{0.5}\text{O})\text{Cu}\) systems.

| Parameter | (La0.5Bi0.5O)CuS | (La0.5Bi0.5O)CuSe | (La0.5Bi0.5O)CuTe |
|-----------|-----------------|-----------------|-----------------|
| \(a (\text{Å})\) | 3.9699 | 3.9398(2) | 3.8691(1) |
| \(c (\text{Å})\) | 8.5791 | 8.5215(4) | 8.5620(4) |
| \(\Delta a (%)\) | — | —0.3981 | 2.6056 |
| \(\Delta c (%)\) | — | 0.6759 | 0.2207 |
| \(V_{\text{cell}} (\text{Å}^3)\) | 135.2083 | 135.9217 | 128.1456 |

**Fig. 2** Trend of lattice parameters of \((\text{La}_{0.5}\text{Bi}_{0.5}\text{O})\text{Cu}\) (Ch = S, Se, Te) systems different Ch from calculation (Calc) and experiments of \((\text{La}_{0.5}\text{Bi}_{0.5}\text{O})\text{Cu}\) systems (Exp).
that (La$_{0.5}$Bi$_{0.5}$O)$_2$CuSe and (La$_{0.5}$Bi$_{0.5}$O)$_2$CuTe systems have the indirect $E_g$ of 0.529 and 0.256 eV (Γ → 0.4Δ), respectively. The term 0.4Δ $\tilde{g}$ denotes the path connecting 0.4Γ to 2Z points. These $E_g$ are lower than that of both (LaO)CuCh (1.67 and 1.44 eV for Ch = S and Se, respectively)$^{37}$ and (BiO)CuCh systems (0.68 and 0.40 eV for Ch = S and Se, respectively)$^{44}$ within the GGA. Furthermore, (La$_{0.5}$Bi$_{0.5}$O)$_2$CuTe system exhibits the indirect $E_g$ of 0.094 eV (Z → 0.4A), which is lower than that of (LaO)CuTe system$^{64}$ and shows the different behaviors with that of the metallic (BiO)CuTe system.$^{44}$ However, this $E_g$ is close to that of (LaO)CuTe system by including the on-site Coulomb repulsion ($U$) and spin–orbit coupling (SOC) corrections.$^{65}$ We suggest that the decrease $E_g$ corresponds to the increase of the lattice parameters as Ch is substituted from S to Te. The increase of the lattice parameters enlengthens the interatomic distances, leaving binding forces valence electrons and the corresponding parent ions reduced. Thus, the valence electrons are easier to move freely and induce the increase of n and $\sigma$. This suggestion assumes that $E_g$ is roughly inversely proportional to n.$^{66}$ Hence, the decrease of $E_g$ may indirectly be correlated with the ionic radii of Ch$^{2-}$ ions.

Experimental $E_g$ of all the systems might be higher than that of the present work because of the limitation of the GGA, usually underestimating $E_g$ in the exact Kohn–Sham band structures.$^{67}$ Furthermore, including $U$ in the calculation might also provide a closer $E_g$ to that of the possible experimental result. However, $U$ is not suitable to be included in a closed-shell system, where its valence orbitals are in the full occupation or empty.$^{68}$ Here, (La$_{0.5}$Bi$_{0.5}$O)$_2$CuCh systems are closed-shell systems. The ionic electronic configurations in (La$_{0.5}$Bi$_{0.5}$O)$_2$CuCh systems are La$^{3+}$: [Xe], Bi$^{3+}$: [Xe] $4f^{14}5d^{10}6s^2$, O$^{2-}$: [He] $2s^22p^6$, Cu$: [Ar] 3d^{10}$, S$^2-$: [Ne] $3s^23p^6$, Se$^2-$: [Ar] $3d^{10}4s^24p^6$, and Te$^{2-}$: [Kr] $4d^{10}5s^25p^6$. Also, the exchange–correlation term in Cu 3d orbital cannot be fully described by $U$.$^{65,67}$ The use of hybrid-functional$^{71-73}$ or GW approximations$^{74}$ might induce the wider $E_g$ than that of the GGA. However, both of them usually overestimate $E_g$ of semiconductors.$^{77-79}$ Furthermore, the Hartree–Fock (HF) exchange in the hybrid-functional approximations can lead to the d-element exchange splitting overestimation.$^{73,80}$ These explanation encourages us to keep the GGA method without $U$ correction, thus, indicates that the calculated properties are sufficient to predict experimental electronic properties.

The valence band (VB) structures of (La$_{0.5}$Bi$_{0.5}$O)$_2$CuCh (Ch = S, Se, Te) show the tuning of heavy hole (HH), light hole (LH), and split-off hole (SOH) states due to the Ch substitution. We are interested in the k-path of R–Z–Γ–M to observe this tuning since this path is near the $E_g$ transition. Along R–Z path, HH and LH states are separated, followed by SOH. The energy separation between HH and LH states is increased by the Ch substitution, while the energy level of SOH state is pushed down. The

![Fig. 3](image-url)
increasing separation between HH and LH states is shown by the decrease and increase of steepness of HH and LH states, respectively. Along Z–Γ path, the HH and LH coincide from 0.8Δ to 0.2Δ points. The SOH state shows a valley in the middle of this path, as its energy level is also pushed down by the Ch substitution. Along Γ–M path, the HH and LH states are separated with the lower separation that of R–Z path. However, this separation is not sensitive to the Ch substitution. On the other hand, the energy level of the SOH state is also sensitively pushed down. We are interested in the shifts of HH, LH, and SOH states at Z and Γ points. By substituting Ch from S to Se, HH, LH, and SOH states show shifts of 137, 122, and −99 meV, respectively, at Z point. At Γ points, HH, LH, and SOH states show shifts of 131, 124, and −88 meV, respectively. By substituting Ch from Se to Te, HH, LH, and SOH states show shifts of 33, −12, and −279 meV, respectively, at Z point. At Γ points, HH, LH, and SOH states show shifts of 0, 3, and −272 meV, respectively. It is indicated that the energy levels of HH and LH states are more sensitive to the Ch substitution from S to Se than that of the SOH state. On the other hand, the energy level of SOH is sensitive to the Ch substitution from Se to Te, while the energy levels of HH and LH are in contrast. This result leads to a shift of split-off energy (Δl) (l = 1, 2) of each system, defined as the energy separation between the HH and SOH states. Table 4 presents the split-off energy (Δl, l = 1, 2) of the systems. The term Δ1 and Δ2 are located at Z and Γ points, respectively. The difference between Δ1 and Δ2 are defined as δ12. For all the systems, we find the result of Δ1 > Δ2, leading to the positive δ12. Interestingly, the Ch substitution increases both Δ1 and δ12. This result shows the significant role of the Ch substitution in tuning the band structures.

Table 4 Calculated split-off energy (Δl) (l = 1, 2) of (La0.5Bi0.5O)CuCh (Ch = S, Se, Te) systems

| System                | Δ1 (Z point) | Δ2 (Γ point) | δ12 = Δ1 − Δ2 |
|-----------------------|--------------|--------------|----------------|
| (La0.5Bi0.5O)CuS      | 350          | 349          | 1              |
| (La0.5Bi0.5O)CuSe     | 586          | 569          | 17             |
| (La0.5Bi0.5O)CuTe     | 897          | 841          | 56             |

Fig. 4 Band structures of (a) (La0.5Bi0.5O)CuS, (b) (La0.5Bi0.5O)CuSe, and (c) (La0.5Bi0.5O)CuTe systems. (d–f) The right panels show zoomed band structures in the range of −1.0 < E_F < 1.0 eV.
3.3. Density of states

Fig. 5 presents the TDOS of (La$_{0.5}$Bi$_{0.5}$O)$_2$CuCh (Ch = S, Se, Te) systems (range: $-8.5 \leq (E - E_F) \leq 5.0$ eV). The TDOS shows the decrease of VB width due to the Ch substitution. We find the VB widths of 6.17, 6.00, and 5.98 eV in (La$_{0.5}$Bi$_{0.5}$O)$_2$CuS, (La$_{0.5}$Bi$_{0.5}$O)$_2$CuSe, and (La$_{0.5}$Bi$_{0.5}$O)$_2$CuTe systems, respectively. Hence, the Ch substitution slightly enhances the energy localization of VB. The VB can be divided into four levels, i.e., lower bonding, upper bonding, nonbonding, and antibonding levels, as summarized in Table 5. Theoretically, a VB consists of bonding, nonbonding, and antibonding levels. In this work, the four divisions are only to differ between the two peaks of bonding levels. The Ch substitution decreases the lower bonding level and nonbonding level widths but increases the antibonding level width. On the other hand, regarding the upper bonding level, (La$_{0.5}$Bi$_{0.5}$O)$_2$CuCuSe and (La$_{0.5}$Bi$_{0.5}$O)$_2$CuTe systems show the lowest and highest level widths, respectively. Furthermore, the Ch substitution decreases the conduction band (CB) width. We find the CB widths of 4.60, 4.34, and 3.91 eV in (La$_{0.5}$Bi$_{0.5}$O)$_2$CuS, (La$_{0.5}$Bi$_{0.5}$O)$_2$CuSe, and (La$_{0.5}$Bi$_{0.5}$O)$_2$CuTe systems, respectively, indicating the enhancement of energy localization of CB.

Fig. 5 also presents the PDOS of O 2p and Bi 6p states (La$_{0.5}$Bi$_{0.5}$O)$_2$CuCh (Ch = S, Se, Te) systems. O 2p states of O1 and O2 have the same DOS shape, thus, O 2p states are mentioned without assigning k. We calculate DOS centroids ($E_{\text{centroid}}$) for analyzing the PDOS using the expression

$$E_{\text{centroid}} = \frac{\sum_{E_{\text{min}}}^{E_{\text{max}}}}{E_{\text{max}} - E_{\text{min}}} \frac{D(E)dE}{D(E)dE} \approx \frac{\sum_{E_{\text{min}}}^{E_{\text{max}}}}{E_{\text{max}} - E_{\text{min}}} \frac{ED(E)dE}{ED(E)dE}$$

(in eV) (6)

where $D(E)$ is the DOS as the function of energy ($E$). (La$_{0.5}$Bi$_{0.5}$O)$_2$CuS, (La$_{0.5}$Bi$_{0.5}$O)$_2$CuSe, and (La$_{0.5}$Bi$_{0.5}$O)$_2$CuTe systems show the DOS centroids of deep O 2p states of $-3.76$, $-3.73$, and $-3.95$ eV, respectively, as well as the upper limits of high O 2p peaks at $-2.54$, $-2.61$, and $-2.73$ eV, respectively. The upper limits are between that of (LaO)$_2$CuCh systems and (BiO)$_2$CuCh systems, implying that the co-existence of La and Bi influences the energy level depth of O 2p states. Notably, O 2p states are fully occupied, while La 5d, La 6s, and Bi 6p states are empty in the ionic bonding scheme. However, we find the low-DOS Bi 6p states are shown in the VB, indicating the strong hybridization of O 2p and Bi 6p states. Moreover, the empty La 5d and La 6s are indicated by the absence of both states near $E_F$. The deep energy level of O 2p states indicates the insulating behavior of [LaBiO$_{1.5}$O$_2$] layers, in which the electrons are stable and difficult to be excited to CB. These insulating layers lead to two-dimensional electron confinement in the conducting [Cu$_2$-Ch1Ch2] layers. This confinement elucidates that (La$_{0.5}$Bi$_{0.5}$O)$_2$CuCh can be inferred as natural superlattice systems, which may provide the thermoelectric applications.15,16

Regarding the thermoelectricity, from eqn (2), we predict $S$ using the term $-(dF(E)/dE)$ calculated at $E = E_F$. In the present work, the term $-(dF(E)/dE)$ corresponds to hole as carriers for $E < E_F$. The minus (−) sign is used since $E_F$ below $E_F$ is converted to binding energy, which is represented with the plus sign, as previously shown in the photoemission spectra.44 Furthermore, we also calculate $n(E)$ expressed as

$$n(E) = D(E)(f(E) \text{ (a.u.)})$$

where $f(E)$ is the Fermi–Dirac distribution function.44 At the ground-state limit, we have $f(E) = 1$ for $E < E_F$. Fig. 6 presents $|dF(E)/dE|$ and $n(E)$ of states (La$_{0.5}$Bi$_{0.5}$O)$_2$CuCh (Ch = S, Se, Te) systems in a short energy range (range: $-0.2 \leq (E - E_F) \leq 0$ eV). Near $E_F$, we find $-(dF(E)/dE)$ of 0.21, 17.96, 27.60 eV$^{-2}$ in (La$_{0.5}$Bi$_{0.5}$O)$_2$CuS, (La$_{0.5}$Bi$_{0.5}$O)$_2$CuSe, and (La$_{0.5}$Bi$_{0.5}$O)$_2$CuTe systems, respectively. We suggest that the higher $S$ of (La$_{0.5}$Bi$_{0.5}$O)$_2$CuSe than that of (La$_{0.5}$Bi$_{0.5}$O)$_2$CuTe might provide the higher thermoelectric power. This result is in contrast to that of our previous report that $S$ of (BiO)$_2$CuTe is lower than that of (BiO)$_2$CuSe.44 However, the larger $ZT$ of (BiO)$_2$CuTe provides the higher thermoelectric power due to the metallic behavior, the higher $\sigma$, and the lower thermal conductivity ($\kappa$) than those of (BiO)$_2$CuSe system.5,15,44 From Fig. 6(b), we show that the Ch substitution enhances $n(E)$ of holes as the carriers, which may lead to the increasing $\sigma(E)$. The term $\sigma$ is correlated with $n(E)$ and $\mu(E)$ with the expression $\sigma(E) = n(E)\mu(E)q$. We have also proven that the decrease of $E_F$ due to the Ch substitution is proportionally related to the increase of $n$. The term $\kappa$ will be presented elsewhere in a future publication. Notably, experimental investigations are opened for clarifying our results.

Fig. 7 presents PDOS of Cu 4s, sub-Chy np [p$_x$, p$_y$, p$_z$], and sub-Cu 3d states in (La$_{0.5}$Bi$_{0.5}$O)$_2$CuCh (Ch = S, Se, Te) systems. This figure shows the details of orbital contributions to the lower bonding, upper bonding, nonbonding, and antibonding levels in the VB. Notably, the degeneracy-lifted Chy np and Cu 3d orbitals may be induced by the PJTE in the fully-occupied Cu 3d orbital, related to the LSD in Cu$_2$H$_2$C$_2$ tetrahedra. Notably, the tetrahedral-type crystal would allow the splitting of...

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**Fig. 5** Total density of states (TDOS) of (a) (La$_{0.5}$Bi$_{0.5}$O)$_2$CuS, (b) (La$_{0.5}$Bi$_{0.5}$O)$_2$CuSe, and (c) (La$_{0.5}$Bi$_{0.5}$O)$_2$CuTe systems. Projected density of states (PDOS) of O 2p (blue) and Bi 6p states (violet) are also presented.
Table 5  Ranges of divisions in valence band structures of (La0.5Bi0.5O)CuCh (Ch = S, Se, Te) systems

| System                  | Lower bonding | Upper bonding | Nonbonding | Antibonding |
|-------------------------|---------------|---------------|------------|-------------|
| (La0.5Bi0.5O)CuS        | −6.28 to −4.58 (1.70) | −4.58 to −3.16 (1.42) | −3.16 to −1.42 (1.74) | −1.42 to −0.21 (1.21) |
| (La0.5Bi0.5O)CuSe       | −6.09 to −4.50 (1.59) | −4.50 to −2.59 (1.91) | −2.59 to −1.35 (1.24) | −1.35 to −0.09 (1.26) |
| (La0.5Bi0.5O)CuTe       | −6.00 to −4.45 (1.55) | −4.45 to −2.67 (1.78) | −2.67 to −1.66 (1.01) | −1.66 to −0.01 (1.65) |

Fig. 6  (a) First derivative of total density of states −(dD(E)/dE) and (b) carriers concentration n(E) of (La0.5Bi0.5O)CuCh (Ch = S, Se, Te) systems as functions of energy (E).

The lower bonding level is contributed by Cu 4s and Chj np orbitals. Furthermore, the energy level of this hybridization slightly increases due to the Ch substitution, indicated by the increase of the energy levels of both orbitals. Furthermore, we find that the DOS profiles of Ch1 np and Ch2 np states are different. The different profiles are induced by structural symmetry distortion and the fact that Ch1 and Ch2 are close to the different La and Bi layers, leading to different chemical bonding between Bi–Ch1 and La–Ch2 bonds. In the lower bonding level, the energy levels of Ch2 np states are higher than that of Ch1 np states. We find the two highest peaks of Ch1 np and Ch2 np states in all the systems, alongside Se2 4Pd/2p peak in (La0.5Bi0.5O)CuSe system. This result indicates that the hybridization between Cu 4s and Chj np along c-axis direction is stronger than that of ab-plane direction.

The upper bonding level is contributed by Cu 3d and Chj np states. In (La0.5Bi0.5O)CuS system, S1 3p/c/p and S2 3p/c/p peaks, located at around −4.0 and −4.1 eV, respectively, are the highest peaks among the sub-Chj np states, as presented in Fig. 7(a). At the same energy levels, we find the degeneracy-lifted Cu13dz and Cu13dp peaks, as well as the degeneracy-lifted Cu23dz and Cu23dp peaks, as shown in Fig. 7(b). This result implies that the upper bonding is more pronounced along ab-plane direction. However, in (La0.5Bi0.5O)CuSe system, Se1 4p, peak, located at around −3.4, is the highest peak among the sub-Chj np states, followed by Se2 4Pd/2p located at −3.8 eV, as depicted in Fig. 7(c). From Fig. 7(d), at both −3.4 and −3.8 eV, there appear Cu13d and Cu13dz (Cu23dz) states, respectively, indicating the slightly more pronounced upper bonding along

Fig. 7  Projected density of states (PDOS) of Cu 4s, sub-Chj np, and sub-Cu 3d states (i = 1, 2; j = 1, 2) in (a and b) (La0.5Bi0.5O)CuS, (c and d) (La0.5Bi0.5O)CuSe, and (e and f) (La0.5Bi0.5O)CuTe systems. Notation dxz(dyz) is used for Cu1(Cu2) since the PDOS of dxz and dyz are the same for Cu1 and Cu2, respectively. This purpose is also used for the notation dx/dy.
c-axis direction. On the other hand, in (La0.5Bi0.5)CuTe system, Te 5p_e peak at −3.4 eV is the highest peak among the sub-Ch/np states, as shown in Fig. 7(e). Fig. 7(f) shows Cu3d_{x^2-y^2} and Cu3d_{x^2} (Cu23d_{x^2}) peaks at the same energy level with that of Te 5p_e states. This result indicates that Te 5p_e states experience the strongest hybridization with Cu 3d states compared to the other sub-Te/np states. We highlight for all the systems that Cu 3d-t_{2g} states strongly hybridize with Ch/np states and also show the larger contribution in the upper bonding level than that of Cu 3d-e_g states.

The nonbonding level is mainly contributed by the localized Cu 3d-e_g states (Cu3d_{x^2-y^2} and Cu3d_{xy}) based on Fig. 7. As the state with the highest peak, Cu3d_{x^2} states are localized at −2.1, −2.4, and −2.1 eV in (La0.5Bi0.5)CuS, (La0.5Bi0.5)CuSe, and (La0.5Bi0.5)CuTe systems, respectively. From Fig. 7(d), (La0.5Bi0.5)CuSe system shows the highest peak of Cu3d_{x^2-y^2} states among all the systems. However, the nonbonding level shows the presence of Cu13d_{yz} (Cu23d_{yz}) and Cu13d_{xy} (Cu23d_{xy}), indicating that Cu 3d-t_{2g} states partially hybridize with Ch/np states. This result is different from the previous suggestion that Cu and Ch ions are bound either along xz, yz, or xy planes. For all the systems, Ch2 np_e also slightly contribute to the nonbonding level, followed by Ch1 np_e states. Additionally, the contribution of Ch1 np_e states is increased by the Ch substitution.

The antibonding level is contributed by Cu 3d and Ch/np states. Based on the bottom panels of Fig. 7, all the systems show the highest peaks of Cu3d_{x^2-y^2} states, located at around −1.2, −1.4, and 1.1 eV in (La0.5Bi0.5)CuS, (La0.5Bi0.5)CuSe, and (La0.5Bi0.5)CuTe systems, respectively. This highest peaks are followed by Cu3d_{yz} peaks located at the close energy levels to those of Cu3d_{x^2-y^2} states. Regarding Ch/np states, all systems show the highest peaks of Ch1 np_e and Ch2 np_e states, located at around −0.9 eV based on the top panels of Fig. 7. In (La0.5Bi0.5) CuS system, we find two high peaks of S1 3p_x/p_y and S2 3p_x/p_y states, which are located at −0.4 and −1.2 eV, respectively. In (La0.5Bi0.5)CuSe and (La0.5Bi0.5)CuTe systems, the highest S1 3p_x/p_y (Te1 5p_x/p_y) and Se2 3p_x/p_y (Te2 5p_x/p_y) peaks are located at −0.3 (−0.1) and −1.1 (−1.2) eV, respectively. This result indicates that the antibonding is more pronounced along ab-plane direction. We also highlight for all the systems that Cu 3d-t_{2g} states strongly hybridize with Ch/np states and also show the larger contribution in the antibonding level than that of Cu 3d-e_g states.

4. Conclusions

The structural and electronic properties of the layered oxochalcogenides (La_{0.5}Bi_{0.5})CuCh (Ch = S, Se, Te) have been investigated based on the first principles. From the structural properties, the LSDs in CuCh1 and CuCh2, and OLa_{0.5}Bi_{0.5} tetrahedra are increased by the Ch substitution, in which the LSD in OLa_{0.5}Bi_{0.5} is stronger than that of CuCh1 tetrahedra. The possible PJTE in the fully-occupied Cu 3d orbital is suggested to be responsible for inducing the LSD in CuCh1 and CuCh2 tetrahedra and to lift the degeneracy level of t_{2g} and e_g states. From the electronic properties, all the systems are semiconductors.
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