A Density Functional Theoretical Study of Honeycomb Layered Nickel Tellurates

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**Highlights**

- $\text{K}_2\text{Ni}_2\text{TeO}_6$ disposition to accommodate new cations for various functionalities.
- Density-functional theory calculations for $\text{A}_2\text{Ni}_2\text{TeO}_6$ ($\text{A} = \text{Rb, Cs, H, Cu, Ag and Au}$).
- Large alkali atoms (Na, Rb and Cs) form a prismatic coordination with oxygen atoms at large interlayer distances.
- Coinage-metal atoms (Cu, Ag and Au) tend to form linear coordinations with oxygen atoms at intermediate interlayer distances.
- Li forms octahedral coordination with oxygen atoms at small interlayer distances.
- Hydrogen atoms form linear coordinations with oxygen atoms forming hydroxyl radical groups.

**Keywords:** First-Principles, Density Functional Theory, Honeycomb Layered Oxides, Stability, Ceramics, Atomic Structure
Abstract
Honeycomb layered tellurates represent a burgeoning class of multi-functional materials with fascinating crystal-structural versatility and a rich composition space. Despite their multifold capabilities, their compositional diversity remains underexplored due to complexities in experimental design and syntheses. Thus, in a bid to expand this frontier, we employ a density functional theory (DFT) approach to predict in silico the crystal structures of new honeycomb layered tellurates embodied by the composition, $A_2Ni_2TeO_6$ ($A =$ alkali and coinage-metal atoms). Here alkali-metal atoms with vastly larger radii (Rb and Cs) are found to engender a prismatic coordination with the oxygen atoms from the honeycomb slabs whilst coinage-metal atoms (Ag, Au and Cu) display a propensity for linear coordination. Further, the $H_2Ni_2TeO_6$ is found to also render a linear coordination wherein the hydrogen atom preferentially establishes a stronger coordination with one of the oxygen atoms to form hydroxyl groups. This work not only propounds new honeycomb layered tellurate compositions but also provides insight into the rational design of multifunctional materials for applications ranging from energy storage to catalysis and optics.

Figure showing the interslab/interlayer distances rendered by the $A_2Ni_2TeO_6$ ($A =$ Li, Na, Cu, Ag, K, Rb and Cs) compositions. The Shannon radii of the monovalent cations is shown in the horizontal scale.
1. INTRODUCTION

Honeycomb layered oxides embodying monovalent atoms such as Li, Na, K, Cu, or Ag, encapsulated between layered hexagonal frameworks of transition metal- or heavy metal oxides, exemplify a vanguard class of nanomaterials endowed with unconventional magnetic interactions, agile ionic mobility, exotic phase transitions and exquisite electrochemical functionalities that betoken monumental advancements in science and technology.[1] These fascinating capabilities have galvanised inquests into honeycomb layered oxides, particularly those entailing pnictogen and chalcogen atom frameworks, for they not only harbour a rich compositional canvas for developing high-voltage materials with high ionic conductivities but also represent an ideal pedagogical platform for investigating piquant magnetic phenomena and paradigm-shifting gravitational systems.[1-45]

Honeycomb layered oxides comprising pnictogen and/or chalcogen frameworks adopt an assortment of chemical compositions such as $A_4MDO_6$, $A_3M_2DO_6$ or $A_2M_2DO_6$, inter alia; where $M$ represents transition metal species such as Cu, Co, Zn, Ni, etc. or s-block metals such as Mg; $A$ denotes alkali- or coinage-metal species e.g., Li, Na, K, Cu, Ag, etc., and $D$ depicts a chalcogen or pnictogen metal species such as Te, Sb, Bi, etc. [1,2,6,8,10-14,18-21,29-31] These compounds present a rich compositional flexibility that allows various combinations and permutations of the $M$ and $D$ species—a recipe for unique magnetic and voltage properties that further expand their range of applications. Despite this chemical diversity, exploration into chalcogen $D$ species such as Te, remains limited, considering the great deal of scientific endeavour dispensed into honeycomb layered oxides entailing pnictogens such as Bi and Sb. [2,8,11,12-14,22,24,27,30]

Notably, honeycomb layered tellurates adopting the $A_2M_2TeO_6$ ($A = \text{Li, Na, K}$) compositions have garnered great utility as energy storage materials for they exhibit superb ionic properties such as elevated conductivities as well as high voltages that undoubtedly supersede those of most antimonates and bismuthates.[1] In fact, tellurates used alongside Ni in $A_2Ni_2TeO_6$ honeycomb layered oxides have been reported to exhibit the highest ionic conductivities and voltages (over 4 V) amongst the honeycomb layered oxides reported to date.[1,17,19-21,23,26,41,42] Therefore, to further expand this compositional space and enhance the functionalities of nickel-based honeycomb layered tellurates, it is imperative to gain insights into related layered structures that can accommodate other alkali atoms — (e.g., Rb and Cs) or coinage metal atoms (such as
Ag and Cu)—a pursuit yet to be undertaken for these tellurates.

The experimental discovery, design, and development of novel materials are heavily encumbered by challenges in synthesis and inexplicable influences of external/environmental factors. For this reason, computation techniques have become an indispensable part of material science research for their efficacy in predicting new materials and their emergent properties under controlled conditions that circumvent the limitations of experimental routes. In particular, density functional theoretical (DFT) methods have garnered traction in manifold applications due to their predictive power rooted in the quantum-mechanical description of electron and atom interactions that not only facilitates the exploration of mesoscopic and microscopic properties but also the prediction of new material compositions alongside their properties down to the atomic scale. As such, DFT has become a uniquely potent tool for predicting new crystal structures with high fidelity besides reproducing material ground state properties with reasonable scaling in respect to system size.

In this study, we aim to augment the compositional space of nickel-based honeycomb layered tellurates by employing DFT calculations to predict original compositions of $A_2Ni_2TeO_6$ ($A = H, Rb, Cs, Cu, Ag, Au$) yet under-reported in experimental and theoretical literature. The computations elucidate the stability and structural configurations of these new compositions comprising vastly large alkali atoms (namely, Rb and Cs), coinage-metal atoms (namely, Ag, Au, and Cu) and hydrogen. The optimised models of the $A_2Ni_2TeO_6$ compositions derived from the computations reveal distinctive prismatic coordinations between large alkali ($A = Rb, Cs$) and oxygen atoms, whilst the coinage-metal ($A = Ag, Au, Cu$) and the hydrogen atoms ($A = H$) exhibit an inclination towards dumbbell-like linear coordinations with two apical oxygen atoms from the transition metal slabs. Further, the predicted crystal model of the $H_2Ni_2TeO_6$ shows that each hydrogen atom preferentially establishes a stronger coordination with one of the oxygen atoms compared to those encompassing coinage-metal atoms, thus forming a relatively more stable hydroxyl group. The present findings not only envisage the vast compositional space of honeycomb layered tellurates but also paves the way for the design and synthesis of these new multifunctional materials that promise to expand the functionalities and applications of honeycomb layered oxides.
2. COMPUTATIONAL METHODOLOGY

The charge density and total energies were optimised to be self-consistent (with a threshold of $10^{-7}$ eV) using the Kohn-Sham formalism. The Perdew-Burke-Ernzerhof expression (GGA-PBE), which is one of the generalised gradient approximations, was adopted as the exchange-correlation functional. Further, a dispersion force correction of the DFT-D3 with Becke-Jonson damping method was adopted to accurately calculate the honeycomb oxide interlayer distance. The inner core region was assessed using the projector-augmented-wavefunction method. The number of valency electrons was set as follows: H ($1s^1$), Li ($2s^1$), Na ($3s^1$), K ($3p^64s^1$), Rb ($4p^65s^1$), Cs ($5s^25p^66s^1$), Cu ($3d^{10}4s^1$), Ag ($4d^{10}5s^1$), Au ($5d^{10}6s^1$), Ni ($3d^84s^2$), Te($5s^25p^4$) and O ($2s^22p^4$). An on-site Coulomb correction (DFT + $U$ method) was adopted, with $U = 4$ eV added to the 3$d$ orbital of Ni. The electronic spins on the Ni sites coupled in an anti-parallel manner can cause spin contamination error. Although the effect of the error in total energy was investigated by the approximated spin projection scheme for DFT, the attained results do not affect the discussion presented herein. The DFT calculations were performed by Vienna Ab initio Simulation Package (VASP) programme.

Structural optimisation was performed for all atoms, lattice constants, and cell dimensions. The crystal structures were relaxed until the threshold was reduced below $10^{-5}$ eV or $10^{-2}$ eV / Å. It is prudent to mention that the honeycomb [Ni$_2$TeO$_6$]$^{2-}$ slab was maintained in all the initial structures used, regardless of the various adjustments made to the atomic positions and lattice constants of the initial K$_2$Ni$_2$TeO$_6$ structures. Moreover, no symmetry restrictions were imposed during the structural optimisation. The energy cut-off was set at 500 eV (wave function) and 2400 eV (charge). $k$-sampling was performed with a 5×5×3 of Γ-centred mesh. Figure 1 shows the optimised crystal structure of K$_2$Ni$_2$TeO$_6$, which was subjected to structural relaxation to assess its stability to accommodate other alkali atoms (viz., H, Li, Na, Rb, Cs) and coinage-metal atoms (Cu, Ag and Au). The optimised lattice parameters for K$_2$Ni$_2$TeO$_6$ along with the optimised structures (A$_2$Ni$_2$TeO$_6$ ($A = H, Li, Na, Rb, Cs, Ag, Au$ and Cu)) have been furnished in Tables S1, S2 and S3. The most stable electronic configurations for A$_2$Ni$_2$TeO$_6$ ($A = Li, Na, Rb, Cs, Ag, Au$ and Cu) were found to be antiferromagnetic, whilst a ferromagnetic state was found for H$_2$Ni$_2$TeO$_6$. Although triclinic structures could be obtained, for the sake of a systematic discussion, the discussion hereafter is based on the stable optimised configurations of the honeycomb structures. Renditions of the crystal structures were performed using VESTA crystallographic software.
**Figure 1. Optimised crystal structural framework of K$_2$Ni$_2$TeO$_6$.** (a) Optimised crystal structural framework of K$_2$Ni$_2$TeO$_6$ when viewed along the [110] zone axis and [001] zone axis. Potassium atoms (in purple) are coordinated with six oxygen atoms (in red) to form a prismatic coordination. The potassium atoms are sandwiched between layers or slabs entailing Ni atoms (dark green) arranged in a honeycomb configuration around Te atoms (in ochre) via the oxygen atoms to form NiO$_6$ and TeO$_6$ octahedra. Note that the crystal structural framework is slightly deviated from the [110] zone axis, in order to explicitly visualise all the atom coordination within the unit cell.

3. **RESULTS AND DISCUSSION**

3.1. **Crystal structures of Na$_2$Ni$_2$TeO$_6$, Rb$_2$Ni$_2$TeO$_6$, Cs$_2$Ni$_2$TeO$_6$ and Li$_2$Ni$_2$TeO$_6$**

K$_2$Ni$_2$TeO$_6$, a plausible precursor material in the topochemical ion-exchange synthesis of honeycomb layered oxides such as Na$_2$Ni$_2$TeO$_6$, was selected for DFT analyses as it displays the widest interlayer distance amongst the nickel-based tellurates reported so far. As such, its lattice structure was assessed to ascertain its disposition to accommodate Na$^+$. An optimised crystal structure of Na$_2$Ni$_2$TeO$_6$ was subsequently obtained, as illustrated in Figures 2a and 2b. The derived lattice parameters furnished in Table S2 (Supporting Information section) exhibit congruence with the experimental values—affirming the exactitude of the optimised structure. In the crystal model, each
Na atom (in yellow) is coordinated with six oxygen atoms (shown in red) from the

Figure 2. Optimised crystal structural frameworks of Na$_2$Ni$_2$TeO$_6$. Optimised crystal structural framework of Na$_2$Ni$_2$TeO$_6$ (with Na coordinated with oxygen in a prismatic coordination and lying below oxygen atoms (in red)) when viewed along (a) [110] zone axis and (b) [001] zone axis. Sodium atoms are shown in yellow. (c)
Optimised crystal structural framework of Na$_2$Ni$_2$TeO$_6$ (with Na coordinated with oxygen in a prismatic coordination but lying directly below Ni atoms (in dark green)) when viewed along [110] zone axis and (d) when viewed along [001] zone axis. (e) Optimised crystal structural framework of Na$_2$Ni$_2$TeO$_6$ (with Na coordinated with oxygen in an octahedral coordination) when viewed along [110] zone axis and (f) when viewed along [001] zone axis. Ni atoms (dark green) are arranged in a honeycomb configuration around Te atoms (in ochre) via the oxygen atoms to form NiO$_6$ and TeO$_6$ octahedra. Note that the crystal structural framework is slightly deviated from the [110] zone axis, in order to explicitly visualise all the atom coordination within the unit cell.

adjacent transition metal slabs/layers forming NaO$_6$ prismatic polyhedron. On the other hand, each transition metal slab comprises six Ni atoms (shown in grey) surrounding each Te atom (shown in mustard yellow) in a honeycomb fashion (Figure 2b). The Na atoms occupy crystallographic sites below the apical oxygen atoms (connecting two Ni atoms and one Te atom in the honeycomb slab), forming a prismatic configuration. This positioning of Na atoms is attributed to the strong electrostatic repulsion imparted by the Ni$^{2+}$–Ni$^{2+}$ and Te$^{6+}$–Te$^{6+}$ residing in the adjacent metal slabs due to shorter interslab distance, which prevents them from occupying crystallographic sites where the electrostatic effect of Te and Ni atoms is immense. Other stable configurations, wherein Na is situated directly below or above Ni atoms, were also observed (shown in Figures 2c and 2d). Figures 2e and 2f show another stable configuration of Na$_2$Ni$_2$TeO$_6$ with Na atoms coordinated octahedrally with six oxygen atoms. The total energy differences between the structures shown in Figure 2a and Figure 2c was found to be -0.24 eV, implying the structure shown in Figure 2a to be more stable. However, the total energy difference between the structure in Figure 2a and that shown in Figure 2e was found to be subtle (0.07 eV), indicating the possibility to attain a stable Na$_2$Ni$_2$TeO$_6$ structure displaying an octahedral arrangement of Na with oxygen atoms. Given the smaller Shannon-Prewitt ionic radius of Na$^+$ compared to that of K$^+$, the Na$_2$Ni$_2$TeO$_6$ crystal renders a smaller interslab/interlayer distance than that of K$_2$Ni$_2$TeO$_6$. This is further corroborated by the c-axis parameter of Na$_2$Ni$_2$TeO$_6$ (Table S2), which is lower than that of K$_2$Ni$_2$TeO$_6$ (Table S1).

The stability and the structural configuration of the K$_2$Ni$_2$TeO$_6$ crystal lattice with the larger Rb and Cs atoms was further investigated by obtaining optimised crystal structures of Rb$_2$Ni$_2$TeO$_6$ (Figures 3a and 3c) and Cs$_2$Ni$_2$TeO$_6$ (Figures 4a and 4c). The pertinent lattice parameters have been furnished in Table S2. In both structures, Rb and
Cs atoms are coordinated with six oxygen atoms from the adjacent transition metal slabs to form prismatic RbO$_6$ and CsO$_6$ polyhedra (Figures 2c and 2e), in a similar manner as the Na$_2$Ni$_2$TeO$_6$ (see Figure 2a) and K$_2$Ni$_2$TeO$_6$ (Figure 1a). Moreover, two stable configurations were attained whereby Rb and Cs atoms occupy crystallographic sites that have Ni atoms (Figures 3a and 4a) or O atoms (Figures 3c and 4c) lying directly above or below. The total energy differences between the obtained structures shown in

![Figure 3. Optimised crystal structural frameworks of Rb$_2$Ni$_2$TeO$_6$. Optimised crystal structural framework of Rb$_2$Ni$_2$TeO$_6$ (with Rb lying below oxygen atoms (in red)) when viewed along (a) [110] zone axis and (b) [001] zone axis. Rubidium atoms are shown in pink. (c) Optimised crystal structural framework of Rb$_2$Ni$_2$TeO$_6$ (with Rb situated directly below Ni atoms (in dark green)) when viewed along [110] zone axis and (d) when viewed along [001] zone axis. Ni atoms are arranged in a honeycomb configuration around Te atoms (in ochre) via the oxygen atoms to form NiO$_6$ and TeO$_6$ octahedra. Note that the crystal structural framework is slightly deviated from the [110] zone axis, in order to explicitly visualise all the atom coordination within the unit cell.](9)
Figures 3a and 3c for Rb$_2$Ni$_2$TeO$_6$, and Figures 4a and 4c for Cs$_2$Ni$_2$TeO$_6$ were 0.17 eV, and –0.09 eV, respectively. When coordinated with six oxygen atoms, Rb and Cs manifest larger Shannon-Prewitt ionic radii (i.e., 1.52 Å for Rb and 1.67 Å for Cs) than the K atoms (1.38 Å), \(^{[61]}\) which endow the Rb$_2$Ni$_2$TeO$_6$ and Cs$_2$Ni$_2$TeO$_6$ structures with larger interslab/interlayer distances than K$_2$Ni$_2$TeO$_6$ (see c-axis lattice parameters shown in Table S2).

Figure 4. Optimised crystal structural frameworks of Cs$_2$Ni$_2$TeO$_6$. Optimised crystal structural framework of Cs$_2$Ni$_2$TeO$_6$ (with Rb lying below oxygen atoms (in red)) when viewed along (a) [110] zone axis and (b) [001] zone axis. Caesium atoms are shown in cyan. (c) Optimised crystal structural framework of Cs$_2$Ni$_2$TeO$_6$ (with Cs situated directly below Ni atoms (in dark green)) when viewed along [110] zone axis and (d) when viewed along [001] zone axis. Ni atoms are arranged in a honeycomb configuration around Te atoms (in ochre) via the oxygen atoms to form NiO$_6$ and TeO$_6$ octahedra. Note that the crystal structural framework is slightly deviated from the [110] zone axis, in order to explicitly visualise all the atom coordination within the unit cell.
Similar to the Na occupancy previously observed (Figure 2b), configurations were obtained where the Rb and Cs atoms are positioned directly above and below the Ni atoms in a honeycomb configuration when observed along the ab plane (Figure 3b and Figure 4b). This positioning can be ascribed to the larger interslab distances of Rb$_2$Ni$_2$TeO$_6$ and Cs$_2$Ni$_2$TeO$_6$ which offset the electrostatic repulsion forces imparted on the alkali atoms by Ni$^{2+}$—Ni$^{2+}$.

It is worth mentioning that the Rb$_2$Ni$_2$TeO$_6$ and Cs$_2$Ni$_2$TeO$_6$ are not ideally suited for energy storage applications, despite their projected high voltages, due to the high molar mass of Rb and Cs that leads to significantly low capacities. Even so, their wide interlayer distances are poised to engender unique two-dimensional (2D) magnetic interactions, making these compositions auspicious platforms for related investigations. Additionally, if experimentally synthesised, the most stable configurations of Rb$_2$Ni$_2$TeO$_6$ and Cs$_2$Ni$_2$TeO$_6$ are postulated to be antiferromagnetic (Table S2), rendering them promising candidates for exploring emergent 2D antiferromagnetic interactions such as those manifested in the Kitaev model. [28]

Following the assessments on the crystallographic occupation of the large Rb and Cs atoms in the K$_2$Ni$_2$TeO$_6$ crystal lattice, the crystal structure was investigated with Li atoms, which definitively display smaller ionic radii than the K and Na atoms (see the c-axis lattice parameter of Li$_2$Ni$_2$TeO$_6$ in Table S2). The optimised crystal structures of Li$_2$Ni$_2$TeO$_6$, viewed along various zone axes, are illustrated in Figure 5. In the same vein as the previous alkali atoms, Li atoms are coordinated with six oxygen atoms from the adjacent metal slabs to form LiO$_6$ with Li residing in crystallographic sites where Ni atoms (Figures 5a and 5b) or oxygen atoms (Figures 5c and 5d) lie directly below and above. Furthermore, an optimised crystal structure where L atoms are coordinated octahedrally with oxygen atoms was also obtained (Figures 5e and 5f). The total energy difference between the structures shown in Figure 5a and Figure 5c is –0.45 eV, which means that the structure shown in Figure 5a is the more stable. However, the total energy difference between the structures shown in Figure 5a and Figure 5e yields a value of 0.77 eV, indicating that the structure shown in Figure 5e (where Li atoms are coordinated octahedrally to oxygen atoms) to be the most stable. Unlike K, Rb and Cs atoms which manifest prismatic coordination of alkali atoms as stable configurations, the Li atoms engender an octahedral coordination with the oxygen atoms (as also noted in a stable configuration of Na$_2$Ni$_2$TeO$_6$). Due to the small ionic
radius of Li (0.76 Å), the LiO$_6$ octahedra (Figure 5e) exhibits a smaller interslab/interslab

Figure 5. Optimised crystal structural frameworks of Li$_2$Ni$_2$TeO$_6$. Optimised crystal structural framework of Li$_2$Ni$_2$TeO$_6$ (with Li coordinated with oxygen in a prismatic coordination and lying below oxygen atoms (in red)) when viewed along (a) [110] zone
axis and (b) [001] zone axis. Lithium atoms are shown in light green. (c) Optimised crystal structural framework of Li$_2$Ni$_2$TeO$_6$ (with Li coordinated with oxygen in a prismatic coordination but lying directly below Ni atoms (in dark green)) when viewed along [110] zone axis and (d) when viewed along [001] zone axis. (e) Optimised crystal structural framework of Li$_2$Ni$_2$TeO$_6$ (with Li coordinated with oxygen in an octahedral coordination) when viewed along [110] zone axis and (f) when viewed along [001] zone axis. Ni atoms are arranged in a honeycomb configuration around Te atoms (in ochre) via the oxygen atoms to form NiO$_6$ and TeO$_6$ octahedra. Note that the crystal structural framework is slightly deviated from the [110] zone axis, in order to explicitly visualise all the atom coordination within the unit cell.

distance with the most stable bonds among the alkali atoms investigated herein. The reason underlying the stable octahedral coordination of LiO$_6$ in Li$_2$Ni$_2$TeO$_6$ can be ascribed as follows. When Li is coordinated with oxygen atoms, their 2s and 2p orbitals take part in the coordination chemistry. Given that the radial distribution of the orbitals tends to hybridise when in close proximity, the orthogonality of the $p_x$, $p_y$ and $p_z$ orbitals is reflected by the predominant octahedral coordination of LiO$_6$. To accommodate the LiO$_6$ octahedra in the honeycomb structure, the adjacent transition metal slabs shift across the $ab$ plane placing the apical oxygen atoms (connecting two Ni atoms and one Te atom in the honeycomb slab) directly above and below the Li atoms crystallographic sites (Figures 5e and 5f).

The observations made from the optimised Li$_2$Ni$_2$TeO$_6$ structure bear significance in rechargeable battery applications after recent reports deemed the layered material to be a propitious high-voltage cathode material. However, Li$_2$Ni$_2$TeO$_6$ was found to adopt various polytypes wherein different coordination between Li and oxygen emerge, depending on the synthesis technique employed. [20] Due to the comparable Shannon-Prewitt ionic radii of Li (0.76 Å in LiO$_6$ octahedra) and Ni (0.69 Å in NiO$_6$ octahedra), [61] certain preparation techniques for instance, high-temperature solid-state ceramics route compel the two atom species to swap their crystallographic positions (a phenomenon referred to as ‘cationic mixing’), thus creating a disordered crystal framework of Li$_2$Ni$_2$TeO$_6$. The occupancy of Ni atoms in the same plane as Li atoms in the disordered Li$_2$Ni$_2$TeO$_6$ framework, significantly inhibits Li diffusion in the alkali atom plane thereby resulting in poor electrochemical performance. [20] As a strategy to improve the electrochemical performance of Li-based honeycomb layered oxides, an ordered Li$_2$Ni$_2$TeO$_6$ (with varied crystal versatility) can be designed via topochemical
ion-exchange (metathesis reaction), which involves a low-temperature heat-treatment of Na$_2$Ni$_2$TeO$_6$ alongside a molten Li salt such as LiNO$_3$.[20] In this context, the present computational results evince the possibility of synthesising ordered Li$_2$Ni$_2$TeO$_6$ polytypes also from K$_2$Ni$_2$TeO$_6$ via topochemical ion-exchange.

3.2. Crystal structure of H$_2$Ni$_2$TeO$_6$

Layered frameworks that can particularly accommodate hydrogen atoms are relatively limited due to their complex syntheses and their highly unstable structures that hinder experimental observations. In fact, layered oxides encompassing hydrogen atoms sandwiched between transition metal slabs have not been reported to date. Nonetheless, we show here that the experimental limitations can be circumvented via DFT computations which aptly predict the optimised structure of H$_2$Ni$_2$TeO$_6$ shown in Figures 6a and 6b. The optimised lattice parameters have been furnished as Table S3. The H$_2$Ni$_2$TeO$_6$ crystal structure shows the hydrogen atoms to be linearly coordinated with two oxygen atoms from the adjacent transition metal slabs forming dumbbell-like conformations. However, the hydrogen atom was observed to preferentially form a stronger bond (closer coordination) with one of the oxygen atoms creating the hydroxyl (OH$^-$) group.

In contrast with the other honeycomb layered tellurate compositions modelled in this study, the most stable structure of H$_2$Ni$_2$TeO$_6$ displays a ferromagnetic state of transition metal atoms (albeit antiferromagnetic states were also observed), as illustrated in Table S3. The high stability of the ferromagnetic state is attributed to the decrease in super-exchange interactions that typically accompany the formation of OH$^-$ groups. [62,63] Further, the theoretical predictions made in this study pave way for future experimental design and synthesis of H$_2$Ni$_2$TeO$_6$ which is envisaged to find niche utility in the realms of solid-state hydrogen storage and catalysis.
Figure 6. Optimised crystal structural frameworks of H$_2$Ni$_2$TeO$_6$. Optimised crystal structural framework of H$_2$Ni$_2$TeO$_6$ when viewed along (a) [110] zone axis and (b) [001] zone axis. Hydrogen atoms are shown in rose pink. Ni atoms (dark green) are arranged in a honeycomb configuration around Te atoms (in ochre) via the oxygen atoms (in red) to form NiO$_6$ and TeO$_6$ octahedra. Note that the crystal structural framework is slightly deviated from the [110] zone axis, in order to explicitly visualise all the atom coordination within the unit cell.

3.3. Crystal structures of Ag$_2$Ni$_2$TeO$_6$, Au$_2$Ni$_2$TeO$_6$ and Cu$_2$Ni$_2$TeO$_6$

The crystal versatility of honeycomb layered oxides, evidenced by their ability to accommodate a variety of atom species within the lattice structures, is a critical distinguishing property of this class of layered oxides. This diversity has been attested by experimental reports on honeycomb layered oxides featuring coinage-metal atoms (such as Ag and Cu) between the honeycomb slabs.\cite{30,64-67} Replacing the alkali atoms with coinage-metal atoms is posited to ameliorate the functionalities of these materials, thereby expanding their range of utility in applications such as catalysis, magnetism, and optics. Therefore, for insight into the stability of these emergent structures, the K$_2$Ni$_2$TeO$_6$ crystal lattice was investigated with Cu, Ag, and Au coinage-metal atoms. Group 11 elements (which consist of Cu, Ag, Au, amongst others) are s-orbital systems with fully closed d-valence electrons. However, these elements are also transition metals and are thus expected to undergo ionisation, leading to the formation of compounds manifesting sd hybridisation.

Figures 7a and 7b show the optimised crystal structure of Cu$_2$Ni$_2$TeO$_6$ viewed along various zone axes. The optimised lattice parameters for Cu$_2$Ni$_2$TeO$_6$, along with those of Ag$_2$Ni$_2$TeO$_6$, and Au$_2$Ni$_2$TeO$_6$ are provided in Table S2. The DFT model shows Cu
Figure 7. Optimised crystal structural frameworks of $A_2Ni_2TeO_6$ ($A = Cu, Ag$ and $Au$). Optimised crystal structural framework of $Cu_2Ni_2TeO_6$ when viewed along (a) [110] zone axis and (b) [001] zone axis. Copper atoms are shown in blue. (c) Optimised crystal structural framework of $Ag_2Ni_2TeO_6$ when viewed along the [110] zone axis and (d) when viewed along [001] zone axis. Silver atoms are shown in grey. (e) Optimised crystal structural framework of $Au_2Ni_2TeO_6$ when viewed along the [110] zone axis and
atoms to be linearly coordinated with two oxygen atoms, forming dumbbell-like conformations. Similar coordinations have also been experimentally observed in Cu-containing Delafossites such as Cu$_3$Co$_2$SbO$_6$ and Cu$_3$Ni$_2$SbO$_6$,\cite{65,66} which signals the possibility of attaining tellurate composition analogues via experimental routes. Likewise, the Ag$_2$Ni$_2$TeO$_6$ optimised crystal structure (Figures 7c and 7d) exhibited dumbbell-like coordinations resembling those in the Cu$_2$Ni$_2$TeO$_6$ structure — indicating their structural comparability. The coordination between the Ag and oxygen atoms predicted here has also been reported by experimental studies on other silver-based honeycomb layered oxides such as the antimonates (Ag$_3$M$_2$SbO$_6$ (M = Ni, Co, Zn))\cite{67} and bismuthates (Ag$_3$Ni$_2$BiO$_6$).\cite{64} Other metastable configurations of Cu$_2$Ni$_2$TeO$_6$ and Ag$_2$Ni$_2$TeO$_6$ that show different coordination have been predicted in the present study (Figures S1 and S2), wherein Ag is octahedrally coordinated to six oxygen atoms in a prismatic fashion (akin to the coordination exemplified in AgRuO$_3$\cite{68}), whilst Cu is coordinated to four oxygen atoms forming CuO$_4$ plaquettes (as those observed in cuprates such as Li$_2$CuO$_2$\cite{69,70}). Unlike Ag and Au, the tendency for Cu atoms to also coordinate with four oxygen atoms (as predicted by DFT) can be ascribed to a stronger $d$-orbital hybridisation of Cu. Although these configurations are predicted to be metastable by the present DFT study, high-pressure synthesis can be a route to access honeycomb layered oxides with such atom coordination as pressure can induce a change in the bonding coordination of compounds.\cite{11}

The predominance of linear coordination amongst coinage-metal atoms with oxygen atoms is attributed to the hybridised $d_{z^2}$ orbitals of the group 11 monovalent cations (Cu$^+$, Ag$^+$, Au$^+$, etc.). This inclination towards dumbbell-like linear coordinations instead of prismatic coordinations engenders larger interlayer distance in Ag$_2$Ni$_2$TeO$_6$ than its Na analogue: in congruence with previous experimental reports on Ag-based honeycomb layered oxides, which further validate the optimised Ag$_2$Ni$_2$TeO$_6$ structure.\cite{49,52} Considering that the detailed experimental synthesis and structural characterisation of Ag$_2$Ni$_2$TeO$_6$ has not yet been reported to date,\cite{31} the results of this study will be instrumental in predicting emergent features of this material that we are currently
pursuing. However, it is worth noting that given the unique chemistry of silver, we can anticipate a diverse assortment of atomic coordinations in Ag$_2$Ni$_2$TeO$_6$, not necessarily predicted by the DFT calculations in the present work.

Nonetheless, the ability to predict novel material compositions—such as H$_2$Ni$_2$TeO$_6$ and Ag$_2$Ni$_2$TeO$_6$—that may go beyond the boundaries of present experimental validation earmarks the expediency of DFT computation methods in quest for novel honeycomb layered oxides. Amongst the coinage-metal based materials investigated, Au-related compounds are far less investigated than the other group 11 element species such as Cu and Ag. In fact, no Au-based layered oxides have been reported to date. Au-based compounds have been found to manifest high activity and selectivity for many reactions—features that are particularly attractive in the fields of catalysis and optics. As such, the stability of Au atoms in the K$_2$Ni$_2$TeO$_6$ lattice framework was investigated, as shown in Figures 7e and 7f. Akin to Cu$_2$Ni$_2$TeO$_6$ and Ag$_2$Ni$_2$TeO$_6$, Au$_2$Ni$_2$TeO$_6$ exhibits a linear coordination of Au atoms with two oxygen atoms in a dumbbell-like conformation. As expected, the Au atoms render a large interlayer distance in the linearly coordinated structure. Given the untapped state of this research space, the Au-based honeycomb layered oxide presented here promises to rekindle interest in the realm of noble gold chemistry since the synthesis and evaluation of Au$_2$Ni$_2$TeO$_6$ herald major advancements in the exploration of the piquant catalytic and optical properties of small gold clusters, mono-atomically dispersed gold, and monovalent gold complexes.

### 3.4. Interlayer distances of $A_2$Ni$_2$TeO$_6$ ($A =$ H, Li, Na, Rb, Cs, Ag, Au and Cu)

As shown in Figure 8, the $A_2$Ni$_2$TeO$_6$ ($A =$ H, Li, Na, Rb, Cs, Ag, Au, and Cu) honeycomb tellurates presented in this study exhibit distinct structures with varying interslab/interlayer distances depending on the species of $A^+$ cations employed. We note here that the straight-line correlation between the interslab distance and the Shannon-Prewitt ionic radius size of the resident $A^+$ cations is only valid for the alkali cations, i.e., Li, Na, K, Rb, and Cs, although the coordination polyhedra formed by Li atoms and oxygen is octahedral, differing from the rest that are prismatic. Generally, a small ionic radius favours octahedral and/or dumbbell/linear coordination with a smaller or intermediate interlayer distance whereas a larger radius predominantly favours a prismatic coordination with the largest interlayer distances. In particular, with regards to coinage-metal atoms (viz., Cu, Ag, and Au), the linear coordination between $A^+$ cations
and the oxygen atoms engenders intermediate interslab distances even with smaller $A^+$ cations. For instance, even though the Shannon-Prewitt ionic radius of monovalent Cu is comparable to that of Li, the interslab distance in the Cu$_2$Ni$_2$TeO$_6$ crystal structure is still larger than that of Li$_2$Ni$_2$TeO$_6$.

**Figure 8.** Interslab/interlayer distances rendered by the $A_2$Ni$_2$TeO$_6$ ($A = \text{Li, Na, Cu, Ag, K, Rb and Cs}$) compositions. The changes in the interslab distances in the $A_2$Ni$_2$TeO$_6$ compositions are derived using first-principles density functional theory calculations. The Shannon$^{[58]}$ radii of the monovalent $A^+$ cations is shown in the horizontal scale. Note that the Shannon ionic radius value of Au when coordinated to two oxygen atoms is not available; thus has not been shown in the plots along with that of H.

The interslab distances of the honeycomb layered tellurates presented in this study significantly influence emergent functionalities such as solid-state cationic diffusion.
In fact, a recent study highlighted the correlation between the coordination structure, the size of the $A^+$ alkali cations, and the resulting ionic conductivity of honeycomb layered oxides. For instance, the small ionic radius of Li$^+$ begets strongly bonded octahedral structures with smaller inter-layer distances that result in limited ionic conductivity. However, the larger ionic radius of K$^+$ yields weakly-bonded prismatic structures with larger inter-layer distances and enhanced ionic conductivities.

On the other hand, the linear coordination between coinage-metal cations such as Ag$^+$ and oxygen atoms precipitates relatively weaker interlayer bonds and consequently intermediate inter-layer distances in the pertinent structures. In principle, the weaker interlayer bonds (and intermediate and large interlayer distances) in linear or prismatic layered structures are expected to create more open voids within the transition metal layers/slabs allowing for facile two-dimensional diffusion of alkali or coinage-metal atoms within the slabs. In this vein, pursuing the design of new honeycomb compositions predicted in this study, such as Rb$_2$Ni$_2$TeO$_6$, Cs$_2$Ni$_2$TeO$_6$, and Ag$_2$Ni$_2$TeO$_6$, can therefore be a worthwhile undertaking in fields such as materials science geared towards various functionalities such as magnetism, catalysis and energy storage solutions.

Nota bene, honeycomb layered oxides display a multitude of slab stacking structures typically characterised by the Hagenmuller-Delmas notation. In this study, the K$_2$Ni$_2$TeO$_6$ used as the initial model structure displays a prismatic coordination of K atoms with two repetitive honeycomb layers (comprising NiO$_6$ and TeO$_6$ octahedra) for each unit cell (P2-Type in Hagenmuller-Delmas notation). As such, the honeycomb layered tellurate compositions predicted in this study also show P2-Type structural configurations. This suggests that the new honeycomb layered oxides can be experimentally reproduced via topotactic ion-exchange. Previous reports have also shown layered oxide structures manifest a plenitude of stacking faults and other topological defects that bring forth fascinating functionalities. Therefore, we should expect the materials predicted herein to exhibit various stacking faults and other topological defects accompanied by unique properties. On a separate note, the coordination chemistry of coinage-metal atoms such as Ag can be expected to show other variegated coordinations besides the typical linear coordination envisioned in this study. This is because some coinage-metal atoms, such as Ag in Ag$_2$NiO$_2$, have been known to exhibit unprecedented sub-valency states (i.e., valency states between +1 and 0) that lead to idiosyncratic structural and bonding properties when sandwiched
between transition metal layers. Therefore, even though first-principles predictions vaticinate the design and prospects of new honeycomb tellurate compositions such as $\text{Ag}_2\text{Ni}_2\text{TeO}_6$ and $\text{Au}_2\text{Ni}_2\text{TeO}_6$, experimental inquests are still vital to advancing this class of materials.

3. CONCLUSION

This study aims to extend the frontier of nickel-based tellurates and diversify their functionalities by employing density functional theory (DFT) to explore the structural configuration of new honeycomb layered tellurates entailing previously unreported cation species such as large alkali atoms (in $\text{Rb}_2\text{Ni}_2\text{TeO}_6$ and $\text{Cs}_2\text{Ni}_2\text{TeO}_6$), coinage-metal atoms (in $\text{Cu}_2\text{Ni}_2\text{TeO}_6$, $\text{Ag}_2\text{Ni}_2\text{TeO}_6$, and $\text{Au}_2\text{Ni}_2\text{TeO}_6$) and hydrogen (in $\text{H}_2\text{Ni}_2\text{TeO}_6$). The theoretical simulations, employing $\text{K}_2\text{Ni}_2\text{TeO}_6$ as the initial structural model, reveal an underlying correlation between the distinct coordination structures engendered by the different species (in this case: large alkali atoms and coinage metal atoms) and their resultant interslab / interlayer distances. The interlayer distance in honeycomb layered tellurates comprising large alkali atoms (Rb and Cs) is seen to be contingent on the ionic radius of the atom, which forms a prismatic coordination with the oxygen atoms from the adjacent honeycomb slabs. On the other hand, coinage-metal atoms (Cu, Ag, and Au) show a proclivity towards linear coordination with two oxygen atoms rendering intermediate interlayer distances independent of their ionic radii. Further, the hydrogen atom is seen to render a linear coordination with two oxygen atoms whilst manifesting a preferential coordination with one of the oxygen atoms that results in the formation of hydroxyl groups. The new honeycomb layered compositions presented herein betoken promising functionalities such as two-dimensional magnetism, optics, catalysis for utility in fields ranging from solid-state hydrogen storage to noble gold chemistry. However, even with the excellent prospects envisioned in this study, experimental techniques remain a requisite in the design and exploration of the new materials due to the possibility of disparate emergent properties such as the variegated bonding properties of Ag atoms. Nonetheless, this work augments the diversity of honeycomb layered tellurates whilst paving the way for future explorations and the rational design of new-fangled honeycomb layered oxides with assorted physicochemical properties.
SUPPLEMENTARY TABLES AND FIGURES

Table S1. Optimised lattice parameters of K$_2$Ni$_2$TeO$_6$. The magnetic atoms (Ni) were assessed in two configurations: ferromagnetic (FM) and antiferromagnetic (AFM) states. The experimentally obtained lattice parameters are shown for a comparison.

| Compound      | State | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\alpha$ (°) | $\beta$ (°) | $\gamma$ (°) |
|---------------|-------|---------|---------|---------|---------------|-------------|--------------|
| K$_2$Ni$_2$TeO$_6$ | AFM   | 5.28176 | 5.28176 | 12.37282 | 90.0000       | 90.0000     | 120.0558     |
|               | FM    | 5.32141 | 5.32141 | 12.49672 | 90.0000       | 90.0000     | 120.1055     |
| Experimental value |       | 5.26060 | 5.26060 | 12.46090 | 90.0000       | 90.0000     | 120.0000     |

Table S2. Optimised lattice parameters for various configurations of A$_2$Ni$_2$TeO$_6$ (A = Li, Na, Rb, Cs, Cu, Ag, and Au). The magnetic atoms (Ni) were assessed in antiferromagnetic (AFM) states.

| Compound      | Structure | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\alpha$ (°) | $\beta$ (°) | $\gamma$ (°) |
|---------------|-----------|---------|---------|---------|---------------|-------------|--------------|
| Na$_2$Ni$_2$TeO$_6$ | Fig. 2a   | 5.21403 | 5.21403 | 10.83093 | 90.3336       | 89.6702     | 129.3777     |
|               | Fig. 2c   | 5.17381 | 5.17454 | 10.91146 | 90.0022       | 89.9080     | 119.9326     |
|               | Fig. 2e   | 5.17516 | 5.17554 | 10.71164 | 90.8184       | 89.1720     | 119.4091     |
| Rb$_2$Ni$_2$TeO$_6$ | Fig. 3a   | 5.33225 | 5.33225 | 12.94207 | 89.9998       | 89.9998     | 120.0310     |
|               | Fig. 3c   | 5.31038 | 5.31032 | 12.87370 | 90.0074       | 89.9047     | 120.0477     |
| Cs$_2$Ni$_2$TeO$_6$ | Fig. 4a   | 5.42700 | 5.42700 | 13.45493 | 90.0001       | 90.0001     | 119.9957     |
|               | Fig. 4c   | 5.40044 | 5.40044 | 13.33245 | 90.0071       | 89.9020     | 119.9932     |
| Li$_2$Ni$_2$TeO$_6$ | Fig. 5a   | 5.16340 | 5.16355 | 10.05834 | 90.1412       | 89.8514     | 120.5663     |
|               | Fig. 5c   | 5.11048 | 5.11045 | 10.10848 | 90.0109       | 89.9975     | 119.9924     |
|               | Fig. 5e   | 5.13412 | 5.13638 | 9.65122  | 90.0785       | 89.9220     | 119.5745     |
| Cu$_2$Ni$_2$TeO$_6$ | Fig. 6a   | 5.24766 | 5.24777 | 11.55000 | 90.0468       | 89.9602     | 119.8259     |
| Ag$_2$Ni$_2$TeO$_6$ | Fig. 6c   | 5.23066 | 5.23123 | 12.47119 | 90.0076       | 89.9901     | 119.8416     |
| Au$_2$Ni$_2$TeO$_6$ | Fig. 6e   | 5.25312 | 5.25337 | 12.31434 | 90.0482       | 89.9593     | 119.6811     |
Table S3. Optimised lattice parameters for various configurations of H$_2$Ni$_2$TeO$_6$.

The magnetic atoms (Ni) were assessed in two configurations: ferromagnetic (FM) and antiferromagnetic (AFM) states. The lattice parameters for the most stable configuration are highlighted in grey.

| Compound  | State | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\alpha$ | $\beta$ | $\gamma$ |
|-----------|-------|---------|---------|---------|---------|---------|---------|
| H$_2$Ni$_2$TeO$_6$ | AFM-1  | 5.26335 | 5.26356 | 9.18956 | 95.7798 | 84.2228 | 119.7717 |
|           | AFM-2  | 5.26488 | 5.26482 | 9.18296 | 96.0979 | 83.9147 | 119.7702 |
|           | AFM-3  | 5.26714 | 5.26683 | 9.18887 | 95.9650 | 84.0158 | 119.7788 |
|           | FM-1   | 5.26230 | 5.26238 | 9.28724 | 90.0835 | 89.9207 | 120.4790 |
|           | FM-2   | 5.28817 | 5.28811 | 9.23936 | 90.4659 | 89.5393 | 120.5527 |
|           | FM-3   | 5.29236 | 5.29344 | 9.28540 | 90.3051 | 89.7239 | 120.5348 |

Figure S1. Crystal structural frameworks of Cu$_2$Ni$_2$TeO$_6$ with Cu atoms (in blue) coordinated to four oxygen atoms. Metastable crystal structural framework of Cu$_2$Ni$_2$TeO$_6$ with Cu in a planar coordination with oxygen atoms when viewed along (a) [110] zone axis and (b) [001] zone axis. Ni atoms (dark green) are arranged in a honeycomb configuration around Te atoms (in ochre) via the oxygen atoms (in red) to form NiO$_6$ and TeO$_6$ octahedra. Note that the crystal structural framework is slightly deviated from the [110] zone axis, in order to explicitly visualise all the atom coordination within the unit cell.
Figure S2. Crystal structural frameworks of Ag$_2$Ni$_2$TeO$_6$ with Ag atoms (in grey) coordinated to six oxygen atoms. Metastable crystal structural frameworks of Ag$_2$Ni$_2$TeO$_6$ with Ag in prismatic coordination with oxygen atoms when viewed along [110] zone axis ((a) and (c)) and [001] zone axis ((b) and (d)). Ni atoms (dark green) are arranged in a honeycomb configuration around Te atoms (in ochre) via the oxygen atoms (in red) to form NiO$_6$ and TeO$_6$ octahedra. Note that the crystal structural framework is slightly deviated from the [110] zone axis, in order to explicitly visualise all the atom coordination within the unit cell.

**Data availability statement**
The datasets (raw/processed data) required to reproduce the results and computer codes are available upon request from the authors.
**CRediT authorship contribution statement**

**Kohei Tada**: Methodology, Investigation, Formal analysis, Data curation, Validation, Writing – original draft. **Godwill Mbiti Kanyolo**: Methodology, Investigation, Validation, Writing - review & editing. **Titus Masese**: Methodology, Investigation, Validation, Writing - review & editing.

**Declaration of Competing Interests**

The authors declare that they have no known competing financial interests or personal relationships that could have unethically impacted the rigour and scientific methods employed in this work.

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**Supplementary material**

Computational methodology associated with this article will also be provided in an online version, at the production stage.

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