Expanding Family of Litharge-Derived Sulfate Minerals and Synthetic Compounds: Preparation and Crystal Structures of [Bi$_2$CuO$_3$]SO$_4$ and [Ln$_2$O$_2$]SO$_4$ ($Ln =$ Dy and Ho)

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Abstract: During the last decades, layered structures have attracted particular and increasing interest due to the multitude of outstanding properties exhibited by their representatives. Particularly common among their archetypes, with a significant number of mineral and synthetic species structural derivatives, is that of litharge. In the current paper, we report the structural studies of two later rare-earth oxysulfates, [Ln$_2$O$_2$]SO$_4$ ($Ln =$ Dy, Ho), which belong indeed to the grandreefite family, and a novel compound [Bi$_2$CuO$_3$]SO$_4$, which belongs to a new structure type and demonstrates the second example of Cu$^{2+}$ incorporation into litharge-type slabs. Crystals of [Bi$_2$CuO$_3$]SO$_4$ were obtained under high-pressure/high-temperature (HP/HT) conditions, whereas polycrystalline samples of [Ln$_2$O$_2$]SO$_4$ ($Ln =$ Dy, Ho) compounds were prepared via an exchange solid-state reaction. The crystal structure of [Bi$_2$CuO$_3$]SO$_4$ is based on alternation of continuous [Bi$_2$CuO$_3$] layers of edge-sharing OBi$_2$Cu$_2$ and OBi$_2$Cu tetrahedra and sheets of sulfate groups. Cu$^{2+}$ cations are in cis position in O5Bi$_2$Cu$_2$ and O6Bi$_2$Cu$_2$ oxocentered tetrahedra in litharge slab. The crystal structure of [Ln$_2$O$_2$]SO$_4$ ($Ln =$ Dy, Ho) is completely analogous to those of grandreefite and oxysulfates of La, Sm, Eu, and Bi.

Keywords: sulfates; litharge; layered structures; copper; lanthanides; crystal structure; synthesis

1. Introduction

Litharge-derived architectures are widely represented by both mineral and synthetic species exhibiting exceptional structural and chemical diversity, as well as a variety of properties. While the numerical majority of representatives belongs to the compounds of f-metals, its structural diversity is provided mostly by just two neighbor elements in the Periodic system, lead and bismuth. The easy formation of layered structures is commonly attributed to the “lone-pair” stereochemical activity of Pb$^{2+}$ and Bi$^{3+}$, which favors their “one-sided” coordination. The majority of both synthetic and mineral contributions come from the chemistry of oxides [1–3] and oxyhalides [4–18], most commonly the representatives of the so-called Sillén family. The latter generally correspond to ordered alternations of litharge-derived slabs and single or double sheets of monoatomic anions of Group 15–17 elements.
For the majority of these architectures, interlayer charge balance requires partial aliovalent substitution for Pb$^{2+}$ and Bi$^{3+}$. Overall, the initially neutral [PbO] litharge slabs are essentially more tolerable to the chemical nature of such substituents compared to charged [BiO]$^+$. For instance, lead-based litharge slabs can accommodate various transition metal-based species (vanadate, chromate, molybdate, tungstate, etc.) while oxides and oxyhalides of bismuth are totally resistant to such substitution (Cd$^{2+}$ (4d$^{10}$), as a post-transition element [19], is not considered).

Structurally related architectures occur when the interlayer gallery hosts various molecular anions (linear triatomic [20,21], trigonal [22–26], or tetrahedral [27–38] (Figure 1a–h). There are three possible orientations of tetrahedral anions between the litharge slabs (Figure 1d–f) two of which are represented in nature by the mineral grandreefite [Pb$_2$F$_2$]SO$_4$ [27] and a slag phase [Ba$_2$F$_2$]S$_2$O$_3$ [28]. Synthetic analogs of [Ba$_2$F$_2$]S$_2$O$_3$ were found among [Ln$_2$O$_2$]CrO$_4$ oxychromates (Ln = Pr–Tb [33]). Synthetic analogs of the grandreefite structure are observed also among selenates ([Pb$_2$F$_2$]SeO$_4$ [34] and [Ln$_2$O$_2$]SeO$_4$, Ln = La, Pr, Nd [35]) and chromates ([La$_2$O$_2$]CrO$_4$ [32]). The same structure was also established for [Bi$_2$O$_2$]SO$_4$ [36] and some rare-earth oxysulfates [Ln$_2$O$_2$]SO$_4$ (La [29], Sm [30] and Eu [31]). In the meantime, a different atomic arrangement was suggested for [Nd$_2$O$_2$]SO$_4$ [37]. The crystal structures of other reported [M$_2$O$_2$]SO$_4$ oxysulfates (M = Pr, Gd–Lu, Y [39], Am–Cf [40,41]) are unknown to date. Initially, the XRD patterns of all Ln and An oxysulfates were indexed in orthorhombic symmetry (I-centered, a ~ b ~ 4 Å, c ~ 13Å [39–41]) with similar patterns suggesting that all the compounds are isostructural. As shown before, just a handful of these were re-investigated, the later rare-earth compounds remaining mostly unaddressed.

![Figure 1. Sillén-type structural architectures in minerals and synthetic compounds. General projection (a) and interlayer (b) in the crystal structure of [Bi$_2$O$_2$]Te [42] and its derivatives hosting molecular anions in the interlayer galleries: [Bi$_2$O$_2$]CN$_2$ [20] (c,d), kettnerite [BiO][CaF][CO$_3$] [26] (e), grandreefite [Pb$_2$F$_2$]SO$_4$ [27] (f), slag phase [Ba$_2$F$_2$]S$_2$O$_3$ [28] (g), and [La$_2$O$_2$]MoO$_4$ [43] (h).](image-url)
The crystal chemistry of bismuth oxy sulfates is more diverse and contains, besides the grandreefite analogue, three relatively complex litharge derivatives incorporating transition metal cations: \([\text{Bi}_6\text{O}_4\text{Co}_2\text{SO}_4]\) with krönikite-type chain anions, \([\text{Bi}_2\text{Co}_3\text{SO}_4]\) and \([\text{Bi}_{5.27}\text{Cu}_{1.6}\text{O}_4]\)[SO_4], recently re-determined by Lü et al. [44]. The latter are of particular interest representing yet only two known examples of transition metal cations (\(\text{Co}^{2+}\) and \(\text{Cu}^{2+}\)) incorporated into the bismuth-oxide litharge layers. Given that the same layers are resistant to such incorporation in oxyhalides [45], two questions arise: what is the role of tetrahedral (sulfate) anions which makes transition metal substitution possible and if other representatives can be prepared. In the current paper, we report the structural studies of two later rare-earth oxy sulfates, \([\text{Ln}_2\text{O}_2\text{SO}_4]\) (\(\text{Ln} = \text{Dy, Ho}\)), which belong indeed to the grandreefite family, and a novel compound \([\text{Bi}_2\text{Cu}_3\text{SO}_4]\), which belongs to a new structure type and demonstrates the second example of \(\text{Cu}^{2+}\) incorporation into litharge-type slabs.

2. Materials and Methods

2.1. Synthesis

Crystals (Figure 2a) of novel \([\text{Bi}_2\text{Cu}_3\text{SO}_4]\) were obtained under high-pressure/high-temperature (HP/HT) conditions. The synthesis was performed using the piston cylinder module of a Voggenreiter LP 1000-540/50 system installed at the Institute of Geosciences, University of Kiel, Kiel, Germany. \(\text{CuSO}_4\) (Aldrich ≥99.0%, 0.119 g) and \(\text{BiOCl}\) (Aldrich ≥99.0%, 0.260 g) were weighed, mixed, and finely ground. The mixture was placed into a platinum capsule (outer diameter = 3 mm, wall thickness = 0.2 mm, length = 12 mm). The capsule was sealed on both sides and placed into the center of a 1/2-inch piston cylinder tâlc–Pyrex assembly. The pressure increased for 5 min at a rate of 0.2 GPa/min, until a working pressure of 1 GPa was reached, whereupon the temperature program was started at a rate of 60 °C/min up to the operating temperature of 600 °C, which was maintained at the set pressure for 6 h. The cooling time was 10 h (cooling rate ≈ 60 °C/h). Simultaneously with cooling, the pressure was released at a rate of 0.1 GPa/h. After room temperature had been reached, the experiment was decompressed during 20 min. The capsule was extracted from the high-pressure assembly and cut for further investigations. The product consisted of grass-green transparent \([\text{Bi}_2\text{Cu}_3\text{SO}_4]\) crystals in association with unreacted \(\text{BiOCl}\).

![Figure 2](image)

**Figure 2.** Green crystals of \([\text{Bi}_2\text{Cu}_3\text{SO}_4]\) (field of view 0.5 mm) (a). Coordination environments of \(\text{Bi}^{3+}, \text{Cu}^{2+},\) and \(\text{S}^{6+}\) cations in the structure of \([\text{Bi}_2\text{Cu}_3\text{SO}_4]\) (b). Weaker Bi-O bonds are shown by thin lines. Ellipsoids are drawn at 50% probability level.
Polycrystalline samples of $[\text{Ln}_2\text{O}_2\text{SO}_4]$ ($\text{Ln} = \text{Dy, Ho}$) compounds were prepared via an exchange reaction similar to $[\text{Ln}_2\text{O}_2\text{CrO}_4]$ [32,33] and $[\text{Ln}_2\text{O}_2\text{SeO}_4]$ [35]. Rare-earth oxychlorides, $\text{LnOCl}$, prepared by thermal hydrolysis of $\text{LnCl}_3\cdot6\text{H}_2\text{O}$, were mixed with potassium sulfate (pre-dried at 140 °C for 6 h) in 2:1.1 ratio, thoroughly ground and placed in silica-jacketed alumina crucibles. The silica tubes were vacuum-sealed and annealed at 825 °C for 48 h (heating rate 50 °C/h, cooling rate 5 °C/h to 650 °C, after which the furnace was switched off. The products were washed several times with distilled water to remove the KCl by-product and excess K$_2$SO$_4$, and air dried.

2.2. Single-Crystal XRD Studies

A single crystal of $[\text{Bi}_2\text{CuO}_3\text{SO}_4]$ was attached to glass fiber using an epoxy resin and mounted on a Bruker SMART APEX II DUO diffractometer (Bruker AXS, Karlsruhe, Germany) equipped with a micro-focus X-ray tube utilizing MoKα radiation. The experimental data set was collected at 150 K. Unit-cell parameters were calculated using least-squares fits. Structure factors were derived using APEX 2 after introducing the required corrections [46]; details on data collection are in Table 1. The structure was solved using direct methods and refined in SHELXL [47]. The data are deposited in CCDC under Entry No. 2021664.

Table 1. Crystallographic data and refinement parameters for $[\text{Bi}_2\text{CuO}_3\text{SO}_4]$ and $[\text{Ln}_2\text{O}_2\text{SO}_4]$ ($\text{Ln} = \text{Dy, Ho}$).

|                   | $[\text{Bi}_2\text{CuO}_3\text{SO}_4]$ | $[\text{Dy}_2\text{O}_2\text{SO}_4]$ | $[\text{Ho}_2\text{O}_2\text{SO}_4]$ |
|-------------------|---------------------------------------|-------------------------------------|-------------------------------------|
| **Space Group**   | C2/c                                  | C2/c                                | C2/c                                |
| **a (Å)**         | 20.0283(7)                            | 13.3682(2)                          | 13.4172(1)                          |
| **b (Å)**         | 5.3970(2)                             | 4.14721(5)                          | 4.15878(4)                          |
| **c (Å)**         | 14.1413(5)                            | 8.0204(1)                           | 8.05626(8)                          |
| **β (°)**         | 128.4450(10)                          | 107.8070(8)                         | 107.6201(8)                         |
| **V (Å³)**        | 1197.19(8)                            | 423.35(1)                           | 428.44(1)                           |
| **$D_x$**         | 6.941                                 | 7.18                                | 7.024                               |
| **2θ range (°).**| 2.60–38.50                            | 10–120                              | 10–120                              |
| **$R_{int}$**     | 0.030                                 | 0.029                               | 0.015                               |
| **$R_{F}$**       | 0.023                                 | 0.043                               | 0.014                               |
| **Gof**           | 1.040                                 | 0.029                               | 0.035                               |
| **CCDC**          | 2021664                               | 2021867                             | 2021874                             |

2.3. Powder XRD Studies

High-resolution data sets were collected for $[\text{Ln}_2\text{O}_2\text{SO}_4]$ ($\text{Ln} = \text{Dy, Ho}$) on a PANalytical–X’Pert diffractometer (Malvern Instruments, Malvern, UK) utilizing CuKα1,2 radiations. The refinement was done using the JANA2006 software (version 2014.11–0) [48]. As in the case of isostructural $[\text{Pb}_2\text{F}_2\text{SeO}_4]$ [34] and $\text{Bi}_2\text{O}_2\text{SO}_4$ [36], indexing the powder patterns was not straightforward as two sets of Miller indices are possible for the strongest reflections yielding two alternative unit cells which led to close residuals upon LeBail full-pattern decomposition. The correct ones, listed in Table 1, were chosen based on results of Rietveld analysis wherein the derived atomic arrangements (with the structure of $[\text{Eu}_2\text{O}_2\text{SO}_4]$ [31] taken as the initial model) were chemically sensible. Due to weak scattering from the oxygen atoms and low sensitivity of the residuals to their coordinates, a mild constraint was imposed on the S–O distances in the $\text{SO}_4^{2–}$ anion. Final Rietveld refinement plots for $[\text{Dy}_2\text{O}_2\text{SO}_4]$ and $[\text{Ho}_2\text{O}_2\text{SO}_4]$ are given in the Supplementary Materials. The data are deposited in CCDC under entries No. 2021867 ($[\text{Dy}_2\text{O}_2\text{SO}_4]$) and 2021874 ($[\text{Ho}_2\text{O}_2\text{SO}_4]$).
3. Results

3.1. Crystal Structure of [Bi$_2$CuO$_3$]SO$_4$

The structure of [Bi$_2$CuO$_3$]SO$_4$ contains two symmetrically unique Bi positions and one Cu position. The Bi1 and Bi2 sites are coordinated by nine and ten O atoms each, respectively (Figure 2b). The general feature of the Bi$^{3+}$ coordination in [Bi$_2$CuO$_3$]SO$_4$ is the presence of four short and very strong Bi-O bonds (2.23–2.37 Å) located in one coordination hemisphere of the Bi$^{3+}$ cations. In the opposite hemisphere, the Bi$^{3+}$ cations form from five to six longer Bi$^{3+}$–O bonds. The distortion of the Bi$^{3+}$ coordination polyhedra is due to the stereoactivity of $s^2$ “lone-pairs”. However, the distortion of bismuth coordination environments is not as strong as usually observed for Pb$^{2+}$ in litharge-derived structures.

The Cu site is coordinated by four O atoms to form a distorted CuO$_4$ square complemented by two apical O$^{2-}$ anions. As a result, a distorted [CuO$_4$O$_2$] octahedron is formed. [CuO$_4$O$_2$] octahedra group in pairs via common edge to form Cu$_2$O$_6$ slabs shown in Figure 2. Cu–Cu distance is 2.79 Å. Unfortunately, we were unable to measure magnetic properties of [Bi$_2$CuO$_3$]SO$_4$ due to the insufficient amount of pure material.

One symmetrically independent S$^{6+}$ cation forms rather symmetrical SO$_4$ tetrahedra. The individual S–O distances are in the range of 1.470(4)–1.491(4) Å, which is in good agreement for well-refined sulfate structures [49].

From the viewpoint of the bond-valence theory the O$_2$-Bi and O$_4$-Cu bonds (O$_4$—additional oxygen atoms not bonded to S) are the shortest and therefore the strongest in the structures of [Bi$_2$CuO$_3$]SO$_4$, which makes it reasonable to consider the Bi-Cu-O substructure consisting of Bi$_2$Cu$_2$ and OBi$_2$Cu tetrahedra interacting with SO$_4$ tetrahedra through relatively weaker Bi-O$_4$ and Cu-O$_4$ bonds. The topology of this oxo-centered [Bi$_2$CuO$_3$]SO$_4$ structural unit (Figure 3a) is two-dimensional and obviously related to the [Bi$_2$O$_2$]$^{2+}$ layer typical for compounds structurally related to litharge.

The crystal structure of [Bi$_2$CuO$_3$]SO$_4$ (Figure 3d) is based on alternation of continuous [Bi$_2$CuO$_3$]$^{2+}$ layers of edge-sharing OBi$_2$Cu$_2$ and OBi$_2$Cu tetrahedra and sheets of sulfate groups. Note that [Bi$_2$CuO$_3$]SO$_4$ belongs to a new structure type. The structure of recently re-investigated [Bi$_2$CoO$_3$]SO$_4$ (Pbca, $a = 5.4153(2)$, $b = 14.2437(6)$, $c = 15.7595(7)$ Å, $V = 1215.59$ Å$^3$) [44] is also based on litharge-type slabs (Figure 3b). Arrangement of Co$^{2+}$ cations within litharge slab is different from that observed for Cu$^{2+}$ in [Bi$_2$CuO$_3$]SO$_4$ (Figure 3e). Cu$^{2+}$ cations are in cis position in O5Bi$_2$Cu$_2$ and O6Bi$_2$Cu$_2$ oxo-centered tetrahedra in [Bi$_2$CoO$_3$]SO$_4$, and Co$^{2+}$ cations are in trans position in OBi$_2$Cu$_2$ oxo-centered tetrahedra in [Bi$_2$CoO$_3$]SO$_4$. While the Co$^{2+}$ are surrounded by Bi$^{3+}$ only and reside at relatively long separations, the Cu$^{2+}$ cluster in pairs results in larger undulation amplitudes in [Bi$_2$CoO$_3$]$^{2+}$ slabs (Figure 3e) compared to [Bi$_2$CuO$_3$]$^{2+}$. All this results in lowering the symmetry from orthorhombic for the Co compound to monoclinic to that of Cu. A defect-free [Bi$_2$O$_2$]$^{2+}$ layer (Figure 3c) has been recently described by us in [Bi$_2$O$_2$](SO$_4$) (Figure 3f) [36].

3.2. Crystal Structure of [Ln$_2$O$_3$]SO$_4$ (Ln = Dy, Ho)

The crystal structure of [Lu$_2$O$_2$]SO$_4$ is completely analogous to those of grandreelite and oxysulfates of La, Sm, Eu, and Bi. It contains one symmetrically independent Ln$^{3+}$ cation (Figure 4a) which is coordinated by eight oxygen atoms. Four Ln–O$_6$ short and strong bonds are formed within the litharge [Ln$_2$O$_3$]$^{2+}$ slab and four Ln–O$_4$ bonds are formed with sulfate groups in the interlayer (O$_4$—the oxygen atoms of the sulfate group). The coordination environments of Ln$^{3+}$ cations are similar to those of Bi$^{3+}$ in [Bi$_2$O$_2$]SO$_4$ and more distantly related to those in [Bi$_2$CuO$_3$]SO$_4$ described above. One S site has a tetrahedral arrangement typical for hexavalent sulfur; the SO$_4$$^{2-}$ tetrahedra are essentially distorted. In general, the structural architecture of [Ln$_2$O$_2$]SO$_4$ (Figure 4b) is similar to [Bi$_2$CuO$_3$]SO$_4$. The current pool of data indicates that structures of the [Ln$_2$O$_2$]SO$_4$ species for Ln = La, Sm, Eu and Ho ([29–31] and this work) are nearly identical except Ln = Nd [37] with suggested trigonal prismatic coordination for Nd$^{3+}$ which is relatively rare. The suggested non-centrosymmetric $Iar{2}22$ space group was not
verified. From our viewpoint, there are no chemical reasons why the \( \text{[Nd}_2\text{O}_2\text{]}\text{SO}_4 \) would adopt a different crystal structure, unless a new polymorph was generated.

Figure 3. \([\text{Bi}_2\text{CuO}_3\text{]}^{2+}\) layer (a) in the crystal structure of \([\text{Bi}_2\text{CuO}_3\text{]}\text{SO}_4\), \([\text{Bi}_2\text{CoO}_3\text{]}^{2+}\) layer (b) in the structure of \([\text{Bi}_2\text{CoO}_3\text{]}\text{SO}_4\) and \([\text{Bi}_2\text{O}_2\text{]}^{2+}\) layer (c) in the structure of \([\text{Bi}_2\text{O}_2\text{]}\text{SO}_4\). General projections of the crystal structure of \([\text{Bi}_2\text{CuO}_3\text{]}\text{SO}_4\) along the \(b\) axis (d), \([\text{Bi}_2\text{CoO}_3\text{]}\text{SO}_4\) along the \(a\) axis (e), and \([\text{Bi}_2\text{O}_2\text{]}\text{SO}_4\) along the \(b\) axis (f).
without very strong distortions of the anionic layer and coordination polyhedra of Bi$^{3+}$ or Pb$^{2+}$. It is possible the polyatomic nature of the sulfate anions which permits to satisfy the coordination requirements of both Bi$^{3+}$ and M$^{2+}$. Therefore, Bi$^{3+}$ behaves as a size analog of Eu$^{3+}$, falling probably beyond the stability limit of oxide selenates. The structure of [La$_2$O$_2$]CrO$_4$ (determined from powder neutron data [32]) exhibits almost regular chromate anions which suggests their relative rigidity. This may explain both why the grandreefite structure is adopted by an only compound of the earliest rare-earth element and why an alternative structure is formed for the compounds of Pr–Tb which is not formed for selenates while the size of CrO$_4^{2-}$ and SeO$_4^{2-}$ is relatively close. Note also the relatively low stability of SeO$_4^{2-}$ against SeO$_3^{2-}$. Close structural relationships between [Ln$_2$O$_2$]CrO$_4$ and [Ba$_2$F$_2$](S$_2$O$_3$) suggest possible existence of some more isostructural compounds. However, while Pb contributes to the fluoride sulfate and selenate, barium contributes only to fluoride thiosulfate but not to derivatives of other tetrahedral anions. This may be caused by very low solubility of PbCrO$_4$, BaSO$_4$ and BaSO$_4$ compared to PbF$_2$ and BaF$_2$, while those of BaF$_2$ and BaSO$_4$, as well as PbSO$_4$ (PbSeO$_4$) and PbF$_2$ are of the same order [34].

Incorporation of transition metal cations in square oxygen nets with the O–O distances of 2.7–2.8 Å would suggest a M–O distance of 1.9–2Å which is slightly below the common range for Cu$^{2+}$ but essentially small for Co$^{2+}$. Therefore, the M$^{2+}$ cations reside above the “liharge” oxygens in the structures of [Bi$_2$MO$_3$]SO$_4$ as clearly seen in Figure 3d,e. Their coordination polyhedron is expanded to a distorted square pyramid (or a particularly stretched octahedron) by the oxygen atoms of sulfate tetrahedra. This is not possible in the oxyhalide or oxychalcogenide structures shown in Figure 1a without very strong distortions of the anionic layer and coordination polyhedra of Bi$^{3+}$ or Pb$^{2+}$. It is possibly the polyatomic nature of the sulfate anions which permits to satisfy the coordination requirements of both Bi$^{3+}$ and M$^{2+}$. Note that both Co$^{2+}$ (3d$^7$) and Cu$^{2+}$ (3d$^9$) exhibit pronounced Jahn–Teller effect which permits gross distortions of octahedral coordination. With other M$^{2+}$ cations like Ni$^{2+}$ (3d$^{8}$) this is expected to be essentially less likely. Furthermore, the arrangement of sulfate...
anions in the structures of [Bi₂MO₃]SO₄ results in very irregular, “one-sided” coordination of Bi³⁺, which is, however, rather common due to high stereochemical activity of its lone-pair. This irregularity would not be favored by rare-earth cations. Indeed, interaction of Ln₂O₃ oxides (Ln ≤ Ho) with CuSO₄ (as well as other sulfates of divalent metals) yields only mixtures of [Ln₂O₃]SO₄ and CuO (or other MO oxides) with no hint ath the intermediate [Ln₂MO₃]SO₄ composition [50]. However, it seems rather likely that some other layered structures may be found among oxysulfates of Bi and Co or Cu.

Supplementary Materials: The following are available online at http://www.mdpi.com/2075-163X/10/10/887/s1. Figure S1. Rietveld refinement plots for [H₂O₂]SO₄ and [Dy₂O₂]SO₄. Table S1. Coordinates and isotropic displacement parameters (Å²) of atoms in [Bi₂CuO₃]SO₄. Table S2. Anisotropic displacement parameters (Å²) of atoms in [Bi₂CuO₃]SO₄. Table S3. Coordinates and isotropic displacement parameters (Å²) of atoms in [Dy₂O₂]SO₄. Table S4. Coordinates and isotropic displacement parameters (Å²) of atoms in [H₂O₂]SO₄.

Author Contributions: O.S. and D.C. designed the study; O.S. and E.N. performed and interpreted single crystal X-ray diffraction experiments; I.P. interpreted powder X-ray diffraction experiments; E.N. performed synthesis of [Bi₂CuO₃]SO₄; D.C. and G.A. performed synthesis of [Ln₂O₃]SO₄ (Ln = Dy and Ho); O.S. and D.C. wrote the paper; A.H. provided materials and work in the high-pressure laboratory. All authors have read and agreed to the published version of the manuscript.

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