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Expanding Family of Litharge-Derived Sulfate Minerals and Synthetic Compounds: Preparation and Crystal Structures of $[Bi_2CuO_3]SO_4$ and $[Ln_2O_2]SO_4$ (Ln = Dy and Ho)

Oleg Siidra^{1,*}, Dmitri Charkin², Igor Plokhikh³, Evgeny Nazarchuk¹, Astrid Holzheid⁴ and Georgy Akimov²

- ¹ Department of Crystallography, Saint-Petersburg State University, University emb. 7/9, 199034 St. Petersburg, Russia; e_nazarchuk@mail.ru
- ² Department of Chemistry, Moscow State University, GSP-1, 119991 Moscow, Russia; d.o.charkin@gmail.com (D.C.); akimov.georgyy@gmail.com (G.A.)
- ³ Institut für Anorganische Chemie der Universität Regensburg, Universitätsstr. 31, D-93040 Regensburg, Germany; ig.plohih@yandex.ru
- ⁴ Institut für Geowissenschaften der Universität Kiel, Olshausenstr. 40, D-24098 Kiel, Germany; astrid.holzheid@ifg.uni-kiel.de
- * Correspondence: o.siidra@spbu.ru; Tel.: +7-812-350-66-88

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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*₂O₂]SO₄ (*Ln* = Dy, Ho), which belong indeed to the grandreefite family, and a novel compound [Bi₂CuO₃]SO₄, which belongs to a new structure type and demonstrates the second example of Cu²⁺ incorporation into litharge-type slabs. Crystals of [Bi₂CuO₃]SO₄ were obtained under high-pressure/high-temperature (HP/HT) conditions, whereas polycrystalline samples of [*Ln*₂O₂]SO₄ (*Ln* = Dy, Ho) compounds were prepared via an exchange solid-state reaction. The crystal structure of [Bi₂CuO₃]SO₄ is based on alternation of continuous [Bi₂CuO₃]²⁺ layers of edge-sharing OBi₂Cu₂ and OBi₃Cu tetrahedra and sheets of sulfate groups. Cu²⁺ cations are in *cis* position in O5Bi₂Cu₂ and O6Bi₂Cu₂ oxocentered tetrahedra in litharge slab. The crystal structure of [*Ln*₂O₂]SO₄ (*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 Pb²⁺ and Bi³⁺, 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 (Cd²⁺ (4d¹⁰), 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 [Pb₂F₂]SO₄ [27] and a slag phase [Ba₂F₂]S₂O₃ [28]. Synthetic analogs of [Ba₂F₂]S₂O₃ were found among [Ln_2O_2]CrO₄ oxychromates (Ln = Pr-Tb [33]). Synthetic analogs of the grandreefite structure are observed also among selenates ([Pb₂F₂]SeO₄ [34] and [Ln_2O_2]SeO₄, Ln = La, Pr, Nd [35]) and chromates ([La₂O₂]CrO₄ [32]). The same structure was also established for [Bi₂O₂]SO₄ [36] and some rare-earth oxysulfates [Ln_2O_2]SO₄ (La [29], Sm [30] and Eu [31]). In the meantime, a different atomic arrangement was suggested for [Nd₂O₂]SO₄ [37]. The crystal structures of other reported [M₂O₂]SO₄ 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 (*l*-centered, $a \sim b \sim 4$ Å, $c \sim 13$ Å [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 $[Bi_2O_2]Te$ [42] and its derivatives hosting molecular anions in the interlayer galleries: $[Bi_2O_2]CN_2$ [20] (c,d), kettnerite $[BiO][CaF][CO_3$ [26] (e), grandreefite $[Pb_2F_2]SO_4$ [27] (f), slag phase $[Ba_2F_2]S_2O_3$ [28] (g), and $[La_2O_2]MoO_4$ [43] (h).

The crystal chemistry of bismuth oxysulfates is more diverse and contains, besides the grandreefite analogue, three relatively complex litharge derivatives incorporating transition metal cations: $[Bi_6O_6]CoO_2(SO_4)_2$ with krönkite-type chain anions, $[Bi_2CoO_3]SO_4$ and $[Bi_{6.27}Cu_{1.6}O_8](SO_4)_3$, recently re-determined by Lü et al. [44]. The latter are of particular interest representing yet only two known examples of transition metal cations (Co²⁺ and Cu²⁺) 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 oxysulfates, $[Ln_2O_2]SO_4$ (Ln = Dy, Ho), which belong indeed to the grandreefite family, and a novel compound $[Bi_2CuO_3]SO_4$, which belongs to a new structure type and demonstrates the second example of Cu²⁺ incorporation into litharge-type slabs.

2. Materials and Methods

2.1. Synthesis

Crystals (Figure 2a) of novel [Bi₂CuO₃]SO₄ 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. CuSO₄ (Aldrich \geq 99.0%, 0.119 g) and BiOCl (Aldrich \geq 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 talc–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 \approx 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 [Bi₂CuO₃]SO₄ crystals in association with unreacted BiOCl.



Figure 2. Green crystals of $[Bi_2CuO_3]SO_4$ (field of view 0.5 mm) (**a**). Coordination environments of Bi^{3+} , Cu^{2+} , and S^{6+} cations in the structure of $[Bi_2CuO_3]SO_4$ (**b**). Weaker Bi-O bonds are shown by thin lines. Ellipsoids are drawn at 50% probability level.

Polycrystalline samples of $[Ln_2O_2]SO_4$ (Ln = Dy, Ho) compounds were prepared via an exchange reaction similar to $[Ln_2O_2]CrO_4$ [32,33] and $[Ln_2O_2]SeO_4$ [35]. Rare-earth oxychlorides, LnOCl, prepared by thermal hydrolysis of $LnCl_3$ ·6H₂O, 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 K₂SO₄, and air dried.

2.2. Single-Crystal XRD Studies

A single crystal of $[Bi_2CuO_3]SO_4$ 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 MoK α 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 $[Bi_2CuO_3](SO_4)$ and $[Ln_2O_2](SO_4)$ (Ln = Dy, Ho).

Single-Ci	ystal XRD		Powder XRD	
	[Bi ₂ CuO ₃](SO ₄)		[Dy ₂ O ₂](SO ₄)	[Ho ₂ O ₂](SO ₄)
Space Group	C2/c	Space Group	C2/c	C2/c
a (Å)	20.0283(7)	a (Å)	13.3682(2)	13.4172(1)
b (Å)	5.3970(2)	b (Å)	4.14721(5)	4.15878(4)
<i>c</i> (Å)	14.1413(5)	<i>c</i> (Å)	8.0204(1)	8.05626(8)
β, °	128.4450(10)	β,°	107.8070(8)	107.6201(8)
V (Å ³)	1197.19(8)	V (Å ³)	423.35(1)	428.44(1)
$D_{\mathbf{x}}$	6.941	$D_{\mathbf{x}}$	7.18	7.024
2θ range (°).	2.60-38.50	2θ range (°).	10–120	10–120
R _{int}	0.030	R_P	0.029	0.015
R_1	0.023	R _{WP} (%)	0.043	0.014
Gof	1.040	R_F (%)	0.029	0.035
CCDC	2021664	CCDC	2021867	2021874

2.3. Powder XRD Studies

High-resolution data sets were collected for $[Ln_2O_2]SO_4$ (Ln = Dy, Ho) on a PANalytical–X'Pert diffractometer (Malvern Instruments, Malvern, UK) utilizing CuKa1,2 radiations. The refinement was done using the JANA2006 software (version 2014.11–0) [48]. As in the case of isostructural $[Pb_2F_2]SeO_4$ [34] and Bi₂O₂SO₄ [36], indexing the powder patters 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 $[Eu_2O_2]SO_4$ [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 SO₄^{2–} anion. Final Rietveld refinement plots for $[Dy_2O_2]SO_4$ and $[Ho_2O_2]SO_4$ are given in the Supplementary Materials. The data are deposited in CCDC under entries No. 2021867 ($[Dy_2O_2]SO_4$) and 2021874 ($[Ho_2O_2]SO_4$).

3. Results

3.1. Crystal Structure of [Bi₂CuO₃]SO₄

The structure of $[Bi_2CuO_3]SO_4$ 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 Bi³⁺ coordination in $[Bi_2CuO_3]SO_4$ is the presence of four short and very strong Bi-O bonds (2.23–2.37 Å) located in one coordination hemisphere of the Bi³⁺ cations. In the opposite hemisphere, the Bi³⁺ cations form from five to six longer Bi³⁺-O bonds. The distortion of the Bi³⁺ coordination of bismuth coordination environments is not as strong as usually observed for Pb²⁺ in litharge-derived structures.

The Cu site is coordinated by four O atoms to form a distorted CuO₄ square complemented by two apical O^{2-} anions. As a result, a distorted [CuO₄O₂] octahedron is formed. [CuO₄O₂] octahedra group in pairs via common edge to form Cu₂O₈ dimers shown in Figure 2. Cu–Cu distance is 2.79 Å. Unfortunately, we were unable to measure magnetic properties of [Bi₂CuO₃]SO₄ due to the insufficient amount of pure material.

One symmetrically independent S⁶⁺ cation forms rather symmetrical SO₄ 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_a -Bi and O_a -Cu bonds (O_a —additional oxygen atoms not bonded to S) are the shortest and therefore the strongest in the structures of $[Bi_2CuO_3]SO_4$, which makes it reasonable to consider the Bi-Cu-O substructure consisting of OBi_2Cu_2 and OBi_3Cu tetrahedra interacting with SO_4 tetrahedra through relatively weaker Bi-O_t and Cu-O_t bonds. The topology of this oxocentered $[Bi_2CuO_3]^{2+}$ structural unit (Figure 3a) is two-dimensional and obviously related to the $[Bi_2O_2]^{2+}$ layer typical for compounds structurally related to litharge.

The crystal structure of $[Bi_2CuO_3]SO_4$ (Figure 3d) is based on alternation of continuous $[Bi_2CuO_3]^{2+}$ layers of edge-sharing OBi₂Cu₂ and OBi₃Cu tetrahedra and sheets of sulfate groups. Note that $[Bi_2CuO_3]SO_4$ belongs to a new structure type. The structure of recently re-investigated $[Bi_2CoO_3]SO_4$ (*Pbca, a* = 5.4153(2), *b* = 14.2437(6), *c* = 15.7595(7) Å, *V* = 1215.59 Å³) [44] is also based on litharge-type slabs (Figure 3b). Arrangement of Co²⁺ cations within litharge slab is different from that observed for Cu²⁺ in $[Bi_2CuO_3]SO_4$ (Figure 3e). Cu²⁺ cations are in *cis* position in O5Bi₂Cu₂ and O6Bi₂Cu₂ oxocentered tetrahedra in $[Bi_2CuO_3]SO_4$, and Co²⁺ cations are in *trans* position in OBi₂Co₂ oxocentered tetrahedra in $[Bi_2CoO_3]SO_4$. While the Co²⁺ are surrounded by Bi³⁺ only and reside at relatively long separations, the Cu²⁺ cluster in pairs which results in larger undulation amplitudes in $[Bi_2CoO_3]^{2+}$ slabs (Figure 3e) compared to $[Bi_2CuO_3]^{2+}$. All this results in lowering the symmetry from orthorhombic for the Co compound to monoclinic to that of Cu. A defect-free $[Bi_2O_2]^{2+}$ layer (Figure 3c) has been recently described by us in $[Bi_2O_2](SO_4)$ (Figure 3f) [36].

3.2. Crystal Structure of $[Ln_2O_2]SO_4$ (Ln = Dy, Ho)

The crystal structure of $[Ln_2O_2]SO_4$ is completely analogous to those of grandreefite 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_a short and strong bonds are formed within the litharge $[Ln_2O_2]^{2+}$ slab and four Ln-O_t bonds are formed with sulfate groups in the interlayer (O_t—the oxygen atoms of the sulfate group). The coordination environments of Ln^{3+} cations are similar to those of Bi³⁺ in [Bi₂O₂]SO₄ and more distantly related to those in [Bi₂CuO₃]SO₄ described above. One S site has a tetrahedral arrangement typical for hexavalent sulfur; the SO₄²⁻ tetrahedra are essentially distorted. In general, the structural architecture of $[Ln_2O_2]SO_4$ (Figure 4b) is similar to [Bi₂CuO₃]SO₄. The current pool of data indicates that structures of the $[Ln_2O_2]SO_4$ species for Ln = La, Sm, Eu, Dy and Ho ([29–31] and this work) are nearly identical except Ln = Nd [37] with suggested trigonal prismatic coordination for Nd³⁺ which is relatively rare. The suggested non-centrosymmetric *I*222 space group was not Bi1

(a)

Bi1 Bi2

07

Bi2

06

Cu1 Cu1

25

verified. From our viewpoint, there are no chemical reasons why the $[Nd_2O_2]SO_4$ would adopt a different crystal structure, unless a new polymorph was generated.

(d)



Figure 3. $[Bi_2CuO_3]^{2+}$ layer (**a**) in the crystal structure of $[Bi_2CuO_3](SO_4)$, $[Bi_2CoO_3]^{2+}$ layer (**b**) in the structure of $[Bi_2CoO_3](SO_4)$ and $[Bi_2O_2]^{2+}$ layer (**c**) in the structure of $[Bi_2O_2](SO_4)$. General projections of the crystal structure of $[Bi_2CuO_3](SO_4)$ along the *b* axis (**d**), $[Bi_2CoO_3](SO_4)$ along the *a* axis (**e**), and $[Bi_2O_2](SO_4)$ along the *b* axis (**f**).

Bi

Cu S O



Figure 4. Cation coordination in the structure of $[Dy_2O_2]SO_4$ (**a**). General projection of the crystal structure of $[Dy_2O_2]SO_4$ along the b axis (**b**). $[Dy_2O_2]^{2+}$ layer (**c**).

4. Discussion

The tetrahedral sulfate, selenate, chromate, and molybdate anions are yet the largest species which can be accommodated in the space between metal-oxide or metal-fluoride litharge slabs. Their effective size essentially exceeds that of the largest monoatomic (Te^{2-}) species. This results in strong distortion (mostly stretching in the *ab* plane) of the [M₂O₂]²⁺ layers. The derivatives of the smallest sulfate anion are the most numerous and include compounds of all rare earths, as well as bismuth. The dissimilarity in bonding to oxygen atoms results in a large distortion of the sulfate tetrahedra; it is their utmost chemical stability that makes these distortions tolerable. According to our results for the Dy and Ho compounds, all $[Ln_2O_2]SO_4$ crystallize in the monoclinic grandreefite structure (Table 1). In the predominantly ionic structure of $[Pb_2F_2]SO_4$ with essentially larger $[Pb_2F_2]^{2+}$ slabs, the configuration of the sulfate anion is close to regular. Selenate is more voluminous and less chemically stable so only a handful of grandreefite-type compounds is known, including those of the earliest rare-earths and the "direct" analog of grandreefite. Comparison of structural data for the [M₂O₂]SO₄ compounds reveals that distances in [Bi₂O₂]SO₄ are very close to those of [Eu₂O₂]SO₄. Therefore, Bi³⁺ behaves as a size analog of Eu^{3+} , falling probably beyond the stability limit of oxide selenates. The structure of [La₂O₂]CrO₄ (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 $[Ln_2O_2]CrO_4$ and $[Ba_2F_2](S_2O_3)$ 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 PbCrO₄, BaSO₄ and BaSO₄ compared to PbF₂ and BaF₂, while those of BaF₂ and BaSO₄, as well as PbSO₄ (PbSeO₄) and PbF₂ 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 Cu²⁺ but essentially small for Co²⁺. Therefore, the M²⁺ cations reside above the "liharge" oxygens in the structures of [Bi₂MO₃]SO₄ 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 Bi³⁺ or Pb²⁺. It is possibly the polyatomic nature of the sulfate anions which permits to satisfy the coordination requirements of both Bi³⁺ and M²⁺. Note that both Co²⁺ (3d⁷) and Cu²⁺ (3d⁹) exhibit pronounced Jahn–Teller effect which permits gross distortions of ochahedral coordination. With other M²⁺ cations like Ni²⁺ (3d⁸) this is expected to be essentially less likely. Furthermore, the arrangement of sulfate

anions in the structures of $[Bi_2MO_3]SO_4$ results in very irregular, "one-sided" coordination of Bi^{3+} , 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 Ln_2O_3 oxides ($Ln \le Ho$) with CuSO₄ (as well as other sulfates of divalent metals) yields only mixtures of $[Ln_2O_2]SO_4$ and CuO (or other MO oxides) with no hint ath the intermediate $[Ln_2MO_3]SO_4$ 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 $[Ho_2O_2]SO_4$ and $[Dy_2O_2]SO_4$. Table S1. Coordinates and isotropic displacement parameters (Å²) of atoms in $[Bi_2CuO_3](SO_4)$. Table S2. Anisotropic displacement parameters (Å²) of atoms in $[Dy_2O_2]SO_4$. Table S4. Coordinates and isotropic displacement parameters (Å²) of atoms in $[Dy_2O_2]SO_4$. Table S4. Coordinates and isotropic displacement parameters (Å²) of atoms in $[Dy_2O_2]SO_4$. Table S4. Coordinates and isotropic displacement parameters (Å²) of atoms in $[Ho_2O_2]SO_4$.

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 $[Bi_2CuO_3]SO_4$; D.C. and G.A. performed synthesis of $[Ln_2O_2]SO_4$ (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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