HIGH-PRESSURE STUDIES OF Bi$_2$S$_3$

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Supplementary Information

S1. Calculated atomic coordinates for Bi$_2$S$_3$

There exist 20 atoms (five distinct atomic sites) in the unit cell of Bi$_2$S$_3$. All of these atoms occupy the 4a Wyckoff position, with the corresponding position vectors defined as:

$$\overrightarrow{Bi_1} = (x_1, 0.25, z_1),$$

$$\overrightarrow{Bi_2} = (x_2, 0.25, z_2),$$

$$\overrightarrow{S_1} = (x_3, 0.25, z_3),$$

$$\overrightarrow{S_2} = (x_4, 0.25, z_4),$$

$$\overrightarrow{S_3} = (x_5, 0.25, z_5),$$

in relative coordinates, where x_n and z_n (n = 1 to 5) are the 10 internal parameters of for the atomic basis. The 20 atom unit cell is obtained by the symmetry operation of the *Pnma* space group. For any basis vector position of the type, (x, 0.25, z), there exist three additional positions, (x + 0.5, 0.25, 0.5 - z), (0.5 - x, 0.75, z + 0.5) and (-x, 0.75, -z), generated by the lattice symmetry. The calculated 10 internal parameters, based on DFT computations, are tabulated in **Table S1**.

Table S1: Calculated postional coordinates for all ions in the Bi$_2$S$_3$ unit cell at various pressures.

P (GPa)	Bi(1)-x	Bi(1)-z	Bi(2)-x	Bi(2)-z	S(1)-x	S(1)-z	S(2)-x	S(2)-z	S(3)-x	S(3)-z
0.424	0.01422	0.67426	0.33969	0.46774	0.04873	0.12986	0.37752	0.05562	0.21473	0.80744
1.197	0.01586	0.6738	0.34167	0.46726	0.04848	0.12982	0.37791	0.05544	0.21295	0.80804
2.065	0.00597	0.67461	0.33428	0.46824	0.05064	0.12998	0.37727	0.05723	0.21822	0.80464
3.028	0.00251	0.67509	0.33162	0.46883	0.05097	0.1297	0.37722	0.05785	0.21946	0.80333
4.065	0.000206	0.67545	0.32945	0.46952	0.05127	0.12952	0.37691	0.05826	0.22053	0.80212
5.077	-0.00229	0.67575	0.32767	0.47027	0.05123	0.12946	0.37667	0.05861	0.22117	0.80105
6.012	-0.00314	0.67614	0.32651	0.47067	0.05131	0.12937	0.37612	0.05863	0.22186	0.79995
7.051	-0.00429	0.6764	0.32528	0.47099	0.05148	0.12931	0.37566	0.05869	0.22238	0.79899
8.027	-0.0065	0.677	0.32326	0.47165	0.05135	0.12865	0.37552	0.05919	0.22276	0.79763
9.016	-0.00751	0.67724	0.32238	0.47196	0.05134	0.12841	0.37542	0.05951	0.22301	0.79658
10.103	-0.00863	0.67757	0.32121	0.47214	0.05146	0.12824	0.37498	0.05971	0.22334	0.79553
14.928	-0.01206	0.67834	0.31774	0.47276	0.05169	0.12749	0.37353	0.06071	0.22431	0.79124
20.088	-0.01516	0.67952	0.31458	0.47334	0.05195	0.1258	0.37304	0.06192	0.22444	0.78754
24.9	-0.01694	0.67976	0.31276	0.47328	0.05209	0.12495	0.37229	0.06318	0.22472	0.78484
30.069	-0.01516	0.67952	0.31458	0.47334	0.05195	0.1258	0.37304	0.06192	0.22444	0.78754
35.033	-0.02042	0.67964	0.3103	0.47151	0.05329	0.12332	0.37054	0.06615	0.22438	0.77903
39.959	-0.02155	0.68002	0.30928	0.47081	0.05355	0.12249	0.37055	0.0666	0.22422	0.77739
45.07	-0.02248	0.68001	0.30838	0.47039	0.05375	0.12184	0.3701	0.06772	0.2241	0.77585

S2. Bond lengths of Bi_2S_3 up to 45 GPa
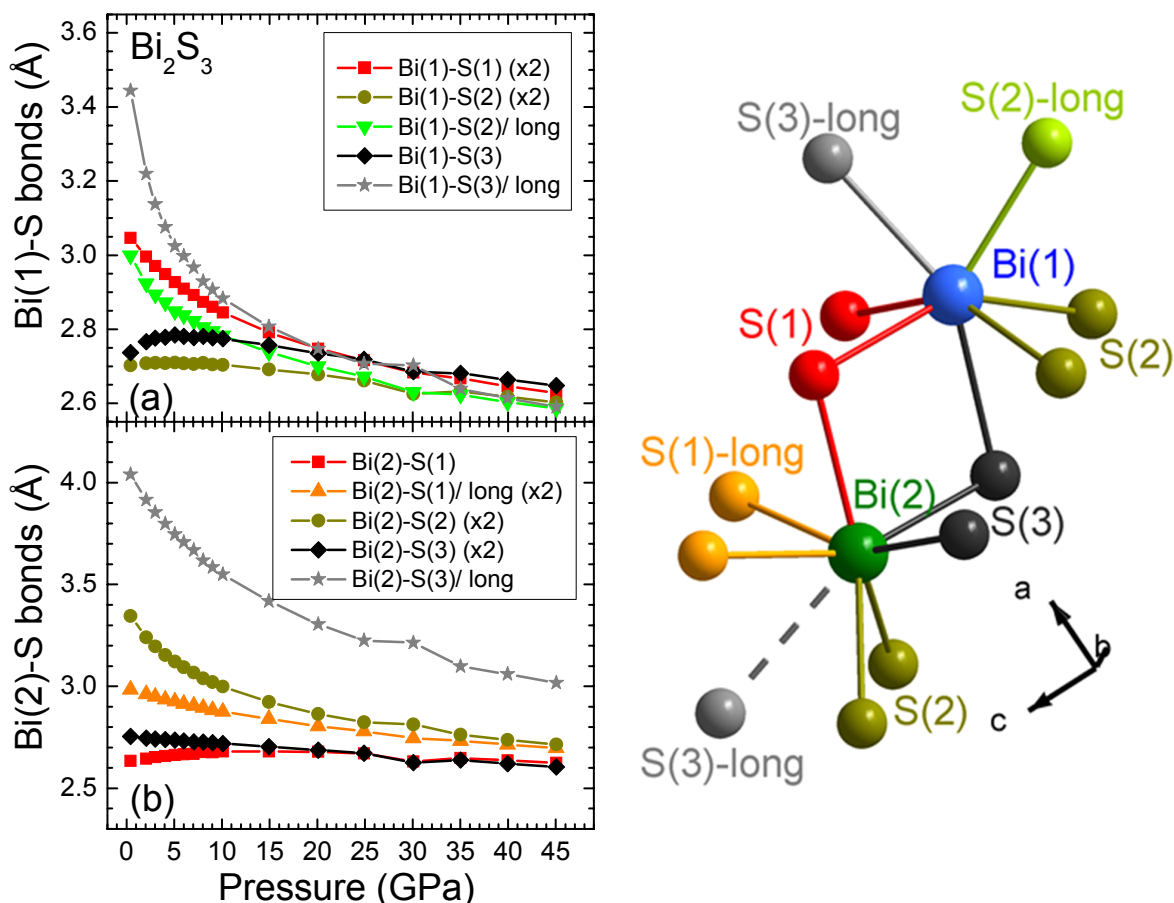
Figure S1: Pressure-induced changes of the (a) Bi(1)-S and (b) Bi(2)-S bond lengths within the $Bi(1)S_7$ and $Bi(2)S_{7+1}$ polyhedra, respectively, for the *Pnma* phase of Bi_2S_3. At low pressures, the S-coordination environment around both Bi(1) and Bi(2) cations is highly asymmetric, as indicated by the large diversity in the Bi-S bond length values of the respective polyhedra. For both Bi(1) and Bi(2) cations we can observe that the effect of pressure is more pronounced for the longer Bi-S bonds (>3 Å). On the other hand, the shorter Bi(1)-S(2), Bi(1)-S(3), and Bi(2)-S(1) bonds elongate up to ~10 GPa; this pressure-induced elongation of the shorter bond distances is typical for LEP-active compounds[1,2]. In addition, pressure "forces" the various Bi-S bond lengths of the $Bi(1)S_7$ polyhedron to adopt a similar value beyond ~20 GPa. This effect can be translated as a pressure-induced symmetrization of the $Bi(1)S_7$ polyhedral units, which is directly connected with significant suppression of the Bi^{3+} LEP stereochemical activity above that pressure (**Appendix**).

APPENDIX: LONE PAIR ACTIVITY OF Bi³⁺

An important crystal-chemical parameter of the A_2B_3 ($A=Sb^{3+}$, Bi^{3+}; $B=O$, S, Se, Te) series is the stereochemical activity of the lone electron pairs (LEPs) present in the Sb^{3+} and Bi^{3+} cations. The LEP activity can affect the structural [3,4], electronic [5], and several other physical properties [6,7] significantly. In a nutshell [for a review see e.g. Ref.[8]], LEPs are cationic valence electrons that do not participate in any direct chemical bonding with the corresponding anions. LEPs appear to occupy space in the local ligand sphere of the respective (central) cation like a regular ligand. The presence of this stereochemically active lone electron pair can result in asymmetric local environments around the central cations, leading to cationic polyhedral distortions. Therefore, the degree of distortion for the respective the cationic polyhedra can provide a reasonable estimate for the LEP stereochemical activity. The distortion of a cationic polyhedron can be quantified by several parameters [9–11]; here, however, we employ the *cation eccentricity* as an indirect measure of the stereochemical activity. The cation eccentricity is defined as the displacement of the cation from the centroid (ideal center) of its coordination polyhedron divided by the average cation-ligand distance [12]. Therefore, the larger the cation eccentricity, the larger the LEP stereochemical activity.

In order to establish a connection between cation eccentricity and LEP stereochemical activity for the *Pnma* structure, we have calculated the cation eccentricities for several R_2S_3 compounds [$R^{3+}=Tm^{13}$, Dy^{14}, Tb^{14}, and Gd^{15}] isostructural to Bi_2S_3, but without any active lone-pairs [**Fig. 6(a)**]. The cation eccentricities for both cationic sites are close to zero for all RE_2Se_3 materials. In addition, the same calculation was performed for Sb_2S_3[2], which has active LEPs [**Fig. 6(a)**]; both Sb cationic sites exhibit a finite value of eccentricities. Since all of these compounds adopt the same crystal structure, it becomes clear that the *Pnma* phase alone does not impose any significant cation eccentricity; it is rather the presence of LEPs that generates the eccentricity of

cation positions in this structure [**Fig. 6(a)**]. Finally, and in order to validate our method further, we have calculated the cation eccentricities for the mixed-valent $Ag_{25}Bi_3O_{18}$[16] compound [**Fig. 6(a)**]. In this structure, both Bi^{3+} (LEP active) and Bi^{5+} (no lone pairs) reside in octahedral sites. As expected, the cation eccentricity for pentavalent bismuth is zero [**Fig. 6(a)**], i.e. Bi^{5+} resides in an undistorted octahedron due to the absence of LEPs. Therefore, the cation eccentricity is a good qualitative measure for the LEP stereochemical activity.

Turning now to Bi_2S_3, in **Fig. 6(b)** we present the pressure dependence of both Bi(1) and Bi(2) cation eccentricities up to 45 GPa. It is important to remind here that the two Bi cations exhibit different coordination environments (**Fig. 1**): Bi(1) coordinates with seven S anions, whereas for Bi(2) the coordination is eightfold (7+1). At low pressures, the coordination of Bi(2) can be viewed as sevenfold due to the initially larger Bi(2)-S(3)/long bond length. Upon pressure increase, however, the S(3) anion "enters" into the Bi(2) primary coordination sphere, thus making the Bi(2) coordination eightfold. In order to be consistent, however, we have assumed a sevenfold coordination for both Bi(1) and Bi(2) at all pressures.
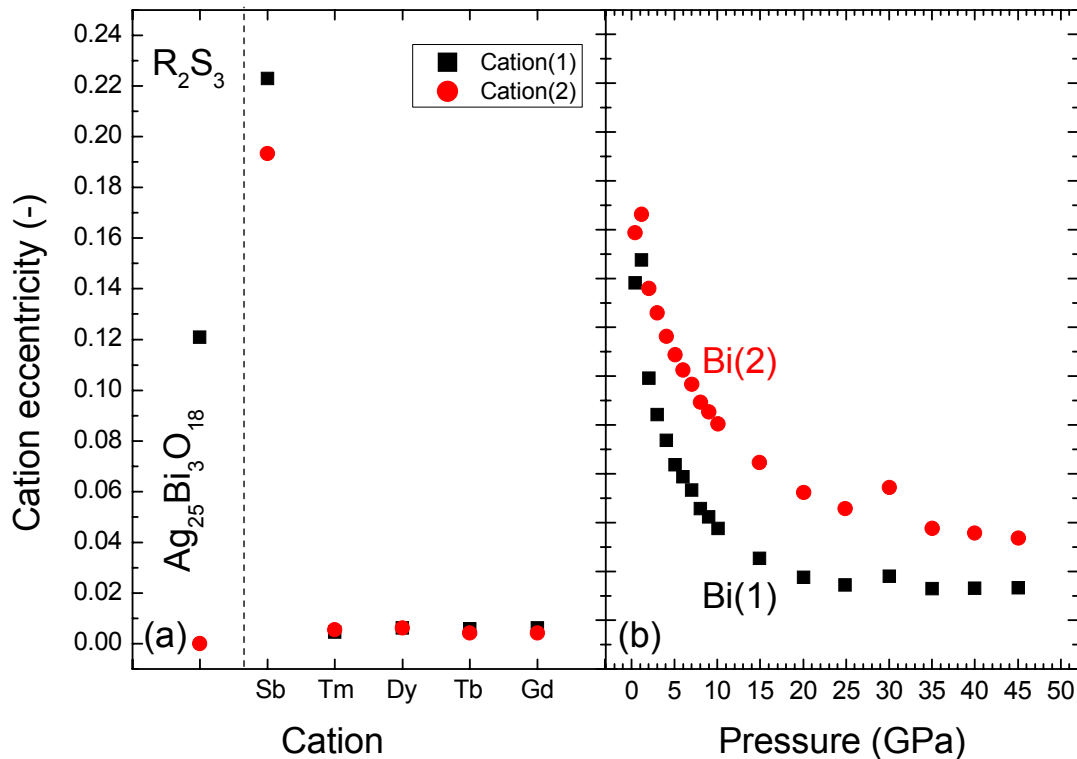
Figure S2: (a) Plot of the R(1) and R(2) cation eccentricities for several R_2S_3 compounds (R^{3+}=Sb, Tm, Dy, Tb, and Gd) with *Pnma* structure. The mixed-valent $Ag_{25}Bi_3O_{18}$ compound, with Bi^{3+} at site (1) and Bi^{5+} at site (2), is also shown for comparison. (b) Pressure-induced variation of the Bi(1) and Bi(2) cation eccentricities for the Bi_2S_3 compound.

From **Fig. 6(b)** we can observe the following pressure-related effects: (I) Both Bi(1) and Bi(2) cation eccentricities decrease in a non-monotonous manner upon increasing pressure, indicating a decrease in the Bi^{3+} LEP stereochemical activity upon compression. The same situation was evidenced for isostructural Sb_2Se_3[17] and Sb_2S_3[2] compounds. (II) The Bi(1) cation eccentricity remains lower than that of Bi(2) at all pressures. (III) The pressure-induced decrease for both Bi(1) and Bi(2) cation eccentricities is more pronounced below ~10 GPa; both eccentricities almost saturate beyond that pressure. (IV) Close examination of the pressure dependence for both cation eccentricities reveals a subtle change in their compressibilities near 4-5 GPa (not

shown), coinciding with the compressibility change of several structural parameters (**Fig. 4**). Given that the cation eccentricities correlate directly with the average cation-ligand distances and the respective bond valences[12], a change in their compressibilities may insinuate the isostructural transition speculated for Bi_2S_3 near that pressure. (IV) By extrapolation of the data, the Bi(1) and Bi(2) cation eccentricities are expected to reach zero values at 108 GPa and 84 GPa, respectively. Hence, a high-pressure structural study extending beyond 1 Mbar will be required for revealing whether the utter suppression of the Bi^{3+} LEP activity can lead to any structural transitions.

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