Supplementary Materials

High pressure investigation of the S-N\textsubscript{2} system up to the megabar range: Synthesis and characterization of the SN\textsubscript{2} solid

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Single crystal X-ray diffraction procedure

An overview of the procedure to obtain the single crystal data is here presented. For the full details, please see ref. 1.

First, it needs to be clear that while the SN$_2$ structure was resolved from single crystal X-ray diffraction data, the data collected at the synchrotron is not solely the reflections belonging to a unique single crystal, but rather from multitudes of single crystals: polycrystals. As described here, the single crystal data is afterwards extracted by choosing a single set of reflections; all associated with a single crystal.

After laser-heating, we first perform an X-ray diffraction mapping of our sample. This allows us to pinpoint the regions with the best and the worst powder data; i.e. with nice homogeneous diffractions rings and with highly spotty reflections. The diffractograms shown in the paper were obtained on sample areas where the powder quality was the highest (diffraction rings as homogeneous as possible). However, the “single crystal” data was acquired at other positions, where the “powder” is the spottiest. Still, we do not acquire reflections belonging solely to one single crystals, but rather the reflections coming from many single crystals. The image plate obtained during the XRD sample mapping (a still image; i.e. without DAC rotation) at 121.7 GPa, from which the position was selected for a step-scan (“single crystal”) data acquisition is shown in Figure S1. The position is chosen on account of the nice diffraction spots belonging to the SN$_2$ phase. The homogeneous powder rings come from the Re gasket.

Figure S1: Still X-ray diffraction image collected on a laser-heated S-N$_2$ sample at 121.7 GPa. The continuous rings belong to the Re gasket while the diffraction spots are produced from multiple SN$_2$ single crystals.
After having acquired step-scans at various positions on the sample, the challenge is to properly analyze the data and find the reflections belonging to only one single crystal. Then, the data may be treated as regular single crystal dataset, albeit with the obvious constraints brought by the DAC, notably a reduced coverage of the Ewald sphere. Identifying the reflections produced by a unique single crystal is possible through the attentive examination of the reflections observed in the Ewald sphere, and especially doable with the modern CrysAlisPro software. Figure S2 represents the Ewald sphere for the data at 121.7 GPa, where all reflections, belonging to all single crystals, are observed. Reflections from a unique single crystal, which are recognized by their periodic arrangement, are visible in red. There are several criteria which allow to verify that a certain set of reflections belongs to a unique single crystal, namely the integration of the intensities which should give a low $R_{int}$, the scale factor should not vary significantly from frame to frame and unwarps should confirm the assignment of the space group (consistent with the space group systematic extinctions). Integrated intensities are then used for solving and refining the crystal structure with standard crystallographic software (in our case, Jana2006). Of course, it may occur that the single crystal data quality is too poor to solve or refine the structure, but as we demonstrate for our case of SN$_2$, statistical characteristics of structural refinement ($R_p$, $wR_p$, etc.) are low, have values one could expect for data collected at ambient conditions, and satisfy standard procedure (developed by the IUCr) of CIF-files checker.

Figure S2: Ewald sphere collected on a laser-heated S-N$_2$ sample at 121.7 GPa. (Above) All reflections retrieved by the CrysAlisPro software from the collected step-scans (through the automatic "peak search" procedure). (Below) In red, the reflections belonging to a unique SN$_2$ single crystal. This is noticed by the periodic arrangement of the reflections, and later validated by the CrysAlisPro software, as described in the text above.
Figure S3: Differential charge density plot at a), c) ambient pressure ($V = 44.5 \text{ Å}^3$) and b), d) at 78 GPa ($V = 36.8 \text{ Å}^3$) obtained by HSE06 calculations in the plane containing both apical and equatorial S-N bonds a) and b), as well as equatorial S-N bonds only c) and d).