Synthesis and stability of xenon oxides $\text{Xe}_2\text{O}_5$ and $\text{Xe}_3\text{O}_2$ under pressure

Agnès Dewaele¹, Nicholas Worth², Chris J. Pickard³⁴⁵, Richard J. Needs², Sakura Pascarelli⁶, Olivier Mathon⁶, Mohamed Mezouar⁶ and Tetsuo Irifune⁷⁸

¹CEA, DAM, DIF, F-91297 Arpajon, France
²TCM Group, Cavendish Laboratory, J J Thomson Avenue, University of Cambridge, CB3 0HE, United Kingdom
³Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom
⁴Department of Materials Science & Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge, CB3 0FS, United Kingdom
⁵Advanced Institute for Materials Research, Tohoku University 2-1-1 Katahira, Aoba, Sendai, 980-8577, Japan
⁶European Synchrotron Radiation Facility, BP220, 38043 Grenoble Cedex, France
⁷Ehime University, 2–5 Bunkyo-cho, Matsuyama 790-8577, Japan
⁸Earth-Life Science Institute, Tokyo Institute of Technology, Tokyo 152-8500, Japan

The noble gases are the most inert atomic group, but their reactivity increases with pressure. Diamond-anvil-cell experiments and ab initio modelling have been used to investigate a possible direct reaction between xenon and oxygen at high pressures. We have synthesized two oxides below 100 GPa, $\text{Xe}_2\text{O}_5$ under oxygen-rich conditions, and $\text{Xe}_3\text{O}_2$ under oxygen-poor conditions. $\text{Xe}_2\text{O}_5$ has been observed using X-ray diffraction methods, its structure identified using ab initio random structure searching, and confirmed using X-ray absorption and Raman spectroscopies. The experiments confirm the recent prediction of $\text{Xe}_3\text{O}_2$ as a stable xenon oxide under high pressure. Xenon atoms adopt mixed oxidation states of 0 and +4 in $\text{Xe}_2\text{O}_5$ and +4 and +6 in $\text{Xe}_3\text{O}_2$. $\text{Xe}_3\text{O}_2$ and $\text{Xe}_2\text{O}_5$ form extended networks incorporating oxygen-sharing $\text{XeO}_4$ squares, while $\text{Xe}_2\text{O}_5$ additionally incorporates oxygen-sharing $\text{XeO}_5$ pyramids. Other xenon oxides ($\text{XeO}_2$, $\text{XeO}_3$) are expected to form at higher pressures. We find that xenon is more reactive under pressure than predicted previously.
The binding of the valence electrons to the ionic core of a noble gas atom decreases with atomic number, opening up the possibility of oxidation for the heaviest of them (Kr, Xe). Since the 1960s, compounds containing xenon in oxidation states of +2, +4, +6 and +8 have been synthesized\(^1\), for instance molecular XeF\(_2\)\(^{2,3}\), XeO\(_3\)\(^4\) and XeO\(_4\)\(^5\). Recently, a new xenon oxide, XeO\(_2\), was synthesized, in which Xe-O bonds form an extended network of XeO\(_4\) squares connected by sharing oxygen atoms at their corners\(^6\). Under ambient conditions, xenon oxides are thermodynamically unstable and are synthesized using xenon fluorides as reactants. At moderate pressures, solid xenon forms weakly bonded compounds with other species, for instance with H\(_2\)O around 1 GPa\(^7\) or O\(_2\) around 3 GPa\(^8,9\). However, its properties change significantly when the pressure is further increased. Xenon transforms sluggishly between 3 and 80 GPa\(^{10-12}\) from a face-centred cubic (fcc) to a hexagonal close packed (hcp) structure, which becomes metallic around 135 GPa\(^{13}\).

Recently, theoretical proposals and experimental evidence have appeared for the formation of strongly bonded and stable xenon compounds under pressure. A recent theoretical study has proposed Xe-Ni and Xe-Fe structures, and found them to be stable against decomposition under conditions found in the Earth’s inner core\(^{14}\). Xenon has been incorporated in quartz at pressures of a few GPa and high temperatures\(^{15}\), and it has been proposed that xenon atoms replace silicon atoms in this structure. The synthesis of a compound of xenon, oxygen and hydrogen was reported recently at around 50 GPa\(^{16}\). The formation of xenon oxides in the Mbar range has been predicted using an evolutionary structure searching algorithm\(^{17}\) and density functional theory (DFT) methods\(^{18-20}\). In Refs. 18 and 19, only the simple stoichiometries XeO, XeO\(_2\), XeO\(_3\) and XeO\(_4\) suggested by low-pressure experimental observations were considered. Hermann and Schwerdtfeger found a Xe\(_3\)O\(_2\) structure in searches and predicted it to be stable above 75 GPa\(^{20}\). However, experimental data for xenon oxides have not been reported previously at the high pressures at which they might become stable. Structure searching methods have been used in conjunction with first-principles DFT calculations to determine structures of boron\(^{21}\), hydrogen\(^{22}\) and many other materials at high pressures. Studies of xenon chemistry\(^{14-16,18-20}\) have been performed in part to help in explaining the anomalously low xenon content of the Earth’s atmosphere\(^23\) in comparison with stony meteorites. One proposal for resolving this “missing xenon paradox” is that xenon is stored in the deep Earth, thus motivating a better understanding of the chemistry of xenon under geological pressures.

We have investigated the stability of compounds of xenon and the most abundant element in the Earth’s mantle, oxygen, under pressure. Experimental results are reported from powder X-ray diffraction (PXRD), X-ray absorption (XAS), and Raman spectroscopy, in laser-heated diamond anvil cells loaded with Xe-O\(_2\) mixtures (O\(_2\) content varying between 11 mol.% and 64 mol.%, see Supplementary Table SI). We have used the ab initio random structure searching (AIRSS) approach\(^{24,25}\) and DFT methods to predict low enthalpy structures at pressures of 83 GPa, 150 GPa and 200 GPa. An ensemble of random structures with reasonable volumes was generated, subject to constraints on the minimum initial distances.
between atoms and on the symmetries of the structures. Each of these structures was relaxed to their local minimum in enthalpy; see the Methods for more information.

Combining experimental and theoretical approaches has enabled us to synthesize and identify two xenon oxide structures at high pressures: \( \text{Xe}_2\text{O}_2 \) (as predicted in Ref. 20) and the new \( \text{Xe}_2\text{O}_5 \).

**Results**

**Oxygen-rich systems.**

Above \( \sim 77 \text{ GPa} \), a reaction was observed under laser heating of Xe-O mixtures with an \( \text{O}_2 \) content higher than 50 mol.% that led to a single product (1), which was characterized by PXRD, XAS and Raman spectroscopies.

The PXRD pattern of product 1 recorded around 83 GPa (Fig. 1a) did not correspond to any of the xenon oxides that have previously been predicted\(^{18-20} \). This pattern was indexed by a tetragonal cell of volume \( V = 247.3 \text{ Å}^3 \), and showed a minor amount of unreacted Xe. The PXRD intensities enabled the determination of the approximate atomic positions of the xenon atoms in the tetragonal cell, but not the precise number and positions of the oxygen atoms because of the low atomic scattering power of oxygen relative to xenon.

Characterization of 1 by XAS at the Xe K-edge showed the presence of Xe-O bonds. XAS near edge spectra of the sample compressed to 82 GPa are presented in Fig. 2a. Fig. 2b shows the extended X-ray absorption fine structure oscillations due to the local environment around the Xe atoms, and Fig. 2c shows their Fourier transform for the heated sample. A simple two shell model including only one Xe-O and one Xe-Xe coordination shell provides a good fit to the data, with 3.0±0.5 oxygen atoms and 5.0±0.6 xenon atoms at separations of 1.93 Å and 3.165 Å, respectively. We saw no evidence for contamination by unreacted xenon of the XAS spectra, and the absence of xenon was further confirmed by PXRD data taken on the same spot (see the Supplementary Information).

To identify the structure of xenon oxide 1, we first used \textit{ab initio} random structure searching (AIRSS) to determine the lowest-enthalpy structures of simple Xe-O stoichiometries — such as Xe, \( \text{Xe}_2\text{O} \), \( \text{XeO} \), \( \text{XeO}_2 \), \( \text{XeO}_3 \), and \( \text{O} \) — and their cell volumes at 83 GPa. We then added together simple stoichiometries, such as \( \text{XeO}_2+2\text{XeO} = \text{Xe}_2\text{O}_4 \). Multiplication by a suitable integer (e.g., \( 3\text{XeO}_2 \)) then provided cell volumes that were compared with the experimental unit cell volume of 1. A close match between theoretical and experimental cell volumes suggests a reasonable candidate structure, which is then checked against the available experimental data (PXRD, XAS and Raman spectroscopy). After several trials, we found that \( 4(\text{XeO}_2+\text{XeO}_2) = 4\text{Xe}_2\text{O}_5 \) provided a good match to the experimental unit cell volume of the xenon oxide. We then used AIRSS with the unit cell constrained to experiment to find the lowest-enthalpy structure of stoichiometry \( \text{Xe}_2\text{O}_5 \) with four formula units per cell. This procedure led us to a \( P4/ncc \) structure that, crucially, was found to have the lowest enthalpy with this stoichiometry (see Supplementary Fig. S2).
Simulated PXRD and XAS data for this theoretical Xe$_2$O$_5$ structure were in good agreement with the experimental data of 1 (see Figs. 1 and 2). The Raman spectrum of 1 was collected at 88 GPa (Fig. 3) and on subsequent pressure decrease (Supplementary Fig. S3). The Raman frequencies and intensities calculated at the same volume in Xe$_2$O$_5$ correctly reproduce this experimental spectrum, although all Raman frequencies are slightly lower (by ~4 \%) than in the experimental spectrum of product 1, which suggests that the bond strength is underestimated in the calculations. The bulk modulus predicted by DFT calculations at this volume (313 GPa, in contrast to the experimentally measured value of 440 GPa, see Table I) further supports this interpretation, and the DFT and experimental data therefore provide strong evidence that the synthesized compound 1 is that of Xe$_2$O$_5$ adopting a $P4/ncc$ structure.

The theoretical structure of Xe$_2$O$_5$ at 83 GPa is illustrated in Fig. 4a. It consists of a three-dimensional framework of corner-sharing XeO$_4$ squares with an Xe-O distance of 1.98 Å. Every second Xe atom bonds with a fifth O atom (Xe-O distance 1.83 Å), forming a XeO$_5$ square pyramid with the Xe atom being slightly below the base of the pyramid. These two similar Xe-O distances could not be resolved in the XAS data and appear as a single (average) Xe-O shell at 1.93Å. Such local geometries have been reported in molecules or solids containing oxidized xenon. This suggests the presence of Xe$^{4+}$ and O$^{2-}$ in XeO$_5$ units (as in XeO$_5$)$^6$ and Xe$^{6+}$ and O$^{2-}$ in XeO$_5$ units (as in [XeF$_5$]$^+$[PtF$_6$]$^-$) $^{26}$. The minimum Xe-Xe distance is 3.19 Å, in agreement with the XAS data, and adjacent xenon atoms are connected by a single oxygen atom. Table I gives the lattice parameters and interatomic separations determined by experiment and DFT.

The experimental density of Xe$_2$O$_5$ is 14\% higher than that of a mixture of xenon$^8$ and O$_2$$^{27}$ with the same stoichiometry and under the same pressure. Xe$_2$O$_5$ thus allows an efficient packing of xenon and oxygen atoms. Oxidation states of the Xe atoms determined using Mulliken, Bader and Hirshfeld charge density analyses$^{28-30}$ are consistent and confirm the oxidation states of +4 or +6 for Xe atoms in Fig. 4a (see Supplementary Table SIII). Xe atoms connected to each other via an oxygen atom have different oxidation states. The shortest distance between a Xe$^{6+}$ ion and the four nearest oxygen atoms not bonded to it is only 2.29 Å (in contrast, for Xe$^{4+}$ this distance is 2.49 Å). This small interatomic separation suggests a weak attraction between these atoms, as in [XeF$_5$]$^+$[PtF$_6$]$^-$ $^{26}$.

The Raman and PXRD data show that the Xe$_2$O$_5$ crystal 1 is metastable down to $\approx$30 GPa (see Supplementary Figs. S3 and S4), and becomes amorphous at lower pressures. However, the Xe-O bonding still remains after pressure release: a Raman mode with a frequency similar to metastable XeO$_4$ $^{31}$ or XeO$_5$ $^{32}$ was recorded at 0 GPa before the diamond anvil cell was opened (Supplementary Fig. S3). The equation of state of Xe$_2$O$_5$ synthesized at 93 GPa was measured under a pressure increase to 99 GPa and subsequent decrease to 30 GPa (Supplementary Fig. S4). It agrees well with the equation of state predicted by DFT, see Table I. Around 80 GPa, the bulk modulus (resistance to compression) of Xe$_2$O$_5$ is approximately 50\% higher than that of pure xenon, indicating strong bonding.
Oxygen-poor systems.

Another xenon oxide, with a lower oxygen content than \( \text{Xe}_2\text{O}_5 \), was also predicted by AIRSS to be stable at high pressures: \( \text{Xe}_3\text{O}_2 \) with an orthorhombic \( \text{Immm} \) structure. These calculations support the prediction of this phase made independently in Ref. 20. In order to investigate the existence of this compound experimentally, Xe-rich Xe-O \( \text{Xe}_2 \text{O}_5 \) mixtures were compressed and heated by laser. For mixtures with an \( \text{O}_2 \) content lower than 25 mol.% a compound 2 was obtained that was indeed shown by PXRD to be \( \text{Xe}_3\text{O}_2 \). Apart from one intense extraneous peak, the Raman spectrum collected for 2 is in agreement with the predicted one for \( \text{Xe}_3\text{O}_2 \) (Fig. 3), which coexists with both Xe and \( \text{Xe}_2\text{O}_5 \) — even for the mixture containing only 11% \( \text{O}_2 \) (Fig. 1), in contrast to the expected mixture of \( \text{Xe}_3\text{O}_2 \) and xenon. This may be due to the presence of an oxygen-rich \( \text{Xe}(\text{O}_2) \) phase in the starting mixture (see Methods). The measured cell volume of \( \text{Xe}_3\text{O}_2 \) was 131.5 Å\(^3\)/2 formula units at 97 GPa, which is 8% denser than a mixture of xenon and \( \text{O}_2 \) at the same pressure.

The structure of \( \text{Xe}_3\text{O}_2 \) obtained with AIRSS is shown in Fig. 4b. \( \text{Xe}_3\text{O}_2 \) contains planar chains of \( \text{XeO}_4 \) squares parallel to the \( b \) axis, sharing oxygen corners as in the structure proposed for \( \text{XeO}_2 \)\(^6\). This suggests a +4 oxidation state for these Xe atoms, bridged by four \( \text{O}^2- \) ions and forming a fully saturated network of \( \text{XeO}_2 \) stoichiometry. This is confirmed by charge density analysis (see Supplementary Table SIV). The layers of \( \text{XeO}_4 \) chains are intercalated with xenon layers, which are found to be unoxidized. As expected from the structure, the \( b \) axis parallel to the strong Xe-O chains undergoes less compression under pressure than the \( a \) and \( c \) axes (Supplementary Fig. S4). There is good agreement between the experimental and DFT values of the lattice parameters and interatomic distances of \( \text{Xe}_3\text{O}_2 \) at 97 GPa, which are summarized in Table I. The \( \text{Xe}^0-\text{Xe}^0 \) and \( \text{Xe}^0-\text{Xe}^{4+} \) distances are comparable to the Xe-Xe distance in pure xenon (3.03 Å)\(^8\) at the same pressure. In Ref. 20, a small transfer of charge between \( \text{Xe}^0 \) and \( \text{Xe}^{4+} \) was calculated and interpreted as stabilizing this mixed valence compound, and our calculations support this analysis.

A \( \text{Xe}_2\text{O} \) oxide with a \( C2/m \) structure has been predicted by DFT searches\(^20\) and confirmed by the current calculations to be stable at high pressure. Indeed, several xenon-rich structures predicted by DFT searches to be stable or close to stability, both previously\(^20\) and in this study, are closely related to \( \text{Xe}_3\text{O}_2 \), but with larger fractions of intercalated Xe atoms, see Fig. S2. In the present experiments, we did not observe any evidence from PXRD for the synthesis of the \( \text{Xe}_2\text{O}-C2/m \) phase.

\( \text{Xe}_2\text{O}_2 \) was found to be metastable down to \( \sim 38 \) GPa before amorphisation. Our DFT calculations predict that \( \text{Xe}_2\text{O}-C2/m \) is stable above 65 GPa, and \( \text{Xe}_3\text{O}_2 \) above 66 GPa. The equation of state of \( \text{Xe}_3\text{O}_2 \) measured on pressure decrease is in good agreement with DFT close to the synthesis pressure (see Supplementary Fig. S4). The measured bulk moduli of \( \text{Xe}_3\text{O}_2 \), in which 2/3 of the xenon atoms are unoxidized, and pure Xe are similar at high pressures. The bulk modulus of \( \text{Xe}_3\text{O}_2 \) at 97 GPa is about double that of \( \text{Xe}_2\text{O}_2 \) at 83GPa, which is compatible with stronger inter-atomic bonding in \( \text{Xe}_3\text{O}_2 \).
Discussion

Enthalpies of formation per atom of the most stable structures found in the searches are plotted against the fraction $x$ of O atoms on a convex hull diagram in Fig. 5. Structures on the hull indicated by filled circles are stable. $\text{Xe}_3\text{O}_2$, $\text{Xe}_2\text{O}_3$ and $\text{Xe}_2\text{O}$ were found to be stable compounds at around 1 Mbar. The substantial differences between the hull plots in Fig. 5 and those of Refs. 19 and 20, which are directly compared in Supplementary Fig. S1, arise from two main sources.

(1) We have searched over 17 stoichiometries (not including pure Xe and O, see Supplementary Fig. S2) to identify possible stable structures with up to 28 atoms in the primitive unit cell, which involved relaxing about $10^5$ structures. Zhu et al.\textsuperscript{19} considered 4 stoichiometries ($\text{XeO}$, $\text{XeO}_2$, $\text{XeO}_3$ and $\text{XeO}_4$), but for each of their predicted structures we found either a lower-enthalpy structure or that the structure was unstable to decomposition into compounds on the convex hull with other stoichiometries. The searches in Ref. 20 were conducted over 8 stoichiometries, which included $\text{Xe}_3\text{O}_2$, which they correctly found to be stable, although they did not consider $\text{Xe}_2\text{O}_3$.

(2) In Refs. 19 and 20 a pseudopotential was used to describe the Xe 4$d$ orbitals. However, this approximation is inaccurate for xenon oxides and pure Xe at high pressures because of the spatial overlap of the Xe 4$d$ orbitals and the higher energy 5$s$ and 5$p$ Xe orbitals, see Supplementary Figs. S5 and S6. For example, calculations for $\text{Xe}_2\text{O}_5$ give an enthalpy of formation from the elemental solids at 83 GPa of -0.37 eV per atom, but only -0.05 eV when the 4$d$ orbitals are described by the pseudopotential, see Supplementary Fig. S7.

The densities of electronic states show substantial transfer of charge from Xe to O atoms in $\text{Xe}_2\text{O}_5$, which suggests strong ionic Xe-O bonding, see Supplementary Figs. S11 and S13. The transfer of charge from Xe to O in $\text{Xe}_2\text{O}_3$ is quite small, which is consistent with the observation that 2/3 of the Xe atoms are in the zero oxidation state.

The electronic band structure of $\text{Xe}_2\text{O}_5$ at 83 GPa is shown in Fig. 6. Band structures and densities of states of the other structures predicted to be stable in some pressure range are provided in Supplementary Figs. S12, S14 and S15. The occupied valence bands of $\text{Xe}_2\text{O}_5$ are divided into an upper part arising from the oxygen 2$p$ and xenon 5$p$ levels with a width of approximately 12 eV, and a lower part from the oxygen 2$s$ and xenon 5$s$ levels with a width of approximately 15 eV. The Xe 4$d$ bands are almost dispersionless and lie at about 60 eV below the highest occupied orbitals, and are not directly involved in chemical bonding.

Using the Perdew–Burke–Ernzerhof (PBE) semi-local density functional\textsuperscript{33}, $\text{Xe}_2\text{O}_5$ was predicted to be an insulator with a band gap of 1.48 eV at 83 GPa, while $\text{Xe}_3\text{O}_2$ was predicted to be semi-metallic with a very low density of states at the Fermi energy (see Supplementary Fig. S12). We also calculated the band gap of $\text{Xe}_3\text{O}_2$ using the HSE06 screened Coulomb functional\textsuperscript{34}, which normally gives larger and more accurate band gaps than PBE. A minimum band gap of about 0.05 eV was found with the HSE06 functional, which is close to the value.
reported in Ref. 20 and suggests that Xe$_2$O$_3$ is a small band gap semiconductor at 83 GPa. Table II provides more information on the calculated band gaps of these xenon oxides.

DFT calculations were performed at higher pressures to investigate the evolution of the convex hull with compression (see Supplementary Table SII). We found the previously unreported phases XeO$_3$-P2$_1$2$_1$2$_1$ and XeO$_2$-Pnma, which become stable above around 131 GPa and 186 GPa, respectively. At about 191 GPa, Xe$_2$O becomes unstable to decomposition into Xe$_2$O$_2$ and Xe; around 197 GPa, Xe$_3$O$_2$ is predicted to decompose into a mixture of XeO$_2$ and XeO$_3$. These phases are depicted in Supplementary Figs. S8 and S9. The structural parameters of these phases are provided in Supplementary Table SV and bandstructures are given in Supplementary Table SVI and Supplementary Figs. S14 and S15. XeO$_3$ is an extended structure with all Xe atoms in a +6 oxidation state. XeO$_2$ consists of distorted versions of the XeO$_2$ chains found in Xe$_3$O$_2$. Both of these structures are more compact than Xe$_2$O$_5$, contributing to their greater stability at higher pressures.

The need for laser heating to induce chemical reactions in Xe-O$_2$ mixtures and the observation that Xe$_2$O$_5$ (Xe$_3$O$_2$) is metastable down to 30 GPa (38 GPa) implies the existence of substantial kinetic barriers between phases. The stability of the xenon oxides is found to increase substantially with pressure, see Fig. 5. The relative stabilities of phases are not expected to be altered significantly by heating to 3000 K.

In summary, we have synthesized two oxides, Xe$_2$O$_2$ and Xe$_2$O$_5$, in laser-heated diamond anvil cells. 

Methods

**Experimental procedures.** Membrane diamond anvil cells were loaded at room temperature with xenon-oxygen mixtures (with a composition determined using O$_2$ and Xe equations of state) in a high-pressure vessel. The mixtures were homogenized in the vessel over 12 hours before loading. After loading, the pressure was increased to 10 GPa and the sample was characterized with Raman spectroscopy. The crystallization of Xe-O$_2$ mixtures under pressure leads to three different solid phases (Xe with O$_2$ impurities, Xe(O$_2$)$_2$ and pure O$_2$). The diamond anvil cell was heated at 420 K for several hours to reduce compositional heterogeneities in the sample chamber. The pressure was then increased to the required value, and the sample was laser-heated for a few minutes at the centre of the sample chamber, on one or both sides. The temperature was estimated to be above 2000 K. The sample was characterized before and after heating with X-ray diffraction (PXRD), X-ray absorption spectroscopy (XAS) and/or Raman spectroscopy (see Supplementary Table SI). The reacted
zone was detected by mapping PXRD or XAS spectra (see Supplementary Fig. S16). In one run, the rhenium gasket was isolated from the sample chamber by a gold ring in order to verify that rhenium did not participate in the chemical reactions.

PXRD experiments were performed on the ID27 beamline of the European synchrotron Radiation Facility, ESRF. The angular dispersive (λ=0.3738 Å) XRD patterns were collected on a MARE345 or a MAR-CCD detector, located at a distance of ∼300 mm from the sample. The X-ray beam was focused by two Kirkpatrick-Baez mirrors and cleaned by two pinholes to a 2×2.7 μm full width at half maximum (FWHM) spot on the sample. PXRD spectra were treated using the Fit2d software and the crystal structure and Xe positions in Xe₂O₅ were determined using Dicvol and Fox software. XAS experiments were performed on the BM23 beamline of the ESRF, at the K-edge of xenon (34.561 keV) calibrated using gaseous xenon. The beam was focused to 4×4 μm² FWHM using a pair of Kirkpatrick-Baez mirrors. We used nano-polycrystalline diamond anvils, which do not create any XAS parasitic signal due to Bragg diffraction. A high quality spectrum was recorded in a wide range in the reciprocal space (kₓₓ = 18 Å⁻¹) which enabled a detailed quantitative analysis of the near-neighbour shells of Xe in the direct space. The XAS spectra were analysed with the Athena and Artemis softwares to determine the local structure around xenon atoms. PXRD was also performed on BM23. On ID27 and BM23, the pressure was measured using the PXRD signal from unreacted xenon or a gold pressure marker placed at the edge of the sample chamber and their ambient temperature equations of state were checked with the rhenium gasket PXRD signal and equation of state. For the Raman measurements, the pressure was obtained using the high-frequency Raman edge of the diamond anvil.

**Ab initio calculations.** We used the CASTEP planewave DFT code with ultrasoft pseudopotentials (4d⁰ 5s² 5p⁶ and 2s² 2p⁶ electrons treated as valence for Xe and O, respectively), for all except the Raman intensity calculations for Xe₂O₅ and the HSE06 calculations, for which norm-conserving pseudopotentials (with Xe 5s² 5p⁶ and O 2s² 2p⁶ electrons treated as valence) were used. A plane-wave basis set energy cutoff of 400 eV was used for the structure searches, and a cutoff of 700 eV was used for the final converged results reported in our paper. We employed the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) density functional for the calculations, except for the calculation of the band gap of Xe₂O₅ with the HSE06 functional. The Brillouin zone was sampled using a k-point grid of spacing 2π×0.07 Å⁻¹ for the structure searches, and a finer spacing of 2π×0.03 Å⁻¹ for the final converged results.

We used AIRSS to search for low-enthalpy structures over a wide range of stoichiometries. Within the basic AIRSS approach a cell volume and shape is selected at random within a reasonable range, atoms are added at random positions to provide the desired stoichiometry, and the system is relaxed until the forces on the atoms are negligible and the pressure takes the required value. Repeating this procedure provides a relatively sparse sampling of the “structure space”. We constrained the minimum separations between atomic pairs (Xe–Xe, Xe–O, O–O) in the initial structures, which helps to space out the atoms appropriately, while retaining a high degree of randomness. We performed searches with various different symmetry constraints, which is useful because low energy structures often possess
symmetries. In this way sampling is focused on the regions of the “structure space” in which chemical intuition suggests that the lowest-enthalpy structures are likely to be found.

Images of structures were generated using VESTA. PXRD patterns were calculated using PowderCell. Densities of electronic states were calculated using OptaDOS.

**Acknowledgements.** The authors acknowledge the European Synchrotron Radiation Facility for provision of beamtime under proposals HS-4067 and HC-767. Financial support was provided by the Engineering and Physical Sciences Research Council (EPSRC) of the UK [EP/J017639/1]. Computational resources were provided by the High Performance Computing Service at the University of Cambridge and the Archer facility of the UK’s national high-performance computing service, for which access was obtained via the UKCP consortium [EP/K014560/1]. C.J.P. is supported by the Royal Society through a Royal Society Wolfson Research Merit Award. Nano-polycrystalline diamond anvils were prepared based on JSPS grants (No. 25220712 and No.15H05829) to T.I. We thank M. Hanfland for use of his laser heating setup, and Paul Loubeyre, Stéphane Mazevet, Chrystèle Sanloup, and John Trail for helpful discussions.

**Author contributions.** A.D. proposed the research; A.D. and R.J.N. coordinated the research. A.D. performed the experiments with the help of O.M. and M.M. at the synchrotron source. T.I. provided the nanopolycrystalline diamond anvils. A.D. and S.P. analysed experimental data. N.W. and C.J.P. performed the theoretical and computational work. R.J.N., A.D. and N.W. wrote the paper. All authors commented on the manuscript.


TABLE I: Comparison of experimental and theoretical properties of Xe$_2$O$_5$ and Xe$_3$O$_2$.
Experimental lattice constants were obtained from the PXRD data. Experimental interatomic distances were obtained using the structures from AIRSS and the experimental lattice constants. Lattice parameters and bond lengths are given at 83 GPa for Xe$_2$O$_5$ and at 97 GPa for Xe$_3$O$_2$. $V_0$ and $K_0$ denote the zero-pressure volume and bulk modulus obtained with a Rydberg-Vinet fit of $P–V$ data plotted in Supplementary Fig. S4. The error bars correspond to a 95% confidence level.

<table>
<thead>
<tr>
<th></th>
<th>Xe$_2$O$_5$</th>
<th>Experimental</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameter $a$ (Å)</td>
<td>4.980</td>
<td>4.978</td>
<td></td>
</tr>
<tr>
<td>Lattice parameter $c$ (Å)</td>
<td>9.970</td>
<td>9.951</td>
<td></td>
</tr>
<tr>
<td>Volume ($Å^3$/4 f.u.)</td>
<td>247.3</td>
<td>246.6</td>
<td></td>
</tr>
<tr>
<td>Bond Xe$^{6+}$-O(1) (Å)</td>
<td>1.83</td>
<td>1.83</td>
<td></td>
</tr>
<tr>
<td>Bond Xe$^{6+}$-O(2) (Å)</td>
<td>1.97</td>
<td>1.97</td>
<td></td>
</tr>
<tr>
<td>Bond Xe$^{4+}$-O (Å)</td>
<td>1.98</td>
<td>1.98</td>
<td></td>
</tr>
<tr>
<td>Bond Xe$^{6+}$-Xe$^{4+}$ (Å)</td>
<td>3.19</td>
<td>3.19</td>
<td></td>
</tr>
<tr>
<td>Rydberg-Vinet $V_0$ ($Å^3$/4 f.u.)</td>
<td>337.2±6</td>
<td>332.8±2.4</td>
<td></td>
</tr>
<tr>
<td>Rydberg-Vinet $K_0$ (GPa)</td>
<td>150±20</td>
<td>161±6</td>
<td></td>
</tr>
<tr>
<td>Rydberg-Vinet $K'_0$ (GPa)</td>
<td>4 (fixed)</td>
<td>4 (fixed)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Xe$_3$O$_2$</th>
<th>Experimental</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameter $a$ (Å)</td>
<td>8.457</td>
<td>8.388</td>
<td></td>
</tr>
<tr>
<td>Lattice parameter $b$ (Å)</td>
<td>3.166</td>
<td>3.195</td>
<td></td>
</tr>
<tr>
<td>Lattice parameter $c$ (Å)</td>
<td>4.904</td>
<td>4.880</td>
<td></td>
</tr>
<tr>
<td>Volume ($Å^3$/2 f.u.)</td>
<td>131.3</td>
<td>130.8</td>
<td></td>
</tr>
<tr>
<td>Bond Xe$^{4+}$-O (Å)</td>
<td>1.99</td>
<td>2.01</td>
<td></td>
</tr>
<tr>
<td>Bond Xe$^{4+}$-Xe$^{4+}$ (Å)</td>
<td>3.17</td>
<td>3.19</td>
<td></td>
</tr>
<tr>
<td>Bond Xe$^{0}$-Xe$^{6+}$ (Å)</td>
<td>3.06</td>
<td>3.05</td>
<td></td>
</tr>
<tr>
<td>Bond Xe$^{6+}$-Xe$^{0}$ (Å)</td>
<td>2.96-3.01</td>
<td>2.95-3.00</td>
<td></td>
</tr>
<tr>
<td>Rydberg-Vinet $V_0$ ($Å^3$/2 f.u.)</td>
<td>262±15</td>
<td>217.8±2.4</td>
<td></td>
</tr>
<tr>
<td>Rydberg-Vinet $K_0$ (GPa)</td>
<td>37.2±8</td>
<td>74.5±4</td>
<td></td>
</tr>
<tr>
<td>Rydberg-Vinet $K'_0$ (GPa)</td>
<td>4 (fixed)</td>
<td>4 (fixed)</td>
<td></td>
</tr>
</tbody>
</table>

TABLE II: Minimum (thermal) and minimum direct (optical) band gaps in eV calculated with the PBE exchange-correlation functional.

(a) Minimum band gap

<table>
<thead>
<tr>
<th>Structure</th>
<th>Pressure (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>83</td>
</tr>
<tr>
<td>Xe$_2$O$_5$-P4/ncc</td>
<td>1.48</td>
</tr>
<tr>
<td>Xe$_3$O$_2$-Immm</td>
<td>0.00</td>
</tr>
</tbody>
</table>

(b) Minimum direct band gap

<table>
<thead>
<tr>
<th>Structure</th>
<th>Pressure (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>83</td>
</tr>
<tr>
<td>Xe$_2$O$_5$-P4/ncc</td>
<td>1.80</td>
</tr>
<tr>
<td>Xe$_3$O$_2$-Immm</td>
<td>0.01</td>
</tr>
</tbody>
</table>
FIG. 1: X-ray diffraction patterns of Xe–O\textsubscript{2} mixtures under pressure. a, b X-ray diffraction patterns of a 33\% Xe–67\% O\textsubscript{2} mixture at about 83 GPa (a) and of a 89\% Xe–11\% O\textsubscript{2} mixture at about 97 GPa (b). The insets show the two-dimensional patterns before circular integration. Prior to laser-heating, the phases were Xe with O\textsubscript{2} impurities and partially amorphized Xe(O\textsubscript{2})\textsubscript{2} in both mixtures. After laser-heating, the phases consist of mostly Xe\textsubscript{2}O\textsubscript{5} (a) and Xe\textsubscript{3}O\textsubscript{5} and Xe\textsubscript{2}O\textsubscript{5} (b), in addition to the reactants. The light blue and purple ticks indicate the positions and predicted relative intensities of the diffraction peaks of Xe\textsubscript{2}O\textsubscript{5} and Xe\textsubscript{3}O\textsubscript{5}, respectively (lattice parameters in Table I). The most intense xenon diffraction peaks have been masked during integration. In both experiments, the Xe PXRD lines (red ticks) are split after laser-heating, which we interpret as arising from a variable content of O\textsubscript{2} impurities.
FIG. 2: Xe K-edge X-ray absorption spectra (XAS) of a 36% Xe – 64% O₂ mixture at about 82 GPa. a, Raw spectra. After heating, a strong absorption line appears at the Xe K-edge absorption onset (around 34.6 keV) at the centre of the laser-heated area, indicating depletion of the 5p states of Xe just above the Fermi level due to oxidation. b, Extended X-ray absorption fine structure function $\chi(k)$, weighted by $k^2$ (where $k$ is the photoelectron wavenumber), extracted from the XAS spectrum after laser-heating (blue: data; dashed green: 2-shell fit; red: fit assuming the Xe₂O₆-P4/ncc structure). c, $|\chi(R)|$ (Å⁻³) amplitude of the Fourier transform of this function (same colours as in b). The two intense peaks reflect the presence of two distinct distances with neighbours around xenon atoms. The abscissa has been rigidly shifted by 0.33 Å to account for the photoelectron scattering phase shift.
FIG. 3: Raman spectra of Xe$_2$O$_5$ and Xe$_3$O$_2$. Raman signals measured for Xe$_2$O$_5$ and Xe$_3$O$_2$ at 88 GPa and 97 GPa, respectively. Peak frequencies have been calculated for Xe$_2$O$_5$ and Xe$_3$O$_2$ at their experimental cell volumes and are plotted as red and green ticks, respectively. Peak intensities have also been calculated for Xe$_2$O$_5$. When the frequencies calculated for Xe$_2$O$_5$ are increased by 4% (bold red ticks), they agree with the measured ones to within ±15 cm$^{-1}$. 

Calculated Raman frequencies:
- Xe$_2$O$_5$; frequencies x1.04
- Xe$_3$O$_2$
FIG. 4: Structures of the stable xenon oxides at 83 GPa. a, Xe$_2$O$_5$ and b, Xe$_3$O$_2$. Xenon atoms are shown in blue shades and oxygen atoms in red shades. The oxygen atoms have an oxidation state of -2, and the darker shade of red indicates an oxygen atom that bonds only to one xenon atom. The oxidation states of the xenon atoms are indicated by different shades of blue. The lightest blue indicates 0 oxidation state, the medium shade +4 and the darkest blue the +6 oxidation state. The xenon atoms in Xe$_2$O$_5$ and Xe$_3$O$_2$ exist in two different oxidation states within each structure, +4 and +6 in Xe$_2$O$_5$ and 0 and +4 in Xe$_3$O$_2$. 
FIG. 5: Convex hull diagram for xenon oxides showing calculated enthalpies of formation per atom from the elements for the predicted stable phases. For a structure of stoichiometry $\text{Xe}_m\text{O}_n$, the enthalpy of formation per atom is given by $\Delta H_f(\text{Xe}_m\text{O}_n) = \frac{H(\text{Xe}_m\text{O}_n) - (mH(\text{Xe}) + nH(\text{O}))}{(m+n)}$, where $H$ denotes the enthalpy of each formula unit under the relevant pressure. The three convex hulls shown are for 83 GPa (green), 150 GPa (red), and 200 GPa (blue). Each coloured circle denotes a structure that is stable against decomposition. The coloured lines joining the enthalpies of the stable structures denote the convex hull.
FIG. 6: Bandstructure and electronic density of states of Xe$_2$O$_5$ at 83 GPa. The electronic bands are shown in blue and the Fermi level is shown as a horizontal black dashed line. The orange line shows the $d$ electron density of states (rescaled to fit on the axes), the red shows the $s$ density of states, and the green shows the $p$ density of states. Note the appearance of a band gap and that the $d$ levels are about 30 eV below the $s$ bands.