Supporting information for article:

Crystal structure of monoclinic hafnia (HfO2) revisited from synchrotron X-ray, neutron diffraction and first-principles

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Supporting Information

We have given here the necessary supporting data with following content:

Content: Section S1: Diffraction pattern of calibrant LaB_6

Section S2: Density functional theory

Section S1: Diffraction pattern of calibrant LaB_6

The sample to detector geometry was determined using the diffraction pattern of standard sample of Lanthanum Hexaboride (LaB_6). Integration of the 2D diffraction patterns to I-2θ plots were carried out using this calibration. The integrated pattern of the calibrant LaB_6 is shown in **Fig. S1**.
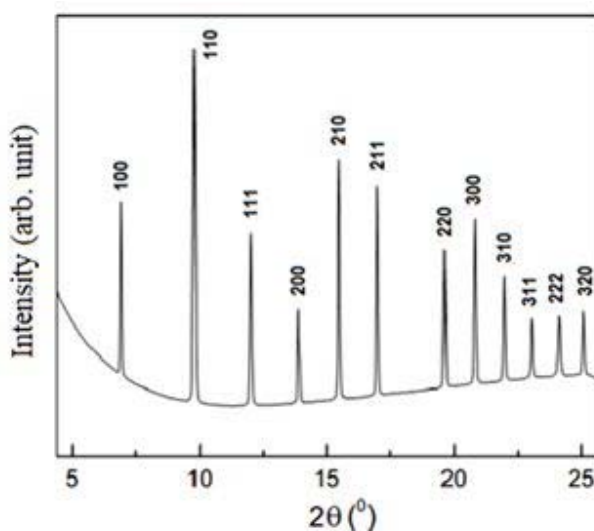

Figure S1 Integrated I-2θ diffraction plot of calibrant LaB_6 in Xpress beamline (λ= 0.5007 Å).

Section S2: Density Functional Theory

All calculations for electronic structure analysis are done based on the CRYSTAL17 programme, as discussed earlier. For O atoms, we opted the all electron basis-sets (Scaranto *et al.*, 2008), whereas for Hf atom empirical core potential basis sets were adopted (Muñoz-Ramo *et al.*, 2007a) due to their robustness which is validated in the previous reports (Muñoz-Ramo *et al.*, 2007b).Coulomb and exchange integrals cut-off during the self-consistent field (SCF) calculations was chosen to 10^{-8} for coulomb overlap tolerance, coulomb penetration tolerance, exchange overlap tolerance, exchange pseudo overlap in direct space and 10^{-16} for exchange pseudo overlap in reciprocal space. The SCF calculation was considered converged when

the difference in energy between two subsequent cycles is lower than 10^{-8} au. The k-mesh was set with a shrinking factor 8 using Pack-Monkhorst methods. During the structural relaxation (both cell volume and lattice position relaxed), the force convergence cut-off was set to 10^{-7}. We have used the Generalized Gradient Approximation (GGA) of the exchange correlation as proposed by Perdew, Ernzerhof and Bruke, so called PBE-GGA functional (Perdew *et al.*, 1996). This latter B3LYP type functional combines the LYP exchange-correlation functional, including 20% Fock exchange i.e. so called B3LYP hybrid functional (Becke, 1993). However, in the HSE06 functional, the Fock exchange is 25%, along with the PBE-GGA exchange and correlation.

All electron full potentials calculations are done with the plane-wave WIEN2K Code (Blaha *et al.*, 2019) and the hybrid calculations (TB-mBJ) Modified Becke-Johnson (mBJ) exchange correlation potential proposed by Tran & Blaha, 2009 as implemented in the WIEN2K code. From the PBE-GGA ground state wave function using $6 \times 6 \times 6$ *k*-mesh and tetrahedron method, the TB-mBJ calculations were performed on the top. The energy and charge convergence were ensured during the self-consistent run using convergence criteria 10^{-8} au and 10^{-6}, respectively. The plane-wave cut-off of 600 eV was ensured with largest muffin-tin radius multiplied with K_{max} value yields 8.0.
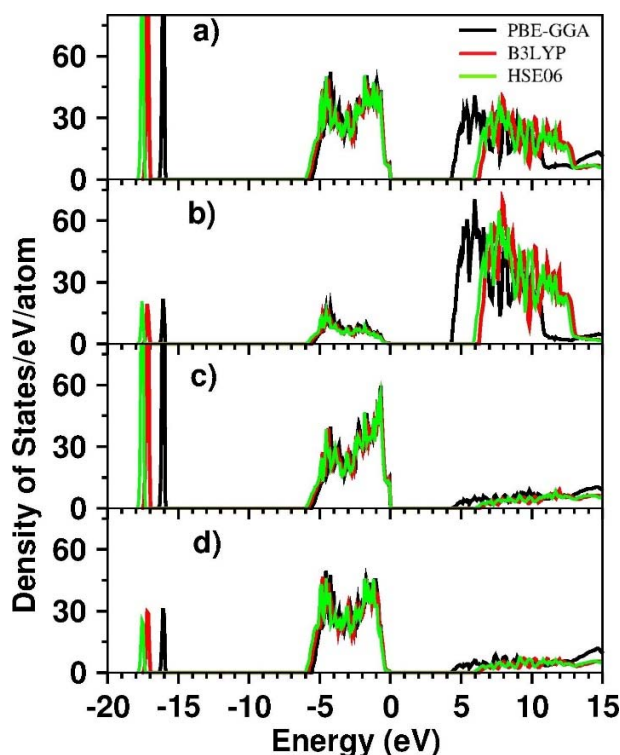

Figure S2 **(a)** Calculated total density of states (DOS), along with the atom projected DOS from **(b)** Hf, **(c)** O1 and **(d)** O2 atoms from PBE-GGA (black shade area), B3LYP (red solid line) and HSE06 (green solid line) functional based calculations.

References

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