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# Supplementary Information: High ionic conductivity in fluorite δ-bismuth oxide-based vertically aligned nanocomposite thin films

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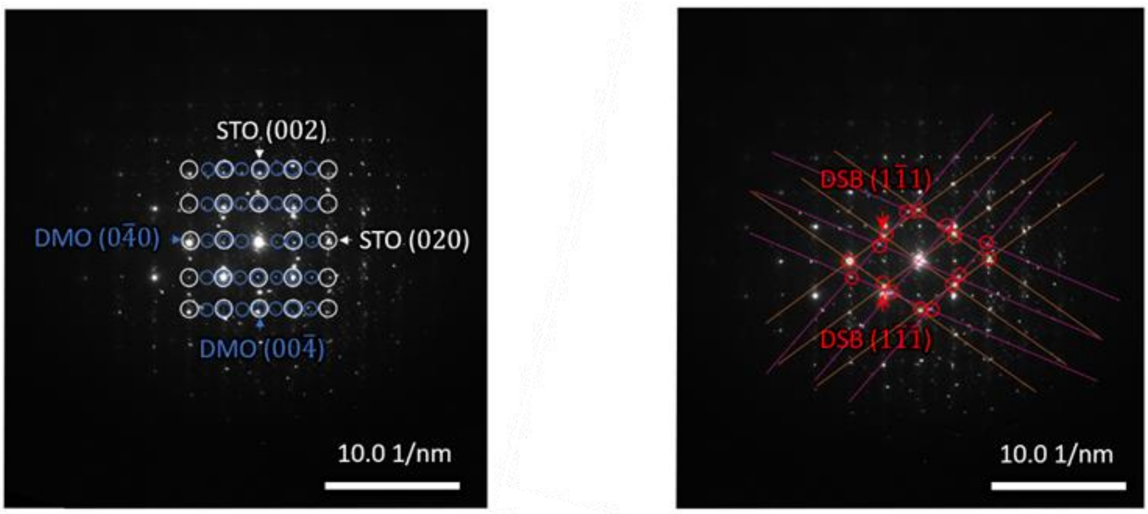


**Fig. S1** Indexed SAED pattern showing DSB, STO and DMO phases. The SAED pattern was simulated using lattice parameters of the respective phases as determined from XRD. The white, blue and red circles correspond to the STO, DMO (relaxed) and DSB diffraction dots, respectively. For DSB, the orange and magenta lines mark two different diffraction patterns for two DSB domains with a slight in-plane rotation, as expected from the broad reflection in the DMO RSM in Fig. 2d. The STO diffraction spots are marked in white. The location of the simulated DMO diffraction spots (both relaxed and strained) are marked by the blue circles. Within these blue circles, there are diffraction sports assigned to the DMO phases. However, it is challenging to separate the strained DMO and relaxed DMO from each other, and from the primary diffraction pattern since they have very similar lattice parameters, and some are overlapped by STO diffraction spots (white circles). This overlap also confirms the close matching between the DMO phase and the STO substrate.

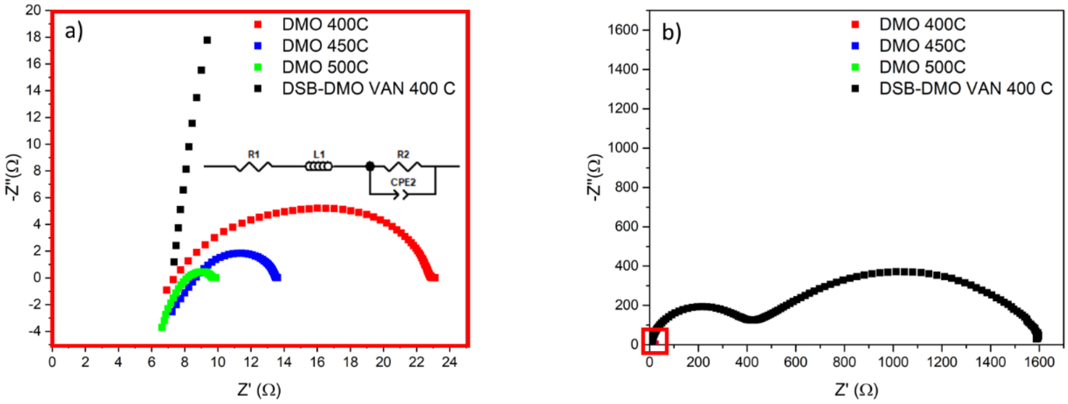


**Fig. S2** (a) Electrical Impedance spectroscopy Nyquist plots of a reference DMO planar film (Ag/Nb-STO/DMO/Pt) at selected temperatures performed with the same experimental conditions outlined in the Experimental Section (b) Nyquist plots on same scale as in Fig. 3b for reference; the red box in (b) highlights the location of the region plotted in (a).

It is clearly seen that the impedance response of this electronic conducting DMO planar system is very different to the impedance of the DSB-DMO VAN system presented in Fig. 3b. The overall impedance of this system is 2 orders of magnitude smaller than observed for the DSB-DMO VAN. The DMO planar film is well modelled by a resistor and inductor in series with an RC circuit (Fig. S2a, inset) i.e. one arc is present, very different to the DSB-DMO system where two clear arcs are observed.

This Ag/Nb-STO/DMO/Pt system also contains the Ag/Nb-STO response, and the contribution of the Nb-STO substrate. By comparison, it is clear that these contributions are also very small to the overall impedance of the system.

Inclusion of the DSB (to form the DSB-DMO VAN) clearly increases the impedance of the system, as seen in Fig. S2b. Noting the non-parallel features in the TEM, and the different EIS features, we can determine that the conduction pathway is through the ionic conducting DSB. If it were not, i.e. if it were through the DMO, the EIS features would look identical to the planar DMO EIS in Fig. S2.