Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Hexagonal perovskite derivatives: a new direction in the design of oxide ion conducting materials

Sacha Fop,*[a] Kirstie S. McCombie,[a] Eve J. Wildman,[a] Janet M. S. Skakle [a] and Abbie C. Mclaughlin [†a]

[a] Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, United Kingdom

* E-mail: sacha.fop1@abdn.ac.uk

† E-mail: a.c.mclaughlin@abdn.ac.uk

Minimum bounding ellipsoid fitting

Polyhedral distortion can be evaluated by analysis of the minimum bounding ellipsoid that comprises all the atoms of the coordination polyhedra [1]. The minimum bounding ellipsoid is defined by the following quantities:

- $R_1 \geq R_2 \geq R_3$**:** principal ellipsoid radii
- **<*R*>:** mean ellipsoid radius, related to the polyhedron size
- **σ(*R*):** ellipsoid radii standard deviation, related to the polyhedral distortion
- ***D:*** displacement vector of the central atom relative to the ellipsoid centre
- **S:** ellipsoidal shape parameter

The PIEFACE software package [1] was employed to perform the minimum ellipsoid fitting. PIEFACE fits an ellipsoid to a set of points in Cartesian coordinates. The minimum bounding ellipsoid is calculated using a Khachiyan minimisation algorithm. Typical ellipsoid fits can be seen in Fig. S1.

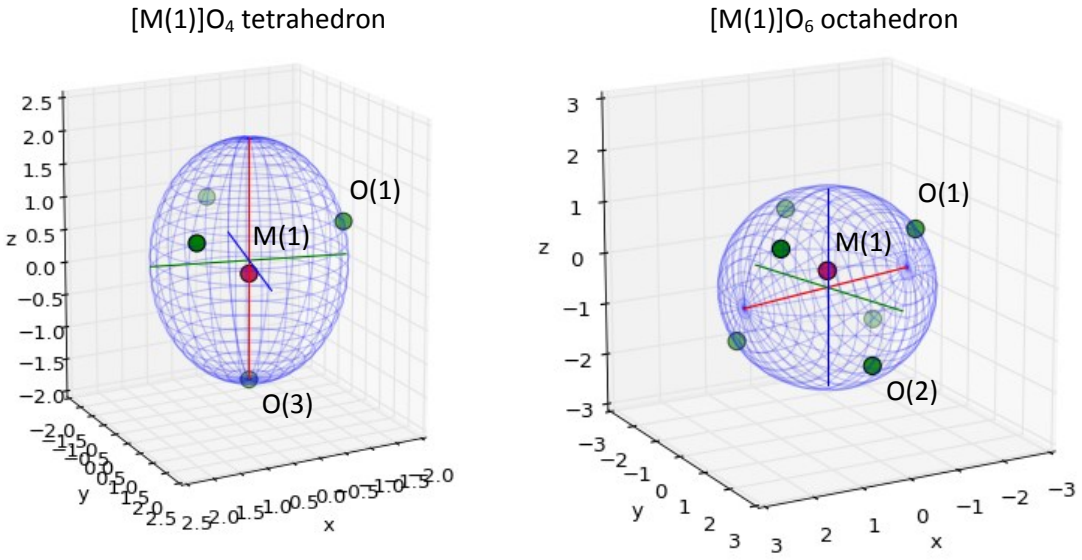

Fig. S1 Minimum bounding ellipsoid fit for the $[M(1)]O_x$ polyhedra in $Ba_3MoNbO_{8.5}$ at 25 °C.

The minimum bounding ellipsoid centre is oriented in opposite directions relative to the metal centres of the tetrahedral and octahedral units, thus resulting in displacement values with opposite signs for the two polyhedra (see Fig.9 in main article).

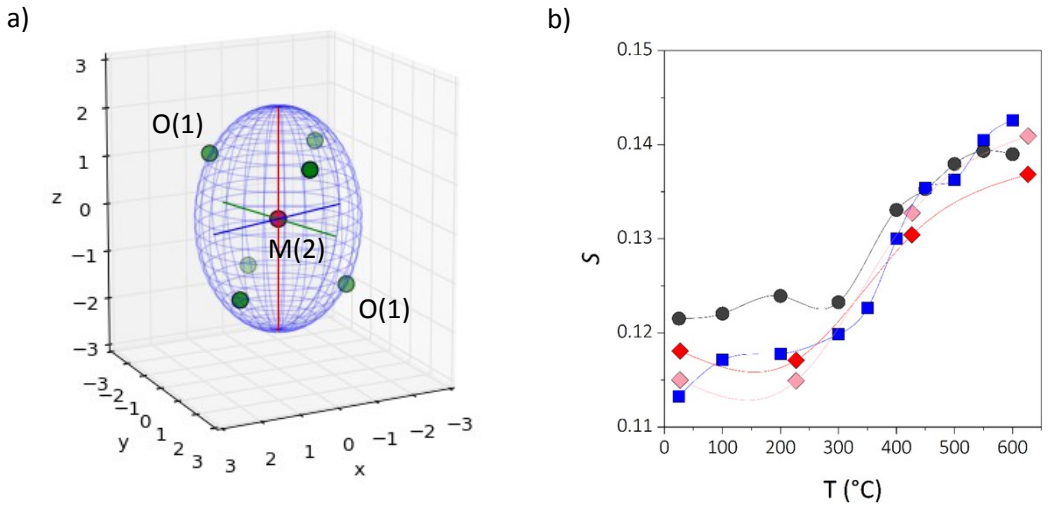

Fig. S1 a) Minimum bounding ellipsoid fit for the $[M(2)]O_6$ octahedra in $Ba_3MoNbO_{8.5}$ at 25 °C. b) Thermal variation of the ellipsoidal shape parameter of the $[M(2)]O_6$ octahedra for selected compositions. As the temperature increases, the $[M(2)]O_6$ octahedra become more axially stretched, expanding parallel to the *c*-axis in agreement with a previous report [2]. Black circles indicate $Ba_3MoNbO_{8.5}$, red and pink diamonds $Ba_3Mo_{1-x}W_xNbO_{8.5}$ x = 0.50 and x = 1.00 respectively, and blue squares $Ba_3W_{1.2}Nb_{0.8}O_{8.6}$.

References

1. J. Cumby and J. P. Attfield, *Nature Communications,* 2017, **8**, 14235.
2. S. Fop, E. J. Wildman, J. T. S. Irvine, P. A. Connor, J. M. S. Skakle, R. Clemens, A. C. Mclaughlin, *Chem. Mater.*, 2017, **29**, 4146-4152