

NdBaScO₄: aristotype of a new family of geometric ferroelectrics?

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Supplementary Information

Synthesis

Stoichiometric mixtures of dried reactant powders (99.9% purity) M₂O₃ (M = Nd, Eu, Yb, Y and Sc) and BaCO₃ were intimately mixed and ground, pelleted and fired at 1000 °C for 12 hours, followed by 1400 °C for 24 hours. A small excess of BaCO₃ (< 5%) was found to improve sample purity.

Second harmonic generation

Powder SHG measurements were performed on a modified Kurtz-NLO system [ref. 1] using a pulsed Nd:YAG laser (Quantel Laser, Ultra 50) with a wavelength of 1064 nm. Fine powder of NdBaScO₄ (EuBaScO₄) was filled in a fused silica tube with an outside diameter of 4 mm. α-SiO₂ powder was also measured at the same condition as a reference. The measurements indicated that NdBaScO₄ (EuBaScO₄) is not SHG active.

[1] S. K. Kurtz and T. T. Perry, *J. Appl. Phys.* 1968, **39**, 3798.

DFT calculations

DFT calculations were performed using the VASP code [2] (version 5.3.3) within its projected augmented wave (PAW) implementation and through the PBEsol approximation for the exchange correlation functional [3]. We treated the f-electrons as frozen core states for Nd (Nd_3 06Sep2000 POTCAR file), the 5s, 5p and 6s as valence states for Ba (Ba_sv 06Sep2000 POTCAR file), the 3s 3p 3d 4s as valence states for Sc (Sc_sv 07Sep2000 POTCAR file), 4s, 4p, 4d and 5s as valence states for Y (Y_sv 25May2007 POTCAR file) and 2s and 2p as valence states for O (O 08Apr2002 POTCAR file). We obtained converged calculations for atomic and cell relaxations and phonons with a cut off energy of 600 eV on the plane wave expansion and 8x4x6 grid sampling for the k-points integration in the reciprocal space. Phonon calculations were calculated using the density functional perturbation theory (DFPT [4]) as implemented in the VASP code. The relaxed cell parameters are a=4.039 Å, b=17.487 Å and c=5.945 Å, which are in good agreement with the experimental ones.

[2] G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758.

[3] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, *Phys. Rev. Lett.*, **100**, 2008, 136406.

[4] X. Gonze and C. Lee, *Phys. Rev. B*, 1997, **55**, 10355.

Crystallography

Powder X-ray diffraction (PXRD) data were collected on a Panalytical Empyrean diffractometer using $\text{CuK}_{\alpha 1}$ radiation. Variable temperature PXRD were collected on a Panalytical Empyrean diffractometer using $\text{MoK}_{\alpha 1}$ radiation. Powder neutron diffraction (PND) data were collected via the GEM Xpress service at the ISIS Spallation Neutron Source, Rutherford Appleton Laboratory, Didcot, UK. Samples were mounted in standard cylindrical vanadium cans. For NdBaScO_4 a small sample ($\sim 1\text{g}$) was used, requiring a data collection time of $\sim 2\text{hrs}$. For YBaScO_4 a larger ($\sim 3\text{g}$) sample was run, for $\sim 1\text{hr}$. Rietveld refinement was carried out using the GSAS package with the EXPGUI interface. For the PXRD refinements fixed models were used, based on the PND refinements, with only profile and lattice parameters being refined. For the PND refinements, simultaneous refinement was carried out against four detector banks, with profile, background, lattice parameters and freely refined coordinates and isotropic displacement parameters for all atoms.

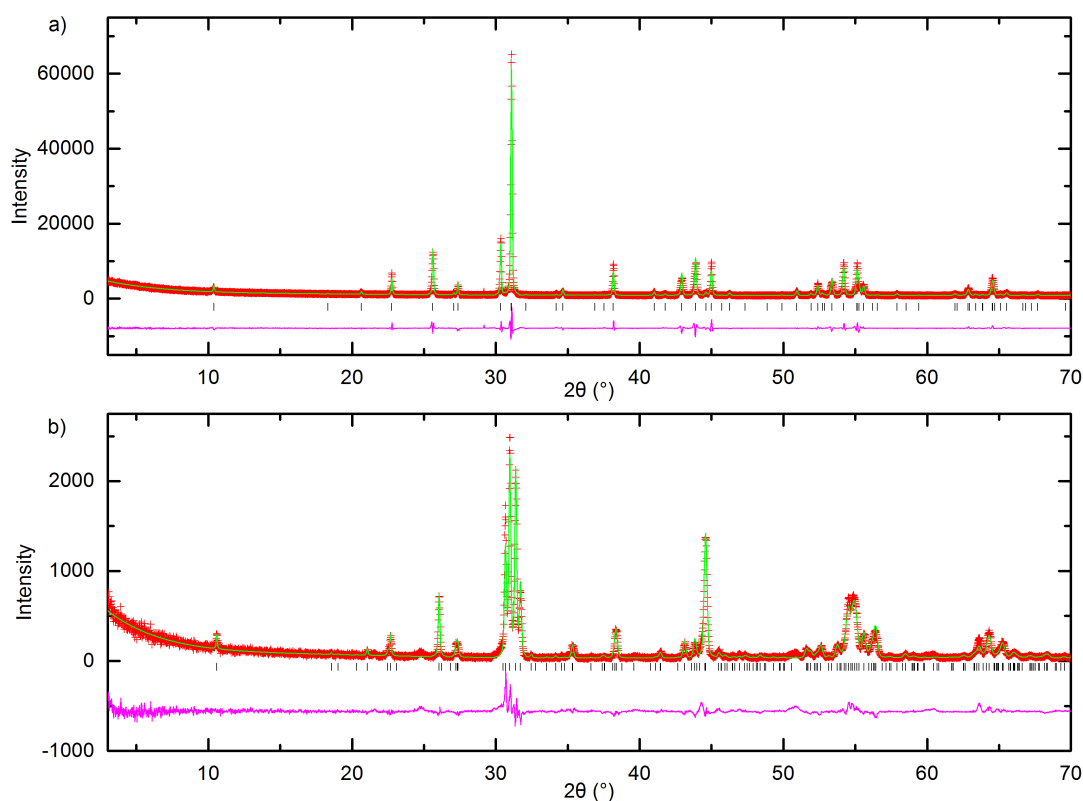


Figure S1. Rietveld plots (PXRD at 25 °C) for EuBaScO_4 , $Cmcm$ model (a) and YbBaScO_4 , $P2_1/c$ model (b).

Table S1 Unit cell parameters from X-ray (or neutron*) Rietveld refinement at ambient temperature.

| | a (Å) | b (Å) | c (Å) | β (deg) | γ (deg) |
|--------------------------------|------------|--------------|-------------|---------------|----------------|
| NdBaScO_4^* | 4.05607(8) | 17.54910(14) | 5.97733(13) | | |
| YBaScO_4^* | 8.8577(14) | 5.8975(9) | 8.1315(13) | 104.037(2) | |
| YBaScO_4^* (trans) | 4.0658 | 17.1880 | 5.8975 | | 90.77 |
| EuBaScO_4 | 4.04403(9) | 17.3639(5) | 5.92613(13) | | |
| YbBaScO_4 | 8.7855(5) | 5.8620(4) | 8.1625(5) | 104.457(3) | |
| YbBaScO_4 (trans) | 4.0812 | 17.0174 | 5.8620 | | 91.03 |

Note: (i) NdBaScO₄ and EuBaScO₄ are refined as orthorhombic, *Cmcm*; YBaScO₄ and YbBaScO₄ are refined as monoclinic, *P2₁/c*. (ii) 'trans' refers to the primitive monoclinic unit cell transformed to the corresponding pseudo-orthorhombic unit cell using the matrix (0,0,1/2; 2,0,1/2; 0,1,0). The resultant γ angles show that the true symmetry remains monoclinic.

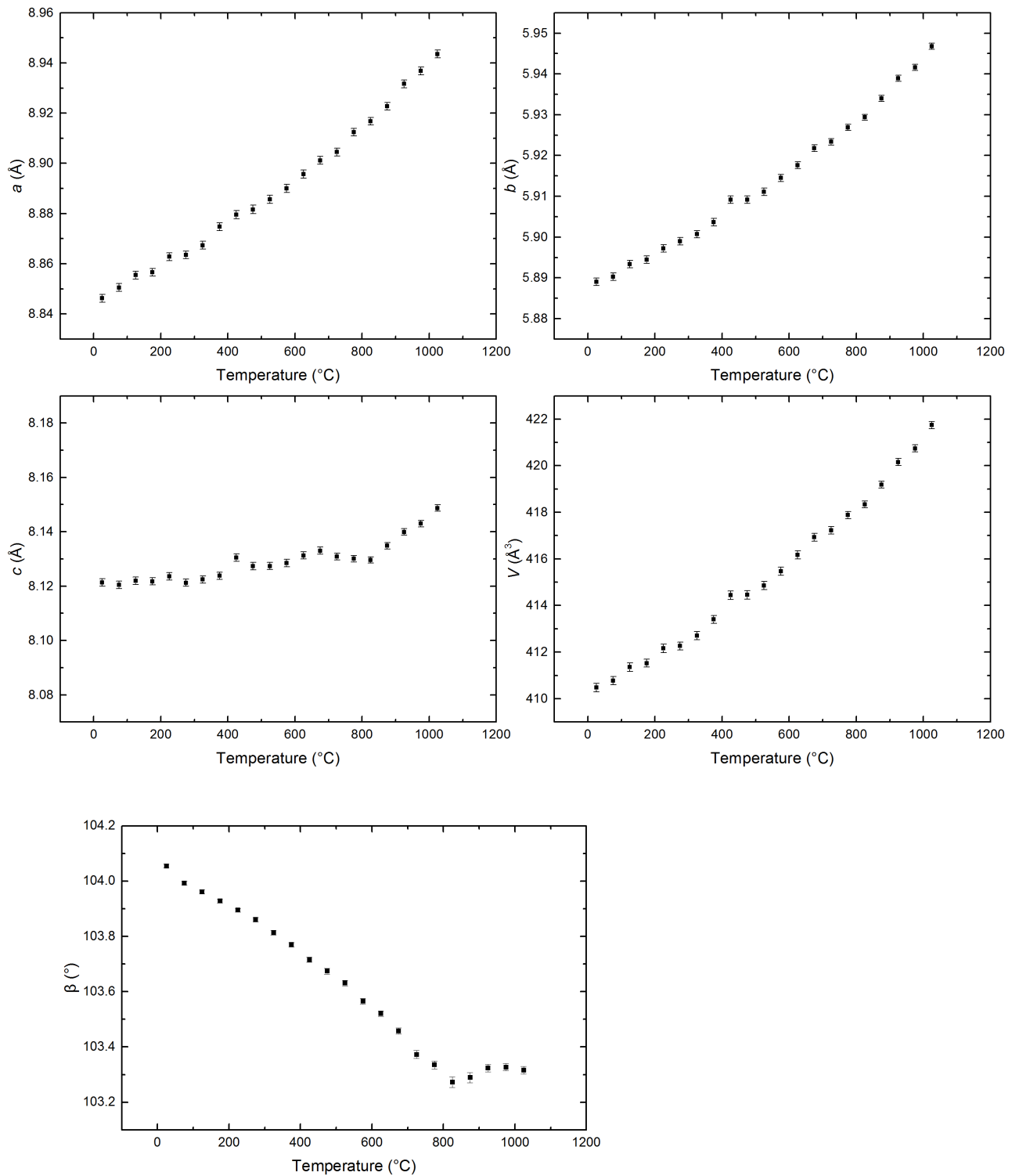


Figure S2 Lattice parameters for YBaScO₄ versus temperature, derived from Rietveld refinements of the monoclinic model (profile and lattice parameters only). Note that the primitive monoclinic lattice parameters at 1025 °C ($a = 8.944(1)$ Å, $b = 5.9468(8)$ Å, $c = 8.149(1)$ Å, $\beta = 103.32(1)$ °) transform to $a = 4.0743$ Å, $b = 17.406$ Å, $c = 5.9468$ Å, $\gamma = 90.15^\circ$ in the corresponding *Cmcm* setting (cf. Table S1). Given the relatively poor data quality and the observed changes in slope of lattice parameters near 800 °C it is likely that there is monoclinic to orthorhombic transition through this temperature range. Neutron diffraction would be necessary to verify this.

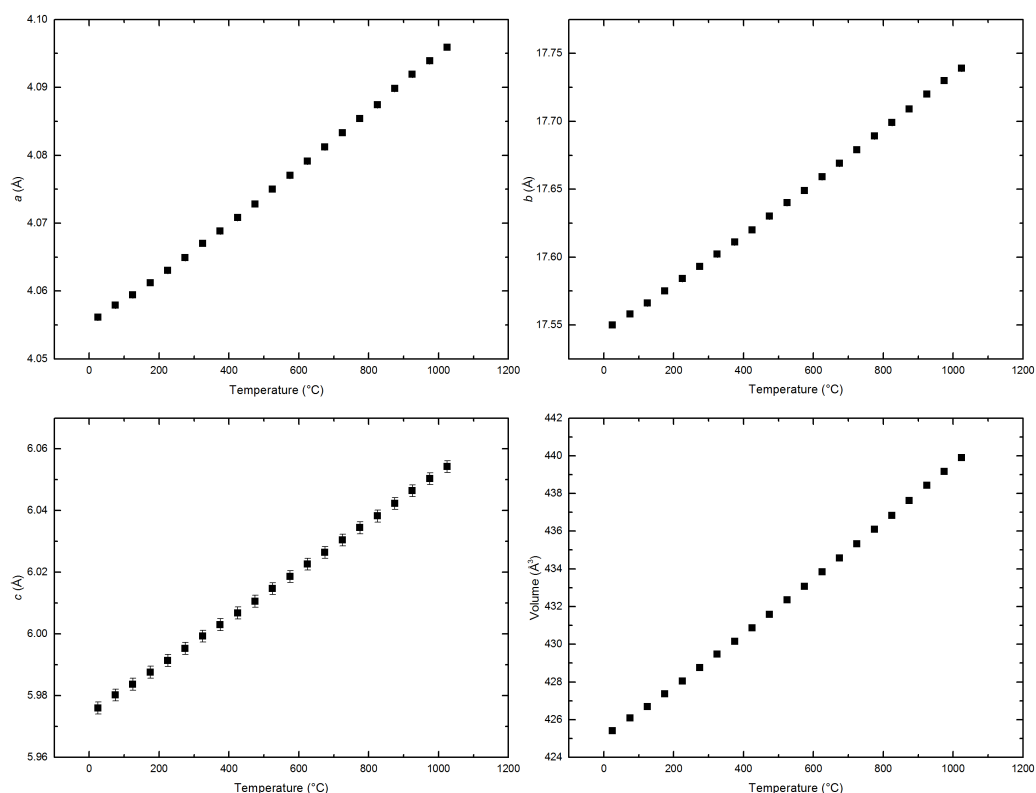


Figure S3 Lattice parameters for NdBaScO₄ versus temperature, derived from Rietveld refinements of the orthorhombic model (profile and lattice parameters only). There is no evidence for any phase transition or unusual thermal evolution within the temperature range studied. Based on a linear approximation the axial thermal expansivities ($\alpha_i = 1/l(dl/dT)$) are $\alpha_a = 9.81 \times 10^{-6} \text{ K}^{-1}$, $\alpha_b = 10.77 \times 10^{-6} \text{ K}^{-1}$, $\alpha_c = 13.09 \times 10^{-6} \text{ K}^{-1}$.

Table S2 Refined atomic parameters from neutron Rietveld refinements at ambient temperature.**(a) NdBaScO₄**

| Atom | x | y | z | U _{iso} (Å ²) |
|------|---|------------|-------------|------------------------------------|
| Nd1 | 0 | 0.72444(6) | 0.25 | 0.0030(3) |
| Ba1 | 0 | 0.42384(9) | 0.25 | 0.0035(3) |
| Sc1 | 0 | 0.08138(5) | 0.25 | 0.0064(2) |
| O1 | 0 | 0 | 0 | 0.0071(3) |
| O2 | 0 | 0.58886(9) | 0.25 | 0.0075(3) |
| O3 | 0 | 0.18158(7) | 0.48068(17) | 0.0099(3) |

(b) YBaScO₄

| Atom | x | y | z | U _{iso} (Å ²) |
|------|-------------|------------|-----------|------------------------------------|
| Y1 | 0.45398(17) | 0.7452(5) | 0.1018(2) | 0.0046(4) |
| Ba1 | 0.1574(3) | 0.2483(7) | 0.0352(4) | 0.0034(4) |
| Sc1 | 0.83057(14) | 0.2607(3) | 0.2074(2) | 0.0080(3) |
| O1 | 0.1944(3) | 0.7952(3) | 0.0491(5) | 0.0043(4) |
| O2 | -0.0124(4) | -0.0104(7) | 0.2619(4) | 0.0107(7) |
| O3 | 0.3982(3) | 0.5585(4) | 0.3317(4) | 0.0099(3) |
| O4 | 0.6548(3) | 0.5172(5) | 0.1180(3) | 0.0092(6) |

Table S3 Bond lengths (Å) and bond valence sums (valence units)**(a) NdBaScO₄**

| | Bond | Valence | | Bond | Valence |
|--------|---------------|----------------|--------|---------------|----------------|
| Nd1-O2 | 2.379(2) | 0.48 | Ba1-O1 | 2.8517(7) x 4 | 0.22 |
| Nd1-O3 | 2.305(1) x 2 | 0.58 | Ba1-O2 | 2.896(2) | 0.13 |
| Nd1-O3 | 2.5651(7) x 4 | 0.29 | Ba1-O1 | 2.9970(2) x 2 | 0.15 |
| | | Σ 2.79 | Ba1-O3 | 3.182(1) x 4 | 0.09 |
| | | | | | Σ 1.70 |
| Sc1-O1 | 2.0670(6) x 2 | 0.56 | | | |
| Sc1-O2 | 2.0323(1) x 2 | 0.61 | | | |
| Sc1-O3 | 2.235(1) x 2 | 0.35 | | | |
| | | Σ 3.03 | | | |

(b) YBaScO₄

| | Bond | Valence | | Bond | Valence |
|--------|-------------|----------------|--------|-------------|----------------|
| Y1-O1 | 2.254(3) | 0.53 | Ba1-O1 | 2.691(4) | 0.33 |
| Y1-O3 | 2.324(4) | 0.44 | Ba1-O1 | 3.035(3) | 0.13 |
| Y1-O3 | 2.253(4) | 0.53 | Ba1-O1 | 3.241(4) | 0.08 |
| Y1-O3 | 2.425(4) | 0.33 | Ba1-O2 | 2.725(4) | 0.30 |
| Y1-O4 | 2.208(4) | 0.60 | Ba1-O2 | 2.819(5) | 0.24 |
| Y1-O4 | 2.384(3) | 0.373 | Ba1-O2 | 2.823(5) | 0.24 |
| | | Σ 2.81 | Ba1-O2 | 3.055(4) | 0.13 |
| Sc1-O1 | 2.055(4) | 0.57 | Ba1-O3 | 3.349(4) | 0.06 |
| Sc1-O1 | 2.070(4) | 0.55 | Ba1-O3 | 3.503(5) | 0.04 |
| Sc1-O2 | 2.069(4) | 0.55 | Ba1-O4 | 2.690(4) | 0.34 |
| Sc1-O2 | 2.095(4) | 0.51 | Ba1-O4 | 3.209(5) | 0.08 |
| Sc1-O3 | 2.306(3) | 0.29 | | | Σ 1.95 |
| Sc1-O4 | 2.166(3) | 0.43 | | | |
| | | Σ 2.91 | | | |