Experimental report

10/04/2024

Proposal: 5-23-783 **Council:** 10/2022

Title: Structural Origins of Dielectric Phenomena in Promising Sr-Na-Nb-based TTB Ferrorelaxors

Research area: Chemistry

This proposal is a new proposal

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Samples: Sr2¿2zCazYzNaNb5¿zZrzO15 (z = 0, 0.025, 0.05)

Instrument	Requested days	Allocated days	From	To
D2B	4	2	17/05/2023	19/05/2023

Abstract:

In the drive to obtain commercially viable materials for use in high-temperature, high-efficiency Class-II capacitors, necessary for the global energy transition, we have developed a promising line of tetragonal tungsten bronze (TTB) ferrorelaxors: Sr2¿2zCazYzNaNb5¿zZrzO15 (z=0-0.05). However, anomalous features in temperature scans of their dielectric properties preclude their commercialisation. With structure-property relationships of TTBs in their infancy, we have identified the potential origins of these anomalies through combined X-ray, electron and DFT studies. To develop a comprehensive theory of the structure-property interplay in these systems, we now require neutron diffraction data to elucidate: (a) the precise oxygen atom positions to describe the nature and evolution of tilts and rotations in the network of NbO6 octahedra, and (b) the existence of a predicted lower-symmetry monoclinic phase. We propose a 4-day experiment using both cryostream and furnace to collect at 8 temperatures for 3 samples between 10 and 725 K. Results will significantly further understanding of this emerging class of functional materials, providing design routes to viable capacitor materials.

Experimental Report

Structural Origins of Dielectric Phenomena in Promising Sr-Na-Nb-based TTB Ferrorelaxors

Background

As global energy supplies shift towards renewable electrics, demand has emerged for Class-II, high efficiency capacitors which can operate over wide and high-reaching (up to >300 °C) temperature ranges.[1] Initial research into commercially viable ceramic perovskite ferroelectrics contained either Bi or Pd oxide, incompatible with the Ni electrode materials currently in common use. This triggered investigation into tetragonal tungsten bronze (TTB, $A1_2A2_4C_4B1_2B2_8O_{30}$) ferrorelaxors, based instead on alkali- and alkali-earth metal Nb oxide systems. In this context, collaborators developed a promising $Sr_2NaNb_5O_{15}$ (SNN) based line of TTBs.[2] These materials exhibit wide-ranging, high relative permittivity and are compatible with Ni electrode systems. However, anomalies exist in the dielectric constants (T1 and T2, seen in Fig. 1) that preclude their commercial use. As part of an interdisciplinary collaboration with groups at the Universities of Durham, Leeds, Manchester and Sheffield (EPSRC grant, EP/V053701/1), our aim is to elucidate the structural behaviour of these materials and its interplay with their properties, building comprehensive structure-property relationships together with collaborators to design and produce further improved materials.

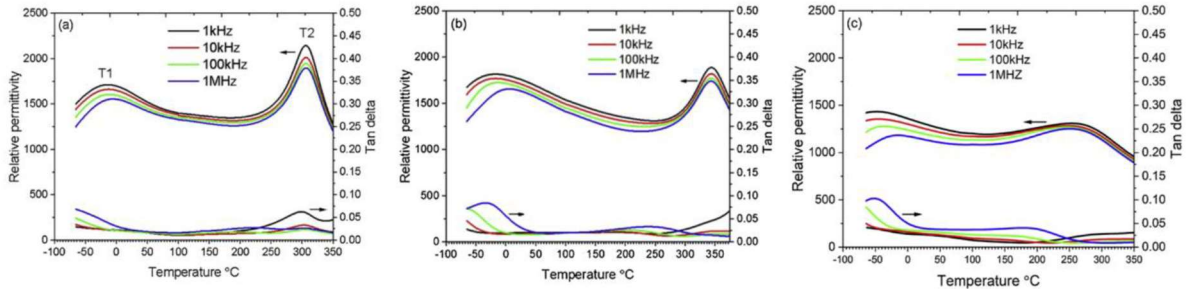

Figure 1. Plots of the relative permittivity (ε_r) and tan delta as relating to dielectric properties in $Sr_{2-2z}Ca_zY_zNaNb_{5-z}Zr_zO_{15}$ for (a) z=0, (b) z=0.025, and (c) z=0.05. Note the large variation in ε_r for particularly (a) and ~25 and 300 °C, replicated to decreasing degrees as z is increased. Figure adapted from reference 2.

While structure-property relationships in the context of perovskite materials are relatively mature, they remain in their infancy for TTBs. Even structural assignment for these samples presents a considerable challenge and, in many cases (SNN included), conflicting reports exist in the literature.[5] Using both synchrotron X-ray powder diffraction (SXRPD) and *in-house* electron diffraction and microscopy, we have elucidated the room-temperature structure of SNN to be a slightly incommensurate form of the *Ama*2 subgroup of the *P*4/*mbm* aristotype in cell basis [(1,−1,0)(2,2,0)(0,0,2)]. Notably, our variable temperature (VT) SXRPD studies find negative thermal expansion of the *c* axis in SNN (Fig. 2), bounded by T1 and T2. Interestingly, the polar structural mode (transforming as the irreducible representation, Γ_{3-}), which leads to off-centre displacements solely along *c*, is only significant below T2. This supports predictions of DFT calculations, performed by collaborators, that the non-polar supergroup of *Ama*2, *Amam*, should be found at higher temperatures. Thus, T2 would initially appear to be related to the softening of the Γ_{3-} mode, associated to a phase transition between the *A*-centred phases.

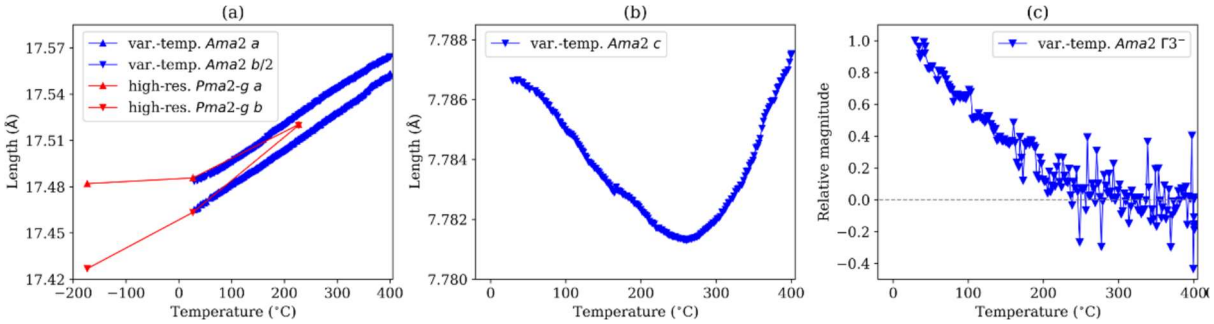

Figure 2. Temperature dependence of (a) the a and b and (b) the c crystallographic cell parameters and (c) the polar Γ_{5^-} distortion mode of SNN from refinements of SXRPD data. For VT, a commensurate Ama2 approximation is refined; for high resolution data we refine a Pma2 model (basis [(1,−1,0)(1,1,0)(0,0,1)]) with g vector 0,~0.48,0.5 describing the incommensurate diffraction. Note the deviation in a,b separation below ~0 °C (a) and indicated maximum in c (b), and the up-turn in thermal expansion at ~270 °C, coincident with suppression of the Γ_{5^-} distortion.

The same DFT work indicated a monoclinic, Aa phase (same cell basis as the room-temperature structure) to be of lower energy still. Although we see little indication of this in the present crystallographic data, we note observations of deviation in both Δa,b and the thermal expansion of c at about T1 (Fig. 2). Moreover, the predicted Aa phase would gain polar modes in the ab plane that might explain the T1 anomaly in the relative permittivity data.

While progress has clearly been made in our aims, the inherent insensitivity of X-rays to oxygen atoms in the presence of far heavier metals severely limits the structural insight that can be gained. Specifically, while understanding of the primary polar distortion has been advanced, being dominated by the displacement of Nb atoms, we have obtained little reliable insight into the complex tilting and rotating of the interconnected NbO6 octahedra that give rise to the A-centred supercell and would affect the predicted lowering to monoclinic symmetry. It is in this context that high-resolution neutron diffraction studies would be of great value. Here, the greater scattering contribution of oxygen will allow for robust refinement of the distortions associated with those lighter atoms, to which our X-ray experiments are otherwise largely blind. Similarly, neutrons will be far more sensitive to the off-centre oxygen displacements that are likely characteristic of the predicted monoclinic phase.

Experimental Measurement

As proposed in the experiment, two samples, SNN y = 0 and SNN y=– 0.05 were measured over the 4 days on D2B in the cryostat and furnace at 10K, 150, 250 K, 295k, 350C, 300C and 350C. The data and sample quality seemed to be exceptionally high.

Results

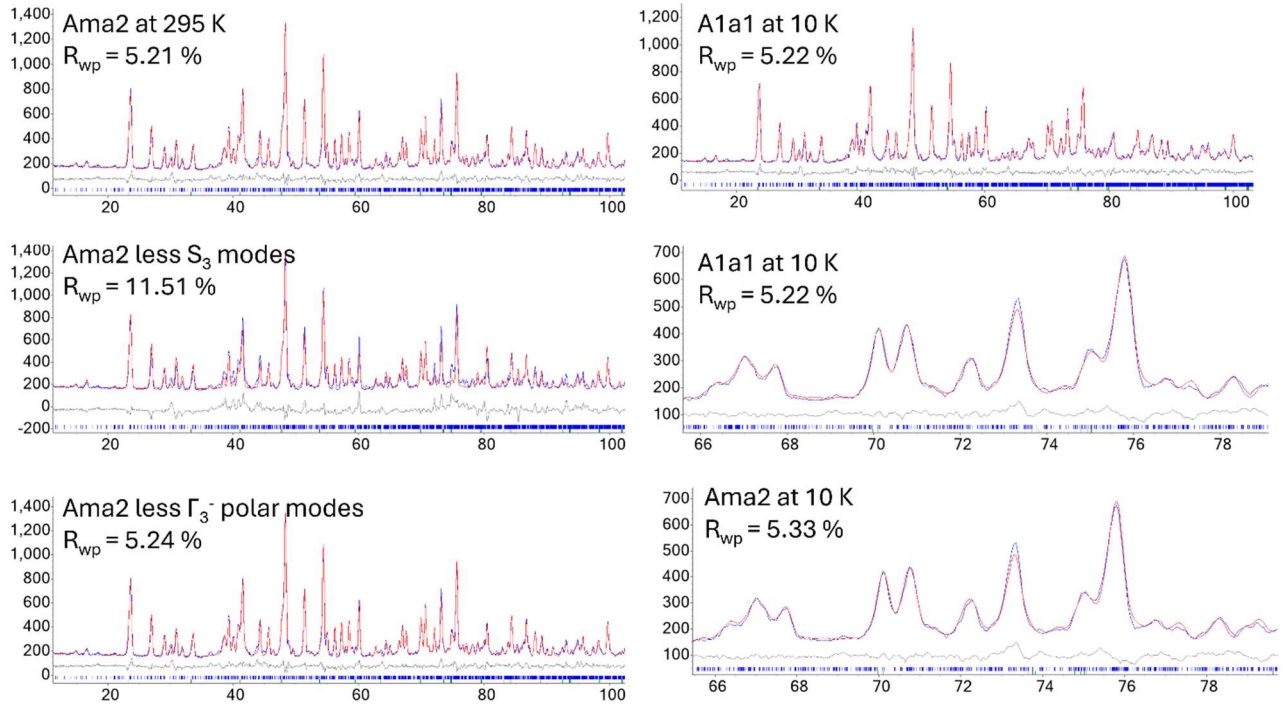

Figure : Powder Neutron Diffraction. Plots of fits to the neutron powder data (SNN, y = 0) for the *Ama*2 at 295 K (top-left) as reported in the paper, (middle-left) minus the S_3 distortion and (bottom-left) instead without the Γ_3^- distortion; and for the *A*1*a*1 model at 10 K (top-right) as reported in the paper, alongside comparable zoom regions of (middle-right) precisely this model and (bottom-right) the *Ama*2 model. Note the more significant impact of refining the Γ_5^- distortion and β angle on the *A*1*a*1 model at 10 K (5.22% *vs*. 5.33%) than the Γ_3^- distortion for the *Ama*2 model at 295 K (5.21% *vs*. 5.24%). For reference, a precisely tetragonal model in *P*4/*mbm* provides an R_{wp} of 12.71%.

The Neutron powder diffraction data collected on D2B on SNN as proved instrumental on verifying the existence of the Aa structural distortion at low temperatures (See Figure). This has result in the completion of our study on the temperature induced phase transitions in SNN. Our paper is currently in press at npj Communications Materials:

Structural origins of dielectric anomalies in the filled tetragonal tungsten bronze, Sr2NaNb5O15.

J. Tidey *et al. accepted npg Communications Materials*, https://doi.org/10.21203/rs.3.rs-3893784/v1

References

[1] J. Watson and G. Castro, J. Mater. Sci: Mater. Electron., 2015, 26, 9226-9235. [2] T. Brown, A.P. Brown, D.A. Hall, T.E. Hooper, Y. Li, S. Mitcklethwaite, Z. Aslam and S.J. Milne, J. Eur. Ceram. Soc., 2021, 41, 3416–3424. [3] E. García-González, A. Torres-Pardo, R. Jiménez and M. González-Calbert, Chem. Mater., 2007, 19, 3575-3580. [4] J. Ravez, J.-P. Budin and P. Hagenmuller, J. Solid State Chem., 1972, 5, 239-246. [5] T.A. Whittle, S. Schmidt and C.J. Howard, Acta Crystallogr., Section B, 2021, 77, 981-985.