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# NdBaScO₄: aristotype of a new family of geometric ferroelectrics?

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**NdBaScO₄ represents the aristotype structure of a new series of <110>-cut layered perovskites; it is suggested that compositional fine-tuning is likely to produce a family of new geometric ferroelectrics, driven primarily by octahedral tilting.**

Several families of layered perovskites are known, most of which may be regarded as derived from 'slicing' the perovskite aristotype $ABX_3$ through *trans*-vertices of the $BX_6$ octahedra (i.e. along one of the parent cubic <100> directions[1]), and inserting additional species between these layers. This gives rise to the well-known Aurivillius, Ruddlesden-Popper (RP) and Dion-Jacobson (DJ) families, of general compositions $(Bi_2O_2)A_{n-1}B_nO_{3n+1}$, $A_{n+1}B_nO_{3n+1}$ and $A'A_{n-1}B_nO_{3n+1}$, respectively. Such materials may have diverse and tailorable compositions and crystal structures, and hence display a wide array of functionalities, including superconductivity, photocatalysis, magnetoresistance and ferroelectricity. The latter property has been well-established in the Aurivillius phases for many years[2], but is a relatively recent observation in the RP and DJ families[3,4,5]. Recent work has suggested that ferroelectricity in these systems often derives from the combination of one or more 'octahedral tilt' modes (which in themselves are intrinsically non-polar), coupling to a soft polar mode[1,6,7]. Another series of layered perovskites, of generic composition $A_nB_nX_{3n+2}$, exists, which derives from slicing the perovskite parent phase along *cis*-vertices (i.e. octahedral edges rather than corners): these phase may be regarded as '<110>-cut' layered perovskites[7]. Within this family there are several examples of both ferroelectric and multiferroic materials, such as $Sr_2Nb_2O_7$[9], $La_2Ti_2O_7$[10] and $BaMnF_4$[11]. Significantly the mechanism of ferroelectricity in this family does *not* rely on the coupling of multiple octahedral tilts and correlated polar modes: instead a single octahedral tilt mode drives the structure directly into a polar symmetry, i.e. these are *proper* rather than *hybrid improper* ferroelectrics[12,13]. For the simplest (i.e. $n = 2$) member of this family,

$ABX_4$, the aristotype structure is shown in Fig. 1(a). The symmetry is centrosymmetric orthorhombic (space group *Cmcm*) and significantly there is no octahedral tilting present. The only well-characterised example of this aristotype structure is $BiReO_4$[14]. Two of the simplest structural distortions of this aristotype rely on 'out-of-phase' or 'in-phase' or tilting of octahedral units along one axis (Fig. 1(c) and 1(e), respectively). Out-of-phase tilting retains centrosymmetricity, whereas in-phase tilting leads naturally to polarity (space group $Cmc2_1$); a mechanism which has been termed 'geometric' or 'topological' ferroelectricity[12]. Examples of both these structure types are known, and we have recently shown (for the example of $LaTaO_4$) that the energetic balance between the two polymorphs can be very fine, such that a phase transition can occur between these two distinct tilted phases as a function of either temperature or composition[13].

The aim of this paper is to introduce a new family of layered perovskites, $LnBaScO_4$, closely related to the $LaTaO_4$ type, which we now show can exist in both the 'out-of-phase-tilted' and aristotype polymorphs. This study was prompted by the recent isolation of the related phase $NdBaInO_4$[15]. The opportunities for compositional and structural diversity here suggests that this structural family is also likely to host the corresponding 'in-phase-tilted' polar polymorph and therefore represents a new family of potential geometric ferroelectrics and, perhaps, multiferroics.

Although the relationship of $NdBaInO_4$ to the $LaTaO_4$ structure type was not recognised in the original report[15], it is evident that insertion of an additional cationic layer between adjacent perovskite-like slabs can convert the $ABX_4$ stoichiometry to $AA'BX_4$, subject to satisfying the necessary charge-balancing and size-matching criteria. This would result in the three idealised polymorphs shown in Fig. 1 (b,d,f), by analogy with those shown in Fig. 1 (a,c,e). The reported structure of $NdBaInO_4$ (monoclinic, space group $P2_1/c$) corresponds to the 'out-of-phase-tilted' polymorph (Fig. 1(d)).
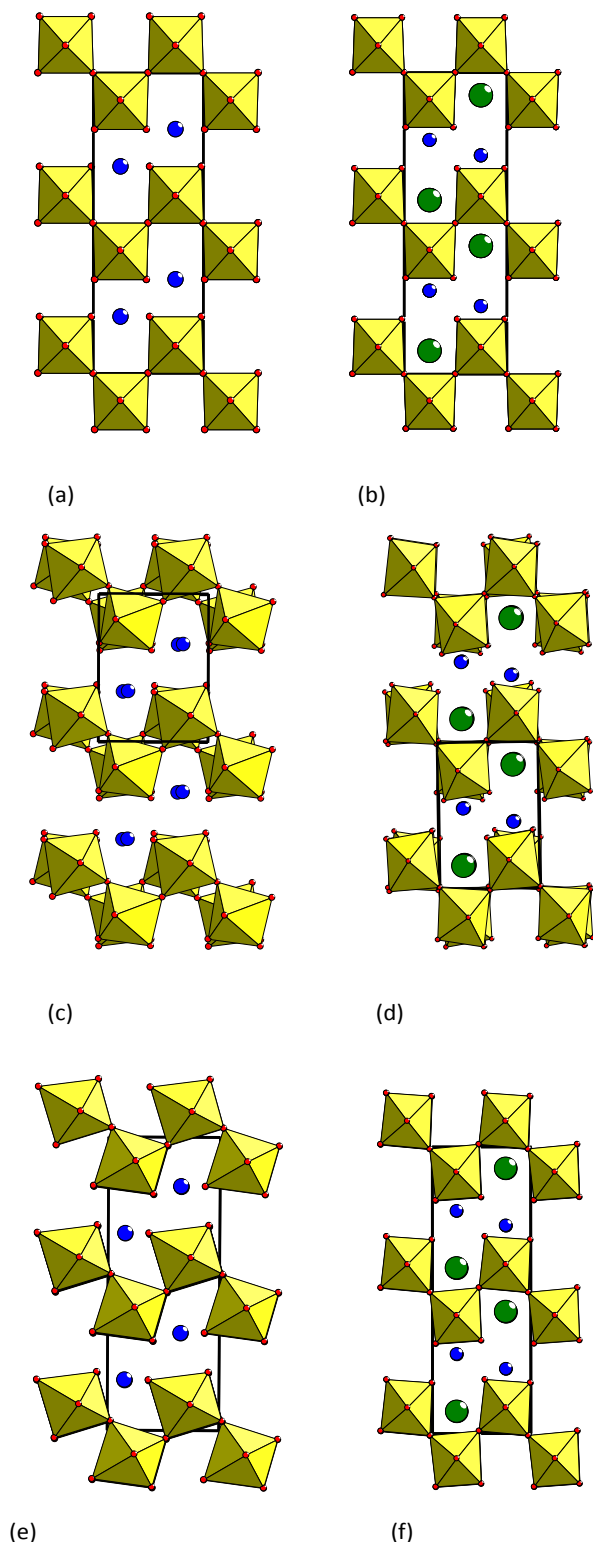
**Fig. 1.** Crystal structures of the three polymorphs of the ABX$_4$ family (a: arisotype, c: 'out-of--phase' tilted, e: 'in-phase' tilted) and the corresponding polymorphs of the new AA'BX$_4$ family (b: NdBaScO$_4$, d: YBaScO$_4$, f: as-yet undiscovered polar phase). A site (Ln): small blue spheres; A' site (Ba): large green spheres.

It is likely that the stability of this structure type (for example compared to potential competitors such as AA'BO$_4$ RP-related phases, which are known for compositions such as LaSrScO$_4$[16]) depends on the significant difference in the A and A' cation sizes, and possibly also on the relative B-cation size and the relative charges of the cations at the three cation sites. Therefore we chose first to prepare the 'most similar' analogue NdBaScO$_4$, keeping the A/A' cation composition constant, and substituting the next smallest trivalent cation at the B-site (cation radii: In$^{3+}$ = 0.80 Å, Sc$^{3+}$ = 0.745 Å for 6-coordination). Subsequently, we then extended this to other lanthanide analogues.

NdBaScO$_4$ was prepared by a conventional solid state method: (see ESI for further experimental details). This method also led to the successful preparation of the LnBaScO$_4$ analogues (Ln = Eu, Y, Yb). Rietveld refinement of powder X-ray diffraction (PXRD) data for NdBaScO$_4$ using the model of NdBaInO$_4$[15] led to a satisfactory fit. However, on closer inspection it was found that a similar fit could be obtained in the higher symmetry aristotype structure type (Cmcm). The two structures are related by a transformation matrix (0,0,1/2; 2,0,1/2; 0,1,0). Powder neutron diffraction was used to ascertain more precise structural details for both NdBaScO$_4$ and YBaScO$_4$. Neutron Rietveld refinements of the three models (Fig. 1 (b,d,f) for NdBaScO$_4$ led to agreement factors ($\chi^2$) 1.77, 1.50 and 1.59, for Cmcm, P2$_1$/c and Cmc2$_1$ models, respectively. Given that the Cmcm model requires significantly fewer variables (only 12, versus the 28 atomic parameters for the P2$_1$/c model) and that the resulting deviations from the aristotype model are very small when allowing the enhanced degrees of freedom, this supported the assertion that NdBaScO$_4$ does indeed adopt the aristotype structure. On the other hand, the refinements unambiguously confirmed that YBaScO$_4$ adopts the 'out-of-phase-tilted' NdBaInO$_4$ structure (Fig. 1(d)). Clearly this difference is likely to be due to cation size influences (cation radii: Nd$^{3+}$ = 1.12 Å, Y$^{3+}$ = 0.0.96 Å for the observed 7-coordination), a suggestion supported by X-ray Rietveld refinements for EuBaScO$_4$ and YbBaScO$_4$, which fit well to the Cmcm and P2$_1$/c models, respectively.

In order to confirm the proposed aristotype structure of NdBaScO$_4$, we carried out second-harmonic generation (SHG) measurements, which showed no signal for either NdBaScO$_4$ or YBaScO$_4$, supporting centrosymmetric models for each. As a final check we undertook density functional theory (DFT) calculations using the VASP code[17] (see ESI for further details). Energy minimisations of the P2$_1$/c and Cmc2$_1$ models for NdBaScO$_4$ converged to the aristotype Cmcm model, whereas for YBaScO$_4$ the P2$_1$/c model is found to have the lowest energy. The Cmcm phase stability of NdBaScO$_4$ is also confirmed by the absence of unstable modes in the calculated phonons at the Γ point and at the zone boundary points.

LaTaO$_4$ exists in the polar Cmc2$_1$ structure (Fig 1(e)) when prepared as described in ref.13. However, earlier studies[18,19] of that composition suggested the centrosymmetric P2$_1$/c polymorph to be more stable at ambient temperature, with a phase transition to the Cmc2$_1$ polymorph occurring around 200 °C. Clearly, in the case of LaTaO$_4$, the two tilted polymorphs are of competitive stabilities. We found that the P2$_1$/c polymorph could be stabilised at ambient temperature by Nd-doping[13] (at composition La$_{0.9}$Nd$_{0.1}$TaO$_4$). Moreover, this phase was itself transformed to the Cmc2$_1$ polymorph on heating to ~ 250 °C.

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Transformation of a centrosymmetric ambient-temperature phase to a polar polymorph on heating[13,18,19] is highly unusual, and it is an intriguing possibility that such subtle polymorphic phase transitions could also occur in the $NdBaInO_4$ / $NdBaScO_4$ family as a function of either temperature or composition. Hence we carried out a variable temperature PXRD study of $YBaScO_4$ and $NdBaScO_4$ (see ESI for details). In the case of $NdBaScO_4$, there is no evidence for a phase transition for 25 °C < $T$ < 1025 °C, with linear, but anisotropic, thermal expansion throughout this region. $YBaScO_4$ retains the out-of-phase tilted structure up to at least 750 °C, but converges towards orthorhombicity at higher T ($\beta$ ~ 90.1°). Due to the relatively poor crystallinity (broad peaks) present in the $YBaScO_4$ sample it is not possible to rule out a phase transition. Indeed, the evolution of the as-refined (monoclinic) unit cell parameters support such a transition around 750 – 800 °C. Interestingly, Fujii et al.[15] also carried out a powder (neutron) study of $NdBaInO_4$ at both 24 °C and 1000 °C. They presented conductivity data, which shows a change of slope around 850 °C. The monoclinic unit cell reported at 1000 °C can, in fact, be transformed to a metrically orthorhombic setting (corresponding to the $Cmcm$ or $Cmc2_1$ polymorphs discussed here), with cell size $a$ = 4.1600, $b$ = 17.9703, $c$ = 6.1185 Å.
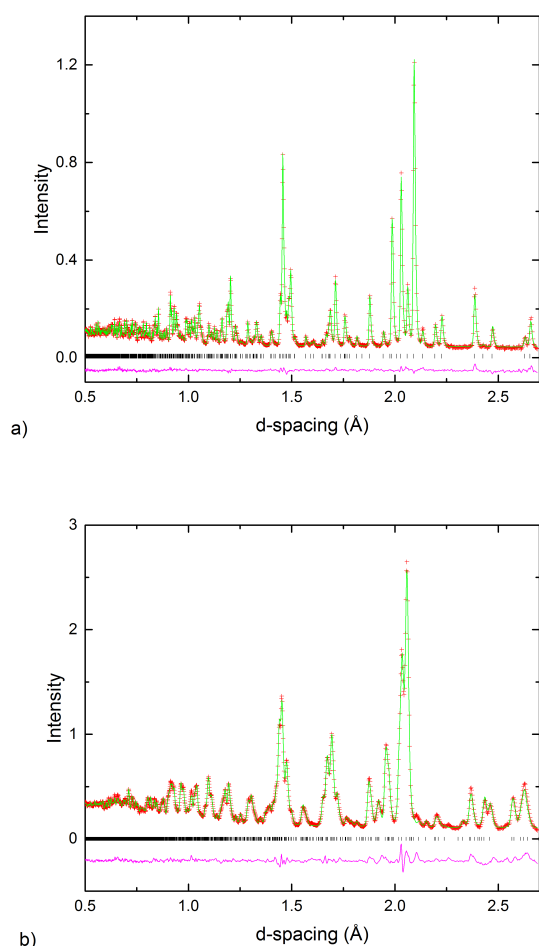
It is possible therefore that the change in slope of conductivity in $NdBaInO_4$ corresponds to a tilt-induced phase transition to either the aristotype or polar orthorhombic phase.

In summary, we have shown that the novel layered perovskite structure type first reported for $NdBaInO_4$ can be extended to other $AA'BX_4$ compositions, specifically for B = Sc, A' = Ba and A = lanthanide. We have shown the relationship between this structural family and the $LaTaO_4$ family, which can occur in three distinct polymorphs, differing in octahedral tilt patterns. It is reasonable that each of the three corresponding polymorphs should exist for the $AA'BX_4$ family. Of these, we have shown that $NdBaScO_4$ adopts the aristotype 'untilted' polymorph of this series, and $YBaScO_4$ adopts the centrosymmetric, 'out-of-phase-tilted' polymorph. Although we have not yet discovered the 'in-phase-tilted' polymorph, which is of interest as a prospective new geometric ferroelectric material, we suggest that the fine energy balance observed between the polymorphs of the $LaTaO_4$ family prompt further study of this new $AA'BX_4$ family. The possibilities for isolating the polar $Cmc2_1$ polymorph include not only variable temperature studies, but also a wider range of compositional and doping opportunities than is available in the $LaTaO_4$ family. For example, having three distinct cation sites allows for a wider range of possible oxidation state combinations at A, A' and B sites and also the exciting possibility of being able to incorporate magnetic cations (e.g. trivalent or tetravalent first-row transition metal species) at the B-sites more readily than can occur in the $LaTaO_4$ family. Multiferroic *oxide* analogues of $BaMnF_4$[20] may therefore be accessible within this new family. Further work on the compositional stability field of this new family and its polymorphs, in particular targeting the polar polymorph, are in progress.

**Fig. 2.** Example Rietveld fits to powder neutron diffraction data for (a) $NdBaScO_4$ (aristotype $Cmcm$ model (see Fig.1(b)) and (b) $YBaScO_4$ (out-of-phase tilted $P2_1/c$ model (see Fig. 1(d)).

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