# Experimental report

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**Title:** Complex ordering in Y1/3TaO3, a new polar A-site deficient perovskite

**Research area:** Materials

**This proposal is a new proposal**


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**Samples:** Y1/3TaO3

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D2B | 3 | 3 | 26/09/2018 | 29/09/2018 |


## Abstract:

The most ubiquitous distortion in ABO3 perovskite oxides and related compounds is rotation or tilting of BO6 octahedra. The oxygen octahedral rotations(OORs) do not break the inversion symmetry in simple perovskites because of the intrinsic nature of octahedral connectivity. However, OORs can break inversion symmetry in layered perovskites such as Ruddlesden-Popper(RP) phases. Recently, our group reported OOR-induced noncentrosymmetry in n = 1 RP NaRTiO4 (R:rare earth), where the inversion symmetry is broken by the combination of OORs and A-site layered ordering.

We now extend our understanding of OORs to A-site deficient perovskites, R1/3TaO3, that exhibit a layered ordering of the R cations and vacancies. Although the crystal structure was previously reported for R=La-Tm, no reliable crystallographic data are available for R=Y. Here, we will reveal the relation between OOR and ferroelectricity in Y1/3TaO3 using neutron powder diffraction. Our goal is to resolve the ambiguity of the OOR patterns in the room-temperature polar and high-temperature "incommensurate" nonpolar phases. This approach will allow a better understanding of phase transition of a new ferroelectric material.

**Complex ordering in $Y_{1/3}TaO_3$, a new polar *A*-site deficient perovskite**

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## Experimental report

Recent theoretical work has identified that oxygen octahedral rotations (OORs) in layered perovskites such as Ruddlesden-Popper phases can generate ferroelectricity through a hybrid improper mechanism. In this context, we focus on *A*-site deficient perovskites, $R_{1/3}TaO_3$ (*R* = rare earth), that exhibit a layered ordering of the *R* cations and vacancies. Although the average crystal structure was previously reported for *R* = La-Tm, no reliable crystallographic data are available for *R* = Y. In this experiment, we carried out neutron powder diffraction (NPD) on D2B for $Y_{1/3}TaO_3$ to resolve unambiguously the OOR pattern in the room-temperature phase and also to identify the high-temperature incommensurate (INC) structure due to the OOR frustration.

Polycrystalline $Y_{1/3}TaO_3$ samples were prepared by the conventional solid-state reaction at 1873 K. Preliminary analysis of synchrotron XRD data at 300 K on the BL02B2@SPring-8 revealed a single phase, crystallizing in an orthorhombic structure with an enlarged unit cell $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$ ($a_p \cong 3.9$ Å is the pseudo-cubic lattice parameter), due to the OOR distortions ($a^-a^-c^+$ in Glazer notation). Considering the reflection conditions in the orthorhombic setting [0*kl*: $k = 2n$ and 0*k*0: $k = 2n$ (*n*: integer)], the possible space groups were $Pb2_1m$ (noncentrosymmetric polar) or *Pbmm* (centrosymmetric nonpolar). However, it was difficult to determine unambiguously the room-temperature crystal structure by using only synchrotron XRD.

In order to identify the room-temperature phase of $Y_{1/3}TaO_3$, we performed a high-resolution NPD experiment, which allows a much more accurate determination of oxygen parameters than XRD. In the measurements, a 4.5-g sample was put in an evacuated vanadium can with an inner diameter of 9 mm. Using a wavelength of 1.594 Å available on D2B, we recorded diffraction patterns up to $2\theta = 160°$ corresponding to a $d_{min}$ of 0.81 Å. The data were analysed using the FullProf suite and JANA2006. The Rietveld plot (see **Fig. 1**) shows a noticeable mismatch in some peak intensities for the *Pbmm* model, indicating that the room-temperature phase likely belongs to ferroelectric $Pb2_1m$ space group. A close inspection reveals that the RT phase may be incommensurately modulated with a short to medium coherence length due to the presence of very few broad additional unindexed peaks, satellites not previously seen by synchrotron XRD.

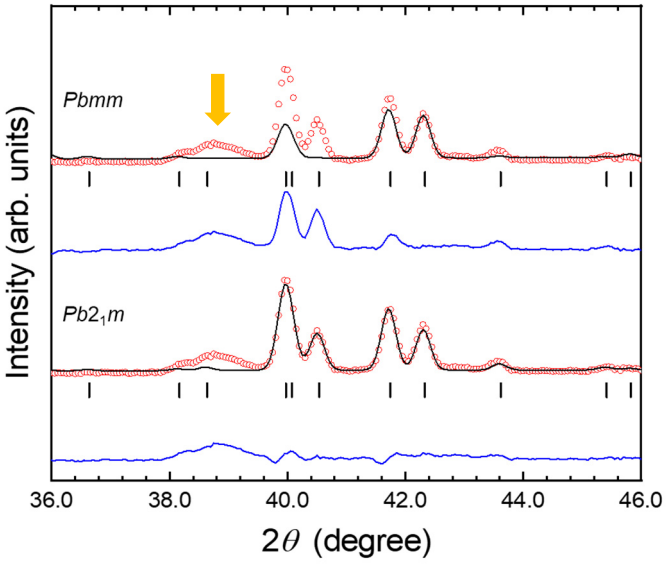


**Fig. 1.** Rietveld plot against D2B data of $Y_{1/3}TaO_3$ measured at 300 K ($\lambda = 1.594$ Å). Unindexed broad peaks around $2\theta = 38.7°$ (marked with an arrow) are associated to an additional unknown RT INC order.

High-temperature NPD data were also recorded using a standard vanadium furnace, from 300 to 1000 K with a step of 100 degrees. We observed a structural phase transition at 700 K and were able to show the disappearance of the few broad satellites hardly observed below 700 K, the appearance of new thin satellites and a drastic reorganization of the main reflections. These results indicate

(consistently with the high-temperature synchrotron XRD data though with much more intense satellites) the presence of a high temperature INC phase of average symmetry $P4/mmm$ ($a_p \times a_p \times 2a_p$ unit cell), stable from 800 to 1000 K whose modulated structure is still unknown.

In addition, we used on D2B a longer wavelength (2.40 Å) at RT and in the high temperature phase (at 800 & 900 K) to better discriminate the satellites and thereby determine the true INC symmetry (see **Figs. 2 & 3**). Through preliminary structural analyses, we now believe it will be possible to determine unambiguously the high-temperature INC structure (superspace group approach) by combining synchrotron XRD, TEM observations and the two-wavelength D2B data. At RT the INC structure will be more difficult to derive, owing to the weakness and limited number of observed superlattice peaks. However superspace structural relationships could help once the high-temperature INC structure will be refined, as well as high resolution TEM experiments.

Finally, using only the main reflections, we have successfully obtained useful information about the OOR distortions by Rietveld refinements of the average structure between 300 and 1000 K.

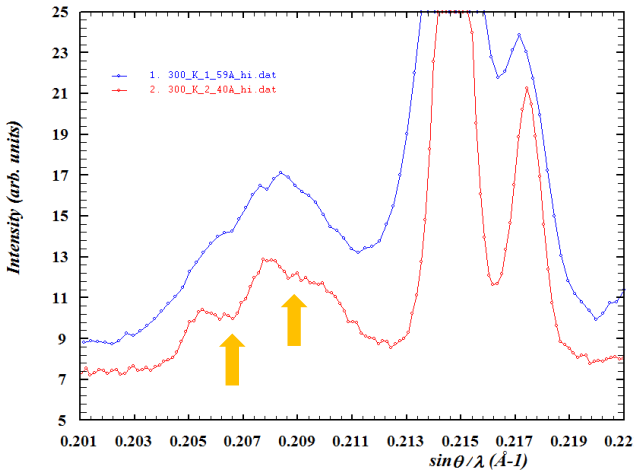


**Fig. 2.** D2B data of $Y_{1/3}TaO_3$ at 300 K within the low temperature orthorhombic phase using two different wavelengths ($\lambda$ = 1.594 Å in blue and 2.398 Å in red). The splitting of the broad satellites on the left of the 103 main reflection is evidenced (see the arrows).

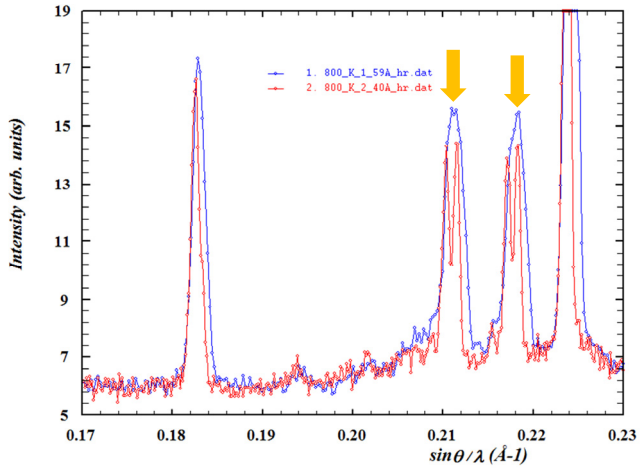


**Fig. 3.** D2B data of $Y_{1/3}TaO_3$ at 800 K within the high temperature tetragonal INC phase using two different wavelengths ($\lambda$ = 1.594 Å in blue and 2.398 Å in red). The splitting of the satellites between the (102)/(110) main reflections – on the left – and the (112) main reflection – on the right – is clearly highlighted (see the arrows).