

Modulated Structures for CsMOB₂O₅ (*M* = Nb, Ta) from Variable Temperature Single-Crystal X-Ray Diffraction Data

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A phase transition was discovered in the CsMOB₂O₅ (*M* = Nb, Ta) compounds using single-crystal X-ray diffraction. A 2x commensurate modulation was identified in CsNbOB₂O₅ for the first time by cooling to 150 K. A modulation vector of $\mathbf{q} = 0.43(1)\mathbf{b}^*$ was also observed in CsTaOB₂O₅ when cooled to 150 K. These results are explained in terms of structural distortions introduced at low temperatures to satisfy the bonding requirements of the Cs-cation.

1. Introduction:

CsNbOB₂O₅ and CsTaOB₂O₅ are members of a family of non-centrosymmetric oxo pyroborates, AMOB₂O₅ (*A* = K, Rb, Cs, Tl; *M* = Nb, Ta) [1-4], which have attracted considerable interest over the past three decades because they satisfy many of the required criteria for nonlinear optical applications, namely, exceptional resistance to laser damage, a high second order susceptibility coefficient, a moderate birefringence, and UV cut-off wavelengths below 290 nm [5]. Previous studies [1-9] have been performed into all of the 8 possible members of the oxo-pyroborate family to investigate their crystal structure and nonlinear optical properties.

The structure of each of the 8 members of the AMOB₂O₅ family has been solved using a superstructure approximation to find that slight changes in the size of the *A*-cation lead to changes in the multiplicity of the modulation in the structure. Figure 1 illustrates how the *A*-site cation (red) occupies the channels created by the bridging borate groups and the chains of niobium-oxygen octahedra (blue). At room temperature (RT), the Cs-cation appears to be large enough to occupy the channels such that no tilting occurs and hence CsNbOB₂O₅ is considered to be the 'parent' structure type [3].

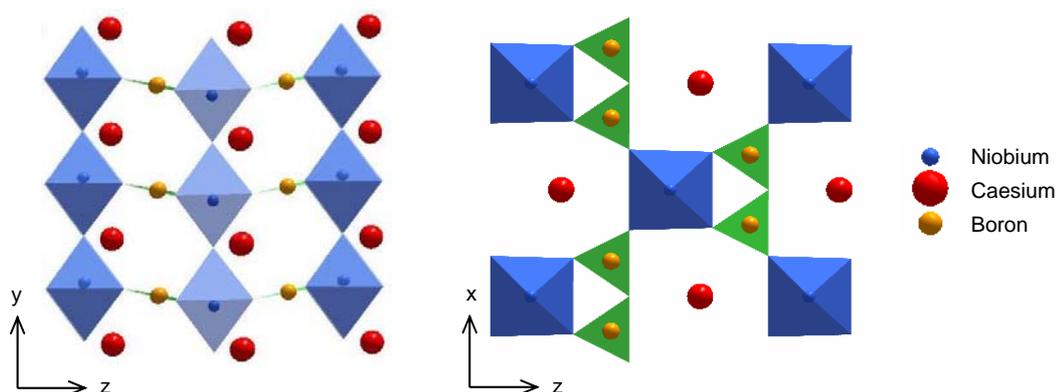


Fig. 1. Projection of the (non-modulated) crystal structure of CsNbOB₂O₅ at RT along the *x*-axis (left), and down the *y*-axis (right). Blue spheres represent niobium atoms, red spheres represent caesium, and orange spheres represent boron atoms. Oxygen atoms are at every corner of each polyhedron, but omitted for clarity.

Insertion of a smaller *A*-site cation requires the surrounding octahedra to tilt inwards in order to maintain satisfactory bonding for all atoms, introducing a structural modulation along the **b**-direction (corresponding to the *Pmn*2₁ setting of CsNbOB₂O₅) [1, 3, 4, 9].

The octahedral tilting within the $A = \text{Tl}$ compounds repeats every two octahedral units (*i.e.* displays a two-fold superstructure), the tilting within the $A = \text{Rb}$ compounds repeats every five octahedral units (*i.e.* a five-fold superstructure), and the $A = \text{K}$ compound repeats every 8 octahedral units (*i.e.* an eight-fold superstructure). To date, the multiplicity of the modulation in the $A = \text{Tl}$, Rb , K compounds has been found to be independent of whether $M = \text{Nb}$ or Ta .

Previous work on the KNbOB_2O_5 and $\text{RbNbOB}_2\text{O}_5$ family members has shown that the modulation that exists at RT is removed at high temperatures, which can be explained by a temperature-induced increase in the effective size of the A -site cation, removing the need for an octahedral tilt and hence removing the modulation.

2. Experimental

Single crystals of $\text{CsNbOB}_2\text{O}_5$ and $\text{CsTaOB}_2\text{O}_5$ were synthesised via a flux growth reaction using Cs_2CO_3 , Nb_2O_5 or Ta_2O_5 , and H_3BO_3 in the stoichiometric ratio 1:2.5:6.5. The starting reagents were heated in a platinum crucible at 1273 K for 20 hours, cooled to 1073 K at 4 K min^{-1} and then to RT at 10 K min^{-1} . The crystals were then separated from the flux by washing with warm distilled water. Single-crystal X-ray diffraction data in this study were collected on a Bruker-Nonius FR591 Rotating Anode Generator *Kappa Apex II* diffractometer, using $\text{Mo-}K_\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$).

Data collection was performed at RT, and then at 150 K, where the crystal was cooled with an Oxford 700+ cryostream. Data were collected using a 4.5 kW setting for 12 hours. Cell indexing was performed using the *CellNow* software package, and precession images were generated using the *Apex II* software package.

3. Results

3.1 $\text{CsNbOB}_2\text{O}_5$

Single-crystal X-ray diffraction data collected at RT verified that no modulation was present as reported by Becker *et al.*[3]. The crystal was then characterised again at 150 K to determine if any satellites could be observed at low temperatures. Precession photographs (Figure 2) were constructed from the single-crystal X-ray diffraction data at RT and 150 K.

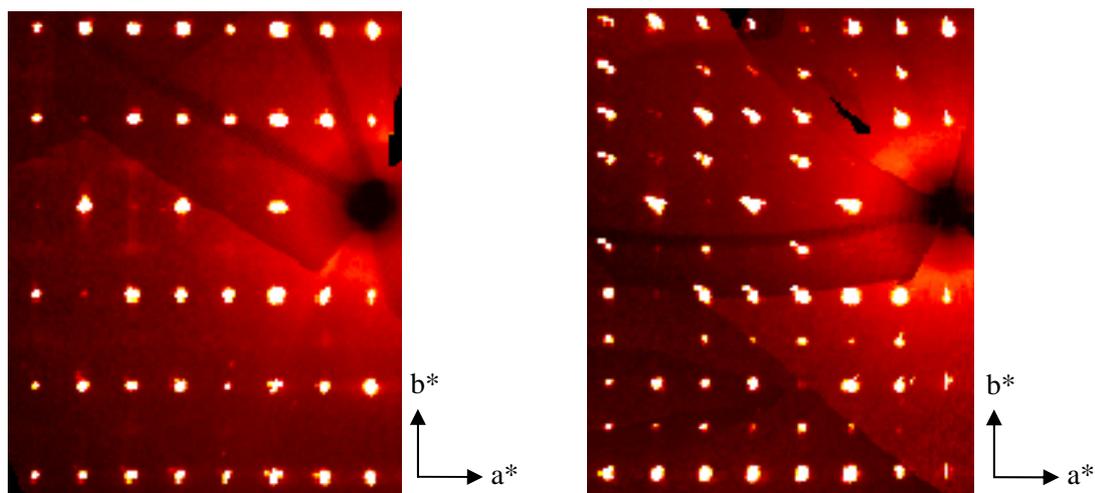


Fig. 2. Reconstructed images of the $[hk0]$ zone axis of $\text{CsNbOB}_2\text{O}_5$ at 298 K (left) and 150 K (right) with satellite reflections present.

Although no evidence of modulation was found at RT, the precession image at 150 K contains clearly observable satellites positioned exactly half way between each row of main reflections, indicating that a commensurate 2x modulation has been adopted by the structure (*i.e.* a modulation vector of $\mathbf{q} = 0.5\mathbf{b}^*$). This observation leads to a doubling of cell parameter a as the temperature is reduced from RT to 150 K (Table 1).

This structural change on cooling is evidence of a phase transition from the parent structure type to a modulated structure. Such a phase transition can be attributed to the reduced thermal energy of the atoms in the structure at low temperatures, requiring an inward tilt of the surrounding niobium-oxygen octahedra to compensate for the change in bonding requirements of an effectively smaller Cs-cation.

3.2 CsTaOB₂O₅

The CsTaOB₂O₅ family member was investigated to resolve the distinctly different observations previously published by two different research groups where it was claimed that CsTaOB₂O₅ adopts an 8x or 1x superstructure, respectively (at RT) [3, 4]. Precession images generated from CsTaOB₂O₅ single-crystal X-ray diffraction data collected at RT contained no satellite reflections and hence no evidence of modulation (Figure 3). However, first order satellites were observed in the precession images generated from data collected at 150 K, showing that a modulation is also introduced into the CsTaOB₂O₅ structure at low temperature. The observed first order satellite reflections are evenly spaced around their corresponding main reflections as shown in the precession image of the [hk0] plane in Figure 3. The positions of the satellites relative to their corresponding main reflections were measured to give a modulation vector of $\mathbf{q} = 0.43(1)\mathbf{b}^*$, providing evidence that the structure adopts an incommensurate modulation at low temperature.

The magnitude of the modulation vector for the CsTaOB₂O₅ structure is different to the CsNbOB₂O₅ structure, although most other family members ($A = \text{Ti, K, Rb}$) exhibit a modulation vector that appears to be independent of whether $M = \text{Nb or Ta}$.

Similarly to the CsNbOB₂O₅ case, the observation of a modulation in CsTaOB₂O₅ is attributed to the reduced size of the Cs-cation, requiring the surrounding octahedra to tilt inwards to maintain a closer-to-ideal bonding environment.

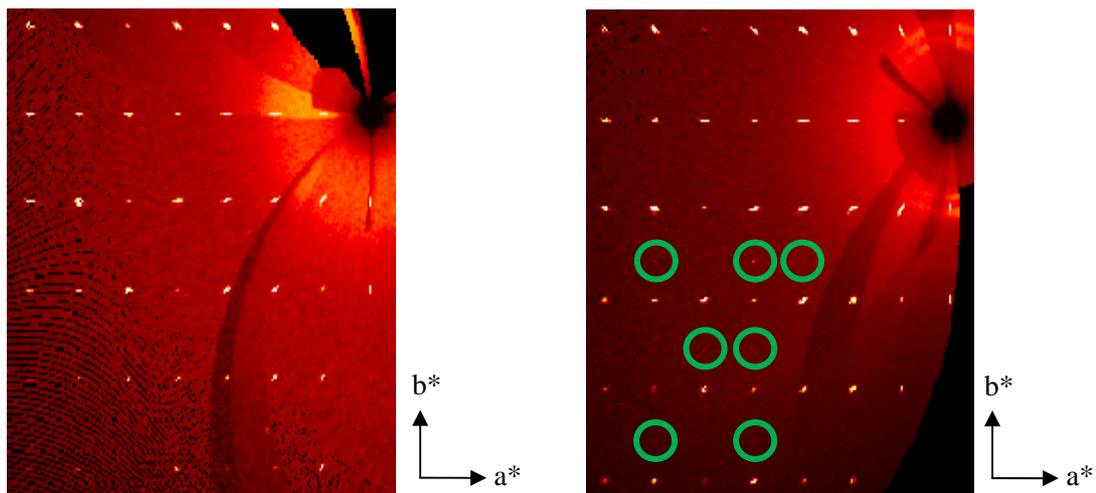


Fig. 3. Reconstructed images of the [hk0] zone axis of CsTaOB₂O₅ at 298 K (left) and 150 K (right) with satellite reflections marked with green circles.

The weakness of the satellites in the CsTaOB₂O₅ precession image at 150 K relative to those in the precession image of CsNbOB₂O₅ at 150 K is explained by the measurement of an incommensurate modulation vector because the first order satellite reflections corresponding to adjacent main reflection do not overlap in an incommensurately modulated structure and hence can be expected to have half the intensity of those observed from a commensurately modulated structure.

Table 1. Cell parameters and modulation information for CsNbOB₂O₅ and CsTaOB₂O₅ at 298 and 150 K.

Compound	CsNbOB ₂ O ₅		CsTaOB ₂ O ₅	
	298 K	150 K	298 K	150 K
a (Å)	7.5359(6)	7.5240(3)	3.9156(2)	3.9124(2)
b (Å)	3.9964(3)	7.9690(5)	7.5654(3)	7.5532(4)
c (Å)	9.7349(8)	9.7240(6)	9.7933(4)	9.7626(5)
q-vector	-	0.5b* (for parent)	-	0.43(1)b*

Differential scanning calorimetry and further temperature dependent XRD of CsNbOB₂O₅ and CsTaOB₂O₅ will be conducted to identify the nature of the transition and the exact temperature at which the transition occurs.

Acknowledgements

The authors would like to thank Dr Paul Jensen and Mr Neeraj Sharma for their assistance with single-crystal X-ray diffraction data collection and analysis.

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