

# Modulated Structures in the $AMOB_2O_5$ Family from Variable Temperature X-Ray Powder Diffraction Data

S. Schmid

*School of Chemistry, The University of Sydney, Sydney NSW 2006, Australia.*

Variable temperature X-ray powder diffraction patterns have been collected for  $RbNbOB_2O_5$  and  $KNbOB_2O_5$  between room temperature and 1073 K. At room temperature both structures are modulated and show satellite reflections in their diffraction patterns. These satellite reflection intensities diminish with increasing temperature and disappear for  $RbNbOB_2O_5$  below 828 K while for  $KNbOB_2O_5$  they are still present at 1073 K.

## 1. Introduction

Non-centrosymmetric oxo pyroborates,  $AMOB_2O_5$  ( $A = K, Rb, Cs, Tl; M = Nb, Ta$ ) [1-3], have attracted considerable interest owing to their potential use as non-linear optical materials. All members of the family possess a common underlying average structure. In addition most exhibit superstructures of varying multiplicities (2, 5 and 8) along the  $b$  axis (corresponding to the  $Pmn2_1$  setting of  $CsNbOB_2O_5$  [4]). The structures of  $RbNbOB_2O_5$  [1] and  $KNbOB_2O_5$  [2] have been refined using a superspace approach [5]. The structure of  $RbNbOB_2O_5$  is incommensurately modulated, despite the apparent value of the modulation wave vector of  $2/5 \mathbf{b}^*$  exactly. In contrast the structure of  $KNbOB_2O_5$  refined significantly better as a commensurate modulated structure and was therefore reported as a superstructure. Given the ambiguity in deciding whether a structure is commensurately or incommensurately modulated using metrics alone, a variability of the magnitude of the modulation wave vector with composition (e.g. for solid solutions) or temperature is usually taken as a means to distinguish between these possibilities, especially if refinement results are inconclusive.

Figure 1 shows the 8x superstructure of  $KNbOB_2O_5$  at RT in two projections, as an example for the whole family of compounds.

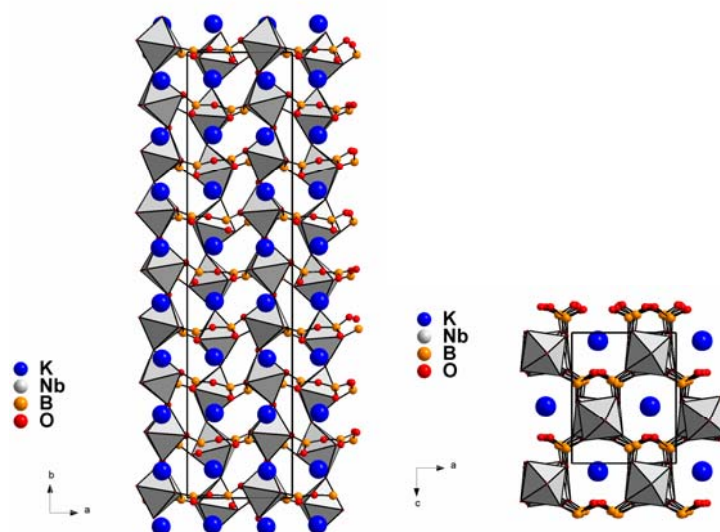


Fig. 1. The structure of  $KNbOB_2O_5$  at RT in the projection along  $c$  (left) and  $b$  (right). Niobium oxygen octahedra are corner connected to chains along  $b$  and these chains are connected by  $B_2O_5$ -groups. The unit cell boundaries are outlined in both projections.

Chains of niobium oxygen octahedra, connected via one corner, are further linked by  $B_2O_5$  groups to create a 3-dimensional structure with large channels running along  $b$ . The projection along  $c$  shows the tilting of octahedra along the chains while the projection along  $b$  shows the rotation of these octahedra in the  $ac$ -plane. The A cations (K, Rb, Cs or Tl) occupy the channels in the structure and depending on the nature of the A cation, commensurate or incommensurately modulated structures with different multiplicities are formed.

In a previous publication it has been suggested that the size of the A-cation is responsible for the modulations that are observed for most members of the  $AMOB_2O_5$  family.  $CsNbOB_2O_5$ , for example, has the largest cation and has not been reported to show a modulation, but rather is considered the parent structure type for this family [4]. For  $CsTaOB_2O_5$  the same structure would be expected, however, it has been reported both with [4] and without modulation [6]. Given the smaller size of K and Rb the niobium oxygen octahedra tilt inward to reduce the size of the channel and satisfy the bonding requirements of these smaller cations.

In this paper we report a variable temperature X-ray powder diffraction study for both  $RbNbOB_2O_5$  and  $KNbOB_2O_5$ . Diffraction patterns were collected from RT up to 1073 K. The results of the analysis of these data will be presented in the following.

## 2. Sample preparation

Powder samples for both  $RbNbOB_2O_5$  and  $KNbOB_2O_5$  were prepared from single crystalline material as described previously [2]. Variable temperature X-ray powder diffraction patterns were recorded at the Australian National Beamline Facility (ANBF), Photon Factory, Tsukuba, Japan. A wavelength of  $\lambda = 1.19646 \text{ \AA}$  was used, as a compromise between the need for high resolution and low absorption. The crystalline powders were contained in glass (RT) or quartz capillaries with 0.3 mm and 0.5 mm internal diameter, respectively. All pattern fitting and refinements were carried out using Jana2006 [7], which allows the use of X-ray powder diffraction data for the refinement of modulated structures.

## 3. Results

Figure 2 shows the powder diffraction pattern from the low angle image plate ( $\sim 4 - 45^\circ 2\theta$ ) for  $RbNbOB_2O_5$ .

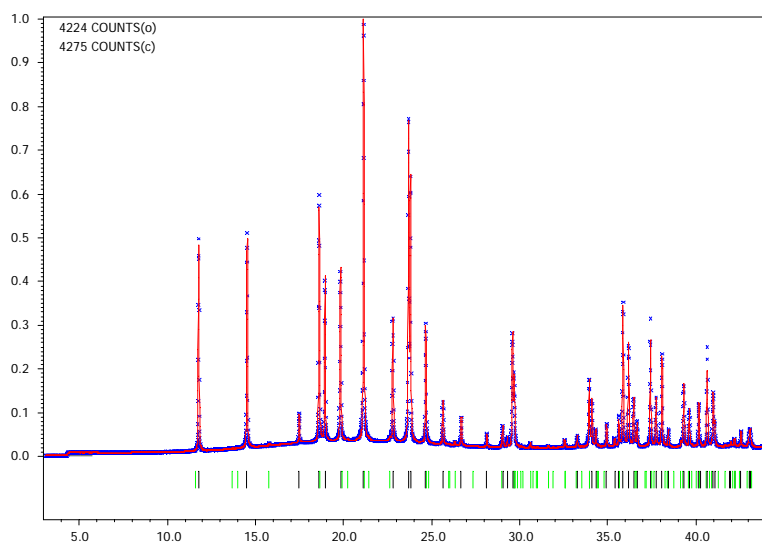


Fig. 2. X-ray powder diffraction pattern for  $RbNbOB_2O_5$  at RT (Australian National Beamline Facility, Photon Factory, Tsukuba, Japan;  $\lambda = 1.19646 \text{ \AA}$ ). Black markers indicate main reflections while green markers signify satellite reflections.

It can be seen from Figure 2 that satellite reflections (green markers) are significantly weaker than main reflections (black markers), which is common for modulated structures. Given the smaller numbers of independently observable reflections in powder diffraction patterns this makes the analysis of modulated structures from powder diffraction data especially difficult.

The diffraction patterns (as shown in Figure 2) recorded at RT were refined using the previously refined structures as starting models with Jana2006. The refinement of the powder diffraction data matches the previously reported structures very well [1, 2].

In Figure 3 only the part of the diffraction between 28 and 34 ° 2θ is shown, since that proved to be the part where satellite reflections are both very well separated from main peaks and also strong enough to be observable.

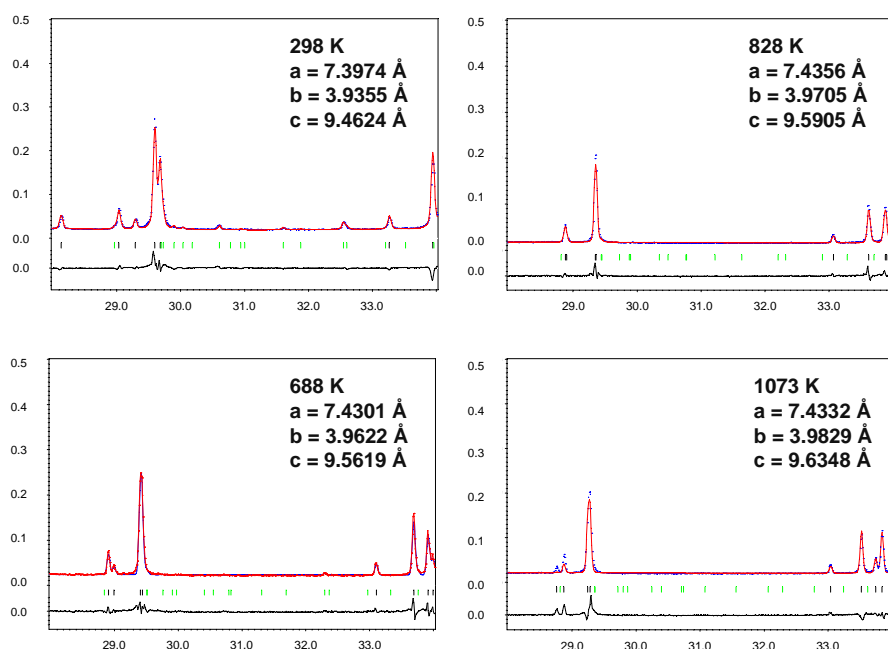


Fig. 3. Diffraction patterns for RbNbOB<sub>2</sub>O<sub>5</sub> at 298, 688, 828 and 1073 K (intensity [arbitrary units] vs. 2θ [°]; Australian National Beamline Facility, Photon Factory, Tsukuba, Japan; λ = 1.19646 Å). Black markers indicate main reflections while green markers signify satellite reflections.

Analysis of the diffraction patterns for RbNbOB<sub>2</sub>O<sub>5</sub> taken from RT up to 1073 K shows that the intensity of satellite reflections diminishes with increasing temperature and is virtually zero from about 750 K (if one interpolates between the diffraction patterns at 688 and 828 K). That shows for the first time that RbNbOB<sub>2</sub>O<sub>5</sub> undergoes a phase transition back to the unmodulated parent structure with space group *Pmn*2<sub>1</sub> on heating.

The KNbOB<sub>2</sub>O<sub>5</sub> phase was investigated in analogous fashion, however, the diffraction patterns show that there is a distinct difference between these two members of the family.

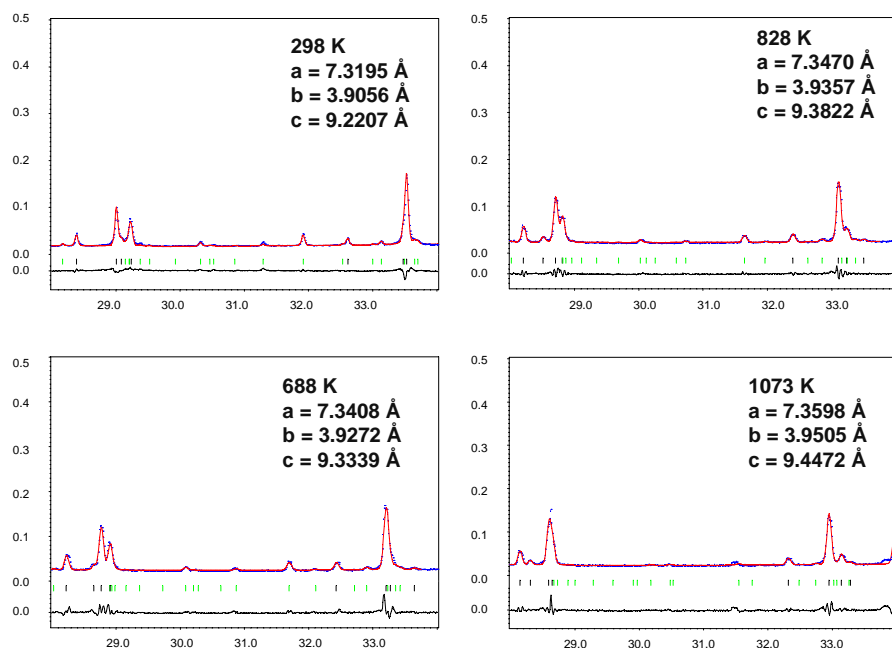


Fig. 4. Diffraction patterns for KNbOB<sub>2</sub>O<sub>5</sub> at 298, 688, 828 and 1073 K (intensity [arbitrary units] vs.  $2\theta$  [°]; Australian National Beamline Facility, Photon Factory, Tsukuba, Japan;  $\lambda = 1.19646$  Å). Black markers indicate main reflections while green markers signify satellite reflections.

Analysis of the diffraction patterns for KNbOB<sub>2</sub>O<sub>5</sub> taken from RT up to 1073 K shows that the intensity of satellite reflections is generally stronger than for RbNbOB<sub>2</sub>O<sub>5</sub> (even at RT). While the satellite intensities diminishes as well with increasing temperature there is still significant intensity observable at 1073 K (the highest achievable temperature at this instrument).

## Conclusion

The observed behaviour of the RbNbOB<sub>2</sub>O<sub>5</sub> and KNbOB<sub>2</sub>O<sub>5</sub> phases confirms the hypothesis that it is the size of the A-site cation that drives the modulation in the structure. While these phase transitions have been observed for the first time it will be instructive to investigate the temperature range in finer steps to confirm the exact transition temperature.

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## References

- [1] S. Schmid, R.L. Withers, D. Corker and P. Baules, *Acta Crystallogr.* **B54**, 558 (2000).
- [2] S. Schmid and T. Wagner, *Acta Crystallogr.* **B61**, 361 (2005).
- [3] A. Baucher, M. Gasperin and B. Cervelle, *Acta Crystallogr.* **B32**, 2211 (1976).
- [4] P. Becker, L. Bohaty and R. Fröhlich, *Acta Crystallogr.* **C51**, 1721 (1995).
- [5] R. L. Withers, S. Schmid and J. G. Thompson, *Prog. Solid State Chem.* **26**, 1 (1998).
- [6] A. Akella and D. A. Keszler, *J. Solid State Chem.* **120**, 74 (1995).
- [7] V. Petříček, M. Dušek and L. Palatinus, JANA2006, Programs for Modulated and Composite Crystals, Institute of Physics, Praha, Czech Republic (2000).