

Structural solution of a new mesoporous $\text{Rb}_3\text{Ta}_5\text{O}_{14}$ phase

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Introduction

In exploring the Ca-Rb-Ta-O phase diagram and attempting to grow new four layered members of the technologically interesting $\text{Rb}_2\text{Ca}_2\text{Ta}_4\text{O}_{13}$ perovskite family, a new structural phase was encountered. Initial XRF and EDAX analyses indicated only Rb and Ta components. Single crystal synchrotron X-ray data using BL-14A [1] was measured for the new compound at 0.85\AA wavelength, chosen to avoid the 0.81\AA Rb absorption edge [2]. Our use of the synchrotron was essential because only a few crystals smaller than 0.05^3 mm^3 were of suitable quality for study. The Diff14A Software [3] was used to drive the horizontal-type 4-circle diffractometer and an eight channel avalanche photodiode detector was used for photon counting [4].

The $\text{Rb}_3\text{Ta}_5\text{O}_{14}$ structure was solved from a half sphere of reflection data using SHELXS97 [5]. Subsequent refinement was done with Xtal3.7 [6]. Absorption coefficients [2] and anomalous dispersion coefficients [7] were taken from the tables of Sasaki. The results have been published [8].

Structure

$\text{Rb}_3\text{Ta}_5\text{O}_{14}$ is a mesoporous material comprised of a network of six distinct TaO_6 octahedra and one TaO_5 trigonal bipyramid which delimit the boundaries of three large Rb filled cavities, as well as the channels that link them. The Ta-O framework appears laminar and consists of two six-membered and one eight membered pyrochlore-like ring system, as indicated in Figure 1. These layers are stacked with a small offset leading to orthorhombic Pnma symmetry and dimensions $a=7.3677(3)$, $b=14.7904(19)$ and $c=25.379(3)\text{\AA}$.

The structure refined well with $wR=0.047$ but large residual densities were observed for two of the four Rb atoms and all four exhibit very large vibrational motion. This suggests that some degree of static or dynamic disorder is associated, could be associated with their coordinating environment. If the Rb atom disorder is static then it may be that the m -symmetry is broken.

The Rb atom environments also appear unusual in that there are chains of Rb-Rb contacts extending through the structural cavities and channels. These have contacts in the range $3.5\text{-}4.1\text{\AA}$, significantly shorter than the 4.95\AA Rb-Rb bonds in metallic (bcc) Rb. This suggests that the chains of Rb atoms in this lattice might behave as one dimensional wires, perhaps exhibiting some unusual conduction properties.

The mesoporous lattice could also be amenable to Li ion replacement, providing a solid electrolyte matrix within which Li ions could be re and de-intercalated as conduction ions.

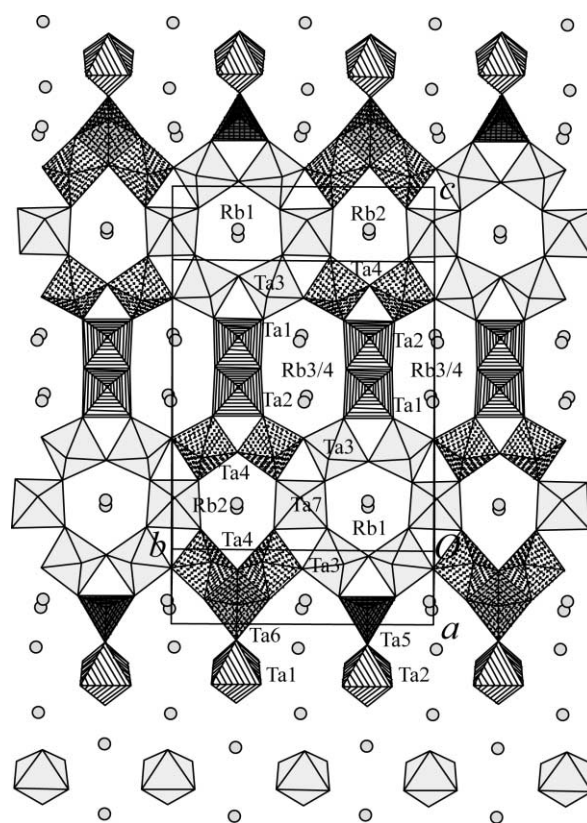


Fig. 1 Pyrochlore like layering in $\text{Rb}_3\text{Ta}_5\text{O}_{14}$

References

- [1] Y. Satow & Y. Iitaka, Rev. Sci. Instrum. **60**, 2390 (1989).
- [2] S. Sasaki, KEK Report 5-24 (1989).
- [3] T.P. Vaalsta & J.R. Hester Diff14A Software.
- [4] S. Kishimoto et al., Rev. Sci. Instrum. **69**, 384 (1998).
- [5] G.M. Sheldrick SHELXS97 Gottingen, Germany (1997)
- [6] Hall et al., Xtal3.7 <http://xtal.crystal.uwa.edu.au/> (2000)
- [7] S. Sasaki, KEK Report 7-26 (1990).
- [8] D. du Boulay et al., Acta. Cryst., **C58**, i40 (2002).

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