Crystal Structure of Ca$_5$Nb$_5$O$_{17}$

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Perovskite-related oxidic compounds of the series $A_nB_nO_{3n+2}$ ($A =$ Ca, Sr or La and $B =$ Ti or Nb) with $n =$ 4, 4.33, 4.5, 5, 6 and 7 have been the subject of much research because of their interesting electronic and dielectric properties which can be adjusted by tuning the oxygen content [1, 2]. The crystal structures of these compounds consist of slabs of corner-linked perovskites stacked along one crystallographic direction. These slabs are $n$ layers of octahedra wide and are interupted by a gap leaving an extra layer of oxygen atoms with respect to the ideal perovskite structure.

The crystal structure of Ca$_5$Nb$_5$O$_{17}$ ($n =$ 5) is monoclinic, $P2_1/c$, with lattice parameters $a =$ 7.7494(3) Å, $b =$ 5.4928(1) Å, $c =$ 32.241(1) Å and $β =$ 96.809(4)$^\circ$. Pseudo-merohedral twinning exists in the crystal structure with a twin law given by a 2-fold axis along $a$-axis resulting in the superposition of reflections $(h k l)$ and $(h -k -(h + l))_{\#1}$ of the respective twin domains. Using synchrotron radiation ($λ =$ 0.7100(2) Å), we were able to measure weak superlattice reflections and thereby determine the crystal structure [3]. The diffraction data at ambient conditions were collected at beamline F1 using a $κ$-diffractometer with a CCD area detector. After integration of the diffraction intensities and subsequent application of absorption correction, 31864 reflections were obtained with maximum $2θ =$ 71.05$^\circ$. The structure refinement converged with residual indices of $R_F =$0.0247 and $wR_{F^2} =$0.0296 for the observed reflections ($I > 3σ$).

The crystal structure comprises slabs of NbO$_6$ octahedra which exhibit a tilt pattern of $a^+c$ whereby neighboring octahedra along $a$-axis are tilted in the same sense and exhibit tilts of opposite sense about the $c$-axis (Fig. 1a, b). The effect of a $c$ tilt has been reported to induce doubling of the $a$ lattice parameter [4, 5] as has been observed in the present study. Ca atoms near the borders of the slabs exhibit irregular coordination geometries whereas those within the slabs are 12-fold coordinated as expected for a perovskite-type structure. In Fig. 1c, Ca5, which is located at the borders of the slabs, is displaced out of the center of the coordinating polyhedra towards the neighboring slab, while Ca1 and Ca3, which are embedded within the slabs, exhibit a distorted cuboctahedron coordination. The deviation of Ca5 from the center of its coordinating polyhedra toward the interlayer regions is consistent with local charge neutrality as there are excess oxygen atoms in these regions. For the Ca atoms within the slabs, the distortion follows from the slight shift of the Ca atoms from the centers of the coordinating cuboctahedra.

The distortion of the NbO$_6$ octahedral groups is minimal within the slabs and it increases towards the borders of the slabs. This is indicated by the smaller spread in bond lengths at the center compared to the borders of the slabs (Fig. 2a). Bond valence sums computed for Nb at different sites in the slabs show that Nb ions near the borders of the slabs have valences close to the formal valence of $5^+$, while those within the slabs have smaller fractional valences (Fig. 2b). This result indicates that the extra electrons in the $4d$ orbitals of Nb are most probably accommodated at Nb sites in the middle of the slabs. This further suggests that the electrical conduction in this compound takes place predominantly in the middle of the slab where the NbO$_6$ octahedra are least distorted.

References

Figure 1: NbO$_6$ octahedra tilting about ($a$) $a^*$ and ($b$) $c^*$ in Ca$_5$Nb$_5$O$_{17}$. Also shown are the sense of tilt of the octahedra. ($c$) Coordination of Ca atoms. Ca1 is in the middle of the slabs while Ca5 is at the border. The dark lines between the O atoms are only a means to clarify the coordination geometries and do not represent chemical bonds. The symbol ⊙ marks the position that Ca5 would occupy in a 12-fold coordination.

Figure 2: ($a$) Bond distances between different Nb atoms and their coordinating O atoms. ($b$) Nb valence for the different Nb sites in the octahedral slab. The Nb atoms are arranged such that the center of the horizontal axis of the graph corresponds to the center of the slab. The black triangle symbol corresponds to Nb atoms on one row along the $c$-axis while the inverted black triangle symbol refers to a second row displaced by $a/2$. The gray circle symbol denotes the average Nb–O distance for a particular Nb site.