

# Poster Presentations

## [MS18-P16] Ordering of pentavalent cations in columbitetantalite.

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Columbite-tantalite (Fe,Mn)(Nb,Ta)<sub>2</sub>O<sub>6</sub> minerals crystallizes in a superstructure of the  $\alpha$ -PbO<sub>2</sub> type, derived by the tripling of the a cell parameter due to the ordering of divalent and pentavalent cations on the two available octahedral sites, named A and B. In nature, these minerals show widely variable degrees of order in agreement with electrostatic energy calculation, which indicate that various cation ordering schemes within octahedral sites lead to similar lattice energies [1]. Nonetheless a thermal treatment induces always the complete ordered state [2,3].

In this work, cation ordering has been induced by thermal treatments in three natural columbite-tantalite crystals with different compositions along the join MnNb<sub>2</sub>O<sub>6</sub>-MnTa<sub>2</sub>O<sub>6</sub>. For each sample, different structural states covering the range of  $Q$  between 0.15 and 1 have been obtained by quenching experiments. Single-crystal X-ray diffraction (SC-XRD) has been used to characterize the structural variations as a function of the ordering degree and of composition. Ordering of divalent cations on A sites and pentavalent cations on B sites causes linear variations of a and c cell parameters, while a non-linear behavior is shown by the b cell parameter. Cation ordering causes volume variations of the two octahedral sites as a consequence of the different ionic radii of the various species. The entrance of the larger Mn<sup>2+</sup> causes an enlargement and a distortion of the A site. Octahedral bond-length distortion parameters show that distortion of the B site, in general more distorted than the A site, increases with ordering due to higher cation-cation repulsion along the B octahedral chain and to second-order Jahn-Teller (SOJT) effect. Octahedral chains respond to modifications of the polyhedra by folding along

the common edge. The relative staggering of the A and B chains depends on the mismatch between the volumes of A and B sites and on the volume of the A site respectively, irrespective of the actual composition and of the degree of order. Difference in the diffusional behaviors of Nb and Ta has been revealed by analyzing variations of refined site occupancies as a function of  $Q$ , thus suggesting that (Fe,Mn)(Nb,Ta)<sub>2</sub>O<sub>6</sub> join cannot be assimilated to a binary M<sup>2+</sup>-M<sup>5+</sup>, but rather to a three components system. Preliminary kinetics studies on this system have shown also that Mn-Ta exchange is much slower than Mn-Nb. Columbite minerals crystallized as a disordered phase and are likely to have subsequently ordered during cooling of the parent rock [4]. The degree of order seems to be related also to the composition and evolution of the pegmatite suites [4,5], and this study shows in association with the geochemical control a crystal-chemical control due to the different distribution rates of the different cations across the octahedral sites.

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