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Origin of diffuse superstructure reflections in labuntsovite-group minerals

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ABSTRACT

The average crystal structures of two natural porous titanosilicates of the labuntsovite group, lemmleinite-Ba and lemmleinite-K, ideally $Na_4K_4Ba_2Ti_8(Si_4O_{12})_4O_4(OH)_4 \cdot 8H_2O$ and $Na_4K_4K_2Ti_8(Si_4O_{12})_4O_2(OH)_6 \cdot 8H_2O$, respectively, have been refined from single crystal X-ray diffraction data. Both samples represent an extensive solid solution with labuntsovite sensu strictu $Na_4K_4D_2Ti_8(Si_4O_{12})_4O_4(OH)_4 \cdot 10H_2O$ where D = Mn, Fe, and Mg. In addition to the sharp Bragg reflections both crystals, space group $C2/m$, a = 14.3, b =13.8, c = 7.75 Å, β = 117°, exhibit diffuse layers at $c^*/2$ intervals indicating faulty superstructures with c = 15.7 Å. The diffuse layers consist of two types of reflections. The dominant type is strongly diffuse and smeared along **a*** indicating an *I*-centered Bravais lattice. The other type is very sharp but also weak and is in agreement with a *C*-centered lattice. Models for both superstructures have been developed on the basis of crystal-chemical principles and their theoretical diffraction patterns have been calculated and compared with the observed diffuse layers yielding excellent qualitative agreement.

X-ray structure refinements of the average structure at –160 and 22 °C indicate temperature independent (static) disorder of Ti within rather rigid TiO_6 octahedra connected to chains that extend along **a.** This Ti disorder is interpreted in terms of long-range order of OH and O in the superstructures where these anions occupy the corner-connecting octahedral apices in an ordered fashion. An additional effect of OH, O order is an ordered arrangement of extraframework Ba (K) that only bonds to O but not to OH sites exposed on the channel walls.

Temperature dependent cell dimensions between –160 and +200 °C suggest a phase transition at ca. –80 °C. However, the structural data obtained from the average structures, refined at –160 and 22 °C, did not allow us to draw crystal-chemical conclusions about the nature of the phase transition. Dehydration of the investigated lemmleinite-Ba starts at ca. 150 °C leading to increasing extraframework disorder and decreasing crystal quality as evidenced by strong smearing of the originally sharp Bragg reflections.