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 Na₄K₄Ba₂Ti₈(Si₄O₁₂)₄O₄(OH)₄ ⋅ 8H₂O and Na₄K₄K₂Ti₈(Si₄O₁₂)₄O₄(OH)₄ ⋅ 10H₂O, respectively, have been refined from single crystal X-ray diffraction data. Both samples represent an extensive solid solution with labuntsovite sensu strictu Na₄K₄D₂Ti₈(Si₄O₁₂)₄O₄(OH)₄ ⋅ 8H₂O, whereas that of lemmleinite-K is Na₄K₄K₂Ti₈(Si₄O₁₂)₄O₄(OH)₄ ⋅ 10H₂O 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 = 12/2 intervals indicating repeated 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 TiO₆ 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 +220 °C suggest a phase transition at ca. ~150 °C leading to increasing superframework disorder and decreasing crystal quality as evidenced by strong smearing of the originally sharp Bragg reflections.

INTRODUCTION

Labuntsovite-group minerals (Chukanov et al. 2002) comprise porous titanium and niobium silicates with a common tetrahedral-octahedral framework topology formed by chains of corner-sharing octahedra (Ti, Nb) extending along a, which are cross-linked by four-membered rings of tetrahedra (Si). Depending on the configuration of the octahedral chains two subgroups are distinguished: (1) The orthorhombic members, space group Pbm, a = 7.4 b = 14.2, c = 7.1 Å (nenadkevichite, M = Nb and korobitsynite, M = Ti) and (2) a variety of monoclinic minerals, space group C2/m, a = 14.3, b = 13.8, c = 7.75 or 15.7 Å, β = 117°. In addition to the substitution of Ti by Nb, the monoclinic labuntsovite-group minerals are distinguished by different substitutions in the porous voids. In the context of this study, the labuntsovite and lemmleinite monoclinic subgroups (Chukanov et al. 2002) are of importance.

In labuntsovite, chains of Ti octahedra are in addition to the four-membered rings of tetrahedra cross-linked by an edge-sharing octahedron (D = Mn, Fe, Mg) where the additional two octahedral apices are formed by H₂O molecules. The remaining porous space is filled by Na, K, and H₂O. The idealized formula of labuntsovite may be written as Na₄K₄D₂Ti₈(Si₄O₁₂)₄O₄(OH)₄ ⋅ 8H₂O where D = Mn, Fe, and Mg. The hyphenated suffix characterizes the species with different octahedral D ions (e.g., labuntsovite-Mn etc.).

Members of the lemmleinite subgroup have no edge-connected D octahedra but instead K or Ba (C site) occupies the same position as the H₂O molecule forming the two octahedral D-site apices in labuntsovite. Thus the substitution may be written as

\[(Fe,Mg,Mn,Zn)\text{O}_6^2+ + 2H_2O \rightarrow □\text{O}_6^2+ + 2(K, 0.5 \text{ Ba})\text{O}_6^2+\]  

(1)

The idealized formula of lemmleinite-Ba is Na₄K₄Ba₂Ti₈(Si₄O₁₂)₄O₄(OH)₄ ⋅ 8H₂O, whereas that of lemmleinite-K is Na₄K₄K₂