

STRUCTURE AND ION-EXCHANGE PROPERTIES OF LABUNTSOVITE GROUP MINERALS

R.K.Rastsvetaeva

Institute of Crystallography RAS, Moscow, Russia

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At present there are a wide range of natural and thynthetic compounds of labuntsovite family with common chemical formula $A_{10-12}M_8[T_4O_{12}]_4(O,OH)_8nH_2O$; $A=Ti, Fe, Mn, Mg, Zn, Na, Ca, K, Ba, Sr, Pb, Cs, H_3O$; $M=Nb, Ti$; $T=Si, Al, Ga$; $n=4-16$ and cell parameters $a=14.18-14.69$, $b=13.7-14.27$, $c=7.74-7.93\text{\AA}$, $\beta=117-118^\circ$ and $a=7.35-7.41$, $b=14.15-14.20$, $c=7.12-7.15\text{\AA}$. They are of interest due to their

zeolite like frameworks and considerable technological importance as ion-exchange materials [1]. The base of their structures is mixed framework consisting of the chains of corner-sharing Ti(Nb) octahedra and square rings of Si tetrahedra. In this framework there is a system of channels filled with different A cations and water molecules.

The structures of eight minerals of the labuntsovite group with different chemical compositions have been studied by XRD:

1. Korobitsynite $Na_{8.8}[Ti_{5.6}Nb_{2.4}(O,OH)_8][Si_4O_{12}]_4 \cdot 14.8H_2O$ [2].
2. Lemmleinite $K_{7.2}Na_4[Ti_{5.6}Nb_{2.4}(OH,O)_8][Si_4O_{12}]_4 \cdot 7.2H_2O$ [3].
3. Vuorijarvite $K_6Na_{1.24}[Na_{1.16}(H_2O)_{2.32}][Nb_{4.4}Ti_{3.6}(O,OH)_8][Si_4O_{12}]_4 \cdot 4H_2O$ [4].
4. H_3O -vuorijarvite $(H_3O)_4Na_2K[Sr_{0.4}(H_2O)_{0.8}][Ti_{4.5}Nb_{3.5}(OH_{4.5}O_{3.5})][Si_4O_{12}]_4 \cdot 4H_2O$ [5].
5. Kuzmenkoite $K_{3.2}(H_3O)_{1.5}Na_{0.35}Ba_{0.1}[Mn_{1.4}(H_2O)_{2.8}][(Ti_{3.2}Fe_{0.8})(Ti_{3.6}Nb_{0.4})(OH_{7.6}O_{0.4})][Si_4O_{12}]_4 \cdot 5.7H_2O$ [6].
6. K-labuntsovite (I) $K_{6.8}Na_4[Mn_{0.4}(H_2O)_{0.8}][Ti_{6.4}Nb_{1.6}(O,OH)_8][Si_4O_{12}]_4 \cdot 8H_2O$ [7].
7. K-labuntsovite (II) $K_{5.6}Na_{4.5}Ba_{0.8}[(Mn,Fe)_{0.25}Mg_{0.05}(H_2O)_{0.6}][Ti_{7.2}Nb_{0.8}(O,OH)_8][Si_4O_{12}]_4 \cdot 8H_2O$ [7].
8. Ba-labuntsovite $Na_4K_4Ba_{2.2}[Mn_{0.9}(H_2O)_{1.8}][Ti_8(O,OH)_8][Si_4O_{12}]_4 \cdot 7.2H_2O$ [8].

All the representatives of the family are subdivided into two subgroups - orthorhombic minerals (space group *Pbam*) and monoclinic ones (space groups *C2/m* or *Cm*). In orthorhombic structures the chains are straight while in the monoclinic ones they are screwy and have S-bend. There is a special position between chains suitable to the additional M(II) octahedron sharing the edges with the chain octahedra.

The orthorhombic minerals are microporous titanium-niobium silicates with the structure of nenadkevichite (korobitsynite) suitable to the substitution of Na atoms by Li and other small ions while the monoclinic representatives are characterized by larger channels of the labuntsovite structure and more appropriate to exchange Na by larger ions and H_3O groups. The structures best suited for ion exchange (lemmleinite type) don't contain any M(II) cations (Ti, Mn, Fe, Mg, Zn ...) which shut some channels.

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