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X-ray Diffraction and IR Spectroscopy Study of Labuntsovite-Group Minerals[1]

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Abstract—The distribution of cations over the positions in the structures of labuntsovite-group minerals was studied by X-ray diffraction analysis and IR spectroscopy. Several types of cation order over the five key positions are established depending on cation composition and their force characteristics. *© 2002 MAIK "Nauka/Interperiodica".*

INTRODUCTION

Minerals of the labuntsovite group are promising ion exchangers, sorbents, and catalyst carriers and therefore can be used in chromatography, catalysis, water purification, etc. Efforts were made to synthesize meso- and microporous materials [1–4] with the use of minerals of the nenadkevichite (representative of the labuntsovite group) structure type taking into account the available data on the natural specimens.

Zeolite properties of many Ti-, Nb-, and Zr-alkali silicates are associated with the differences in the force characteristics of the cation–oxygen chemical bonds. It is well known that a quantitative characteristic of a bond is the force constant derived from the second partial derivative of the total potential energy with respect to the deviation of the bond length from its equilibrium value. The corresponding stretching frequencies determined from IR spectra can be considered as a measure of force characteristics. The classification of the force characteristics into "high" and "low" ones is arbitrary. In this study, the force characteristics of the bonds, whose cation–oxygen stretching frequencies are either lower than 400 cm^{-1}, range from 400 to 700 cm^{-1}, or are higher than 700 cm^{-1} will be referred to as low, moderate, and high, respectively. It should be noted that the values of the force characteristics decrease with an increase in the coordination number and the elongation of the bond.

Transition elements (along with silicon) possessing high force characteristics of the bonds with oxygen play the key role in the structures of most of the minerals under consideration and provide the formation of three-dimensional frameworks, whereas the cations with low force characteristics and water molecules are located in their cavities.

CRYSTAL CHEMISTRY OF LABUNTSOVITE-GROUP MINERALS

The general crystallochemical formula of the monoclinic members of the labuntsovite group with ordered cations can be written as (Z = 1): $A_4B_4C_{4-2x} \cdot [D_x(H_2O)_{2x}][M_8(O,OH)_8][Si_4O_{12}]_4 \cdot nH_2O$, where $n \approx 8$, $x = 0–2$, A = Na, Ca, Sr, H$_3$O, or □; B = K, Na, H$_3$O, or □; C = K, Ba, H$_3$O, or □; D = Mn^{2+}, Fe^{2+}, Mg, Zn, or □; M = Ti or Nb; and □ is a vacancy (letters A, B, C, and D not only denote the particular set of cations but also correspond to certain structure positions or groups of positions, if the latter are split).

The labuntsovite group includes more than twenty minerals, which are widespread in the massifs of the Kola Peninsula and Greenland. Fourteen minerals of this group were recognized by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Their chemical compositions (wt %) lie within the following ranges: Na$_2$O, 0–14; K$_2$O, 0–15; CaO, 0–7; Sr–O, 0–8; BaO, 0–17; MgO, 0–2; FeO, 0–5; MnO, 0–7; ZnO, 0–7; TiO$_2$, 1–27; and Nb$_2$O$_5$, 0–39. Some structurally studied minerals of the labuntsovite group are listed in Table 1.

The structures of all the minerals of the labuntsovite group can be described as mixed frameworks consisting of infinite chains of titanium- or niobium-octahedra sharing vertices along the *a* axis. The chains are linked to each other via the [Si$_4$O$_{12}$]-rings along two other directions. The SiO$_4$-tetrahedra share vertices with the Ti(Nb)O$_6$-octahedra. The structural similarity of the mixed frameworks is seen from the fact that their unit-

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Table 1. Symmetry and unit-cell parameters of some structurally studied minerals of the labuntsovite group

Mineral	Sp. gr.	a, Å	b, Å	c, Å	β, deg	Reference
Nenadkevichite	*Pbam*	7.41	14.20	7.15	90	[5]
Korobitsynite	*Pbam*	7.35	14.15	7.12	90	[6]
Abuntsovite	*C2/m*	14.18	13.70	7.74	117.0	[7]
Labuntsovite-Mn	*C2/m*	14.29	13.85	7.78	116.8	[8]
Labuntsovite-η	*C2/m*	14.30	13.82	7.79	116.8	[9]
Lemmleinite-K(1)	*C2/m*	14.33	13.83	7.79	117.1	[10]
Lemmleinite-K(2)	*C2/m*	14.42	13.91	7.80	116.9	[10]
Lemmleinite-Ba	*C2/m*	14.22	13.75	7.77	116.7	[11]
Paralabuntsovite	*I2/m*	14.24	13.77	15.57	116.8	[8]
Niobium-rich analogue of labuntsovite	*Cm*	14.45	13.91	7.836	117.4	[12]
Lemmleinite-K(3)	*C2/m*	14.39	13.90	7.83	117.6	[13, 14]
"Monoclinic nenadkevichite"	*C2/m*	14.75	14.37	8.01	117.4	[15]
Vuoriyarvite-K	*Cm*	14.69	14.16	7.86	117.9	[16]
Kuzmenkoite-Mn	*Cm*	14.37	13.91	7.81	117.1	[17, 18]
Alsakharovite	*Cm*	14.45	13.91	7.836	117.4	[19]
Karupmollerite-Ca	*C2/m*	14.64	14.21	7.91	117.4	[20]
Gutkovaite-Mn	*Cm*	14.36	13.89	7.814	117.4	[21]
Tsepinite-Na	*Cm*	14.60	14.27	7.93	117.4	[22]

Note: Data for the monoclinic members of the labuntsovite group are given in the unified setting, which corresponds to the monoclinic angle β.

cell parameters are comparable, even if the representatives of this mineral group are described by different symmetries (Table 1). Large alkali and alkaline-earth cations and water molecules occupy the cavities of the structures.

Framework consisting of the Ti(Nb)O_6-octahedra and four-membered rings of the SiO_4-tetrahedra. The framework of the composition $[M_4(O,OH)_4(Si_4O_{12})_2]$ is negatively charged depending on the Ti : Nb ratio in the M-octahedra. The axes of the M-octahedra in the chains are tilted with respect to each other in the ac-plane, which imparts the zigzag shape to these chains. The M–O–M angles characterizing the mutual inclination of octahedra in the chains are approximately equal to (135°–138°) for all the minerals of the labuntsovite group. However, the directions of inclination substantially differ as well as the angles of mutual rotation of octahedra. In orthorhombic structures, the chains are straightened in the ac-plane, so that the chain axis is parallel to the x axis of the unit cell. In monoclinic structures, these structural elements are more complicated because of the rotation of the octahedra about their axes and the additional inclination with respect to each other in the ab-plane, so that the axis of the chain passing through the shared vertices of the octahedra is bent in a wavelike fashion. In this case, there are prerequisites for the formation of additional octahedra at the sites of mutual approach of the chains, so that the additional octahedra share edges with the chain octahedra. This transformation of the chains in the monoclinic structures leads to deformation of the silicon–oxygen rings. As a result, these rings are no longer planar and symmetrical cycles with Si–O–Si angles of 150° and 172° (orthorhombic structures). The angles of rotation of the tetrahedra in the monoclinic structures now range within 135°–154°, which offers the possibilities of identifying the minerals of the labuntsovite group from their IR spectra.

Zeolite-like cavities. The differences in the frameworks of the orthorhombic (Fig. 1) and monoclinic (Fig. 2) minerals of the labuntsovite group are reflected in the character of filling of the zeolite-like cavities. The orthorhombic minerals (sp. gr. *Pbam*) include niobium-rich nenadkevichite [5] and its titanium analogue korobitsynite [6] with the idealized general formula $Na_8(Nb,Ti)_4(O,OH)_4[Si_4O_{12}]_2 \cdot nH_2O$, where $n \approx 8$ ($Z = 1$). These structures have relatively small similar cavities, in which sodium atoms substantially dominate over other cations. The Na atoms are located in eight- and nine-vertex coordination polyhedra with the shortest Na–O distance of 2.2 Å, which hinders the incorporation of large cations such as K^+ and Ba^{2+} into the structures of the orthorhombic members of the labuntsovite group. All the other members of this group belong to the monoclinic system. Their structures contain large cavities of different shapes and sizes, which are denoted by the letters A, B, and C according to the nomenclature used for this mineral group [23] and the letter by D in the case of the formation of additional octahedral complexes. In all the structurally studied

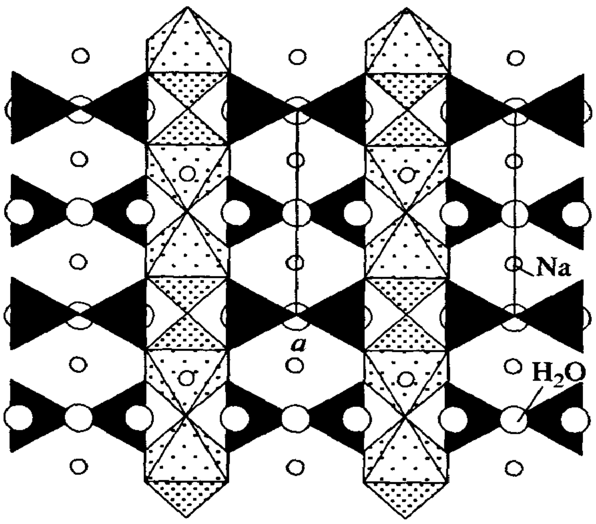

Fig. 1. Structure of the orthorhombic representatives of the labuntsovite group.

minerals of the labuntsovite group, the selective incorporation of extraframework cations into the *A*, *B*, *C*, and *D* positions was observed. This makes it possible to reveal the following characteristic features of the ordering of cations and water molecules in the series of structurally studied minerals of the labuntsovite group.

The *A* position is occupied predominantly by sodium atoms. It should be noted that four sodium atoms provide the maximum possible occupancy. Although the multiplicity of the *A* position is equal to 8, the pairs of crystallographically equivalent positions are located at such close distances (2.5 Å) that they cannot be simultaneously occupied by cations. In the monoclinic structures, the single *A* position can be split into the *A*(1) and *A*(2) subpositions spaced by 1.6–1.7 Å. One of these positions is still occupied by Na cations, whereas the other position is occupied by larger cations, such as Sr in the structure of the Zn, Ti-containing representative of the labuntsovite group [19], K in niobium-rich labuntsovite [12], and H_3O in tsepinite-Na [22]. In most of the labuntsovites, the *A*(2) position is occupied by H_2O molecules and is involved in the coordination environment around the *A*(1) position displaced for a longer distance.

The main difference between kuzmenkoite $K_4[Mn_2(H_2O)_4][(Ti,Nb)_8(O,OH)_8][Si_4O_{12}]_8 \cdot 8H_2O$ [17, 18] and the minerals with the labuntsovite structure is that the *A*(1) position in the former mineral is vacant because of the low sodium concentration, with the *A*(2) position being partly occupied by H_3O and H_2O. In the structurally studied calcium-rich labuntsovite-like minerals [15], the *A* position is vacant to a large degree because calcium is not incorporated into this position at a low sodium concentration. An analogous situation was also observed in the structure of karupmollerite-Ca $\square_4(K_{1.03}Na_{0.87})(Ca_{0.57}Na_{0.30}Ba_{0.02})(Ca_{1.39}Mn_{0.02}) \cdot (Nb_{2.71}Ti_{1.20}Fe_{0.05})(Nb_{2.63}Ti_{1.28}Fe_{0.05})[Si_4O_{12}]_4(O,OH)_8 \cdot 11H_2O$ studied by the Rietveld method [20].

An essentially different distribution of the extraframework cations is observed in the structure of gutkovaite-Mn, which is a low-sodium and, at the same time, Ca-containing representative of the labuntsovite group [21]. The Ca atoms in this mineral are ordered and occupy one of two positions related by a twofold axis, whereas these two positions in the structures of typical labuntsovites are statistically occupied by sodium. Compared to the Na-nine-vertex polyhedron (the average Na–O distance is 2.65 Å) in the labuntsovite structure, the Ca-polyhedron in gutkovaite-Mn is reduced to a seven-vertex polyhedron (the average Ca–O distance is 2.48 Å). In low-potassium (K ≤ 4) labuntsovites, all the potassium atoms are located in the *B* position [10, 23], which can also be split into partly

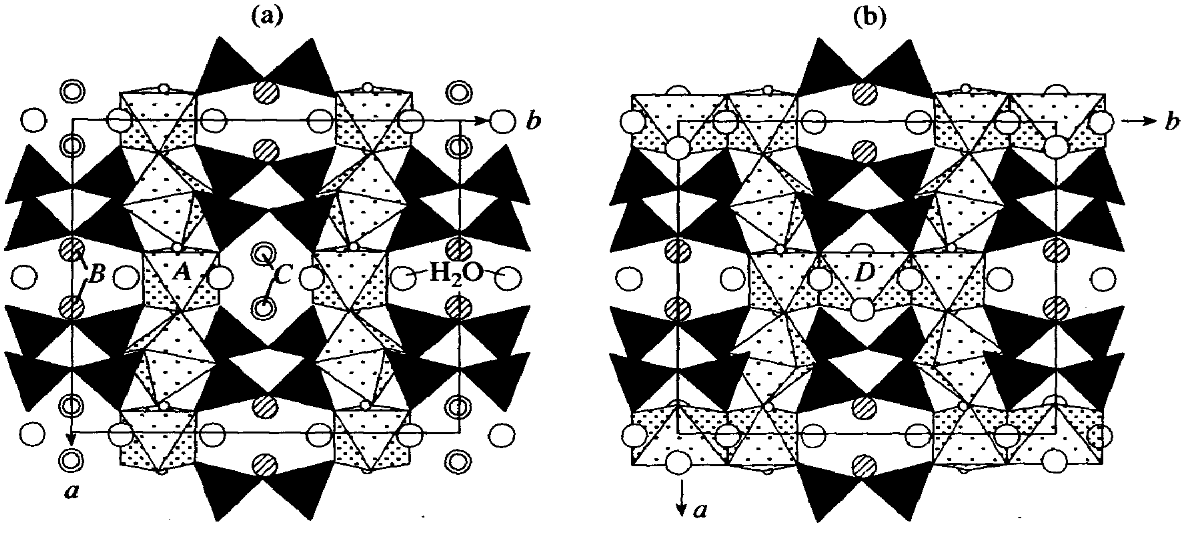

Fig. 2. Structure of the monoclinic representatives of the labuntsovite group (a) without an additional complex between the chains of the MO_6-octahedra and (b) with the additional $D(H_2O)_2$ complexes.

occupied subpositions. The structure of vuoriyarvite-K [16], which differs from most of the other minerals of the labuntsovite group, is characterized by the presence of a large number of extraframework positions spaced by close distances, including the positions around the *B* position. The disorder in the structure of this mineral is seen from the nonequivalence of all the four tetrahedra of the silicon–oxygen ring and all Nb(Ti)–O bonds in all the octahedra, the nonsymmetric splitting of the extraframework partly vacant positions, and, as a consequence, the absence of a center of inversion.

Vuoriyarvite-K is structurally similar to its Na,Ti-rich analogue—tsepinite-Na $(Na, H_3O, K, Sr, Ba)_2(Ti,Nb)_2[Si_4O_{12}](OH,O)_2 \cdot 3H_2O$ [22] from the Khibiny massif. In particular, the structure of tsepinite-Na has eight extraframework positions occupied by large cations (Na, K, Ba, Sr, Ca, and H_3O^+). However, six of these positions are usually vacant. Two positions have occupancies of ~0.6. Three other positions contain H_3O^+ ions with occupancies of 0.35, 0.26, and 0.39 (the H_3O–O distances are 3.12, 3.19, and 2.93 Å, respectively).

The partial replacement of K by H_3O was observed in some other members of the labuntsovite group, for example, in the Zn,Ti-containing representative [19]. Direct evidence of the incorporation of oxonium ions into the labuntsovite structure is lacking. At the same time, the presence of H_3O^+ ions in labuntsovites is consistent with the chemical compositions of many specimens (a deficiency of extraframework cations often accompanied by a high water content), which is confirmed by the IR spectroscopy data. The IR spectrum of the structurally studied specimen of tsepinite-Na [24] has additional bands at 3250, 2940, and 1700 cm^{-1} and is characterized by high absorption intensity in the region of Si–O–Si stretching vibrations (1000–1200 cm^{-1}). For the H_3O^+ ion with the symmetry C_{3v}, the calculated frequencies (cm^{-1}) are as follows: $\nu_1(A_1) = 3160$; $\nu_{2\delta}(A) = 1050$–1140; $\nu_3(A) = 3320$, and $\nu_{4\delta} = 1730$–1740. Apparently, the involvement of the oxonium cations in hydrogen bonding leads to a lowering of their symmetry and induces low-frequency shifts of their spectral bands. Since the $\nu_{2\delta}(A)$ band overlaps with the ν(Si–O–Si) band, the precise determination of its position is difficult.

The *B* position is most often surrounded by two water molecules, $H_2O(1)$ and $H_2O(2)$, involved in the coordination sphere of the sodium atoms, and each of these water molecules is also bound to one of the large cations (K or Ba).

In monoclinic structures, the chains of the (Ti,Nb)-octahedra can be cross-linked via additional octahedra located at the sites where the chains approach each other (Fig. 2b). These additional octahedra share edges with the octahedra of the chains. The "cross-linking" *D* position can be occupied by both $R = Mn^{2+}$, Fe^{2+}, Mg, or Zn ions and the larger ions, such as Ca, Na, or Sr. It should be noted that divalent cations R^{2+}, i.e., the cations with relatively high force characteristics, are incorporated into this position as $[R(H_2O)_2]^{2+}$ complexes. The water molecules involved in these complexes are located at the vertices of the "cross-linking" octahedron and occupy the *C* position. If the positions of the H_2O molecules and *C* cations in the labuntsovite structure virtually coincide (the distance between these positions is no larger than 0.3 Å), an interesting instance of alternative isomorphism is observed:

$$\underset{C}{2(\mathrm{K, Ba})} + \underset{D}{\square} \longleftrightarrow \underset{C}{2\mathrm{H_2O}} + \underset{D}{(\mathrm{Mn, Fe, Mg, Zn})}.$$

For the labuntsovite group, the continuous isomorphism according to this scheme occurs throughout the range of the occupancies of the *C* and *D* cation positions (i.e., from 0 to 4 and from 2 to 0, respectively). Of the "*D*-occupied" (and, consequently, "*C*-vacant") minerals with a labuntsovite structure, labuntsovite-Mn, labuntsovite-Fe, and labuntsovite-Mg have already been described [23].

The fact that the additional (cross-linking) octahedral positions are occupied mainly by the divalent Fe, Mn, Mg, and Zn cations was confirmed in a series of structural studies [10, 11]. However, the *D* position is often vacant (lemmleinite [13] and tsepinite [22]) and can also be occupied mainly by sodium (vuoriyarvite [16]) or calcium (monoclinic nenadkevichite [15]) cations. The unusual position occupied by strontium with the occupancy of 0.22 was observed in tsepinite-Na. This position can be interpreted as octahedral (an analogue of the *D* position). However, compared to the usual cross-linking cations, the strontium atoms are displaced from the centers of the squares that are formed by the oxygen atoms shared by the Ti,Nb-octahedra. The average, minimum, and maximum Sr–O distances are 2.35, 2.16, and 2.50 Å, respectively.

The shape of the chain (or the degree of its straightening) depends on the size of the cation in the key *D* position. This is reflected in the change in the unit-cell parameter *a* along the chain and, to a lesser extent, in the change in the unit-cell parameter *b*, which is exemplified by several structurally studied minerals of the labuntsovite group [22]. In particular, the average distances in the *D*-octahedra and the unit-cell parameter *a* are as follows (*A*): 2.0–2.1 and 14.2–14.3 in labuntsovites, 2.2 and 14.4 in kuzmenkoite-Mn, 2.3 and 14.7 in vuoriyarvite-K (containing Na in the *D* position), 2.3 and 14.75 in monoclinic nenadkevichite (Ca), and 2.35 (for Sr) and 14.6 in tsepinite-Na (Sr + vacancy).

As was mentioned above, the *B* position is occupied mainly by potassium cations. The excessive (above four atoms per unit cell) potassium atoms are incorporated into the *C* position where they compete with barium atoms and water molecules. It should be noted that the potassium atoms virtually share their positions with the H_2O molecules located at the vertices of the *D*-octahe-

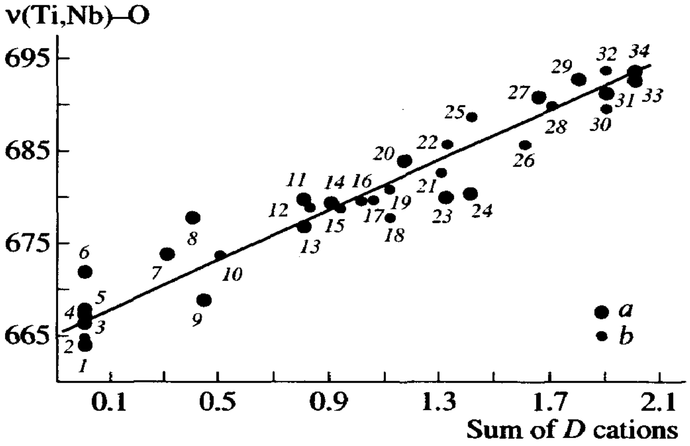

Fig. 3. Dependence of the position of the (Ti,Nb)-O stretching-vibration band on the content of *D*-cations in the minerals of the labuntsovite group according to the data of (*a*) structural studies and (*b*) chemical analysis. The experimental points are numbered in correspondence with the following specimens: *1*, *2*, and *3* (korobitsynite); *4* and *5* (nenadkevichite); *6*, *7*, *8*, and *10* (lemmleinite-K); *9* (tsepinite-Na); *11* (paralabuntsovite-□); *12*, *14*, and *15* (labuntsovite-□); *13* (lemmleinite-Ba); *16* (labuntsovite-Fe); *17*, *21*, *22*, and *26* (labuntsovite-Mg); *18* (paralabuntsovite-Mg); *19*, *21*, and *23* (labuntsovite-Mn); *20* (vuoriyarvite-K); *24* (karupmollerite-Ca); *25*, *27*, and *30* (kuzmenkoite-Mn); *28* (kuzmenkoite-Zn); *29* (organovaite-Mn); *31* (gutkovaite-Mn); *32* and *33* (organovaite-Zn); *34* (parakuzmenkoite-Fe).

dra, whereas the heavy barium atoms are more rigidly fixed at distances of 0.3 Å from the H_2O positions. In a labuntsovite structure with the more than two Ba atoms (lemmleinite-Ba) [11], the Na, K, and Ba cations were demonstrated to be completely ordered in the *A*, *B*, and *C* positions, respectively, with barium atoms in the latter position being dominant.

Karupmollerite-Ca [20] is characterized by a substantial deficiency of extraframework cations (2.8 out of 12 theoretically possible cations) with a simultaneous increase in the H_2O content. Although this mineral is structurally similar to kuzmenkoite-Mn, the *C* position in its structure is occupied by the Ca and Na cations in contrast to other minerals of the labuntsovite group, in which this position is occupied by Ba and K cations. In the structure of karupmollerite-Ca, the *C* position is displaced from the *D* position ("moves apart" from it, with the *D*–*C* distance being 2.41 Å) and from the H_2O position in the vertex of the *D*-octahedron (the *C*–H_2O distance is 0.82 Å). For comparison, the corresponding distances in lemmleinite-Ba are 2.11 and 0.29 Å, respectively. The Ca and Na cations (partly, Ba cations) statistically (by ~23%) occupy the *C* position and alternate with the *D* cations, with *D* dominating over *C* (~70 and 23%, respectively).

Lemmleinite-K [10] occupies a special place among minerals with a labuntsovite structure. This mineral is the potassium-limiting member of the isomorphous family described by the above scheme, i.e., contains no cations in the *D* positions, whereas the *C* position is almost fully occupied by K.

IR SPECTROSCOPY

The fact that the constituent elements of labuntsovites have different force characteristics of the cation–oxygen bonds enables one to successfully use both IR spectroscopy and X-ray diffraction analysis. Thus, the force constants can be directly determined from IR spectroscopic data, because these constants are proportional to the ratio of the squared frequency of the corresponding normal vibrations to the reduced mass of these vibrations.

The minerals of the labuntsovite group can be identified from their IR spectra because of the differences in the Si–O–Si angles in the four-membered silicon–oxygen rings, which, in turn, depend on the deformation of the octahedra in the chains. In the region of Ti(Nb)–O stretching vibrations (660–700 cm^{-1}), the IR spectra of minerals of the labuntsovite group have a strong narrow band. The fact that this band is not split in the spectra of multiphase samples throughout the entire range of the Ti : Nb ratio indicates that the Ti- and Nb-octahedra are involved in normal chain vibrations as virtually indistinguishable oscillators. The Ti(Nb)–O stretching frequencies depend primarily on the occupancy $x/2$ of the cross-linking *D*-octahedra (see the crystallochemical formula). The interactions between Ti(Nb)-octahedra in the chains are stronger than those between chain octahedra and *D*-octahedra. Therefore, the latter interactions can be considered as perturbations.

According to the theory of vibrations in the cluster approximation [25], these perturbations for a chain consisting of N links are described by the dynamic matrix $\Delta\check{D}$. This matrix has the dimensionality $N \times N$, and the elements of its principal diagonal are equal to Δd_0 (with a probability of $x/2$) or 0 (with a probability of $1 - x/2$). According to the first-order perturbation theory, the shift of the kth (Ti,Nb)–O stretching band is described by the following equation [26]:

$$\Delta\nu_k(N, x)^2 = g^*_{0k}\Delta\check{D}\mathbf{g}_{0k},$$

where $\mathbf{g}_{0k}$ is the kth zeroth-order eigenvector, whose ith component (with due regard for only the short-range interactions between the octahedra) is $\overset{i}{\mathbf{g}}_{0k} = [2/(N+1)]^{1/2}\sin[ik\pi/(N+1)]$. In the IR spectrum, the edge mode of the frequency branch with $k = 1$ is active. Consequently, the following equation can be written:

$$\Delta\nu(N, x)^2 = [2/(N+1)]\sum_{i=1}^{N}(x/2)\Delta d_0\sin^2[(i\pi)/(N+1)]. \quad (1)$$

Table 2. Crystallochemical role of cations with different force characteristics of the cation–oxygen bond

Cations	Isomorphism	Presence of vacancies	Splitting of positions	Stretching frequencies, cm^{-1}
Si	–	–	–	900–1100
Ti, Nb, Zr, $^{[4]}Fe^{2+}$, Fe^{3+}	+	–	–	660–700
Mn, $^{[6]}Fe^{2+}$, Mg, Zn, $^{[6]}Ca$	+	+	–	440–470
Na, K, $^{[>6]}Ca$, Sr, Ba, H_3O^+	+	+	+	<400

Summing up from $i = 1$ to $i = N$ at $N \longrightarrow \infty$, we obtain

$$\Delta\nu^2(x) = \nu^2(x) - \nu_0^2 = cx,$$

where ν_0 is the Ti(Nb)–O stretching frequency in the case of a completely vacant D position, x is the number of atoms (per unit cell) in the D position, and c is a constant. If the nondiagonal elements of the dynamic matrix $\check{D}$ that describes the interactions between oscillators are much smaller than the diagonal elements, i.e., $\nu(x) - \nu_0 \ll \nu_0$, the latter equation can be rewritten as $\nu(x) = \nu_0 + (c/2\nu_0)x$.

Thus, the position of the Ti(Nb)–O stretching band must linearly correlate with the occupancy of the D position. This conclusion was experimentally confirmed. We measured IR spectra of all the minerals of the labuntsovite group characterized either chemically or structurally. The spectra were recorded on a Specord 75 IR spectrophotometer with the spectral slit width of 1.2 cm^{-1} (for the wave numbers ranging from 400 to 1200 cm^{-1}). The samples were prepared as pellets with potassium bromide. The wave numbers were determined with the use of polystyrene and gaseous ammonia as the standards. For the structurally studied specimens, the occupancies of the D positions plotted on the graph (Fig. 3) were determined from the experimental structural data. For the remaining specimens, the occupancies were determined as an excessive (above eight atoms per unit cell) number of the octahedrally coordinated atoms (Ti, Nb, Fe, Mg, Mn, Zn).

The idealized dependence (1) was determined on the assumption that the perturbing cross-linking octahedra in the D position are identical, whereas other perturbing factors are absent. The first condition implies that the cross-linking octahedra possess close force characteristics, thus giving rise to approximately equal elements of the vibrational dynamic matrix responsible for the interactions between the links of the adjacent chains via the cross-linking octahedra. Most likely, the scatter in the points plotted on the graph in Fig. 3 results primarily from the differences in the arrangement and occupancies of the extraframework positions.

The correlation between the stretching frequencies for the chains and the occupancy of the D position allows one to make some preliminary conclusions about the character of the structures of new minerals belonging to the labuntsovite group without resorting to X-ray diffraction analysis.

The differences in the force characteristics of the cation–oxygen bonds determining the role of the cations in the structures of the specimens of the labuntsovite group can be seen from Table 2, where the cations are arranged in order of decreasing stretching frequencies. The last column in Table 2 indicates the ranges of the characteristic stretching vibration frequencies of the corresponding polyhedra, which reflect the force characteristics of four groups of cations (according to the IR spectroscopic data). In particular, this table accounts for the ever more pronounced tendency of Group IV elements to be replaced by vacancies. Probably, this tendency is associated with specimen decationization (in this case, the charge is compensated with the replacement of H_2O with H_3O^{+1} or, e.g., by the oxidation of iron or manganese to the trivalent state). For Group III elements, the complex isomorphism involves not only the replacement of both atoms by other atoms but also the replacement of complexes by other complexes.

CONCLUSIONS

To summarize, the following conclusions can be drawn.

The D cations give rise to substantial local perturbations of the force field (in the case of complete occupancy of the D position, the observed shifts of the (Ti,Nb)–O stretching bands in the IR spectra under the influence of the D cations reach 30 cm^{-1}), so that their effect must be taken into account, in particular, in the interpretation of the ion-exchange properties of the labuntsovite-group minerals.

Perturbations induced by the D cations only slightly depend on the nature of these cations. Thus, the D position can be occupied by Ca, Sr, and Na cations along with "typical" D cations (Mg, Mn, Fe, and Zn) that have close ionic radii and a coordination number of 6.

In some cases, IR spectroscopy enables one to obtain information on the distribution of the cations that play a dual role in the structures of zeolite-like minerals, without resorting to X-ray diffraction analysis. This is of particular importance in the cases where X-ray diffraction studies cannot be performed because of the poor quality of the crystals. In particular, such cations as Ca, Sr, or Na can occupy both the D position (at low coordination numbers) and large cavities of the framework, where they are characterized by high coordination numbers. This is particularly true for the representatives of the labuntsovite group that are virtually free of Mg, Mn, Fe, and Zn ions and contain about two atoms, Ca + Sr, for every 16 Si atoms. The frequencies in the maxima of the (Ti,Nb)–O stretching bands for different specimens vary over a wide range, which corresponds to the distribution of these cations both over the *D* position and the extraframework positions.

Along with the Ca, Sr, and Na cations, some transition-metal cations can also play a dual role in the structures of labuntsovite-like minerals. For example, the total amount of manganese and zinc in some specimens is substantially higher than the theoretical limit for the *D* cations (two atoms for every 16 silicon atoms) and can be equal to three or more atoms. The presence of excessive Mn + Zn ions does not lead to a substantial increase in the ν(Ti,Nb–O) frequency, and, hence, the excessive ions act as typical extraframework ions. Apparently, in this case the potassium or barium ions in the *C* position are replaced by complexes of the $[Zn(H_2O)_2]^{2+}$ type.

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