

STRUCTURE OF INORGANIC COMPOUNDS

Crystal Structures of Two Ancylite Modifications

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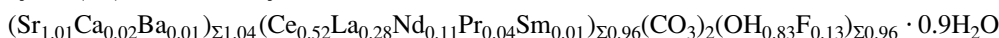
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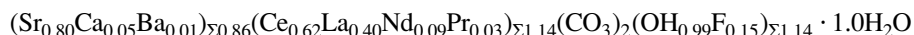
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Abstract—The crystal structures of two ancylite specimens from Khibiny massif (the Kola Peninsula, Russia)—ancylite-(Ce) from alkali hydrothermalites



and ancylite-(Ce) from carbonatites—have



been refined by the Rietveld method. A focusing STOE-STADIP diffractometer with a bent Ge(111) primary monochromator was used ($\lambda\text{MoK}_{\alpha_1}$ radiation, $2.16^\circ < 2\theta < 54.98^\circ$; reflection number 237–437). All the computations for ancylite from alkali hydrothermalites were performed within the sp. gr. $Pmc2_1$, $a = 5.0634(1) \text{ \AA}$, $b = 8.5898(1) \text{ \AA}$, $c = 7.2781(1) \text{ \AA}$, $V = 316.55(1) \text{ \AA}^3$, $R_{wp} = 1.90$; the computations for ancylite from carbonatites were performed within the sp. gr. $Pmcn$, $a = 5.0577(1) \text{ \AA}$, $b = 8.5665(2) \text{ \AA}$, $c = 7.3151(2) \text{ \AA}$, $V = 316.94(1) \text{ \AA}^3$, $R_{wp} = 2.38$ in the anisotropic approximation of thermal vibrations of cations and oxygen atoms. © 2002 MAIK “Nauka/Interperiodica”.

INTRODUCTION

Ancylite-(Ce) described by the formula $(\text{Sr}, \text{Ca})_{2-x}\text{REE}_x(\text{CO}_3)_2(\text{OH}, \text{F})_x \cdot n\text{H}_2\text{O}$ (with $x \approx 1.0\text{--}1.5$, $n \approx 1$) is one of the rare earth carbonates occurring in many alkaline massifs (the Khibiny, Sebljavr, the Kola peninsula, Vuorijarvi, Sallanlatva, and Northern Karelia (Russia), Mont Saint-Hilaire (Canada), Narssarsuk (Greenland), etc.). It is also characteristic of late low-alkali hydrothermal formations associated with apaitic rocks and carbonatites.

The ancylite family consists of five minerals described by the general formula $M_{2-x}^{2+}\text{REE}_x(\text{CO}_3)_2(\text{OH})_x \cdot n\text{H}_2\text{O}$, namely, ancylite-(Ce) and ancylite-(La) with $M^{2+} = \text{Sr}$ [1], calcioancylite-(Ce) [2] and calcioancylite-(Nd) [3] with $M^{2+} = \text{Ca}$, and gysinite-(Nd) [4] with $M^{2+} = \text{Pb}$. The crystal structure of ancylite-(Ce) was first determined within the sp. gr. $Pmcn$ in 1975 [5]. The metal atoms in the structure are located in ten-vertex polyhedra forming a three-dimensional framework (Fig. 1).

We studied crystal structures of two ancylite-(Ce) modifications found in specimens from Khibiny massif (the Kola Peninsula): the ancylite-(Ce) from alkali hydrothermalites (the Lovchorrite Mine, the Hackman Valley) described by the formula $(\text{Sr}_{1.01}\text{Ca}_{0.02}\text{Ba}_{0.01})_{\Sigma 1.04} \cdot (\text{Ce}_{0.52}\text{La}_{0.28}\text{Nd}_{0.11}\text{Pr}_{0.04}\text{Sm}_{0.01})_{\Sigma 0.96}(\text{CO}_3)_2(\text{OH}_{0.83}\text{F}_{0.13})_{\Sigma 0.96} \cdot 0.9\text{H}_2\text{O}$ (sp. gr. $Pmc2_1$) (specimen 52) and ancylite-(Ce) from carbonatites (the region of the

Tulilukht Bay) described by the formula $(\text{Sr}_{0.80}\text{Ca}_{0.05}\text{Ba}_{0.01})_{\Sigma 0.86}(\text{Ce}_{0.62}\text{La}_{0.40}\text{Nd}_{0.09}\text{Pr}_{0.03})_{\Sigma 1.14} \cdot (\text{CO}_3)_2(\text{OH}_{0.99}\text{F}_{0.15})_{\Sigma 1.14} \cdot 1.0\text{H}_2\text{O}$ (sp. gr. $Pmcn$) (specimen 54). Since the IR spectra obtained from these two

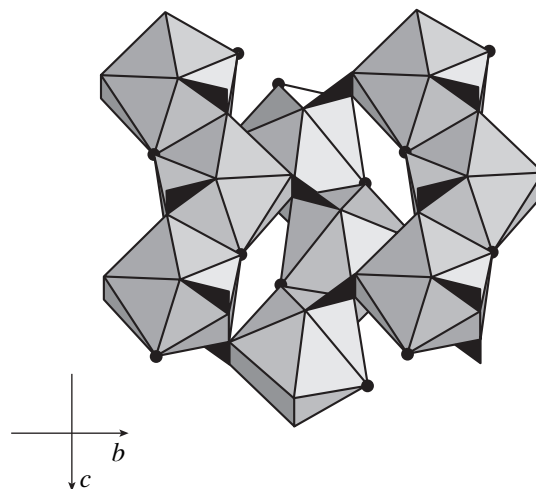


Fig. 1. Projection of an ideal ancylite structure onto the (100) plane. The CO_3^{2-} groups are indicated by black triangles. The black circles indicate the O(3) position in the structure of ancylite from carbonatites (specimen 54) corresponding to the O(31) and O(32) positions in the structure of ancylite from alkali hydrothermalites (specimen 52).

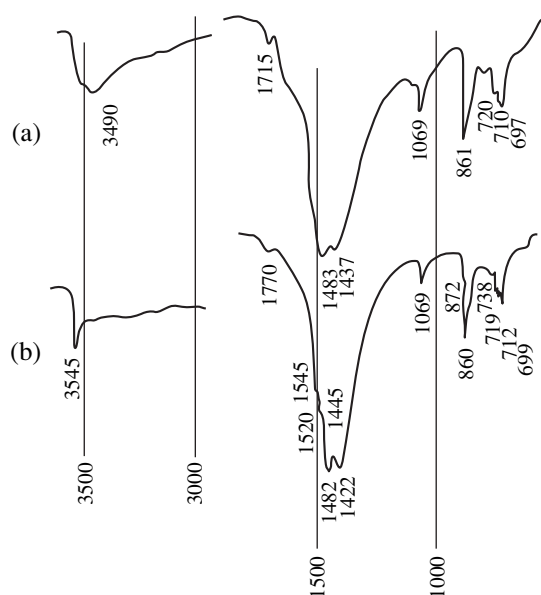


Fig. 2. IR spectra of ancylites from (a) alkali hydrothermalites and (b) carbonatites. The numbers indicate frequencies in cm^{-1} .

specimens (Fig. 2) were essentially different, we undertook their structural investigation.

EXPERIMENTAL

Ancylite-(Ce) from alkali hydrothermalites from the Hackman Valley (specimen 52) forms bright yellow aggregates of split platelike crystals with a thickness of up to 0.5 mm forming, in turn, cellular pseudomorph after the hexagonal prismatic mineral (probably burbankite) in association with feldspar, natrolite, eudialyte, aegirine, astrophyllite, and apatite. Ancylite-(Ce) from calcite carbonatites from the region of the Tululukht Bay (specimen 54) is an aggregate of white split

isometric crystals up to 0.3 mm in length forming together with strontianite a cavernous pseudomorph after burbankite.

The chemical compositions of the specimens (cations, fluorine, Table 1) was studied by electron microprobe analysis (Camebax SX 50, analyst N.N. Kononkova, Moscow State University).

The powder specimens were prepared from the specially selected homogeneous ancylite grains. The X-ray diffraction spectra were obtained on a focusing STOE-STADIP diffractometer with bent Ge(111) primary monochromator $\lambda\text{MoK}\alpha_1$ radiation, $2.16^\circ < 2\theta < 54.98^\circ$, with a total number of reflections of 437 (specimen 52); $5.00^\circ < 2\theta < 44.98^\circ$, with a total number of reflections of 237 (specimen 54). All the computations were made by the WYRIET program, version 3.3 [6] within the sp. gr. $Pmc2_1$ (specimen 52) and the sp. gr. $Pm\bar{c}n$ (specimen 54). The initial structure model refined within the sp. gr. $Pm\bar{c}n$ was the model suggested by Dal Negro, Rossi, and Tazzoli [5]. The model refined within the sp. gr. $Pmc2_1$ was also based on the structure of highly symmetric ancylite but with due regard for the absence of the plane n .

Specimen 54 showed the presence of strontianite impurity (4.2%) and, therefore, the refinement was performed for two phases simultaneously—ancylite and strontianite as the second phase.

We used ionic scattering curves. The profile peak was approximated according to the Pearson-VII function at 6FWHM. The asymmetry was refined at $2\theta < 40^\circ$. The refinement was performed with gradual inclusion into the process of new parameters to be refined and constant automatic modeling of the background until the attainment of a stable R factor. Upon the refinement in the isotropic approximation, the reliability factor R_{wp} was 2.87% (specimen 52) and 2.67% (specimen 54).

Some parameters of the data acquisition and the results of the structure refinement of ancylites in the

Table 1. Chemical composition (wt %) and the formulas of studied ancylites

Components	Specimen 52	Specimen 54	Components	Specimen 52	Specimen 54
CaO	0.34	0.68	Sm_2O_3	0.31	0.09
SrO	27.65	21.24	F	0.64	0.73
BaO	0.46	0.36	CO_2	(23.28)	(22.44)
La_2O_3	12.10	16.64	$(\text{H}_2\text{O})_1$	(1.98)	(2.27)
Ce_2O_3	22.50	25.53	$(\text{H}_2\text{O})_2$	(4.32)	(4.92)
Pr_2O_3	1.76	1.37	$-\text{O}=\text{F}_2$	0.27	0.31
Nd_2O_3	4.93	4.03	Total	(100.00)	(100.00)

Note: 1. Specimen 52 is ancylite from alkali hydrothermalites from Lovchorrit Mine and Hackman Valley of the compositions $(\text{Sr}_{1.01}\text{Ca}_{0.02}\text{Ba}_{0.01})_{\Sigma 1.04}(\text{Ce}_{0.52}\text{La}_{0.28}\text{Nd}_{0.11}\text{Pr}_{0.04}\text{Sm}_{0.01})_{\Sigma 0.96}(\text{CO}_3)_2(\text{OH}_{0.83}\text{F}_{0.13})_{\Sigma 0.96} \cdot 0.9\text{H}_2\text{O}$. Specimen 54 is ancylite from carbonatites from the region of Tululukht Bay $(\text{Sr}_{0.86}\text{Ca}_{0.05}\text{Ba}_{0.01})_{\Sigma 0.92}(\text{Ce}_{0.62}\text{La}_{0.40}\text{Nd}_{0.09}\text{Pr}_{0.03})_{\Sigma 1.14}(\text{CO}_3)_2(\text{OH}_{0.99}\text{F}_{0.15})_{\Sigma 1.14} \cdot 1.0\text{H}_2\text{O}$. 2. The calculated values are given in parentheses; the number of OH-groups (to which the $(\text{H}_2\text{O})_1$ value corresponds) was calculated from the stoichiometry; the number of water molecules $(\text{H}_2\text{O})_2$ was calculated from the difference of the total.

Table 2. Unit-cell parameters and the refined data for crystal structures of two ancylite specimens

Characteristic	Specimen 52	Specimen 54	Characteristic	Specimen 52	Specimen 54
a , Å	5.0634(1)	5.0577(1)	R_p	1.45	1.87
b , Å	8.5898(1)	8.5665(2)	R_{wp}	1.90	2.38
c , Å	7.2781(1)	7.3151(2)	R_{exp}	1.83	2.87
V , Å ³	316.55	316.94	R_B	1.53	1.34
Sp. gr.	$Pmc2_1$	$Pmcn$	R_F	1.43	1.63
2 θ -range, deg	2.16–54.98	5.00–44.98	s^*	1.04	0.83
Number of reflections	437	237	DWD^{**}	0.81	1.04
Number of refined parameters	90	50	σ_x^{***}	1.660	1.587

* $s = R_{wp}/R_{exp}$, R_{exp} is the expected value of R_{wp} .

** Durbin–Watson statistics [8].

*** Factor used for calculating standard deviations [9].

Table 3. Atomic coordinates, isotropic temperature parameters ($\text{\AA}^2$), and occupancies of the positions in ancylite-(Ce) from alkali hydrothermalites (specimen 52), sp. gr. $Pmc2_1$

Atom	Characteristic	Value	Atom	Characteristic	Value
$M(1)$	x	0	O(11)	x	0
	y	0.0977(5)		y	0.418(4)
	z	0.6437(5)		z	0.271(3)
	B_j	0.48(5)	O(12)	B_j	2.1(8)
	q (Sr)*	0.486(2)		x	0.5
	q (RE + Ba)**	0.486(2)		y	0.919(4)
	q (Ca)	0.016(6)		z	0.244(2)
$M(2)$			O(21)	B_j	1.4(8)
	x	0.5		x	0.277(2)
	y	0.5897(5)		y	0.122(2)
	z	0.8475(5)		z	0.352(2)
	B_j	0.66(5)	O(22)	B_j	1.3(5)
	q (Sr)	0.498(2)		x	0.223(2)
	q (RE) **	0.498(2)		y	0.617(2)
C(1)			O(31)	z	0.151(2)
	x	0		B_j	1.5(5)
	y	0.554(6)		x	0
	z	0.191(2)		y	0.204(3)
C(2)	B_j	1.9(9)	O(32)	z	0.992(3)
				B_j	1.4(9)
	x	0.5		x	0.5
	y	0.056(6)		y	0.660(3)
	z	0.308(2)		z	0.516(3)
	B_j	1.8(9)		B_j	1.0(8)

Notes: 1. Refinement was made for the composition $(\text{Sr}_{0.49}\text{RE}_{0.48}\text{Ca}_{0.02}\text{Ba}_{0.01})_{\Sigma 1.00}(\text{Sr}_{0.50}\text{RE}_{0.50})_{\Sigma 1.00}(\text{CO}_3)_2(\text{OH}, \text{F})_{0.98} \cdot 0.9\text{H}_2\text{O}$. The number of OH-groups was calculated from the stoichiometry; the number of water molecules was calculated from the difference of the total.
2. The refinement for RE was made with the use of the f -curve of cerium.

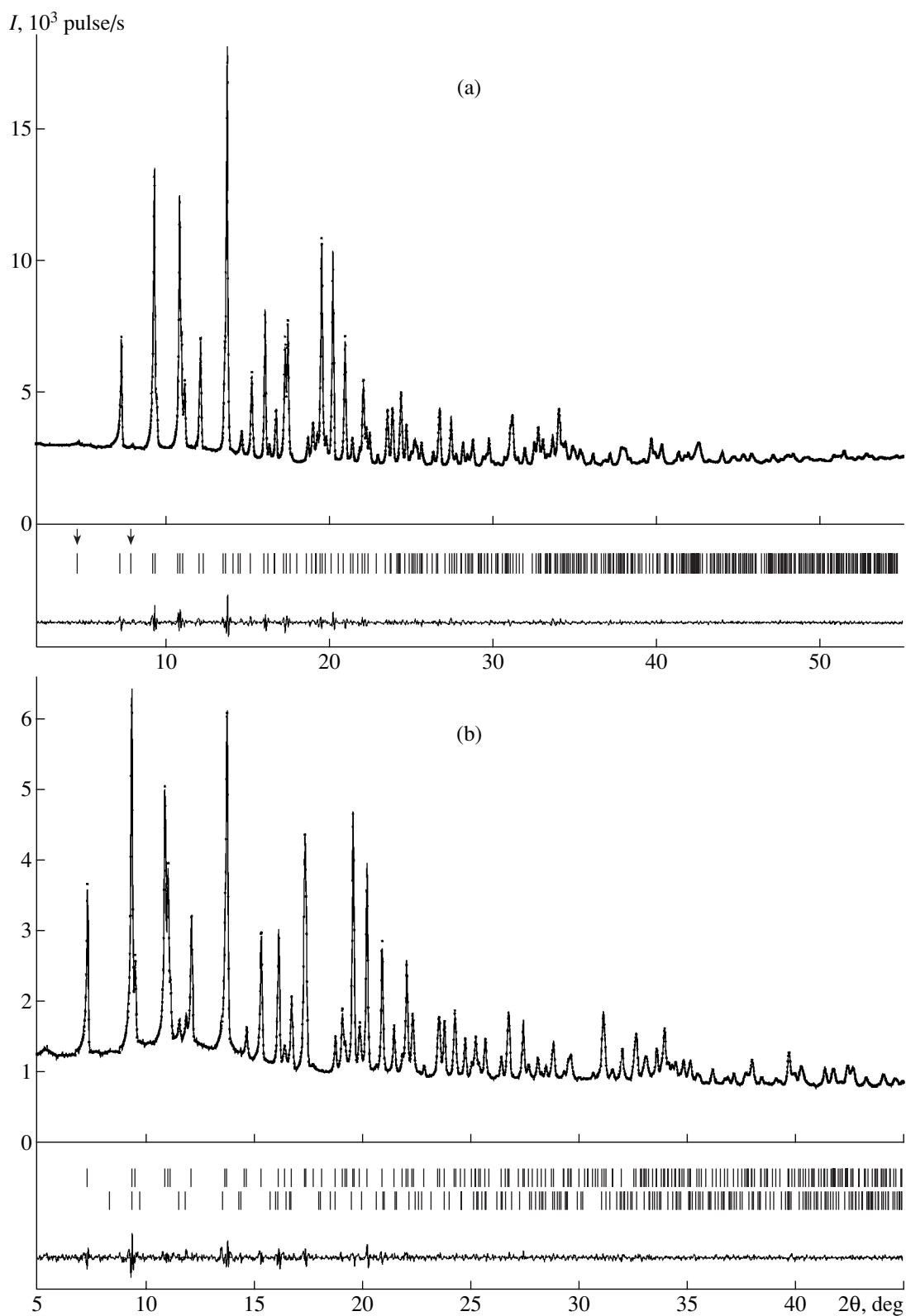


Fig. 3. Experimental (solid line) and calculated (dots) X-ray diffraction spectra from ancyrites (a) specimen 52 and (b) specimen 54. Arrows indicate the additional reflections in the spectrum from ancyrite from alkali hydrothermalites ($2\theta = 4.739^\circ$, $d = 8.579 \text{ \AA}$, $hkl = 010$ and $2\theta = 8.020^\circ$, $d = 5.072 \text{ \AA}$, $hkl = 100$) which violate the law of systematic absences for the sp. gr. *Pmcn*. The specimen from carbonatites has a strontianite impurity (the lower line diagram).

Table 4. Atomic coordinates and isotropic temperature parameters ($\text{\AA}^2$) and occupancies of the positions in ancylite-(Ce) from carbonatites (specimen 54), sp. gr. *Pmcn*

Atom	Characteristic	Value	Atom	Characteristic	Value
<i>M</i>	<i>x</i>	1/4	O(1)	<i>x</i>	3/4
	<i>y</i>	0.3409(3)		<i>y</i>	0.3286(2)
	<i>z</i>	0.6482(3)		<i>z</i>	0.7336(2)
	<i>B_j</i>	0.96(2)		<i>B_j</i>	2.7(5)
	<i>q</i> (RE + Ba)*	1.153(3)	O(2)	<i>x</i>	0.5266(2)
	<i>q</i> (Sr)	0.798(4)		<i>y</i>	0.1223(1)
	<i>q</i> (Ca)	0.056(8)		<i>z</i>	0.8525(2)
C	<i>x</i>	3/4		<i>B_j</i>	1.2(3)
	<i>y</i>	0.1961(4)	O(3)	<i>x</i>	1/4
	<i>z</i>	0.8154(5)		<i>y</i>	0.4183(2)
	<i>B_j</i>	3.7(9)		<i>z</i>	0.9736(2)
				<i>B_j</i>	2.7(5)

Notes: 1. Refinement was made for the composition $(RE_{1.13}Sr_{0.80}Ca_{0.06}Ba_{0.02})_{\Sigma 2.01}(CO_3)_2[(OH, F)_{1.15}(H_2O)_{1.0}]_{\Sigma 2.15}$. The number of OH-groups was calculated from the stoichiometry; the number of water molecules was calculated from the difference of the total.
 2. The refinement for RE was made with the use of the *f*-curve of cerium.

anisotropic (metal and oxygen atoms) and isotropic (carbon atoms) approximations are listed in Table 2. Figure 3 shows the experimental (solid line) and the calculated (dots) X-ray diffraction spectra of ancylites. The coordinates and the isotropic temperature corrections for atoms and the position occupancies are indicated in Tables 3 and 4.

The IR spectra of ancylites prepared in the shape of tablets with KBr were obtained on a Specord 75 IR spectrophotometer.

DISCUSSION

The crystal structure of ancylite-(Ce) was first solved within the sp. gr. *Pmcn* as a derivative of the aragonite structure in 1975 [5]. Our results obtained for ancylite-(Ce) from carbonatites (specimen 54) agree well with the data of this first structure determination [5]. Divalent Sr, Ca, Ba cations and rare earth elements in ancylite are located in ten-vertex polyhedra formed by O(1), O(2), and O(3) oxygen atoms. Ten-vertex polyhedra share triangular O(1)–O(3)–O(2) faces and form chains along the *c*-axis. In turn, these chains form a three-dimensional framework via (CO_3) -triangles, with each triangle being surrounded with three *M*-polyhedra sharing their edges (Fig. 1).

The average distances in the polyhedra are *M*–O 2.63, C–O 1.31 Å (specimen 54) and *M*(1)–O 2.69, *M*(2)–O 2.62, C(1)–O 1.29, and C(2)–O 1.29 Å (specimen 52).

Unlike the X-ray diffraction pattern from ancylite from carbonatites (Fig. 3b), the X-ray diffraction pattern from ancylite from alkali hydrothermalites (Fig. 3a) has some additional reflections ($2\theta = 4.739^\circ$, $d = 8.579$ Å,

$hkl = 010$ and $2\theta = 8.020^\circ$, $d = 5.072$ Å, $hkl = 100$), which violate the law of systematic absences for the sp. gr. *Pmcn*. Therefore, the structure of this mineral was refined within the less symmetric group *Pmc2*₁ in which the cations (Sr, Ca, Ba, and RE) are located in two crystallographically nonequivalent positions *M*(1) and *M*(2). Since the ratio of the number of divalent cations to the total number of rare earth elements in this specimen was close to 1 : 1, we first assumed that *M*²⁺ and RE occupy two separate positions and that the lowering of the symmetry is caused by cationic ordering. However, the structure refinement showed that both these positions are occupied statistically (Table 3) and the lowering of the symmetry in the structure of this ancylite modification is caused by the displacement of atoms from the special positions to the general ones. The disappearance of the plane *n* is associated with the split of each position in the above structure into two nonequivalent positions (Tables 3 and 4), with the differences in the coordinates of each pair of atoms being much more pronounced than the accuracy of the determination of these coordinates.

The calculation of the local balance by the method suggested in [7] and the allowance for possible hydrogen bonds allowed us to single out O atoms, (OH)[–] groups, and H₂O molecules in the anionic part of the structure. In the structure of ancylite from carbonatites (specimen 54), the O(1) and O(2) positions are occupied by O atoms, whereas the O(3) position is statistically filled with (OH)[–]-groups and H₂O-molecules. In the structure of low-symmetric ancylite from alkali hydrothermalites (specimen 52), the OH[–]-groups and H₂O molecules are orderly distributed over the O(32) and O(31) positions, respectively.

The IR spectrum of ancylite from alkali hydrothermalites (specimen 52) (Fig. 2a) has a band at 3480–3490 cm^{-1} corresponding to the stretching vibrations of OH^- groups forming relatively weak hydrogen bonds. Sometimes, we also observed a shoulder at 3530–3540 cm^{-1} , which is attributed to free OH -groups whose number is considerably less than the number of these groups linked by hydrogen bonds. The water molecules form rather strong hydrogen bonds, which manifest themselves in the IR spectrum as a broad band with the maximum at 2900–3000 cm^{-1} . The triply degenerate band of bending vibrations of CO_3^{2-} anions is split into four to six components, which indicates the presence of CO_3 -groups of at least two kinds. At the same time, the presence of an unsplit band due to fully symmetric stretching vibrations of CO_3^{2-} groups at 1068 cm^{-1} indicates a considerable violation of the local symmetry of carbonate anions only for one kind of CO_3^{2-} groups.

The IR spectrum of ancylite from carbonatites (specimen 54) considerably differs from that of ancylite from alkali hydrothermalites in that it has a narrow intense band at 3540–3545 cm^{-1} and a narrow band at 739 cm^{-1} (Fig. 2b) attributed to the stretching and bending vibrations of OH^- anions forming no hydrogen bonds, whereas no hydroxyl groups linked by a hydrogen bond are present at all (the absence of the band at 3480–3490 cm^{-1}).

Thus, we can state that there exist two ancylite modifications which are crystallized in two different space groups of the orthorhombic system and have essentially different X-ray and IR-spectroscopic characteristics. Taking into account the corresponding crystallochemical data, these modifications should be described by

different formulas (Tables 3 and 4). The representative sampling of IR spectra of ancylites from numerous alkaline massifs over the entire world allows us to state that both ancylite modifications occur widely in nature.

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