

TABLE I. Revdite: Coordinates (for x , $\times 10^4$; for y and z , $\times 10^3$) of Basis Atoms and Equivalent Thermal Parameters

Atom	x/a	y/b	z/c	B_{equ}
Si1	2025(1)	208(1)	680(1)	0,7(1)
Si2	2997(1)	492(1)	-10(1)	1,6(1)
Si3	2727(1)	498(1)	573(1)	1,6(1)
Si4	4522(1)	465(1)	680(1)	3,0(2)
Si5	4528(1)	28(1)	679(4)	2,6(2)
Si6	4528(1)	244(1)	8(2)	2,3(2)
Si7	2973(1)	282(1)	319(1)	1,2(1)
Si8	4741(1)	247(1)	430(2)	2,4(2)
Na1	3658(1)	489(2)	128(2)	3,1(2)
Na2	2082(1)	489(2)	957(2)	2,8(2)
Na3	1302(1)	492(2)	833(1)	2,3(2)
Na4	3830(2)	250(2)	867(2)	2,0(2)
Na5	463(2)	245(1)	14(2)	2,9(2)
Na6	5000	492(3)	0	1,9(5)
Na7	1175(2)	254(2)	134(2)	2,5(2)
Na8	5000	1(3)	0	1,3(5)
Na9	2507(2)	265(2)	-5(2)	4,2(5)
O1**	239(3)	252(2)	576(3)	1,3(3)
O2*	2427(2)	489(2)	502(2)	0,8(2)
O3*	1727(2)	235(2)	602(2)	1,9(3)
O4**	2762(4)	153(3)	790(4)	2,5(5)
O5*	1184(4)	505(4)	202(4)	1,9(5)
O6*	750(2)	497(3)	370(2)	2,5(2)
O7*	2796(3)	146(2)	274(3)	1,3(3)
O8	2920(2)	366(1)	105(2)	0,6(2)
O9*	3813(4)	491(3)	802(4)	2,0(5)
O10*	3661(3)	256(2)	186(3)	1,7(4)
O11*	1327(5)	252(3)	806(5)	2,2(5)
O12*	4244(2)	493(3)	632(2)	1,9(2)
O13	3265(2)	502(2)	948(2)	1,4(2)
O14**	4133(4)	496(4)	216(3)	2,7(5)
O15**	3510(3)	495(4)	448(4)	3,1(4)
O16	2081(3)	127(2)	852(3)	2,9(3)
O17**	1015(4)	258(2)	451(4)	2,5(5)
O18**	1528(3)	489(3)	553(3)	2,9(4)
O19**	1602(4)	261(4)	226(4)	3,0(5)
O20	2776(2)	504(3)	810(2)	1,6(2)
O21*	3258(3)	248(2)	382(3)	1,6(3)
O22**	855(3)	505(3)	783(3)	1,6(3)
O23**	3401(4)	261(3)	777(3)	1,5(4)
O24**	4003(3)	252(2)	545(3)	2,3(3)
O25	2863(3)	369(2)	486(4)	1,5(4)
O26**	1692(2)	512(2)	50(2)	1,8(2)
O27	2127(4)	135(2)	506(4)	1,6(4)
O28*	4211(4)	254(3)	46(4)	4,1(5)
O29	4593(3)	114(2)	885(3)	2,8(3)
O30	283(3)	398(2)	257(3)	2,9(3)
O31*	2247(3)	342(2)	194(3)	1,9(3)
O32	4733(3)	238(2)	197(3)	2,2(3)
O33	2187(3)	339(2)	726(3)	1,3(3)
O34	4598(3)	378(2)	888(3)	2,6(4)
O35**	255(4)	394(3)	798(4)	3,8(4)
O36	4641(3)	114(2)	496(3)	2,6(3)
O37	4636(3)	382(2)	493(3)	2,5(3)
O38**	260(4)	97(3)	786(4)	4,0(4)
O39*	282(3)	95(2)	257(3)	3,6(4)
O40	5000	241(3)	500	2,0(5)
O41**	794(3)	248(2)	917(3)	2,6(3)

¹Values of anisotropic thermal factors may be obtained from the authors.

*Hydroxyl atom.

**Water molecule.

TABLE II. Revdite: Interatomic Distances (Å)

Na-octahedra					
Na1 — O13	2,32(1)	Na3 — O11*	2,34(3)	Na4 — O28*	2,26(2)
O10*	2,36(2)	O22**	2,39(2)	O23**	2,32(2)
O15**	2,43(2)	O18**	2,40(2)	O9*	2,45(3)
O9*	2,49(3)	O26**	2,43(1)	O10*	2,47(2)
O14**	2,55(2)	O10*	2,64(2)	O5*	2,48(3)
O11*	2,72(3)	O5*	2,70(3)	O24**	2,51(2)
	(2,48)		(2,48)		(2,42)
Na7 — O19**	2,31(2)	Na9 — O31*	2,20(2)		
O41**	2,39(2)	O4**	2,37(3)		
O17**	2,44(3)	O8	2,47(1)		
O11*	2,49(3)	O33	2,48(2)		
O5*	2,55(3)	O7*	2,61(2)		
O9*	2,65(3)	O16	2,75(2)		
	(2,41)		(2,48)		
Na-antiprisms					
Na6 — O38**	2,39(3)	Na8 — O35**	2,33(2)		
O38**	2,39(3)	O35**	2,33(2)		
O39*	2,42(2)	O30	2,42(2)		
O39*	2,42(2)	O30	2,42(2)		
O34	2,48(2)	O29	2,50(2)		
O34	2,48(2)	O29	2,50(2)		
	(2,43)		(2,42)		
Na-pyramids					
Na2 — O26**	2,27(1)	Na5 — O41**	1,97(2)		
O31*	2,29(2)	O35**	2,29(2)		
O33	2,30(2)	O38**	2,32(2)		
O7*	2,38(2)	O39*	2,52(2)		
O4*	2,46(3)	O30	2,54(2)		
	(2,34)		(2,33)		
Si-tetrahedra					
Si1 — O3*	1,65(1)	Si2 — O13	1,50(1)	Si3 — O25	1,62(2)
O16	1,44(2)	O5*	1,57(1)	O20	1,63(1)
O27	1,56(2)	O20	1,61(1)	O2*	1,63(1)
O33	1,57(2)	O16	1,81(2)	O27	1,69(2)
	(1,56)		(1,62)		(1,64)
O — O	(2,54)	O — O	(2,64)	O — O	(2,68)
Si4 — O12*	1,5, (1)	Si5 — O6*	1,52(1)	Si6 — O29	1,55(2)
O34	1,69(2)	O29	1,66(2)	O34	1,57(2)
O39*	1,69(2)	O30	1,67(2)	O32	1,68(2)
O37	1,70(2)	O36	1,69(2)	O28*	1,79(2)
	(1,65)		(1,64)		(1,65)
O — O	(2,68)	O — O	(2,66)	O — O	(2,70)
Si7 — O21*	1,58(1)	Si8 — O40	1,42(1)		
O25	1,60(2)	O36	1,52(2)		
O7*	1,66(1)	O37	1,54(2)		
O8	1,69(1)	O32	1,60(2)		
	(1,63)		(1,52)		
O — O	(2,65)	O — O	(2,48)		

the structure in the automatic mode, or a wide variation of the calculated parameters in the direct method. Therefore, in order to select the most reliably set of phases in the multivariate method we used⁵ the NQUEST estimate, employing the ratios between the phases of four reflections (negative quartets). From the 398 strongest normalized structure amplitudes we generated 6000 triple products and in the automatic mode we compiled 46 negative quartets. After calculation of 64 phase variants, the multivariate method selected eight sets,

having selected the second set as the best according to the ROC+NQUEST criterion. The *E* synthesis constructed according to this set corresponded to $R_{hkl} = 0.188$. The method of successive approximations after four iterations reduced the value of the *R* index from 0.305 to 0.255 and revealed a fragment of the structure which, after the appropriate transition, served as the starting-point for correction of the phases in the complete cell in the acentric variant, and then in the space group $P\bar{1}$. The model of the structure obtained from 53

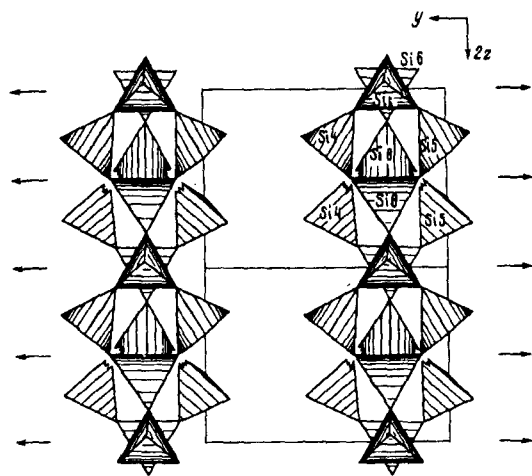


FIG. 2. Bands $[\text{Si}_8\text{O}_{15}(\text{OH})_6]$ in (100) projection at level of about $x/2$.

electron density peaks, identified with the atoms Si, Na, and O, was refined in the isotropic approximation to $R_{hkl} = 0.23$. Analysis of the model revealed that the cause of its incompleteness and inaccuracy lies in the inaccurate choice of the unit cell and symmetry. The transition with the matrix 210/010/001 to the monoclinic cell with parameters $a = 53.83(4)$, $b = 9.972(9)$, $c = 6.907(4)$ Å, $\beta = 96.78(1)^\circ$, $V = 3680(8)$ Å³ enabled us to refine the structural fragment from $1785|F|$, averaged in the space group $C2$, to $R_{hkl} = 0.16$ (in the space group $C2/m$ the R index remained higher, about 0.20). From the F synthesis we located the missing atoms:

one Si atom, three O atoms, and a water molecule. Refinement of the complete model reduced the R index to 0.132 in the isotropic approximation and 0.084 in the anisotropic one.

The final coordinates of the basis atoms and the interatomic distances are given in Tables I and II.

At this stage we formulated the crystal-chemical formula and determined the contents of the unit cell of revdite: $\text{Na}_{16}[\text{Si}_4\text{O}_6(\text{OH})_5]_2[\text{Si}_8\text{O}_{15}(\text{OH})_6](\text{OH})_{10} \cdot 28\text{H}_2\text{O}$, $Z = 2$, $d_{\text{exp}} = 1.94$, $d_{\text{calc}} = 1.93$ g/cm³. In this formula, the O atoms, the OH groups, and the H₂O molecules are distinguished on the basis of a calculation of the local balance of valence forces on the anions.⁶

A characteristic feature of the structure of revdite is the presence of two different tetrahedral bands, not bound together. One of these is the band $[\text{Si}_4\text{O}_6(\text{OH})_5]$ (Fig. 1), which geometrically resembles the bands of the synthetic crystals $\text{Li}_2\text{Mg}_2[\text{Si}_4\text{O}_{11}]$ (Ref. 7). The silicon-oxygen bands of both structures, constructed from fourfold tetrahedral rings, are readily compared with the more corrugated bands of vlasovite.⁸

The second silicon-oxygen complex of the revdite structure is unusual. This combination of two bands, lying at different levels along the x axis and mutually displaced, is of the first type (Fig. 2). The configuration of this complex (Si, O) anion with the formula $[\text{Si}_8\text{O}_{15}(\text{OH})_6]$ is similar to the recently established tetrahedral group $[\text{Si}_8\text{O}_{21}]$ in the structure of the synthetic silicate $\text{Cs}_4(\text{NbO})_2[\text{Si}_8\text{O}_{21}]$ (Ref. 9).

In the projections in Figs. 3 and 4 we clearly see the constitution of the whole structure, which can be described as an openwork framework of Na polyhedra, in the channels in

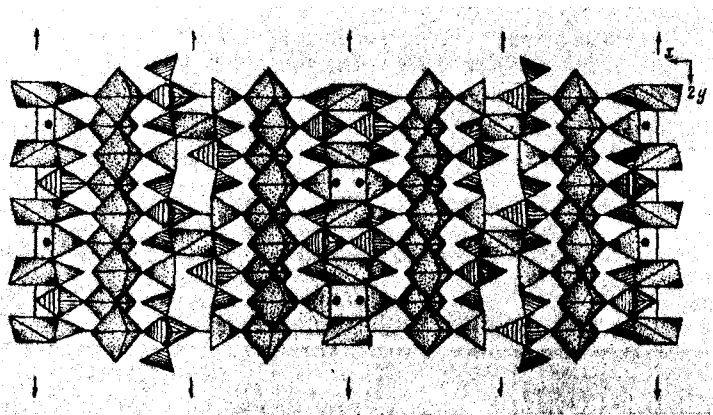


FIG. 3. Projection of revdite structure on (001) plane. Sodium polyhedra are marked by dots, (Si, O) tetrahedra by hachure, and water molecules by black circles.

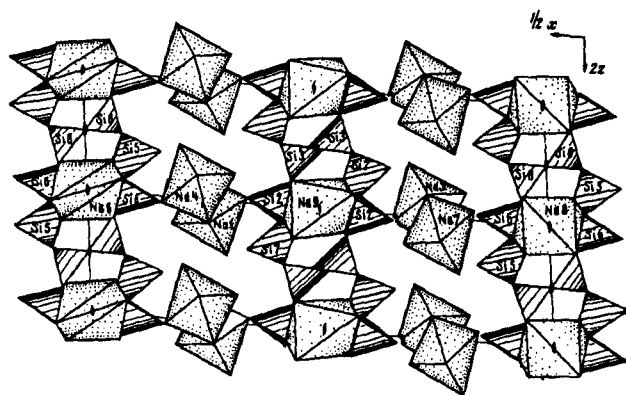


FIG. 4. Projection of revdite structure on (010) plane. Notation: same as previous figure.

which there are single and double bands of Si tetrahedra, stretching along [001], and alternating along [100]. Of the nine independent Na atoms, five lie in octahedra, two in tetragonal pyramids, and two in trigonal antiprisms. The Na₁, 3, 4, 7 polyhedra form columns parallel to [010] and joined by the Na₂, 9 polyhedra, and also by the polyhedra Na₅, 6, 8, which in turn form a hollow tube within which are the water molecules. The O1 atom of the H₂O molecule is not included in the Na₅ polyhedron owing to the long distance Na₅-O1 = 3.11 Å.

The combination of the above (Si, O) bands into a unified structure is new in respect of silicates and their analogs, characterized by the presence of different tetrahedral complexes.¹⁰ Apparently, the factor which reduces the stresses in this exceedingly unstable structure of revdite is the presence of "loose" low-discharge Na⁺ cations with fairly large coordination numbers, and also of easily polarized water molecules and (OH)⁻ groups.

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X-ray structural investigation of the crystals of the monohydrate of *L*-arginine hydrobromide C₆H₁₄O₂N₄HBr · H₂O

G. N. Nabakhtiani, N. G. Furmanova, and L. G. Chachkhiani

Institute of Crystallography, Russian Academy of Sciences

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By x-ray structural analysis the authors refine the crystal structure of *L*-arginine hydrobromide monohydrate C₆H₁₄O₂N₄HBr · H₂O, the crystals of which were obtained from the system KBr-HBr-*L*-arginine-H₂O at pH=9 (molar ratio of KBr:*L*-arginine 1:1). The authors have made a comparative analysis of the structures of *L*-arginine hydrobromide monohydrate and the isostructural *L*-arginine hydrochloride monohydrate. On the basis of the revealed differences in the structures they explain the difference in the nonlinear optical properties of the crystals of these compounds.

INTRODUCTION

In contemporary technology increasing use is being made of new organic materials with high nonlinear characteristics. Some of them are crystals of salts of *L*-arginine. Among these compounds the leader is *L*-arginine phosphate monohydrate (*LAP*) and its deuterated analog (*d-LAP*) (Ref. 1). It is reckoned that the guanidine and carboxyl groups of *L*-arginine are "responsible" for the nonlinear-optical properties of these compounds. In the opinion of the same authors, the hydrogen bonds and anions in the structure do not in themselves have an appreciable influence on the nonlinear-optical properties of the materials, but only form the mutual arrangement of the carboxyl and guanidine groups of the different molecules. However, as shown by investigations on powders,² there is marked difference in the intensities of the second harmonics not only in *LAP* and *L*-arginine hydrobromide monohydrate (*LAB*), which belong to the same space group *P2*₁ but have different structures,^{3,4} but also in the isostructural *LAB* and *L*-arginine hydrochloride monohydrate (*LACH*).⁵

Since the structure of *LAB* (Ref. 4) was determined in

1966 with poor accuracy (photographic method, *R* = 0.102), therefore for a detailed comparison of its geometrical parameters with the corresponding values for *LACH*, it appeared expedient to refine the structure of *LAB* from diffractometric data.

Note that, as shown by investigations of its physical properties, *LAB* is a good piezoelectric material.⁶ Its piezomodulus *d*₂₁₁ is three times as great as the *d*₁₁₁ coefficient of quartz.

PREPARATION OF CRYSTALS

Crystals of *LAB* are, as a rule, obtained from solutions containing *L*-arginine and HBr at pH = 3.4 (Ref. 6). We studied the behavior of the system C₆H₁₄O₂N₄-KBr-HBr-H₂O with a 1:1 molar ratio of *L*-arginine to KBr. At pH = 9 we obtained single crystals by slow evaporation at room temperature. According to the chemical analysis data, the resulting single crystals contained 29.68% Br, 20.42% N, 17.21% O and 26.30% C. For the formula of *LAB* we calculated C₆H₁₄O₂N₄HBr · H₂O: 29.25% Br, 20.51% N, 17.57%