

CRYSTALLOGRAPHIC MODEL OF DOUBLE ALUMINUM LITHIUM
HYDROXIDE USING STRUCTURAL CRYSTAL OPTICS DATA

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Structural crystal optics was used to construct a model for the structure of double aluminum lithium hydroxide in the $P6_3cm$ space group. The model accounts for most of the physicochemical properties of this compound.

Amorphous aluminum hydroxides obtained by prior synthesis or directly in the reaction medium are efficient adsorbents for the extraction of lithium from natural brines and industrial solutions [1-3]. This reaction gives a double hydroxide, $LiOH \cdot 2Al(OH)_3 \cdot (2-4)H_2O$ (DALH-OH) [4] or a double lithium aluminum hydroxo salt with the general formula $Li_xAn^{x-} \cdot 2Al(OH)_3 \cdot (2-4)H_2O$ (DALH-An), where An = Cl, Br, I, and CO_3 [5]. The reaction products, as a rule, crystallize poorly, thereby hindering the study of their structure and formation mechanism. Thus, the available data on the structure of DALH-An are limited and contradictory [7-9]. An x-ray diffraction structural analysis of a DALH-An compound indicated that it has laminar structure by analogy with hydrargillite with retention of the a_0 and b_0 unit cell parameters [6-10] and dense packing type [11]. However, the position occupied by the lithium ions in the structure of DALH-An remained unclear.

In the present work, we determined the location of lithium and its coordination and selected a crystallographic model for the compound, which permits not only the confirmation but also the prediction of some physicochemical properties of this class of compounds.

In this study, we used $LiOH \cdot 2Al(OH)_3 \cdot (2-4)H_2O$ (DALH-OH) obtained by the reaction of hydrargillite with aqueous solutions of lithium hydroxide under equilibrium conditions and the products of the intercalation of lithium salts [4, 6, 7]. In studying powders, a structural crystal optics method was used, entailing the construction of a crystal chemical or crystallographic model based on conclusions concerning the nature and arrangement of the chemical bonds and atoms using crystal optics and structural refractometry data [12, 13]. Other physicochemical methods such as x-ray diffraction structural analysis, thermal analysis, IR spectroscopy, and chemical analysis as well as various crystal chemical methods were used in constructing the model.

According to the crystal optics data, DALH-OH is the most highly symmetric form of all the forms of DALH-An since the (0001) cross-sections have trigonal form and are isotropic. The anomalous angle $2V$ is only 5° . Other forms of DALH-An (An = Cl, Br, and I) display anisotropy of the (0001) sections and have large $2V$ angles [7]. The x-ray diffraction structural determination of monoclinic symmetry with a very low monoclinicity angle (0.7°) for DALH-OH [8] close to that for bayerite (0.3°) and hydrargillite (0.5°) [10] is in accord with the assignment of DALH-OH to the most highly symmetrical form of DALH-An.

Figure 1 shows the change in the main refraction index n with increasing aluminum content (the water content per cation did not vary) in the series $LiOH \cdot H_2O$ -DALH-OH- $Al(OH)_3$. Structural refractometry methods were used in this analysis [8]. The experimental data showed that the properties of DALH-OH are rigorously additive relative to the properties of the extreme points as in the case of a mixture of two phases. On the other hand, the double hydroxide has an x-ray diffraction pattern differing from the starting phases.

The additive composition at the DALH-OH point corresponds to the chemical formula $LiOH \cdot 2Al(OH)_3 \cdot 2H_2O$. We should note that the experimental data indicate that DALH-OH may contain either two or four water molecules, having identical refraction indices $n_g = 1.554 \pm 0.01$, $n_p = 1.545 \pm 0.001$ ($N_g \parallel C$). The insensitivity of the refraction indices to the amount of

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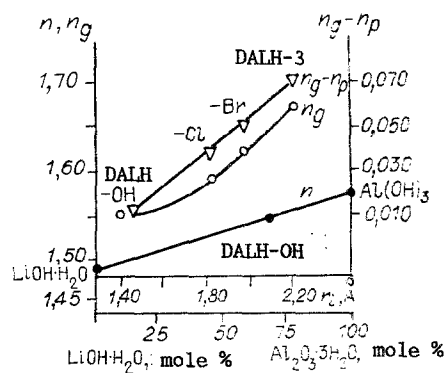


Fig. 1. Additive line of the main refraction index relative to the amounts of Al_2O_3 and LiOH in the compounds studied and increasing n and the birefringence with change in the anion bound to lithium. The size of the point corresponds to the experimental error limits.

water in the compound (the changes are within the error limits of the experimental determination) indicates weak chemical bonds of the additional water molecules, which penetrate into the structure of this compound with different structural pattern elements. Such cases have been reported extensively for oxygen compounds. The additivity of the optical properties indicates a single laminar structural pattern for all three compounds, i.e., unity is found for the structural patterns of the solid phases at the extreme points with the pattern for the double compound (mean point) with the same cation coordination numbers. The coordination of the cations has the predominant effect on the refraction index (the polyhedron forms in the layers may be different [13]).

If the lithium ion in its hydroxide had a coordination number of 6 with retention of the laminar pattern, the value of n would be increased by more than 0.02-0.03, which is known from the polymorphism data [12, 13]. Thus, the straight line given in Fig. 1 would be a curve. The tetrahedral coordination of lithium is also indicated by the similarity of the experimental refraction of DALH-OH to the additive value calculated as the sum of the refractions of $\text{LiOH}\cdot 2\text{H}_2\text{O}$ and $2\text{Al}(\text{OH})_3$ with coordination number 4 and 6 for lithium and aluminum, respectively.

The existence of an independent lithium layer containing anions and water molecules along with lithium is indirectly indicated by the experimental results obtained upon treating DALH-An with water when 90-100% of the lithium is transferred to the liquid phase, while the solid residue is virtually pure hydrargillite [14].

The symmetry of the lithium hydroxide layer should obey the trigonal dense packing symmetry if the inserted anions augment it (Fig. 2). Thus, the architecture of the arrangement of the lithium tetrahedra cannot be identical to the pseudotetragonal structure of $\text{LiOH}\cdot 2\text{H}_2\text{O}$. Furthermore, a tetragonal pyramid as in the structure of LiOH is impossible. If we orient three $\text{Li}-\text{OH}$ bonds almost in the (0001) planes and one $\text{Li}-\text{OH}$ bond parallel to the C-axis, the tetrahedron should be polar and acquire trigonal symmetry. Any other orientation of the tetrahedron would lead to a breakdown in the three-fold symmetry axis. The stoichiometry constant of the compound ($\text{Li}:\text{An} = 1:1$) also indirectly indicates polarity of the arrangement of the $\text{Li}-\text{An}$ bond. A vertical orientation of the $\text{Li}-\text{An}$ bond is indicated by the crystal optics data on monoaxial nature and trigonal symmetry of DALH-OH crystals and the increase in birefringence in the vertical plane of the crystal proportional to the increase in the radius of the inserted anions (Fig. 1).

The inserted hydroxide ions or other anions may be arranged in DALH-OH by either hexagonal or cubic dense packing. In the case of hexagonal packing (Fig. 2a), the anion layers A and B alternate: $\text{Ba}(\text{B})\text{AB}(\text{A})$. Let us examine the consequences of this process in the (0001) plane (Fig. 3). The hexagonal dense packing of the oxygen atoms in hydrargillite contains a three-fold axis [15] extending from the apices and centers of the cell triangles, which determines the multiplicity of all the atoms. Two octahedral cavities in the centers of the cell triangles are occupied by aluminum ions, forming a corundum ring. The third cavities form channels parallel to the C-axis. If the lithium ions occupy any tetrahedral cavities (I), the effect of the three-fold axes leads to an increase in their multiplicity to three for aluminum multiplicity equal to two, which is not in accord with the chemical formula of this compound. If the lithium ions are found in the octahedral cavities of the aluminum or lithium layers along the cell corners (position II), the lithium multiplicity equal to one is retained but six $\text{Li}-\text{O}$ bonds will give an identical contribution to the refraction index measured parallel to the C-axis similarly to the $\text{Al}-\text{OH}$ bonds. In this case, an increase in birefringence in the vertical plane will not be observed in going from OH types to Cl, Br, and I types of the compound studied. When a

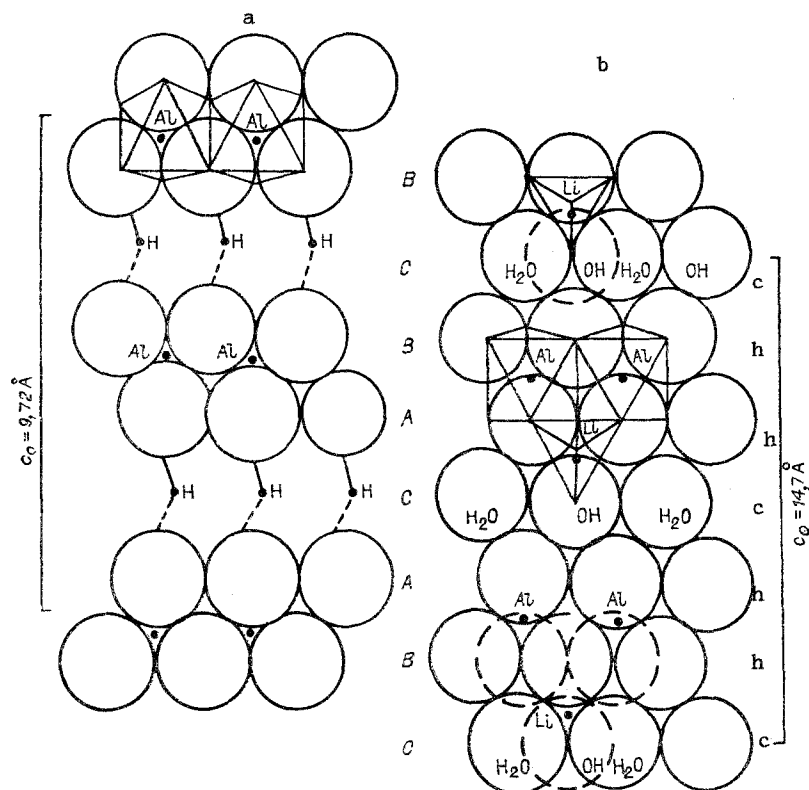


Fig. 2. Cross section of the $(10\bar{1}0)$ plane of the unit cell: a) hydrargillite with displacement of the aluminum layers by $O-H \cdots O$ bonds and b) DALH-OH with display of the $Al-(OH)$ and $Li-(OH)$ bonds and positions of the water molecules and lithium and aluminum ions.

coordination number of 4 is found from the lithium ion in this position, the inclined position of the $Li-An$ bond in the two variants for arrangement of the $Li(OH)_4$ tetrahedron will lead to anisotropy of the (0001) cross section, which is also in accord with the experimental data.

The cubic variant for arrangement of the anions in the lithium layer leads to the formation of mixed-laminar dense packing (Fig. 4). In contrast to cubing packing ABCABC, we observed the following alternation of layers: $(C)BA(C)AB(C)BA$ (Fig. 2b) and hexalaminar packing CBACABC (within the unit cell). This packing is symmetrical relative to the central c-type layer [15] (the anions upon insertion occupy the octahedral cavities, forming a c-type [cubic] layer). The lithium ion may occupy a position in the tetrahedral cavity opposite the inserted hydroxide ion without breaking the bond in the inserted $Li-OH$ (Cl, Br, I) molecule. The $Li-An$ bond is vertical and the multiplicities of Li and An are unity. The formation of the lithium tetrahedron is achieved through three other bonds with the closest hydroxide ions of the aluminum octahedral layer already present in the structure of $Al(OH)_3$. Thus, the facility of the intercalation of lithium salts into $Al(OH)_3$ is explained [7]. The vertical cross section of the oxygen layers will not differ from the analogous cross section of ABABAB packing (Fig. 2b) since the c-type layer is shifted relative to the position of the A layer along the X-axis and they coincide in this projection. When the oxygen diameter in the layer is 2.6 \AA (contraction of the diameter due to dense packing of the layers), the complete set of layers in the model hexalaminar packing corresponds to the experimental parameter $c_0 = 14.7 \text{ \AA}$. In the (0001) cross-section, we see that the inserted anion occupies one of the three dense packing positions in the c-type layer on the three-fold axes (Fig. 3). The two other positions are occupied by water molecules, which insert along with $LiOH$ from the aqueous solution. Thus, the layer should correspond to the formula $LiOH \cdot 2H_2O$.

Alternation of $[Li^4OH \cdot 2H_2O]$ and $[Al^6(OH)_3]^*$ leads to an empirical formula of DALH-OH: $LiOH \cdot 2H_2O \cdot Al_2(OH)_6$ or $Li_2O \cdot 2Al_2O_3 \cdot 11H_2O$. Chemical analysis gives the most frequently deter-

*The superscripts indicate the coordination.

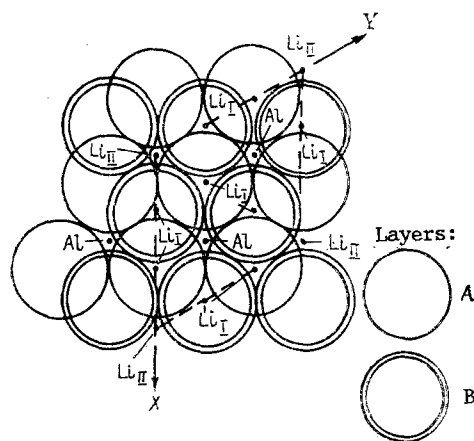


Fig. 3. Projection of the bilaminar hexagonal packing onto (0001). The possible positions of lithium ions (positions I and II) are shown in the P cell.

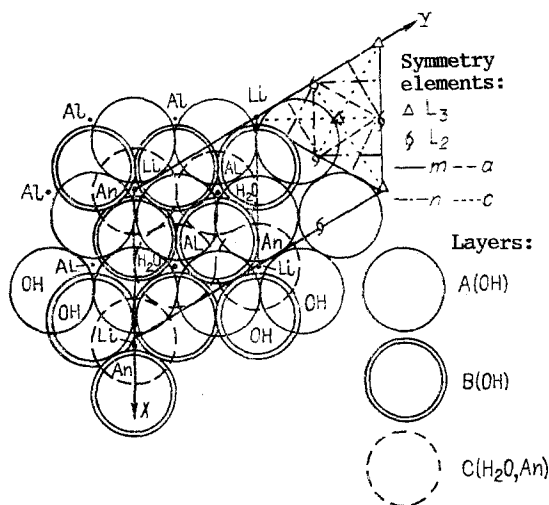


Fig. 4. Projection of the structure of DALH-OH onto (0001) on the basis of hexalaminar mixed packing. Layers A, B, and C of the anions are shown ($1/2$ parameter C_0 relative to height).

mined (mean) formula $\text{Li}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot (10.3-10.6)\text{H}_2\text{O}$ [4]. Since the bonds of the lithium cation with water are not equivalent, as indicated above, while the hydrogen bonds with the OH groups are very weak, not all the dense packing sites of the c-type layer may be occupied by water molecules, which leads to variation in the composition relative to the water content.

It is unlikely that the lithium ion may "fall into" the octahedral cavity located below the tetrahedral cavity in the next layer (Fig. 4) since the bond lengths in the $\text{Li}(\text{OH})_4$ tetrahedron have a definite value. An increase in the length of the vertical Li-OH bond should lead to a weakening of its effect on the optical indices, which is not in accord with the increase in birefringence and values of n for DALH-An (An = Cl, Br, I).

Since the symmetry of mixed lamimer packings is a function of the h-type layers [15], the trigonal (hexagonal) symmetry is retained. The space group should be sought over a system of three-fold axes passing through at least a portion of the axes of the vertical mirror planes. These requirements require the elimination of P-cells, containing only symmetry axes, especially since such compounds and minerals have a constant needle habitus, while platelets with twinning relative to (0001) are characteristic for DALH-OH. Since the lithium tetrahedra are polar, the $\bar{3}$ and $\bar{6}$ rotoinversion axes and horizontal symmetry planes are impossi-

TABLE 1. Coordination of the Ions for DALH-OH with $P6_3cm$ Space Group

Atom	Multiplicity	Position	Coordinates
Li	2	<i>a</i>	0 0 1/2 0 0 7/12
Al	4	<i>b</i>	1/3 2/3 3/4; 2/3 1/3 3/4 1/3 2/3 1/4; 2/3 1/3 1/4
O	6	<i>c</i>	1/3 0 1/6; 0 1/3 1/6; 2/3 2/3 1/6 2/3 0 2/3; 0 2/3 2/3; 1/3 1/3 2/3
	6	<i>c</i>	2/3 0 1/3; 0 2/3 1/3; 1/3 1/3 1/3 1/3 0 5/6; 0 1/3 5/6; 2/3 2/3 5/6
OH(Cl)	2	<i>a</i>	0 0 0 0 0 1/2
H ₂ O	4	<i>b</i>	1/3 2/3 0; 2/3 1/3 0 1/3 2/3 1/2; 2/3 1/3 1/2

ble. These limitations lead to a set of six space groups: $P31m$, $P3m1$, $P3c1$, $P31c$, $P6_3mc$, and $P6_3cm$. Figure 4 shows the cell symmetry elements arising for the atomic arrangement described above. Three vertical mirror planes traverse only in the directions of the crystallographic X, Y, and *i* axes. Thus, of the remaining group, we select $P31m$ and $P6_3cm$. A portion of the atomic positions of both groups are almost identical. The emergence of the screw axes by $1/2X$ and $1/2Y$ with three-fold axes at the centers of the cell triangles indicates the existence of a 6_3 axis at the cell corners. The additional existence of glide planes along the C-axis through the cell diagonals indicates the $P6_3cm$ group.

The atomic coordinates in the selected space group are shown in Table 1. Parameter Z was calculated using the vertical projection (Fig. 2b). The lithium ion and the associated inserted hydroxide ion occupy position (*a*) with coordinates (00Z), Al occupies the 1/3, 2/3, and Z position as the water molecules in the c-type layer. The oxygen atoms are displaced at the position (*c*) with multiplicity three and X0Z coordinates in the h-type layers.

Thus, the structure of DALH-OH as the most highly symmetrical form of DALH-An may be described satisfactorily in the framework of a crystallographic model using a hexalaminar mixed packing and space group $P6_3cm$, permitting us to explain most of the physicochemical properties of this compound. The lithium and aluminum ions are located in different layers of the structure described by the following structural formula: $[Li^+OH \cdot 2H_2O] \cdot Al_2^6(OH)_6$. The lithium tetrahedron is polar.

LITERATURE CITED

1. J. Kelly, *J. Appl. Biotechnol.*, **28**, 469-475 (1978).
2. M. Frenkel, A. Clasner, and S. Sarig, *J. Phys. Chem.*, **84**, 507-512 (1980).
3. Ding Xue Kang, Xiang-Mu Shen, and Xue-Juan Won, *J. Chem. Technol. Biotechnol.*, **31**, 683-690 (1981).
4. N. P. Kotsupalo, V. A. Pushnyakova, and A. S. Berger, *Zh. Neorg. Khim.*, **23**, No. 9, 2514-2520 (1978).
5. V. P. Danilov and I. I. Lepeshkov, Abstracts of the 12th Mendeleev Congress on General and Applied Chemistry [in Russian], Part, 1, Moscow (1981), p. 29.
6. A. P. Nemudryi, V. P. Isupov, N. P. Kotsupalo, et al., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim.*, **4**, No. 11, 28-37 (1984).
7. A. P. Nemudryi, V. P. Isupov, N. P. Kotsupalo, and V. V. Boldyrev, *Zh. Neorg. Khim.*, **31**, No. 5, 1146-1156 (1986).
8. E. T. Devyatkina, N. P. Kotsupalo, N. P. Tomilov, et al., *Zh. Neorg. Khim.*, **28**, No. 6, 1420-1429 (1983).
9. C. J. Serna, J. L. Rendon, and J. E. Iglesias, *Clay and Clay Minerals*, **30**, No. 3, 180-185 (1982).
10. R. Rothbauer, F. Zigan, and H. O'Daniel, *Z. Krist.*, **B125**, 317 (1967).
11. I. A. Poroshina, N. P. Kotsupalo, M. I. Tatarintseva, et al., *Zh. Neorg. Khim.*, **23**, No. 8, 2232-2237 (1978).
12. S. S. Batsanov, *Structural Refractometry* [in Russian], Vysshaya Shkola, Moscow (1976).

13. I. A. Poroshina, Zh. Fiz. Khim., 64, No. 5, 1155-1159 (1980).
14. V. A. Pushnyakova, V. D. Belykh, V. P. Isupov, et al., Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim., 6, 57-63 (1984).
15. N. V. Belov, Outline of Structural Mineralogy [in Russian], Nedra, Moscow (1976).

REFINEMENT OF THE CRYSTAL STRUCTURE OF $Pb_5(GeO_4)(VO_4)_2$
RELATIVE TO THE POWDER DIFFRACTION PATTERNS PROFILE

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The Rietveld method for analyzing the profile of powder diffraction patterns was used to study the crystal structure of $Pb_5(GeO_4)(VO_4)_2$, which has been assigned to the apatite structural type [space group $P6_3/m$, $a = 10.099(3)$, $c = 7.400(2)$ Å, $Z = 2$]. The refinement results ($R_p = 0.51$, $R_{wp} = 0.073$, $R_b = 0.022$) using the PFSR program indicated that, in contrast to apatite with the general formula $A_4B_6(XO_4)_6Y_2$, the lead cations in $Pb_5(GeO_4)(VO_4)_2$ occupy both A(4f) and B(6h) positions, while the anionic position Y remains vacant. In turn, the germanium and vanadium cations are randomly located in the tetrahedral position X. Analysis of the cation-anion distances indicates an unusual geometry of the anionic environment of one of the lead cations [located in the (6h) position], which may be described, to a first approximation, by a distorted pentagonal pyramid. Such coordination of this cation may be ascribed to its possession of an unshared electron pair.

Monocrystals of $Pb_5(GeO_4)(VO_4)_2$ hold significant interest as materials for acoustico-optical devices. These crystals are superior in some ways to the materials now used for such equipment [1, 2]. Nevertheless, no information is available on their atomic structure. It has only been proposed that crystals of $Pb_5(GeO_4)(VO_4)_2$ belong to the apatite structural family $A_4B_6(XO_4)_6Y_2$ [3]. The lack of data on the crystal structure of this compound led us to study its structure by x-ray diffraction structural analysis. Since samples of $Pb_5(GeO_4)(VO_4)_2$ are available in only small amounts and contain small monocrystals, it was preferable to use the full-profile method for treating powder diffraction data. This method is based on minimalization of the difference between the experimental and calculated dependence of the scattering intensity on the reflection angle (diffraction pattern profiles) by the method of least squares. In the present work, results are given for a refinement of the instrumental and structural parameters of $Pb_5(GeO_4)(VO_4)_2$ using all points of the recorded diffraction pattern.

EXPERIMENTAL

Fine yellow monocrystals of $Pb_5(GeO_4)(VO_4)_2$ were obtained by spontaneous crystallization from the melt. The quantitative chemical analysis of these crystals was carried out by local x-ray spectral analysis on a Cameca MB-1 microprobe and supported the assigned chemical formula. Traces of potassium and fluorine, which are often present in the apatite structure, were not found. We should also note that the IR spectra taken on a Perkin-Elmer spectrometer showed that OH⁻ groups are not present in the crystals.

A powder sample prepared by careful grinding of fine monocrystals was used for this study. The method for preparing the sample entailing spraying of finely ground powder into the cell virtually excluded the formation of texture in the sample studied. The x-ray diffraction experiments were carried out on a DRON-3 diffractometer at $18^\circ \leq 2\theta \leq 80^\circ$ using $CuK\alpha$ radiation monochromatized by a balance filter. The measurements were carried out by

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