

atoms of the five basal water molecules. Table IV lists the principal characteristics of the hydrogen bonds of the structure. Of the six independent F atoms, only the two F (5) and F (6) are not involved in the hydrogen bonds. These link the Zr eight-pointed polyhedra and Mn octahedra; in the latter the Mn-F (5) and Mn-F (6) are the strongest (2.09 Å), and in the former the Zr (1)-F (6) and Zr (2)-F (5) bonds are second in value 2.03 and 2.05 Å, respectively. Each water molecule is incorporated into the structure by a donor for a bond pair by the scheme



The water molecule H (1) O (4) H (2), the oxygen atom of which is in intimate contact with the manganese

atom [Mn-O (4) = 2.13 Å], is bounded by two of these hydrogen bonds. The O atoms of the other water molecules are also involved (each of them) in a single hydrogen bond, in which they act as acceptors.

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Sazhinite, $\text{Na}_2\text{Ce}[\text{Si}_6\text{O}_{14}(\text{OH})] \cdot n\text{H}_2\text{O}$: a new representative of the dalyite family in crystal chemistry

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On the basis of a three-dimensional set of $I(hkl)$ (obtained by the photographic method with a KFOR-3 camera in λMo , 394 reflections) the authors have made a complete x-ray diffraction investigation of the mineral sazhinite, $\text{Na}_2\text{Ce}[\text{Si}_6\text{O}_{14}(\text{OH})] \cdot n\text{H}_2\text{O}$, where $n \geq 1.5$. The parameters of the orthorhombic unit cell are $a = 7.50 \pm 0.03$, $b = 15.62 \pm 0.06$, $c = 7.35 \pm 0.03$ Å, $V = 861$ Å³, $Z = 2$, sp. gr. *Pmm*2. The atomic coordinates, found from Patterson and Fourier syntheses, were refined by the method of least squares in the isotropic approximation to $R(hkl) = 0.119$. The interatomic distances are: in the seven-vertex figures, Ce-O = 2.29-2.94; in the tetrahedra, Si-O = 1.51-1.72; in the five-vertex figures, Na-O = 2.44-2.63 (with two H₂O ligands at about 3 Å). The structure is based on infinite corrugated networks of Si tetrahedra built up to xonotlite bands of the dalyite type. On the basis of this Si radical the dalyite family is distinguished in crystal chemistry, including three minerals (dalyite, sazhinite, and armstrongite) and two artificial phases, $\text{K}_3\text{NdSi}_6\text{O}_{15}$ and $\text{K}_2\text{Be}_2\text{Si}_6\text{O}_{15}$.

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Sazhinite is a new silicate of sodium and rare earths of the cerium group; it was first described in 1974 and was assigned the approximate formula $\text{Na}_3\text{CeSi}_6\text{O}_{15} \cdot 6\text{H}_2\text{O}$ (Ref. 1). According to Laue and oscillation x-ray patterns, the mineral is orthorhombic and has the unit-cell parameters¹ $a = 7.50(3)$, $b = 15.62(6)$, $c = 7.35(3)$ Å, $V = 861$ Å³, $Z = 2$.

A three-dimensional set of intensities was obtained photographically from an irregularly shaped specimen (KFOR-3 camera, λMo , $0kl-4kl$ scanning, and also $hk0-hk1$). In all we registered 394 reflections with $\sin \theta/\lambda \leq 0.68$ Å⁻¹. This small number of reflections, decaying very rapidly with rise of $\sin \theta/\lambda$, agrees with the previous conclusion¹ that sazhinite has a defect structure; this followed from observations of the "blurred" IR spectra.

The absence of systematic extinctions of reflections led to the diffraction class *mmmP*---, containing the Fedorov groups *Pmmm*, *Pmm*2, and *P222*. In our further analysis we found that the true group is $C_{2v}^1 = \text{Pmm}2$.

All the structural calculations were effected on a

BESM-4 computer by means of the Rentgen-70 program.² From the three-dimensional distribution of the function $P(uvw)$ only the positions of the heavy Ce atoms could be confidently determined. The coordinates of the next heaviest Si atoms were found by successive approximations of the electron density. The ambiguity of the locations of these atoms derived from the $P(uvw)$ distribution revealed when the multiplicities of the probable positions were refined. The remaining atoms (Na and O) were then determined with the aid of ordinary and difference electron density syntheses. The model found for the structure was refined by the MLS (method of least squares) in the isotropic approximation to $R = 0.119$, which is quite satisfactory for registration of intensities by the photographic method. The final atomic coordinates and thermal parameters are listed in Table I, and the corresponding interatomic distances in Table II.

As the above considerations suggest, B_{tot} was unusually high in this silicate (3.8 Å²). Among the individual B_{iso} we can pick out $B(\text{O}_{13}) = 10.02$, which may cast doubt on the existence of the atom $\text{O}_{13}(\text{H}_2\text{O})$ in the structure.

TABLE I. Positional and Thermal Parameters of Sazhinite Structure*

Atom	x/a	y/b	z/c	B _{iso}	Atom	x/a	y/b	z/c	B _{iso}
Ce	0	0.260	0.004	3.55	O ₄	0.192	0.114	0.565	2.56
Si ₁	0.284	0.094	0.760	3.29	O ₅	0.171	0.398	0.487	5.69
Si ₂	0.298	0.402	0.295	2.88	O ₆	0.254	0.500	0.232	3.95
Si ₃	0	0.164	0.496	4.39	O ₇ (OH)	0	0.189	0.276	4.56
Si ₄	0	0.365	0.592	3.74	O ₈	0	0.259	0.604	4.57
Na ₁	0.500	0.261	0.005	3.86	O ₉	0	0.392	0.789	6.36
Na ₂	0.222	0.500	0.875	6.87	O ₁₀	0.500	0.113	0.688	4.45
O ₁	0.257	0	0.823	3.69	O ₁₁	0.500	0.402	0.377	5.18
O ₂	0.245	0.335	0.139	5.18	O ₁₂ (H ₂ O) ₁	0.500	0.373	0.766	4.22
O ₃	0.241	0.171	0.916	3.58	O ₁₃ (H ₂ O) ₂	0	0	0.138	10.02

*The standard deviations are not given on account of the poor quality of the experimental data.

TABLE II. Principal Interatomic Distances in (Å) *

Ce polyhedron		Na polyhedra	
Ce-O ₇	2.29	Na ₁ -O ₂ (2)	2.44
-O ₃ (2)	2.36	-O ₃ (2)	2.48
-O ₂ (2)	2.40	(H ₂ O) ₁	2.48
-O ₈	2.60	Na ₂ -O ₉ (2)	2.45
-O ₈	2.94	-O ₆	2.63
Si tetrahedra			
Si ₁ -O ₁	1.56	Si ₂ -O ₂	1.61
-O ₄	1.62	-O ₆	1.63
-O ₃	1.69	-O ₁₁	1.63
-O ₁₀	1.72	-O ₅	1.71
O ₁ -O ₄	2.64	O ₂ -O ₆	2.67
-O ₃	2.76	-O ₁₁	2.80
-O ₁₀	2.72	-O ₅	2.80
O ₁ -O ₃	2.76	O ₆ -O ₁₁	2.62
-O ₁₀	2.48	-O ₅	2.54
O ₃ -O ₁₀	2.73	O ₁₁ -O ₅	2.60
Si ₃ -O ₇	1.66	Si ₄ -O ₉	1.51
-O ₈	1.68	-O ₃ (2)	1.58
-O ₄ (2)	1.72	-O ₈	1.66
O ₇ -O ₈	2.64	O ₉ -O ₃ (2)	2.56
-O ₄ (2)	2.82	-O ₈	2.49
O ₈ -O ₄ (2)	2.70	O ₃ -O ₈ (2)	2.67
O ₄ -O ₄	2.88	-O ₃	2.37

*Figures in parentheses are numbers of equivalent bonds.

However, the corresponding peak was constantly present in all the electron density syntheses, and omission of O₁₃ in the course of the MLS refinement led to an appreciable increase in the final R index.

In Table II we find the distance Si₄-O₉ = 1.51 Å, which is apparently underestimated owing to the paucity of the original experimental data. Nevertheless, we cannot fail to notice that the bond between Si₄ and the nonbridging (free) atom O₉ must be relatively short. This conclusion follows from the requirement of local valence balance and is supported by the related structure of K₃NdSi₆O₁₅ (Ref. 3) in which the analogous bond has a length of 1.54 Å.

The sazhinite structure is based on a layered silicon-oxygen radical of the daylyite type [Si₆O₁₅]_∞ which is shown in two projections in Fig. 1. The principal component of this layer is the xonotlite band composed of eight-membered rings of tetrahedra running parallel to [100]. Adjacent bands (along Y) are related by a mirror plane, and owing to their condensation there arises a network with eight-membered, six-membered, and four-membered loops, infinite in two dimensions. From the endwise projection (Fig. 1a) we clearly see that this network is not plane but wavy. The first Si radicals of this type were found in the structure of dalyite K₂ZrSi₆O₁₅ (Ref. 4), and then in another natural zirconium silicate, armstrongite,

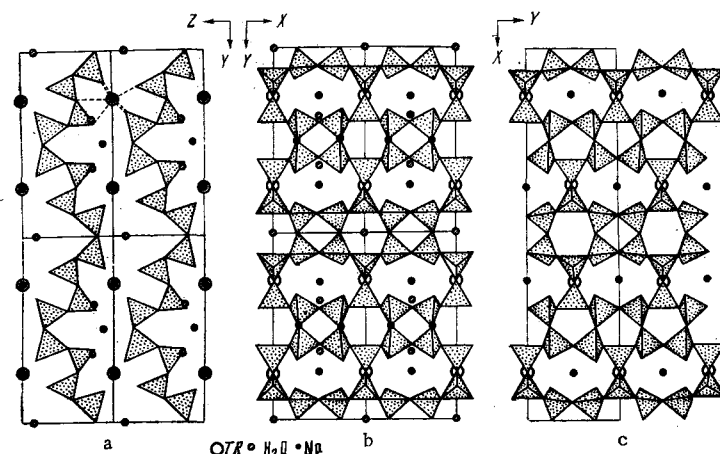


FIG. 1. Two projections of structure of sazhinite (a, b) and plan of crystal structure of H₂NaNdSi₆O₁₅ · nH₂O (c).

$\text{CaZrSi}_6\text{O}_{15} \cdot 2.5\text{H}_2\text{O}$ (Ref. 5). It is also found in the artificial rare earth phase $\text{K}_3\text{NdSi}_6\text{O}_{15}$ (Ref. 3).

In the crystal structure of sazhinite in the Z direction (7.35 Å) these networks alternate with cation layers in which a special role is played by the high-valence Ce^{3+} atoms lying at the points of a slightly distorted cubic lattice with a period of about 7.5 Å. To a first approximation the coordination sphere of Ce can be described as a distorted octahedra including all the free O vertices of the Si tetrahedra. With this approach, the structural motif of sazhinite can be treated as a mixed framework $\{\text{Ce} \cdot [\text{Si}_6\text{O}_{15}]_{\infty}^{3-}\}_{\infty}$, which is also found in dalyite.⁶ Admittedly, the correctness of this approach is somewhat marred by the fact that as well as the six nearest neighbors at 2.36–2.60 Å the Ce has as an additional seventh ligand one of the bridging O atoms lying at a distance of 2.94 Å. If this is taken into account, the coordination sphere of the Ce takes the form of a singly-capped octahedron which shares one edge with a neighboring Si tetrahedron.

As well as Ce, in the cation layer of the structure there are all the Na atoms, as seen in Fig. 1a. Some of the alkali cations (Na_1) lie in distorted tetragonal pyramids (c.n. 5) linked via opposite edges of the base to the cerium "octahedra" and forming with them infinite columns along the *a* axis (7.5 Å). Between the Na_1 , Ce columns there are rows of mutually isolated Na_2 ions, each surrounded by three O atoms at distances of 2.5–2.6 Å and two molecules (H_2O)₁ at a distance of about 3 Å. The (H_2O)₂ molecules do not come into the coordination sphere of the cations.

As a result of our investigation we found the unit cell of sazhinite to contain 2Ce, 12Si, 4Na, and 33O. On the basis of the local valence balance, three of these O atoms were identified with water molecules and two were taken to be hydroxyl ions which symbolize the free vertices of the Si_3 tetrahedra (Table I).

Summing up, the formula of the investigated specimens of the mineral can be written in the form $\text{Na}_2\text{CeSi}_6\text{O}_{14} \cdot (\text{OH}) \cdot 1.5\text{H}_2\text{O}$ (for *Z* = 2). This differs from the original formula¹ in having lower Na and H₂ contents. Of course, one reason for this discrepancy may be inaccuracy of the chemical analysis. But we must point out that the final electron density syntheses of sazhinite contained a number of spurious peaks, which when identified with light atoms (O or Na) impair the agreement between the experimental and theoretical results. Moreover, these maxima may indicate that the structure contains ions or molecules which do not occupy strict crystallographic positions but occur in variable amounts statistically in the lattice of the mineral. Considering the probability of this resemblance of sazhinite to a zeolite, its general formula may be written as $\text{H}_x\text{Na}_{3-x}\text{CeSi}_6\text{O}_{15} \cdot n\text{H}_2\text{O}$ (*n* ≥ 1.5).

It is not unimportant to note that in certain respects the structure of sazhinite is similar to that of its artificial Nd analog $\text{H}_2\text{NaNdSi}_6\text{O}_{15} \cdot n\text{H}_2\text{O}$, which has recently been determined on the basis of diffractometric intensity registration.⁷ In particular, the Na deficit, which is even more marked than that in sazhinite, is here compensated by statistical incorporation of H atoms in the lattice. Moreover, the position of the H_2O , which is estimated to be present to the extent of 1–2 molecules per formula unit, remained undetermined, and could not be precisely fixed.

Despite the similarity of their chemical formula and powder patterns,⁷ the natural and artificial phases are not isostructural. The main difference between sazhinite and the Na, Nd silicate is that although in both structures the silicon–oxygen radicals are condensation products of xonotlite bands, these radicals are "polymorphic varieties" of networks with the empirical formula $[\text{Si}_2\text{O}_5]_{\infty}$. Until recently three topologically distinct dimeta networks $[\text{Si}_2\text{O}_5]_{\infty}$ were known, differing in the mode of condensation of the xonotlite bands⁸: a) the apophyllite type, made up of equal numbers of eight-membered and four-membered rings of tetrahedra; b) the okenite type, made up of eight-membered and five-membered rings in the proportion 1 : 2; c) the dalyite type, made up of eight-membered, six-membered, and four-membered rings in the proportion 1 : 1 : 1. To this list we must now add another type – the dimeta network of the above-mentioned Na, Nd silicate.⁷ The loops of this network are of all four types of rings, present in the proportions 2 : 1 : 2 : 1 (in order of descending numbers of tetrahedral ring links).

We can imagine the network (Fig. 1c) to be divided up into infinite blocks of the dalyite type, each two xonotlite bands wide. Whereas in the case of sazhinite (dalyite) the network as a whole is the product of condensation of these blocks aided by the *m* planes (Fig. 1b), the radical of the artificial Na, Nd silicate results from the condensation of the same blocks, but with *g* planes passing through the peripheral vertices of the tetrahedra²) (Fig. 1c). In the upshot, the dimeta network of the silicate in question is a sort of "alloy" of the dalyte and okenite radicals. Its specific structure causes base centering of the unit cell and doubling of one of its periods (*a*) in comparison with the sazhinite lattice (Table III).

From the above data it follows that at present we know of several crystal structures based on the "dalyite" silicon–oxygen radical – a corrugated network containing eight-membered, six-membered, and four-membered rings of tetrahedra. From this we can infer the existence of the crystal–chemical family of dalyite in which sazhinite is one representative (Table III). In Table III, as well as the above compounds, we feature beryllosilicate $\text{K}_2\text{Be}_2 \cdot \text{Si}_6\text{O}_{15}$ (Ref. 9), the inclusion of which is justified by the hypothesis that the functions of the octahedral (*M*) cations are fulfilled in this case by pairs of Be tetrahedra linked via their edges ("binuclear octahedra"). Let us consider some structural characteristics of the family.

Within the dalyite network (Fig. 1b) the minimal repeat periods are determined by the dimension of one eight-membered ring along the axis of the xonotlite band and also by the width of the band in the perpendicular direction. This can be arbitrarily expressed by the symbol (1)–(1). Evidently the third period of the minimum unit cell must contain only one silicon–oxygen layer (network), leading to the symbol (1)–(1)–(1). In Table III all the parameters of the real cells (in the notation of the original articles) are arranged in conformity with the adopted series of periodicities for convenience in comparison of the analogous directions in the crystal structures. In the next column of the table we give the arbitrary symbols indicating the numbers of eight-membered rings, xonotlite bands, and Si–O layers belonging to the corresponding periods of the real lattices.

TABLE III. Some Structural Characteristics of the Crystal-Chemical Dalyite Family

Compound (mineral)	Fedorov gp.	z	Unit-cell parameter (Å)	Symbol of structural motif	M-polyhedron	C.n. of A cation
$K_2ZrSi_6O_{15}$ (dalyite)	<i>P1</i>	1	$c=7.00$; $a=7.51$; $b=7.73$ $\alpha=106$; $\beta=113.5$; $\gamma=99.5^\circ$	1-1-1	Octahedron	8
$K_2Be_2Si_6O_{15}$	<i>Cmc2₁</i>	4	$a=7.485$; $c=11.148$; $b=15.453$	1-2-2	"Binuclear" octahedron	7
$K_3NdSi_6O_{15}$	<i>Pbam</i>	4	$c=7.276$; $a=16.011$; $b=14.984$	1-2-2		6.7
$Na_2HfCeSi_6O_{15} \cdot 4.5H_2O$ (sazhinite)	<i>Pmm2</i>	2	$a=7.50$; $b=15.62$; $c=7.35$	1-2-1	Singly capped octahedron	5
$CaZrSi_6O_{15} \cdot 2.5H_2O$ (armstrongite)	<i>C2</i>	4	$b=14.16$; $a=14.04$; $c=7.81$ $\beta=109^\circ 33'$	2-2-1		6

The simplest three-unity symbol characterizes the progenitor of the family, dalyite, in which all three parameters are close to 7 Å. This periodicity, typical of representatives of the second chapter in the crystal chemistry of silicates,¹⁰ follows directly from the geometry of the Si radical only for the first direction which coincides with the axis of the xonotlite band. The second period, along which we can distinguish a chain of the batistite type, depends on the degree of deformation of the silicon-oxygen layer (its "crumpling" into folds), and the third also depends on the radii of the atoms filling the interlayer space. The multiplicity of all the parameters of the "group of seven" can be explained by the features of the cation motif, namely its pseudocubic sublattice with a period of about 7 Å which has the high-valence M cations at its points. Only in K, Be silicate is one edge of the M subcell shortened to about 5.5 Å, and this reflects the marked crumpling of the Si radical into folds (parameter *c* in Table III). Another feature of the cation motifs of all the representatives of the family lies in the columns of alternating high-valence (M) and low-valence (A) cations running parallel to the xonotlite bands. In the former cases (dalyite, armstrongite) they constitute the whole motif; in the others, the columns are interlain with rows or columns of A polyhedra (sazhinite, K, Nd, silicate).

As well as the explicit signs of the similarity of the structures, they have their own individual features imposed by the stoichiometry and qualitative composition of the particular compounds. This applies primarily to the ways in which the xonotlite bands are linked into infinite layers of the dalyite type. Figure 2 illustrates four schemes of condensation to which the arrangement of the component in the real structures may reduce. Here the rectangular blocks nominally represent the ends of the xonotlite bands extending along the normals to the plane of the paper. Scheme 1, corresponding to the structures of dalyite and armstrongite, is characterized by stepwise arrangement of the blocks, which are related by dyad axes or centers of inversion. In scheme 2 the band blocks lie in two layers and are related by a slip plane parallel to the layer. The corresponding motif is similar to what observed in the structure of $K_3NdSi_6O_{15}$. Scheme 3 illustrates the sawtooth profile of the silicon-oxygen network of sazhenite, where the xonotlite bands are inclined toward one another and are related by a vertical mirror plane.

Finally, scheme 4 answers to the structure of K, Be silicate, and differs from the preceding ones in that the adjacent bands overlap at the crests and troughs. This shortens the identity period in a direction perpendicular to the folds of the Si, O layer (compare the corresponding parameter in Table III).

The different representatives of the family also have different arrangements of cation and anion layers which vary with the number and type of A or M cations. Thus if we look along the third lattice period (according to Table III), the M atoms are protected to the centers of the four-membered rings in dalyite, to the centers of the six-membered rings in armstrongite, to the boundaries of two eight-membered rings in sazhenite, and so on. Nevertheless in all cases there is octahedral (or similar sevenfold) coordination of the M cation. This is due to the above-mentioned capacity of the flexible Si radical to "crumple" in different ways into folds; together with this there is also distortion of the xonotlite bands themselves; this is manifested in compression and extension, bending, and twisting of the eight-membered rings on account of various rotations of their component Si tetrahedra. Another mechanism helping to match the cation and anion layers is the frequently observed shift of adjacent dalyite networks, causing monoclinic (or triclinic) distortion of the lattice or complication of its symmetry on account of additional glide operations.

The above features of the dalyite family reflect the well-known crystal-chemical feature that the silicon-oxygen radical plays a subordinate part in the formation

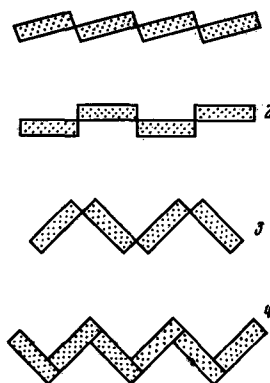


FIG. 2. Four schemes of condensation of xonotlite bands in infinite layer of the dalyite type.

of silicates.¹⁰ The large alkali or alkaline-earth A cations are enclosed in the cavities in the $\{M[Si_6O_{15}]\}_{\infty\infty}^{n-}$ framework, compensating its overall negative charge which depends on the valence of the M atom.

The specific geometry of the dalyite networks (the presence of wide eight-membered rings) governs the marked volume of the cavities and their incommensurability with the A cations of relatively small radius. On the basis of factual material we can suppose that the optimal "fillers" of the mixed framework in the case of the given family are K^+ ions, which are always uniformly surrounded by O atoms in the framework (dalyite, K, Nd silicate, K-beryllosilicate). For Na^+ and Ca^{2+} the cavities are too capacious, and during crystallization they tend to capture H_2O molecules, which on the one hand give more uniform coordination of the A cations, and on the other, make the structure more compact. This may partly explain the known hydrophobic nature of potassium⁹ and the corresponding hydrophilic nature of Na-Ca in silicates.

¹⁾ In contrast with Ref. 1, the crystallographic axes were chosen in conformity with the standard setting $c < a < b$.

²⁾ The total period in the glide direction is here equal to the minimal translation along the xonotlite band.

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A study of the distribution of valence electrons in crystals. II. Calculation of the electron structure of lithium formate deuterate from diffraction data

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The authors investigate the electron structure of lithium formate deuterate $HCOOLi \cdot D_2O$ according to diffraction data. The initial experimental data, obtained from a precision x-ray experiment, contained information on the redistribution of valence electrons in the crystal. The experimental charge distribution differs from the theoretical in its greater polarity; this may be attributed to molecular interaction in the crystal. The dipole bond moments calculated for the water molecule in the point charge approximation are 1.39 D and 1.19 D, and the total dipole moment is 1.52 D.

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As the object of an investigation of the electron density distribution by the method suggested in Ref. 1, the authors chose lithium formate deuterate (LFD), $HCOOLi \cdot D_2O$. This crystal has an exceptional capacity for second harmonic generation: The intensity is 20 times greater than for KH_2PO_4 crystals.² It has no center of symmetry, and possesses pyroelectricity, piezoelectricity, and ferroelectricity, and also nonlinear optical properties. In conjunction with its high dielectric strength, these properties are the basis of the wide use of LFD as a material for laser technique. A knowledge of the details of the electron structure of LFD is important for understanding the nonlinear optical properties of the crystal³ and for calculating

its nonlinear optical susceptibilities.⁴

Crystals of LFD are colorless and easily soluble in water. Lithium formate was dissolved in heavy water at 45°C. The salt had previously been kept in a drying cupboard at 95-96°C. The marked temperature dependence of the solubility of the salt enabled us to grow the crystals by reducing the solution temperature. A seed was glued to the crystal holder. The growth rate did not exceed 0.35 mm/day. We finally got a crystal of high quality from the x-ray diffraction aspect.

The crystal structure of lithium formate hydrate has been investigated by the x-ray diffraction⁵ and neutron