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X-RAY-DIFFRACTION STUDY OF THE STRUCTURE OF BERBANKITE $(Na, Ca)_3$ $(Ca, Sr, Ba, TR)_3$ (Co_3)

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A complete x-ray diffraction study of the rare-earth carbonate berbankite is presented. The parameters of the hexagonal cell are $a = 10.52 \pm 0.04$, $c = 6.51 \pm 0.02$ Å, $Z = 2$, space group $P6_3mc$. The structure is characterized by widely-developed isomorphic relationships of the cations, which are arranged in two groups: A = Na and Ca, B = Cs, Sr, Ba, and TR (TR = transition). The general formula of the mineral is $A_3B_3(CO_3)_5$.

The rare-earth carbonate berbankite is distinguished from the majority of anhydrous carbonates both by the complexity of its chemical composition, in which the univalent cation (Na^+) is accompanied by a whole series of divalent cations (Ca, Sr, Ba) and rare earths, and by its unusually low birefringence (no more than 0.012). Both these features are of considerable interest both from the purely structural and general mineralogical points of view. The first x-ray study [1] showed that berbankite crystallized in the hexagonal system. The most probable space group was given as $D^4_{6h} - P6_3/mmc$, and the generalized chemical formula for the mineral was expressed in the form $Na_2R_4(CO_3)_5$, with two of these "molecules" per unit cell (R = Ca, Sr, TR, Ba, Na).

We studied samples of berbankite obtained from the Kol'sk peninsula; these were kindly presented by Yu. L. Kapustin. Using the Laue and oscillation methods in an RKOP camera, we verified the hexagonal symmetry of the mineral (Laue class 6/mmm) and determined the unit-cell parameters: $a = 10.52 \pm 0.004$ and $c = 6.51 \pm 0.02$ Å, which practically coincided with the data presented in [1]. On the basis of the experimental density $\rho = 3.58$ g/cm^3 and chemical analysis of the mineral, we calculated the contents of the unit cell for the berbankite sample under examination $(Na_{5.5}Ca_{2.4}TR_{1.5}Sr_{1.3}Ba_{1.3}) \cdot (CO_3)_{10}$, corresponding to the general formula $R_{12}(CO_3)_{10}$. Here we may note that the TR in berbankite was 85% represented by cerium and lanthanum; in calculating the molecular weight of TR_2O_3 we used data published earlier for rare earths [2].

The experimental data (developments of layer lines obtained by rotating around the a and c axes) were obtained in KFOR cameras, using Mo radiation, with isometric sections of single crystals 0.2 to 0.3 mm in diameter. The intensities of the reflections were measured visually, using a photographic-density scale in steps of $\sqrt[4]{2}$. The values of F^2 were calculated by the standard method, allowing for the Lorentz and polarization factors; absorption was not taken into account. Among the $hh\overline{2h}l$ and $000l$ reflections on the layer lines, only those with $l = 2n$ were present. This law of systematic extinctions leads to an x-ray group $6/mmmP-/--c$ containing three space groups $D^4_{6h} - P6_3/mmc$, $D^4_{3h} - P\bar{6}2c$, and $C^4_{6v} - P6_3mc$. The high piezoactivity of the berbankite crystals observed when studying the powdered mineral (A. F. Solov'ev, Moscow State University) eliminated the earlier-proposed centrosymmetric space group D^4_{6h} [1] from further consideration. Of the acentric groups, by analyzing two-dimensional Patterson syntheses we chose the $P6_3mc$ group as the most probable, and this was confirmed in subsequent analysis of the structure.

Judging by the complexity of the chemical composition of berbankite, we might well imagine ab initio that there would be widely developed mutual isomorphic relationships between the atoms in its structure. For this reason it was hard to make any judgement regarding the crystal-chemical role of any particular component (apart from O and C). Nevertheless, the following two variants appeared to be the most probable: 1) a complete lack of order among the large cations, occupying one general 12-fold position, and 2) a partial degree of order with two 6-fold complexes of $x\bar{x}z$ points in m symmetry planes [3].

It was found from the P(xy) and P(yz) Patterson projections that the cell contained a group of six cations sharply distinguished as regards scattering power ("heavy" atoms). It was logical to suppose that this group comprised cations with the highest atomic numbers Z. Hence, in constructing the first electron-density syntheses (simply taking account of the "heavy" atoms), we used an effective atomic number Z for the latter, calculating this as the weighted mean of the atomic numbers of Sr, Ba, TR, and some of the Ca, making up a total of six atoms per cell. The use of the heavy-atom method was in fact only successful for the centrosymmetric electron density projection $\sigma(xy)$. This indicated that, in addition to the six specified "heavy" atoms, the cell contained one more crystallographically independent group of cations, also occupying a single six-fold complex of points in m symmetry planes. The presence of two nonequivalent groups of cations with the same multiplicity in the berbankite structure determined the general form of the crystal-chemical formula of the mineral: $A_6B_6(CO_3)_{10}$ or $A_3B_3(CO_3)_5$ with N = 2. On introducing the coordinates of the next-heavy cations of group A into the second approximation of the calculation for $\sigma(xy)$, all the light atoms in the cell were located.

At this stage it became possible to approach the determination of the Z_{eff} of the A and B groups of cations more rigorously, i.e., ultimately, to determine the nature of the isomorphic substitutions in the structure. For this purpose we used the available coordinates of all the atoms and studied the dependence of the R factor for the hk0 zone of reflections on the values of Z_A and Z_B (for a constant value of the sum $Z_A + Z_B = 52$). A criterion of the validity of this operation was that the signs of the structure amplitudes should not change on changing the value of Z_{eff}. The results appear in Table 1.

It follows from the data presented in Table 1 that the minimum value of R corresponds to the combination of cations for which the difference in the total scattering powers of the atoms of groups A and B is a maximum.[1] This situation is only realized when the whole weight of the sodium (the lightest of all the large cations) participating in the composition of the mineral is concentrated in group A, while the remaining "vacant" positions of the corresponding complex of points are occupied by the next-lightest cation, calcium. Hence the final formula of berbankite is $(Na, Ca)_3(Ca, Sr, Ba, TR)_3 \cdot (CO_3)_5$. It may be noted that the distribution of cations obtained by this purely experimental approach agrees with the crystal-chemical characteristics of the corresponding ions and also with the character of their mutual isomorphic relationships, observed in other natural compounds.

TABLE 1. The R Factor as a Function of the Effective Values of Z_A and Z_B

No.	Z_A	Z_B	R (hk0), %
1	9	43	10.7
2	12	40	9.9
3	13	39	10.5
4	14	38	11.3
5	17	35	14.2

TABLE 2. R Factors in the Berbankite Structure (Without Considering $F_{exp} = 0$)

Zone of reflections	No. of independent $F_{exp} \neq 0$	$(\sin\theta/\lambda)_{max}$	R, %	B, $Å^2$
$hk0$	72	1.06	9.9	0.85
$hk1$	47	0.80	10.4	1.3
$hk3$	46	0.80	8.1	1.5
$0kl$	84	0.80	9.9	2.0

TABLE 3. Coordinates of the Basal Atoms of Berbankite

Atoms	Positions	x/a	y/b	z/c
A = (Na, Ca)	6 (c)	0.527	0.473	0.317
B = (Ca, Sr, Ba, TR)	"	0.841	0.159	0
O_I	12 (d)	0.377	0.082	0.617
O_{II}	6 (c)	0.134	0.067	0.326
O_{III}	"	0.598	0.196	0.992
O_{IV}	"	0.460	0.230	0.340
C_I	"	0.416	0.208	0.533
C_{II}	2 (a)	0	0	0.826
C_{III}	2 (b)	0.333	0.667	0.492

Starting from the cation distribution thus established, we refined the x and y coordinates of all the atoms in the cell by the method of successive approximations. The refined form of the $\sigma(xy)$ projection appears in Fig. 1. The side projection $\sigma(yz)$ was unsuitable for determining the third coordinate of the atoms owing to the overlapping of a considerable number of these, and also because of

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[1] The first line in Table 1 refers to an artificially underestimated Z_A and overestimated Z_B, not corresponding to the chemical composition of the mineral under consideration.

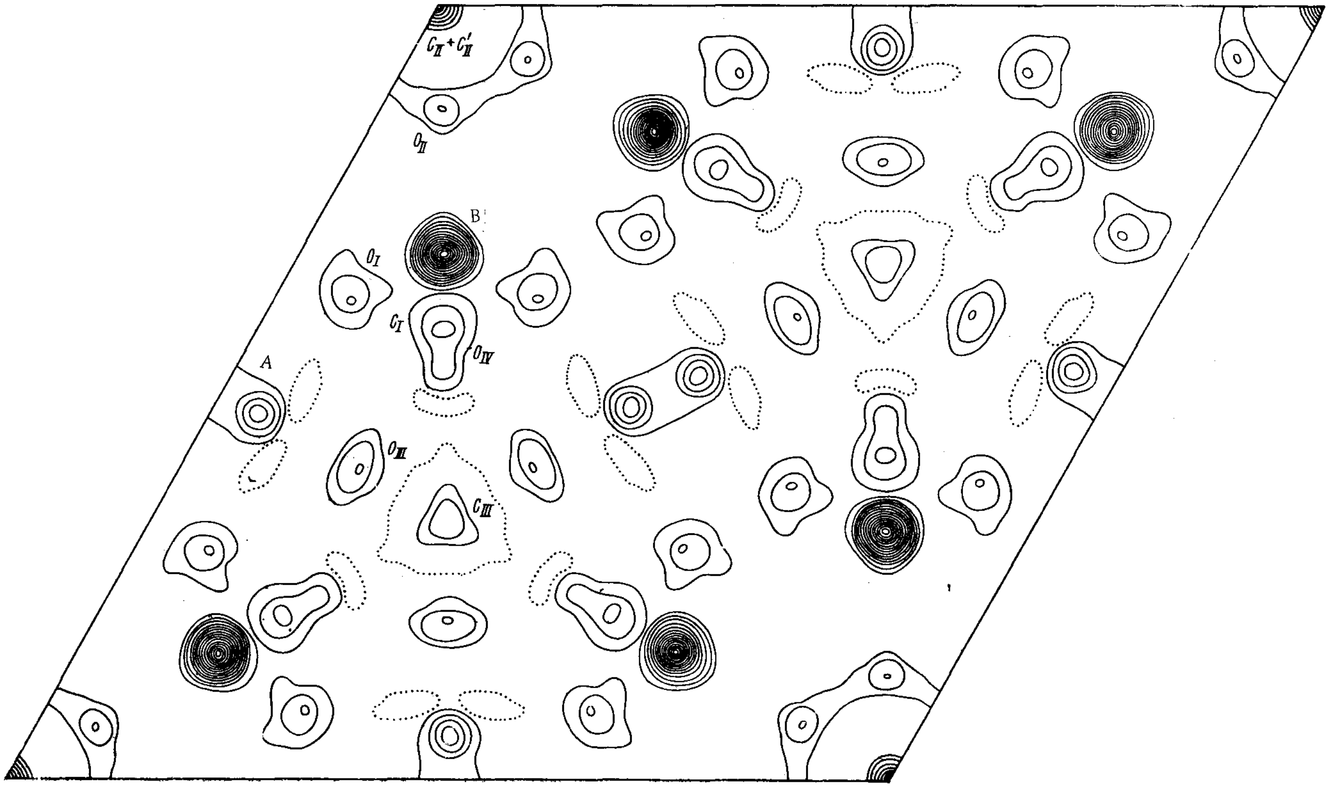

Fig. 1. Electron-density projection σ(xy). Isolines drawn every 9.3 electrons/Å^2 for the B cations and every 7 electrons/Å^2 for the remaining atoms.

the sharp pseudosymmetry due to the centrosymmetric arrangement of the large cations. Hence in order to establish the z parameters roughly we used several cycles of approximations with respect to the weighted projections $\sigma_1^{\sin,\cos}(xy)$ and $\sigma_3^{\sin,\cos}(xy)$. The resultant coordinates were refined with respect to the side projection (yz) by means of difference syntheses of electron density. The contributions of atoms with reliably established parameters were successively eliminated from the experimental amplitudes F(0k*l*). Tables 2 and 3 show the final values of the R factors and coordinates of the basal atoms in the structure.

Two different types of coordination polyhedra correspond to the two crystallographically different sorts of cations in the berbankite structure. The cations of group A are placed in characteristic eight-pointed figures, constituting a combination of a distorted trigonal prism with four-sided pyramids constructed on two of its side faces. The axes of the prism are arranged parallel to the horizontal edges and short diagonal of the cell. The coordination number of the B cations equals 10. The corresponding ten-pointed polygon has twelve triangular and two quadrangular faces and is almost an exact copy of the polyhedron surrounding the rare-earth atoms in the structure of $Nd(NO_3)_3 \cdot 6H_2O$ [4]. The two types of berbankite polyhedra described have m point symmetry. In addition to these the structure contains three crystallographically independent sorts of CO_3 triangles oriented in different ways in space.

The base of the structure is formed by infinite skeletal lattices of B polyhedra parallel to (0001), linked to each other at common vertices by 3 and 6 axes (Fig. 2a). Two such layers correspond to the cell period c; these are rotated through 60° with respect to each other in accordance with the law of the 6_3 axis. The polyhedra in the upper stage fit into the spaces between the polyhedra of the lower stage like gear teeth, touching them along common edges. In the direction of the c axis the translationally identical ten-pointed polyhedra have no elements in common with each other, but are connected through obliquely situated C triangles. This motif of B polyhedra also contains empty vertical channels passing perpendicularly to the layers in question along the 6_3 and 3 axes and also through the middles of the edges and the middle of the short cell diagonal. Horizontally oriented C triangles are arranged in the channels of the first and second types, while the channels of the third type contain A cations. The eight-pointed polyhedra corresponding to these form infinite zigzag columns in which neighboring polyhedra are directly adjacent to one another along the triangular faces (Fig. 3). Two A polyhedra belong to each c period. Each column is linked by two threefold axes to four similar columns, contact between these being established by the common vertices of the A polyhedra and inclined C triangles (Fig. 2b). The columns are connected very closely with the layers of B polyhedra: The different types of polyhedron touch each other with their common triangular faces, each of them being compressed between four polyhedra of a different sort.

The interatomic distances in the berbankite structure agree closely with the established distribution of cations between the A and B groups. The lengths of the A–O bonds in the (Na, Ca) eight-pointed polyhedra equal 2.29 (2), 2.48 (1), 2.49 (2), 2.55 (1), and 2.62 Å (2) with an average of 2.48 Å. The cation-anion distances in the B polyhedron are: 2.54 (2), 2.56 (1), 2.71 (1), 2.76 (2), 2.77 (2), and 2.79 Å (2), with an average of 2.70 Å. The value of the O–O edges, without allowing for the shortest of these and those existing in common with the C triangles, lies between 2.81 and 3.58 Å in both polyhedra. The interatomic distances in the carbonate groups are C_I–O 1.30 (2) and 1.32 Å (1), C_{II}–O 1.22 Å (3) and C_{III}–O 1.26 Å (3). The edges of the corresponding C triangles are 2.24-2.25 Å, 2.11 Å, and 2.17 Å.

The berbankite structure is in good agreement with Pauling's second rule: The maximum deviation of the sum of the positive valence forces converging at oxygen atoms from 2 never exceeds 5%. The structure explains the anomalously low birefringence in berbankite crystals. Of the ten plane carbonate groups CO_3 contained in the unit cell, four are oriented perpendicularly and the other six at an angle of 23° to the principal axis of the crystal. In addition to this, by the laws of hexagonal symmetry the latter six C triangles have different azimuthal orientations. Any preferential influence of the carbonate groups on the polarization of light in the crystal is thus entirely eliminated. An analogous effect was observed earlier in the hexagonal structure of jeremejevite, $AlBO_3$, where the role of the C triangles was taken over by similarly situated triangular BO_3 groups [5].

The structural type of berbankite meanwhile remains an anomaly among the known crystal structures of other minerals, in particular carbonates. It is important to note that an unalterable condition for the existence of this structure is an isomorphic interrelationship between the large ca-

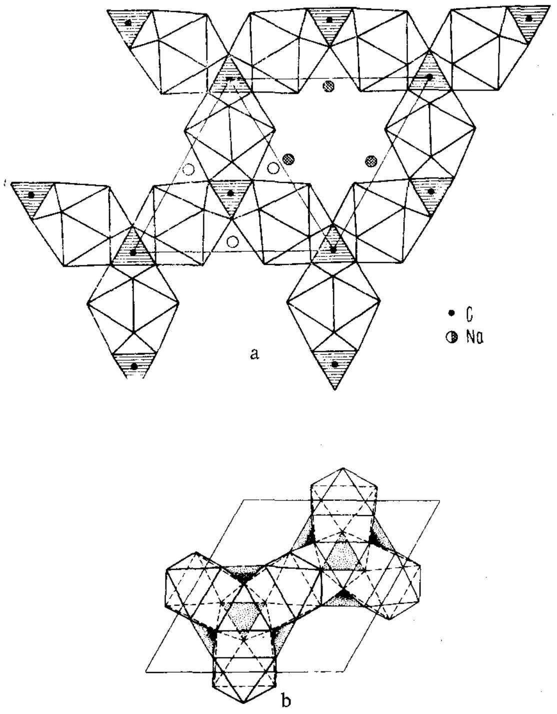

Fig. 2. Projection of the berbankite structure on the (0001) plane: a) layer of B polyhedra; b) motif of A polyhedra.

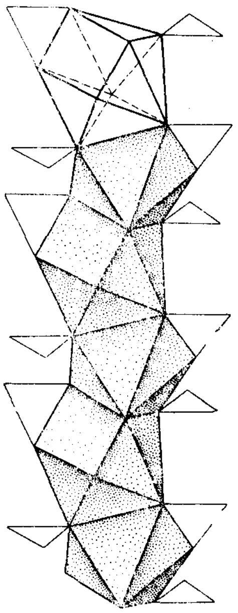

Fig. 3. Column of eight-pointed A polyhedra.

tions, at least in one of the groups A or B. If in fact we call the average valence of the A and B cations in berbankite w_A and w_B respectively, it then follows from the general formula $A_3B_3(CO_3)_5$ that

$$3w_A + 3w_B = +10 \text{ or } w_A + w_B = +{}^{10}/_{3}. \qquad (1)$$

The fractional value of the last sum demands a fractional value of the valence of the cations composing one or both of the groups in question, and this is only possible in the presence of isomorphic substitutions between the cations.

In the natural samples studied such substitutions occur in both A and B groups, the A group consisting of 90% Na. The present investigation reveals a low probability that Na atoms will enter the large B cation group. This conclusion is supported by the fact that the number of Na atoms in the composition of known varieties of the mineral is always smaller than six per unit cell. Let us imagine a case in which the A group consists of pure Na. This case would correspond to "berbankite" having isomorphic relations of the cations in only one group (B). In this event $w_A = +1$, and from Eq. (1) we have $w_B = +{}^{7}/_{3}$, whence the ratio of di- and tervalent cations in group B should be 2:1; the corresponding formula has the form $Na_3M^{2+}_{2.0}M^{3+}_{1.0}(CO_3)_5$.

If we consider that in the real berbankite structure the effective ionic radius of the B cations (1.11 Å) corresponds to Sr^{2+} (1.12 Å), being close to the radius of Ce^{3+} (1.07 Å), the formula may be written more specifically in the form $Na_3(Sr_2Ce) \cdot (CO_3)_5$. The "limiting" composition found should correspond to the most "rare-earth" variety of berbankite, since increasing the number of TR^{3+} atoms in the formula of the mineral (above unity) inescapably leads to an infringement of stoichiometry. Passing to oxides, we may say that the maximum possible amount of TR_2O_3 in the bulk chemical analysis of berbankite should not exceed about 22 wt.%. It is interesting in this connection to note that, among all the natural berbankites (taken from six different mineral fields) known at the present time, the proportion of TR_2O_3 always lies within the range 9.0 to 20.0 wt.%.

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