CRYSTAL STRUCTURE OF CARBOCERNAITE

\[(Na, Ca)(TR, Sr, Ca, Ba)(CO_3)_2\]

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The properties of the mineral carbocernaite AB(CO_3)_2 = (Na, Ca) (TR, Sr, Ca, Ba) (CO_3)_2 were studied by x-ray diffraction. The mineral is rhombic with the following parameters: \(a = 6.41\), \(b = 7.30\), \(c = 5.23\) \(\AA\), \(N = 2\). The space group is \(C_{2v}^2\)-Pb2m. The coordination numbers are: A cations 7, B cations 10. The mineral constitutes a new structural type. Proposed structural analogs of carbocernaite with simple compositions include the compounds NaTR(CO_3)_2, where TR = La or Ce.

Carbocernaite is a mineral characterized by a complex cation composition; however, the empirical, generalized formula of this compound belongs to the simple MCO_3 = (Ca, Na, TR, Sr, Ba)CO_3 type, where TR are predominantly tervalent La and Ce [1]. The usual interest in the x-ray diffraction study of a mineral with unknown structure was intensified in the case of carbocernaite by the possibility of determining the characteristics of isomorphic substitutions; it was desired to find whether all the cations in the structure were really crystallographically equivalent, or, in other words, whether the formula given in [1] was truly the crystal-chemical formula of the mineral in question. We note that experience in the structural examination of a mineral of similar composition, berbankite, (Na, Ca, TR, Sr, Ba)_6(CO_3)_5 = (Na, Ca)_3(TR, Sr, Ba, Ca, Ba)(CO_3)_5 [2], suggested that in the case of carbocernaite also we might expect at least two independent cation positions.

The material for study was obtained from Yu. L. Kapustin; we had an unlimited supply of grains of the mineral obtained from the Kol'sk peninsula (accompanied by the corresponding chemical-analysis records [1]) and also fragments of carbocernaite crystals from other countries, which unfortunately had not been subjected to chemical analysis. Even at the first stages of the research it became evident that the x-ray-diffraction pictures of the single crystals from the Kol'sk peninsula were of low quality (diffuse reflections and asterisms); for this reason the rest of the experiments were carried out on a foreign sample, which gave a very sharp diffraction picture. Here we should note that the absence of direct evidence regarding the chemical composition of the specific material constituted no serious obstacle to the x-ray study; comparison of published [1, 3] data relating to the compositions of samples of carbocernaite obtained from various sites shows that variations were only slight, and in determining the structure of the mineral we therefore started from averaged figures leading to the empirical formula \((Na_{0.21}Ca_{0.43}TR_{0.21}Sr_{0.21}Ba_{0.04})CO_3\).

X-ray diffraction pictures obtained in the RKOP camera indicated that the mineral had the same symmetry and lattice parameters [Laue class mmm, \(a = 6.41 \pm 0.03\), \(b = 7.30 \pm 0.03\), \(c = 5.23 \pm 0.02\) \(\AA\), \(N = 4(MCO_3)\)], as those obtained in the previous investigation [1]. On analyzing the x-ray goniometric developments of the layer lines obtained with Mo radiation in the KFOR camera we established a single law for the systematic extinctions of reflections. Among reflections of the 0k0 type, only those with \(k = 2n\) were present in the x-ray diffraction photographs. This led to the x-ray group mmmPb-, including three space groups: \(D_{2h}^3\)-Pbmm, \(C_{2v}^2\)-Pb2m and \(C_{2v}^4\)-Pbm2. Since carbocernaite crystals had a high piezoactivity (established by A. F. Solov'ev in Moscow State University), the centrisymmetric group \(D_{2h}^3\) was eliminated from consideration. Subsequently the true group of the mineral was determined: \(C_{2v}^2\)-Pb2m. The intensities of the reflections were measured visually, using a photographic-density scale in steps of \(4^2\). The values of \(R^2\) were found in the usual way, allowing for the kinematic and polarization factors. A correction for absorption was not introduced, owing to the small dimensions of the crystals (about 0.2 mm).

Since the carbocernaite cell contains four MCO_3 "molecules," we had to locate four M(Ca + Na + ... ) cations, four carbon atoms, and twelve oxygen atoms. In each of the space groups and \(C_{2v}^2\) and \(C_{2v}^4\) the multiplicity of the...
general position equals four and that of the particular positions, two \cite{4}. Hence in the case of either of the two non-centrosymmetric groups there are only two variations for the sitting of the cations: either all four M statistically occupy points of general position, or the whole set of cations is divided into crystallographically-independent groups A and B, occupying two-fold positions on 2-fold axes or in mirror planes. A similar alternative exists for the four carbon atoms. In the initial stage of the investigation it was hard to say anything definite regarding the positions of the remaining atoms in the structure.

By analyzing the Patterson projections $P(uv)$, $P(uw)$, and $P(vw)$ respectively plotted from 117, 84, and 66 non-zero reflections, we obtained useful information regarding the structure of carbocernaite. Thus we were able to establish that the most probable space group of the mineral was $C_{2h}^{2} - Pb2_1m$, while the cations of the structure were distributed over points of particular positions in $m$ planes and formed two independent groups, differing sharply in their over-all scattering power. The most convincing proof of these conclusions came from the $P(uw)$ and $P(vw)$ projections. In both syntheses the highest maxima were concentrated exactly on the $w = \frac{1}{2}$ lines. Since the $C_{2h}^{2}$ group in the Pb$m_2$ aspect chosen does not contain symmetry elements fixing the position of atoms the z axis, this characteristic feature of the arrangement of the Patterson peaks can only be explained on the basis of the other possible group Pb$2_1m$, in which the horizontal $m$ planes constitute such fixing elements.

It thus followed from the analysis that the contents of the carbocernaite cell could be represented in the form $A_2B_2(CO_3)_m$ with $f_{A}^{\text{eff}} < f_{B}^{\text{eff}}$. It is clear that the greatest contrast in the x-ray scattering of groups A and B will be found when $A = Na + Ca$ and $B = Tr + Sr + Ba$. Since the total number of $(Na + Ca)$ atoms in the cell of known samples of carbocernaite is always greater than two, the final variation of the proposed grouping of cations in the structure took the form $A = Na, Ca; B = Tr, Sr, Ca, Ba$. On the basis of this cation distribution and our "average" composition, we then calculated the "effective" scattering powers: $Z_{A}^{\text{eff}} = 16$ and $Z_{B}^{\text{eff}} = 41$. We note that the grouping of the cations taken also corresponded to the well-known principle of grouping by reference to ionic radii.\text*\footnote{In the B group the Ca and Ba atoms play a subordinate part. Nevertheless, if we consider the relative numbers of these atoms and determine some average radius for them, this comes close to the radius of the Tr(Sr) atoms.}