On a peculiarity of the piezoeffect in carbonate-cancrinite crystals

I. B. Kobyakov, A. A. Levin, and Yu. I. Smolin

Institute of General and Inorganic Chemistry, USSR Academy of Sciences

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In the course of an x-ray study of the structure of carbonate-cancrinite in an electric field, an anomalously large deformation of the CO_3 ion, located in channels and tightly coupled to the aluminosilico-oxygen framework was observed. A model of the action of the channels on such a lattice characteristic of the piezoeffect has been developed for zeolites. The theoretical value of the piezomodulus $d_{33} = 28.3\times 10^{-12}$ C/N and the experimental value $d_{15} = -16.5\times 10^{-12}$ C/N of carbon cancrinite were found to be higher than the piezomoduli of the strongest linear piezoelectric substances known at present.

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Crystals of carbonate-cancrinite are described by the general formula $Na_6Ca(AlSiO_4)_6\cdot CO_3\cdot nH_2O$. In spite of the fact that cancrinite has been considered as a centrally symmetric crystal in the mineralogical literature,[1] in its natural samples, which are polycrystalline formations with a certain ordering of the blocks, a strong piezoelectric effect has been observed.[2,3] Since the presence of defects in the natural samples has a significant effect on the piezoelectric activity, a method of growing carbonate-cancrinite under hydrothermal conditions has been developed,[4–6] and apparently homogeneous single crystals with volumes up to several cm^3 have been obtained. The crystals are colorless, transparent and have a density $\rho = 2427 \pm 2$ kg/m^3. The predominant forms of the artifical crystals are hexagonal prism $\{11\bar{2}0\}$ and hexagonal dipyramid $\{11\bar{2}1\}$. Less developed are the hexagonal prism $\{01\bar{1}0\}$ and pinacoid $\{000\bar{1}\}$ faces. The investigation of the real structure has shown their low quality; the crystals are strained, they crack quickly after growing, they contain numerous inclusions of the mother liquor in the form of "channels" which extend along the Z axis. Moreover, a significant change in the chemical composition has been observed in various parts of the crystals and even within the limits of a single crystal.

We have undertaken to measure the piezoelectric constants of artificial carbonate-cancrinite by a resonance method, and also to determine by the method of structural analysis the elements responsible for the amplification of the piezoelectric activity of the crystal. The results of measurement of the resistivity ρ, the tangent of the dielectric loss angle tan δ, the permittivity ε_{ii}^T, and the piezomoduli d_{ij} at room temperature are shown in Table I. The data of the table (small value of ρ_Z and large value of tan δ_Z) indicate the presence of more crystal defects in the Z direction, which leads to a significant underestimation of the values of the piezomoduli d_{33} and d_{31} as measured by the resonance method. This statement is also confirmed by the fact that $Q = 30$–70 for the vibration of rods, excited through piezomoduli d_{33} and d_{31}, while $Q \approx 1000$ for vibration of plates excited by piezomoduli d_{14} and d_{15}. Moreover, the inclusions of the mother liquor in "channels" parallel to the Z axis, and containing mainly water ($\varepsilon = 81$), are the reason for the increased values of the permittivity ε_{33}^T of the carbonate-cancrinite. Recognizing that ε of ice falls off rapidly with decrease in the temperature ($\varepsilon = 72.5$ at $T = 268$ K and $\varepsilon = 3.5$ at $T = 213$ K at a frequency of 1 kHz) and consequently cannot exhibit any effect on ε of the cancrinite at low temperatures, we measured the temperature dependence of ε_{33}^T of the cancrinite at a frequency of 1 kHz. The results are shown in Table II, from which it is seen that even $\varepsilon_{33}^T = 9.9$ at $T = 200$ K.

TABLE I

Measured value	Calculated value	Measured value	Calculated value
ρ_X	50÷70	ρ_Z	1–3
tg δ_X	0.04	tg δ_Z	0.5
$\varepsilon_{11}{}^T$	11.9÷12.3	$\varepsilon_{33}{}^T$	17.6–21.6
d_{15}	–(11.3÷16.5)	d_{33}	2.2÷2.9
d_{14}	4.8÷5.8	d_{31}	0– –1

Note: Here ρ is in 10^{10} Ohm-cm, d in 10^{-12} C/N.

A detailed determination of the structure of natural carbonate-cancrinite has been made in Ref. 7. We have carried out a refinement of the structure in artificial samples, for which the piezomoduli d_{ij} were measured, with account of the large piezoelectric activity of the crystal—and in an electric field.[8] Samples of the following composition were investigated:

$Na_7Ca_{0,9}(AlSiO_4)_6\cdot(CO_3)_{1,4}\cdot 2.1H_2O$.

Measurement of the parameters of the unit cell ($a = 12.635 \pm 0.005$, $c = 5.115 \pm 0.003$ Å) and the intensity of the reflections were made on a crystal which was machined to a spherical shape with diameter of 0.32 mm. The symmetry of the diffraction picture and of the extinction pointed to the space groups $P\,6_3$ and $P\,6_3/\mathrm{m}$. Measurement of the intensity was carried out on a single-crystal diffractome-

TABLE II. Temperature dependence of the permittivity ε_{33}^T of artificial carbonate-cancrinite.

T, K	$\varepsilon_{33}{}^T$	T, K	$\varepsilon_{33}{}^T$
80	9.2	230	10.2
150	9.6	250	11.0
200	9.9	280	20.0

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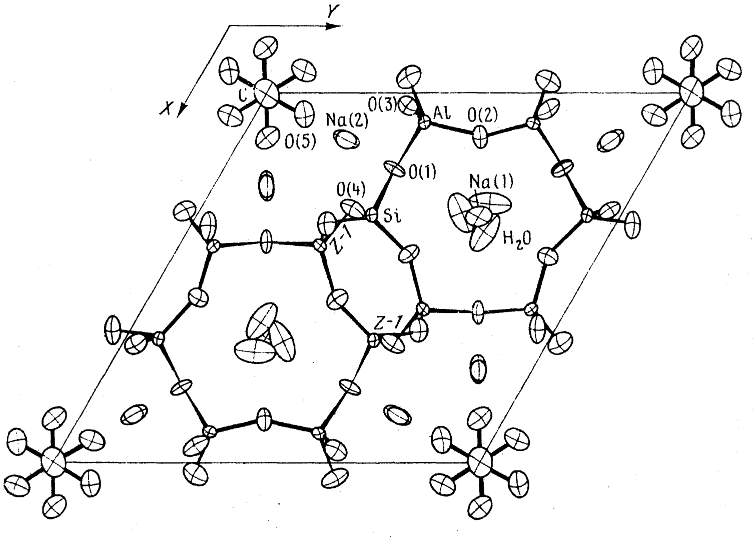

FIG. 1. Projection of the structure of carbonate-cancrinite on the plane {0001}.

ter by the method of a perpendicular beam with use of Mo K_α radiation that was rendered monochromatic by a graphite monochromator. Measurements of the reflection of six layer lines were carried out ($l = 0$–5). Corrections for polarization and the kinematic factor were introduced.

As an initial model, we chose the coordinates of the framework atoms from Ref. 7. With the help of a series of successive difference syntheses with intermediate refinement by the method of least squares,[9,10] we determined the locations of the nonnetwork atoms Na, O and C. After finding all the atoms, we refined the determination of the structure by the method of least squares from 1000 measurements of $F(h,k,l)$. In this case the atomic factors of neutral atoms were used.[11] In the final stages, the occupation factors of the positions of the nonnetwork atoms were included in the list of refined parameters, subject to the valence-balance condition. To reduce the correlation between the occupation factors and the thermal properties of the atoms, refinement of the former was carried out on an array of $F(h,k,l)$ with $\sin\theta/\lambda \leqslant 0.35$ Å^{-1}. The final value of the R factor was 0.04. In Table III we give the coordinates of the basis atoms. The occupations of the positions of the nonnetwork atoms are as follows: Na_1 2.01(3), Na_2 6.38(2), H_2O 2.01(6), CO_3 1.19. The structure of the synthetic cancrinite is shown in Fig. 1, where the atoms are shown in the form of thermal-oscillation ellipsoids. The six-membered rings of Si and Al tetrahedra are closed around the triad axes 1/3, 2/3 and 2/3, 1/3. Each ring is joined to six neighboring rings. The CO_3 group is located on the 6_3 axis and is characterized by the following geometries C–O_5 1.291 Å, $<O_5$–C–O_5 120.00(9)°. The Na_2 atom is the link between this group and the framework atoms; its polyhedron is formed both by the oxygen atoms of the CO_3 group and by the oxygen atoms of the framework. The other Na_1 atom is located on the triad axis and is coordinated through the O_1 and O_2 atoms and the water molecules. The water molecule in the cancrinite structure is located near the triad axis, and for this position the traid axis is statistically satisfied; the occupation factor of the position is 1/3.

In the case of weak piezoelectrics (for example, quartz), the displacement of the atoms when an electric field is applied to the crystal is small and cannot be recorded by the x-ray method. In the case of strong piezoelectrics, similar to cancrinite, particularly when there is nonuniform displacement of the atoms, the largest displacements can probably be recorded by the method of structure analysis. For this purpose, a cancrinite crystal in the form of a regular dodecahedral prism 2.3 mm in height and 0.4 mm in diameter was fixed to the goniometric head of a diffractometer by conducting glue; on the other end of the crystal, we fixed (also by conducting glue) a copper electrode connected to a high-voltage supply by a thin wire.

The intensities were measured by the "stationary counter, stationary crystal" method for a fixed period in an electric field (+ 1.5 kV and then—1.5 kV) applied parallel to the C_6 axis. The background noise was then subtracted and the ratio of the measured intensities was calculated. In this manner we measured the intensities of 1520 independent nonequivalent reflections. This procedure enabled us to increase the accuracy of the measurements because of the statistics, since the crystal was always located in the maximal

TABLE III. Coordinates and mean square errors of the atoms.

ATOM	x/a	y/b	z/c	ATOM	x/a	y/b	z/c
Al	0.0772(1)	0.4121(1)	0.75	Na_1	$^2/_3$	$^1/_3$	0.1354(14)
Si	0.3300(1)	0.4115(1)	0.7500(4)	Na_2	0.1254(2)	0.2521(2)	0.2943(6)
O_1	0.2019(2)	0.4035(2)	0.6586(8)	H_2O	0.378(3)	0.701(2)	0.179(4)
O_2	0.1157(3)	0.5619(3)	0.7248(10)	O_5	0.1179(7)	0.0603(7)	0.173(4)
O_3	0.0329(3)	0.3526(3)	0.0588(9)	C	0	0	0.173(7)
O_4	0.3161(3)	0.3582(3)	0.0486(9)				

reflection position; it also permitted us to eliminate all errors due to inaccuracy of the adjustment, to extinction, and to the other factors, because they are the same for measurements at + 1.5 and − 1.5 kV. The displacements of the atoms were estimated in the refinement by the method of least squares from the array of structure factors $F(h,k,l)$, which was obtained by multiplication of $F(h,k,l)$ calculated in the determination of the structure, by the corresponding intensity ratios raised to the power $\frac{1}{2}$, obtained in the measurement of the crystal in an electric field. The results of the refinement showed that only the displacements of the carbon atom of the carbonate group exceeded the rms error by a factor of 2. The oxygen atom in the carbonate group was shifted in the opposite direction by about 0.001 Å, a value equal to the error of the determination. The displacements of all the other atoms were significantly less and did not exceed the errors in their determination. In other words, the carbonate cation acquired the shape of an umbrella. The distance from the carbon atom to the plane of the oxygen atoms became equal to 0.0036 ± 0.0015 Å at $U = 3$ kV. Thus, under the influence of an electric field, the most deformed element of the cancrinite structure was the CO_3 ion.

The x-ray studies led us to two basic conclusions:

1) If we take it into account that the presence of the piezoeffect excludes the space group $P\,6_3/m$, then our results finally confirm the results of Ref. 7—the space group of carbonate-cancrinite is $P\,6_3(C\,6_3)$, the point group is C_6.

2) Since the CO_3 ion is tightly bound to the aluminosilico-oxygen framework (this is evidenced, in particular, by the fact that carbon dioxide is released from the crystal at a temperature above 900 °C) the large value of its deformation under the action of an applied electric field should lead to an increase in the deformation of the entire crystalline cell. This means that the presence of the CO_3 ion in the channels of cancrinite stimulates an increase in the piezoelectric activity of the crystal.

Starting out from this idea, we have obtained expressions for the piezomoduli d_{33} and the permittivity ε_{33}^T of carbonate-cancrinite. The x-ray data allow us to state that under the action of an applied electric field the O and C atoms in the carbonate ion are displaced in such a way that their center of mass does not change its position. We denote the displacement of the C atom relative to the plane of the O atoms by Δq; then, within elastic limits,

$$\Delta q = k\cdot\Delta c, \tag{1}$$

where Δc is the deformation of the cell parameter c and k is a proportionality coefficient. Since

$$S_3 = \Delta c/c = s_{33}T_3, \tag{2}$$

where S_3 is the deformation, s_{33} is the elastic compliance, T_3 is the mechanical stress, we have

$$\Delta q = kcs_{33}T_3. \tag{3}$$

Then the dipole moment μ of the CO_3 ion can be represented in the form

$$\mu = (\partial\mu/\partial q)\,\Delta q = (\partial\mu/\partial q)\,kcs_{33}T_3. \tag{4}$$

Starting out from the x-ray data, we find that the polarization vector P_3 is almost completely determined by the polarization of the CO_3 ion; then

$$P_3 = \frac{n\mu}{V} = \frac{n}{V}\left(\frac{\partial\mu}{\partial q}\right)kcs_{33}T_3, \tag{5}$$

where n is the number of CO_3 ions in the unit cell and V is the volume of the unit cell.

We write down the equations of the piezoeffect for our case:

$$S_3 = s_{33}{}^{E}T_3 + d_{33}E_3, \tag{6}$$

$$D_3 = \varepsilon_0E_3 + P_3 = d_{33}T_3 + \varepsilon_0\varepsilon_{33}{}^{T}E_3. \tag{7}$$

In the absence of field ($E_3 = 0$) we get from Eq. (7)

$$P_3 = d_{33}T_3, \tag{8}$$

and with account of Eq. (5),

$$d_{33} = \frac{n}{V}\left(\frac{\partial\mu}{\partial q}\right)kcs_{33}{}^{E}. \tag{9}$$

Assuming that the deformation of the CO_3 ion is proportional to the intensity of the applied electric field, we obtain

$$\Delta q = (\partial q/\partial E_3)\,E_3. \tag{10}$$

In the absence of mechanical stress ($T_3 = 0$) we get from Eq. (6)

$$S_3 = d_{33}E_3 \tag{11}$$

and with account of Eq. (2)

$$\Delta c = cd_{33}E_3. \tag{12}$$

From Eqs. (1), (10), and (12) we have

$$k = \frac{1}{cd_{33}}\left(\frac{\partial q}{\partial E_3}\right) \tag{13}$$

and with account of Eq. (9)

$$d_{33} = \left[\frac{ns_{33}{}^{E}}{V}\left(\frac{\partial\mu}{\partial q}\right)\left(\frac{\partial q}{\partial E_3}\right)\right]^{1/2}, \tag{14}$$

while from Eqs. (4) and (5)

$$\varepsilon_{33}{}^{T} = 1 + \frac{P_3}{\varepsilon_0E_3} = 1 + \frac{n}{V\varepsilon_0E_3}\left(\frac{\partial\mu}{\partial q}\right)\Delta q. \tag{15}$$

Our measurements enabled us to obtain data necessary for the calculation of d_{33} and ε_{33}^T: $V = 7.07\times10^{-28}$ m³; $n = 1.2$; the elastic compliance, determined by the resonance and pulsed ultrasonic method,

$$s_{33}{}^{E} = 1.22\cdot10^{-11}\ \mathrm{m^2/N},\quad \partial q/\partial E_3 = 27.6\cdot10^{-20}\ \mathrm{m^2/V},$$
$$E_3 = 1.3\cdot10^{6}\ \mathrm{V/m},\quad \Delta q = 3.6\cdot10^{-13}\ \mathrm{m}.$$

We have taken the value of the derivative of the dipole moment with respect to displacement of the atoms in the CO_3 ion out of its plane under the effect of an electric field from Ref. 12: $\partial\mu/\partial q = 1.4\cdot10^{-19}$ C. Substituting these data in formulas (14) and (15), we obtain the following numerical values:

$$d_{33} = 28.3\cdot10^{-12}\ \mathrm{C/N},\quad \varepsilon_{33}{}^{T} = 8.4.$$

Comparison of the numerical value of the piezomulus d_{33} with the measured $d_{15} = -16.5\times10^{-12}$ C/N shows that these quantities are sufficiently close to one another. In this case we must keep it in mind that the d_{15} of cancrinite is much larger than the analogous piezomoduli of all known linear pieoelectrics (for example, in the case of ZnO,

$d_{15} = -8.3\times 10^{-12}$ C/N). The calculated value of the permittivity ε_{ss}^{T} is somewhat below the value measured at low temperatures ($\varepsilon_{33}^{T} = 9.9$ at $T = 200$ K), where the effect of the inclusions of matrix solution has not been taken into account. This difference can be attributed to the fact that in our model we have used only the polarization of the CO_3 ions and have neglected the polarizations of the aluminosilicooxygen framework.

To test our model, we carried out the following experiment: the crystal was heated to 500 °C, after which the piezoeffect disappeared. These same samples were studied further by x-ray methods. It turned out that the water was removed from the structure channels, as a result of which a certain rearrangement of the structure took place; the CO_3 ion had the shape of an umbrella without application of a field and was not deformed in an electric field.

The experiments described above and the calculations leads us to the conclusion that the channels in zeolites can have a significant effect on the lattice characteristics of the crystals, such as the piezoeffect.

[1] A. G. Berekhin, Mineralogiya (Mineralogy), Gostekhizdat, 1950.
[2] V. A. Koptsik, Izv. Akad. Nauk SSSR, Ser. Fiz. **20**, 219 (1956).
[3] V. A. Koptsik and I. B. Kobyakov, Kristallografiya **4**, 223 (1959) [Sov. Phys. Crystallogr. **4**, 201 (1960)].
[4] B. N. Litvin and L. N. Dem'yanets, Kristallografiya **6**, 799 (1961) [Sov. Phys. Crystallogr. **6**, 643 (1962)].
[5] F. A. Belimenko, I. B. Kobyakov, V. E. Khadzhi, and V. K. Novik, Reports of papers, Fifth All-Union Conference on Crystal Growth, Tbilisi, 1977, p. 82.
[6] B. N. Litvin, I. B. Kobyakov and F. A. Belimenko, Kristallografiya **26**, 822 (1981) [Sov. Phys. Crystallogr. **26**, 465 (1981)].
[7] O. Z. Jarchow, Z. Kristallogr. **122**, 407 (1965).
[8] Yu. I. Smolin, Yu. F. Shepelev, I. K. Butikova and I. B. Kobyakov, Kristallografiya **26**, 63 (1981) [Sov. Phys. Crystallogr. **26**, 33 (1981)].
[9] W. R. Busing, K. O. Martin and H. A. Levy, Oak Ridge Nat. Lab. Rept. ORNL-TM-305, Tennessee, 1962.
[10] V. I. Andrianov, Z. Sh. Safina and B. L. Tarnopols'kiĭ, Zh. Struk. Khim. **15**, 911 (1974).
[11] H. P. Hanson, F. Herman, L. D. Lea and S. Skillman, Acta crystallogr. **17**, 1040 (1964).
[12] M. V. Belousov, D. E. Pogarev and A. A. Shiltin, Fiz. Tverd. Tela (Leningrad) **11**, 2697 (1969) [Sov. Phys. Solid State **11**, 2185 (1970)].

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