

Asymmetric thermal vibrations of atoms and pyroelectricity in cancrinite

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The crystal structure of CO₃-cancrinite was analyzed by applying a generalized structure factor expression of the Gram-Charlier expansion to the least-squares refinement performed by using the X-ray intensities measured on single crystals at 173, 293, 473, and 673 K. No satellite reflection or diffuse scattering was observed. The space group is $P6_3$ with unit cell $a = 1.2604(3)$ and $c = 0.51144(8)$ nm at 173 K, and $a = 1.2709(4)$ and $c = 0.5202(6)$ nm at 823 K. The temperature behavior for the dehydration and the unit cell dimensions were considerably different from those previously reported for CO₃-cancrinite, which shows superstructure reflections.

Two position vectors were assigned to each of the framework atom sites or the CO₃ site for examining its asymmetric probability density function—one for the free energy minimum and another for the potential energy minimum. Two polarization vectors were obtained for a unit cell from those position vectors and ion charges. The rigid ion contributions to the pyroelectric coefficients $p^{(\sigma)}$ (measured under a constant stress σ) and the secondary coefficient $p^{(2)}$ were finally estimated from the temperature dependences of the polarization vectors.

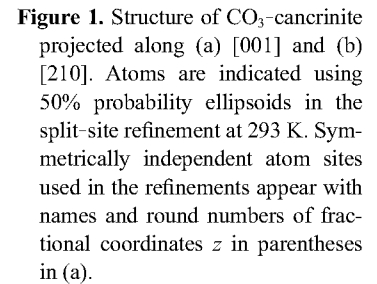
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INTRODUCTION

Cancrinite is a tectosilicate mineral belonging to a polar space group $P6_3$ (Grundy and Hassan, 1982), which allows the crystal to polarize electrically along the hexagonal c -axis. Figure 1 illustrates the structure of cancrinite in projections along [001] and [210]. Symmetrically independent atom sites obtained from the split-site refinement in the present study are shown in Figure 1a; the z -coordinates are rounded off and given in parentheses. Some measurements of the pyroelectric coefficients have been reported for CO₃-cancrinite at temperatures 4.2–500 K by Drozhdin et al. (1975) and Kozlov et al. (1989). These authors found that the temperature dependence of the pyroelectric coefficient $p^{(\sigma)}$, which was measured under a constant mechanical stress σ , is non-monotonic, including sign changes below 100 K, and has some polarization relaxations. Most of these studies have pointed out the importance of water molecules in the absolute values of $p^{(\sigma)}$, although the interpretation of temperature behaviors is not unique. Drozhdin et al. (1975) considered two cases, wherein the primary and secondary (the piezoelectric ef-

fect due to thermal expansions) effects are predominant, whereas Kozlov et al. (1989) considered the temperature dependence of the primary effect as the reason for the sign change. In a more general interpretation, another possibility has been pointed out on the basis of the compensation between the two values of the changes in polarization—one value for the aluminosilicate framework and another for one or more mobile structural elements possessing nonzero intrinsic dipole moments (Galitskii, 1981). Many compounds contain molecules or complexes in channels or voids in their structures, which are bound to lattice skeletons by weak hydrogen bonds. Galitskii (1981) focused on the influence of the disorder of dipolar structural elements on total pyroelectric polarization by considering the correlation between the anomalous behaviors of pyroelectric coefficients and the hindering of the mobility of dipolar structural elements.

Previous studies on the pyroelectricity of cancrinite have primarily employed the measured pyroelectric coefficients of cancrinite without having any detailed descriptions of atomic configurations in the crystal. In general, we can estimate the thermodynamic equilibrium position of an atom κ , $\mathbf{r}_{\kappa}^{(e)}$, i.e., the position corresponding to the free energy minimum of thermally strained crystals, as


$$p_{\alpha}^{(1)} = \frac{1}{V_{\text{cell}}} \sum_{\kappa=l}^n q_{\kappa} \frac{\partial r_{\kappa\alpha}^{(\text{e})}}{\partial T} - p_{\alpha}^{(2)} \quad (\alpha = 1 \text{ to } 3) \quad (1),$$

In a refinement using X-ray or neutron diffraction

The cancrinite structure, which can accommodate polar or charged units in its channels and cages, provides a good example for evaluating the roles of the framework atoms and extra-framework atoms or units in the spontaneous polarization and its temperature coefficients. In the

present study, we report the results of the application of a generalized least-squares method to determine the individual atomic p.d.f.'s in a CO_3 -cancrinite sample at different temperatures; further, we apply the position data obtained from p.d.f.'s to calculate the two values of polarization vectors and their temperature coefficients, $p^{(0)}$, $p^{(2)}$, and then $p^{(1)}$ in a rigid-ion approximation. The results are compared with the literature values for pyroelectric measurements to evaluate the feasibility of our process, and then they are used in discussing the atomic mechanisms of pyroelectric coefficients in cancrinite.

SAMPLES AND CHEMICAL ANALYSES

The crystals of cancrinite used in the present study were found coexisting with sodalite in pegmatitic rocks at Ilmen Mountains (Ural). A piece of granular block of approximately 1 cm length was crushed into fragments, and transparent and colorless crystals, mostly tabular or prismatic, were collected. An X-ray powder measurement was conducted for these crystals, and it showed a diffraction pattern that identified it as CO_3 -rich cancrinite. Thermogravimetry (TG) measurements revealed a quick and large decrease in weight at around 1200 K. This weight loss is comparable to the weight loss at 1220 K that was assigned to the release of CO_2 from a CO_3 -cancrinite sample obtained from Dunganon Township, Bancroft (Canada), by Hassan (1996). Some fragments were examined by using a polarized microscope and X-ray photographic methods for determining the quality of the specimens and diffraction characteristics including symmetry (Laue group $6/m$) and crystal data. The X-ray single-crystal photographs showed clear diffraction spots as usually obtained from good quality crystals. In a preliminary step, we compared the Russian specimens with those from Litchfield, Maine (USA), by taking precession pictures. The Maine specimen showed rather sharp superstructure spots, and their positional relationship with the main reflections appeared similar to those previously reported for the Canadian samples (Grundy and Hassan, 1982). On the other hand, no satellite or diffuse reflections were observed in the case of the Russian crystals (the operating conditions for the X-ray experiment were nearly identical to those for the Main sample). Hence, in the present study, the Russian crystals were chosen to avoid structural complications related to the origin of the superstructure. Our sample had higher Na content than Ca. It is noteworthy that, according to Foit et al. (1973), materials from the two localities, which they studied, commonly showed superstructure reflections and had an unusually high Ca content.

Electron probe micro-analyzer (EPMA, JEOL

8800R) measurements were performed for Si, Al, Ca, Na, K, and S at 14–16 points in the polished surface of the crystals: these elements were nearly homogeneously distributed in the section of the crystals. The amount of CO_3 was first estimated with the weight loss at around 1200 K in the TG measurements. The chemical composition, excluding H_2O , is given as $\text{Si}_{6.30}\text{Al}_{5.71}\text{Ca}_{0.95}\text{Na}_{6.84}(\text{CO}_3)_{1.21}(\text{SO}_4)_{0.15}$ for 24 O atoms of the framework. The structural formula of cancrinite can be expressed as $\text{X}_2\text{Y}_6[(\text{T1})(\text{T2})(\text{O1})(\text{O2})(\text{O3})(\text{O4})]_6\text{A}_2\text{W}_2$, where both X and Y are the sites for Na and Ca; T1 and T2 for Si and Al; A for CO_3 with a C atom and three symmetrically equivalent O atoms represented as O5; W for H_2O with an O atom denoted as O6; and O1 to O4 for the framework O atoms. SO_4 could be accommodated in site A, but it is ignored in the present refinement. In the X-ray least-squares refinement, the content of site A was refined to be 1.66 CO_3 instead of 1.21, whereas a site W had high H_2O content (for example, 1.98 at 293 K).

X-RAY MEASUREMENTS

Three single-crystal specimens, which were ground with a Bond grinder to pseudospheres of radii of approximately 0.14–0.15 mm, were prepared for X-ray diffraction measurements. Integrated intensities were measured at 173 K with a charge coupled device (CCD) diffractometer (RIGAKU Mercury), and at 293, 493, and 673 K using a 4-circle diffractometer (RIGAKU APCS). The unit cell dimensions were measured at 13 temperatures, 12 of which were above room temperature (with the 4-circle diffractometer) and one was below room temperature (with the CCD diffractometer), separately from the intensity measurements. Figure 2 illustrates the temperature dependence of unit cell dimensions a and c ; weak but sharp falls can be observed at around 673 K. The cell dimensions were fitted taking nine temperatures below 673 K with a cubic equation having the following form:

$$a \text{ (or } c) = uT^3 + vT^2 + w \quad (2),$$

where u , v , and w are the parameters to be determined, and T is temperature. Figure 2 also shows the linear thermal expansion coefficients α_1 and α_3 calculated using the parameters determined; they change along the upward convex curves with a maxima at around 350 K and become nearly zero (α_1) and negative (α_3) at approximately 673 K. All the X-ray measurements were performed using graphite-monochromatized $\text{MoK}\alpha$ radiation. The low temperature was attained using a N_2 gas-flow cooling device placed on the CCD diffractometer, where the temperature was controlled within ± 1 K at 173 K. High tempera-

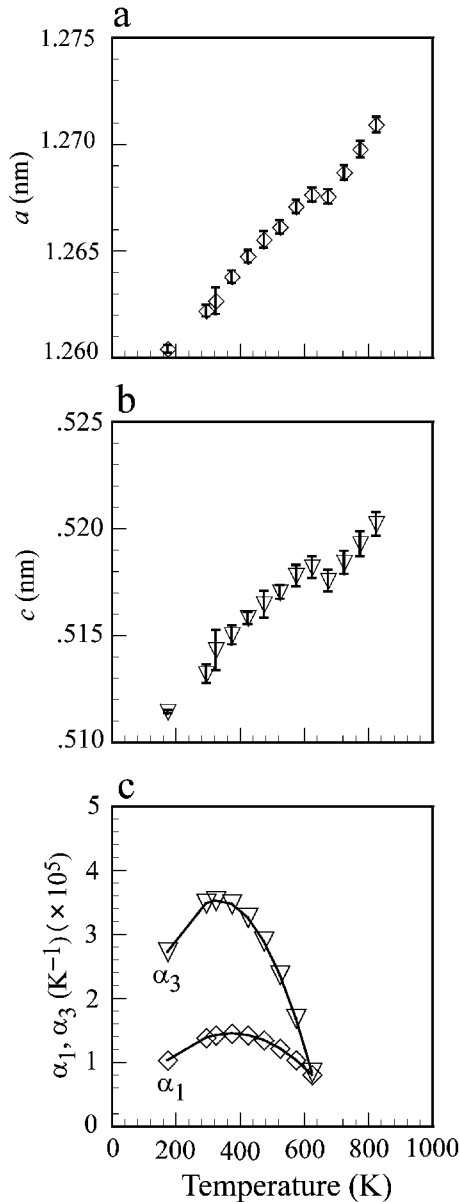


Figure 2. Temperature dependences of unit-cell dimensions (a) a and (b) c , both in nm, and (c) linear thermal expansion coefficients α_1 and α_3 (K^{-1}), both multiplied by 10^5 in CO_3 -cancrinite. Error bars correspond to one e.s.d. α_1 and α_3 were calculated with parameters obtained after fitting nine sets of a and c below 623 K using equation (2). The parameters in this fitting are as follows: u (nm/K^3) = -4.38×10^{-11} , v (nm/K^2) = 4.916×10^{-8} , w (nm) = 1.25915, and goodness of fit $R^2 = 0.998$ for a , and u = -5.454×10^{-11} , v = 5.451×10^{-8} , w = 0.51015, and $R^2 = 0.993$ for c .

tures were attained using an electric furnace, and the temperature was regulated within a range of ± 1 K around the set temperatures at a distance of approximately 1 mm from the center of the crystal. The preliminary hexagonal diffraction symmetry determined from the photographic methods was confirmed with an overall internal agreement for equivalent reflections—1.4% for 1138 equiva-

lent groups at 173 K. With the given Laue group symmetry, two space groups— $P6_3$ and $P6_3/m$ —are possible; the possibility of the latter is eliminated at this stage because of the possibility of pyroelectricity.

By using a 4-circle diffractometer, integrated intensities were measured in the ω - 2θ scan mode for the reflections of $2\theta \leq 70^\circ$ for half the reflection sphere. In the case of the measurements using the CCD diffractometer, intensity data were collected within the full sphere of $2\theta \leq 50^\circ$. The measured intensities were converted to structure factors or their squares after applying Lp corrections; the absorption was negligible and $\mu r < 0.089$. Averages over equivalent reflections for the point group 6 were taken, and those larger than the corresponding 3σ were used in the refinements at 293, 473, and 673 K or at 173 K.

X-RAY SINGLE-CRYSTAL ANALYSES

According to Jarchow (1965), the electron density distribution around O6 of the water molecule showed a strong possibility of disorder over the three positions around the 3-fold axis. Grundy and Hassan (1982) also demonstrated another type of disorder at one of the oxygen atoms (O5) and at the carbon atom in two parts along the 6_3 -axis. These authors successfully refined the structure using a split-site model. Our Fourier syntheses for the room temperature data showed electron density distributions suggesting the possibility of almost identical disorders around the same atom sites as in the previous studies.

The present least-squares refinements were applied to both the split-site model of Grundy and Hassan (1982) and an ordinary model; however, in contrast to the former, no specific assumption regarding the atomic p.d.f.'s was made in the ordinary model. The results of the split-site refinement were obtained to draw structural pictures and to compare with the literature data. The possibilities of positional disorder as well as the relationship between asymmetric p.d.f.'s and spontaneous polarization in the crystal are discussed on the basis of results of the refinement of the ordinary model employing higher-order terms of p.d.f.'s in the Gram-Charlier expansion (Johnson and Levy, 1974). A least-squares program LSGCEX (Kihara, 1990) was used for the refinements with coefficients up to the fourth-order term. In the beginning, the positive (or negative) direction of the c -axis (from Grundy and Hassan (1982)) was determined for all the spherical specimens by comparing the R -factors in the least-squares refinements with the sets of reflections indexed for the two possible orientations. Significant differences resulted; for example, the value was 0.018 for one dataset, while it was 0.024 for another dataset, both at 293 K in the final stage. In the least-squares refinement, the atomic ratio C/O5 was

restrained at 1/3. (In the split-site refinement, the two sites at C and O5 were distinguished as C1 and O51, respectively, for the lower one and C2 and O52, respectively, for the upper; further restraints were applied to maintain both the ratios for C1/O51 and C2/O52 at 1/3). The spherical atomic scattering factors were obtained from the table of Cromer and Waber (1974), and the anomalous dispersions were obtained from the table of Cromer (1974). The quantity minimized was $\sum w(|F_o| - k|F_c|)^2$, where k is a scale factor and w is a weighting function $1/s^2(|F_o|)$ with a standard deviation $s(|F_o|)$, estimated by counting statistics.

In the refinements at the four temperatures, the occupancy parameter at site X converged to full occupation by Na. The content of A was nearly constant at around 83% (corresponding to 1.66 in the chemical formula) at the lower three temperatures, but it reduced to 75% at 673 K. The protons of H₂O in site W were not identified in the electron density maps, but a valence calculation has suggested for the protons to coalesce in the water molecules with O6 (as mentioned subsequently). The occupancy of O6 converged to values in the range from 90 to 99% at the lower three temperatures, whereas the least-squares calculations of any parameter for O6 failed at 673 K. A difference Fourier synthesis with the F_c 's calculated using the structural parameters refined without O6 showed no

significant residuals around the expected positions. This temperature is close to that of the dips observed in the cell-dimension curves. With respect to these points, we assumed that most water molecules escaped from the correct sites in the event related to the anomaly observed in the cell dimensions, and the final least-squares cycles for 673 K were performed without O6.

As the CO₃ and H₂O contents decreased at high temperatures, the least-squares refinement was continued with the variable compositions of O, CO₃, and Na at sites W, A, and Y, respectively, while maintaining the compositions for the sites of the framework atoms—Na in X and Ca in Y—constant. Among the higher-order coefficients c^{ijk} and d^{ijk} (i, j, k and $\ell = 1$ to 3), only limited numbers of those were found to be significant or crucial at most sites. However, among others, A(C) was special; the enormously elongated bimodal p.d.f. was successfully simulated with only two coefficients, c^{333} and d^{333} .

RESULTS OF STRUCTURE REFINEMENTS

Table 1 summarizes the crystallographic and refinement data at the four temperatures. Table 2 lists the atomic coordinates (first-order coefficients) and the occupancies in the higher-order refinements; further, the averaged displacements over all directions calculated from anisotropic

Table 1. Crystallographic and refinement data for CO₃-cancrinite at 4 temperatures

X ₂ Y ₆ (T1T2O ₄) ₆ A ₂ W ₂ , X=Na, Y=0.807Na+0.158Ca, T1=Si, T2=0.951Al+0.049Si, A=0.605CO ₃ +0.07SO ₄ , W=H ₂ O, Space group P6 ₃ , Z=1				
	173 K (CCD, Mo K α)	293 K (4-circle diffractometer, Mo K α)	473 K (4-circle diffractometer, Mo K α)	673 K (4-circle diffractometer, Mo K α)
Used reflections ($ F_o \geq 3\sigma(F_o)$)	1241 for 4°<2 θ <50°	1971 for 4°<2 θ <70°	1757 for 4°<2 θ <70°	1649 for 4°<2 θ <70°
<i>a</i> (nm)	1.2604(3)	1.2631(3)	1.2659(3)	1.2681(3)
<i>c</i> (nm)	0.51144(8)	0.51320(5)	0.51676(4)	0.51827(4)
<i>V</i> _{cell} (nm ³)	0.70366(7)	0.70906(8)	0.71715(7)	0.72177(7)
Anharmonic ¹⁾				
<i>N</i> _p	179	179	179	186
<i>R</i> (<i>R</i> _w) [*]	0.0164(0.0218) ²⁾	0.0179(0.0259) ²⁾	0.0328(0.0374)	0.0457(0.0478)
Split-site model ²⁾				
<i>N</i> _p	100	100	100	91
<i>R</i> (<i>R</i> _w) [*]	0.030(0.023)	0.026(0.038)	0.039(0.046)	0.053(0.058)

^{*} $\sum w(|F_o| - k|F_c|)^2$ was minimized; $w = 1/\sigma^2(|F_o|)$; k , a scale factor; and σ , the standard deviation of $|F_o|$, based on the counting statistics.
 $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$.

*N*_p is the number of parameters refined in the least-squares method.

¹⁾ The sites for X, Y, O6, C, and O5 were refined with coefficients up to the fourth order. The sites for the framework O atoms from O1 to O4 corresponded to those up to the third order, while those for T1 and T2 were refined with second-order coefficients at 173, 293, and 473 K, and those with third-order coefficients at 673 K.

²⁾ Harmonic refinement for split-site model.

Table 2. Contents and first-order coefficients, x , y , and z , of the atomic sites in refinements with coefficients up to fourth-order terms at different temperatures

	Sites*	Contents (%)	x	y	z	$8\pi^2 \langle u^2 \rangle_{\text{iso}} \times 10^2$
173K	X (2 b 3)	100 Na	2/3	1/3	0.1328(12)	2.33(6)
	Y (6 c 1)	79.8(3)Na+15.8 Ca	0.1250 (2)	0.2526(2)	0.2920(4)	1.58(4)
	T1 (6 c 1)	100 Si	0.32804(3)	0.41074(4)	0.75 *	0.43(2)
	T2 (6 c 1)	95 Al+5 Si	0.07539(4)	0.41257(4)	0.7507(2)	0.43(2)
	O1 (6 c 1)	100 O	0.2024(2)	0.4031(2)	0.6694(6)	0.88(5)
	O2 (6 c 1)	100 O	0.1151(2)	0.5642(2)	0.7239(6)	1.32(6)
	O3 (6 c 1)	100 O	0.0301(2)	0.3507(2)	0.0612(5)	0.94(6)
	O4 (6 c 1)	100 O	0.3147(2)	0.3586(3)	0.0444(5)	0.99(6)
	W(O6) (2 a 3)	94(2) O	2/3	1/3	0.685(2)	13.8(5)
	A(C) (2 a 3)	81.0(8) C	0	0	0.775(7)	18(2)
293K	A(O5) (6 c 1)	81.0 O	0.0581(5)	0.1169(4)	0.781(2)	17.4(7)
	X	100 Na	2/3	1/3	0.1323(11)	2.95(5)
	Y	79.7(3)Na+15.8 Ca	0.12486(9)	0.2525(1)	0.2917(3)	1.99(3)
	T1	100 Si	0.32819(3)	0.41079(2)	0.75 *	0.561(9)
	T2	95 Al+5 Si	0.07528(3)	0.41256(3)	0.75085(9)	0.57(1)
	O1	100 O	0.2030(2)	0.4048(2)	0.6607(5)	1.12(3)
	O2	100 O	0.1142(2)	0.5637(2)	0.7271(5)	1.61(4)
	O3	100 O	0.0292(2)	0.3502(2)	0.0594(4)	1.14(3)
	O4	100 O	0.3151(2)	0.3582(2)	0.0421(4)	1.18(4)
	W(O6)	99(2) O	2/3	1/3	0.689(2)	13.9(5)
473K	A(C)	81.7(7) C	0	0	0.779(4)	19(2)
	A(O5)	81.7 O	0.0576(4)	0.1164(4)	0.780(2)	18.1(6)
	X	100 Na	2/3	1/3	0.132(3)	5.4(2)
	Y	78.8(5)Na+15.8Ca	0.1254(2)	0.2542(2)	0.2890(6)	4.34(6)
	T1	100 Si	0.32859(4)	0.41106(4)	0.75 *	0.84(2)
	T2	95 Al+5 Si	0.07515(5)	0.41283(5)	0.7508(2)	0.87(2)
	O1	100 O	0.2041(3)	0.4070(3)	0.6696(8)	1.69(5)
	O2	100 O	0.1126(3)	0.5631(3)	0.7321(9)	2.24(5)
	O3	100 O	0.0259(3)	0.3485(4)	0.0539(7)	1.65(5)
	O4	100 O	0.3164(3)	0.3554(4)	0.0369(7)	1.64(5)
673K	W(O6)	94(4)	2/3	1/3	0.696(4)	21(2)
	A(C)	83(1) C	0	0	0.782(6)	16(2)
	A(O5)	83 O	0.0559(9)	0.1127(7)	0.781(3)	20.3(7)
	X	100 Na	2/3	1/3	0.132(4)	7.5(2)
	Y	77.0(7) Na+1.58Ca	0.1256(3)	0.2551(3)	0.2855(9)	4.10(6)
	T1	100 Si	0.3288(2)	0.4116(2)	0.75 *	1.34(3)
	T2	95 Al+5 Si	0.0753(2)	0.4137(2)	0.7502(6)	1.40(3)
	O1	100 O	0.2043(4)	0.4075(5)	0.675(1)	2.58(8)
	O2	100 O	0.1139(4)	0.5636(4)	0.733(2)	3.22(8)
	O3	100 O	0.0235(5)	0.3484(5)	0.0501(10)	2.43(7)
	O4	100 O	0.3185(5)	0.3548(5)	0.0337(10)	2.40(8)
	W(O6)**	---	---	---	---	---
	A(C)	75(2) C	0	0	0.775(10)	17(2)
	A(O5)	75 O	0.054(2)	0.1104(10)	0.783(5)	24(2)

Atomic displacements averaged over all directions $\langle u^2 \rangle_{\text{iso}}$ (nm²) were obtained from harmonic refinements.

The atomic site names are followed by the number of positions, Wyckoff notation, and point symmetry in parentheses.

Ratio C to O was restrained at 1/3. The estimated standard deviations are indicated in parentheses.

* Fixed during refinements.

** Vacant.

temperature factors in the refinement of the ordinary model terminated after the second-order terms are listed. The atomic distances and angles were calculated for the coordinates obtained in the refinements after omitting the higher-order terms for convenience to compare with literature values. The distances and angles in Table 3 are comparable with those listed in Grundy and Hassan (1982). The T1-O and T2-O distances appear consistent with the

contents of T1 (fully occupied by Si) and T2 (fully occupied but mostly by Al). The T1-O and T2-O distances (O from O1, O2, O3, and O4), which, in most cases (except for T1-O3 and T2-O4) have weak negative temperature dependences, were corrected for thermal displacements; a simple rigid bond model given by Downs et al. (1992) was employed. The corrections resulted in larger T-O values, but remained only at about 1-estimated standard de-

Table 3. Selected atomic distances and angles for atomic mean positions

(a) Distances (nm) $\times 10$				
Site	173K	293K	473K	673K
T1				
- O1	1.610(2) (1.612)	1.612(2) (1.614)	1.608(2) (1.611)	1.606(4) (1.611)
- O2	1.608(2) (1.611)	1.609(2) (1.612)	1.605(3) (1.610)	1.602(3) (1.609)
- O3	1.622(2) (1.624)	1.622(2) (1.624)	1.622(3) (1.625)	1.623(4) (1.627)
- O4	1.622(2) (1.624)	1.620(2) (1.622)	1.619(3) (1.622)	1.615(3) (1.619)
Mean	1.620(1)	1.616(1)	1.614(2)	1.612(2)
O1 - O2	2.600(2)	2.601(2)	2.600(3)	2.594(3)
O1 - O3	2.607(3)	2.610(3)	2.603(4)	2.600(5)
O1 - O4	2.652(3)	2.652(2)	2.644(4)	2.635(5)
O2 - O3	2.681(3)	2.680(3)	2.682(4)	2.682(6)
O2 - O4	2.679(3)	2.680(3)	2.676(4)	2.679(6)
O3 - O4	2.605(2)	2.603(2)	2.600(3)	2.597(4)
Mean	2.637(2)	2.638(2)	2.634(2)	2.631(2)
T2				
-O1	1.729(2) (1.731)	1.729(2) (1.731)	1.726(2) (1.729)	1.724(4) (1.728)
-O2	1.722(2) (1.725)	1.720(2) (1.723)	1.713(4) (1.718)	1.712(3) (1.718)
-O3	1.734(2) (1.736)	1.737(2) (1.739)	1.736(3) (1.739)	1.729(3) (1.732)
-O4	1.745(2) (1.747)	1.749(2) (1.751)	1.751(3) (1.754)	1.755(3) (1.759)
Mean	1.733(1)	1.734(1)	1.732(2)	1.730(2)
O1 - O2	2.768(3)	2.764(3)	2.761(4)	2.751(5)
O1 - O3	2.822(2)	2.827(2)	2.821(3)	2.813(4)
O1 - O4	2.787(3)	2.792(3)	2.785(3)	2.782(5)
O2 - O3	2.905(2)	2.906(2)	2.901(5)	2.904(4)
O2 - O4	2.914(2)	2.913(2)	2.915(5)	2.922(4)
O3 - O4	2.763(2)	2.769(2)	2.768(3)	2.761(4)
Mean	2.827(1)	2.829(1)	2.825(2)	2.822(2)
X				
- O1 $\times$ 3	2.877(2)	2.866(2)	2.854(2)	2.857(3)
- O2 $\times$ 3	2.429(2)	2.444(2)	2.469(3)	2.461(4)
- O6 (lower)	2.342(7)	2.355(8)	2.318(26)	-----
- O6 (upper)	2.891(7)	2.883(8)	2.903(23)	-----
Mean	2.644(2)	2.646(2)	2.649(5)	2.659(4)
Y				
- O1	2.496(2)	2.524(2)	2.568(3)	2.605(4)
- O3	2.428(2)	2.445(2)	2.457(3)	2.473(4)
- O4	2.441(2)	2.459(2)	2.472(3)	2.484(3)
- O51 *	2.429(7) 2.440(7) 2.462(5)	2.407(7) 2.448(7) 2.472(5)	2.455(13) 2.475(12) 2.498(10)	2.492(20) 2.487(13) 2.506(11)
- O52 *	2.432(10) 2.439(7) 2.455(9)	2.457(11) 2.429(8) 2.461(9)	2.450(24) 2.504(25) 2.475(26)	2.491(26) 2.520(40) 2.491(20)
- O3	2.882(2)	2.875(2)	2.845(3)	2.839(4)
- O4	2.914(3)	2.906(3)	2.870(3)	2.862(5)
C1 - O51	1.296(8)	1.292(7)	1.265(12)	1.264(11)
C2 - O52	1.308(8)	1.291(7)	1.265(13)	1.299(41)
C1 - C2	1.204(60)	1.195(49)	1.229(52)	1.091(169)
O51 - O52	1.207(14)	1.229(16)	1.298(28)	1.280(43)

* Either O51 or O52 can coordinate with Y-site cations.

(b) Bond angles in degrees for T1-O-T2 and O-C-O				
	173 K	293 K	473 K	673 K
T1-O1-T2	146.4(1)	147.4(1)	149.8(2)	151.5(2)
T1-O2-T2	151.1(1)	151.86(9)	153.2(2)	152.2(2)
T1-O3-T2	133.2(2)	133.8(2)	135.1(2)	136.6(2)
T1-O4-T2	133.18(8)	133.71(7)	135.0(2)	136.2(2)
O51-C1-O51	118.7(7)	119.8(4)	120.0(6)	119.5(11)
O52-C2-O52	118.7(10)	119.5(7)	120(2)	115.5(50)

Distances corrected with a simple rigid bond model are also shown for each T-O bond in parenthesis.

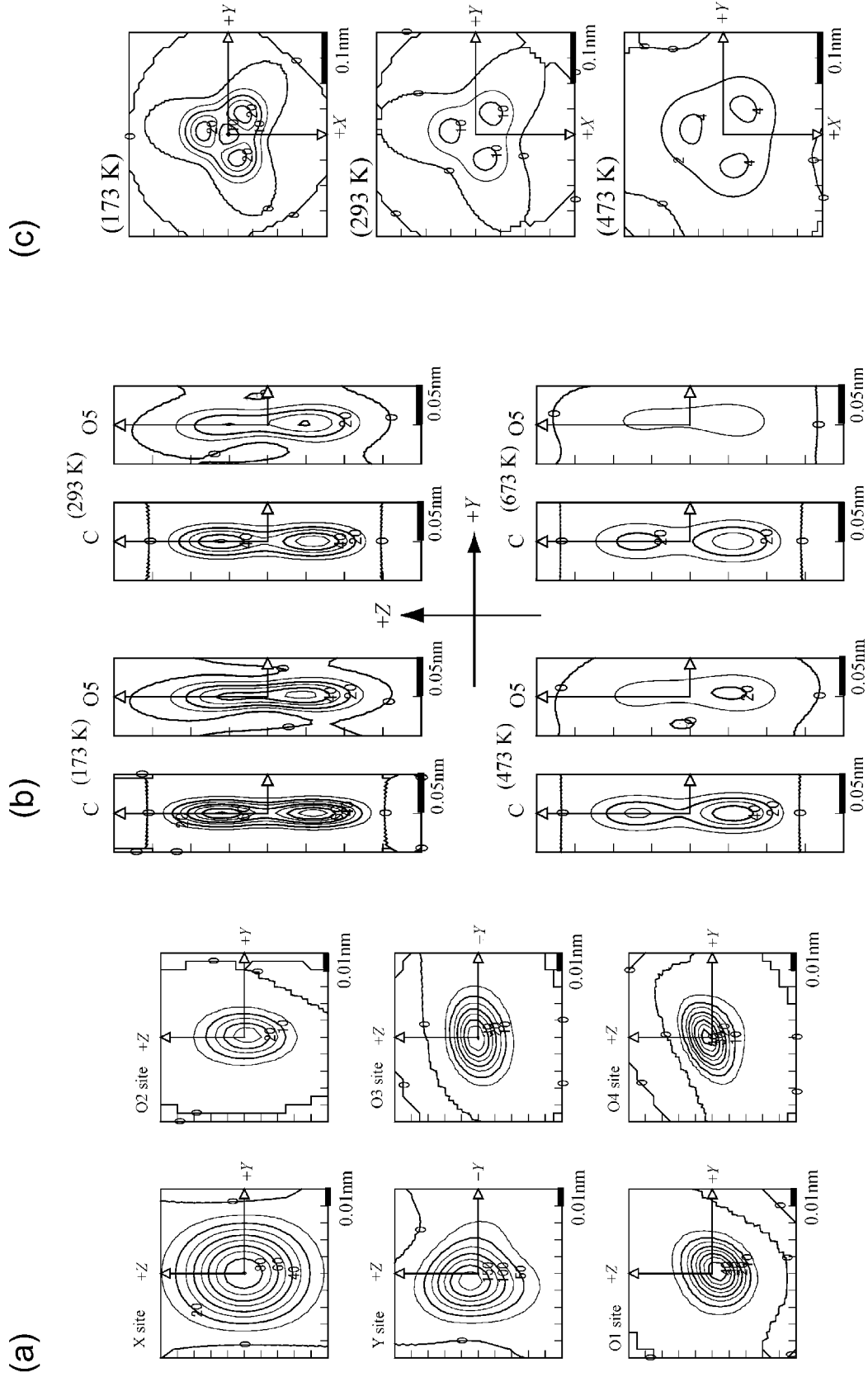


Figure 3. Probability density functions (nm⁻³) in sections passing reference positions for atom sites in refinements with higher-order coefficients. The orthogonal coordinates X , Y , and Z are chosen to be in $[210]$, $[010]$, and $[001]$, respectively. (a) (100)-sections at sites X and Y , and sites for framework O atoms (O1, O2, O3, and O4) at 293 K. Contours are scaled down by 10^2 for sites X and Y , by 10^3 for O1, O2, O3, and O4. (b) (100)-sections at site A (C and O5) at 173, 293, 473, and 673 K. Contours are scaled down by 10^2 . (c) (001)-sections at site W(O6) at 173, 293, and 473 K. Contours are scaled down by 10^2 .

viations (e.s.d.).

The position vectors $\mathbf{r}_\kappa^{(e)}$ and $\mathbf{r}_\kappa^{(m)}$ were obtained by analyzing the atomic p.d.f., $\rho_\kappa(\mathbf{u}')$, which was calculated using an equation expressed in the repeated summation convention as follows:

$$\rho_\kappa(\mathbf{u}') \approx \hat{\rho}_\kappa(\mathbf{u}') \left[1 + \frac{1}{3!} c_{\kappa}^{ijk} H_{ijk}(\mathbf{u}') + \frac{1}{4!} d_{\kappa}^{ijkl} H_{ijkl}(\mathbf{u}') \right] \quad (3),$$

where an orthogonal coordinate system $X//[210]$, $Y//[010]$, and $Z//[001]$ was chosen for the displacement vector $\mathbf{u}'$ of the atom from its position represented by the first-order coefficient x^i , i.e., x , y , and z , tabulated in Table 2; H represents the multidimensional Hermite polynomial tensors; and $\hat{\rho}_\kappa(\mathbf{u}')$, the Gaussian p.d.f. with the mean and dispersion chosen such that the first and second terms disappear (Johnson and Levy, 1974). In the present study, $\hat{\rho}_\kappa(\mathbf{u}')$ in equation (3) was calculated using the first- and second-order coefficients in the higher-order refinements. The (100) sections of the p.d.f. maps at the X, Y and framework O sites are shown for 293 K in Figure 3a; here, all the sections pass the origins of the p.d.f.'s, i.e., the atomic positions given by the higher-order refinements. In the case of sites A and W, the (100) and (001) sections are shown in Figure 3b and c, respectively.

DISCUSSIONS

The present specimen is considerably different from the CO_3 -cancrinite specimens reported by Hassan (1996) and Hassan et al. (2006), which were obtained from Bancroft, Canada, with respect to the diffraction characteristics and the behavior of the water molecule at different temperatures. The cancrinite specimen in this study is somewhat identical to a hydrothermally synthesized NO_3 -cancrinite (Fechtelkord et al., 2001) specimen, which shows no superstructure reflections.

Anisotropic and anharmonic atomic probability density functions

The p.d.f.'s at the framework atom sites (T1, T2, and O from O1 to O4) and the extra-framework cation sites (X and Y) are unimodal. At the T1 and T2 sites, the mean-square displacements (m.s.d.) are much smaller than those at the rest atom sites (Table 2), and their weak anisotropy can be barely observed in the ellipsoid drawing in Figures 1 and 4. At 173, 293, and 473 K, the higher-order coefficients at T1 and T2 were refined with values smaller than

the corresponding e.s.d.'s, indicating that the asymmetric departures of $\mathbf{r}^{(e)}$ from $\mathbf{r}^{(m)}$ are insignificant at these sites. The rest atom sites were refined with significant anharmonic coefficients. The two X-O6 separations are characteristically different from one another. Despite this pronounced asymmetry in the close-neighbor geometry, the asymmetry of the p.d.f. at X is not as significant as expected. Sites W and A show triple- and double-mode p.d.f.s, respectively, and will be separately described below.

A-site and disorder

The p.d.f. at site A is strongly elongated along [001], which shows that the two maxima are separated by approximately 0.12 nm in the cases of both C and O5 (Fig. 3b). Each mode at both C and O5 finds its counter one nearly at the same height z . This parallel appearance strongly suggests that CO_3 is displaced dynamically or statically along the 6_3 -axis keeping it nearly parallel with (001). The double modes at site A are denoted as A1 (lower) and A2 (upper). (If necessary, the double modes at C and O5 may be separately represented by C1 and C2 and O51 and O52, respectively.)

A CO_3 unit can occupy either A1 or A2 keeping its triangular plane nearly in (001). In Figure 4, the atomic arrangements around the sites A and Y are projected along 6_3 in order to observe the possible differences between the two cases—(a) A1 occupied and (b) A2 occupied. Eight O atoms are located near the site Y; among them, six are at 0.24–0.25 nm, and the other two are at approximately 0.29 nm at the relevant temperatures. Among the six nearest O atoms, three (O1, O3, and O4) belong to the framework, whose positions are to be kept nearly constant for both (a) and (b), but the remaining three belong to CO_3 (O5). In case (a), the three framework O atoms form a distorted trigonal prism with two O5 atoms at height z , for example, 0.67, and an O5 atom at $z = 1.17 (1/2 + z)$. However, in case (b), a distorted octahedron is formed with an O5 atom at $z = 0.91$ and two O5 atoms at $z = 0.41 (z - 1/2)$. The three distances for Y–O5 range from 0.24 to 0.25 nm with an average of 0.2444 nm for case (a) and 0.2442 nm for (b), for example, at 173 K (Table 3). In this manner, the CO_3 unit, whose triangular plane is nearly parallel to (001), can be maintained either in A1 or A2. Figure 4c illustrates another view of the positional relation for Y–O5 between the two cases in the projection along [110]. In either case (a) or (b), O5 is almost symmetrically located with respect to Y along [001]. In other words, in either case—whether A1 or A2 is occupied by CO_3 —the relation Y–O5 remains effectively constant. Site A definitely has a double-minimum o.p.p., and it may be assumed that

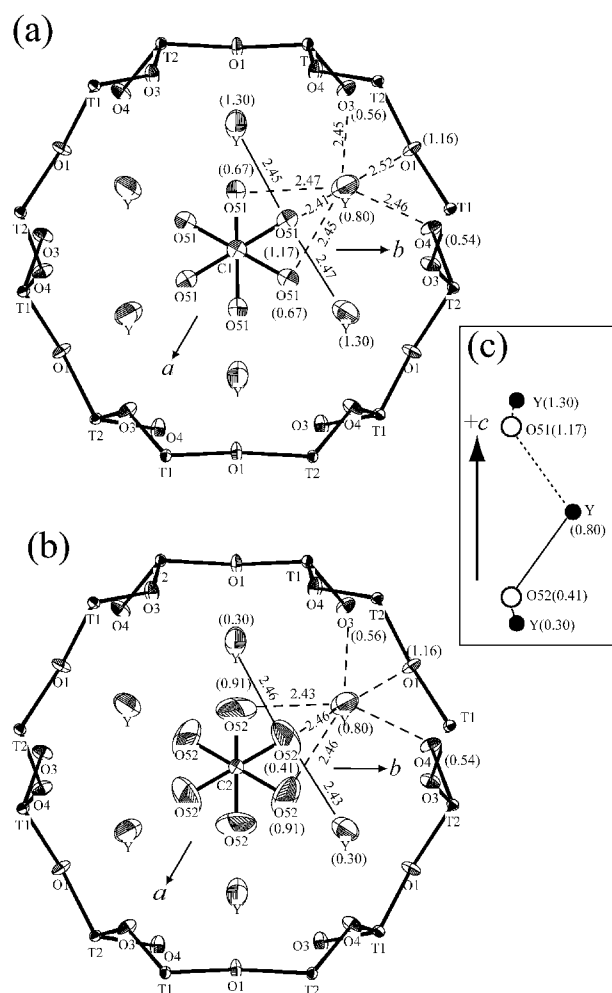


Figure 4. Projections of partial atomic arrangements along [001] around sites A and Y inside the channel running along [001]. Values are at 293 K. (a) CO₃ occupying well A1 (C1 and O51) and (b) CO₃ occupying well A2 (C2 and O52). In (a) and (b), a site Y at $z = 0.80$ is chosen to show the coordination by neighboring six O atoms with broken lines. O51 at $z = 1.17$ in (a) and O52 at $z = 0.41$ in (b) are also chosen to show their relationship with neighboring Y-sites at $z = 1.30$ and 0.30 with solid lines. (c) Another view of the positional relation between Y and O5 in a projection along [110]. Two cases are shown—dotted line for O51 and solid line for O52. Numbers in parentheses represent atomic fractional z -coordinates. The relevant Y–O distances are indicated along the bonds in nm.

their depths are nearly equal at A1 and A2.

W-site and disorder

The water molecule is located inside the cage penetrated by the 3-fold axis. In Figure 1, which is drawn with the results of the split-site refinement at 293 K, O6 appears thrice around the 3-fold axis. The calculated bond valences (Brese and O'Keeffe, 1991) of the framework O atoms from O1 to O4, and O5 of CO₃ are nearly ideal, except in

the case of O2, only if the identified atoms in the refinement are considered. The deficiency at O2, 0.13 v.u., could be compensated by the hydrogen bonding with the protons attached to O6. The two protons, denoted as H1 and H2, are expected to be symmetrically independent of each other with symmetry 1. The p.d.f. maps for O6 in (001) show that triple peaks deviated away by more than 0.08 nm from the 3-fold axis at 173 and 293 K, but it changed to a peak (with fewer features) in three directions at 473 K (Fig. 3c). Hence, the o.p.p. at O6 is suggested to be, at least, of a triple minimum, over which O6 is equally disordered. If the disorder is of the triple minima, H1 and H2 must also be disordered, respectively, over the symmetrically equivalent three positions switching the counter O2 atoms of the hydrogen bonding; hence, the H1–H1 and H2–H2 vectors must appear at every 120° in (001). (Vector H1–H2 also appears at every 120°, but not necessarily in (001).) In a PMR study, Sokolov et al. (1977) found that the proton–proton vector in (001) reorients at every 120° with a frequency that is greater than 10^4 Hz at 250 K. The observation of Sokolov et al. (1977) only suggests that the dynamical disorder of H₂O occurs over the three minima. Further, this disorder causes no change in the polarization along the c -axis. As is frequently mentioned in literatures (for example, Drozhdin et al., 1975 or Kozlov et al., 1989), if the water molecule in the W-sites contributes to the pyroelectricity, an angular change in the z -component of the O–H1 or O–H2 bond is probably involved, which is basically not related to the concerned disorder.

The observed temperature dependences of the unit-cell dimensions or linear thermal expansion coefficients α_1 and α_3 suggest that drastic dehydration occurs between 623 and 673 K, but it is preceded by a continuous dehydration that began at approximately 350 K. Our least-squares result for the occupancy at W still remains high at 94(4)% at 473 K. Besides this apparent inconsistency—the reason is still not known—it is noteworthy that the m.s.d. of O6 increases quickly in (001) from 0.138(2) nm² at 173 K to 0.302(8) nm² at 473 K, while the corresponding m.s.d.'s in [001] have rather small values from 0.026(5) to 0.036(8) nm². This data suggests that the water molecules move away from site W through the four-membered rings of the cage.

Asymmetric probability density functions and pyroelectricity

The changes in the spontaneous polarization vector ΔP with temperature change ΔT in a rigid-ion model can be calculated using the following equation:

$$\Delta \mathbf{P} = \frac{1}{V_{\text{cell}}} \sum_{\kappa=1}^n q_{\kappa} \Delta \mathbf{r}_{\kappa} \quad (4).$$

Here q_{κ} is the charge of the κ -th ion in a unit cell with volume V_{cell} , and $\Delta \mathbf{r}_{\kappa}$ is the displacement of the ion after the temperature changes. In pyroelectric crystals, vector $\Delta \mathbf{P}$ is parallel to the unique polar axes. As previously noted, we may have two close but different values, i.e., $\mathbf{r}_{\kappa}^{(m)}$ and $\mathbf{r}_{\kappa}^{(e)}$, for each atom; equation (4) can then be calculated to different values for these two values. The polarization calculated with the set of $\mathbf{r}_{\kappa}^{(e)}$ might correspond to the measured one under a constant stress σ (Mair and Wilkins, 1981).

In a single-minimum o.p.p., an atom undergoes thermal vibrations in the single well. After a change in temperature, in reality, bond distances and angles in the crystal vary because of asymmetric (anharmonic) potentials for every atom pair, thereby causing the crystal to be strained with the new positions of minima $\mathbf{r}_{\kappa}^{(m)}$. We assume that the polarization calculated with the set of $\mathbf{r}_{\kappa}^{(m)}$ corresponds to the secondary effect of pyroelectricity. Equation (1) can then be rewritten as follows:

$$p_{\alpha}^{(1)} = \frac{1}{V_{\text{cell}}} \left[\sum_{\kappa=1}^n q_{\kappa} \left(\frac{\partial r_{\kappa\alpha}^{(e)}}{\partial T} - \frac{\partial r_{\kappa\alpha}^{(m)}}{\partial T} \right) \right] \quad (5).$$

The positions, $\mathbf{r}_{\kappa}^{(m)}$ and $\mathbf{r}_{\kappa}^{(e)}$, can be obtained uniquely from the corresponding p.d.f. map in single-minimum o.p.p. cases. Even in the case of multiple-minimum o.p.p., it is still straightforward to determine $\mathbf{r}_{\kappa}^{(e)}$ and thereby the unique center of gravity of p.d.f.. However, $\mathbf{r}_{\kappa}^{(m)}$, as intended in equation (5), may not be any of the minima. In the case of multiple-minimum o.p.p., either a unimodal or multimodal p.d.f. may result, depending on the nature of the disorder. In other words, the form of o.p.p. is not necessarily obvious in an observed p.d.f. map, and $\mathbf{r}_{\kappa}^{(m)}$ must be determined carefully.

In cancrinite, the p.d.f. at the sites for X, Y and the framework atoms (T1, T2, O1, O2, O3, O4) is unimodal, and there are no obvious indications for the o.p.p. to be multiple-minimum. We assumed that all these sites are of single-minimum potential, and their $\mathbf{r}_{\kappa}^{(m)}$ can be identified with the corresponding modes of the p.d.f.'s. As described previously, the o.p.p. at site A can be reasonably assumed to be of double minimum, and symmetrical at the mid point between A1 and A2. The mid point is thus chosen to represent $\mathbf{r}_{\kappa}^{(m)}$. The asymmetry observed in the p.d.f. at this site (Fig. 3b) reflects the conditions experienced by the crystal. It is noteworthy that the Canadian specimen showed an equal site-occupancy for A1 and A2 (Grundys and Hassan, 1982), which is definitely different from our result. The (averaged) content of CO_3^{2-} at A1 and A2 may

vary with temperature, and these changes, if any, must cause the change of pyroelectric coefficient.

The p.d.f. at each atom site was calculated for the nodes of three-dimensional arrays that are regularly separated with the origins placed on the reference positions, i.e., the first-order coefficients (x^j) in a refinement. The error in the p.d.f. was estimated for the standard deviations of all the relevant parameters determined in the least-squares refinements. The position of the centroid for the p.d.f., i.e., $\mathbf{r}_{\kappa}^{(e)}$, was determined as the zero-moment position for such an array of nodes, separated by 0.002 nm in the three Cartesian axes. On the other hand, the modes were searched through the array of nodes meshed at 0.0001 nm, which is sufficiently small as compared to those due to the estimated errors in the p.d.f. (The position data $\mathbf{r}_{\kappa}^{(e)}$ and $\mathbf{r}_{\kappa}^{(m)}$ together with the full atomic parameters are collected in Appendix.)

Since no proton positional data was determined in the refinement, considered were the partial structures with the W site replaced by a vacancy. The polarization vector $\mathbf{P}(p_1 p_2 p_3)$ per volume was calculated taking the unit cell given in Figure 1 at the relevant temperatures. In the cancrinite structure, p_1 and p_2 are both zero, and hereafter, $\mathbf{P}$ is represented as p_3 without the subscript "3." The two kinds of coordinates at each atom site, i.e., $\mathbf{r}_{\kappa}^{(e)}$ and $\mathbf{r}_{\kappa}^{(m)}$, provided two different values of p ; they are denoted as p_E and p_M , respectively. In Figure 5a, the values of p_E (circles) and p_M (triangles)—calculated with assumed formal charges—are plotted. Both p_E and p_M appear to show smooth temperature dependences. Since $p^{(e)}$ and $p^{(m)}$ in Kozlov et al. (1989) are plotted on continuous non-linear curves below approximately 400 K, the temperature derivative $\delta p / \delta T$, which can be expected to give the rigid ion contribution to the pyroelectric coefficient, was estimated on the curves p_E and p_M fitted with the cubic equations in the form of equation (2). Any linear term must disappear in this fitting, since $\delta p / \delta T$ is to be zero at 0 K. Furthermore, both p_E and p_M were set equal at 0 K since contributions from thermal vibrations will be absent. The two curves fitted with a common w are also shown in Figure 5a. As the temperature increases from 0 K, the curve for p_E first appears to be nearly horizontal or slightly increasing; this is followed by a continuous fall in the high temperature region. In contrast, p_M first increases up to approximately 500 K and then begins to fall.

Figure 5b illustrates the three curves for $\delta p_M / \delta T$, $\delta p_E / \delta T$, and $\delta p_E / \delta T - \delta p_M / \delta T$, calculated using the parameters determined above. $\delta p_M / \delta T$ is positive and increases up to approximately 250 K; it then decreases and goes to a negative region above 500 K. The curves for $\delta p_M / \delta T$ and the thermal expansion coefficients (Fig. 2c) appear to share a common tendency. A secondary pyroelectric coefficient

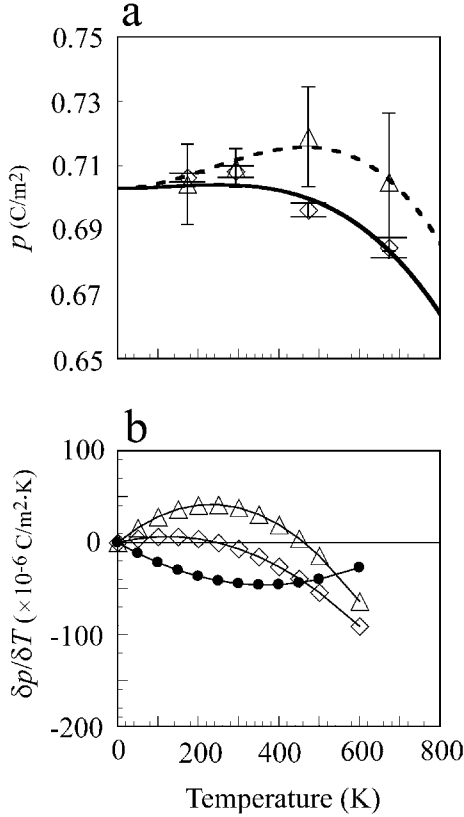


Figure 5. Temperature dependences of spontaneous polarizations, (a) p_E and p_M and (b) their temperature derivatives in rigid-ion calculations for the partial structure of CO_3 -cancrinite. p_E (diamonds) and p_M (triangles) were calculated with atom positions corresponding to free energy minimum and potential energy minimum, respectively. Error bars indicate 1 e.s.d. for p_E or of errors corresponding to 1 e.s.d. of p.d.f. for p_M . $\delta p_E / \delta T$ (diamonds), $\delta p_M / \delta T$ (triangles), and $\delta p_E / \delta T - \delta p_M / \delta T$ (solid circles) were calculated using the parameters determined by fitting p_E and p_M with equation (2) constraining w to be common for both $\delta p_E / \delta T$ and $\delta p_M / \delta T$. The parameters in this fitting were as follows: u ($\text{C}/\text{m}^2 \cdot \text{K}^3$) = -1.43396×10^{-10} , v ($\text{C}/\text{m}^2 \cdot \text{K}^2$) = 5.3238×10^{-8} , and $R^2 = 0.90$ for p_E , and $u = -2.5828 \times 10^{-10}$, $v = 1.7932 \times 10^{-7}$ and $R^2 = 0.88$ for p_M . Lines are only as guide for eyes.

$p^{(2)}$ is calculated in practice using known measured coefficients d_{ij} , c_{jk} , and α_k . For the point group of cancrinite, $p^{(2)}$ can be calculated using

$$p^{(2)} = d_{3j} c_{jk} \alpha_k \quad (6).$$

Kozlov et al. (1989) noted that the term $d_{33}c_{3k}\alpha_k$ makes the predominant contribution to $p^{(2)}$ at 298 K. From Kozlov et al. (1989), assuming that d_{33} , d_{31} , and c_{jk} are constant over a wide temperature range such as 290–650 K, we expect that the temperature dependence of $p^{(2)}$ of cancrinite must strongly reflect that of α_1 and α_3 . As shown in Figure 2, the expansion coefficients, particularly α_3 , quickly decreases above 350 K. Hence, $p^{(2)}$ cal-

culated with equation (6) must deviate from the straight line assumed by Kozlov et al. (1989) at high temperatures. This characteristic is well represented by $\delta p_M / \delta T$, even though it is considerably—approximately 10 times—larger than the reported value of $p^{(2)}$. The $\delta p_E / \delta T$ curve is also comparable with the characteristic features shown for $p^{(\sigma)}$ measured by Kozlov et al. (1989). The sign change also occurs in our $\delta p_E / \delta T$, but at considerably higher temperatures of around 250 K. Although, as shown, $\delta p_M / \delta T$ and $\delta p_E / \delta T$ are not necessarily in good quantitative agreement with $p^{(2)}$ and $p^{(\sigma)}$, we expect that the primary coefficient $p^{(1)}$, whose rigid ion contribution is estimated by the difference $\delta p_E / \delta T - \delta p_M / \delta T$, is probably negative over a wide range of temperatures above 0 K.

The polarizations p_E and p_M were also calculated for another partial structure, in which, in addition to site W, site A is also replaced by vacancy. The $\delta p / \delta T$ curves (not shown) show no obvious changes from the corresponding curves for the former partial structure, except at high temperatures around 673 K at which the two curves for $\delta p_E / \delta T$ and $\delta p_M / \delta T$ become closer than in Figure 5b. This probably suggests that the effect of the A-site disorder is not significant for the pyroelectric coefficient at low temperatures, but becomes significant at high temperatures.

Concluding remarks

The atom sites in CO_3 -cancrinite—other than the double-minimum CO_3 site and the triple-minimum H_2O site—mostly have single-minimum o.p.p. The rigid ion contribution to the pyroelectric coefficients $p^{(\sigma)}$ and $p^{(2)}$ of this mineral was estimated by analyzing the asymmetric atomic p.d.f.'s, omitting H_2O . Our estimates reproduce the characteristic features of measured $p^{(\sigma)}$ and theoretically expected $p^{(2)}$ with the thermal expansion and other data. Sign changes from positive to negative occur in both $p^{(2)}$ and $p^{(\sigma)}$ with increasing temperature; but at independent temperatures of each other. This results in negative $p^{(1)}$ through a wide temperature range. In an atomic view, the change in $p^{(2)}$ is a result of the displacements of atomic positions corresponding to the potential energy minimum in the crystal. The decrease in $p^{(2)}$ at higher temperatures is macroscopically related to the decrease in the linear thermal expansion coefficient α_3 . The effect of omitting H_2O is probably not significant to affect the present qualitative conclusions.

Although the number of temperatures for the structure analyses, four in the present case, was scarce, we believe that the present rigid-ion approach barely succeeded in taking advantage of the asymmetric atomic p.d.f.'s to determine the atomic mechanism of the secondary coefficient $p^{(2)}$ and then the primary coefficient $p^{(1)}$ for the can-

crinite sample.

DEPOSITORY MATERIAL

Appendix is available online from <http://www.jstage.jst.go.jp/browse/jmps>.

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