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Sodalite: High-temperature structures obtained from synchrotron radiation and Rietveld refinements

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ABSTRACT

The structural behavior of sodalite, ideally $Na_8[Al_6Si_6O_{24}]Cl_2$, at room pressure and from 28 to 982 °C on heating, was determined by using in situ synchrotron X-ray powder diffraction data (λ = 0.92007(4) Å) and Rietveld refinement. The sample was heated at a rate of about 9.5 °C/min and X-ray spectra were collected at intervals of about 15 °C. The cubic unit-cell parameter for sodalite increases smoothly and non-linearly to 982 °C. The percent volume change between 28 and 982 °C is 4.8(2)%. Between 28 and 982 °C, the Al-O and Si-O distances are constant, while the Al-O-Si angle increases from 138.29(1) to 146.35(2)° by 5.06(2)°. Simultaneously, the angle of rotation of the AlO_4 tetrahedron, φ_{Al}, decreases from 22.1 to 16.9°, a difference of 5.2°, while the angle of rotation of the SiO_4 tetrahedron, φ_{Si}, decreases from 23.6 to 18.0°, a difference of 5.6°. Moreover, the $[Na_4Cl]^{3+}$ clusters expand with increases in the Na-Cl bond length by 0.182(4) Å, and corresponding increases in the short Na-O bond length by 0.093(2) Å, and decreases in the longer Na-O* distance by 0.108(1) Å. Large displacement parameters occur for the Na and Cl atoms, and as the weaker Na-Cl bond expands with temperature, the Na atoms move toward the plane of the framework six-membered rings, which causes the framework tetrahedra to rotate and results in a relatively high rate of expansion of the structure. The framework TO_4 tetrahedra distort slightly with temperature. If the Na atom reaches approximately the plane of the six-membered ring, the expansion will be retarded, but sodalite melts before this occurs. Sodalite melts at about 1079 °C and begins to lose NaCl. The NaCl component is lost in two stages: about 4.5 wt% of NaCl is lost slowly at about 1150 °C, and about 7.0 wt% of NaCl is lost at a faster rate at about 1284 °C.

INTRODUCTION

The room-temperature structure of sodalite (space group $P\bar{4}3n$), ideally $Na_8[Al_6Si_6O_{24}]Cl_2$, was determined by Pauling (1930) and refined by Löns and Schulz (1967) and Hassan and Grundy (1984). The sodalite framework structure is characterized by four-membered rings on the (001) plane, and these rings are linked to form six-membered rings parallel to (111) (Fig. 1). These rings have an ordered distribution of Al and Si atoms. The sodalite or β-cage encloses $[Na_4Cl]^{3+}$ clusters. The Cl atoms are at the corners and center of the unit cell and the Na atoms are on the threefold axes adjacent to the six-membered rings. The Cl atom is tetrahedrally coordinated by four Na atoms, while the Na atom is fourfold coordinated by one Cl atom and three framework O atoms.

The thermal expansion of sodalite and structurally related materials were studied by high-temperature powder X-ray diffraction (e.g., Taylor 1968; Henderson and Taylor 1978). The thermal expansion of sodalite was studied by McMullan et al. (1996) using high-temperature single-crystal neutron diffraction data. However, the cell parameters obtained by McMullan et al. (1996) and previous studies are not similar, especially at higher temperatures. Fechtelkord (2000) discussed sodium ion dynamics in sodalite at high-temperatures using ^{23}Na MAS NMR. Hassan and Grundy (1984) developed a geometric model to explain the thermal-expansion mechanism for sodalite, but high-temperature structural data were not available to test this model. Recently, simultaneous differential thermal analysis (DTA) and thermogravimetry (TG) data were also obtained for sodalite (Antao and Hassan 2002), and these data were combined with the high-temperature structural data obtained in this study.

The present study was carried out to determine the structural behavior of sodalite to 982 °C using in situ synchrotron X-ray powder diffraction data and Rietveld structure refinements. No previous study has been done on sodalite using these techniques, so it would be of interest to compare the present results with those obtained previously using different experimental techniques. Data from this study will also be used to resolve some of the inconsistencies in the literature. Finally, the thermal expansion of sodalite is discussed in terms of the observed structural changes and the model of Hassan and Grundy (1984).

EXPERIMENTAL METHODS

The blue sodalite sample used in this study is from Bancroft, Ontario. This sample was also studied by Hassan and Grundy (1984). Chemical analysis of this sample has shown that its nominal composition is close to ideal, i.e., $Na_8[Al_6Si_6O_{24}]Cl_2$ (see Hassan and Grundy 1984). The crystals of sodalite were hand-picked and crushed to a powder using an agate mortar and pestle. High-temperature synchrotron X-ray powder diffraction experiments were performed at beam-line X7B of the National Synchrotron Light Source at Brookhaven National Laboratory. The sample was loaded in a quartz capillary (diameter = 0.5 mm, open to air at one end) and was oscillated during the experiment over a θ range of 10°. The high-temperature X-ray

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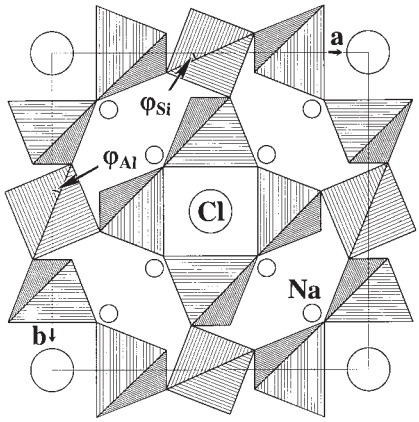

FIGURE 1. Projection of the structure of sodalite down [001] showing the lower half of the unit cell. The TO_4 tetrahedra are ordered and the angles of rotation of these tetrahedra are indicated by φ_{Al} and φ_{Si}. φ is the angle between the cell edge and the projection of the tetrahedral edge on (001).

diffraction data were collected with in situ synchrotron radiation ($\lambda = 0.92007(4)$ Å) at room pressure and from 25 to 982 °C. The sample was heated at a rate of about 9.5 °C/min using a horseshoe-shaped heater controlled using a thermocouple element near the capillary. The raw diffraction data were collected in regular intervals of about 15 °C. The data were collected to a maximum 2θ of about 50° [$(\sin\theta/\lambda) < 0.46$ Å^{-1}]. An imaging plate (IP) detector (Mar345, 2300 × 2300 pixels) mounted perpendicular to the beam path was used to collect full Debye-Scherrer rings with an exposure time of 10 s. In a separate experiment, an external LaB_6 standard was used to determine the sample-to-detector distance, tilt angle, wavelength, and tilting angle of the IP. The diffraction patterns recorded by the IP were integrated using the Fit2d program (Hammersley 1996).

RIETVELD STRUCTURE REFINEMENTS

Of the numerous diffraction traces collected, fourteen patterns were chosen at regular temperature intervals for treatment with the Rietveld method, using the GSAS, and EXPGUI programs (Larson and Von Dreele 2000; Toby 2001). For the room-temperature structure, the starting atomic coordinates, cell parameter, isotropic displacement parameters, and space group, $P\bar{4}3n$, were those of Hassan and Grundy (1984). The refined atomic coordinates were then used as input for the next higher-temperature structure. The site occupancies were fixed to the idealized chemical formula for sodalite. Refinement of the occupancy factors for the Na and Cl atoms indicate this formula to be appropriate, consistent with our previous chemical analysis (see Hassan and Grundy 1984).

In the initial stages, the background was fitted by using the shifted Chebyschev analytical function with 24 terms, and the profiles were fitted using the pseudo-Voigt function and an asymmetry correction term (GV, GW, LY, and asym). A full-matrix least-squares refinement varying a scale factor, cell parameter, atomic coordinates, and isotropic displacement parameters converged rapidly. Isotropic displacement parameters were used for all the atoms, but the Al and Si atoms were constrained to have equal values. In Rietveld structure refinements, it is common to use isotropic displacement parameters, even for simple structures such as the spinels (e.g., Harrison et al. 1998; Redfern et al. 1999), and to constrain similar atoms to have equal isotropic displacement parameters (e.g., Post et al. 2003). Using decreasing weights, soft constraints were used for the T–O distances, as we do not expect them to vary with temperature. Because of these constraints, their contribution to χ^2 was about 6% at different temperatures. Finally, the background (24 terms) and profile parameters (4 terms;), a scale factor, a cell parameter, and structural parameters (8 variables) were also allowed to vary, and the refinement proceeded to convergence. The total number of variables for each refinement was 38, and the number of observed reflections was about 65. The number of observations (data points) was about 1988. The structures refined well at all temperatures. Synchrotron powder X-ray diffraction patterns are shown in Figure 2, as examples. The cell parameters and the Rietveld structure refinement statistics at various temperatures are listed in Table 1. The atomic coordinates and isotropic displacement parameters are given in Table 2, and selected bond-distances and angles are listed in Table 3.

RESULTS AND DISCUSSION

Structure of sodalite

The general structural features of sodalite have been described in the introduction, and the structure obtained at 28 °C is shown in Figure 1. This structure is similar to that obtained by Hassan and Grundy (1984). The Al-O and Si-O distances are 1.7419(1) and 1.6201(1) Å, respectively, indicating that the Al and Si atoms are fully ordered (Table 3).

The Na atom is coordinated by one Cl and three O atoms at a distance less than 2.5 Å (Table 3). In sodalite, there are three O1* atoms at a further distance [3.0774(4) Å at 28 °C] that play an important role in the thermal behavior. The Cl atom is tetrahedrally coordinated by Na atoms.

Cell parameter

The variation in the *a* unit-cell parameter for sodalite with temperature is shown in Figure 3, together with the least-squares

TABLE 1. Sodalite: Rietveld refinement* and unit-cell parameters at various temperatures

T (°C)	*a* (Å)	R_p	R_{wp}	Exp. R_{wp}	R_F^2	χ^2	N_{obs}
†SC20	8.8823(7)						
28	8.88696(5)	0.0223	0.0324	0.0264	0.0318	1.527	65
43	8.88689(5)	0.0214	0.0313	0.0265	0.0289	1.416	65
58	8.88850(5)	0.0210	0.0303	0.0265	0.0302	1.328	65
104	8.89540(5)	0.0223	0.0318	0.0266	0.0329	1.451	65
164	8.90171(5)	0.0217	0.0314	0.0267	0.0353	1.403	65
270	8.91423(6)	0.0238	0.0339	0.0270	0.0392	1.602	65
376	8.92782(7)	0.0242	0.0352	0.0273	0.0376	1.687	67
482	8.94177(7)	0.0234	0.0340	0.0275	0.0453	1.551	65
588	8.95963(7)	0.0223	0.0324	0.0278	0.0418	1.382	67
694	8.97427(7)	0.0234	0.0340	0.0281	0.0497	1.492	67
800	8.99003(8)	0.0247	0.0362	0.0283	0.0532	1.655	67
906	9.01287(9)	0.0258	0.0375	0.0286	0.0567	1.741	70
967	9.02374(10)	0.0268	0.0379	0.0288	0.0610	1.765	70
982	9.02748(10)	0.0277	0.0392	0.0289	0.0632	1.868	70

* R_p = pattern *R*-factor = $\{\Sigma|(I_o - I_c)|\}/\Sigma I_o$; R_{wp} = weighted pattern *R*-factor = $\{\Sigma[w(I_o - I_c)^2]/\Sigma[wI_o^2]\}^{1/2}$, where I_o = observed intensity, I_c = calculated intensity, and $w = 1/I_o$; R_p and R_{wp} are the fitted values obtained without background subtraction. Exp R_{wp} = expected value of $R_{wp} = R_e$. R_F^2 = *R*-structure factor based on observed and calculated structure amplitudes = $\{\Sigma|(F_o^{1/2} - F_c^{1/2})|\}/\Sigma F_o^{1/2}$; $\chi^2 = [R_{wp}/R_e]$; where $R_e = [(N - P)/(\Sigma wI_o^2)]^{1/2}$, where *N* is the no. of observations (data points ≈ 1988) and P is the no. of variables (scale, background (24), and profile terms (4) = 29; cell and structural parameters = 9; total = 38 = P); Nobs. = no. of observed reflections ~ 65.

† SC20 represents single-crystal data at 20 °C from Hassan and Grundy (1984).

TABLE 2. Positional and isotropic displacement parameters (U × 100 Å²) at various temperatures for sodalite

Atom†/*T*		*SC20	28	43	58	104	164	270	376	482	588	694	800	906	967	982
‡Al	U	0.79(5)	0.51(4)	0.491(34)	0.498(33)	0.604(35)	0.66(4)	0.90(4)	0.83(4)	1.16(4)	1.06(4)	1.22(4)	1.30(5)	1.50(5)	1.55(5)	1.64(6)
O	x	0.1390(3)	0.13974(1)	0.13946(1)	0.13979(1)	0.14038(1)	0.14064(1)	0.14122(1)	0.14165(1)	0.14229(1)	0.14272(1)	0.14333(1)	0.14369(1)	0.14428(1)	0.14471(1)	0.14460(1)
	y	0.1494(3)	0.15013(1)	0.14984(1)	0.15017(1)	0.15074(1)	0.15099(1)	0.15155(1)	0.15194(1)	0.15255(1)	0.15294(0)	0.15351(1)	0.15384(1)	0.15438(1)	0.15479(1)	0.15467(1)
	z	0.4383(2)	0.43895(1)	0.43876(1)	0.43908(1)	0.43992(1)	0.44052(1)	0.44178(1)	0.44303(1)	0.44450(1)	0.44612(1)	0.44772(1)	0.44922(1)	0.45155(1)	0.45286(1)	0.45305(1)
	U	1.20(4)	0.24(5)	0.18(5)	0.26(4)	0.44(5)	0.57(5)	0.92(5)	1.04(6)	1.49(6)	1.71(6)	2.07(6)	2.38(7)	2.96(8)	3.24(8)	3.34(8)
Na	x	0.1778(2)	0.1779(1)	0.1781(1)	0.1781(1)	0.1782(1)	0.1785(1)	0.1788(2)	0.1798(2)	0.1800(2)	0.1816(2)	0.1822(2)	0.1835(2)	0.1854(2)	0.1864(2)	0.1868(2))
	U	1.96(5)	1.77(5)	1.66(5)	1.82(5)	2.28(6)	2.61(6)	3.47(7)	3.87(8)	4.97(8)	5.41(8)	6.31(9)	6.92(11)	8.13(12)	8.66(13)	8.92(14)
Cl	U	2.47(5)	2.40(6)	2.38(6)	2.55(6)	3.11(7)	3.63(7)	4.65(8)	5.71(9)	7.00(10)	8.65(11)	10.16(12)	12.00(15)	14.98(18)	16.67(20)	17.17(21)

† Al is at (1/4, 0, 1/2); Si is at (1/4, 1/2, 0); Na at (x, x, x); Cl at (0, 0, 0).
‡ $U_{Al} = U_{Si}$.
* SC20 represents single-crystal data at 20 °C from Hassan and Grundy (1984).

TABLE 3. Bond distances (Å) and angles (°) at various temperatures (°C) for sodalite

Bonds or angle/*T*		*SC20	28	43	58	104	164	270	376	482	588	694	800	906	967	982
Al-O	4×	1.742(2)	1.74188(9)	1.74199(4)	1.74199(4)	1.74199(4)	1.74200(4)	1.74200(4)	1.74201(4)	1.74200(4)	1.74201(4)	1.74201(4)	1.74201(4)	1.74202(4)	1.74202(4)	1.74201(4)
O-Al-O	4×	108.7(1)	108.442(5)	108.544(2)	108.436(2)	108.262(2)	108.199(2)	108.050(2)	107.961(2)	107.799(2)	107.726(2)	107.578(2)	107.519(2)	107.410(2)	107.304(2)	107.357(2)
	2×	111.0(1)	111.550(9)	111.342(3)	111.563(3)	111.917(3)	112.047(3)	112.353(3)	112.536(4)	112.870(3)	113.021(3)	113.327(3)	113.450(4)	113.678(4)	113.898(4)	113.788(4)
Si-O	4×	1.620(2)	1.62011(9)	1.62001(5)	1.62002(5)	1.62001(5)	1.62000(5)	1.62001(6)	1.62000(6)	1.61999(6)	1.61998(5)	1.61999(5)	1.61999(6)	1.61999(6)	1.61998(6)	1.61998(6)
O-Si-O	4×	107.7(1)	107.466(5)	107.571(2)	107.458(2)	107.281(2)	107.217(2)	107.067(2)	106.980(2)	106.818(2)	106.749(2)	106.601(2)	106.546(2)	106.441(2)	106.335(2)	106.392(2)
	2×	113.0(1)	113.560(9)	113.343(3)	113.577(3)	113.947(3)	114.080(3)	114.394(3)	114.578(3)	114.920(3)	115.065(3)	115.378(3)	115.496(3)	115.718(4)	115.943(4)	115.823(4)
Al-O-Si		138.2(1)	138.288(9)	138.286(4)	138.339(4)	138.575(4)	138.791(4)	139.222(5)	139.695(5)	140.188(5)	140.826(4)	141.356(5)	141.935(5)	142.788(5)	143.202(5)	143.347(5)
†φAl		22.4	22.1	22.2	22.1	21.7	21.5	21.0	20.6	20.0	19.4	18.8	18.3	17.4	16.9	16.9
φSi		23.9	23.6	23.7	23.5	23.2	22.9	22.4	21.9	21.3	20.7	20.0	19.5	18.6	18.0	18.0
Na-O	3×	2.353(2)	2.357(1)	2.355(1)	2.358(1)	2.365(1)	2.369(1)	2.380(1)	2.388(1)	2.401(1)	2.409(1)	2.422(1)	2.430(1)	2.444(1)	2.450(1)	2.451(1)
Na-O*	3×	3.078(1)	3.0774(4)	3.0807(3)	3.0763(3)	3.0679(4)	3.0632(4)	3.0537(4)	3.0442(4)	3.0333(4)	3.0211(4)	3.0090(5)	2.9979(5)	2.9808(5)	2.9693(5)	2.9694(6)
<Na-Cl>		2.716(1)	2.717(0)	2.718(0)	2.717(0)	2.716(0)	2.716(0)	2.717(0)	2.716(1)	2.717(1)	2.715(1)	2.716(1)	2.714(1)	2.712(1)	2.710(1)	2.710(1)
Na-Cl		2.736(1)	2.739(2)	2.742(2)	2.742(2)	2.746(2)	2.752(2)	2.761(2)	2.780(2)	2.788(2)	2.818(2)	2.832(3)	2.858(3)	2.894(3)	2.914(3)	2.921(3)

† φ is calculated from geometry of the structure, so no errors are reported.
*SC represents single-crystal data at 20 °C from Hassan and Grundy (1984).

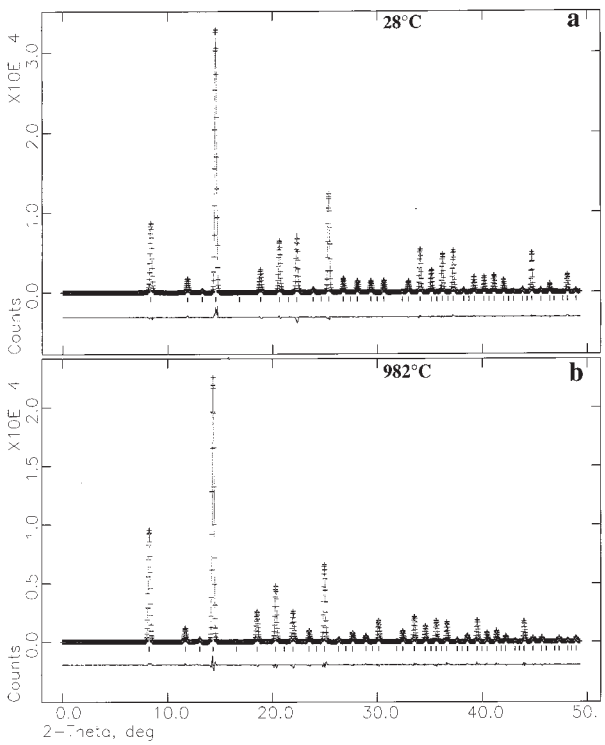

FIGURE 2. Synchrotron X-ray powder diffraction patterns for sodalite: (**a**) at 28 °C, and (**b**) at 982 °C, together with the calculated and difference plots from Rietveld refinements. For the pattern at 28 °C, the 100% peak at 14.56° on the 2θ axis is indexed as 211 and has a FWHM of 0.203°.

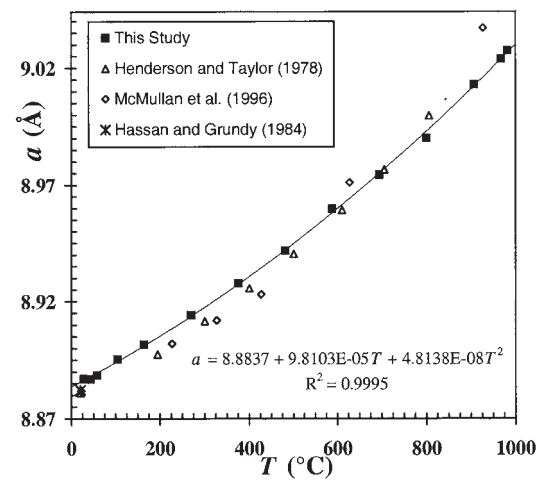

FIGURE 3. The *a* unit-cell parameter increases smoothly with temperature. The least-squares fit to the data is given as an insert. Data from the literature are given for comparison. Error bars are smaller than the symbols.

fit to the data, which is given as an insert. The *a* parameter increases non-linearly with temperature. The data yield a smooth expansion curve without changes or discontinuities that may indicate changes in the sodalite sample up to 982 °C. Sodalite melts at about 1079 °C and begins to lose NaCl. The NaCl component is lost in two stages: about 4.5 wt% of NaCl is lost slowly at about 1150 °C and about 7.0 wt% of NaCl is lost at a faster rate at about 1284 °C (Antao and Hassan 2002). Therefore, sodalite did not change composition significantly in the temperature range used in this study. The unit-cell parameter for

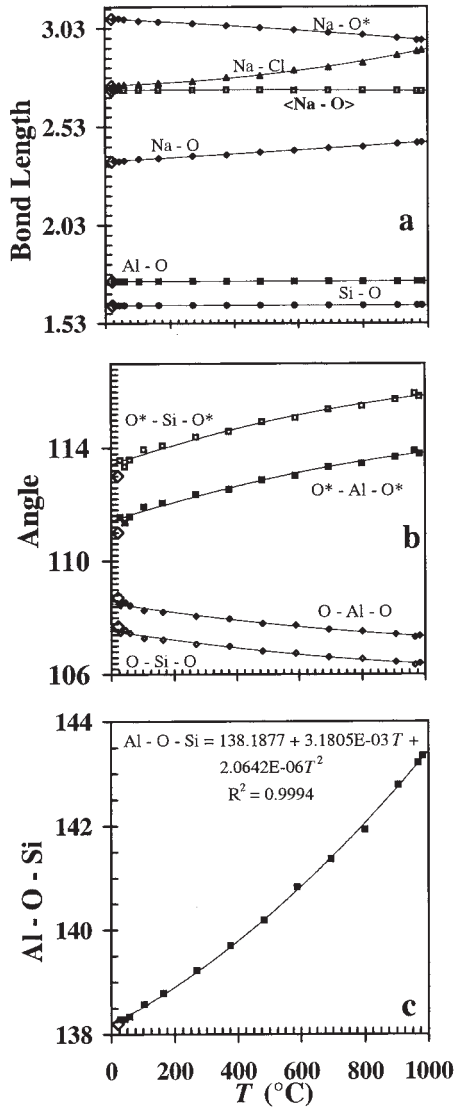

FIGURE 4. (**a**) Variations of the bond distances with temperature. The Na-Cl distance increases with temperature, while the long Na-O* distance decreases, and the Na-O distance increases, but the average <Na -O> and T-O distances are constant. (**b**) Variations of the framework TO_4 bond angles with temperature. (**c**) Variations of the framework Al-O-Si bridging angle with temperature. Error bars are not seen if smaller than the symbols. The room temperature structural data (open diamonds) from Hassan and Grundy (1984) are included for comparison.

sodalite at 28 °C obtained in this study [Table 1; a = 8.88696(5) Å] is slightly different from that obtained by Hassan and Grundy [1984; a = 8.882(1) Å]. The thermal-expansion data for sodalite from Henderson and Taylor (1978) and McMullan et al. (1996) are not the same as those obtained in this study, but the trend in their data is similar (Fig. 3). Significant differences are oberved, but the data from Henderson and Taylor (1978) matched our data more closely than that of McMullan et al. (1996). The a parameter expansion is given by the least-squares fit (all T in °C): $a = 8.8837 + 9.8103 \times 10^{-5}T + 4.8138 \times 10^{-8}T^2$ (Fig. 3). The coefficient of linear thermal expansion, $\alpha_a = (da/dT)(1/a)$, calculated

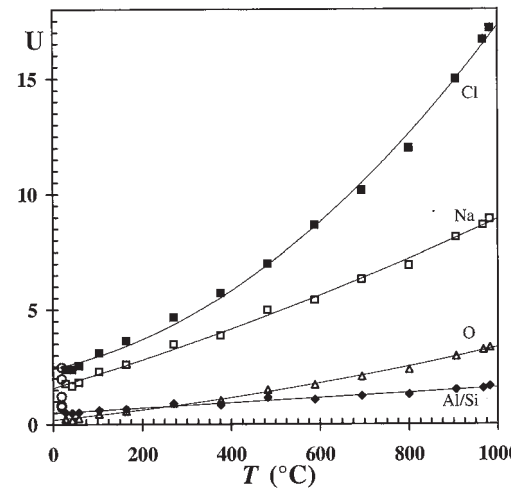

FIGURE 5. Variations of the isotropic displacement parameters, U, with temperature. The U values for Na and Cl increase significantly with temperature. Error bars are smaller than the symbols. The room temperature structual data (open circles) from Hassan and Grundy (1984) are included for comparison.

from the above equation, varies between 1.134×10^{-5} °C^{-1} at 28 °C and 2.134×10^{-5} °C^{-1} at 982 °C. The volume expansion is given by the least-squares fit: $V = 701.1243 + 2.3008 \times 10^{-2}T + 1.2163 \times 10^{-5}T^2$. The coefficient of volume thermal expansion, $\alpha_V = (dV/dT)(1/V)$, varies between 3.375×10^{-5} °C^{-1} at 28 °C and 6.374×10^{-5} °C^{-1} at 982 °C. The unit-cell volume increases between 28 and 982 °C by 4.8(2)%.

Framework

The framework of sodalite consists of corner linked TO_4 tetrahedra (T = Si, Al). The structure refinements indicate that these tetrahedra are fully ordered. Both the AlO_4 and SiO_4 tetrahedra contain two independent T-O bonds and they are constant with increasing temperature (Fig. 4a). The T-O distances were not corrected for thermal motions because isotropic displacement parameters were used. However, McMullan et al. (1996) have corrected for thermal motion and observe that between 22 and 927 °C, the differences in uncorrected values, –0.015 (Si-O) and –0.012 Å (Al-O), are changed by applied corrections to +0.004 and +0.006 Å, which, if meaningful, may indicate bond-stretching at the highest temperatures. The variations of the TO_4 tetrahedral angles are shown in Figure 4b. The smaller O-T-O angles do not vary as much as the larger O*-T-O* angles. From 28 to 982 °C, the Al-O-Si angle increases from 138.29(1) to 143.35(1)°, a difference of 5.06(2)° (Fig. 4c).

Cage clusters

The sodalite or β-cage enclose $[Na_4Cl]^{3+}$ clusters that expand with temperature. The orientation of these clusters is fixed by Na-O bonds to the framework oxygen atoms. The Na-Cl bond length increases by 0.182(4) Å from 28 to 982 °C. From 28 to 982 °C, the long Na-O* distance decreases by 0.108(1) Å, while the short Na-O bond distance increases by 0.093(2) Å, but the average <Na-O> distance is constant (Fig. 4a). The Na atom, therefore, moves toward the plane of the six-membered rings,

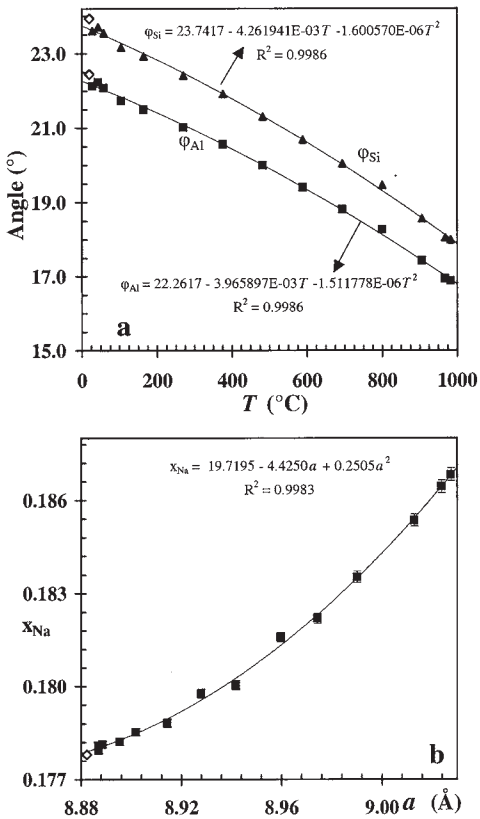

FIGURE 6. (**a**) Variations of the angles of rotations, φ_{Al} and φ_{Si}, of the AlO_4 and SiO_4 tetrahedron respectively, with temperature (see Fig. 1), and (**b**) variations of the Na atomic coordinate, x_{Na}, with the *a* parameter. In (**b**), error bars are not seen if smaller than the symbols. The room temperature structual data (open diamonds) from Hassan and Grundy (1984) are included for comparison.

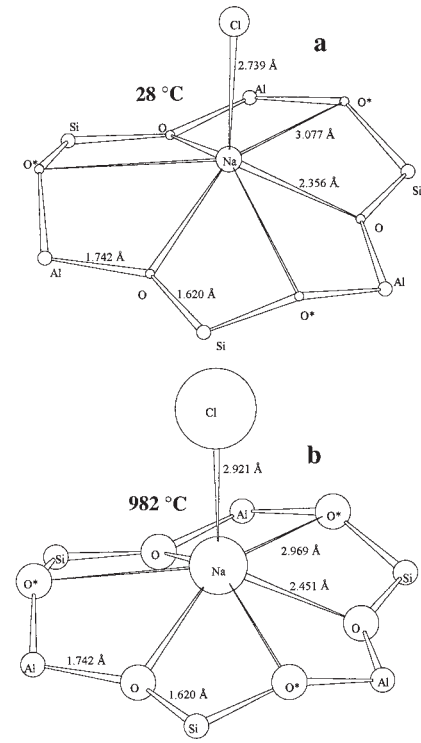

FIGURE 7. Comparison of the Na coordination in sodalite at (**a**) 28 °C and (**b**) at 982 °C. The displacement parameters are shown to scale at the 50% probability level. A six-membered ring is also shown. The O* atoms do not form typical Na-O bonds as they are too long. The long Na-O* distance decreases with temperature as the Na atom moves toward the six-membered ring.

where it comes closer to the framework oxygen atom, O*, that was further away at room temperature. The movement of the Na atom occurs because the weaker Na-Cl bond increases with temperature. We observed no Na atom jumping from the present occupied 8e site to a vacant 8e site on the opposite side of a six-membered window. This would also require puckering of the six-membered ring in the opposite direction (McMullan et al. 1996; Fechtelkord 2000).

Isotropic displacement parameters

Figure 5 shows the variations of the isotropic displacement parameters for the atoms in sodalite. The framework atoms have small U parameters [U(Al/Si) < U(O)] and they increase slightly with temperature. The displacement parameters for Na atoms, and in particular, those for Cl atoms increase considerably with temperature. Unlike the framework atoms, the Na and Cl atoms, therefore, play a crucial role in the thermal expansion of sodalite.

The thermal-expansion mechanism for sodalite

The geometrical model for the thermal expansion of sodalite (Hassan and Grundy 1984), when combined with the thermal analyses of sodalite (Antao and Hassan 2002), and the present results, give a comprehensive description of the thermal behavior of sodalite. In the thermal expansion of sodalite, the weaker Na-Cl bond increases, as indicated by large displacement parameters for the Na and Cl atoms. As the Na atom migrates toward the plane of the six-membered ring, the framework tetrahedra rotate. The AlO_4 and SiO_4 tetrahedra are rotated by angles φ_{Al} and φ_{Si}, respectively (see Fig. 1). These rotational angles are calculated at different temperatures using equation 8 of Hassan and Grundy (1984) and their variations with temperature are shown in Figure 6a. Between 28 and 982 °C, φ_{Al} decreases from 22.1 to 16.9°, a difference of 5.2°, while φ_{Si} decreases from 23.6 to 18.0°, a difference of 5.6°. These changes are comparable to the increase in the Al-O-Si angle of 5.06(2)°. In addition, the framework TO_4 tetrahedra distorts slightly with temperature, as discussed above. These rotations induce a high degree of expansion.

As the Na-Cl bonds expand, the Na atoms move along <111> toward the plane of the six-membered rings. The change of the Na coordinate, x_{Na}, with the *a* cell parameter is given in Figure 6b (compare Fig. 6 of Hassan and Grundy 1984). If the Na atom reaches (1/4, 1/4, 1/4), then it is midway between two Cl atoms and approximately in the plane of the six-membered ring. The Cl atom would then be coordinated by eight Na atoms, and the Na atom coordinated by two Cl and six framework O atoms causing the expansion rate to decrease. In sodalite, melting occurs before the Na atom reaches (1/4, 1/4, 1/4). A comparison

of the coordination of the Na atom and its location with respect to a six-membered ring is shown in Figure 7 for the structure at 28 and 982 °C.

In this study, synchrotron X-ray diffraction is combined with thermal data (DTA/TG), to give a complete picture of the thermal behavior of sodalite. In sodalite, thermal expansion occurs mainly by expansion of the $[Na_4Cl]^{3+}$ clusters, causing the framework tetrahedra to rotate by angles φ_{Al} and φ_{Si}. The changes in these rotational angles are associated with a comparable increase in the Al-O-Si bridging angle. As these rotations proceed smoothly with temperature, so does the increase in the cell parameter.

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