

Häüyne: phase transition and high-temperature structures obtained from synchrotron radiation and Rietveld refinements

I. HASSAN^{1,*}, S. M. ANTÃO² AND J. B. PARISE²

¹ Department of Chemistry, University of the West Indies, Mona, Kingston 7, Jamaica

² Mineral Physics Institute & Department of Geosciences, State University of New York, Stony Brook, NY 11794-2100, USA

ABSTRACT

The structural behaviour of a häüyne with a chemical composition of $\text{Na}_{4.35}\text{Ca}_{2.28}\text{K}_{0.95}[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4)_{2.03}$, at room pressure and from 33 to 1035°C on heating, was determined by using *in situ* synchrotron X-ray powder diffraction data ($\lambda = 0.92249(5)$ Å). The satellite reflections in häüyne are lost at ~400°C and a true substructure results because of this phase transition. There is a discontinuity in the *a* unit-cell parameter at ~585°C. The *a* parameter increases rapidly and non-linearly to 585°C, but above 585°C, the expansion rate decreases. The percent volume change between 33 and 576°C is 2.0(3)%, and 0.6(3)% between 593 and 1035°C. Between 33 and 1035°C, the Al–O, Si–O and S–O distances are constant. Between 33 and 576°C, the angle of rotation of the AlO_4 tetrahedron, φ_{Al} , changes from 11.5 to 5.8°, while the angle of rotation of the SiO_4 tetrahedron, φ_{Si} , changes from 12.4 to 6.3°. The Al–O–Si bridging angle changes from 150.05(2) to 153.08(1)° from 33 to 576°C. Beyond 585°C, φ_{Al} and φ_{Si} angles remain nearly constant even though the maximum rotation of the tetrahedra is not achieved. Moreover, the Al–O–Si angle continues to increase at a slower rate from 585 to 1035°C by 1.05(2)°. From 33 to ~585°C, the K atom position migrates at a slower rate than the Na and Ca atoms, and the structure expands at a high rate. Beyond 585°C, all the atomic positions of the interstitial cations (Na^+ , K^+ , Ca^{2+}) remain nearly constant and the expansion of the structure is retarded.

KEYWORDS: häüyne, phase transition, high-temperature structures, synchrotron radiation, Rietveld refinement.

Introduction

HÄÜYNE, ideally $\text{Na}_6\text{Ca}_2[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4)_2$, is a sulphatic sodalite-group mineral, as are nosean and lazurite. These minerals contain SO_4^{2-} as the dominant interstitial anion, and they generally show complex satellite reflections (e.g. Saalfeld, 1961; Taylor, 1968; Schulz, 1970; Hassan *et al.*, 1985). The satellite reflections indicate that the structures of sulphatic sodalites are modulated incommensurately, so these minerals were studied by transmission electron microscopy (TEM), (e.g. Morimoto, 1978; Tsuchiya and Takeuchi, 1985; Hassan and Buseck, 1989*a,b*; Hassan, 2000). The häüyne specimen used in this study contains

weakly developed satellite reflections (Hassan and Grundy, 1991; Hassan and Buseck, 1989*b*).

The room-temperature structure of häüyne (space group $P\bar{4}3n$) was refined by Hassan and Grundy (1991). The framework structure of häüyne is characterized by four-membered rings in the faces of the unit cell, and these rings are linked to form six-membered rings about the corners of the unit cell (Fig. 1). These rings have an ordered distribution of Al and Si atoms. The cages in häüyne can accommodate a variety of interstitial cations and anions by cooperative rotation of the AlO_4 and SiO_4 tetrahedra by angles φ_{Al} and φ_{Si} , respectively, from their positions in a fully expanded state where φ_{Al} is zero (Fig. 1). In häüyne, the SO_4^{2-} group occurs as the dominant interstitial anion and the interstitial cations are Na^+ , Ca^{2+} and K^+ . These cations occupy three nearby 8(c) positions on the body

* E-mail: ishmael.hassan@uwimona.edu.jm
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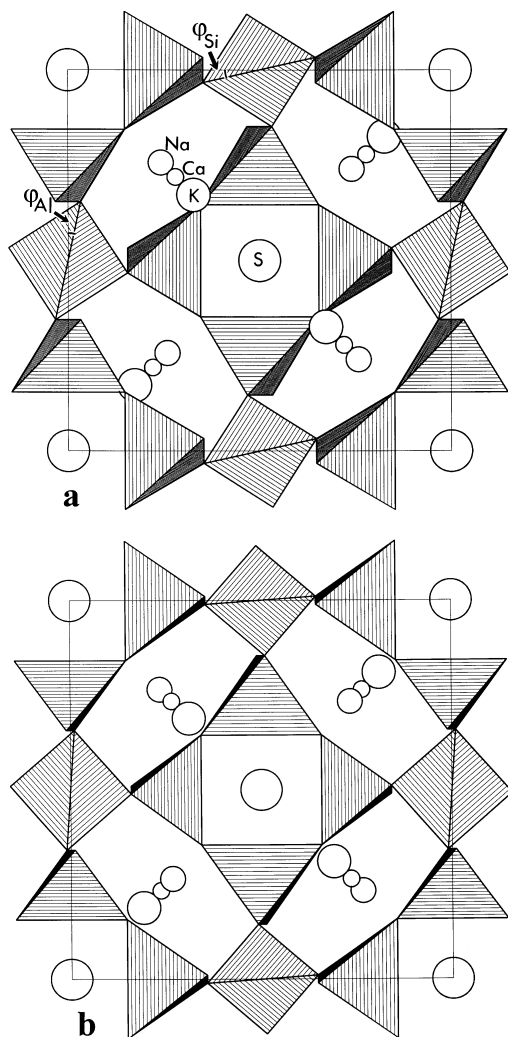


FIG. 1. Projection of the structure of h  yne down [010] showing the lower half of the unit cell. The TO_4 tetrahedra are ordered and the angles of rotation of these tetrahedra are indicated by ϕ_{Al} and ϕ_{Si} , with respect to the cell edges. (a) structure at 33  C and (b) expanded structure at 1035  C showing the changes in the ϕ_{Al} and ϕ_{Si} rotational angles. ϕ is the angle between the cell edge and the projection of the tetrahedral edge on (001).

diagonals of the cubic cell. The SO_4^{2-} groups may occupy two independent positions at the centre of the cell; one SO_4^{2-} group is rotated 90   with respect to the other. However, the interstitial cations force the S atom off the 2(a) position at the centre of the cell to an 8(c) position (see Hassan and Grundy, 1991).

Although the thermal expansion of sodalite and structurally related materials was studied by high-temperature powder X-ray diffraction (XRD) (e.g. Taylor, 1968; Henderson and Taylor, 1978), no previous high-temperature structural work was done on h  yne. The present study was carried out to determine the structural behaviour of h  yne to 1035  C using *in situ* synchrotron X-ray powder-diffraction data and Rietveld structure refinements. The satellite reflections in h  yne should be destroyed with increasing temperature where a phase transition should occur and result in a true substructure. The thermal expansion of h  yne is discussed in terms of the observed structural changes and the geometric model of Hassan and Grundy (1984). This study provides further insights into the structural behaviour of sodalite-group minerals, several of which were recently determined (Hassan *et al.*, 2004; Antao *et al.*, 2003, 2004).

Experimental methods

The h  yne sample used in this study is from Valle Biachella, Sacrofano, Italy, and has a composition of $Na_{4.35}Ca_{2.28}K_{0.95}[Al_6Si_6O_{24}](SO_4)_{2.03}$ (see Hassan and Grundy, 1991). The crystals of h  yne 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 15  . The high-temperature XRD data were collected using *in situ* synchrotron radiation ($\lambda = 0.92249(5)$   ) at room pressure and temperature from 33 to 1035  C. The sample was heated at a rate of $\sim 9.5^\circ\text{C}/\text{min}$ using a horseshoe-shaped heater and controlled using a thermocouple element near the capillary. The diffraction data were collected in regular intervals of $\sim 17^\circ\text{C}$. The data were collected to a maximum 2θ of $\sim 50^\circ$ [$(\sin\theta/\lambda) < 0.46$   ⁻¹]. An imaging plate (IP) detector (Mar345, 2300 $\times$ 2300 pixels) mounted perpendicular to the beam path was used to collect full-circle Debye-Scherrer rings with an exposure time of 15 s. In a separate experiment, an external LaB₆ standard was used to determine the sample-to-detector distance, wavelength, and tilt 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 XRD traces collected, 26 were selected at regular temperature intervals for treatment with the Rietveld method, using the *GSAS* and *EXPGUI* programs (Larson and Von Dreele 2000; Toby, 2001). All the strong reflections can be indexed on the basis of space group $P43n$, which is a pseudo space group for h  y  ne as it contains weak satellite reflections, <1.5% of the strongest 211 reflection. Because of their low intensity, they were ignored in the subsequent structure refinements. For the room-temperature structure, the starting atomic coordinates, cell parameters, isotropic displacement parameters, and space group, $P43n$, were those of Hassan and Grundy (1991). The refined atomic coordinates were then used as input for the next higher-temperature structure. Initially, the site occupancy factors (sofs) in the structural model were set to the nominal chemical composition of $\text{Na}_{4.35}\text{Ca}_{2.28}\text{K}_{0.95}[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4)_2$. Refinement of the sofs for the interstitial cations (Na, Ca and K) and S atom indicate this formula to be appropriate. The sofs obtained for these atoms are similar to those obtained by Hassan and Grundy (1991), and although they were held constant at the different temperatures, they were refined at several temperatures to check for any significant deviations from that at room temperature.

Initially, the background was modelled using a 24-coefficient Chebyshev polynomial function of the first kind, and the reflection profiles were fitted using the Gaussian function corrected for asymmetry (asym term, GW and GV). The zero shift was set to zero at all temperatures, as the instrument was calibrated with a LaB_6 standard. The 24-coefficient Chebyshev polynomial modelled the background ‘‘hump’’ of the quartz capillary quite well. However, above 350  C, the beam intensity dropped by $\sim 1/3$ as judged from the counts for the strongest 211 reflection at $14.2^\circ 2\theta$. Then it was necessary to model the background with 36 coefficients instead of 24. Subsequently, all the refinements were re-done using 36 coefficients. Because of the change in intensity, the peak to background ratio is quite poor for the 211 reflection because it is located on the background ‘‘hump’’ of the quartz capillary. However, as the background was fitted quite well, the data are still quite good, but the low χ^2 at high temperatures is a result of the low peak-to-background ratio, and the structural results are comparable at all temperatures. A full-matrix

least-squares refinement varying a scale factor, a cell parameter, atomic coordinates, and isotropic displacement parameters converged rapidly. Similar atoms were constrained to have equal isotropic displacement parameters, namely $U_{\text{Al}} = U_{\text{Si}}$; $U_{\text{Na}} = U_{\text{K}} = U_{\text{Ca}}$; and $U_{\text{O1}_s} = U_{\text{O2}_s}$ for the SO_4^{2-} group. Soft constraints were used for $T\text{--O}$ ($T = \text{Al, Si}$) and S--O distances and the statistical weights were decreased during the refinements. Because of these constraints, their contribution to χ^2 was ~ 0.005 (i.e. 0.5%) at different temperatures. Finally, the background (36 terms), profile parameters (3 terms), a scale factor, a cell parameter, and structural parameters (12 variables) were allowed to vary, and the refinement proceeded to convergence. The structures refined well at all temperatures. The number of variables was 53 at the end of the refinement, and the number of observed reflections was from 65 to 69. The number of observations (data points) over the 2θ range was ~ 1990 . Synchrotron powder XRD traces are shown in Fig. 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

Satellite reflections in h  y  ne

Satellite reflections that occur in the h  y  ne sample used in this study are easily observed in selected-area electron diffraction (SAED) patterns (see Fig. 2 of Hassan and Buseck, 1992). In the synchrotron powder XRD traces, while several very weak satellite reflections are observed; a weak satellite reflection occurring at $\sim 7^\circ 2\theta$ is easily seen (arrow; Fig. 2a). The satellite reflections were not excluded in the structure refinement because they are weak. The satellite reflections were observed from 33 to 390  C, but not in the trace at 407  C and higher temperatures (see Fig. 2b,c), so the ordering that gives rise to the satellite reflections in h  y  ne is destroyed at $\sim 400^\circ\text{C}$ (between 390 and 407  C traces). The disappearance of the satellite reflections indicates a change in space group, which is now truly $P43n$, and gives rise to a structural phase transition, which was not otherwise detected in the structural parameters.

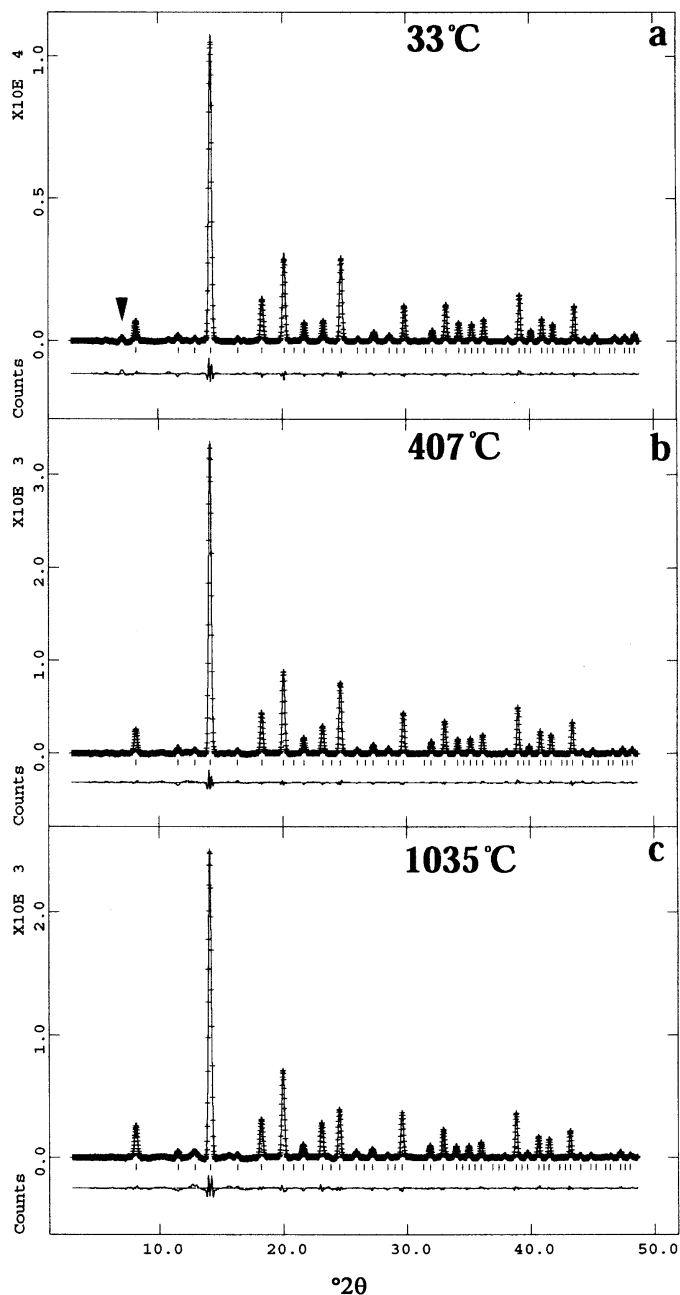


FIG. 2. Synchrotron powder XRD traces for h  yne: (a) at 33  C, (b) at 407  C, and (c) at 1035  C together with the calculated and difference plots from Rietveld refinements. A strong satellite reflection is indicated by an arrow in (a).

The intensity of the satellite reflections decreases with temperature and they disappear at and above 407  C.

Cell parameters

The *a* cell parameter for h  yne increases smoothly and non-linearly with temperature, but

there is a discontinuity at 585  C (temperature chosen midway between 576 and 593  C; Fig. 3). Beyond 585  C, the rate of expansion is retarded.

TABLE 1. Häüyne: Rietveld refinement* and unit-cell parameters at various temperatures (°C).

T (°C)	a (Å)	R_p	R_{wp}	Exp. R_{wp}	R_F^2	χ^2	N_{obs}
33	9.1236(1)	0.0124	0.0173	0.0252	0.0350	0.4812	65
101	9.1318(1)	0.0139	0.0209	0.0253	0.0359	0.6978	67
152	9.1375(1)	0.0139	0.0211	0.0253	0.0372	0.7078	67
203	9.1424(1)	0.0127	0.0183	0.0255	0.0297	0.5266	65
254	9.1455(1)	0.0121	0.0171	0.0254	0.0406	0.4609	67
305	9.1528(1)	0.0120	0.0169	0.0255	0.0328	0.4500	65
356	9.1583(1)	0.0043	0.0061	0.0271	0.0393	0.0505	67
373	9.1589(1)	0.0042	0.0061	0.0272	0.0347	0.0501	67
390	9.1642(1)	0.0039	0.0056	0.0273	0.0361	0.0426	67
407	9.1637(1)	0.0038	0.0055	0.0275	0.0401	0.0410	67
441	9.1694(1)	0.0036	0.0053	0.0276	0.0397	0.0372	67
492	9.1737(1)	0.0035	0.0055	0.0277	0.0347	0.0402	67
542	9.1798(1)	0.0036	0.0054	0.0280	0.0454	0.0380	67
576	9.1852(1)	0.0035	0.0049	0.0280	0.0353	0.0311	69
593	9.1907(1)	0.0031	0.0045	0.0281	0.0405	0.0262	69
644	9.1947(1)	0.0036	0.0049	0.0284	0.0372	0.0310	69
695	9.1968(1)	0.0033	0.0047	0.0284	0.0411	0.0276	69
712	9.1990(1)	0.0036	0.0053	0.0284	0.0415	0.0354	69
729	9.1993(1)	0.0032	0.0048	0.0285	0.0419	0.0287	69
746	9.2010(1)	0.0033	0.0049	0.0285	0.0485	0.0304	69
797	9.2025(1)	0.0034	0.0050	0.0286	0.0416	0.0317	67
848	9.2050(2)	0.0031	0.0044	0.0288	0.0554	0.0235	69
899	9.2076(2)	0.0032	0.0044	0.0289	0.0540	0.0232	67
950	9.2091(2)	0.0034	0.0048	0.0291	0.0617	0.0273	69
1001	9.2093(1)	0.0041	0.0055	0.0289	0.0479	0.0375	69
1035	9.2103(1)	0.0046	0.0064	0.0288	0.0561	0.0506	67

* 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 =

$\{\Sigma[(F_o^{1/2} - F_c^{1/2})]/\Sigma F_o^{1/2}\}^2$

$\chi^2 = [R_{wp}/R_e]$; where $R_e = [(N - P)/(\Sigma wI_o^2)]^{1/2}$, where N is the number of observations (data points ≈ 1992) and P is the number of variables (including structural, background and profile terms ≈ 53); N_{obs} = number of observed reflections ≈ 67 .

The unit-cell parameter for häüyne at 33°C obtained in this study (Table 1; $a = 9.1236(1)$ Å) is slightly different from that obtained by Hassan and Grundy (1991; $a = 9.120(6)$ Å), but they are within experimental error. The a parameter expansion between 33 and 576°C is given by the least-squares fit (all T in °C): $a = 9.1213 + 9.5586 \times 10^{-5}T + 2.4947 \times 10^{-8}T^2$ (Fig. 3). The coefficient of linear thermal expansion, $\alpha_a = (da/dT)(1/a)$, calculated from the above equation, varies between $1.066 \times 10^{-5}^\circ\text{C}^{-1}$ at 33°C and $1.354 \times 10^{-5}^\circ\text{C}^{-1}$ at 576°C. The α_a between 593 and 1035°C calculated from: $a = 9.1229 +$

$1.5450 \times 10^{-4}T - 6.7698 \times 10^{-8}T^2$, varies between $8.075 \times 10^{-6}^\circ\text{C}^{-1}$ at 593°C and $1.560 \times 10^{-6}^\circ\text{C}^{-1}$ at 1035°C (Fig. 3). The volume expansion between 33 and 576°C is given by the least-squares fit: $V = 758.8724 + 2.3822 \times 10^{-2}T + 6.6119 \times 10^{-6}T^2$. The coefficient of volume thermal expansion, α_V , varies between $3.194 \times 10^{-5}^\circ\text{C}^{-1}$ at 33°C and $4.057 \times 10^{-5}^\circ\text{C}^{-1}$ at 576°C. The α_V between 593 and 1035°C calculated from: $V = 759.1402 + 3.9157 \times 10^{-2}T - 1.7141 \times 10^{-5}T^2$, varies between $2.425 \times 10^{-5}^\circ\text{C}^{-1}$ at 593°C and $4.702 \times 10^{-6}^\circ\text{C}^{-1}$ at 1035°C. The percent volume change between 33 and 576°C is

TABLE 2. Positional and isotropic displacement parameters ($U \times 100 \text{ \AA}^2$) at various temperatures ($^{\circ}\text{C}$) for haitiye.

T ($^{\circ}\text{C}$) Atom ^s	33	101	152	203	254	305	356	373	390	407	441	492	542
Al/Si	U 1.23(5)	1.75(6)	1.83(6)	1.75(5)	1.72(5)	1.77(4)	1.77(4)	1.77(4)	1.78(4)	1.73(4)	1.75(4)	1.74(5)	1.77(5)
O	x 0.14399(2)	0.14451(3)	0.14465(3)	0.14469(2)	0.14518(2)	0.14542(6)	0.14579(2)	0.14581(2)	0.14594(2)	0.14602(2)	0.14606(2)	0.14629(2)	0.14677(2)
	y 0.15560(2)	0.15602(2)	0.15622(2)	0.15625(2)	0.15674(2)	0.15677(5)	0.15731(2)	0.15733(2)	0.15746(2)	0.15754(2)	0.15756(2)	0.15779(2)	0.15826(2)
	z 0.46841(4)	0.47021(5)	0.47116(5)	0.47184(4)	0.47320(4)	0.47489(5)	0.47623(4)	0.47637(4)	0.47749(4)	0.47760(4)	0.47862(3)	0.47991(4)	0.48246(4)
	U 1.81(7)	2.20(9)	2.34(9)	2.40(8)	2.55(7)	2.80(7)	2.95(6)	2.94(5)	3.07(5)	3.02(6)	3.12(5)	3.27(7)	3.60(8)
K	x 0.1601(12)	0.1608(16)	0.1611(16)	0.1613(14)	0.1623(12)	0.1635(12)	0.1625(11)	0.1624(10)	0.1637(10)	0.1607(12)	0.1632(10)	0.1635(14)	0.1640(15)
Ca	x 0.1986(3)	0.1978(3)	0.1983(4)	0.1989(3)	0.1988(3)	0.1998(3)	0.2004(2)	0.2005(2)	0.2013(2)	0.2014(3)	0.2022(2)	0.2029(3)	0.2038(3)
Na	x 0.2439(5)	0.2430(5)	0.2439(5)	0.2442(5)	0.2438(4)	0.2443(4)	0.2451(4)	0.2454(4)	0.2463(4)	0.2455(4)	0.2470(4)	0.2477(6)	0.2502(8)
K/Ca/Na	U 0.47(10)	0.14(12)	0.31(12)	0.40(11)	0.45(9)	0.74(9)	0.26(8)	0.21(8)	0.41(8)	0.35(8)	0.51(7)	0.37(10)	0.57(11)
S	U 19.4(3)	20.1(3)	20.4(3)	20.9(3)	21.5(3)	21.5(3)	22.1(2)	21.8(2)	22.1(2)	22.1(2)	22.1(2)	22.6(3)	23.2(3)
Ol _s	x 0.40256(2)	0.40266(3)	0.40272(3)	0.40277(2)	0.40279(2)	0.40298(6)	0.40293(2)	0.40294(2)	0.40299(2)	0.40298(2)	0.40304(2)	0.40308(2)	0.40314(2)
Ol _{2s}	x 0.59744(2)	0.59734(3)	0.59728(3)	0.59723(2)	0.59721(2)	0.59702(6)	0.59708(2)	0.59707(2)	0.59702(2)	0.59702(2)	0.59696(2)	0.59692(2)	0.59686(2)
Ol _s /Ol _{2s}	U 14.8(7)	14.3(7)	14.3(7)	15.0(7)	16.2(6)	16.43(57)	17.8(5)	17.1(5)	17.7(5)	18.8(6)	18.5(5)	18.5(7)	19.6(7)

T ($^{\circ}\text{C}$) Atom ^s	576	593	644	695	712	729	746	797	848	899	950	1001	1035
Al/Si	U 1.62(4)	1.71(4)	1.64(5)	1.85(5)	1.80(6)	1.76(6)	1.63(6)	1.95(6)	1.93(7)	1.98(7)	2.03(8)	2.06(5)	2.05(6)
O	x 0.14685(2)	0.14697(2)	0.14690(2)	0.14679(2)	0.14695(2)	0.14670(2)	0.14693(2)	0.14683(2)	0.14668(2)	0.14653(2)	0.14647(2)	0.14644(2)	0.14647(2)
	y 0.15832(1)	0.15844(1)	0.15836(1)	0.15824(1)	0.15839(1)	0.15814(1)	0.15837(1)	0.15827(1)	0.15811(2)	0.15795(1)	0.15788(1)	0.15785(1)	0.15788(2)
	z 0.48384(3)	0.48555(3)	0.48630(3)	0.48640(3)	0.48758(3)	0.48666(3)	0.48817(3)	0.48810(3)	0.48814(3)	0.48825(3)	0.48834(3)	0.48830(4)	0.48868(4)
	U 3.94(7)	4.12(7)	4.19(8)	4.26(8)	4.34(9)	4.20(10)	4.28(10)	4.46(10)	4.49(11)	4.59(12)	4.46(12)	4.57(8)	4.74(9)
K	x 0.1693(11)	0.1684(12)	0.1717(12)	0.1703(14)	0.1711(16)	0.1709(18)	0.1738(16)	0.1730(16)	0.1759(19)	0.1727(20)	0.1729(21)	0.1727(13)	0.1732(16)
Ca	x 0.2055(3)	0.2075(3)	0.2091(4)	0.2092(4)	0.2089(5)	0.2094(5)	0.2096(5)	0.2098(5)	0.2090(6)	0.2098(6)	0.2099(6)	0.2101(4)	0.2103(4)
Na	x 0.2521(7)	0.2563(9)	0.2573(10)	0.2579(10)	0.2563(12)	0.2574(13)	0.2572(14)	0.2575(13)	0.2571(15)	0.2557(17)	0.2549(17)	0.2545(11)	0.2541(13)
K/Ca/Na	U 1.06(9)	1.11(9)	1.50(11)	1.15(11)	1.34(13)	1.59(14)	2.63(13)	1.57(13)	1.68(15)	2.04(17)	2.01(18)	2.22(12)	2.89(13)
S	U 23.5(3)	24.2(3)	24.4(3)	25.7(3)	25.4(4)	25.6(4)	24.2(4)	25.2(4)	25.3(4)	25.6(5)	26.7(5)	26.6(3)	26.2(4)
Ol _s	x 0.40320(2)	0.40325(2)	0.40330(2)	0.40332(2)	0.40335(2)	0.40335(2)	0.40336(2)	0.40338(2)	0.40341(1)	0.40344(1)	0.40345(2)	0.40345(2)	0.40346(2)
Ol _{2s}	x 0.59680(2)	0.59675(2)	0.59671(2)	0.59668(2)	0.59666(2)	0.59666(2)	0.59664(2)	0.59662(2)	0.59659(1)	0.59657(1)	0.59655(2)	0.59655(2)	0.59654(2)
Ol _s /Ol _{2s}	U 19.0(5)	19.5(5)	19.9(5)	22.2(6)	22.1(7)	21.9(8)	19.6(7)	22.0(7)	22.0(8)	21.4(9)	26.8(0)	23.4(6)	23.5(7)

^s Al is at ($1/4$, 0, $1/2$); Si at ($1/4$, $1/2$, 0); Na, Ca, K, Ol_s and Ol_{2s} are at (x , x , x); S at (0, 0, 0)

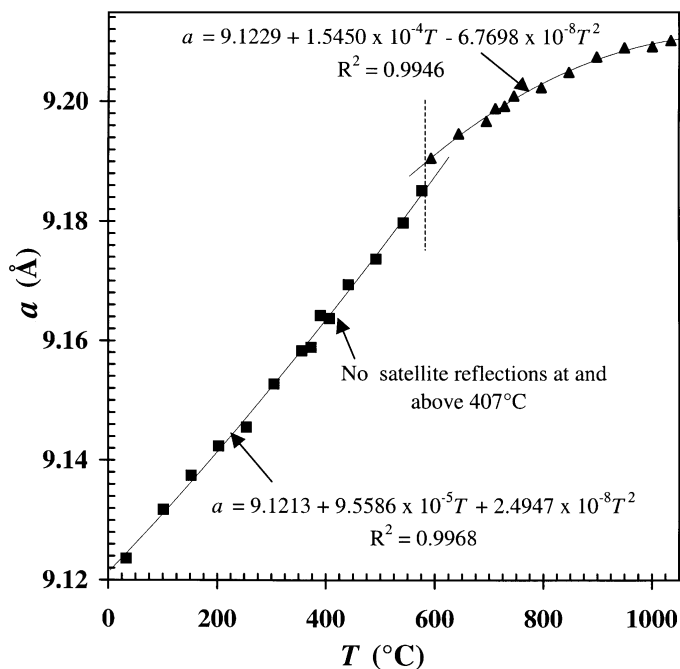


FIG. 3. The thermal-expansion curve for haüyne contains a discontinuity at 585°C. Equations for the least-squares fit to the data are given as inserts. Error bars are smaller than the symbols.

2.0(3)%, and 0.6(3)% between 593 and 1035°C, for a total volume change of 2.9(3)%.

The percent volume change in sodalite between 28 and 982°C is 4.8(2)% (Hassan *et al.*, 2004), and is greater than that in haüyne. Following mineral formation, haüyne contains larger-size cage clusters, e.g. $[\text{Na}_3\text{CaSO}_4]^{3+}$ compared to $[\text{Na}_4\text{Cl}]^{3+}$ clusters in sodalite. Consequently, haüyne starts off with a larger unit cell at room temperature, 9.1236(1) Å compared with 8.8870(1) Å for sodalite. In addition, at room temperature, haüyne ($\varphi_{\text{Si}} = 12.4^\circ$) is in a less collapsed state than that in sodalite ($\varphi_{\text{Si}} = 23.6^\circ$), as can be judged from the tetrahedral rotational angles. This suggests that the larger clusters in haüyne resist contraction following mineral formation.

Structure of haüyne

The general structural features of haüyne have been described and the structure obtained at 33°C is shown (Fig. 1). This structure is similar to that obtained by Hassan and Grundy (1991), except that the SO_4^{2-} group is disordered, one SO_4^{2-} group is rotated 90° with respect to the other, and

the S atom was kept on the 2(a) site. The Al–O and Si–O distances are 1.7418(1) and 1.5971(2) Å, respectively (Table 3), compared to 1.742(5) and 1.597(4) Å obtained by Hassan and Grundy (1991). These results indicate that the Al and Si atoms are fully ordered and this ordering does not change with temperature.

The interstitial cations (Na^+ , K^+ , Ca^{2+}) occupy three nearby 8(e) positions on the 3-fold axes and are coordinated by three O atoms that have short bonds and three O' atoms that are further away. The O and O' framework oxygen atoms are equivalent atoms because they are related by symmetry. The interstitial cation co-ordinations are completed by bonds to O1_S and O2_S atoms of the SO_4^{2-} groups (Table 3). As the SO_4^{2-} group is disordered and the S atom was kept on the 2(a) site, the displacement parameter for the S atom is quite large. Moreover, the S– $\text{O1}/2_\text{S}$ bonds of the disordered SO_4^{2-} group were constrained to be equal. Therefore, the displacement parameters are also quite large for the O1_S and O2_S atoms of the SO_4^{2-} group because these O atoms must be positionally disordered as the S atom is actually located off the 2(a) site (see Hassan and Grundy, 1991).

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

<i>T</i> (°C)	33	101	152	203	254	305	356	373	390	407	441	492	542
Bonds or angle													
Al–O	4 × 1.7418(1)	1.7418(2)	1.7418(2)	1.7418(2)	1.7418(2)	1.7401(4)	1.7418(1)	1.7418(1)	1.7419(1)	1.7419(1)	1.7419(1)	1.7420(1)	1.7420(1)
O–Al–O	4 × 107.96(1)	107.81(1)	107.79(1)	107.79(1)	107.63(1)	107.61(2)	107.47(1)	107.47(1)	107.44(1)	107.41(1)	107.42(1)	107.36(1)	107.22(1)
O'–Al–O'	2 × 112.54(1)	112.84(2)	112.90(2)	112.89(1)	113.22(1)	113.26(4)	113.55(1)	113.56(1)	113.61(1)	113.67(1)	113.66(1)	113.79(1)	114.09(1)
Si–O	4 × 1.5971(2)	1.5971(2)	1.5971(2)	1.5971(2)	1.5970(2)	1.5976(5)	1.5971(2)	1.5971(2)	1.5970(2)	1.5970(2)	1.5970(2)	1.5971(2)	1.5970(2)
O–Si–O	4 × 106.91(1)	106.76(1)	106.73(1)	106.74(1)	106.57(1)	106.57(2)	106.41(1)	106.41(1)	106.38(1)	106.35(1)	106.36(1)	106.30(1)	106.15(1)
O'–Si–O'	2 × 114.73(1)	115.05(2)	115.10(2)	115.09(1)	115.44(1)	115.44(4)	115.79(1)	115.80(1)	115.85(1)	115.92(1)	116.03(1)	116.35(1)	116.35(1)
Al–O–Si	150.05(2)	150.43(2)	150.71(2)	150.94(2)	151.10(2)	151.60(5)	151.72(2)	151.76(2)	152.02(2)	151.99(2)	152.28(1)	152.49(2)	152.80(1)
*φ _{Al}	11.5	10.8	10.5	10.2	9.7	9.1	8.6	8.5	8.1	8.1	7.7	7.3	6.3
φ _{Si}	12.4	11.6	11.3	11.0	10.5	9.8	9.3	9.2	8.8	8.7	8.3	7.8	6.8
K–O	3 × 2.817(1)	2.830(13)	2.838(14)	2.844(12)	2.848(10)	2.855(10)	2.878(9)	2.880(9)	2.880(9)	2.907(10)	2.897(9)	2.908(12)	2.928(13)
K–O'	3 × 3.014(7)	2.998(8)	2.992(8)	2.988(7)	2.972(6)	2.957(6)	2.952(6)	2.952(6)	2.939(5)	2.954(6)	2.937(5)	2.927(8)	2.908(8)
K–O1 _s	3 × 2.484(16)	2.496(20)	2.500(21)	2.504(18)	2.518(16)	2.593(19)	2.523(14)	2.522(14)	2.541(14)	2.502(15)	2.536(13)	2.540(19)	2.549(20)
†K–O2 _s	1 × 0.990(20)	1.004(25)	1.009(25)	1.014(23)	1.031(19)	1.055(19)	1.037(17)	1.036(17)	1.059(16)	1.011(19)	1.052(16)	1.058(23)	1.068(24)
†K–S	1 × 2.529(20)	2.543(25)	2.549(25)	2.554(23)	2.571(19)	2.593(19)	2.577(17)	2.576(17)	2.599(16)	2.551(19)	2.592(16)	2.598(23)	2.608(24)
<K–O/O>	2.916(7)	2.914(8)	2.915(8)	2.916(7)	2.910(6)	2.906(6)	2.915(5)	2.916(5)	2.910(5)	2.931(6)	2.917(5)	2.918(7)	2.918(8)
Ca–O	3 × 2.542(2)	2.563(2)	2.570(2)	2.574(2)	2.586(2)	2.5963(19)	2.605(1)	2.606(1)	2.612(1)	2.613(2)	2.618(1)	2.626(2)	2.644(2)
Ca–O'	3 × 2.871(1)	2.859(1)	2.852(1)	2.847(1)	2.835(1)	2.8227(10)	2.810(1)	2.809(1)	2.800(1)	2.799(1)	2.792(1)	2.781(1)	2.759(1)
Ca–O1 _s	3 × 3.000(4)	2.991(5)	3.000(5)	3.010(4)	3.010(4)	3.026(4)	3.035(3)	3.037(3)	3.050(3)	3.050(4)	3.064(3)	3.075(4)	3.090(5)
†Ca–O2 _s	1 × 1.598(5)	1.588(5)	1.599(6)	1.610(5)	1.610(4)	1.630(4)	1.639(4)	1.641(4)	1.656(4)	1.656(4)	1.672(4)	1.684(5)	1.701(5)
Ca–S	1 × 3.138(5)	3.128(5)	3.139(6)	3.150(5)	3.149(4)	3.168(4)	3.178(4)	3.181(4)	3.195(4)	3.196(4)	3.212(4)	3.224(5)	3.241(5)
<Ca–O/O>	2.707(1)	2.711(1)	2.711(1)	2.710(1)	2.710(1)	2.710(1)	2.708(1)	2.707(1)	2.706(1)	2.706(1)	2.705(1)	2.704(1)	2.702(1)
Na–O	3 × 2.382(1)	2.397(1)	2.404(1)	2.409(1)	2.419(1)	2.4320(12)	2.440(1)	2.441(1)	2.449(1)	2.450(1)	2.458(1)	2.467(1)	2.482(1)
Na–O'	3 × 2.864(1)	2.848(1)	2.843(1)	2.839(1)	2.825(1)	2.8142(13)	2.804(1)	2.803(1)	2.797(1)	2.794(1)	2.790(1)	2.781(1)	2.764(2)
Na–O1 _s	1 × 2.507(7)	2.525(8)	2.514(8)	2.510(8)	2.519(7)	2.515(7)	2.503(6)	2.499(6)	2.487(6)	2.499(7)	2.479(7)	2.469(10)	2.432(12)
Na–O2 _s	1 × 2.314(7)	2.304(8)	2.320(8)	2.328(8)	2.322(7)	2.335(7)	2.348(6)	2.353(6)	2.370(6)	2.357(7)	2.382(7)	2.396(10)	2.438(12)
<Na–O/O>	2.623(1)	2.622(1)	2.623(1)	2.623(1)	2.622(1)	2.623(1)	2.622(1)	2.622(1)	2.623(1)	2.622(1)	2.623(1)	2.624(1)	2.623(1)
S–O1 _s /O2 _s	4 × 1.5398(3)	1.5397(4)	1.5397(4)	1.5397(3)	1.5398(3)	1.5381(10)	1.5399(3)	1.5398(3)	1.5399(3)	1.5400(3)	1.5400(3)	1.5400(3)	1.5400(3)

† These distances arise from the disorder of the SO₄ group and are not real bonds. *φ is calculated from geometry of the structure, so no errors are given.

Table 3. (contd.)

T (°C)	576	593	644	695	712	729	746	797	848	899	950	1001	1035
Bonds or angle													
Al-O	1.7420(1)	1.7420(1)	1.7420(1)	1.7420(1)	1.7420(1)	1.7420(1)	1.7420(1)	1.7420(1)	1.7420(1)	1.7420(1)	1.7420(1)	1.7420(1)	1.7420(1)
Al-O	4 × 1.7420(1)	4 × 1.7420(1)	4 × 1.7420(1)	4 × 1.7420(1)	4 × 1.7420(1)	4 × 1.7420(1)	4 × 1.7420(1)	4 × 1.7420(1)	4 × 1.7420(1)	4 × 1.7420(1)	4 × 1.7420(1)	4 × 1.7420(1)	4 × 1.7420(1)
O'-Al-O	107.21(1)	107.18(1)	107.23(1)	107.27(1)	107.23(1)	107.32(1)	107.240	107.28(1)	107.34(1)	107.40(1)	107.43(1)	107.44(1)	107.44(1)
O'-Al-O'	114.10(1)	114.15(1)	114.06(1)	113.97(1)	114.06(1)	113.88(1)	114.032	113.95(1)	113.82(1)	113.69(1)	113.63(1)	113.61(1)	113.62(1)
Si-O	4 × 1.5970(1)	4 × 1.5970(1)	4 × 1.5970(1)	4 × 1.5970(1)	4 × 1.5970(1)	4 × 1.5970(1)	4 × 1.59696	4 × 1.5970(1)	4 × 1.5970(1)	4 × 1.5970(2)	4 × 1.5970(1)	4 × 1.5970(2)	4 × 1.5970(2)
O-Si-O	4 × 106.14(1)	4 × 106.12(1)	4 × 106.16(1)	4 × 106.22(1)	4 × 106.17(1)	4 × 106.26(1)	106.184	4 × 106.23(1)	4 × 106.29(1)	4 × 106.36(1)	4 × 106.39(1)	4 × 106.40(1)	4 × 106.39(1)
O'-Si-O'	2 × 116.36(1)	2 × 116.40(1)	2 × 116.31(1)	2 × 116.20(1)	2 × 116.30(1)	2 × 116.10(1)	116.268	2 × 116.18(1)	2 × 116.03(1)	2 × 115.89(1)	2 × 115.83(1)	2 × 115.80(1)	2 × 115.82(1)
Al-O-Si	153.08(1)	153.36(1)	153.58(1)	153.70(1)	153.80(1)	153.83(1)	153.926	154.00(1)	154.14(3)	154.28(1)	154.35(1)	154.37(1)	154.41(2)
* ϕ_{Al}	5.8	5.2	4.9	4.9	4.5	4.8	4.3	4.3	4.3	4.3	4.2	4.2	4.1
ϕ_{Si}	6.3	5.6	5.3	5.3	4.8	5.2	4.6	4.6	4.6	4.6	4.6	4.6	4.4
K-O	3 × 2.898(9)	2.923(10)	2.904(10)	2.917(12)	2.922(13)	2.915(14)	2.891(15)	2.912(13)	2.891(15)	2.919(16)	2.918(17)	2.919(11)	2.919(12)
K-O'	3 × 2.874(6)	2.870(6)	2.851(6)	2.860(7)	2.848(8)	2.857(9)	2.826(9)	2.838(8)	2.826(9)	2.844(10)	2.843(10)	2.845(7)	2.840(8)
K-O1 _s	3 × 2.619(15)	2.609(16)	2.654(16)	2.635(19)	2.647(21)	2.645(24)	2.713(25)	2.674(22)	2.713(25)	2.670(27)	2.673(28)	2.671(18)	2.678(21)
†K-O2 _s	1 × 1.154(18)	1.141(19)	1.195(19)	1.172(23)	1.186(25)	1.184(28)	1.265(30)	1.218(26)	1.265(30)	1.214(32)	1.218(33)	1.215(21)	1.223(25)
†K-S	1 × 2.694(18)	2.681(19)	2.735(19)	2.712(23)	2.726(25)	2.724(28)	2.805(30)	2.758(26)	2.805(30)	2.754(32)	2.758(33)	2.755(21)	2.763(25)
<K-O/O>	2.886(5)	2.897(6)	2.878(6)	2.889(7)	2.885(8)	2.886(8)	2.859	2.875(8)	2.859(9)	2.882(8)	2.881(9)	2.882(7)	2.880(7)
Ca-O	3 × 2.649(2)	2.654(2)	2.654(2)	2.655(2)	2.667(3)	2.657(3)	2.674(4)	2.668(3)	2.674(4)	2.672(3)	2.673(3)	2.672(2)	2.675(2)
Ca-O'	3 × 2.748(1)	2.733(1)	2.727(1)	2.727(1)	2.719(1)	2.727(1)	2.719(2)	2.716(1)	2.719(2)	2.719(1)	2.719(1)	2.720(1)	2.717(1)
Ca-O1 _s	3 × 3.114(4)	3.146(5)	3.169(6)	3.171(6)	3.168(7)	3.175(8)	3.171(9)	3.182(7)	3.171(9)	3.183(8)	3.185(8)	3.188(5)	3.191(6)
†Ca-O2 _s	1 × 1.729(4)	1.764(5)	1.790(6)	1.793(7)	1.789(7)	1.797(9)	1.793(10)	1.805(8)	1.793(10)	1.806(9)	1.808(9)	1.811(6)	1.815(7)
Ca-S	1 × 3.269(4)	3.304(5)	3.330(6)	3.333(7)	3.329(7)	3.337(9)	3.333(10)	3.345(8)	3.333(10)	3.346(9)	3.348(9)	3.351(6)	3.355(7)
<Ca-O/O>	2.698(1)	2.693(1)	2.690(1)	2.691(1)	2.693(1)	2.692(2)	2.697	2.692(1)	2.697(1)	2.696(2)	2.696(2)	2.696(1)	2.696(1)
Na-O	3 × 2.492(1)	2.502(1)	2.508(1)	2.510(1)	2.520(1)	2.514(1)	2.527(2)	2.525(1)	2.527(2)	2.531(1)	2.533(2)	2.534(1)	2.537(1)
Na-O'	3 × 2.759(2)	2.756(2)	2.754(3)	2.756(3)	2.742(3)	2.754(4)	2.743(5)	2.743(4)	2.743(5)	2.740(4)	2.738(4)	2.738(3)	2.734(3)
Na-O1 _s	1 × 2.404(12)	2.339(14)	2.326(16)	2.317(17)	2.343(20)	2.325(21)	2.333(25)	2.325(21)	2.333(25)	2.355(26)	2.370(27)	2.376(17)	2.382(21)
Na-O2 _s	1 × 2.471(12)	2.540(14)	2.557(16)	2.568(17)	2.543(20)	2.561(21)	2.559(25)	2.565(21)	2.559(25)	2.538(26)	2.525(27)	2.520(17)	2.514(21)
<Na-O/O>	2.625(1)	2.629(1)	2.631(1)	2.633(1)	2.631(2)	2.634(2)	2.635	2.634(2)	2.635(3)	2.635(2)	2.636(2)	2.636(1)	2.635(2)
S-O1 _s /O2 _s	4 × 1.5400(3)	1.5401(2)	1.5401(4)	1.5401(3)	1.5401(3)	1.5401(3)	1.5400(2)	1.5401(3)	1.5400(2)	1.5400(2)	1.5400(3)	1.5401(3)	1.5400(3)

† These distances arise from the disorder of the SO₄ group and are not real bonds. * ϕ is calculated from geometry of the structure, so no errors are given.

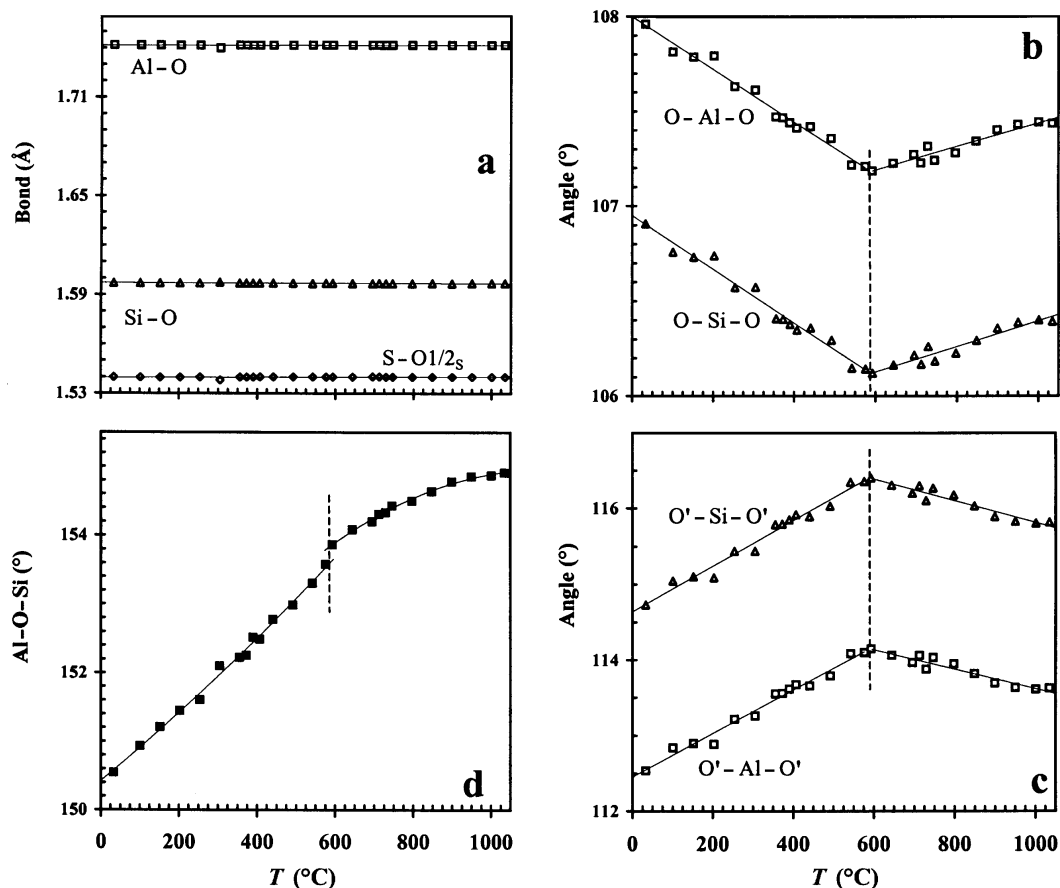


FIG. 4. (a) The Al–O, Si–O, and S–O1/2_s distances are constant with temperature. (b, c) Variation of the framework TO₄ bond angles with temperature. (d) Variation of the Al–O–Si bridging angle with temperature. The dashed vertical lines are drawn at 585°C.

Framework

Each of the AlO₄ and SiO₄ tetrahedra contains one independent T–O bond and these T–O bond distances are constant with temperature (Fig. 4a). In the framework tetrahedra, the smaller O–T–O angles vary opposite to the larger O'–T–O' angles (Fig. 4b,c). These O–T–O angles reach a minimum/maximum value at the discontinuity at 585°C. Moreover, the Al–O–Si bridging angle shows a discontinuity at 585°C (Fig. 4d). From 33 to 576°C, the Al–O–Si angle increases from 150.05(2) to 153.08(1)°, a difference of 3.03(2)°. Between 593°C and 1035°C, the bridging angle increases at a reduced rate by 1.05(2)°. At 1035°C, the Al–O–Si angle is 154.41(2)°, so from 33 to

1035°C, this angle increases by 4.37(2)°. In sodalite, from 28 to 982°C, the Al–O–Si angle increases by 5.06(2)° (Hassan *et al.*, 2004).

Cage clusters

The cage contains interstitial cations (Na⁺, Ca²⁺ and K⁺) that are on three nearby 8(e) positions (see Tables 2, 3 and Fig. 5). The SO₄^{2−} group in a cage occupies two positions that are rotated by 90° with respect to each other and the S atom occupies the 2(a) site. This geometry leads to regular tetrahedral groups with both S–O1_s and S–O2_s distances of 1.5398(3) Å at 33°C, which is reasonable for an S–O bond. The S–O1/2_s distances were constrained to be equal and they are constant with temperature (Fig. 4a). The

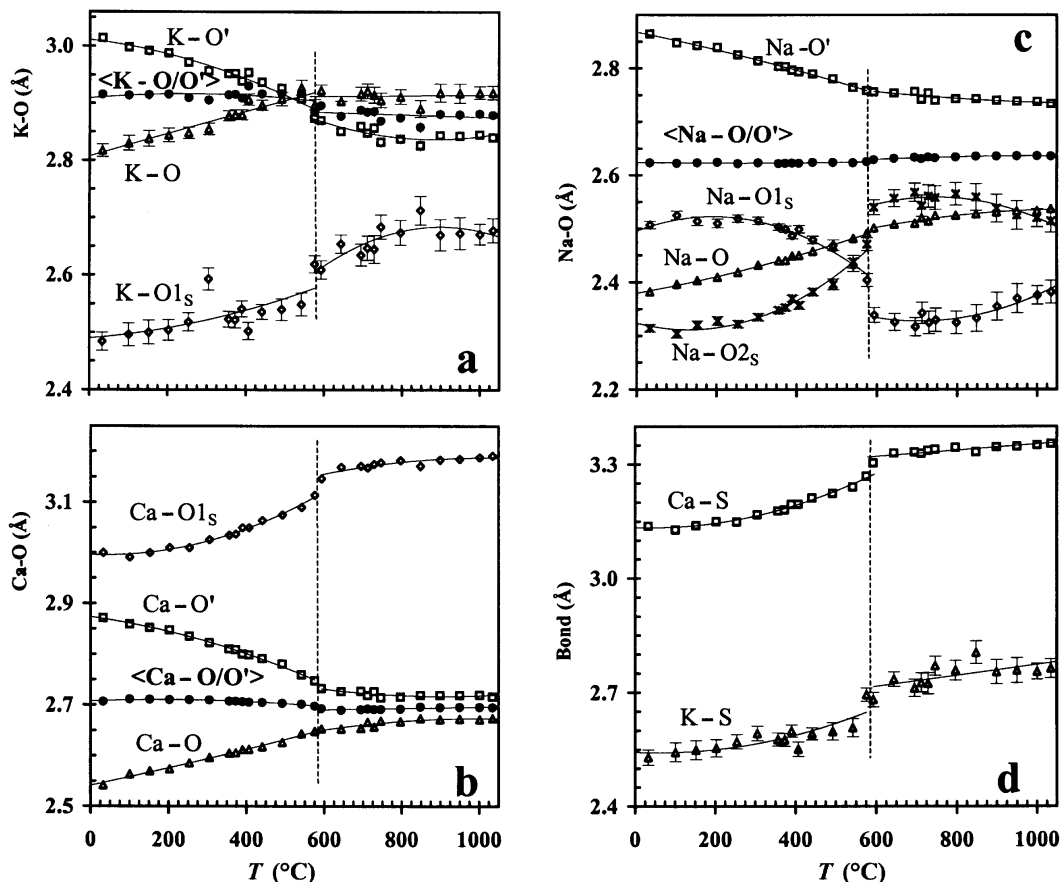


FIG. 5. Variation of the interstitial atom distances with temperature. (a) K–O, (b) Ca–O, (c) Na–O distances, and (d) Ca–S and K–S distances. The short K–S distance indicates that the S atom must move from the 2(a) to an 8(e) site. Error bars are not seen if smaller than the symbols. The dashed vertical lines are drawn at 585°C.

presence of K atoms in a cage and the resulting short K–S distance (Table 3; Fig. 5d) indicates that the S atom of the SO_4^{2-} group must be moved from the 2(a) to an 8(e) site, as was observed by Hassan and Grundy (1991). However, this displacement was not modelled in the present study and as a result, the isotropic displacement parameters for the atoms of the SO_4^{2-} group are quite large (Fig. 6).

From 33 to 585°C, the K–O and K–O_{1s} distances increase smoothly while the K–O' distance decreases smoothly, but the average $\langle\text{K–O/O'}\rangle$ distance is nearly constant (Fig. 5a). At 542°C, the K–O and K–O' distances are nearly equal, and beyond 585°C, the K–O' distance decreases further and then levels off while the K–O distance is nearly constant. The expansion of the K–O_{1s} bond could cause the

framework tetrahedra to rotate, but beyond 585°C, the K–O_{1s} distance continues to increase and then levels off where there is no further rotation of the tetrahedra (Fig. 5a).

The Ca atom has a similar coordination to the K atom, so the Ca–O distances show similar trends to the K atom (Fig. 5b). The Ca–O_{1s} distance increases smoothly, shows a slight break at 585°C, then increases a little further and levels off at high temperatures. From 33 to 585°C, the Ca–O bond increases smoothly while the Ca–O' distance decreases smoothly, but the average $\langle\text{Ca–O/O'}\rangle$ distance is nearly constant throughout (Fig. 5b). The expansion of the Ca–O_{1s} bond could cause the framework tetrahedra to rotate, but beyond 585°C, the Ca–O and Ca–O' distances are nearly constant, and no rotation of the tetrahedra occurs (Fig. 5b).

The Na atom has a different coordination to the K and Ca atoms, but the Na–O distances show similar trends (Fig. 5c). From 33 to 585°C, the Na–O bond increases rapidly but smoothly while the Na–O' bond decreases rapidly, whereas the average $\langle \text{Na–O/O'} \rangle$ distance is nearly constant (Fig. 5c). Beyond 585°C, the Na–O and Na–O' distances are changing at a considerably reduced rate to the maximum temperature (Fig. 5c). However, the Na atom is also bonded to both O1_S and O2_S atoms of the SO_4^{2-} group and the Na–O1/2_S distances decrease or increase smoothly throughout the temperature range. At ~542°C, Na–O1/2_S distances are nearly identical, and at 585°C, there is a sharp and significant break in these distances. The variation of the Na–O1/2_S distances could cause the framework tetrahedra to rotate. The short K–S distance (Fig. 5d) indicates that the S atom of the SO_4^{2-} group must be moved from the 2(a) to an 8(c) site, as was observed by Hassan and Grundy (1991).

Isotropic displacement parameters

The variation of the isotropic displacement parameters, U , for the atoms in haüyne is shown (Fig. 6). The framework atoms and the interstitial cations (Na^+ , Ca^{2+} and K^+) have normal U parameters and they increase slightly with temperature. The U parameters for the atoms of the

SO_4^{2-} group (S, O1_S = O2_S) are unusually high because of disorder and they increase with temperature.

The thermal-expansion mechanism for haüyne

The geometrical model for the thermal expansion of sodalite (Hassan and Grundy, 1984) is combined with the present results to describe the thermal behaviour of haüyne. In the thermal expansion of haüyne, the cage clusters may expand and force the interstitial cations towards the plane of the six-membered ring, which causes the framework tetrahedra to rotate. The AlO_4 and SiO_4 tetrahedra are rotated by angles φ_{Al} and φ_{Si} , respectively (see Fig. 1) and are calculated at different temperatures using equation 8 of Hassan and Grundy (1984), and their variation with temperature is shown (Fig. 7). Between 33 and 585°C, φ_{Al} changes from 11.5 to 5.8°, a difference of 5.7°, while the φ_{Si} changes from 12.4 to 6.3°, a difference of 6.1°. These changes are comparable to changes in the Al–O–Si angle from 150.05(2) to 153.08(1)°, a difference of 3.03(2)° from 33 to 585°C. Beyond 585°C, φ_{Al} and φ_{Si} angles remain nearly constant even though the maximum rotation of the tetrahedra is not achieved, which occurs when φ_{Al} is zero. However, beyond 585°C, the angles in the framework TO_4 tetrahedra change with temperature (Fig. 4b,c). During the

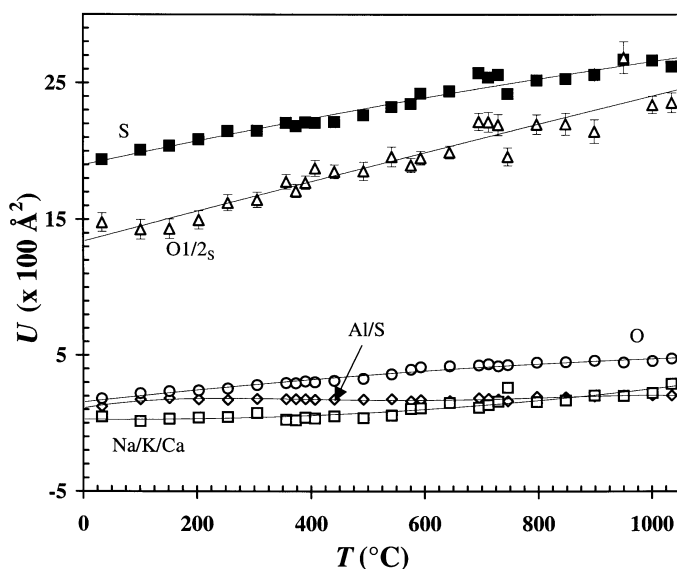


FIG. 6. Variation of the isotropic displacement parameters, U ($\times 100 \text{ \AA}^2$), with temperature. The atoms of the framework have normal values, while those for the SO_4^{2-} group have large values because of positional disorder.

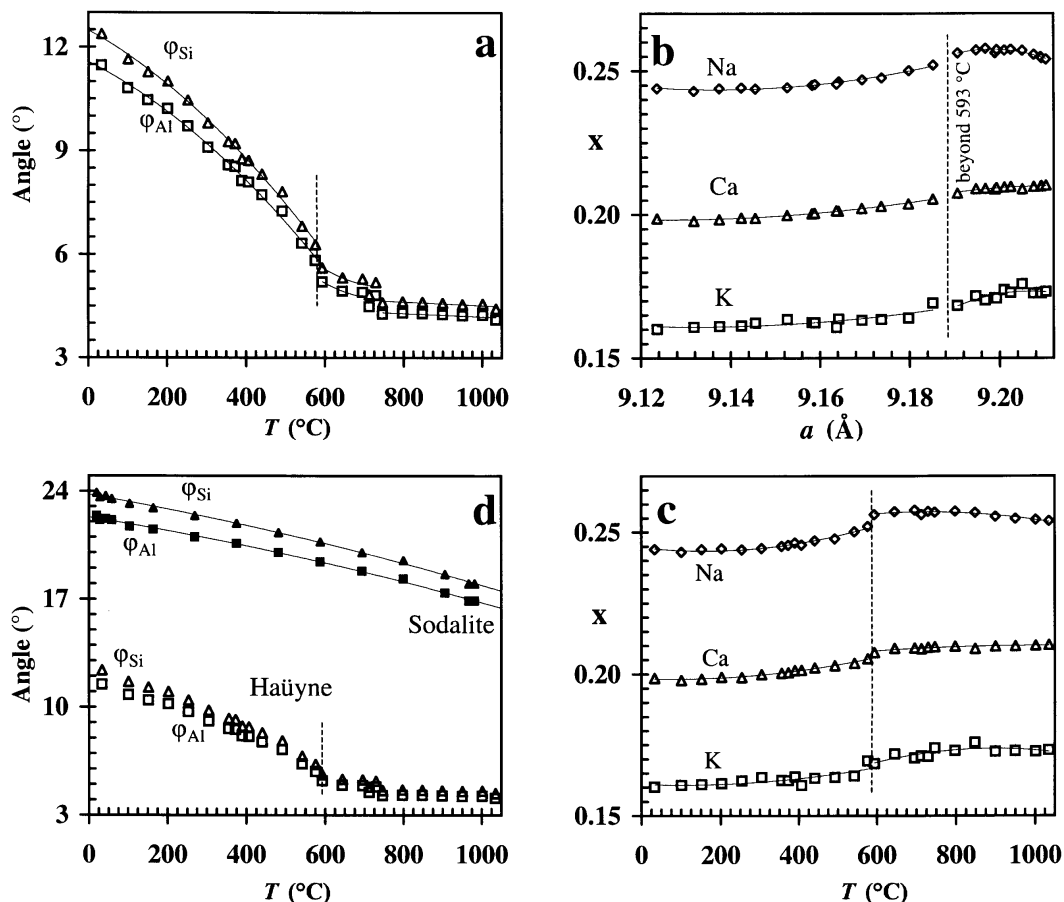


FIG. 7. (a) Variation of the angles of rotation, φ_{Al} and φ_{Si} , of the AlO_4 and SiO_4 tetrahedron with temperature (see Fig. 1). Beyond 585°C, these angles are nearly constant. The dashed vertical lines are drawn at 585°C. (b) Variation of the atomic coordinate of the interstitial cation, x , with the a cell parameter, and (c) with temperature. (d) Comparison of the TO_4 rotational angles for sodalite and h  yne. Error bars are not seen if smaller than the symbols.

stage where rotations of the tetrahedra occur, a high rate of expansion is achieved and when the rotations are stopped, the expansion rate decreases considerably (Figs 3 and 7). In sodalite, between 28 and 982°C, φ_{Al} changes from 22.1 to 16.9°, a difference of 5.2°, while the φ_{Si} changes from 23.6 to 18.0°, a difference of 5.6°, and the Al–O–Si angle increases by 5.06(2)°. At room temperature, the structure of h  yne is in a less collapsed state compared to sodalite, but with increasing temperature, the change in rotation of the tetrahedra in h  yne and sodalite are similar, ~5.5°. However, the tetrahedra in h  yne are rotated by $\varphi_{Si} = 5.6^\circ$ at 593°C, while about the same magnitude of rotation ($\varphi_{Si} = 5.6^\circ$) occurs in sodalite at 982°C (Fig. 7d).

As the structure expands, the interstitial cations move along $\langle 111 \rangle$ towards the plane of the six-membered rings. The change of the interstitial cation coordinate, x , with the a cell parameter and temperature are given (Fig. 7b,c). From 33 to 585°C, the x value for Na and Ca atoms changes at a higher rate than the x value for the K atom, which is nearly constant, and the structure expands at a high rate (Fig. 7c). Beyond 585°C, all the interstitial cations have x values that remain nearly constant, and the expansion of the structure is retarded. Therefore, the movement of the Na and Ca atoms along $\langle 111 \rangle$ allows the tetrahedra to rotate in h  yne. If the interstitial cations reach ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$), which is midway between the centre and a corner of the cell and

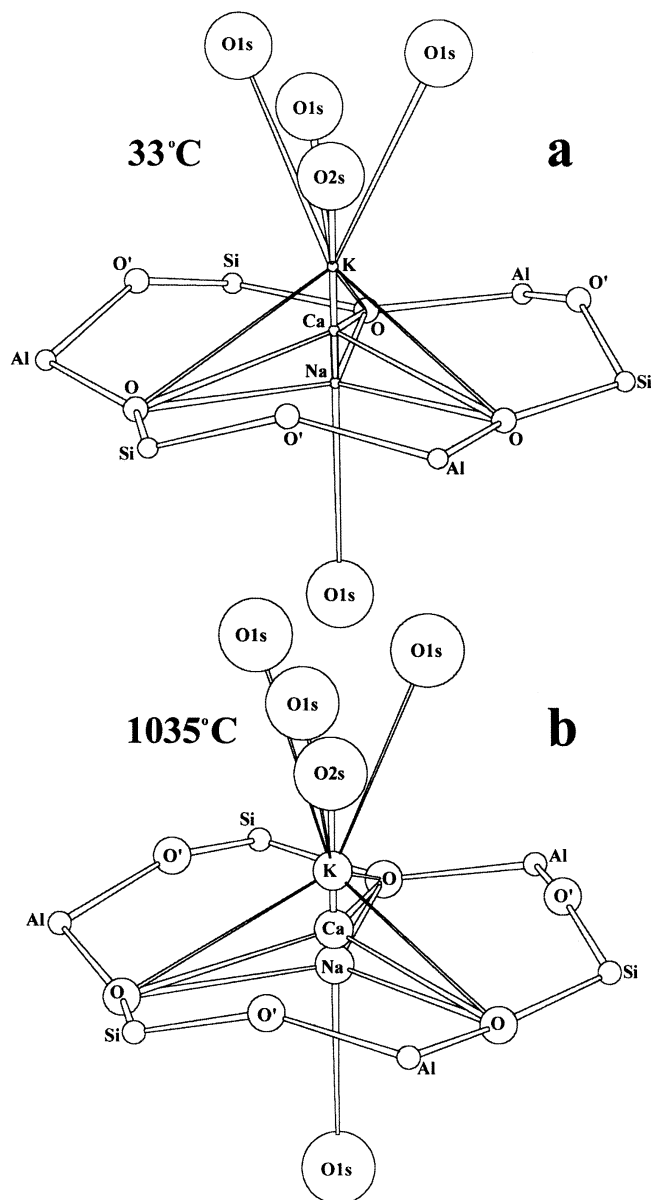


FIG. 8. Comparison of the coordination of the interstitial cations in h  yne at (a) 33  C and (b) at 1035  C. The displacement parameters are shown to scale at the 20% probability level. A six-membered ring is shown. The O' atoms do not form typical cation–O bonds as they are too long. The long cation–O' distance decreases with temperature as the interstitial cations moves towards the plane of the six-membered ring. The Na atom is nearly in the plane of the three O atoms when $x = 0.25$, the x values for Na, K and Ca atoms change until 585  C. Thereafter, all the interstitial cation positional parameters have x values that are nearly constant above 585  C.

approximately in the plane of the six-membered rings, the expansion rate is expected to decrease. However, only the Na interstitial cations are near

($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) in h  yne at and beyond 542  C, and as the x value for the Na atom beyond 542  C is nearly constant at 0.25, further rotation of the

tetrahedra is considerably reduced (Fig. 7). In particular, at 542°C the Na interstitial cation has an x value that is nearly 0.25, the Na–O1/2_s distances, especially, are nearly equal, and the Na and three O atoms are approximately in the same plane (Table 3, Fig. 5c). Thereafter, differences in Na–O1/2_s distances are considerable, particularly at 593°C, and discontinuities in most of the structural parameters occur at 585°C. Therefore, if a single event is responsible for the discontinuity in the thermal-expansion curve for haüyne at 585°C, it has to be the location of the Na cation at $x = 0.25$, when the Na–O1/2_s distances are nearly equal at 542°C. A comparison of the coordination of the interstitial cations and their locations with respect to a six-membered ring is shown in Fig. 8 for the structures at 33 and 1035°C.

In haüyne, thermal expansion occurs mainly by expansion of the cage clusters, which causes the interstitial Na and Ca atoms to move along $\langle 111 \rangle$ and allows the framework tetrahedra to rotate. The change in these rotational angles, φ_{Al} and φ_{Si} , is comparable to the increase in the Al–O–Si bridging angle. As these rotations occur smoothly with temperature up to 585°C, so does the cell parameter. At 542°C, the Na cation has an x value that is nearly equal to 0.25, and the Na–O1/2_s distances are nearly equal. Beyond 585°C, the thermal expansion is considerably reduced, and further rotation of the tetrahedra ceases.

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