Disordered but primitive gallosilicate hydro-sodalite: Structure and thermal behaviour of a framework with novel cation distribution

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ABSTRACT

The structure of a new gallosilicate sodalite $|Na_{6.16(1)}(H_2O)_8|[Ga_{1.04(1)}Si_{0.96(1)}O_4]_6$ described in space group $P\bar{4}3n$ with lattice parameter a = 885.208(7) pm is reported. For such a sodalite with a deviation from a 1:1 ratio in the framework cations a body-centred structure in space group $I\bar{4}3m$ could be expected. The structure shows structural stress resulting from this unusual substitution by a high strain visible in reflections which are forbidden by symmetry in $I\bar{4}3m$. Distinct amounts of Ga and Si are redistributed on the opposite crystallographic position. The second coordination sphere of Si was examined by ^{29}Si MAS NMR, the absence of OH$^-$ in the sodalites cages was checked by FTIR- and Raman spectroscopy. The intensity distribution of MAS NMR signal is modelled using a new technique to calculate the framework metal second neighbour coordination. The confirmed distribution leads to a low thermal stability of the cubic sodalite indicated by a new intermediated phase which could be regarded as a triclinic distorted cancrinite with three-time increased c lattice parameter. This intermediate phase decomposes at around 1000 K to a beryllonite-type sodium gallosilicate.

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1. Introduction

Sodalites are a well-known group of zeolitic materials, consisting of a framework of corner sharing MO_4 tetrahedra, building the so-called *sod*-cages. These *sod*-cages contain extra-framework cations (in most cases Na$^+$), necessary for charge compensation, anions and/or water. Fischer and Baur [1] gave a comprehensive overview on observed sodalite structures and their chemical composition. An alternative structural description via different stacking patterns of sheets of not connected $(M^1M^2O_4)_3$ six-ring sheets leads either to cancrinite (…AB… stacking in <001> direction), sodalite (…ABC… stacking in <111> direction) [2] or the so called intermediate phase with a distinct stacking disorder [3,4]. Generally, the resulting structures could be described in the cancrinite case in hexagonal space-groups (often $P6_3$) with lattice parameter a around 1260 p.m. and c around 520 p.m. in the aluminosilicate system (e.g. Ref. [5]), slightly larger ones are observed in the gallosilicate system ($a \approx 1278$ p.m., $c \approx 528$ p.m.

[6]). The second stacking sequence, leading to sodalite structures, is predominantly described in cubic space groups, where the most prominent one is $P\bar{4}3n$ [1].

In the compound described here Ga^{3+} and Si^{4+} form the framework, Na$^+$ and H_2O are the cage filling constituents. Such gallosilicate hydro-sodalites and their synthesis have been described first by Suzuki and co-workers [7] reporting no structural data but a lattice parameter of 885.6 p.m. The gallosilicate hydro-sodalites reported by McCusker et al. [8] ($P\bar{4}3n$, Si/Ga = 1.26, a = 885.62(1) pm) and Newsam and Jorgensen [9] ($P\bar{4}3n$, Si/Ga = 1.252, a = 884.75(1) pm) are no pure hydro-sodalites but basic/hydro-sodalites, containing a distinct amount of OH$^-$ groups in their cages. In both cases the Si/Ga ratio is greater than 1. Nenoff et al. (1994) [10] reported a pure gallosilicate hydro-sodalite ($P\bar{4}3n$, Si/Ga = 1, a = 886.14(2) pm) and excluded the presence of OH$^-$ groups. Gesing [11] synthesized a primitive ($P\bar{4}3n$, Si/Ga = 1, a = 885.92(3) pm) and a body-centred ($I\bar{4}3m$, Si/Ga = 1.5, a = 884.148(4) pm) gallosilicate hydro-sodalite. In the latter work the local Si environment was examined by ^{29}Si MAS-NMR, showing in the first case a single signal with a chemical shift of -75.6 ppm and in the latter one five signals in the chemical shift range

Table 1
Details of PXRD data collection and refinement of $|Na_{6.16(1)}(H_2O)_8|[Ga_{1.04(1)}Si_{0.93(1)}O_4]_6$.

Powder	white, <63 μm
Wavelength/pm	154.0596(1), 154.4493(1)
μ/cm^{-1}	113.2(5)
$2\theta_{min}$/°	10
$2\theta_{max}$/°	130
2θ stepwidth	0.0167
N(points)$_{measured}$	7480
N(hkl)$_{measured}$	125
N(parameter)$_{refined}$	21
space group	$P\bar{4}3n$
a/pm	885.374(5)
Volume/10^6 p.m.^{3}	693.65(2)
T/K	300(1)
R_{wp}	8.74
R_{Bragg}	2.21

Table 2
Atomic parameters of $|Na_{6.16(1)}(H_2O)_8|[Ga_{1.04(1)}Si_{0.93(1)}O_4]_6$ (equal values are constrained to each other).

Atom	Site	x	y	z	occupancy	B_{iso}
Ga1	6d	1/4	0	1/2	0.17(1)[a]	0.73(2)[b]
Si1					0.83(1)[a]	0.73(2)[b]
Si2	6c	1/4	1/2	0	0.14(2)[a]	0.73(2)[b]
Ga2					0.86(2)[a]	0.73(2)[b]
O1	24i	0.1503(3)	0.1331(3)	0.4246(3)	1	1.0(1)
Na1	8e	0.14324	x	x	0.77(2)	3.6(2)
Ow	8e	0.37285(38)	x	x	1	3.1(3)

[a] Constrained to unity on each site.
[b] Constrained to each other.

of −75.5 ppm to −100.8 ppm corresponding to a local $Si(O_4Ga_4)$, $Si(O_4Ga_3Si)$, $Si(O_4Ga_2Si_2)$, $Si(O_4GaSi_3)$ and $Si(O_4Si_4)$ environment, respectively. The presence of OH$^-$ ions was excluded by vibrational spectroscopy.

From a structural point of view a cubic sodalite with a statistical occupancy on the framework tetrahedral site ($M^1/M^2 \neq 1$, with M^1 and M^2 carrying different charges) should crystallize in space group $I\bar{4}3m$, with the M atoms on a **12d** site. A M^1/M^2 ratio of 1 generally means an ordered distribution of the two species and thus leads from the aristotype $Im\bar{3}m$ via the fully expanded structure in $Pm\bar{3}n$ to the partially collapsed structure described in space group $P\bar{4}3n$ with the M^1 and M^2 atoms on the **6c** and **6d** sites, respectively. Substitution on one of these M sites with an equally charged species retains the space-group [12], substitution with differently charged species inevitably leads to a charge compensating substitution on the other M site, leading to a reduction of symmetry to space group $I\bar{4}3m$.

The dehydration and thermal decomposition of aluminosilicate hydro-sodalites and basic/hydro-sodalites have been examined by Felsche and Luger [13,14]. They observed the dehydration of several $|Na_{6+x}(OH)_x(H_2O)_n|[AlSiO_4]_6$ compounds and observed that the compounds with x = 2, n = 4 and x = 0, n = 8 show a dehydration to one resulting phase. The compound with x = 1 and n = 4 shows a splitting (or bifurcation) of the (110) and (211) reflections, which was interpreted as the dehydration to a two-phase mixture of an empty sodalite (x, n = 0) and a basic sodalite (x ≠ 0, n = 0). The dehydration and decomposition of $|Na_6(H_2O)_8|[GaSiO_4]_6$ was examined by Gesing [11] and it was shown that the sodalite shows only amorphous humps in the X-ray diffraction pattern between 823 K and 923 K and at higher temperatures the crystallization of a hexagonal beryllonite-type $NaGaSiO_4$ ($P6_3$, with lattice parameters a = 881.5(12) pm and c = 845.6(10) pm at 1073 K). Between 323 K and 523 K the gallosilicate hydro-sodalite expands from 886.0(4) pm to 890.1(8) pm, which gives an average linear thermal expansion coefficient of $\bar{\alpha}_a\,^{523}_{323} = 23(1)\,10^{-6}$ K^{-1}, with respect to the lattice parameter a.

This study presents the results of in-depth structural examinations of a gallosilicate hydro-sodalite with an unusual distribution of the framework atoms and its thermal stability.

2. Experimental

$NaGaO_2$ was synthesized by mixing dry Na_2CO_3 with Ga_2O_3 in a 1:1 ratio and heating it for 24 h at 1123 K in a corundum crucible. A possible incorporation of Al from the crucible in the $NaGaO_2$ could

not be observed (see supporting information). 10 mmol $NaGaO_2$ and Na_2SiO_3 were separately stirred for 10 min with 12.5 mL deionized H_2O to form gels. These gels were mixed with 2 g Na_2CO_3, filled in polytetrafluoroethylene-coated steel autoclaves and heated in an open furnace at 453 K for 41 h.

Temperature-dependent (TD) powder X-ray diffraction data were collected between 300 K and 1300 K in 20 K steps on a Philips X'Pert Pro diffractometer (Panalytical, Almelo, Netherlands), using a HTK1200N high-temperature chamber (Anton Paar, Graz, Austria) and CuK$\alpha_{1,2}$ radiation. The instrument was equipped with a Ni-Filter and an X'Celerator detector system. Rietveld refinements were carried using "DiffracPlus Topas 4.2" (Bruker AXS GmbH, Karlsruhe, Germany) software and the fundamental parameter approach on the refinements. The fundamental parameter set was obtained by fitting instrumental parameters against a LaB$_6$ standard reference material and has been verified by Si standard reference material. Further details of the refinements are given in the Results and discussion section. An autocorrelation analysis of the TD X-ray data was carried out according to the procedure given in Ref. [15].

FTIR data in the spectral range from 370 cm^{-1} to 5000 cm^{-1} were collected on a Bruker Optics IFS 66v spectrometer, measuring 64 scans with a spectral resolution of 2 cm^{-1}. The samples were prepared by the KBr-pellet method: A finely ground mixture of 2 mg sample with 200 mg of KBr was compacted in a closed die for 7 min using a pressure of 10^5 N. Raman spectra were collected on a Horiba LabRAM Aramis spectrometer utilizing an Olympus BX-41 confocal microscope and a laser exiting a wavelength of $\lambda = 633$ nm. The sample was slightly pressed to get a smooth and flat sample surface.

Simultaneous thermogravimetric and dynamic difference calorimetry measurements were carried out using a Mettler Toledo TGA/DSC 3 + system. 9.962(1) mg of sample was measured in a corundum crucible in the temperature range of 303 K–1373 K. A heating rate of 10 K/min, a cooling rate of 20 K/min and an N_2 atmosphere as protective gas with a flow-rate of 20 mL/min was utilized.

^{29}Si MAS NMR spectra were recorded using a Bruker 500 WB spectrometer operating at 11.7 T; the corresponding Larmor frequency was 99.4 MHz, the rotating frequency 15 kHz and a standard 4.0 mm probe head (Bruker WVT-type) was employed. The 1D spectrum was recorded with a single pulse sequence accumulating 400 scans with a delay of 10 min. The pulse length was 4 μs at a power level of 200 W. Si(SiMe$_3$)$_4$ served as secondary reference to determine the chemical shifts. The controlled temperature of the bearing gas (300.0 K) and calibration curve with the reference material leads to an estimated sample temperature of 338(2) K. The long relaxation delay guarantees full longitudinal relaxation of all spectral components and was optimized by a classical saturation recovery experiment.