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Synthesis and crystal structure of gallosilicate- and aluminogermanate tetrahydroborate sodalites $Na_8[GaSiO_4]_6(BH_4)_2$ and $Na_8[AlGeO_4]_6(BH_4)_2$

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Abstract

Tetrahydroborate enclathrated sodalites with gallosilicate and aluminogermanate host framework were synthesized under mild hydrothermal conditions and characterized by X-ray powder diffraction and IR spectroscopy. Crystal structures were refined in the space group P-43n from X-ray powder data using the Rietveld method. $Na_8[GaSiO_4]_6(BH_4)_2$: $a = 895.90(1)$ pm, $V = 0.71909(3) \times 10^{-6}\,\text{nm}^3$, $R_P = 0.074$, $R_B = 0.022$, $Na_8[AlGeO_4]_6(BH_4)_2$: $a = 905.89(2)$ pm, $V = 0.74340(6) \times 10^{-6}\,\text{nm}^3$, $R_P = 0.082$, $R_B = 0.026$. The tetrahedral framework T-atoms are completely ordered in each case and the boron atoms are located at the centre of the sodalite cages. The hydrogen atoms of the enclathrated BH_4^- anions were refined on x, x, x positions, restraining them to boron–hydrogen distances of 116.8 pm as found in $NaBD_4$.

The IR-absorption spectra of the novel phases show the typical bands of the tetrahedral BH_4^- group as found in the spectrum of pure sodium boron hydride.

The new sodalites are discussed as interesting BH_4^--containing model compounds which could release pure hydrogen.

Keywords: Hydrothermal synthesis; Gallosilicates; Aluminogermanates; Crystal structure; Powder diffraction; IR spectroscopy

1. Introduction

The cubic framework structure of sodalites with general composition $Na_8[T_1T_2O_4]_6X_2$ is formed by a space-filling array of truncated octahedral cages each built up of tetrahedral TO_4 units. The framework T-atoms are usually Si and Al but even others like Ge or Ga can be introduced during synthesis [1]. Each sodalite cage is filled by an ion complex $[Na_4X]^{3+}$, where X presents a monovalent anion or anion group. According to the host guest interactions the cage filling ions and the type of framework T-atoms are both responsible for the chemical and physical behaviour of a certain sodalite species. In the past decades sodalites were synthesized with various host T-atoms and guest anions. An overview on the classical works was given by Barrer [2]. Despite the great variety in chemical composition of sodalites the tetrahydroborate anion BH_4^- found in the borontetrahydride salts although important as possible hydrogen source has not been used as cage filling ion up to now. The reason for this less attention could be the high reactivity of salts like $Al(BH_4)_3$, $LiBH_4$ or $NaBH_4$ with water. In the literature there was only one early proposal of Barrer for a dry way impregnation of pre-formed zeolites like X and Y with hydride salts [2], but filling of small ß-cages is impossible by impregnation method. No direct ways of synthesis were worked out for a long time, but during our recent investigations on rhodanide and cyanate sodalites [3,4] we succeeded in preparation of tetrahydroborate sodalite $Na_8[AlSiO_4]_6(BH_4)_2$ for the first time [5].

Because sodalites are expected to be an interesting model system for studying simple principles of hydrogen storage in small cavities of framework structures, as proposed in Ref. [6], we extended our experimental work here on synthesis and structure of tetrahydroborate filled sodalites with gallosilicate and aluminogermanate framework.

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Substitution of framework atoms by germanium or gallium is of special interest to study interactions of enclathrated tetrahydroborate guest anions with a host framework of certain composition. The improvement of our knowledge on these structural features is essential for future applications of hydrogen containing sodalites as well as for the modification of zeolites A, X and Y according to a fine tuning of ß-cage size by framework T-atom substitution. In this sense the aim of the present paper is to establish synthesis and crystal structure of $NaBH_4$-containing gallosilicate and aluminogermanate sodalites as new model compounds for a secure long time incorporation of tetrahydroborate in a solid matrix.

2. Experimental procedure

Hydrothermal syntheses were carried out in 50 mL Teflon coated steel autoclaves. According to our experience from studies of tetrahydroborate incorporation in the aluminosilicate system fine-tuning of synthesis temperature, NaOH concentration and reaction time [5] could be performed by a series of screening experiments. Here the temperature was varied between 353 and 433 K. Reaction periods of 12–48 h were tested and the concentration of NaOH solution (Fluka 71691) was varied from 16 to 1 M.

The gallosilicate tetrahydroborate enclathrated sodalite was prepared by alkaline hydrothermal treatment of a solid mixture of gallium oxide (Fluka 48540) and sodium silicate (Aldrich 30,781-5). This mixture was filled into the Teflon lined autoclave onto the $NaBH_4$ salt (Merck 806373). The solid educts were placed within the liner and sodium hydroxide solution was added before the autoclave was rapidly closed and placed in a furnace.

In order to obtain pure sodalite in the aluminogermanate system a beryllonite analogous phase $NaAlGeO_4$ was employed, as described by Fleet [7] for syntheses of aluminogermanate halide sodalites. This phase was prepared from a mixture of 10 mmol GeO_2 (Alfa 721100), 5 mmol γ-Al_2O_3 (Merck 1095) and 5 mmol Na_2CO_3 (Merck 6398) heated at 1473 K for 12 h. After quenching to room temperature it was crystallized at 1073 K for 48 h. One gram of this material was then given into the Teflon liner after first filling in the 2 g $NaBH_4$ salt (Merck 806373).

In all cases the products were washed with water and dried at 353 K for 24 h before they were characterized by X-ray-powder diffraction (XRD) as well as IR spectroscopy.

X-ray powder data were collected on a STOE STADI P diffractometer using Cu$K\alpha_1$ radiation in a Debye–Scherrer geometry. The diffractometer was equiped with a focusing germanium (1 1 1) monochromator and a positional sensitive detector. The measurements were carried out with a step width of 0.1°, a channel width of 0.02° and a measuring time of 7 min per step. The least-squares refinements were done with the Rietveld analysis program Topas 2.1 [8].

Infrared spectra were taken using a FTIR spectrometer Bruker IFS66v. For the measurements the samples were diluted by KBr (about 1 mg sample in 200 mg KBr) and pressed into pellets and measured relatively to the KBr pellet as a reference.

3. Results

3.1. Synthesis

Screening experiments revealed that increasing temperatures above 393 K already favour the decomposition of the tetrahydroborate anions before encapsulation within the sodalite framework cavities. The influence of temperature on the decomposition kinetics was already known from the thermal behaviour of pure $NaBH_4$ salt [9]. Care must be taken here because rapid decomposition causes the formation of hydrogen within the autoclave! This observation is valid for both the gallosilicate as well as the aluminogermanate reaction system. After a reaction at increasing temperature above 393 K mainly species like $(H_3O_2)^-$ known from basic sodalite [10] and hydroxoborate [11] were detected inside the sodalite cages and tetrahydroborate anions were found only in very small amounts.

The influence of reaction time was further investigated and as in the aluminosilicate system a period of 24 h was selected as the favoured time in both the gallosilicate and the aluminogermanate system. Remarkable amounts of hydrogen within the autoclaves were detected at longer reaction periods because of the progress of hydrolysis of $NaBH_4$ salt. In contrast, in a series of 12 h reaction time in each case the conversion of the educts was improper.

Using high NaOH concentrations during the synthesis leads to another problem. The decomposition kinetics of the salt during hydrolysis reaction is strongly influenced by the alkalinity [12–14]. Increasing alkalinity yields to a remarkable decrease of kinetics of $NaBH_4$ hydrolysis reaction but under the same high alkaline conditions problems with sodalite crystallization were observed in both reaction systems due to the individual solubility behaviour of the Ga- and Ge-containing educts. In the gallosilicate system NaOH concentrations higher than 6 M shifted the conversion of the educts to low values as a result of the high solubility of gallium oxide in a strong alkaline solution. Nucleation rate of sodalite was rather low under these conditions.

In the aluminogermanate system a reverse behaviour was found at NaOH concentrations higher than 4 M. Basic sodalite with only low degree of tetrahydroborate enclathration was observed as a result of very rapid dissolution of the Ge-beryllonite and a high nucleation rate of sodalite. Due to the concentration gradient between OH^- anions and BH_4^- anions in the early stage of reaction under the used static experimental conditions crystallization of basic sodalite was thus the result at higher alkalinities in the aluminogermanate system. The unstirred (static) autoclaves were used in all our experiments to prevent more rapid hydrolysis of the boronhydride salt by stirring the solution.

Best results in the gallosilicate system were obtained using a mixture of 0.5 g gallium oxide, 1.5 g sodium-metasilicate, 2 g $NaBH_4$ and 10 mL of the 6-M sodium hydroxide solution. After a reaction time of 24 h at a temperature of 393 K pure phase tetrahydroborate enclathrated gallosilicate sodalite of composition $Na_8[GaSiO_4]_6(BH_4)_2$ could be synthesized, as shown below by the other analytical methods. Idiomorphic crystals of about 2 μm grain size were observed under these conditions.

Optimised results in the aluminogermanate system were obtained using a 4 M NaOH solution. The reaction was performed at a temperature of 393 K for 24 h i.e. under the same conditions, as in the case of gallosilicate tetrahydroborate sodalite crystallization. One gram of the mentioned beryllonite together with 2 g $NaBH_4$ and 10 mL of the NaOH solution were used. In the aluminogermanate case the crystals are somewhat bigger and of very good quality. Idiomorphic sodalite crystals of about 5 μm grain size were observed here.

3.2. *IR spectroscopy*

The IR spectra of both new sodalites obtained in the mid-infrared and far-infrared regions are given in Fig. 1 compared with the spectrum of pure sodium borontetrahydride salt (Merck 806373). In both spectra of the sodalites the enclathrated tetrahydroborate anions can be clearly detected by intense absorption bands at 1143 cm^{-1} (ν_4), 2286 cm^{-1} ($2\nu_4$), 2241 cm^{-1} (ν_3) and 2390 cm^{-1} ($\nu_2+\nu_4$) of the BH_4^- tetrahedral group as compared with spectrum of Fig. 1a for the pure salt consistent with literature data [15–18]. The spectrum of gallosilicate tetrahydroborate sodalite (Fig. 1b) indicate the pure character of the sample. Cage fillings like water known from hydrosodalite or $(H_3O_2)^-$ as in basic sodalite are negligible in this product [10]. In contrast the spectrum of the aluminogermanate tetrahydroborate sodalite (Fig. 1c) shows some impurities. A small water content (vibration mode at 1650 cm^{-1} and broad band in the 3100–3600 cm^{-1} region) is found beside some $(H_3O_2)^-$ anions. A very small amount of carbonate anions are also existing within the sample according to the ν_{as} mode near 1450 cm^{-1}. These observations are in agreement with former investigations on sodalite synthesis in the aluminosilicate system where it was found that the amount of carbonate and water became higher within the products at sodium hydroxide concentrations <4 M solutions [5].

In the range of the framework modes both spectra show major differences concerning the positions and shapes of the signals and even the number of framework vibrations. The spectrum of the gallosilicate sodalite framework (Fig. 1b) shows two clear resolved maxima at 922 and 945 cm^{-1} for the asymmetric T–O–T vibrations. For the ν_s modes two very close adjacent signals with vibrations at 642 cm^{-1} and a shoulder at 624 cm^{-1} as well as a peak at 556 cm^{-1}can be seen from Fig. 1b and finally the framework bending mode was found as one sharp signal at 457 cm^{-1}. The spectrum of the aluminogermanate sodalite (Fig. 1c) shows one asymmetric T–O–T mode at 858 cm^{-1}, two symmetric T–O–T vibrations (609 and 636 cm^{-1}) and a T–O deformation mode at 387 cm^{-1}.

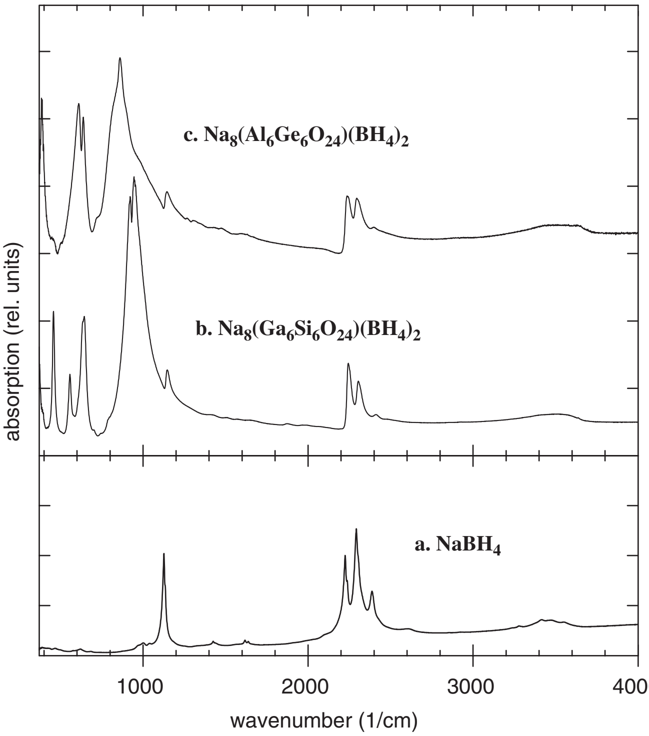
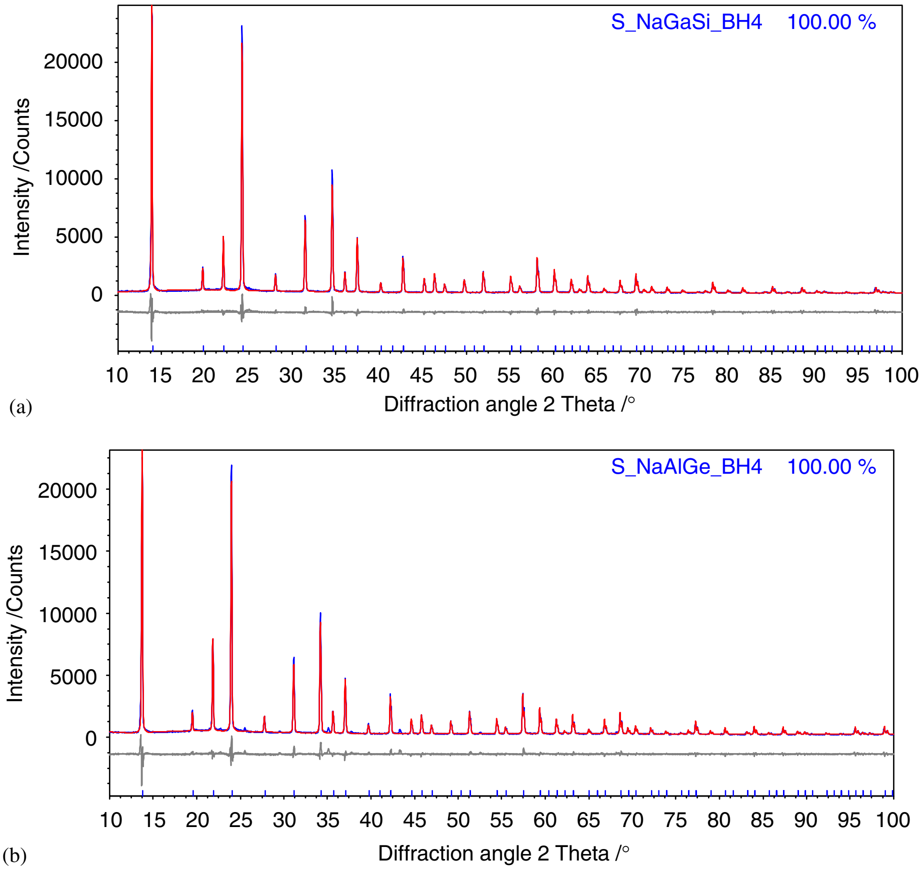


Fig. 1. IR-spectra of pure $NaBH_4$ salt [Merck 806373] (a), gallosilicate tetrahydroborate sodalite (b) and aluminogermanate tetrahydroborate sodalite (c).

3.3. *XRD and structure refinement*

The X-ray powder diagrams of the new phases are given in Figs. 2a and b. Additionally to the powder pattern the differences between observed and calculated intensities and the observed reflections are included in this figure. The cubic lattice parameter $a = 895.90(1)$ pm was refined for the gallosilicate sodiumtetrahydroborate sodalite $Na_8[GaSiO_4]_6(BH_4)_2$. The pattern gave no hints of any crystalline or amorphous impurities. For the aluminogermanate phase $Na_8[AlGeO_4]_6(BH_4)_2$ the peaks could be indexed uniquely according a refined cubic cell parameter $a = 905.89(2)$ pm. In contrast to the gallosilicate sodalite the pattern of the aluminogermanate product shows small signals of a crystalline impurity and the background of pattern gives hints on some amounts of amorphous material.

The X-ray powder data of both new sodalites have been further analysed by Rietveld method. As starting atomic parameters those of chloride sodalite were used [19] replacing the Cl anion by the BH_4^- group with boron in the centre of the sodalite cage and hydrogen on x, x, x



(a)

(b)

Fig. 2. (a) Rietveld plot of gallosilicate tetrahydroborate sodalite with observed intensities, difference between observed and calculated intensities and the possible reflections. (b) Rietveld plot of aluminogermanate tetrahydroborate sodalite with observed intensities, difference between observed and calculated intensities and the possible reflections.

positions, restraining them to distances of 116.8 pm as found in $NaBD_4$ (ICSD-no. 61442[1] [20] to take the electrons into account. Six Chebychev polynomial background parameters, the zero point of the counter, the scale factor, Fundamental profile parameters, the cell parameter and the variable positional parameters were refined in each case. The refinement results are given in Figs. 2a and b together with the plot of the powder diagram for both phases as already mentioned above.

The refined positional-, displacement- and occupancy-parameters for both sodalites are given in Table 1. The Tables include *R*-values [8], cell parameters (a) and cell volume (*V*). Silicon and gallium atoms of the gallosilicate sodalite are tetrahedrally coordinated by oxygen atoms with distances of 161.1(3) and 181.9(3) pm, in the Ga–Si sodalite, respectively. The boron atom of the BH_4^- anion is located at the centre of the sodalite cage. The hydrogen atoms are positionally ordered on the three-fold axis close to the centre of a triangle formed by three sodium atoms (Fig. 3). The Na atoms itself have three oxygen atoms at 234(4) pm as well as three H atoms at 253(1) pm as nearest neighbours (Fig. 3). For we have constrained the B–H distance during the refinement of the BH_4^- anions further experiments like neutron diffraction are necessary to clarify the absolute orientation of the BH_4^- group.

In aluminogermanate sodalite Ge and Al atoms are tetrahedrally coordinated by oxygen atoms with distances of 173.0(3) and 174.9(3) pm. In the same manner as in gallosilicate sodalite (Fig. 3) the Na atoms in the aluminogermanate phase have three oxygen atoms at 234(4) pm and three H atoms at 257(5) pm as nearest neighbours. The hydrogen atoms are located on the same crystallographic positions as found for the gallosilicate phase.

4. Conclusions

Tetrahydroborate anions have been successfully enclathrated within the ß-cages of sodalites with gallosilicate as well as aluminogermanate framework. Although $NaBH_4$ salt is very sensitive to hydrolysis, nevertheless anion incorporation was possible by mild hydrothermal synthesis at low temperature, short reaction time and optimized alkalinity using a 6-M NaOH in the gallosilicate—and 4 M solution in the aluminogermanate system. For both reaction systems the temperature of 393 K in combination

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[1] Additional material can be ordered referring to the no. CSD at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich technische Information mbH, D 76344Eggenstein-Leopoldshafen, Germany.

Table 1
Atomic parameters of gallosilicate tetrahydroborate sodalite $Na_8[GaSiO_4]_6(BH_4)_2$ (SG P-43n: $a = 895.90(1)$ pm, $V = 0.71909(3)\,nm^3$, $R_{WP} = 0.097$, $R_P = 0.074$, $R_B = 0.023$, $R_e = 0.043$) and aluminogermanate tetrahydroborate sodalite $Na_8[AlGeO_4]_6(BH_4)_2$ (SG P-43n: $a = 905.89(2)$ pm, $V = 0.74340(6)\,nm^3$, $R_{WP} = 0.112$, $R_P = 0.082$, $R_B = 0.026$, $R_e = 0.043$)

Atom	P-43n	Occup.	*x*	*y*	*z*	B ($10^2\,nm^3$)
$Na_8[GaSiO_4]_6(BH_4)_2$						
Na	8e	1.02(2)^{1}	0.1731(3)	*x*	*x*	2.7(2)
Ga	6d	1.0	1/4	0	1/2	1.1(2)^{2}
Si	6c	1.0	1/4	1/2	0	1.1(2)^{2}
O	24i	1.0	0.1336(3)	0.1513(3)	0.4310(4)	1.9(2)
B	2a	1.1^{1}	0	0	0	3.2(8)^{3}
H	8e	1.1^{1}	0.4371(38)	*x*	*x*	3.2(8)^{3}
$Na_8[AlGeO_4]_6(BH_4)_2$						
Na	8e	1.02(3)^{4}	0.1740(4)	*x*	*x*	2.5(2)
Al	6d	1.0	1/4	0	1/2	1.4(2)^{5}
Ge	6c	1.0	1/4	1/2	0	1.4(2)^{5}
O	24i	1.0	0.1425(4)	0.1441(4)	0.4296(5)	1.6(2)
B	2a	1.1^{4}	0	0	0	3.2(8)^{6}
H	8e	1.1^{4}	0.4401(38)	*x*	*x*	3.2(8)^{6}

$^{1-6}$ Parameters with the same numbers were constrained to each other.

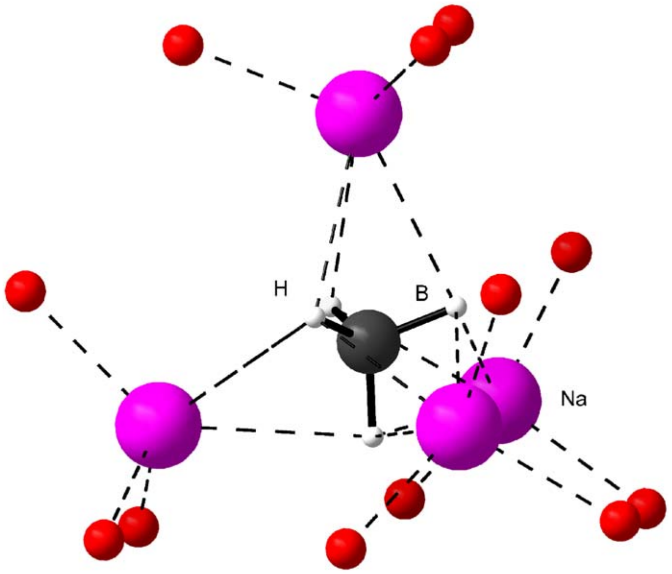

Fig. 3. Coordination of the non-framework atoms in the gallosilicate tetrahydroborate sodalite together with three oxygen atoms of the framework around each sodium atom.

with the low-reaction time of 24 h were found to be ideal, because higher temperatures and longer periods of reaction favour the decomposition of the boron hydride salt and heterogeneous products of tetrahydroborate enclathrated sodalite together with basic sodalite were formed.

Crystal structures have been refined in the space group P-43n. For both new sodalites the boron atoms were found at the centre of the sodalite cage. The hydrogen atoms of the enclathrated BH_4^- anions were refined on x, x, x positions, restraining them to boron—hydrogen distances of 116.8 pm as found in $NaBD_4$. Further experiments like neutron diffraction are necessary to clarify the absolute orientation of the BH_4^- group inside the sodalite cages.

The refined lattice parameters of the novel sodalites are higher as compared with aluminosilicate tetrahydroborate sodalite ($a = 891.61(2)$ pm; [5]). Interesting differences in thermal reaction behaviour of the enclathraed BH_4^- can be predicted due to the relations of cage openings and framework expansion [21]. The new sodalites are interesting BH_4^--containing model compounds which could release pure hydrogen. Such investigations will be presented in a forthcoming paper.

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