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Synthesis, crystal structure and temperature-dependent behavior of gallogermanate tetrahydroborate sodalite $|Na_8(BH_4)_2|[GaGeO_4]_6$

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ABSTRACT

Tetrahydroborate enclathrated gallogermanate sodalite was successfully synthesized under mild hydrothermal conditions and characterized by X-ray powder diffraction and Fourier transform infrared (FTIR) spectroscopy. The crystal structure was refined in space group $P\bar{4}3n$ using the Rietveld method: $a = 912.581(1)$ pm, $V = 760.0(1) \cdot 10^{-6}$ pm^3, $R_B = 0.019$. Within the sodalite cage formed by corner-sharing oxygen coordinated gallium and germanium tetrahedra, the hydrogen atoms of the enclathrated BH_4^- anions were refined on 8e (*x*, *x*, *x*) crystallographic position. The boron–hydrogen distances were restrained to 124.7 pm as calculated from the respective bond valence sums. High temperature behavior was investigated using temperature-dependent X-ray diffraction, FTIR and Raman spectroscopy and TG-DTA methods. A two-step sodalite decomposition reaction to the beryllonite analogous phase $NaGaGeO_4$ was observed. The temperature-dependent development of the sodalite structural parameters evaluated by Rietveld analysis of the XRD data indicate a beginning transformation of the enclathrated $NaBH_4$ at about 528 K followed by a decomposition of the sodalite framework starting at about 648 K. These findings are confirmed by the results obtained from temperature-dependent Raman and FTIR data evaluation.

1. Introduction

The cubic sodalite framework structure consisting of closed packed truncated octahedra was first reported in 1929 and refined in space group $P\bar{4}3n$ (T_d^4) by Jaeger [1] for the crystal structure of nosean, a sulphate variety of sodalite showing a statistical distribution of one sulphate anion over two cages. One year later, Pauling [2] published the crystal structure of chloride sodalite, $|Na_8Cl_2|[AlSiO_4]_6$, which was later confirmed by Löns and Schulz [3] (for historical details see Baur and Fischer [4]). The structure building truncated octahedra (toc), classically described as β- or sodalite cages, are built up by tetrahedral TO_4 units being connected via common O-atoms [3–6]. The T-atoms are placed in the center of each TO_4 tetrahedron occupying the corners of the β-cages [3–6]. Each β-cage exhibits six four-ring and eight six-ring windows built up by linked TO_4 tetrahedra, whereas the cubic sodalite framework structure is formed by the closed packed β-cages via their common four- and six-ring windows [3–8]. Usually in every β-cage, an ion complex $[M_4X]^{3+}$ (M: monovalent cation) is situated, with the monovalent X^- anion being located in the center of the cage [3–10]. Sodalites with electrostatically neutral cage fillings (templates), e.g. hydro-sodalite [11,12] or anhydrous sodalite [13], or with enclathrated multivalent anions [14] and cations, e.g. alkaline earth metals, are also known. The sodalite framework is able to adapt itself to the size of various guest anions by the tilting mechanism [6,8].

The usage of zeolites as potential media for hydrogen storage was suggested by Barrer [7] and Weitkamp et al. [15]. In this context, especially the enclathration of hydride salts into sodalite cages provides an interesting model system to study principles of hydrogen storage in zeolite A, X and Y cavities, which have β-cages within their structure. An incorporation of hydrogen species in the form of the hydride salt $NaBH_4$ was already obtained from mild hydrothermal syntheses for sodalites with alumosilicate, alumogermanate and gallosilicate frameworks [16,17]. With regard to the fine-tuning and controlled change of β-cage properties in zeolites the complete substitution of alumosilicate framework atoms by Ga and Ge could be of interest with regard to the framework-guest interactions. Sodalites with gallogermanate host framework have been synthesized with different enclathrated guest species, e.g. Cl^-, Br^-, I^- [18], H_2O [19] and in the form of large optically clear basic sodalite crystals [20]. Using organic molecules as structure directing agents [21] gallogermanate sodalites containing tetramethylammonium or ethylenediamine can be synthesized. Additionally, gallogermanate zeolite structures like faujasite and

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thomsonite [22], natrolite [23], analcime [21] or cancrinite [24] have been reported.

In the present paper, we describe the hydrothermal synthesis of gallogermanate tetrahydroborate sodalite. Because of the different solubility of Ga_2O_3 and GeO_2, the beryllonite analogous phase $NaGaGeO_4$ was used as a reactant to ensure an equal release of Ga- and Ge-ions into the hydrothermal solution. The corresponding $NaAlGeO_4$ [25] beryllonite was already used by Buhl et al. [17] as reactant for the synthesis of alumogermanate tetrahydroborate sodalite. Furthermore related hydrothermal synthesis routes with other reactants like kaolinite for alumosilicate and oxide mixtures for gallosilicate tetrahydroborate sodalite were successfully performed [16,17]. Additionally, results of the temperature-dependent studies on gallogermanate tetrahydroborate sodalite are presented in order to get more insight on the interaction between the guest anions and the framework atoms. This will help to clarify the influence of the sodalites T-atoms on physical properties like the thermal stability. It has already been shown, that the framework compensates an increasing T-atom size by decreasing the T–O–T-bond angle [19] resulting in an increasing framework tilt. Therefore, with increasing volume of the sodalite cage the sizes of the inter-cage pores (six-ring window diameter) decreases [19]. These changes in structural features enable more possibilities to finely tune the properties of β-cages in zeolite structures like Zeolite A [26] for technical applications.

2. Experimental

The reactant $NaGaGeO_4$ [25,27] was prepared by mixing 10 mmol GeO_2, 5 mmol Ga_2O_3 and 5 mmol Na_2CO_3 in a ball mill for 1 h. This mixture was molten in a platinum crucible at 1473 K for 24 h and subsequently quenched at room-temperature. Crystallization of the resulting glass was achieved by a second heat treatment at 1073 K for 48 h. Hydrothermal syntheses were carried out in 50 mL Teflon coated steel autoclaves. Because it was not possible to synthesize gallogermanate tetrahydroborate sodalite with layered reactants in a one pot synthesis, as described by Buhl et al. [16,17], separate suspensions of $NaGaGeO_4$ and $NaBH_4$ in sodium hydroxide solutions were prepared and combined before the hydrothermal treatment.

As summarized in Table 1, different experimental conditions (i.e. temperature and time) and ratios of the reactants $NaGaGeO_4$ and $NaBH_4$ were used. The best product (No. 5, Table 1) was obtained using 1 g $NaGaGeO_4$ and 1 g $NaBH_4$-granulate, which were each briefly stirred in 1 mL 2 M NaOH solution at ~338 K. Both suspensions were combined with additionally adding 1 mL 2 M NaOH solution. After four hours hydrothermal treatment at 423 K the sample was washed with deionized water and dried 1 h at 383 K.

X-ray powder diffraction (XRPD) data were collected on a Bruker D8 Advance diffractometer equipped with a primary Ge(111) monochromator in a Debye-Scherrer geometry, using $Cu_{K\alpha 1}$ radiation and a quartz capillary, 0.3 mm in diameter, as a sample holder. The diffraction pattern was recorded in three segments in order to rise the measuring time towards higher diffraction angles (Fig. 1). Each measurement was performed with a step width of 0.01° 2θ. Data from 10° to 50° 2θ were collected with 10 s/step, from 48° to 90° 2θ with 20 s/step and from 88° to 130° 2θ with 40 s/step. The crystal structure of the title compound was refined combined for all the segments by the Rietveld method using Bruker Topas 4.2 (Bruker AXS GmbH, Karlsruhe, Germany) software. In the first segment $NaGaGeO_4$ was additionally included as a second phase. The structural parameters of $NaGaGeO_4$ were taken from Robben et al. [27] and fixed during the refinements, except for the lattice parameters and the scale factor. In the second and third segment this phase was not included due to unobserved scattering contributions.

Fourier transform infrared (FTIR) spectra were measured on a Bruker Vertex 80v FTIR spectrometer in a spectral range from far (FIR) to mid (MIR) (30–5000 cm^{-1}) infrared. For the FIR measurements, the sample was incorporated into a PE matrix (2 mg sample in 50 mg PE) and measured relatively to a PE reference pellet. Accordingly, a KBr matrix and reference were used for the FTIR data collection in the MIR (1 mg sample in 200 mg KBr). The FIR and the MIR spectra were combined in order to obtain a continuous FTIR spectrum by adjusting the intensities of the FIR spectrum to the intensities of the MIR spectrum in their common overlapping wavenumber area.

Simultaneous thermal analysis (TG-DTA) was carried out up to 973 K (heating rate: 5 K/min) under dry synthetic air (80 vol-% N_2 and 20 vol-% O_2, flow rate: 30 ml/min) on a Netzsch STA 449 F3 Jupiter TG-DTA unit.

Temperature-dependent (TD) XRD data were collected on a PANalytical X'PertPro MPD diffractometer equipped with an Anton Paar HTK1200 N heating chamber, using $Cu_{K\alpha 1,2}$ radiation, a secondary Ni-filter and a X'Celerator detector. All measurements were carried out between 5° and 120° 2θ with a step width of 0.0167° and a total measuring time of 100 s per step collecting 6881 data points. Patterns were taken in 10 K steps within a temperature range from 298 K to 978 K with 5 min holding time at every temperature step to reach near equilibrium conditions. The resulting pattern were evaluated by the Rietveld method (Topas 4.2, Bruker AXS GmbH, Karlsruhe, Germany). During the refinements, general parameters (e.g. scale factors, one background parameter and sample height error) were optimized. Profile shape calculations were performed based on standard instrumental parameters using the fundamental parameter approach implemented in the program and fitted to a LaB_6 standard measurement. The lattice parameters and average crystallite sizes of both phases were refined. Structural data of the sodalite and $NaGaGeO_4$ were used in an analogous manner to the room temperature measurement.

TD-FTIR spectra were recorded in the spectral MIR range (370–5000 cm^{-1}) on a Bruker IFS 66v/S FTIR spectrometer, equipped with an in-house build furnace and a manually adjustable temperature controller unit (Eurotherm 810). In order to avoid a K^+–Na^+ cation exchange between pellet and sample at elevated temperatures, the sample was incorporated into a NaCl matrix (1 mg sample in 200 mg NaCl) and measured relatively to a 200 mg NaCl

Table 1
|Na8(BH4)2|[GaGeO4]6 hydrothermal synthesis parameters.

No.	Molar batch ratio Na_2O:Ga_2O_3:GeO_2:$NaBH_4$:H_2O	Temp./K	Time/h	SOD[a]/wt%	$NaGaGeO_4$/wt%
1	4:1:2:26:170	383	2	85(1)	15(1)
2	7:1:2:53:339	383	2	80(1)	20(1)
3	4:1:2:26:170	383	4	94(1)	6(1)
4	4:1:2:26:170	383	8	94(1)	6(1)
5	4:1:2:26:170	423	4	97(1)	3(1)

[a] SOD = $|Na_8(BH_4)_2|[GaGeO_4]_6$ plus $NaGaGeO_4$ as second phase. Both phase fractions/wt% were determined by quantitative Rietveld calculations.