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THE PROPERTIES OF SALT-FILLED SODALITES. I. THERMAL DECOMPOSITION REACTIONS OF HYDROXOBORATE SODALITE

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ABSTRACT

Differential scanning calorimetric investigations of tetrahydroxoborate sodalite $Na_8[AlSiO_4]_6[B(OH)_4]_2$ and low temperature polarization microscopic studies indicate structural phase transitions of sluggish character of different samples, covering the temperature range 270–300 K. Sodalite samples show cubic symmetry ($a_0 = 9.010(1)$ Å at 310 K) above 300 K but superstructure characteristics on single-crystal precession and Guinier powder diffraction photographs below 270 K. This pattern could be indexed to orthorhombic symmetry ($a_0 = 25.510(1)$ Å, $b_0 = 12.750(1)$ Å, $c_0 = 9.020(1)$ Å at $T \leqslant 270$ K). Variations of the transition characteristics in the DSC curves of the species from the high temperature run (773 K) and those synthesized at 573 K are discussed.

Thermoanalysis (thermogravimetry, differential thermogravimetry and differential thermoanalysis), coupled with mass spectrometry, of the sodalite samples shows a significant expansion of the framework at elevated temperatures (573–825 K), when a total of four molecules of H_2O are released in a two-step decomposition reaction. The decomposition behaviour indicates the existence of a hydrogen bonding system between framework and non-framework oxygens and is discussed in terms of the destruction of these bonds during heating.

INTRODUCTION

The development of new materials, especially catalysts, involves the study of the effects of salt enclathration as well as the substitution of the tetrahedral aluminosilicate framework sites by heteroatoms on the thermal stability and reactivity of porous tectosilicates [1–5]. Because of their structural relations to the zeolite family, sodalites are favoured for studying

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the properties of salt-imbibed cages [6]. Scarce experimental data are available for borate-imbibed sodalites on polycrystalline samples, grown under mild conditions at 353 K, encapsulating arbitrary amounts of hydrate water and base as well as sodium borate [5].

The present paper reports on structural phase transitions and thermal decomposition reactions of single-crystal products of tetrahydroxoborate sodalite $Na_8[AlSiO_4]_6[B(OH)_4]_2$, grown under more rigorous conditions. A structural characterisation by X-ray diffraction data and magic angle spinning (MAS) NMR results is given elsewhere [7].

EXPERIMENTAL

Single crystals of tetrahydroxoborate sodalite $Na_8[AlSiO_4]_6[B(OH)_4]_2$ were synthesised hydrothermally at 573 K (pressure, 100 MPa) and at 773 K (pressure, 150 MPa) in steel autoclaves having an interior volume of 8 ml. Sealed silver tubes have been employed as sample containers (6 mm diameter, 90 mm length). The crystallisation temperature was measured with calibrated thermocouples. The pressure was generated by compressed argon gas, using a special supercharger. Starting substances were prepared by heating kaolinite (Fluka 60609) at 1773 K for 2 h. This product was used for hydrothermal runs in 8 M NaOH (Riedel–de Haen 30620) mixture together with boric acid (Riedel–de Haen 31146) as a liquid phase for synthesis. The excess of boric acid (4.5 mol l^{-1}) resulted in an $Al_2O_3 : B_2O_3$ ratio of 1 : 10.

After a reaction period of 5 days, single crystals with average dimensions of 0.5 mm were obtained. They were examined by electron microprobe analysis and X-ray Guinier powder diffraction at temperatures of 270 K and 310 K and ^{29}Si as well as ^{11}B MAS NMR experiments, described in ref. 7. Ordering of silicon and aluminium atoms corresponding to an Si : Al ratio of 1.02 has been confirmed. Each sodalite cage contains one tetrahydroxoborate anion. This is in agreement with the salt inclusion isotherm given in ref. 5 for high B_2O_3 contents of the initial solutions. Because of the ^{11}B MAS NMR experiment a substitution of boron for aluminium in the framework of amounts $\leqslant 0.1$ can be excluded. Moreover, no cell parameter reduction has been observed for increasing concentrations of boric acid employed in systematic replacement experiments. Diminished cell parameters were obtained for other tecto- and layer silicates, indicating the substitution of boron for aluminium in the TO_4 sites [8,9]. The X-ray diffraction data reveal cubic symmetry for the high temperature form of tetrahydroxoborate sodalite ($a_0 = 9.010(1)$ Å at 310 K) but a superstructure diffraction pattern for the low temperature form, which has successfully been indexed to the orthorhombic system ($a_0 = 25.510(1)$ Å, $b_0 = 12.750(1)$ Å, $c_0 = 9.010(1)$ Å at 270 K) [7].

A diffraction heating photograph at 293–1000 K was taken at a heating rate of 20 K h^{-1} in an N_2 atmosphere (quartz glass capillary, internal gold standard), using a modified high resolution Guinier camera, assembled from the Enraf–Nonius heating device. Thermoanalysis was carried out on a Netzsch STA 429 thermoanalyser (N_2 atmosphere, heating rate 1 K min^{-1} and 10 K min^{-1}) coupled with a mass spectrometer (Balzers QMG-511) as described by Eppler and Selhofer [10]. A Perkin–Elmer DSC-2 differential scanning calorimeter was used for the calorimetric measurements. A heating microscopic investigation of the single crystals was carried out on a Zeiss polarization microscope coupled with a Mettler FP84 heating device and a cooling arrangement with fluid nitrogen.

RESULTS

Phase transition

Curves from the differential scanning calorimetry (DSC) are given in Figs. 1(a) and 1(b) for the species grown at 573 K and 773 K respectively. Both curves indicate structural phase transitions in the temperature range 270–310 K. The different nature of the intermediate state of these higher order transitions is not yet clear. The transition temperature interval is in agreement with the polarization microscopic studies. Cooling below 270 K yields a domain structure, showing birefringence according to the symmetry reduction from the cubic to the orthorhombic form for both species of tetrahydroxoborate sodalite. The X-ray diffraction heating photograph (see Fig. 3) and the corresponding evaluation of the unit cell dimensions vs. temperature (see Fig. 4) indicate the existence of another high temperature form (HTII) of $Na_8[AlSiO_4]_6[B(OH)_4]_2$ at temperatures of 470–570 K (cubic symmetry, $a_0 = 9.044(1)$ Å). Thus the following transition scheme from low temperatures (LT) to higher temperatures (HT) can be proposed:

$$\text{LT form} \xrightarrow{270\text{K} \leqslant T \leqslant 310\text{K}} \text{HT form I} \xrightarrow{470\text{ K}} \text{HT form II}$$

X-ray powder diffraction data of the LT form at 270 K (orthorhombic symmetry, $a_0 = 25.510(1)$ Å, $b_0 = 12.750(1)$ Å, $c_0 = 9.020(1)$ Å) and of the high temperature form HTI at 310K (cubic symmetry, $a_0 = 9.010(1)$ Å) are given in ref. 7.

The nature of the structural phase transition of $Na_8[AlSiO_4]_6[B(OH)_4]_2$ shows some resemblance to that of the basic hydrosodalites $Na_8[AlSiO_4]_6(OH)_2 \cdot nH_2O$ [6,11,12], and as well the ferroic type of structural phase transition, as discussed in refs. 13–15 for aluminate sodalite, $Ca_8[Al_{12}O_{24}](WO_4)_2$. Accordingly, the structural phase transitions in the samples of tetrahydroxoborate sodalite originate from temperature-induced orientational order–disorder or dynamics of the intracage $[B(OH)_4]^-$ tetrahedra.

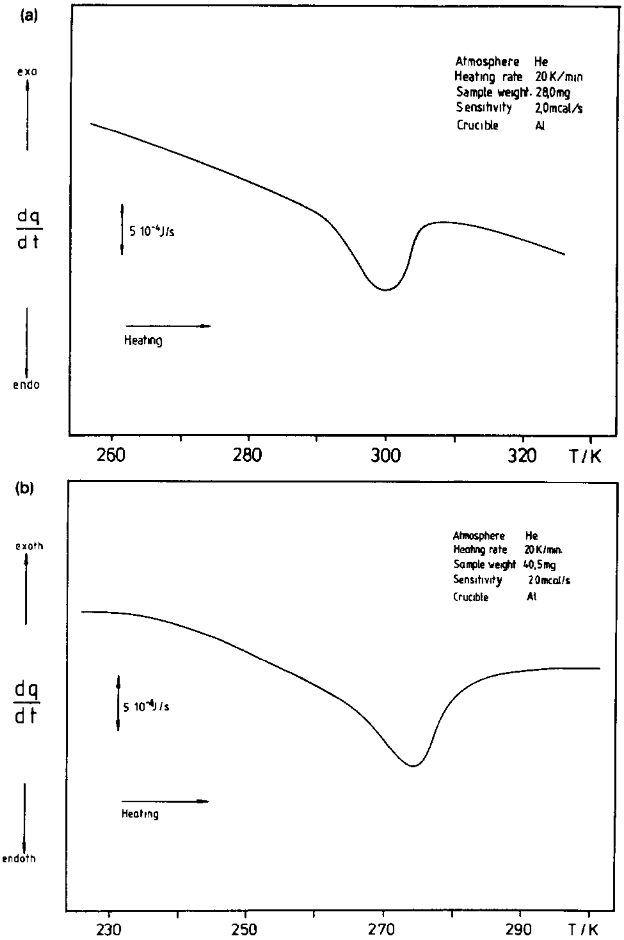

Fig. 1. The course of the heat flow (DSC) with temperature during the structural phase transitions of tetrahydroxoborate sodalite: (a) synthesised at 573 K and 100 MPa; (b) synthesised at 773 K and 150 MPa.

Thermal decomposition behaviour

Results of the simultaneous thermoanalysis and X-ray heating diffraction data on the thermal decomposition reaction of $Na_8[AlSiO_4]_6[B(OH)_4]_2$ are shown in Figs. 2 and 3. Because of the different heating rates and the open system conditions of the thermoanalytical method, the transition temperatures differ somewhat. During heating a two-step decomposition reaction takes place. In the temperature ranges 573–873 K (centre of gravity at 773 K) and 873 K–938 K (centre of gravity at 900 K) four molecules of H_2O are released owing to the total decomposition of the enclathrated tetrahydroxoborate anion, yielding a loss in weight of $\approx 7\%$:

$$Na_8[AlSiO_4]_6[B(OH)_4]_2 \xrightarrow{573-938\ K} 6NaAlSiO_4 + 2NaBO_2 + 4H_2O\uparrow$$

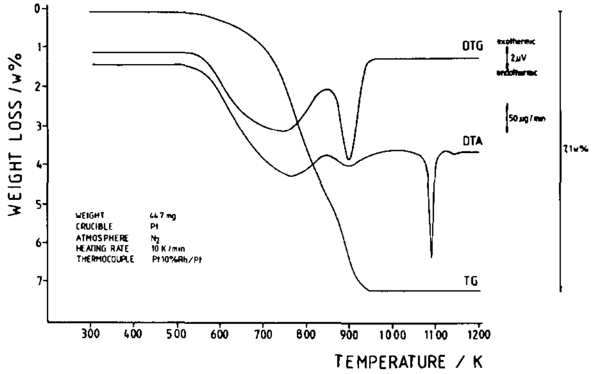

Fig. 2. Simultaneous thermoanalysis (TG (DTG)–DTA) of tetrahydroxoborate sodalite.

After the loss of about one water molecule out of the total number of four a significant change in the X-ray heating diffraction pattern takes place: new reflections appear at low 2θ values (Fig. 3). This observation as well as the single broad DTA and DTG signals indicate a complex continual phase transition during this decomposition step. The accompanying powder pattern could not be indexed to the usual cubic 9 Å cell but for instance to a pseudocubic cell of fourfold volume ($a_0 = 18.302(1)$ Å, $c_0 = 9.151$ Å; tetragonal).

Corresponding to the decomposition step at elevated temperatures the X-ray diffraction heating photograph shows drastic changes, indicating the destruction of the sodalite framework and the release of the imbibed salt species owing to the formation of a nepheline-like phase and sodium metaborate.

A characteristic variation of the unit cell volume results from the thermal decomposition process. At low temperatures up to 470 K the increase of the

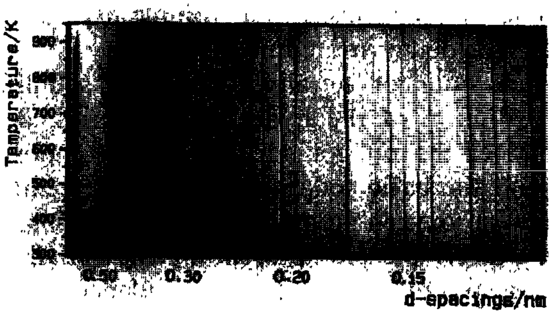

Fig. 3. X-ray diffraction heating photograph of tetrahydroxoborate sodalite (notice the conversion to a nepheline-like phase at elevated temperatures).

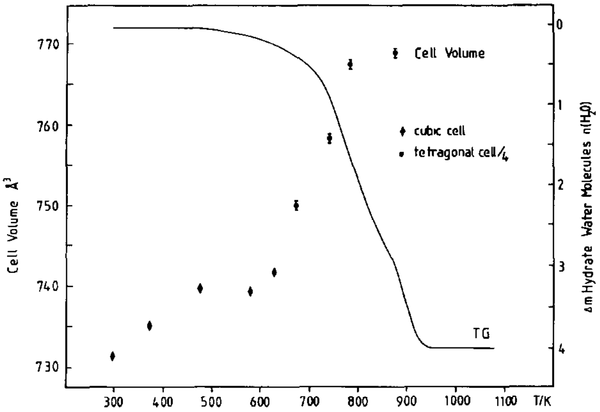

Fig. 4. The course of the unit cell volume on thermal decomposition of tetrahydroxoborate sodalite (heating rate for the thermogravimetry, 1 K min^{-1}; 0.33 K min^{-1} for the X-ray diffraction heating experiment).

volume is due to a linear expansion coefficient in the range of 10^{-5} K^{-1}, but a slight decrease could be observed in the subsequent 100 K interval. However, according to the DTG characteristics no loss in weight of the sample could be observed. From this behaviour, accompanied by diffuse reflections on the X-ray diffraction heating photograph, a further·cubic phase (HT form II, as described above) of the same composition ($Na_8[AlSiO_4]_6[B(OH)_4]_2$) but with orientational disorder of the $[B(OH)_4]^-$ tetrahedra can be postulated.

With the beginning of the first decomposition step at 573 K the unit cell volume increases slightly owing to the release of one water molecule out of the maximum number of three at the end of this step. During further decomposition within this step the unit cell volume increases drastically, as shown by the shift of the reflections to lower 2θ values and the appearance of new reflections described above. A formal comparison between the unit cell volume of the cubic cell of tetrahydroxoborate sodalite at 310 K and one-quarter of the tetragonal cell at 825 K yields a total volume expansion of 4.9% during the release of $3H_2O$, as demonstrated in Fig. 4.

The thermal decomposition behaviour of tetrahydroxoborate sodalite shows a resemblance to the dehydration of the hydrosodalite series, described in ref. 6. The authors explained the antagonistic thermal decomposition behaviour of the non-basic and the basic sodalites in terms of significant differences of interaction between oxygen atoms of the framework and oxygens of the imbibed hydrate water molecules. For non-basic sodalites X-ray Rietveld as well as neutron structure analysis gave evidence for a hydrogen bonding system between framework and non-framework oxygens [16,17]. The significant expansion of these sodalites during heating is due to the destruction of those hydrogen bonds [6]. As well as different O–H bond lengths of the hydrate water molecules such a bonding system also affects the Si–O–Al bond angle [17]. Similar bonding characteristics of the non-framework hydroxyl groups and framework oxygens may be inferred for tetrahydroxoborate sodalites from their thermal behaviour. A further analysis of the space-filling elements and the postulated hydrogen bonding system is in progress [18].

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