

The properties of salt-filled sodalites. Part 3. Synthesis and thermal behaviour of basic and non-basic carbonate enclathrated sodalites

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Abstract

Carbonate-enclathrated basic sodalite $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})(\text{CO}_3)_{0.5} \cdot 3\text{H}_2\text{O}$ has been synthesized under hydrothermal conditions at 353 K. According to the formation of cancrinite or intermediate phases between sodalite and cancrinite, the hydrothermal synthesis of sodalites with higher carbonate contents seemed to be impossible. To overcome these difficulties, a two-step anion exchange reaction at elevated temperatures in a CO_2 atmosphere has been established, using basic nitrite sodalite as a starting material. As a result of the exchange reactions, a non-basic water-free carbonate sodalite $\text{Na}_8[\text{AlSiO}_4]_6(\text{CO}_3)$ could be prepared.

In addition to the determination of the crystal data of both new sodalites, their IR and MAS-NMR spectroscopic patterns and their thermal decomposition behaviour have been investigated. High-temperature Guinier-Simon photographs reveal the onset of a maximal framework expansion for the non-basic carbonate sodalite, whereas a decrease in the unit-cell volume could be observed for the basic sample at elevated temperatures. This thermal behaviour indicates special but different host-guest interactions for both phases due to the dynamics of the enclosed guest ions.

INTRODUCTION

Thorough investigations of several sodalite compounds have indicated that these tectosilicates could be applied as model systems for “reservoir minerals” because of their large variety of chemical composition resulting from cation exchange, substitution of framework atoms or extended formation of solid solutions [1–6]. In particular, the enclathration of hazardous components from waste materials or reactions with waste gases, such as carbon dioxide, and the resulting gas incorporation into the [4⁶⁶⁸] cages of sodalites can be regarded as a versatile tool for materials science and waste management [7].

Some earlier studies on hydrothermal synthesis in the presence of carbonate anions have been published [8–10], but most of the experimental

work was carried out on the crystallization of cancrinites or of intermediate phases between cancrinites and sodalites.

In order to obtain more information on the hydrothermal enclathration of sodium carbonate into the β -cages of sodalite, hydrothermal synthesis in the $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{Na}_2\text{CO}_3-\text{H}_2\text{O}$ system was carried out. The thermal decomposition behaviour of the obtained products has been studied using simultaneous thermal analysis, as well as high-temperature X-ray powder diffraction and spectroscopic measurements. As well as IR spectroscopy, MAS-NMR was employed for further characterization of the new phases.

An alternative method of synthesizing carbonate-imbibed sodalite is the high-temperature anion exchange reaction of basic nitrite sodalite in a CO_2 atmosphere, which is a suitable method for the formation of water-free carbonate sodalite. The starting material was selected according to the well-known thermal properties of basic nitrite sodalite [7]. The anion exchange reaction within the sodalite cages is a result of the combination of two different types of guest molecules in the starting sodalite, "reactive" molecules ($\text{NaOH} \cdot \text{H}_2\text{O}$) and "inert" molecules (NaNO_2).

EXPERIMENTAL

Synthesis

The hydrothermal runs were carried out at low temperatures and pressures in the $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{Na}_2\text{CO}_3-\text{H}_2\text{O}$ system, using 50 ml teflon-lined steel autoclaves heated up to 353 or 473 K (with a resulting autogeneous pressure of up to 10.0 MPa). They were filled with 1 g of kaolinite (Fluka 60609) and 45 ml of an 8 M NaOH solution (Merck 6495; carbonate impurities $\geq 1\%$), freshly prepared under open system conditions. In a second series of runs, 0.53 g of sodium carbonate (Merck 6392) was added to the initial materials. After a reaction time of 24 h, the powdery products were washed with water and dried at 353 K.

For the high-temperature anion exchange reactions, a polycrystalline sample of composition $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH} \cdot \text{H}_2\text{O})(\text{NO}_2)$ was used as the starting material. This basic nitrite sodalite was grown hydrothermally as described in ref. 7. The high-temperature exchange reaction was carried out in a two-step heating process in a flowing CO_2 atmosphere (4.6 l h^{-1}) on a Mettler TA 146 thermoanalyser, first at 973 K for up to 1 h, followed by a second step at 1073 K for another hour.

In addition, ^{29}Si -MAS-NMR spectra of the initial sample and the resulting carbonate-containing product were recorded on a Bruker CXP-300 spectrometer in order to detect any structural deviations resulting

during heating. The spectra were recorded with a multinuclear double-bearing probehead. Chemical shifts were referenced to TMS = 0 ppm with Q_8M_8 (trimethyl-silylester of double four-ring silicate) as an intermediate reference.

Characterization

All the polycrystalline samples were prepared for subsequent X-ray powder diffraction studies, using the Guinier technique (Cu $K\alpha_1$ radiation, internal Si standard, LSQS refinement of the unit-cell parameter and determination of the relative intensities by densitometry). The chemical composition of the aluminosilicate framework of the samples (the Si/Al ratio) was determined from the chemical shifts in the ^{29}Si -MAS-NMR spectra according to the method given by Engelhardt et al. [11]. The concentration of the guest molecules were analysed by thermogravimetry in combination with stepwise IR spectroscopy to distinguish between OH^- , H_2O and CO_3^{2-} .

The thermal decomposition behaviour of the new sodalite phases was followed by simultaneous thermal analysis on a Mettler TA 146 thermo-analyser, including thermogravimetry (TG), differential thermal analysis (DTA) and differential thermogravimetry (DTG). High-temperature X-ray powder diffractometry was also performed, using the Enraf-Nonius Guinier-Simon camera (Cu $K\alpha_1$ radiation).

RESULTS

Hydrothermal synthesis of basic carbonate sodalite hydrate

The hydrothermal runs clearly indicate the structure-controlling role of the carbonate concentration in the initial materials. Sodalite formation is favoured by very small concentrations of carbonate anions in the starting mixtures. The 8 M NaOH used for the hydrothermal runs was freshly prepared under open system conditions and contained carbonate impurities of >1%. These low carbonate levels allow the formation of carbonate-imbibed basic sodalite at a temperature of 353 K. Higher concentrations of carbonate always lead to formation of the cancrinite structure or to crystallization of phases intermediate between sodalite and cancrinite according to stacking errors [9,10]. The best reaction conditions for formation of a basic carbonate sodalite of composition $\text{Na}_8[\text{AlSiO}_4]_6$

(OH)(CO₃)_{0.5} · 3H₂O can be estimated as a temperature of 353 K, autogeneous pressure and a duration of 24 hours.

Using these mild reaction conditions, the products were always obtained as white polycrystalline powders. The grain size of the polycrystallites was around 1.0 μm. The X-ray powder data of basic carbonate sodalite Na₈[AlSiO₄]₆(OH)(CO₃)_{0.5} · 3H₂O are summarized in Table 1(a).

TABLE 1

The X-ray powder data of basic and non-basic carbonate sodalites

<i>h</i>	<i>k</i>	<i>l</i>	2θ _{obs} (deg)	<i>d</i> _{obs} (Å)	<i>I</i> / <i>I</i> ₀ (%)	<i>h</i>	<i>k</i>	<i>l</i>	2θ _{obs} (deg)	<i>d</i> _{obs} (Å)	<i>I</i> / <i>I</i> ₀ (%)
(a) Basic carbonate sodalite hydrate, Na ₈ [AlSiO ₄] ₆ (OH)(CO ₃) _{0.5} · 3H ₂ O, cubic, <i>a</i> ₀ = 8.900(1) Å											
1	1	0	14.039	6.303	83	4	4	2	62.569	1.483	16
2	1	1	24.479	3.634	100	6	0	0			
3	1	0	31.749	2.816	54	5	3	2	64.477	1.444	13
2	2	2	34.987	2.569	66	6	1	1			
3	2	1	37.783	2.379	21	5	4	1	68.239	1.373	12
3	3	0	43.081	2.098	53	6	2	2	70.086	1.342	10
4	1	1				6	3	1	71.904	1.312	6
3	3	2	47.905	1.897	6	4	4	4	73.669	1.285	8
4	2	2	50.173	1.817	18	5	5	2	79.004	1.211	13
4	4	0	58.624	1.573	22	6	3	3			
4	3	3	60.618	1.526	24	7	2	1			
5	3	0									
(b) Non-basic carbonate sodalite Na ₈ [AlSiO ₄] ₆ (CO ₃), cubic, <i>a</i> ₀ = 8.996(1) Å											
1	0	0	9.879	8.947	9	5	2	1	55.984	1.641	9
1	1	0	13.917	6.358	85	4	4	0	57.942	1.590	35
2	0	0	19.720	4.498	13	5	3	0	59.906	1.543	26
2	1	0	22.072	4.024	7	4	3	3			
2	1	1	24.210	3.673	100	6	0	0	61.829	1.499	20
2	2	0	28.039	3.180	5	4	4	2			
3	0	0	29.772	2.998	6	6	1	1	63.716	1.460	25
2	2	1				5	3	2			
3	1	0	31.412	2.846	62	6	2	0	65.595	1.422	5
2	2	2	34.496	2.598	84	5	4	1	67.409	1.388	11
3	2	0	35.950	2.496	7	6	2	2	69.193	1.357	30
3	2	1	37.363	2.405	25	6	3	1	70.981	1.327	11
4	0	0	40.040	2.250	12	4	4	4	72.762	1.299	15
4	1	1	42.596	2.121	60	7	1	0	74.517	1.272	8
3	3	0				5	5	0			
4	2	2	49.598	1.837	12	7	2	1	77.983	1.224	26
5	1	0	51.770	1.764	44	6	3	3	79.688	1.202	6
4	3	1				6	4	2			
4	3	2	54.920	1.670	5	7	3	0			
5	2	0									

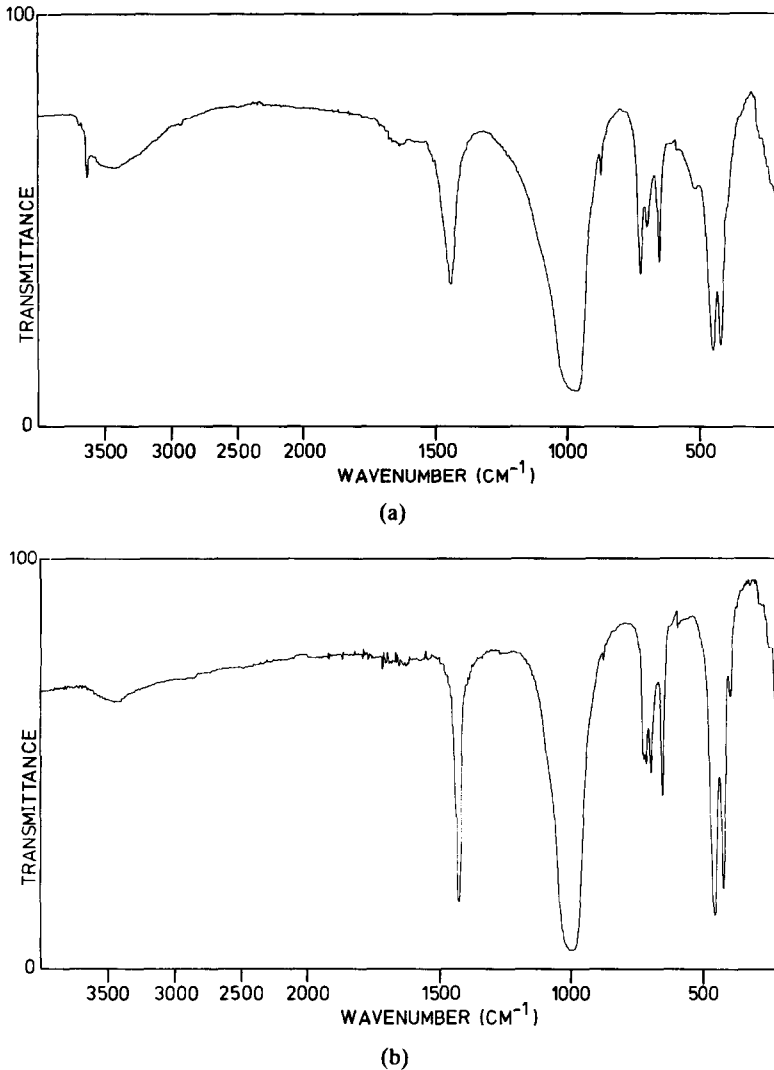


Fig. 1. IR absorption spectra of carbonate sodalites: (a) $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})(\text{CO}_3)_{0.5} \cdot 3\text{H}_2\text{O}$ (basic carbonate sodalite hydrate); (b) $\text{Na}_8[\text{AlSiO}_4]_6(\text{CO}_3)$ (non-basic carbonate sodalite).

The concentration of the guest species carbonate, water and hydroxide, were calculated from thermogravimetry (see Fig. 3(a), below). The IR spectroscopic characterization of the products also reveal the different amounts of the enclathrated guest species, as shown in Fig. 1(a) for $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})(\text{CO}_3)_{0.5} \cdot 3\text{H}_2\text{O}$: absorption bands at 3640 cm^{-1} , (OH^-); $3600\text{--}3000\text{ cm}^{-1}$ and 1650 cm^{-1} (H_2O); and 1450 and 880 cm^{-1} (CO_3^{2-}). The vibrations of the aluminosilicate framework are typical for sodalite, as described by Henderson and Taylor [12].

In addition to the structural information obtained from IR spectroscopic data, the ^{29}Si -MAS-NMR spectra of basic carbonate sodalite are shown in

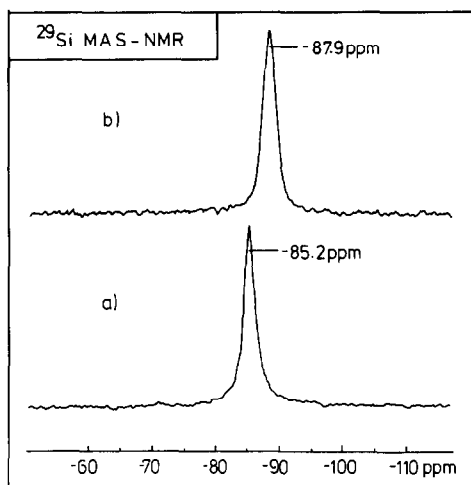
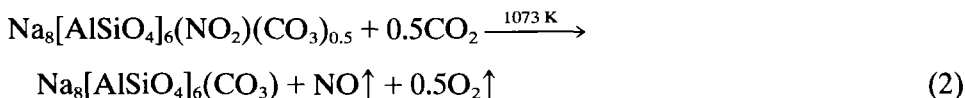
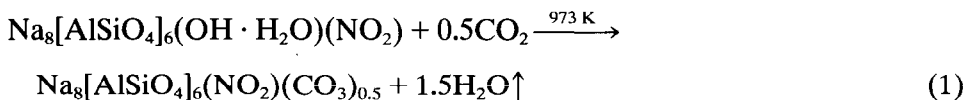


Fig. 2. ^{29}Si -MAS-NMR spectra of the carbonate sodalites: (curve a) basic carbonate sodalite hydrate, obtained from hydrothermal synthesis; (curve b) non-basic carbonate sodalite from the high-temperature anion exchange experiment.

Fig. 2(a). The single peak with a chemical shift of $\delta = -85.2$ ppm clearly indicates the alternating ordering of the Si and Al atoms in the TO_4 -sodalite frameworks, i.e. Si(4Al) units [11]. The chemical shift also correlates well with the unit-cell parameter.

Formation of non-basic carbonate sodalite $\text{Na}_8[\text{AlSiO}_4]_6(\text{CO}_3)$ by high-temperature anion exchange reactions

The high-temperature anion exchange reaction in a CO_2 atmosphere led to the formation of a non-basic carbonate sodalite according to the reaction steps



Stepwise IR spectra of the product after the first and second reactions clearly indicate the decomposition of the guest molecules $\text{NaOH} \cdot \text{H}_2\text{O}$ during the first step and the imbibition of carbonate. At elevated temperatures during the second reaction step, the decomposition of the nitrite occurs accompanied by further carbonate enclathration.

The X-ray powder data of this new carbonate-intercalated sodalite are

given in Table 1(b). Unlike the basic carbonate sodalite hydrate, a (100) reflection can be observed for the non-basic phase. This indicates a nosean-like alternating arrangement of the divalent carbonate anions in 50% of the sodalite cages, with the remaining 50% of the cages unfilled. The non-basic, anhydrous character of the new sodalite phase $\text{Na}_8[\text{AlSiO}_4]_6(\text{CO}_3)$ can be seen from the IR spectrum in Fig. 1(b).

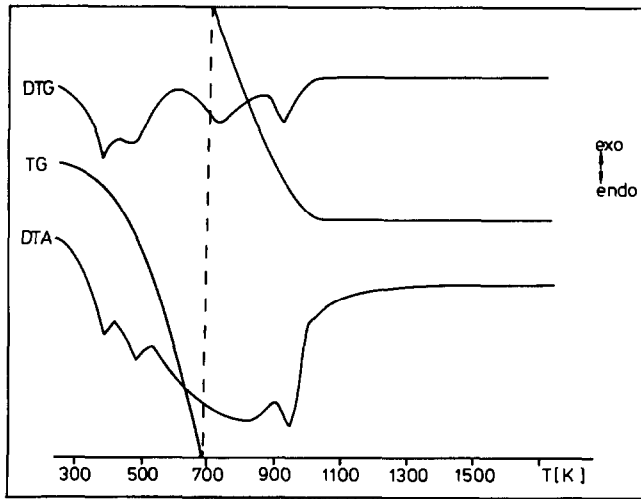
In addition to the structural information from the X-ray powder data as well as from the IR investigation, the ^{29}Si -MAS-NMR spectrum of the non-basic carbonate sodalite is shown in Fig. 2(b). The single peak with a chemical shift of $\delta = -87.8$ ppm indicates the alternating ordering of the Si and Al atoms in the TO_4 -framework, i.e. Si(4Al) units [11]. As already described for the hydrothermally grown basic carbonate sodalite hydrate, the chemical shift also correlates well with the unit-cell parameter. The singlet in the NMR spectrum also provides evidence for the unchanged sodalite framework, with Si/Al = 1.0 after the heating procedure.

Thermal decomposition reactions (Ar atmosphere)

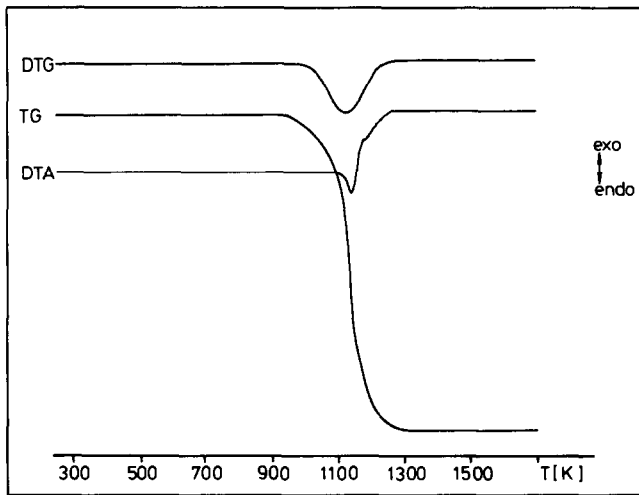
Basic carbonate sodalite hydrate

The results of the simultaneous thermoanalysis of basic carbonate sodalite in an Ar atmosphere are given in Fig. 3(a). During heating up to the total collapse of the sodalite structure, a complex decomposition reaction occurs in the temperature region between 373 and 1123 K. Exclusively endothermic reaction steps can be observed accompanied with the loss of water molecules, hydroxyl groups and carbon dioxide. Thermal decomposition starts over a relatively wide temperature range from 373 to 793 K with the dehydration of the sample. Here two water molecules are lost at low temperatures up to 493 K, followed by loss of another H_2O molecule at 793 K (DTA maximum). This decomposition from a basic carbonate sodalite hydrate to a water-free hydroxycarbonate sodalite seems to be a complex reaction with higher activation energies than for the thermal loss of zeolitic water only from common hydrosodalites [3]. The total loss in weight from the two steps is 5.4 wt.% (thermogravimetry). The dehydration reactions are followed by two further thermal events at higher temperatures. In the temperature interval 966–1023 K, an overlapping of the thermal dehydroxylation and the carbonate decomposition can be obtained together with the total collapse of the sodalite structure.

The thermal decomposition has also been studied by high-temperature X-ray powder diffraction. The change in the lattice parameter during heating, calculated from a Guinier–Simon film, is shown in Fig. 4(a). During the dehydration reaction and the loss of two of the three water molecules, the sodalite framework partly collapses, as shown by the significant shift in the reflections on the Guinier–Simon film. This drastic



(a)



(b)

Fig. 3. Simultaneous thermal analysis of carbonate sodalites (argon atmosphere; heating rate 8 K min^{-1}): (a) $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})(\text{CO}_3)_{0.5} \cdot 3\text{H}_2\text{O}$ (basic carbonate sodalite hydrate; weight 115 mg); (b) $\text{Na}_8[\text{AlSiO}_4]_6(\text{CO}_3)$ (non-basic carbonate sodalite; weight 91 mg).

shrinkage of the cell volume seems to be closely related to the thermal behaviour of carbonate-free basic sodalites [3] during their dehydration. The resulting anhydrous form of composition $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})(\text{CO}_3)_{0.5}$ shows only linear thermal expansion and no variation in the cell volume by the tilt mechanism of the flexible sodalite framework [3, 13].

At elevated temperatures, the totally new pattern of a stuffed carnegieite phase $(\text{Na}_2\text{O})_{1/6}\text{NaAlSiO}_4$ [14] can be observed, followed by the reflections of a nepheline-like phase on the Guinier–Simon film.

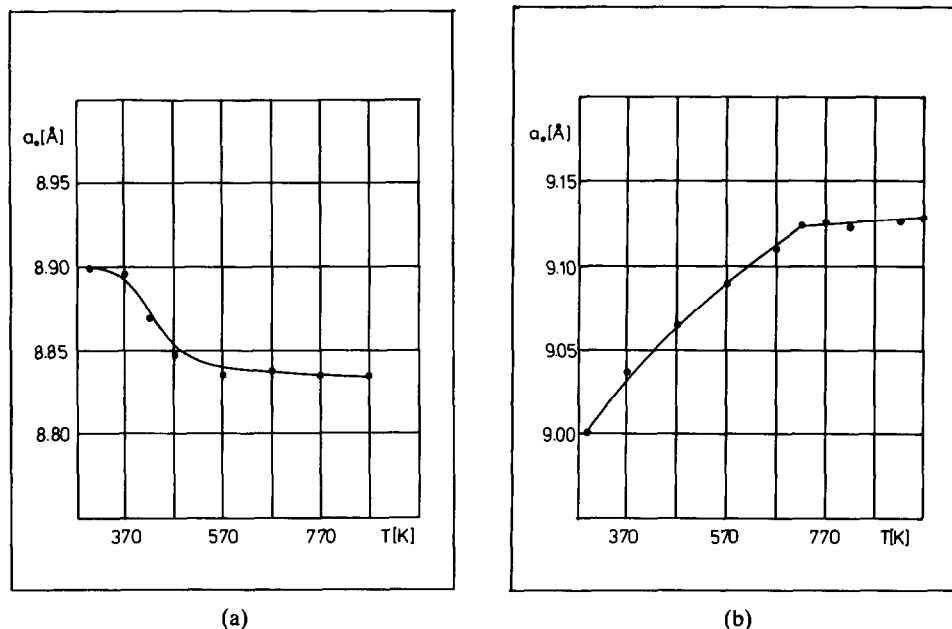
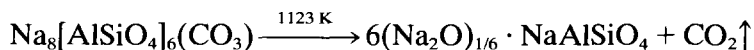


Fig. 4. The change in the unit-cell parameter during the thermal decomposition, calculated from the Guinier–Simon film (heating rate 0.3 K min^{-1}): (a) $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})(\text{CO}_3)_{0.5} \cdot 3\text{H}_2\text{O}$ (basic carbonate sodalite hydrate); (b) $\text{Na}_8[\text{AlSiO}_4]_6(\text{CO}_3)$ (non-basic carbonate sodalite).

Non-basic carbonate sodalite $\text{Na}_8[\text{AlSiO}_4]_6(\text{CO}_3)$

The thermogram of non-basic carbonate sodalite $\text{Na}_8[\text{AlSiO}_4]_6(\text{CO}_3)$ is shown in Fig. 3(b). From this figure, as well as the results of the high-temperature X-ray diffraction experiment given in Fig. 4(b), a totally different thermal behaviour can be observed compared with that of the basic carbonate sodalite hydrate. $\text{Na}_8[\text{AlSiO}_4]_6(\text{CO}_3)$ has a higher thermal stability up to 973 K in argon. At elevated temperatures, decomposition occurs in a one-step endothermic reaction with a DTA maximum at 1123 K



Here the decomposition of the enclathrated carbonate is accompanied by the total destruction of the sodalite framework and the formation of a “stuffed” carnegieite, which transforms into nepheline at higher temperatures. In addition to these thermal transitions, the changes in the Guinier–Simon film indicates a discontinuity of the thermal expansion of the sodalite framework near 873 K without any weight loss of the sample. Here the sodalite framework achieves its fully expanded state, as can be seen from the variation of the unit-cell parameter shown in Fig. 4(b). Thereafter the framework expansion is only due to the linear thermal expansion of Si–O and Al–O bonds, and it is much lower than the expansion by the tilt mechanism. This behaviour is reminiscent of the

nitrate sodalites [15] and is also well known for sodalites containing large cage anions, such as nosean or hauyne, as described by Henderson and Taylor [13].

CONCLUSION

The investigations on the formation and thermal decomposition reactions of carbonate sodalites described here may answer some questions posed in intra-zeolite chemistry: zeolites A, X and Y also consist of sodalite cages as the basic structural building-units. The sodalites can be regarded as a model system in the study of “pure β -cage reactions” of zeolites. Moreover, a knowledge of the results is essential for zeolite synthesis in the presence of carbonate impurities in the mother liquor.

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