

Jerzy FIJAŁ *, Marek TOKARZ *

CRYSTALLOCHEMICAL PROPERTIES OF SYNTHETIC OH- AND Cl-FORMS OF SODALITE

UKD 549.621.56.07.08+54—36:549.621.56.07.08+546.13]:548.3:546.04

Abstract. Some crystallochemical properties of OH- and Cl-forms of sodalite obtained by direct synthesis from pure components and by way of transformation of kaolinite in an alkaline medium were compared, and the differences between these forms were noted.

It has been found that the presence of Cl⁻ ions in the crystal lattice of sodalite increases the degree of its crystalline perfection. This fact has been attributed to the crystal field symmetry round these anions.

The thermal behaviour of the two forms has also been found to be different. The calcination of OH-sodalite is attended with a considerably greater weight loss than the calcination of Cl-form. This can be partly accounted for by the hydrophilic nature of OH-form and the thermal dissociation of OH groups, and partly by the presence of a phase with the structure close to cancrinite in the reaction products, i.e. a phase with larger channel diameters. Slow dehydration of the Cl-form of sodalite at 200—400°C leaves nothing but water molecules, referred to as residual H₂O, strongly coordinated by sodium cations, in cavities of the sodalite framework. The electric field of cations is responsible for the dissociation of H₂O molecules with the formation of H₃O⁺ ions. The presence of the latter was detected with spectroscopic methods.

It has also been found that the OH- and Cl-forms of sodalite show different stability in an aqueous medium. Intense washing of OH-sodalite with water results in the partial removal of Na⁺ ions and transformation of this form into hydrosodalite (H₂O-sodalite).

INTRODUCTION

Sodalite belongs to the group of feldspathoids, i.e. framework aluminosilicates, the structure of which is more readily accessible to foreign ions and molecules than the structure of feldspars. The lattice of feldspathoids has cavities into which fit complementary cations, as well as non-stoichiometric "excess" cations and anions and water molecules. On account of their ion-exchange and sorption properties, these minerals have also been assigned to zeolites.

* Institute of Geology and Mineral Deposits, Academy of Mining and Metallurgy in Cracow (Kraków, al. Mickiewicza 30).

The list of samples and the conditions of synthesis

Sample symbol	Kind of non-stoichiometric ions	Starting materials	Intensity of washing with water
S - 16 a	Na ⁺ Cl ⁻ }	silica sol	cold washed
S - 16 b	Na ⁺ Cl ⁻ }	+ sodium aluminate + NaOH + NaCl + H ₂ O	hot washed
S - 17 a	Na ⁺ Cl ⁻ }	silica sol	cold washed
S - 17 b	Na ⁺ Cl ⁻ }	+ sodium aluminate + NaOH + H ₂ O	hot washed
K - 3 a	Na ⁺ Cl ⁻ }	kaolinite (Kalno)	cold washed
K - 3 b	Na ⁺ Cl ⁻ }	+ NaOH + H ₂ O	hot washed
K - 14 a	Na ⁺ Cl ⁻ }	kaolinite (Kalno)	cold washed
K - 14 b	Na ⁺ Cl ⁻ }	+ NaOH + NaCl + H ₂ O	hot washed

The framework of sodalite is made up of alternate $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra linked by sharing oxygen atoms in such a way that they form a truncated octahedron bounded by tetra- and hexagonal rings, respectively 1.5 and 2.3 Å in diameter. There are cavities in this framework, and Cl^- anions usually fit into their centre. Na^+ cations, compensating for the framework negative charge that results from the Si/Al substitution in the tetrahedra, and balancing the Cl^- charge, are distributed in the hexagonal rings and surround these anions (Lons, Shultz 1967; Taylor, Henderson 1978).

Synthesis from strongly alkaline solutions gives hydroxysodalite (OH-sodalite), which contains OH^- groups and water molecules in place of excess Cl^- anions (Barrer et al. 1968). Up till now the studies of sodalite have concentrated mainly on the description of its structure, while its crystallochemical properties or the presence and effect of non-stoichiometric "excess" cations and anions on these properties have aroused less interest (Barrer et al. 1968; Barrer, Cole 1970; Shipper, Lauthouwers 1972). The reason for this is presumably the fact that the size of the "cage" as well as of the channels and windows in the structure of sodalite severely limits the possibilities of exchange and diffusion of these non-stoichiometric "excess" cations and the modification of their composition. It should be made clear that non-stoichiometric "excess" cations are here understood to mean those Na^+ ions that are present in the structure of sodalite not because they have to compensate for the negative charge on its framework resulting from the Si/Al substitution, but because they balance the charge on Cl^- anions that are in the centre of the sodalite cage. Barrer (1970) defines these ions as salt "inclusions" in the structure of sodalite.

There have been attempts to exchange the "excess" ions without changing the structural parameters of sodalite (Barrer et al. 1968; Barrer, Cole 1970). Na^+ cation can only be exchanged for Li^+ as the ionic radii of other cations are too large. More difficult still is anion exchange because the diffusion of so large ions from inside the sodalite cage is virtually impossible. Different anionic forms of sodalite have been obtained, but this has been accomplished not by ion exchange but by the introduction of various anions into the mixture of initial components. The modifications obtained in this way contained "excess molecules" of the following salts: NaBr , NaJ , NaClO_3 , NaClO_4 , Na_2WO_4 , Na_3PO_4 .

The purpose of this paper is to explain the structural function of "excess" cations and anions in the structure of sodalite. The investigations to be described here were an attempt to elucidate the role of Cl^- ion, and particularly its effect on the symmetry and ordering of the structure of Cl-sodalite. The considerations were based on the results of X-ray, IR spectroscopic and chemical analysis. Since some forms of sodalite are subject to hydrolysis, this phenomenon was also investigated, and so were structural changes accompanying the calcination of synthetic sodalite.

MATERIALS AND METHODS

Investigations were carried out on samples of synthetic OH- and Cl-sodalite obtained by synthesis from pure chemical components and through alkaline transformation of kaolinite from the Kalno deposit

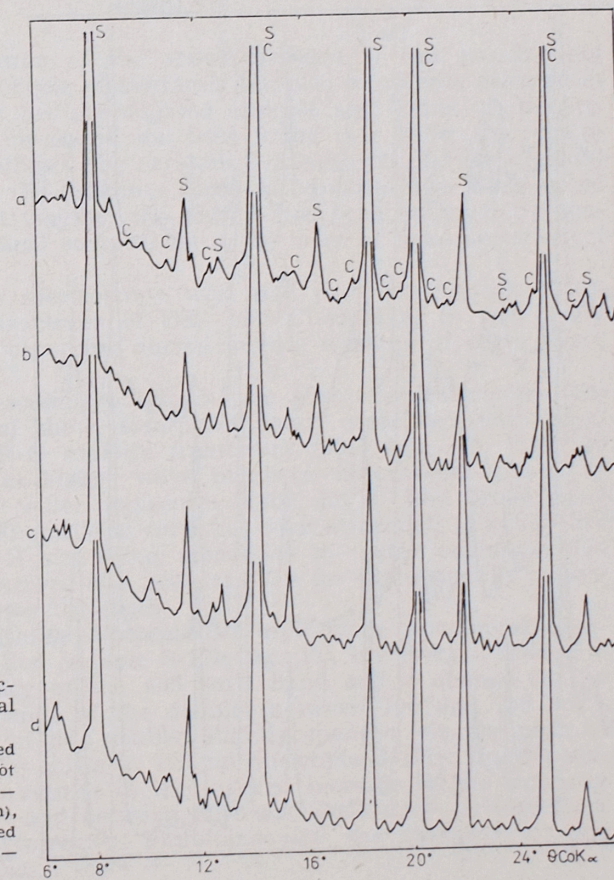


Fig. 1. X-ray diffraction patterns of artificial OH- and Cl-sodalite
 a - S-17a (cold washed OH-form), b - S-17b (hot washed OH-form), c - S-16a (cold washed Cl-form), d - S-16b (hot washed Cl-form). S - sodalite; C - cancrinite

(Lower Silesia). The conditions of synthesis were described in a paper of Tokarz (1978). After the completion of synthesis, all samples were separated from solution and cold washed with distilled water. Then the samples dried at room temperature were divided into two parts, one of which was at once subjected to investigations while the other was intensely hot washed again with distilled water and dried at room temperature. The list of samples and their symbols are given in Table 1.

The products of syntheses were identified with X-ray and IR spectroscopic methods as sodalite (figs. 1, 2). Samples K-3a, b and K-14a, b have also been found to contain a small admixture of unaltered mica (illite) (fig. 2).

X-ray powder patterns were recorded with a TUR-M-61A diffractometer, using Fe-filtered $\text{CoK}\alpha$ radiation ($\lambda=1.78892 \text{ \AA}$). Minerals were identified on the basis of ASTM data. Also crystallite size was determined by Laue's method involving half-width measurements.

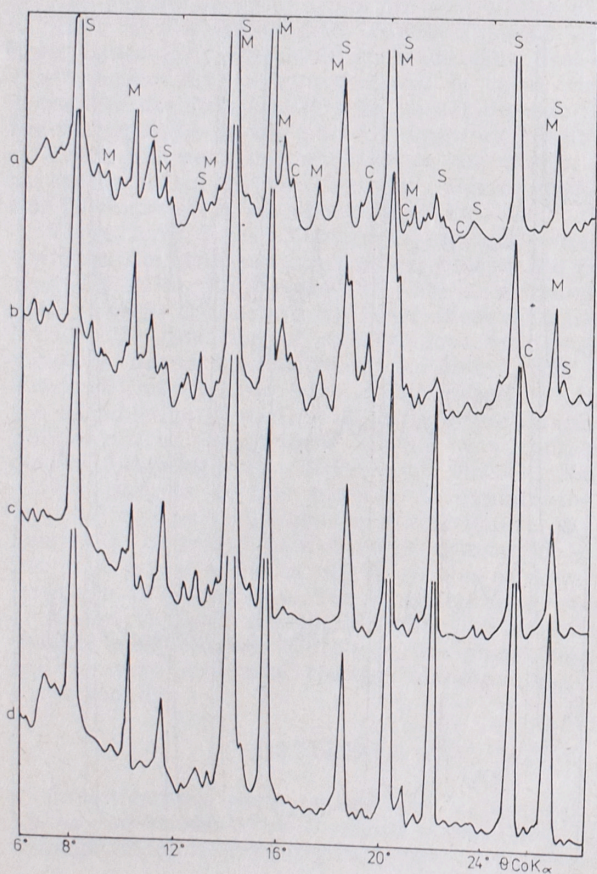


Fig. 2. X-ray diffractograms of OH- and Cl-sodalite obtained by alkaline transformation of kaolinite from the Kalno deposit (Lower Silesia)

a — K-3a (cold washed OH-form), b — K-3b (hot washed OH-form), c — K-14a (cold washed Cl-form), d — K-14b (hot washed Cl-form). S — sodalite; C — cancrinite; M — mica/illite

Infrared absorption spectra were obtained with a C. Zeiss UR-10 spectrometer, using two measuring techniques that required two different kinds of samples. In one case samples prepared in KBr discs were used, and spectra were recorded between 400—1800 and 3000—3800 cm^{-1} . In order to investigate the behaviour of sodalite during calcination at 20—600°C, samples were prepared in the form of thin self-supporting films obtained by pressing the material to be studied, and placed in a high-temperature vacuum absorption cell ensuring a vacuum of 10^{-3} mm Hg . Spectra were recorded at room temperature after the samples had been heated at 150, 300, 450, 500 and 580°C. Each sample was heated at the given temperature until the successively recorded spectra did not show any changes in shape. Infrared spectra were recorded in the ranges 1300—1800 and 3000—3800 cm^{-1} .

The following methods of chemical analysis were used: gravimetric analysis for SiO_2 , complexometric titration with EDTA for Al_2O_3 , Volhard titrimetry for Cl, and flame photometry for Na. Water content was calculated from TG curve.

RESULTS

Due to the application of the above methods, it was possible not only to identify the products of synthesis but also to observe differences or similarities between the investigated samples and forms of sodalite. As regards the crystallite size, it has been found that under the comparable conditions of synthesis, the crystallite size in the Cl-form of sodalite is larger than in OH-sodalite. These differences have been noted irrespective of the fact whether the sample has been obtained by synthesis from pure chemical components or by way of transformation of kaolinite.

Infrared absorption spectroscopy was used to observe subtle differences between the structures of OH- and Cl-sodalite, as well as to describe the processes occurring during intense washing of these forms with water.

The spectra of OH-sodalite obtained from pure chemical components (sample S-17a, fig. 3a) show absorption bands associated with basal vibrations of the Al-Si-O sodalite framework (435, 465, 665, 710, 738 and 1000 cm^{-1}) and, at higher wave numbers, absorptions caused by bending vibrations of water molecules (1660 cm^{-1}). The broad band appearing between 3000 and 3650 cm^{-1} has been attributed to symmetric and antisymmetric O-H stretching vibrations in water molecules. On the slope of this band there is a peak at 3639 cm^{-1} , presumably caused by OH^- groups occupying the cages.

The intense hot washing of sample S-17a produces pronounced changes in infrared absorption (sample S-17b, fig. 3b), involving a reduction in the relative intensity of the 435 cm^{-1} band and a change in the mutual intensity of bands of the doublet between 700 and 750 cm^{-1} . The position of bands of this doublet slightly changes, viz. the peak at 740 cm^{-1} (sample S-17a) shifts to 735 cm^{-1} (sample S-17b). Intense washing with water also results in the marked increase in the intensity of bands at 1660 cm^{-1} and between 3000 and 3650 cm^{-1} , arising from vibrations of water molecules. Simultaneously the intensity of the 3630 cm^{-1} band decreases.

The chemical composition of the samples (%)

Sample No	SiO ₂	Al ₂ O ₃	Na ₂ O	Cl	H ₂ O	Si/Al	Stoichiometric Na ⁺	Non-stoichiometric	Sum of Na ⁺ ions
S — 17 a	34.44	29.59	24.12	—	11.70	1.03	13.34	4.55	17.89
S — 17 b	33.73	29.51	22.20	—	12.96	1.01	13.30	3.17	16.47
S — 16 a	36.03	29.49	25.71	8.92	1.7	1.08	13.28	5.79	19.07
S — 16 b	35.72	29.37	25.22	8.43	2.15	1.07	13.24	5.47	18.71
K — 3 a	34.88	30.81	21.18	—	11.93	0.99	13.89	1.82	15.71
K — 3 b	32.25	28.88	18.95	—	12.80	0.98	13.02	1.04	14.06
K — 14 a	35.88	27.87	24.62	8.8	3.10	1.13	12.56	5.71	18.27
K — 14 b	36.00	28.33	24.92	8.8	3.20	1.12	12.78	5.71	18.49

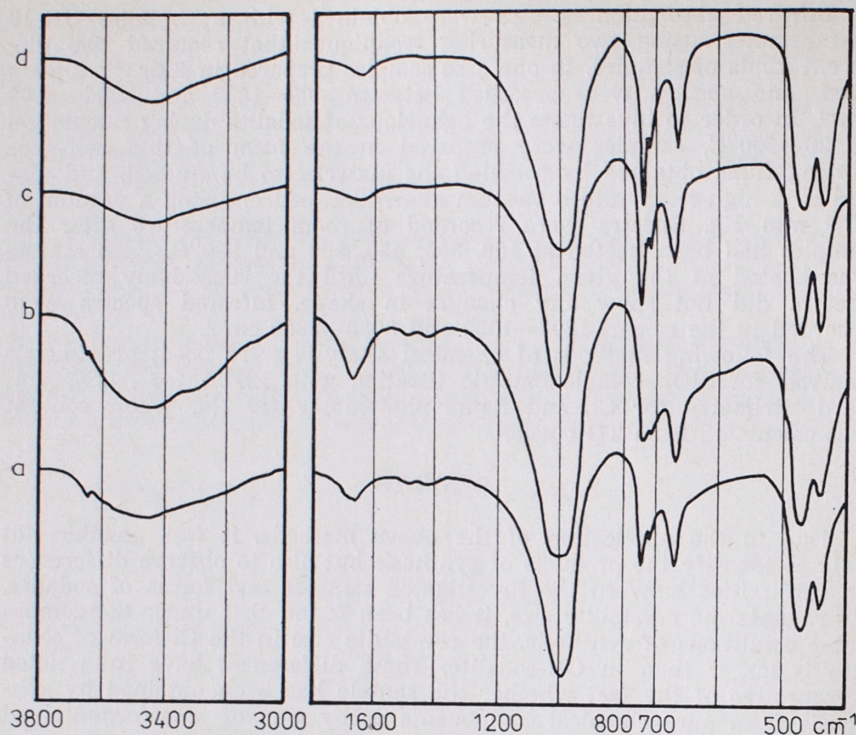


Fig. 3. Infrared spectra of artificial OH- and Cl-sodalite obtained using KBr discs technique

a — S-17a (cold washed OH-form), b — S-17b (hot washed OH-form), c — S-16a (cold washed Cl-form), d — S-16b (hot washed Cl-form)

The differentiation of OH-sodalite spectra, depending on the intensity of washing with water, has been attributed to the reactions of hydrolysis causing partial removal of Na⁺ cations loosely bound to the framework and their replacement by protons. The phenomenon of hydrolysis was also observed by Ward (1971) for some cationic forms of zeolites. The results of chemical analyses also lend support to this inference because it has been found that the content of non-stoichiometric "excess" Na⁺ cations in OH-sodalite samples intensely hot washed with water decreases compared with the cold washed samples (Table 2).

Infrared spectra of the products of transformation of kaolinite (sample K-3 and K-14, fig. 4) differ markedly from the spectra of products obtained by synthesis of sodalite from pure components (samples S-16 and S-17, fig. 3). The latter display additional absorptions from (CO₃)²⁻ anions at 1412 and 1475 cm⁻¹ and bands arising from Si-O and Al-O vibrations in the region between 500 and 700 cm⁻¹ (560, 620, 635 and 695 cm⁻¹). A pronounced change has also been noted in the shape of the doublet caused by ν₄ vibrations of sodalite (435 and 465 cm⁻¹), due to additional absorption in this range. This change has been attributed

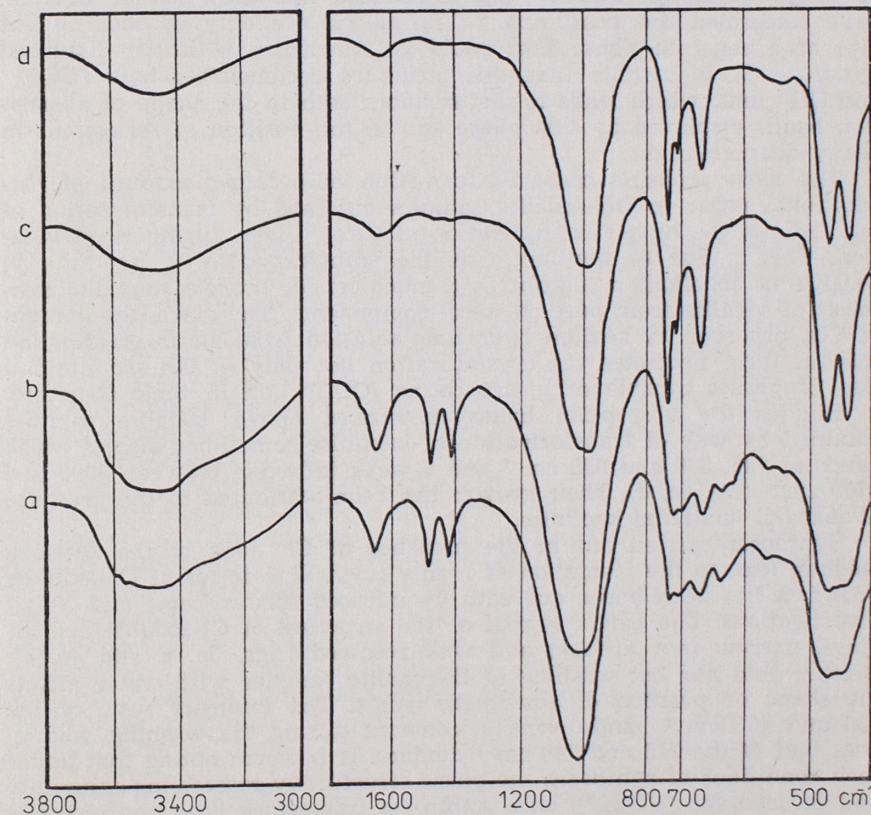


Fig. 4. Infrared spectra of OH- and Cl-sodalite obtained by alkaline transformation of kaolinite from the Kalno deposit (KBr discs technique)

a — K-3a (cold washed OH-form), b — K-3b (hot washed OH-form), c — K-14a (cold washed Cl-form), d — K-14b (hot washed Cl-form)

to the formation of a crystalline phase structurally resembling cancrinite. The absorption bands of this phase appear in varying amounts whenever $(\text{CO}_3)^{2-}$ ions are present in the reaction medium. The lack of distinct correlation between the intensity of bands from carbonate ions and the intensity of washing indicates that this absorption does not arise from a separate, soluble carbonate phase of the soda or trona type. On the basis of the intensity of the discussed absorption bands, the content of this phase in OH-sodalite samples obtained by way of transformation of kaolinite in the alkaline medium has been determined at 10–15%. In X-ray diffraction patterns (figs. 1a, b and 2a, b) reflections with the following d_{hkl} values have been assigned to this phase: 5.45, 4.64, 4.11, 3.21, 3.02, 2.95, 2.73, 2.607, 2.498, 2.249, 2.166, 2.099 Å. They are close to the respective values for cancrinite. The diffraction patterns, on the other hand, show no reflections attributed by Barrer and Cole (1970) to the supposed sodalite variety containing sodium carbonate as "excess salt". Additional syntheses, in the course of which Na_2CO_3 in an amount of 40 g/l of alkaline solution was introduced into the reaction medium, have confirmed the possibility of formation not only of sodalite but also of a separate phase that could be cancrinite with the disturbed structure. It is feasible that this structure accommodates both $(\text{CO}_3)^{2-}$ and OH^- ions, which leads to disturbances both in the shape of absorption bands displayed by this phase and in the position of reflections in X-ray diffractograms.

The most probable cause of formation of a larger amount of this additional phase in OH-sodalite samples obtained by transformation of kaolinite, is the higher concentration of $(\text{CO}_3)^{2-}$ ions during crystallization. This is due to the fact that the transformation of kaolinite to sodalite in an alkaline solution is a much longer process than the synthesis of sodalite from pure chemical components. Therefore, the amount of CO_2 absorbed by sodium hydroxide solution from air is greater and this, in turn, promotes the crystallization not only of OH-sodalite but also of phases capable of incorporating $(\text{CO}_3)^{2-}$ ion in their structure.

Besides the absorption bands mentioned above, sodalite samples obtained by way of transformation of kaolinite sometimes display weak bands at 535, 560 and 928 cm^{-1} and a weak inflexion between 3600 and 3700 cm^{-1} (fig. 4c, d). Their growth has been attributed to the presence of relics of unaltered kaolinite.

Syntheses carried out in the presence of Cl^- ions in the reaction medium lead to the formation of highly crystalline forms of Cl-sodalite. This fact has been borne out both by infrared spectroscopic and X-ray investigations. The bands typical of the structure of Cl-sodalite are intense, narrow (not diffuse) and well resolved (figs. 3c, d and 4c, d). Neither cold nor hot washing of Cl-sodalite samples with water affects the shape or position of absorption bands. The intensity ratio of the 438 and 468 cm^{-1} bands remains constant during the washing, and so does that of the 715 and 740 cm^{-1} doublet. It is worth noting that under such conditions of synthesis, the phase structurally resembling cancrinite and incorporating $(\text{CO}_3)^{2-}$ ions within its framework does not virtually form because the 620, 635 and 695 cm^{-1} bands, which have been attributed to this phase, are missing in the spectra. Only very weak bands between 1400 and 1500 cm^{-1} , and in some samples also at 630 cm^{-1} , may testify to the presence of trace amounts of this phase.

In X-ray diffraction patterns (figs. 1c, d and 2c, d) reflections arising from the lattice plans of Cl-sodalite have a higher intensity than in the case of OH-sodalite. The measurements of crystallite size have also fully confirmed the larger diameter of crystallites in Cl-sodalite samples (Table 3).

From the above considerations it appears that the most reliable data, allowing a fast identification of the discussed forms of sodalite, are yielded by infrared absorption spectroscopy. Additional information on the crystal chemistry of OH- and Cl-forms of sodalite was given by infrared spectroscopic investigations utilizing a high-temperature vacuum absorption cell. Due to its use, it was possible to follow changes in the infrared absorption of samples in response to the increasing calcination temperature. Figure 5 shows spectra of a Cl-sodalite sample (K-14a) calcined at 150, 300, 450,

Table 3
The crystallite size of OH- and Cl-sodalites

Sample No	Diameter of crystallites (μm)
S — 17 b	0.11
S — 16 b	0.29
K — 3 b	0.07
K — 14 b	0.13

500 and 580°C at a pressure of 10^{-3} mm Hg. Spectra were recorded after the sample had been cooled to room temperature. The investigations provided information on the manner of binding of water to this form of sodalite. Most diagnostic in this respect is the region of bending vibrations of water molecules between 1500 and 1750 cm^{-1} . It is known that most of them are coordinated by Na^+ cations. The interaction between these cations and water molecules changes markedly with the increasing calcination temperature. On this basis, three forms of occurrence of water can be distinguished.

One form is represented by weakly bound water molecules that are located outside the inner coordination sphere of Na^+ cations, or are very loosely bound to these cations. They fill cavities in the framework of Cl-sodalite, displaying a broad absorption band with a peak at 1640 cm^{-1} , which is most pronounced in unheated sample (fig. 5a). This band decreases continuously in intensity as the temperature increases, until it disappears completely at 450°C (fig. 5b, c, d).

The second kind of water molecules are those strongly bound to Na^+ cations, and therefore occurring within the inner coordination sphere. Their bending vibrations are responsible for the strong absorption at 1600 cm^{-1} . Thermal stability of this water is somewhat higher as the 1600 cm^{-1} band does not change in intensity in the range of 20–300°C (fig. 5a, b, c), and only the heating at higher temperatures results in dehydration and desorption of these water molecules. At 450°C the intensity of the 1600 cm^{-1} band is insignificant (fig. 5d). The two ways of water binding correspond well to the splitting of the dehydration peak in the range of 100–400°C, visible on DTA and DTG curves (Tokarz — priv. comm.).

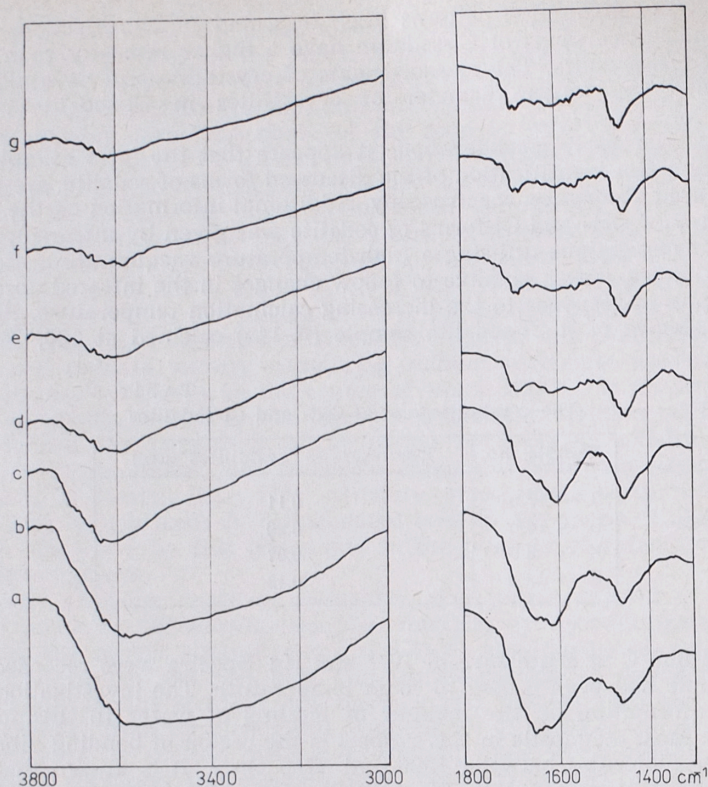


Fig. 5. IR-spectra of K-14a sample (Cl-sodalite) representing various degree of calcination
 a — room temperature, b — 150°C, c — 300°C, d — 450°C, e — 500°C, f — 580°C, g — after rehydration. Sample prepared in form of thin self-supporting film. Spectra recorded using vacuum cell

The band appearing at 1685 cm^{-1} , particularly pronounced after preliminary dehydration of the sample at 300°C (fig. 5c, d, e, f), gives rise to a large number of controversies. The present authors are of the opinion that it is to be attributed to the presence of H_3O^+ ions formed as a result of the dissociation of residual water molecules most strongly bound to Na^+ cations. The attribution of this absorption, as well as of the very broad band occurring between 3000 and 3600 cm^{-1} , refers to earlier papers (Kubisz 1968; Fijał, Olkiewicz 1978). An alternative explanation for the development of the 1685 cm^{-1} band may also be the presence of overtones of the basal bands of sodalite. However, this band has not been recorded in the spectra of OH-sodalite (fig. 7).

The lattice of Cl-sodalite calcined at temperatures higher than 500°C partly collapses (becomes somewhat distorted). This leads to a decrease in the channel diameter and hinders rehydration. The shape of spectrum (fig. 5f) substantiates the hypothesis that the entrapped residual water

molecules bound to Na^+ cations, which are in this case strong Lewis centres, undergo intense dissociation, presumably with the formation of H_3O^+ ion. The absorption occurring close to 3630 cm^{-1} (fig. 5a—f) is caused by O—H stretching vibrations of hydroxyl groups present in the structure of mica (illite). This mica constitutes an insignificant admixture in the initial kaolinite, which virtually is not subject to transformation during synthesis (Tokarz 1978).

Similar conclusions emerge from the analysis of infrared spectra of a Cl-sodalite sample obtained by synthesis from pure chemical components (S-16a) and calcined at the same temperature intervals but at less intense evacuation, i.e. at low water vapour pressure. Under these conditions, dehydration proceeds at a considerably slower rate. Nevertheless, the previous observations concerning three forms of water occurrence in the structure of Cl-sodalite have been confirmed (fig. 6). The fairly intense absorption band between 3000 and 3800 cm^{-1} is owing to the presence of both molecular water, strongly bound to Na^+ cations, and presumably H_3O^+ groupings, as well as to O—H vibrations of hydroxyl groups. In particular, the 3725 cm^{-1} band is to be attributed to Si—OH silanol groups, whereas the bands centered at 3540 and 3630 cm^{-1} may be caused by stretching vibrations of both OH^- groups formed as a result of dissociation of residual water on Na^+ cations and OH^- groups coordinated by Al^{3+} lattice cations in places where the bonds have been disrupted (Ward 1971).

Spectra of Cl-sodalite obtained using the vacuum absorption cell also confirm the presence of $(\text{CO}_3)^{2-}$ anions in the samples. It has been found that hydration has a marked effect on the shape and breadth of ν_3 bands between 1350 and 1500 cm^{-1} arising from carbonate ions bound in the framework of the cancrinite-like phase (fig. 6). Due to the progressive loss of water, the symmetry of band from $(\text{CO}_3)^{2-}$ ions increases markedly so that after calcination at 150°C and higher temperatures there is only a single narrow band with a peak at 1440 cm^{-1} in the spectra. Its position does not change after calcination at higher temperatures.

Infrared spectra of OH-sodalite (K-3a, fig. 7) show that dehydration of this form of sodalite proceeds in a somewhat different way compared with the Cl-form. The spectra have revealed the presence of only two kinds of water molecules occurring in the structure of this mineral. The band at 1655 cm^{-1} corresponds to loosely bound water molecules occupying vacancies in the framework. These molecules are readily removed as the calcination temperature increases so that the sample outgassed at 150°C contains only their trace amounts (fig. 7b). At 300°C the 1655 cm^{-1} band disappears (fig. 7c).

The other kind of H_2O molecules is represented by water strongly bound to Na^+ cations, displaying absorption at 1590 cm^{-1} . This kind of water, as in the Cl-form of sodalite, shows considerably higher thermal stability for the 1590 cm^{-1} band does not virtually change in intensity up to 300°C (fig. 7c). At higher temperatures the band decreases in intensity and disappears at 580°C (fig. 7e).

It is interesting to note that no absorption that could be attributed to H_3O^+ ions (close to 1700 cm^{-1}) has been observed for the OH-form of sodalite.

An analysis of the spectrum in the region of higher wave numbers

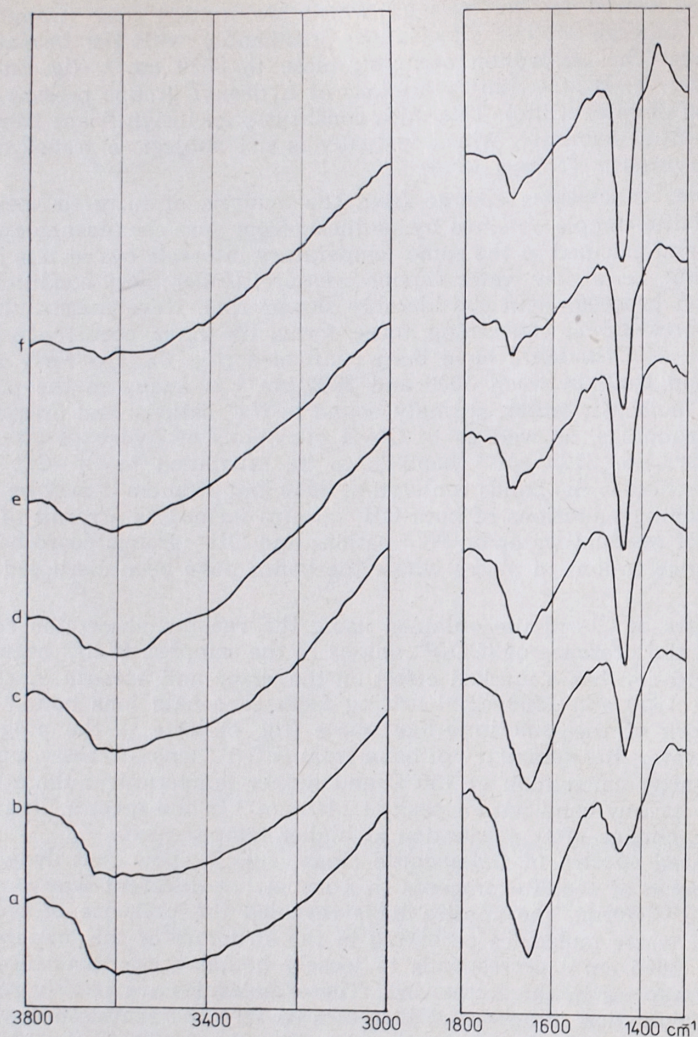


Fig. 6. IR-spectra of S-16a sample (Cl-sodalite) representing various degrees of calcination
a — room temperature, *b* — 150°C, *c* — 300°C, *d* — 450°C, *e* — 500°C, *f* — 580°C. Sample prepared in form of selfsupporting film. Spectra recorded using vacuum cell

yields data on the progressing dehydration of the framework, which is reflected in the rapid reduction in the intensity of the broad, diffuse band occurring between 2600 and 3750 cm^{-1} and caused by symmetric and antisymmetric O—H vibrations in water molecules. The progressing dehydration of the sample is responsible for the bands arising from OH⁻ valency groups at 3600—3750 cm^{-1} . The peak at 3625 cm^{-1} has been

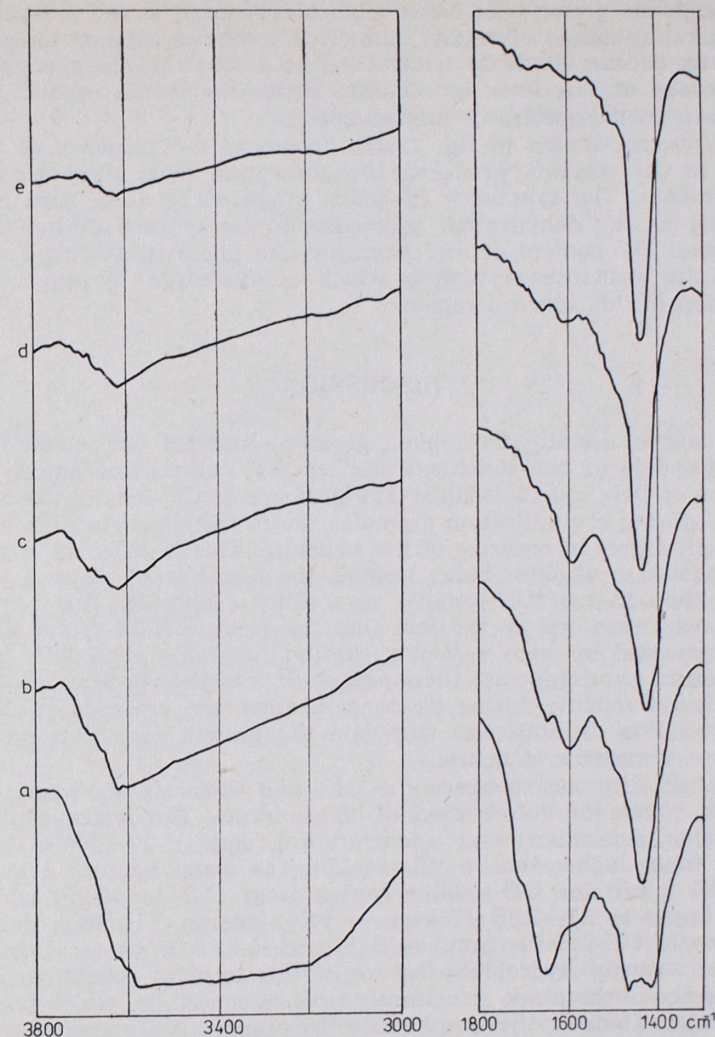


Fig. 7. IR-spectra of K-3a sample (OH-sodalite) representing various degrees of calcination
a — room temperature, *b* — 150°C, *c* — 300°C, *d* — 450°C, *e* — 580°C. Sample prepared in form of selfsupporting film. Spectra recorded using vacuum cell

associated with the insignificant admixture of mica (illite) that did not undergo transformation during synthesis (fig. 7*c, d, e*). The 3665 cm^{-1} band, appearing initially in the spectra recorded after calcination at 150 and 300°C and disappearing almost completely after heating at 450°C (fig. 7*b, c, d*), has been attributed to O—H stretching vibrations of hydroxyl groups balancing the charge on Na⁺ cations.

Though the presence of water molecules strongly bound to Na^+ cations is a potential source of acidity, the (H_3O^+) protons formed under these conditions become instantly neutralized as a result of the reaction with OH^- groups of this form of sodalite. Hence the bands from H_3O^+ ion are absent in the spectra of this sample.

The spectra shown in fig. 7 also document the presence of $(\text{CO}_3)^{2-}$ anions in the reaction products, the absorption from these ions being fairly intense. The symmetry of bands produced by these ions changes markedly as the dehydration proceeds, as was to case in the Cl-form of sodalite. The content of the cancrinite-like phase containing carbonate ions in its structure is higher, which is evidenced by more intense absorption in this spectral region.

DISCUSSION

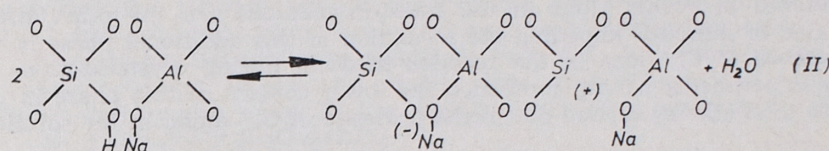
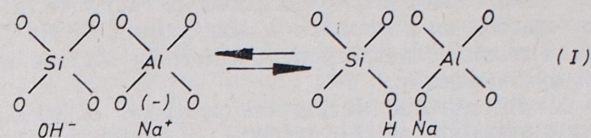
The above investigations have greatly extended our understanding of the function of non-stoichiometric "excess" cations and anions in the structure of OH- and Cl-sodalite. The presence of Cl^- ions in the reaction medium during crystallization promotes the formation of sodalite exhibiting a high degree of ordering of the structure. This is reflected in the size of Cl-sodalite crystallites being formed, the diameter of which is always greater than that of OH-sodalite crystallites (Table 3). This regularity can be accounted for by the fact that the electric field round Cl^- ions is characterized by high symmetry while the field round OH^- ions is asymmetric. Assuming that these anions fit into the specified cavities in the lattice of sodalite during its crystallization, the presence of Cl^- ions in the reaction medium will stimulate the growth of a better ordered and more symmetric structure.

Another difference between the OH- and Cl-forms of sodalite is the different course of dehydration of these forms. The water content in OH-sodalite, determined over a temperature range of 20–400°C, is three to four times higher than in Cl-sodalite. The water content determined from TG curve for OH-sodalite varies from 11.7 to 12.9% while for Cl-sodalite it is 1.7–3.2% (Tokarz — priv. comm.). The high degree of hydration of OH-sodalite (samples S-17 and K-3) is to be associated both with the strongly hydrophilic nature of this form of sodalite and with the presence of the phase structurally close to cancrinite, which has much larger cages. These cavities can be filled by proportionally greater amounts of water than in the case of OH-sodalite.

The way in which the OH- and Cl-forms of sodalite give off water during calcination indicates that dehydration is not a continuous process but involves several distinct stages. This information is provided by infrared spectra obtained using the high-temperature absorption cell. It has been found that both forms of sodalite contain two kinds of water: 1) water loosely bound to Na^+ cations and filling up cavities in the framework of sodalite; 2) water strongly coordinated by Na^+ cations, displaying absorption close to 1600 cm^{-1} ; this water is removed from OH-sodalite over the temperature range between 200–450°C, and from the Cl-form between 200 and 550°C.

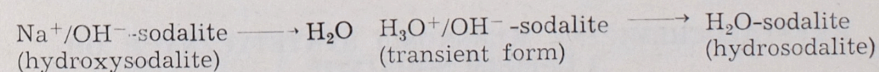
The calcination of OH-sodalite involves thermal dissociation of hydro-

xyl groups of this form, which results in the formation of Lewis-type acid-basic centres. There form cations having coordinations numbers of three, which are acid centres, and coordination-unsatisfied oxygen ions that are basic centres. These reactions proceed over a wide temperature range from 350 to 800°C, presumably according to the following scheme:



From infrared spectroscopic investigations it appears that H_3O^+ ions form in Cl-forms of sodalite as a result of thermal dissociation of residual water molecules in the strong electric field of sodium cations by which they are coordinated. These ions display absorption at 1685 cm^{-1} and a broad band between 2600 and 3600 cm^{-1} coinciding with O—H vibrations of water molecules. The absence of bands from H_3O^+ ions, particularly close to 1680 cm^{-1} , in the spectra of OH-forms of sodalite can be accounted for by the reaction that takes place between the protons being formed during their dissociation and the structural OH^- groups.

The effect of washing of hydroxysodalite samples with water confirms the presence of two kinds of Na^+ cations in the structure, one corresponding to Na^+ cations that compensate for the negative charge on the lattice, resulting from the Si/Al substitution in the tetrahedra, the other being "excess" Na^+ ions fitting into cavities in the framework of hydroxysodalite. Cations of the first kind are strongly bonded to the framework, and therefore little susceptible to hydrolysis, whereas cations of the second kind can be readily removed from the structure if samples are washed, especially hot washed, with water for a sufficient length of time. The mechanism of this process can be explained by the following scheme:



The H_3O^+ ion, present at the transitional stage, becomes instantly neutralized, entering into reaction with the structural OH^- group. In this way hydrosodalite forms, containing water molecules in cavities.

From infrared spectroscopic investigations and chemical analyses it appears that this reaction failed to proceed to completion in the samples studied. This is presumably due to the existence of diffusion barriers

impeding the removal of "excess" Na^+ cations from the structure of hydroxysodalite, especially in the case of well crystallized forms of this mineral, in which the diffusion distance is respectively longer. It has been noticed that the removal of "excess" Na^+ cations, which are loosely bound in the structure of sodalite, is attended by a change in bond symmetry of the Al—Si—O framework of sodalite. The band centered close to 435 cm^{-1} and caused by ν_4 vibrations of SiO_4^{4-} tetrahedra may in this case be regarded as a measure of the content of Na^+ cations in the structure. As a result of washing with water, the surface area of this band diminishes systematically.

Though the conditions used during the synthesis of sodalite favour primarily the crystallization of this mineral, it cannot be ignored that simultaneous crystallization of certain amounts of a phase structurally resembling cancrinite takes place. Its amount largely depends on the presence of $(\text{CO}_3)^{2-}$ ions in the reaction medium. On the other hand, a kind of inhibitor impeding the formation of this additional phase is the presence of Cl^- ions in the reaction medium during crystallization, all the experiments having confirmed the lower content of this phase in the case of syntheses carried out in the presence of Cl^- anion in the solution.

Translated by Hanna Kisielewska

REFERENCES

- BARRER R. M., COLE J. F., STICHER H., 1968: Chemistry of soil minerals. Part V. Low temperature hydrothermal transformation of kaolinite. *J. Chem. Soc. (A)*.
 BARRER R. M., COLE J. F., 1970: Chemistry of soil minerals. Part VI. Salt entrainment by sodalite and cancrinite during their synthesis. *J. Chem. Soc. (A)*.
 FIJAŁ J., OLKIEWICZ S., 1978: Hydronium ion as probable cause of acidity of calcinated H-form of montmorillonite. *Min. Pol.* 9, 2.
 KUBISZ J., 1968: Rola dodatnich jonów wodorowo-tlenowych w minerałach. *Prace Min.* 11.
 LONS J., SCHULZ H., 1967: Strukturverfeinerung von Sodalith, $\text{Na}_8\text{Si}_6\text{Al}_6\text{O}_{24}\text{Cl}_2$. *Acta Cryst.* 23.
 SCHIPPER D. J., LAUTHOUWERS Th. W., 1972: Bromide incorporation in sodalite. *Inorg. Nucl. Chem. Letters.* 8.
 TAYLOR D., HENDERSON C. M. B., 1978: A computer model for the cubic sodalite structure. *Phys. Chem. Miner.* 2.
 TOKARZ M., 1978: Hydrothermal transformation of kaolinite in an alkaline environment. *Min. Pol.* 9, 2.
 WARD J. W., 1971: Infrared spectroscopic studies of zeolites. *Adv. Chem. Series* 101.

Jerzy FIJAŁ, Marek TOKARZ

KRYSTALOCHEMICZNE WŁASNOŚCI SYNTETYCZNYCH OH- I Cl-FORM SODALITU

Streszczenie

Porównano niektóre krystalochemiczne własności OH- i Cl-form sodalitu otrzymanych przez bezpośrednią syntezę z czystych składników chemicznych, jak też poprzez przeobrażenie kaolinitu w środowisku alka-

licznym. Zwrócono przede wszystkim uwagę na szereg różnic między tymi formami.

Zaobserwowano wpływ obecności jonów Cl^- w sieci krystalicznej sodalitu na podwyższenie krystaliczności tego minerału, co przypisano wyższej symetrii pola wokół anionów Cl^- niż OH^- .

Odmienne jest też termiczne zachowanie się obu form. Znacznie większy ubytek masy towarzyszy kalcynacji OH-sodalitu w porównaniu z formą chlorkową tej substancji. Należy to tłumaczyć po części hydrofilnym charakterem formy OH, jak też dysocjacją termiczną grup OH, a także obecnością w produktach reakcji fazy o strukturze bliskiej kankrynitowi (faza ta zawiera kanały o większej niż sodalit średnicy). Powolny proces odwadniania formy chlorkowej sodalitu, w temperaturach $200\text{--}400^\circ\text{C}$, pozostawia w lukach strukturalnych jedynie mocno koordynowane przez kationy sodowe drobiny wody, tzw. H_2O resztkową. Wpływ pola elektrycznego kationów prowadzi do dysocjacji drobin H_2O z wytworzeniem jonów H_3O^+ , których obecność udowodniono metodami spektroskopowymi.

Stwierdzono też odmienną stabilność form OH- i Cl- sodalitu w środowisku wodnym. Intensywne przemywanie wodą OH-sodalitu prowadzi do usunięcia części jonów Na^+ w wyniku hydrolizy i przejście tej formy w tzw. hydrosodalit (H_2O -sodalit).

OBJAŚNIENIA FIGUR

- Fig. 1. Dyfraktogramy rentgenowskie syntetycznych próbek OH- i Cl-sodalitu
 a — próbka S-17a (przemywana na zimno), b — próbka S-17b (przemywana na gorąco), c — próbka S-16a (przemywana na zimno), d — próbka S-16b (przemywana na gorąco). S — sodalit, C — kankrynit
- Fig. 2. Dyfraktogramy rentgenowskie próbek Cl- i OH-sodalitu otrzymanych przez transformację kaolinitu ze złoża Kalno
 a — próbka K-3a (przemywana na zimno), b — próbka K-3b (przemywana na gorąco), c — próbka K-14a (przemywana na zimno), d — próbka K-14b (przemywana na gorąco). S — sodalit, C — kankrynit, M — mika/illit
- Fig. 3. Spektrogramy absorpcyjne w podczerwieni syntetycznych OH- i Cl-form sodalitu (technika prasowanych pastylek z KBr)
 a — próbka S-17a (przemywana na zimno), b — próbka S-17b (przemywana na gorąco), c — próbka S-16a (przemywana na zimno), d — próbka S-16b (przemywana na gorąco)
- Fig. 4. Spektrogramy absorpcyjne w podczerwieni OH- i Cl-form sodalitu otrzymanych przez transformację kaolinitu ze złoża Kalno
 a — próbka K-3a (przemywana na zimno), b — próbka K-3b (przemywana na gorąco), c — próbka K-14a (przemywana na zimno), d — próbka K-14b (przemywana na gorąco)
- Fig. 5. Spektrogramy absorpcyjne w podczerwieni próbki K-14a (Cl-sodalit) reprezentujące różne stadia kalcynacji
 a — temperatura pokojowa, b — 150°C , c — 300°C , d — 450°C , e — 500°C , f — 580°C , g — po rehydratacji
- Fig. 6. Spektrogramy absorpcyjne w podczerwieni próbki S-16a (Cl-sodalit) reprezentujące różne stadia kalcynacji
 a — temperatura pokojowa, b — 150°C , c — 300°C , d — 450°C , e — 500°C , f — 580°C . Widma rejestrowano w kuwecie próżniowej stosując preparat w formie samonośnej błonki
- Fig. 7. Spektrogramy absorpcyjne w podczerwieni próbki K-3a (OH-sodalit) reprezentujące różne stadia kalcynacji
 a — temperatura pokojowa, b — 150°C , c — 300°C , d — 450°C , e — 580°C . Widma rejestrowano w kuwecie próżniowej, stosowano preparat w formie samonośnej błonki

КРИСТАЛЛОХИМИЧЕСКИЕ СВОЙСТВА СИНТЕТИЧЕСКИХ ОН- И СИ-ФОРМ СОДАЛИТА

Резюме

Сравниваются некоторые кристаллохимические свойства Он- и Си-форм содалита, полученных путем непосредственного синтеза из чистых химических элементов, а также путем преобразования каолинита в щелочном среде. Обращается прежде всего внимание на ряд различий между этими формами.

Констатируется влияние присутствия ионов Cl^- в кристаллической сети содалита на повышение кристалличности этого минерала, что приписывается более высокому симметрии поля вокруг анионов Cl^- чем OH^- .

Разным является также термическое поведение обеих форм. Значительно более высокий убыток массы сопровождается кальцинацию Он-содалита в сравнении с Си-формой. Это следует объяснять в части гидрофильным характером формы Он и термической диссоциацией группы Он, а также наличием в продуктах реакции фазы со структурой близкой канкриниту (эта фаза содержит каналы, диаметр которых больше чем содалита). Медленный процесс обезвоживания Си-формы содалита в температурах 200—400°C, оставляет в структурных пробелах только сильно координируемые натриевыми катионами частицы воды, т.нз остаточную H_2O . Влияние электрического поля катионов приводит к диссоциации частиц воды с образованием ионов H_3O^+ , наличие которых доказано спектральными методами.

Констатируется также разную стабильность форм Он- и Си-содалита в водной среде. Интенсивная промывка водой Он-содалита приводит к устранению части ионов Na^+ в результате гидролиза и переход этой формы в т.нз гидросодалит (H_2O -содалит).

ОБЪЯСНЕНИЕ ФИГУРЫ

- Фиг. 1. Рентгеновские дифрактограммы синтетических проб Он- и Си-содалита
a — проба К-3а (холодная промывка), *b* — проба К-3б (горячая промывка),
c — проба S-16а (холодная промывка), *d* — проба S-16б (горячая промывка).
S — содалит, **c** — канкринит
- Фиг. 2. Рентгеновские дифрактограммы проб Си- и Он-содалита полученных путем трансформации каолинита из месторождения Кально
a — проба К-3а (холодная промывка), *b* — проба К-3б (горячая промывка),
c — проба К-14а (холодная промывка), *d* — проба К-14б (горячая промывка).
S — содалит, **c** — канкринит, **M** — слюда/иллит
- Фиг. 3. ИК-спектры синтетических Он- и Си-форм содалита (Техника пресованных таблеток из КВг)
a — проба S-17а (холодная промывка), *b* — проба S-17б (горячая промывка),
c — проба S-16а (холодная промывка), *d* — проба S-16б (горячая промывка)
- Фиг. 4. ИК-спектры Он- и Си-содалита полученных путем трансформации каолинита из месторождения Кально

a — проба К-3а (холодная промывка), *b* — проба К-3б (горячая промывка).
c — проба К-14а (холодная промывка), *d* — проба К-14б (горячая промывка)

- Фиг. 5. ИК-спектры пробы К-14а (Си-содалит) представляющие разные стадии кальцинации
a — температура комнатная, *b* — 150°C, *c* — 300°C, *d* — 450°C, *e* — 500°C, *f* — 580°C, *g* — после регидратации
- Фиг. 6. ИК-спектры пробы S-16а (Си-содалита) представляющие разные стадии кальцинации
a — температура комнатная, *b* — 150°C, *c* — 300°C, *d* — 450°C, *e* — 500°C, *f* — 580°C. Спектры регистрировались в вакуумкамере применяя препарат в форме самоносной пленки
- Фиг. 7. ИК-спектры пробы К-3а (Он-содалит) представляющие разные стадии кальцинации
a — температура комнатная, *b* — 150°C, *c* — 300°C, *d* — 450°C, *e* — 580°C. Спектры регистрировались в вакуум-камере применяя препарат в форме самоносной пленки