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Structural characterization of the hydrous layer silicate Na-RUB-18, $Na_8Si_{32}O_{64}(OH)_8 \cdot 32H_2O$ and derivatives with XPD-, NPD-, and SS NMR experiments

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Abstract

The structural characterization of hydrous layer silicates using X-ray- and neutron powder diffraction studies and complementary experiments with solid state NMR is presented for a variety of materials of the RUB-18 family. The parent Na-RUB-18 shows interesting temperature dependent proton dynamics and proton conduction which is studied with NMR and neutron diffraction experiments. The silicic acid H-RUB-18 crystallises without intercalate water and with considerable distortion of the original structure. Acetone and alanine intercalated in H-RUB-18 occupy the channel-like void of the interlayer space by re-arranging the original stacking motive upon uptake. The article is a summary on work on this family of materials presenting new results in perspective with results already available in the literature.

Keywords: RUB-18; Octosilicate; Rietveld analysis; Proton dynamics; Proton conduction; Amino acid intercalation

1. Introduction

Layered silicates are abundant minerals in sedimentary systems but are also produced in chemical industries in large quantities for production of paints, washing powder production, fillers, catalysts and supports, etc. [1]. The group of hydrous sodium layer silicates (Table 1) plays an outstanding role in such that most materials have been known for more than 50 years, however, most of their crystal structures and their physical properties are still unknown. The particular interest in studying hydrous layer silicates comes from their importance in geoscience as storage and exchange materials and from their economical impact as industrial minerals.

Our interest in structural studies of hydrous layer silicates (HLS) is derived from their specific physical and chemical properties. Because of the easy access of interlayer space they serve as model compounds for the study of surface properties and the interaction of silicate surfaces with water, hydrated cations, and organic molecules. For this purpose hydrous sodium layer silicates are perfectly suited because of their simple chemical composition, of their "buried" interfaces with periodic ordering, thus accessible for diffraction, of the hydrophilic/hydrophobic nature of the surface, of the complicated ion exchange properties, of the intercalation and sorption of organic molecules with various functional groups, such as amino acids, sugars, alcohols, etc.

In the following article a summary of results of diffraction and NMR-spectroscopic experiments is presented leading to a most complete structural characterization of Na-RUB-18 and some of its derivatives. Na-RUB-18 is the Na member of the family of materials with RUB-18 silicate structure type and is isostructural to octosilicate and ilerite. Since a proposed structure model for ilerite and octosilicate were proofen wrong, the trivial-names should be

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Table 1
Natural and synthetic hydrous sodium layer silicates

Material name	Chemical composition	Crystal structure	Crystal structure of derivatives
Kanemit	$NaHSi_2O_5 \cdot 3H_2O$	Structure known	No structural data on derivatives
Makatite	$Na_2Si_4O_9 \cdot 5H_2O$	Structure known	No structural data on derivatives
Magadiite	$Na_2Si_{14}O_{29} \cdot 11H_2O$	Structure unknown	No structural data on derivatives
Kenyaite	$Na_2Si_{22}O_{45} \cdot 10H_2O$	Structure unknown	No structural data on derivatives
Octosilicate, Na-RUB-18	$Na_8Si_{32}O_{64}(OH)_8 \cdot 32H_2O$	Structure known	Structural data of some derivatives are known

discredited. In this article, Na-RUB-18 is the name used instead. With various materials of RUB-18-type structure as test cases it should be demonstrated, how complex and complicated the crystal structure of hydrous layered silicates can be. Despite this, with up-to-date characterization experiments, insight into structure and properties of this class of materials is within reach. Using high resolution powder X-ray and neutron diffraction, and solid state MAS NMR characterization, as complementary techniques, features and properties specific for this family of hydrous layered silicates are highlighted. In order to present a most exhaustive picture of structure and properties of the family of materials in an overview, the article will resort partially on findings already published in literature, however, the majority of results shown here are original.

2. Experimental

Na-RUB-18 was synthesized according to procedures described in the literature [2–4]. Ion exchange to the acidic form, H-RUB-18, was carried out with dilute acetic acid or citric acid, at room temperature. The exchange was carried out in a beaker and repeated several times until the washings was Na-free. Acetone was intercalated into H-RUB-18 by immersing the silicate in acetone for 5 min. Alanine was intercalated into H-RUB-18 by immersing the silicic acid in an aqueous solution of alanine in its betain form.

For X-ray experiments a Siemens D5000 diffractometer was used with monochromatized Cu-Kα_1 radiation and a Braun position sensitive detector. Neutron powder diffraction experiments were carried out at the high resolution powder diffractometer D2B at ILL, Grenoble. Rietveld analysis for structural characterization was carried out with the program suite FullProf [5]. Structure plots were generated with Ball and Sticks [6].

Solid state MAS NMR experiments were carried out on a 9.4 Tesla Bruker ASX 400. All experiments were performed on Bruker probes with 7mm rotors for ^{29}Si and 4mm rotors for ^{1}H and ^{13}C.

3. Results and discussion

3.1. Synthesis of materials of the RUB-18 family

The parent material, Na-RUB-18, is directly synthesized whereas all other modifications have been obtained by secondary treatment, i.e., ion exchange or intercalation reactions. A summary is given in Table 2 with various RUB-18 materials in their as made form. Sodium-RUB-18 is of high crystallinity, α-H-RUB-18 and Ca-RUB-18 are slightly less perfect. All other modifications show significant disorder, however, lattice parameters and NMR-analyses confirm the integrity of the motive of the basic silicate layer.

3.2. Structure analyses and description of structures of Na-RUB-18

The crystal structure of Na-RUB-18 was solved from powder X-ray diffraction data [4]. The high degree of crystallinity which is unexpected for hydrous layer silicates allowed for detailed description of structural features including the intercalate water associated with the charge balancing Na-cation and silanol groups of the silicate layer. Technical details of the structure refinements are given in Table 1 of Supplementary data, Fig. 1 shows the structure

Table 2
Crystallographic summary of various members of the RUB-18 family of materials

Material	Space group	*a*, *b*	*c*	Diffraction analysis
α-H-RUB-18	$I4_1/amd$	7.383(5)	29.76(3)	X
β-H-RUB-18		7.40(5)	26.0(1)	X
Li-RUB-18	$I4_1/amd$	7.43(1)	37.15(1)	X
Na-RUB-18	$I4_1/amd$	7.33(1)	44.32(1)	X, N
K-RUB-18	$P4_12_12$ or $P4_32_12$	7.34(1)	40.92(1)	X
Rb-RUB-18	$I4_1/amd$	7.39(1)	41.92(1)	X
Cs-RUB-18	$I4_1/amd$	7.39(1)	42.65(1)	X
Ca-RUB-18	$P4_1212$ or $P4_3212$	7.53(1)	36.81(1)	X, N
Ace-H-RUB-18	$P4_1212$ or $P4_3212$	7.48(1)	37.34(1)	X, N
Ala-H-RUB-18	$P4_1212$ or $P4_3212$	7.33(1)	36.24	N

X = X-ray powder diffraction, N = neutron powder diffraction.