



Synthesis and characterization of a sulfur containing hydroxy sodalite without sulfur radicals



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ABSTRACT

A new sulfur containing hydroxy sodalite (S–SOD) of high thermal and hydrothermal stability was synthesized and characterized. XRD measurements showed some differences to normal hydroxy sodalite (H–SOD). But the S–SOD is also quite different from natural sulfur containing sodalites like ultramarine blue. IR- and RAMAN-spectroscopy measurements detected no sulfur radicals in the structure of S–SOD, which was already assumed because of the colorless powder of S–SOD. ²⁹Si-, ²⁷Al- and ²³Na–MAS–NMR measurements were conducted to determine the order of the structure and the type of incorporation of the sulfur into the sodalite structure. The sulfur is most likely coordinated statistically on every possible oxygen position in the structure. The pore size of the S–SOD was determined by positron annihilation measurements and is suitable for hydrogen separations.

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1. Introduction

Sodalite is a rock-forming mineral with the general formula $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24} \cdot (\text{X})$ with $\text{X} = \text{Cl}^-$, CO_3^{2-} , SO_4^{2-} , OH^- and so on [1,2]. It is typically formed under hydrothermal conditions. The anions and the cation sodium can be exchanged during heating processes with metal salts [2]. Solutions are often used for this purpose.

Ultramarine is a natural sulfur containing sodalite. The blue pigment can be extracted from the azure stone. Since the 19th century, ultramarines can also be synthesized in different colors like green, red and violet. The change in colors is due to different sulfur radicals, which are connected in the sodalite cages. These color giving centers (chromophores) were widely investigated and proclaimed to be S_3^* , S_2^* and S^* radicals [3–5].

The synthetic hydroxy or hydro sodalites with the formula $\text{Na}_{6+y}\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_y \cdot n\text{H}_2\text{O}$ can be differentiated due to the content of water and hydroxy ions [6]. For $y = 2$ it is called a basic form and for $y = 0$ a nonbasic form. The maximal value for water is $n = 8$. The high water containing structures can be dewatered, but if the water molecule of the hydroxy-group leaves the sodalite

framework above 600 °C–700 °C, the structure collapses and a carnegieite type is formed [7]. This process is not reversible and the resulting powder cannot adsorb water anymore. Therefore, hydroxy sodalite is not thermal stable.

Sodalite exhibits a size of the β -cage in the range of the kinetic molecule diameter of hydrogen (0.29 nm) and is a candidate for hydrogen and water separation technologies. In the last few years, a lot of hydroxy sodalite (H–SOD) membranes were synthesized [7–9], but this type of membrane is not stable at higher temperatures, which is necessary at power plant applications. Also hydrothermal conditions are a problem. This can be explained cause of the dewatering processes of hydroxy sodalites. In consequence of this, a new sulfur containing hydroxy sodalite (S–SOD) was developed at Fraunhofer IKTS [10], which is much more stable than a normal hydroxy sodalite and can be used in membrane applications [11]. This new material is going to be characterized in this study.

2. Experimental

The sulfur containing hydroxy sodalite (S–SOD) was synthesized by classical hydrothermal synthesis. An H–SOD synthesis solution is often prepared by mixing an aluminate and a silicate solution [12]. By using an additional third solution of sodium sulfide nonahydrate

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in water, S–SOD crystals can be obtained. In every other way the S–SOD synthesis can be compared to the one of H–SOD.

2.1. S-SOD synthesis

An aluminate solution was prepared by dissolving 2.5 g sodium aluminate (Sigma Aldrich) and 33.5 g sodium hydroxide (VWR) in 70 g deionized water. The silicate solution was prepared by mixing 6.5 g sodium metasilicate pentahydrate (PQ Nederland B.V.) and 30 g sodium hydroxide in 70 g water. In a third solution 55 g sodium sulfide nonahydrate (ABCR) was dissolved in 90 g water. The silicate and the sulfide solution were added to the aluminate solution, thereby the color changed to orange. The mixture was stirred for 1 h and then synthesized for 20 h at 80 °C in an autoclave. The resulting colorless powder was washed and dried for 2 h at 120 °C.

2.2. Characterization

For comparison with known structures, H–SOD and partly ultramarine blue (commercial, Kremer Pigmente GmbH & Co. KG) were measured with the same setups as S–SOD. By XRD measurements on a Bruker D8 Advance using Cu K α radiation, the purity of the powders was characterized. The crystal sizes and morphology were determined by field emission scanning electron microscopy (FE–SEM) with the help of a Zeiss Ultra 55 plus with an EDAX Trident XM4 sensor for energy dispersive X-ray (EDX) spectroscopy. For Simultaneous Thermogravimetry & Differential Scanning Calorimetry (TG–DSC) the NETZSCH STA 409 PC/PG was used. Water adsorption measurements were done by the device VTI SA of Texas Instruments. The IR spectra were determined with the Diamond ATR (FIR and MIR) Nicolet iS50 of Thermo Fisher Scientific and the RAMAN measurements were either done with the DXR MicroRaman (laser 532 nm, 10 mW, magnification 50x) of Thermo Fisher Scientific or with the Dispersive Raman Microscope SENTERRA (laser 532 nm, 20 mW or 785 nm, 100 mW, magnification 50x) of Bruker.

The solid state nuclear magnetic resonance (NMR) measurements were carried out using a Bruker AV400 spectrometer.

Positron annihilation measurements were conducted at the Institute of Physics of the Martin-Luther-University Halle-Wittenberg. A standard fast–fast positron lifetime spectrometer having a time resolution of FWHM = 230 ps was used. After source-background subtraction, the spectra were decomposed in four lifetime components.

3. Results and discussion

3.1. XRD

The XRD patterns of H–SOD, S–SOD and ultramarine blue (UMB) are shown in Fig. 1. The diffraction peaks of S–SOD are slightly shifted to smaller 2-Theta-values than the peaks of H–SOD. The peaks of ultramarine blue are shifted to even smaller 2-Theta-values. This can be due to an increasing sulfur content from H–SOD over S–SOD to ultramarine blue. Hence, the additional sulfur leads to changes in the lattice parameters.

The ratios of the intensities of the main reflections (at 2-Theta-values of 24°–25°, 34°–35° and 42°–43°) are altered for S–SOD in comparison to H–SOD and ultramarine blue. For S–SOD the intensity of the peak at 34°–35° is higher than the intensity of the peak at 42°–43°. Texturing and modification of the surface of the crystals could explain changes in the peak intensities, but the powders of H–SOD and ultramarine blue exhibit the same ratios in spite of their differences. Another explanation is, that the sulfur in the S–SOD is coordinated in a different way than in ultramarine

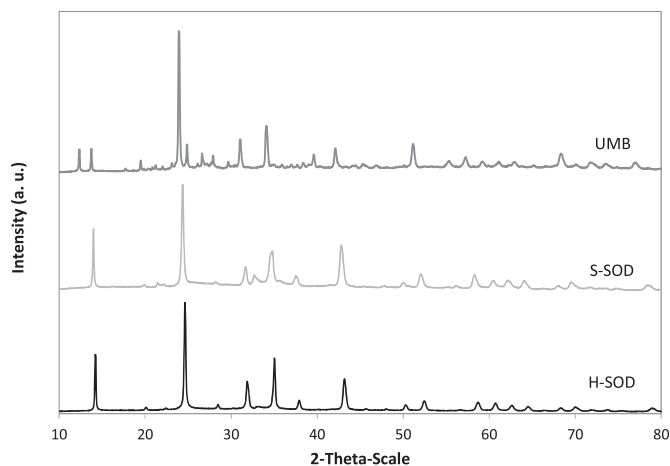


Fig. 1. XRD patterns of H–SOD, S–SOD and ultramarine blue (UMB).

blue. The sulfur can be coordinated in the lattice and not only in the β -cages.

Furthermore, it is noted that the XRD pattern of ultramarine blue shows more peaks than the other patterns. Thus, the cubic ultramarine blue is slightly contaminated with other phases like the hexagonal cancrinite, which often occurs as a secondary phase.

3.2. FE-SEM and EDX

The SEM images of H–SOD and S–SOD show polycrystalline particles with a more or less spherical morphology. The H–SOD powder (see Fig. 2) appears to consist of several spherical fused discs, from which in turn more crystals grow out. In comparison to that, the S–SOD particles are grown to full balls with a cauliflower-like structure, partially intersecting rings on the outer sides of the beads are still visible (see Fig. 3).

The EDX measurements of H–SOD and S–SOD show a very similar composition (see Table 1). The ratio of sodium oxide, aluminum oxide and silicon oxide is nearly the same, but S–SOD additionally contains sulfur. The ratio of Si: Al is nearly 1: 1 for H–SOD and a little bit higher for S–SOD. The higher sodium content in a basic hydrosodalite in comparison to a non-basic form is compensated by adding hydroxide ions. Therefore, the sodium content in the H–SOD which exceeds 6 mol may be associated to

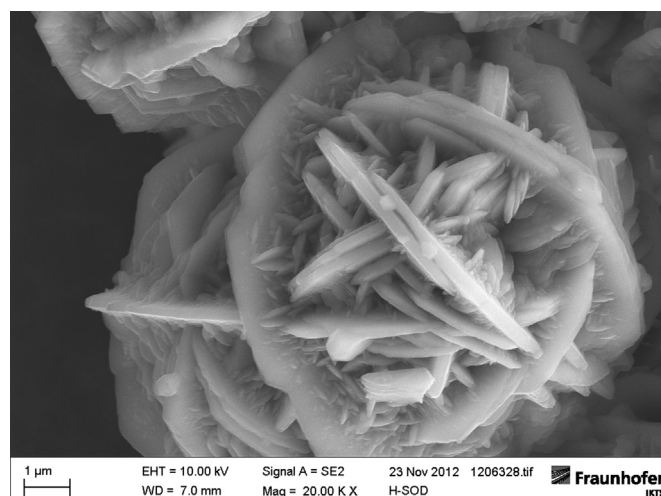


Fig. 2. SEM image of H–SOD.

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