# Dehydration diffusion of $B(OH)_4$-sodalite investigated by micro-Raman spectroscopy on single crystals and combined TG/IR on powders

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**Introduction:** An investigation of the dehydration mechanism of $(Na_8(Al_6Si_6O_{24})(B(OH)_4)_2)$ (= $B(OH)_4$-SOD) could be interesting for a better understanding and control of hydrogen release and reload of $BH_4$-SOD, too [1]. The formation of zoned crystals with cage fillings by $[BH_4]$-anions in the central part towards $[BO_2]$-, $[B(OH)_4]$-, $[BO(OH)_2]$- containing sodalite cages in the outer zones were observed. Therefore, the question arises how the water and related species are transported through such type of the sodalite cages. For $B(OH)_4$-SOD it has been reported that dehydration occurs in two consecutive steps [2]. Such investigations were carried out on polycrystalline powders of typically submicron crystal sizes. Since crystals of sizes up to few tenth of a mm of $B(OH)_4$-SOD could be grown we tried to analyse their dehydration profiles and H/D exchange experiments using mirco-Raman spectroscopy. In a second step combined TG/IR investigations were carried out in order to validate that dehydration occurs diffusion controlled.

**Experimental:** Clear crystals of sizes typically up to 0.5 mm in diameter were grown hydrothermally in closed Ag-tubes. Such crystals gain cracks during dehydration at the used temperatures (300, 350, 400°C, heating between 0.5 and 24 h). Using the micro-Raman technique (Bruker Senterra, 532 nm, 20 mW) measurements could be carried out in crack free parts. The measurements were carried out moving the focus of the confocal beam stepwise from the surface into the interior of the crystal. Cross section profiles verify the results obtained in depth profiles. H/D exchange experiments were carried out by bathing the crystals in 80%/20% $D_2O/H_2O$ liquid at temperatures between 50 and 120°C in closed tubes. The H/D exchange was characterized by micro-Raman spectroscopy, too. As synthesized polycrystalline material were characterized by XRD (Bruker D8) and were investigated thermogravimetrically (Setsys Ev. 1750, Setaram, flowing He 20 ml/min) with 5°C/min heating/cooling rate and 10 min holding times at temperatures between 80 and 500°C. The formation of $[BO_2]$-, $[BO(OH)_2]$- and [B(OH)4]-cage filling species were followed by FTIR absorption (KBr-method, Bruker Vertex 80v).

**Results:** The Raman spectra show the formation of $[BO[OH)_2]$-species beside $[B(OH)_4]$ cage fillings along profiles, which typically extends between 5 and 20 µm into the crystals. A relative decrease in the intensities of B-$(OH)_4$ active Raman vibration at 750 $cm^{-1}$ could be evaluated with respect to the framework Si-$O_4$-peak at 444 $cm^{-1}$. Data evaluation (error function analysis) reveals an Arrhenius behavior of the effective diffusion coefficients in the range between $4*10^{-12}$ and $2.5*10^{-10}$ $cm^2/s$, Ea ≈ 1.3 eV, shown in Fig. 1. The relative change of OD/OH related peak intensity in the Raman spectra from the surface into the interior of the crystals were evaluated, too. Effective diffusion coefficients are between $1.5*10^{-10}$ and $4*10^{-11}$ $cm^2/s$ with Ea ≈ 0.4 eV, also shown in Fig. 1. Additional data shown in Fig. 1 were obtained using some approximation to the dehydration effects on the polycrystalline powder along with $D_p = s^2/t$. For t the holding time (10 min) were used. For s the diameter of an outer shell of spherical crystals were estimated according to the mass loss obtained by the TG measurement. According to XRD analysis average crystal sizes are between 100 and 150 nm which were used as an lower (triangles down) and upper (triangles up) limit of the diameter of spherical crystals. Data are given for holding temperatures between 140 and 250 °C and at 350, 400 and 450°C according to the two consecutive reaction steps, respectively. Dehydration related exclusively to the first reaction step $[B(OH)_4]^- \Rightarrow [BO(OH)_2]^- + H_2O$ occurs between 140°C and about 250°C. Between 250 and 350°C $[BO_2]$-, $[BO(OH)_2]$- and [B(OH)4]-cage filling species were observed, related to the spread in crystal sizes and their different profilings. For temperatures 350, 400 and 450°C the IR absorption spectra indicates that the second step, i.e. $[BO(OH)_2]^- \Rightarrow [BO_2]^- + H_2O$, could be evaluated separately.

**Discussion:** The regression line to single crystal related dehydration data obtained between 300 and 400°C (dashed line) well approximates to powder related data at temperatures between 140 and 200°C. This indicates that dehydration here holds the same diffusion mechanism. Deviations seen with increasing temperature above 200°C can be related to the small size of the crystals in the polycrystalline material and the assumption of an incoming sharp dehydration front to the crystal spheres instead of profiles of irregular shaped crystals, which start to interfere in crystals. This reveals a systematic decrease in $D_p$ with increasing temperature. For the second dehydration step the lower activation energy indicates a lower barrier which can be related to structural changes of the sodalite. The apparently lower value of $D_o$ in $D = D_o\exp\text{-}E_a/kT$ is related to the lower concentration of (OH)-groups in $BO(OH)_2$-SOD compared to $B(OH)_4$-SOD.

**Conclusion:** The results imply a rather fast diffusion of protons and thus a high probability for defect formation in their sub lattice. Proton jumps may occur through the four-ring windows of the sodalite. This effect might support jumps of $OH^-$ through six-rings, which can occur only if these are opened by Na-defect formation as the velocity determining step. Extrapolating Na-self diffusion data obtained by Levi and Lutze [3] for NaCl-SOD to 180°C indicate that this seems to be sufficient. It may be noted that $B(OH)_4$-SOD generally contain some $H_2O$ molecules due to the hydrothermal synthesis. Evaluation of IR-absorption spectra imply that a formula unit of $Na_{7.9}(Al_6Si_6O_{24})(B(OH)_4]_{1.9}{*}0.83H_2O$ could be given for certain crystals. The effect of $H_2O$ cage fillings could lead to missing Na-ions which could open pathways for enhanced dehydration and diffusion, which requires further investigations.

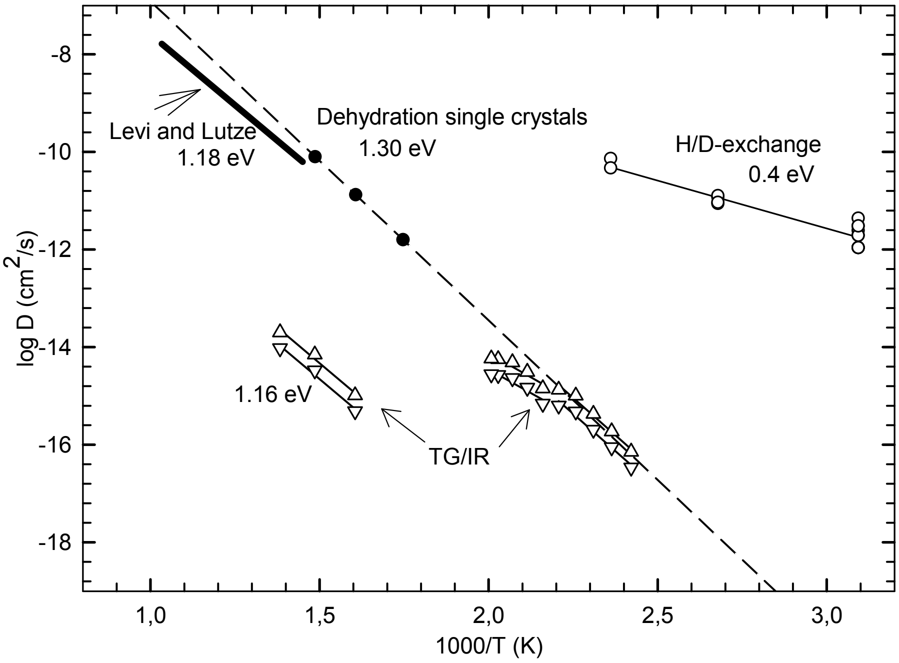

Figure 1: Arrhenius plot of diffusion coefficients from micro Raman profiles on single crystals (filled and open circles) and using powder related data (triangles). Levi and Lutze [3]: Na tracer diffusion of NaCl-sodalite.

## References

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