

**MS41 P13**

**Mechanical properties and structure of nanoporous and bulk borosilicate glass.** I.P.Shakhverdova<sup>a</sup>, P.Paufler<sup>d</sup>, S.K.Filatov<sup>b</sup>, R.S.Bubnova<sup>c</sup>, M.Reibold<sup>a</sup>, J.M.Feldkamp<sup>a</sup>, C.G.Schroer<sup>a</sup>, B.Müller<sup>d</sup>, A.A.Levin<sup>a</sup>, D.C.Meyer<sup>a</sup>, <sup>a</sup>*Inst.Strukturphysik, TU Dresden*; <sup>b</sup>*Dpt. Crystallography, St. Petersburg State Univ.*, <sup>c</sup>*Inst. Silicate Chem.RAS, St. Petersburg*; <sup>d</sup>*Inst. Phys. Chemie, Friedrich - Schiller-Univ. Jena, Germany*  
E-mail: [paufler@physik.tu-dresden.de](mailto:paufler@physik.tu-dresden.de)

**Keywords: Porous glass, sodium borosilicate, hardness**

Mechanical properties of bulk (BG) 18.1Na<sub>2</sub>O·16.9B<sub>2</sub>O<sub>3</sub>·65SiO<sub>2</sub> (mol. %) and nanoporous (NPG) 0.2Na<sub>2</sub>O·3.8B<sub>2</sub>O<sub>3</sub>·96SiO<sub>2</sub> (mol. %) sodium borosilicate glass were investigated by nano- (*TriboScope*<sup>TM</sup>) and microindentation (*Shimatsu HMV2000*). The nano- (*H*) and microhardness (*H<sub>M</sub>*) as well as Young's moduli of NPG and BG were different. While both *H* and *H<sub>M</sub>* varied between ~ 10 and ~ 7 GPa for the BG, values for NPG were an order of magnitude lower (~0.5 GPa). Young's moduli were detected of ~ 82 GPa and ~5 GPa for BG and NPG, respectively [1]. Additionally, cracks around the indent have been observed during the microindentation of BG, whereas none of them could be detected in NPG. From the length of cracks of BG, the fracture toughness *K<sub>c</sub>* ~ 1.67 – 1.94 MPa m<sup>1/2</sup> was estimated following the procedure described in [2]. The structure of glasses was investigated by X-ray powder diffraction (Cu-*K<sub>α</sub>* and Mo-*K<sub>α</sub>* radiation). For both glasses correlation distances of short-range order were found close to those of crystalline compounds with similar chemical composition (quartz, tridymite, cristobalite). However, no significant difference in the structures of BG and NPG could be detected. So, we can conclude, that the difference in mechanical properties is basically affected by the absence of porosity in BG. Morphology of pores and their distribution were investigated by  $\mu$ -SAXS tomography (HASYLAB beamline BW4) [3] and transmission electron microscopy (FEI TECNAI F20/Cs-corrected TEM). According to the TEM study, the pores are of ~ 20 nm size.

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**MS41 P14**

**Al/Si and Ca/Eu short range order in Ca/Eu-bicchulite, studied by FTIR spectroscopy.** Nouri-Said Rahmoun<sup>a</sup>, Lars Peters<sup>b</sup>, Karsten Knorr<sup>a</sup>, Wulf Depmeier<sup>a</sup>, <sup>a</sup>*Institut of Geosciences, University Kiel, Germany*, <sup>b</sup>*Chemistry Department University of Durham, UK*  
E-mail: [nsr@min.uni-kiel.de](mailto:nsr@min.uni-kiel.de)

**Keywords: FTIR spectroscopy, sodalites, short-range order**

Recently, Al-rich aluminosilicates of the solid solution series  $[\text{Ca}_{4-x}\text{Eu}_x(\text{OH})_8][\text{Al}_{12-x}\text{Si}_x\text{O}_{24}]\text{-SOD}$ ,  $0 \leq x \leq 4$ , were synthesised and the structures were characterised by X-ray diffraction and <sup>27</sup>Al MAS NMR [1]. The crystal structure corresponds to that of the mineral bicchulite,  $[\text{Ca}_8(\text{OH})_8][\text{Al}_8\text{Si}_4\text{O}_{24}]$ . Hetero-cubane like  $\text{Ca}_4(\text{OH})_4$  clusters are located in the cages of this sodalite (SOD)-type framework [2,3], formed by all-corner connected SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra. In the structure refinements Al/Si and Eu/Ca were assumed to be distributed statistically. However, broadening of <sup>27</sup>Al NMR resonance lines in Al-rich samples [1] pointed towards local order that could not be further specified. Here, powder infrared spectra of the samples synthesised and investigated by [1] were measured at room temperature with a Fourier transform spectrometer Bruker IFSS/66v, in order to further study local structural effects related to the co-substitution of Al for Si and Eu for Ca.

Spectra taken in the hydroxyl region yield information related to the local structural states of the hetero-cubane like clusters. Three different short range order patterns could be identified. Depending on *x*, different concentrations of  $\text{Ca}_4(\text{OH})_4$ ,  $\text{EuCa}_3(\text{OH})_4$ , and  $\text{Eu}_2\text{Ca}_2(\text{OH})_4$  clusters are found, whereas  $\text{Eu}_3\text{Ca}(\text{OH})_4$  or  $\text{Eu}_4(\text{OH})_4$  clusters are not observed. Hence, short range order is maintained such that each SOD cage of an all-alumina framework contains two Ca and two Eu per cluster.

The framework absorption bands (1400 to 350 cm<sup>-1</sup>) of the solid solution series can be grouped into three sets: Asymmetric stretching  $\nu_{\text{as}}(\text{T-O-T})$ , symmetric stretching  $\nu_s(\text{T-O-T})$  and bending modes  $\delta(\text{O-T-O})$ , where T represent tetrahedrally coordinated Si or Al. The positions of the different modes shift linearly towards lower wave numbers for increasing Al content. The shifts are correlated with the change of the tetrahedra angles vs. the cell parameter [1]. Furthermore, Al-rich samples show a splitting of the bending mode. This is interpreted as the additional change of the local environment of Al due to the co-substitution of Eu<sup>3+</sup> for Ca<sup>2+</sup>. Finally, changes in the line shape, resulting from cation ordering, are studied by autocorrelation analysis. In particular, samples of intermediate composition of the solid solution series have the highest values of the line broadening parameter,  $\square_{\text{corr}}$ , suggesting that they are characterised by a relatively high degree of local structural heterogeneity.

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**MS41 P15**

**Polytypism in micas from Black Hill and apparent polytypism in micas from Alto Paranaibo.**

E. Mesto<sup>a</sup>, F. Scordari<sup>a</sup> <sup>a</sup>*Dipartimento Geomineralogico, Università degli Studi di Bari*  
E-mail: [f.scordari@geomin.uniba.it](mailto:f.scordari@geomin.uniba.it)

**Keywords: Trioctahedral micas, polytypism, twinning.**

Micas are commonly found minerals of igneous and metamorphic rocks which form in a wide range of chemical and physical conditions. This particular feature

can be understood on the ground of the compositional variation and different cation arrangement connected with the intensive parameters change during the crystallization process. Recent studies of cation site partitioning in Ti-rich  $1M$  polytype from Black Hill (Australia) using a multi-technical approach [1] showed the occurrence of Fe, as  $Fe^{2+}$  and  $Fe^{3+}$ , and Ti, as  $Ti^{3+}$  and  $Ti^{4+}$ . While Titanium populates both octahedral and tetrahedral site, Fe is located only at the octahedral position. In addition Mg and Fe distribution was shown to be shared out in approximately equal amounts across M1 and M2 site.

The present study investigates the  $2M_1$  polytype coexisting with  $1M$  form, from Black Hill. Structural analysis showed similar M1 and M2 cation distribution in both polytypes with some noteworthy differences regarding occupancy of the octahedral cations. More specifically, while Mg and Fe randomly populate both M1 and M2 site in the  $1M$  polytype, these cations are distributed in orderly manner in the  $2M_1$  polytype, resulting in symmetry change from  $C2/m$  ( $1M$ ) to  $C2/c$  ( $2M_1$ ) as well as  $c$  parameter doubling. This work also investigates an apparent polytype, observed in the trioctahedral micas from Alto Paranaibo igneous province (Southeastern Brazil). Crystal chemistry of  $1M$  polytype from this locality was investigated by [2]. By making use of the multitechnical approach, [3] recently reanalysed one of the sample quoted in [2] and labelled Ma1. A number of interesting new results were found: Na is lodged at octahedral site, Ti at both octahedral and tetrahedral sites and all  $Fe^{3+}$  at tetrahedral site and  $Fe^{2+}$  populating the same octahedral site. Further investigations showed that the Ma1 can also form apparent polytypes, i.e. twinnings of  $1M$  polytype which simulate diffraction of polytype patterns with long periodicity ( $c \approx 30 \text{ \AA}$ ). Structure refinement of the twinned crystal ( $R = 3.9\%$ , carried out on the family reflections) indicated that the twin law is  $[310]_0$ , the twin index is 3 and the volume element ratio is roughly  $0.85 : 0.09 : 0.06$ . The same conclusions were reached by [4] when studying ferric phlogopites from Ruiz Peak (Northern Chile).

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#### MS41 P16

**The influence of anthropogenic salinization on the soil mineralogy** Yulia S.Simakova, *Institute of Geology KomiSC RAS, Syktyvkar, Russia.*  
E-mail: [cryst@geo.komisc.ru](mailto:cryst@geo.komisc.ru)

**Keywords: crystal chemistry of clays transformation layer silicates, mineral characterization as soil components**

The objects of our investigation are the soils from the Seriogovo salt plug territory where salt mineral waters deposits are situated. Seriogovo salt plug is confined to Mezen syncline of Russian platform.

Samples were obtained from 7 soil cross sections near the Seriogovo salt deposit: R-4, R-6, R-7, PR-1 – uncontaminated (background) and R-5, R-8, R-9 – saline cross sections at the depth 0-103 cm. Soil-forming rocks at this sections are morainic loams underlying by sandstones.

The mineralogical composition of the clay fraction ( $<2 \mu\text{m}$ ) of samples was determined by x-ray diffractometry. The  $d(060)$ -values were used to distinguish dioctahedral (1.510  $\text{\AA}$ ) and trioctahedral (1.538  $\text{\AA}$ ) minerals.

X-ray analysis indicates that almost all clay samples of background sections contain smectite, illite, chlorite, kaolinite with dominated smectite. In clay samples of saline soils chlorite, vermiculite, interstratified chlorite/vermiculite, kaolinite, illite and galite are contained. Chlorite became the predominant 14- $\text{\AA}$ -mineral. We can propose that interlayer octahedral layers are more stable than exchangeable cations of clay minerals' crystal structure in the saline environment.

The XRD patterns for the clay fraction of the uncontaminated section has an intense peak of 1.540  $\text{\AA}$  and a smaller peak of 1.507  $\text{\AA}$  suggesting that in this samples trioctahedral minerals are dominated, but also samples contains some dioctahedral minerals. The samples of the saline section also has both trioctahedral and dioctahedral minerals but the intensity of the peak for the dioctahedral mineral, however, is proportionally larger than in the uncontaminated clay.

The investigations display the difference between the clay minerals of saline and background soil samples of Seriogovo deposits because of their transformation under the al changes. The expandable layer silicates typical for the soils transformed to the unexpandable dioctahedral soil chlorite. Transformation reactions involve the introduction of non-exchangeable hydroxyl-Al polymers into the interlamellar space of pre-existing smectite or vermiculite [1]. The results presented suggest that chlorite was formed diagenetically by prolonged periodic percolation of salt brines through pervious layer silicates.

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#### MS41 P17

**Crystal Structure and twinning of the new stannide  $Sr_{42}Li_{29}Sn_{74}$ .** Qinxing Xie, Michael Wörle, Reinhard Nesper. *Laboratory of Inorganic Chemistry, ETH Zurich, Switzerland.* E-mail: [woerle@inorg.chem.ethz.ch](mailto:woerle@inorg.chem.ethz.ch)

**Keywords: crystal structures of new compounds, twinning, bond order, tin compounds**

Synthesis, physical properties, crystal structure, band structure calculations and bonding analysis of the new stannide  $Sr_{42}Li_{29}Sn_{74}$  is reported. The compound crystallizes in the space group  $P2/m$ . The lattice constants are  $a = 15.266(4) \text{ \AA}$ ,  $b = 4.930(1) \text{ \AA}$ ,  $c = 37.87(1) \text{ \AA}$ ,  $\beta = 101.592(3)^\circ$ . All examined crystals were twinned, resulting in an pseudo-orthorhombic crystal system. The anionic partial structure consists of all-cis Sn-chains, stacked Sn-five-rings which are interconnected by 2-bonded Sn-atoms, and isolated Sn-atoms. (c.f. Fig. 1).

