

MS41 P13

Mechanical properties and structure of nanoporous and bulk borosilicate glass. I.P.Shakhverdova^a, P.Paufler^d, S.K.Filatov^b, R.S.Bubnova^c, M.Reibold^a, J.M.Feldkamp^a, C.G.Schroer^a, B.Müller^d, A.A.Levin^a, D.C.Meyer^a, ^a*Inst.Strukturphysik, TU Dresden*; ^b*Dpt. Crystallography, St. Petersburg State Univ.*, ^c*Inst. Silicate Chem.RAS, St. Petersburg*; ^d*Inst. Phys. Chemie, Friedrich - Schiller-Univ. Jena, Germany*
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Mechanical properties of bulk (BG) 18.1Na₂O·16.9B₂O₃·65SiO₂ (mol. %) and nanoporous (NPG) 0.2Na₂O·3.8B₂O₃·96SiO₂ (mol. %) sodium borosilicate glass were investigated by nano- (*TriboScope*TM) and microindentation (*Shimatsu HMV2000*). The nano- (*H*) and microhardness (*H_M*) as well as Young's moduli of NPG and BG were different. While both *H* and *H_M* 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_c* ~ 1.67 – 1.94 MPa m^{1/2} was estimated following the procedure described in [2]. The structure of glasses was investigated by X-ray powder diffraction (Cu-*K_α* and Mo-*K_α* 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 μ -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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Al/Si and Ca/Eu short range order in Ca/Eu-bicchulite, studied by FTIR spectroscopy. Nouri-Said Rahmoun^a, Lars Peters^b, Karsten Knorr^a, Wulf Depmeier^a, ^a*Institut of Geosciences, University Kiel, Germany*, ^b*Chemistry Department University of Durham, UK*
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Recently, Al-rich aluminosilicates of the solid solution series $[\text{Ca}_{4-x}\text{Eu}_x(\text{OH})_8][\text{Al}_{12-x}\text{Si}_x\text{O}_{24}]$ -SOD, $0 \leq x \leq 4$, were synthesised and the structures were characterised by X-ray diffraction and ²⁷Al 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 SiO₄ and AlO₄ tetrahedra. In the structure refinements Al/Si and Eu/Ca were assumed to be distributed statistically. However, broadening of ²⁷Al 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⁻¹) 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 Eu³⁺ for Ca²⁺. 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_{corr} , suggesting that they are characterised by a relatively high degree of local structural heterogeneity.

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

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