

MS15-P14 **Crystal chemistry and electronic structures of thiooxo metallates** A. J. Lehner and C. Röhr, *Institut f. Anorg. u. Analyt. Chemie, Universität Freiburg, Germany*
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Since their first mention [1], solutions of brightly colored oxidosulphido molybdate or tungstate anions have been studied by vibrational and optical spectroscopy [2]. Surprisingly, the crystal structures of the alkali salts $A_2[(Mo/W)O_{4-x}S_x]$ were not known except for few examples like $Cs_2[MoOS_3]$ [3], when we started resynthesizing these compounds. The synthesis was achieved by passing H_2S through aqueous solutions of the corresponding alkali oxido molybdates. Recently, we presented detailed crystal structures of the salts $A_2[MO_{4-x}S_x]$ ($A = NH_4, K, Rb, Cs; x = 1-3, M = Mo$ [4], W [5]) and hydrates of monosulphido molybdates and tungstates of K, Rb and Cs [6]. While the trisulphido salts all crystallize with the β - $K_2[SO_4]$ type, which is also formed by the tetrasulphido salts, the disulphido salts exhibit several polymorphic forms (e. g. $Cs_2[MoO_2S_2]$, $C2/c: V_{\text{formula unit}} = 197.4 \cdot 10^6 \text{ pm}^3$; $Pbcn: V_{\text{f.u.}} = 199.2 \cdot 10^6 \text{ pm}^3$; $P2_1/c: V_{\text{f.u.}} = 202.1 \cdot 10^6 \text{ pm}^3$). The formation of these phases is highly dependent on the counter cation and can be controlled by solvent and crystallization conditions. The crystal chemistry of the disulphido molybdates and tungstates is rationalized by discussing the coordination, packing and coulomb energies. The effect of the different structure types can also be detected by UV/Vis spectroscopy. Based on the structural data and UV/Vis spectra, the relations of structure and properties, using FP-LAPW bandstructure and MO calculations as theoretical simulations are presented. Because of their controllable stoichiometry and thus band energies, mixed oxidosulphido metallates $[MO_{4-x}S_x]$ are a very suitable model system to study the influences of A, M, x and crystal packing/structure type on optical properties of insulators. The influences of M and x on orbital and band energies are discussed by comparing the experimental spectra in solution and in the solid state. Accordingly, the calculated MO schemes of oxidosulphido molybdates, tungstates and fictive chromates are discussed in comparison with band energies calculated from crystal structure data (e. g. exp. vs. calc. band gap of $K_2[(Mo/W)O_2S_2]$, $C2/c: 2.07/2.51$ vs. $2.34/2.84 \text{ eV}$).

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MS15-P15 **Boron in Mullites.** Hanna Lührs^a, Reinhard X. Fischer^a, Hartmut Schneider^{a,b}, John V. Hanna^c, Scott P. King^c ^aUniversity of Bremen, Germany, ^bUniversity of Köln, Germany, ^cUniversity of Warwick, UK
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Mullite is one of the most important synthetic materials for advanced structural and functional ceramics. The crystal structure of mullite with the composition $Al_2[Al_{2+2x}Si_{2-2x}]O_{10-x}$ can incorporate a large variety of ions [1]. A solid-solution series between mullite and $Al_{18}B_4O_{33}$ was proposed by [2]. Griesser [3] studied the incorporation of boron into mullite based on a 1:2 substitution of Si by B and proposed that about half the SiO_2 can be replaced by B_2O_3 . In this work a series of boron doped mullites (B-mullite) was prepared from single-phase gels based on a 1:1 substitution of Si by B, starting from a 3:2 mullite composition ($Al_{4.5}Si_{1.5}O_{9.75}$). By means of simultaneous thermal analysis (STA), XRD at ambient and high temperature, neutron diffraction, FTIR, and ^{11}B , ^{27}Al , and ^{29}Si MAS Solid State NMR the syntheses, properties, and crystal structure of B-mullite were studied.

Evidence for the incorporation of boron into the crystal structure of mullite was derived from investigation of the in-situ phase formation by means of STA and HT-XRD. A linear relationship between mullite-formation temperature and initial boron content was observed. Further evidence is given by the development of the lattice parameters: For B-mullites a significant decrease in lattice parameters b and c with increasing amount of boron was observed, clearly exceeding the range of variation expected due to a change in the Si/Al ratio. Based on the phase composition and the development of lattice parameters, it was shown that more than one third of the Si can be replaced by B. However, alumina impurities indicate that there is no complete solid solution between mullite and aluminum borate. Long annealing at $1400^\circ C$ leads to an increase of lattice parameters b and c and decomposition of B-mullite to boron-free mullite and α -alumina. However, long-term stability at $800^\circ C$ was proved. Due to the incorporation of B into the mullite structure the mean thermal expansion coefficient was reduced by 15% in comparison to boron-free mullite. The strongest reduction of thermal expansion was observed parallel to the b -axis (21.5%). The expansion of the unit-cell volume was reduced by 16%. Due to the low scattering factor for X-rays and the small weight of boron, chemical and crystal-structure investigations of B-mullites are extraordinarily difficult. The presence of threefold coordinated boron was confirmed by FT-IR spectroscopy and ^{11}B MAS NMR spectroscopy. The measured values of the ^{11}B quadrupole interaction yielded $C_Q = 2.59 \text{ MHz}$ and $\eta_Q = 0.15$; the low η_Q value suggests that the B site possesses a near-three fold axis of rotation. Rietveld refinements based on powder neutron diffraction data indicated that boron resides in three-coordination linking the octahedral chains. As the refinements resulted in unusually long B-O distances a displacement of the oxygen positions has also to be considered, resulting in a distortion of the octahedra.

The trigonal B-position allows for the formation of additional oxygen vacancies due to the substitution of $2Si^{4+}$ by $2B^{3+}$. In addition the strong B-O bonding in c -direction can explain the significant reduction of lattice parameter c due to the incorporation of boron.

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