

Structural and spectroscopic properties of SnMBO₄ (M = Al, Ga)

Sarah Wittmann¹, M. Mangir Murshed^{1,2}, Vitaliy Bilovol³, Thorsten M. Gesing^{1,2}

¹Universität Bremen, Institut für Anorganische Chemie und Kristallographie, Leobener Straße 7, D-28359 Bremen, Germany, swittman@uni-bremen.de, ²Universität Bremen, MAPEX Center for Materials and Processes, Bibliothekstraße 1, D-28359 Bremen, Germany, ³Universidad de Buenos Aires, Facultad de Ingeniería Laboratorio de Sólidos Amorfos, Av. Paseo Colón 850, C1063ACV, Buenos Aires, Argentina

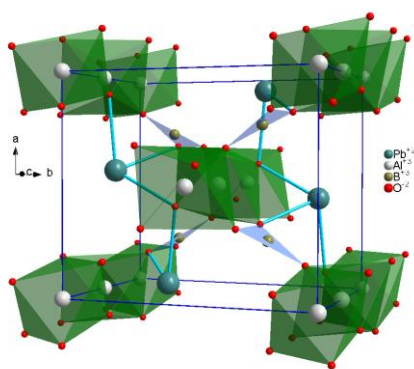


Figure 1: Crystal structure of PbAlBO₄ with AlO₆ octahedra, planar BO₃ groups and PbO₄ square pyramids

Mullite-type compounds EMBO₄ (E₂M₂B₂O₈ ≡ O8-phase) have drawn a considerable interest due to the influence of the stereochemical activity of the 6s² lone electron pairs (LEPs) of Pb²⁺ cation on the crystal-chemico-physical properties. The crystal structure of the O8-phase in the mullite-type setting is described in the orthorhombic space group *Pnam*, where the MO₆ octahedra build an edge-sharing chain running parallel to the crystallographic *c*-axis [1]. The octahedral chains are bridged by trigonal planar BO₃ groups connected by the distorted PbO₄ square pyramids. The influence of the LEP and the rigidity of the planar BO₃ groups play important roles to stabilize the O8-structures. In response to the toxicity of lead and the associated environmental issues, replacement

of Pb²⁺ by suitable LEP-containing divalent cation is a demanding alternative. As such, mullite-type SnAlBO₄ and SnGaBO₄ are synthesized. Whereas the almost similar cationic size of Sn²⁺ and Pb²⁺ predict a complete replacement of Pb²⁺ by Sn²⁺ in the O8-structure, the significantly different Wang-Liebau eccentricity parameter [2] and the susceptibility of Sn²⁺ into Sn⁴⁺ oxidation requires ingenious exploitation of the solid-state reactions. The crystal structural features are obtained from the X-ray powder data Rietveld refinements. Lattice parameters of *a* = 719.10(13) pm, *b* = 773.93(15) pm, *c* = 584.03(3) pm and *V* = 316.41(10) · 10⁶ pm³ for SnAlBO₄ and *a* = 727.60(4) pm, *b* = 791.20(4) pm, *c* = 584.03(3) pm and *V* = 336.47(13) · 10⁶ pm³ for SnGaBO₄ are obtained. Bond valence sum indicate that tin and the M-elements are slightly under bonded whereas boron is slightly over bonded, which can be explained in terms of the contraction of the BO₃ group and the distortion of the MO₆ octahedra via strong influence of the 5s² LEPs of Sn²⁺ cation. The ¹¹⁹Sn-Mössbauer spectra support the coordination and the oxidation state of tin. The vibrational features obtained from the Raman spectroscopy complement both X-ray and Mössbauer results. SnAlBO₄ and SnGaBO₄ possess high bandgap energy of 3.69(1) eV and 3.89(1) eV, respectively, obtained from the UV/Vis diffuse reflectance spectra; the direct nature of the electronic transition is analyzed using RATD (Reflection-Absorption-Tauc-DASF) analysis.

[1] T.M. Gesing, C.B. Mendive, M. Curti, D. Hansmann, G. Nenert, P.E. Kalita, K.E. Lipinska, A. Huq, A.L. Cornelius, M.M. Murshed, Structural properties of mullite-type Pb(Al_{1-x}Mn_x)BO₄, *Z. Kristallogr.-Cryst. Mater.* 228(10) (2013) 532-543. DOI:10.1524/zkri.2013.1640

[2] M. Curti, C.B. Mendive, T. Bredow, M. Mangir Murshed, T.M. Gesing, Structural, vibrational and electronic properties of SnMBO₄ (M = Al, Ga): a predictive hybrid DFT study, *J Phys Condens Matter* 31(34) (2019) 345701. DOI:10.1088/1361-648X/ab20a1

Sarah Wittmann acknowledges support by DFG under grant number GE1981/14-1.