

MS13-1-6 Temperature-dependent structural and spectroscopic properties of mullite-type SnMBO₄
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Abstract

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 the Pb²⁺ cation on the crystal-chemical and 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 cations 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. Structural information's were obtained from Rietveld refinements and 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 were refined. Bond valence sums 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. Temperature-dependent ¹¹⁹Sn-Mössbauer spectra support the coordination and the oxidation state of tin. Temperature-dependent X-ray investigations (10 K – 850 K) show very small thermal expansion coefficients with a maximum of 10•10⁻⁶ K⁻¹ at 800 K without any anomaly pointing to a phase transition. The vibrational features obtained from Raman spectroscopy complement both X-ray and Mössbauer spectroscopic results. SnAlBO₄ and SnGaBO₄ possess band-gap energies of 3.42(2) eV and 2.62(4) eV, respectively, determined from the UV/Vis diffuse reflectance spectra. The indirect nature of the electronic transition is analyzed using RATD (Reflection-Absorption-Tauc-DASF) analysis.

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References

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Figure 1: Crystal structure of PbAlBO₄

