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

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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) pm³ for SnAlBO₄ and a = 727.60(4) pm, b = 791.20(4) pm, c = 584.03(3) pm and V = 336.47(13) 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 Sn⁴⁺ 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.


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