Synthesis and characterization of indium-containing sillenite

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Bi₂₄MO₄₀ (M = Zn²⁺, Fe³⁺, Ti⁴⁺ and P⁵⁺ etc.) compounds belong to sillenite family with non-centrosymmetric space group (I23) – the prerequisite for piezoelectric and non-linear optical properties [1]. The stereochemical activity of the 6s² lone electron pairs (LEP; E) of Bi³⁺ cation can additionally serve for interesting crystal-physico-chemical properties. Indium containing sillenite-type Bi₂₅InO₄₀ has been synthesized using solid state method. X-ray powder data Rietveld refinement suggests bismuth to be found both at 24f and 2a Wyckoff positions, forming BiO₅ and BiO₄ polyhedral geometry, respectively for a cut-off distance of 260 pm. Whereas the BiO₄ tetrahedron is almost regular (Bi-O = 200.50(2) pm and 200.56(2) pm), the BiO₅ pyramid is highly distorted (Figure 1) with a maximum deviation of about 45.3 pm (max. 257.8(1) pm and min. 212.5(1) pm) mainly due to LEP activity of the Bi³⁺ cation [2]. Therefore, one might claim this coordination as nido-BiO₅:E octahedra, with the LEP pointing to the nido-position. The occupancy of the 2a position was converged to be shared by both indium and bismuth. The calculated bond valence sum of 4.03 v.u. leads to conclude that 2a site is equally shared by In³⁺ and Bi⁵⁺ cations. While Raman spectral bands between 400 cm⁻¹ and 600 cm⁻¹ are characteristic of the Bi₂₄O₄₀ cluster, the asymmetric sharp feature between 810 cm⁻¹ and 840 cm⁻¹ can be assigned to the M-O stretching bands of the MO₄ tetrahedra. Assuming the Raman scattering cross sections of the Bi-O and In-O bonds in the tetrahedral site to be similar, the fitted two spectral components at about 825 cm⁻¹ and 829 cm⁻¹ comprise of 57 % and 43 % occupancy of Bi⁵⁺ and In³⁺, which is different than that of calculated from the X-ray data. However, in this regard an estimated uncertainly of amount 10 % of the Raman spectral analysis should be considered. Analysis of the UV/Vis diffuse reflectance spectrum using the Reflectance-Absorbance-Tauc-DASF (RATD) methods, the indium containing sillenite possesses a direct bandgap of 2.08(2) eV. The bandgap value in this range may hint to a possible light photocatalytic activity of this indium containing sillenite.