Synthesis and characterization of indium-containing sillenite

Md. Imran Hossain[1], M. Mangir Murshed[1,2], Thorsten M. Gesing[1,2]

[1]University of Bremen, Institute of Inorganic Chemistry and Crystallography, Leobener Straße 7, D-28359 Bremen, Germany, mdimran@uni-bremen.de, [2]MAPEX Center for Materials and Processes, Bibliothekstraße 1, Universität Bremen, D-28359 Bremen, Germany

$Bi_{24}MO_{40}$ (M = Zn^{2+}, Fe^{3+}, Ti^{4+} and P^{5+} etc.) compounds belong to sillenite family with non-centrosymmetric space group (*I*23) – the prerequisite for piezoelectric and non-linear optical properties [1]. The stereochemical activity of the $6s^2$ lone electron pairs (LEP; E) of Bi^{3+} cation can additionally serve for interesting crystal-physico-chemical properties. Indium containing sillenite-type $Bi_{25}InO_{40}$ has been synthesized using solid state method. X-ray powder data Rietveld refinement suggests bismuth to be found both at 24*f* and 2*a* *Wyckoff* positions, forming BiO_5 and BiO_4 polyhedral geometry, respectively for a cut-off distance of 260 pm. Whereas the BiO_4 tetrahedron is almost regular (Bi-O = 200.50(2) pm and 200.56(2) pm), the BiO_5 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 Bi^{3+} cation [2]. Therefore, one might claim this coordination as nido-BiO_5E octahedra, with the LEP pointing to the nido-position. The occupancy of the 2*a* 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 2*a* site is equally shared by In^{3+} and Bi^{5+} cations. While Raman spectral bands between 400 cm^{-1} and 600 cm^{-1} are characteristic of the $Bi_{24}O_{40}$ cluster, the asymmetric sharp feature between 810 cm^{-1} and 840 cm^{-1} can be assigned to the M-O stretching bands of the MO_4 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 Bi^{5+} and In^{3+}, 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 visible light photocatalytic activity of this indium containing sillenite.

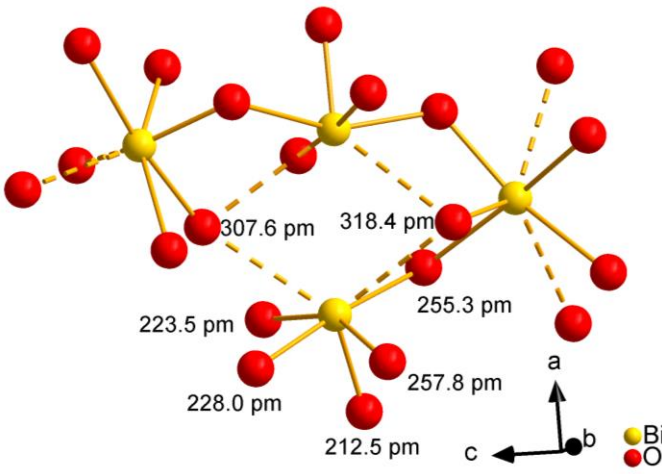

Figure 1. Coordination of BiO_5 pyramid

[1] P.S. Halasyamani, K.R. Poeppelmeier, Noncentrosymmetric oxides, Chemistry of Materials 10(10) (1998) 2753-2769. Doi:10.1021/cm980140w

[2] R.J. Betsch, W.B. White, Vibrational spectra of bismuth oxide and the sillenite-structure bismuth oxide derivatives, Spectrochimica Acta Part A: Molecular Spectroscopy 34(5) (1978) 505-514. Doi:10.1016/0584-8539(78)80047-6