Poster

Structural and spectroscopic characterisation of schafarzikite-type PbSbMO$_4$ (M = Cr, Fe, Mn)

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Due to different stereo-chemical activities of the lone electron pairs (LEPs) of 5s^2 (Sb^{3+}) and 6s^2 (Pb^{2+}) cations in metal oxides, PbSbMO$_4$ (M = Fe, Cr, Mn) would be an excellent playgroup to understand how a mixed influence of LEP-containing cations on a given *Wyckoff* position play roles for the phases crystal-physico-chemical properties.

We present the synthesis and characterization of PbSbMO$_4$ (M = Fe, Cr, Mn) which are isostructural to the mineral schafarzikite ($FeSb_2O_4$). The crystal structures are analysed based on X-ray powder diffraction data (XRPD) followed by Rietveld refinements, confirming each phase to crystallize in the $P4_2/mbc$ space group. Moreover, samples of $PbSbCrO_4$ and $PbSbFeO_4$ were analysed using 3D electron diffraction (3D ED); the resulting unit-cell parameters well agree with those from XRPD data within less than 0.5 %. Differences between the unit cell volumes of the three compounds are explained in terms of different cationic size between Cr^{3+}, Fe^{3+} and Mn^{3+}. Both kinematic and dynamic refinements are applied after appropriate data reduction [1], which confirm the tetragonal space group for both $PbSbCrO_4$ and $PbSbFeO_4$. The strength of the stereo-chemical activity of the LEP is measured using the Wang-Liebau eccentricity parameter [2]. The vibrational properties are characterized by Raman and FTIR spectroscopy data complement the local structural features of the schafarzikite structure-types. The optical band gaps are evaluated from the UV/Vis diffuse reflectance spectra using the RATD methods, leading to types of transition as well. This study highlights how the crystal-chemical properties are associated with the strength of the stereo-chemical activity of LEPs in these novel mullite-type O8 compounds.

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