Abstract

$YBi_2O_{3.5+\delta}Se_{1-x}Cl_x$: A family of semiconductors with a charge- and defect-tunable triple fluorite layer

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The design and development of new materials is crucial for advanced next-generation technologies, necessitating the modification of materials with tuneable atomic and electronic frameworks. This is often achieved by addition or replacement of metals and cations. Substitution of anions is also possible; here, we present the $YBi_2O_{3.5+\delta}Se_{1-x}Cl_x$ family which represent a new class of layered mixed anionic semiconductor materials with complete substitution of Cl by Se charge balanced by the introduction of oxide vacancies. The introduction of Se anions into the visible band gap material YBi_2O_4Cl shifts the band gap from 2.4 to 1.2 eV. This coupled Se/Cl substitution with O vacancy generation enables defect-engineered, tuneable new layered materials with tailored electronic properties in the visible band gap region, opening new pathways for development of semiconductors, thermoelectrics, and mixed oxide ion conductors.

We have synthesized a layered rare earth Bi-based oxyselenide ($YBi_2O_{3.5}Se$), isostructural to $LaBi_2O_4Cl$ and features selenium (Se^{2-}) in place of chlorine (Cl^-) in its composition by an aliovalent substitution not usually possible. The $LaBi_2O_4Cl$ structure, in theory, could host disordered dimers by substitution of Cl^- with Se^- as seen in the similar material La_2O_2Sb with Sb^{2-} on a square net, shifting off centre from its central special position. However, instead of reduction of Se^{2-} to a formal Se^{1-} as would be the case for the formula YBi_2O_4Se, we find that for every Cl atom substituted by Se from the formula YBi_2O_4Cl, the compound loses 1/2 of an oxygen atom from the triple fluorite layer, confirmed by neutron diffraction data.

To understand the relationship between the oxygen vacancies and aliovalent substitution on the Se/Cl site, the series $YBi_2O_{3.5+\delta}Se_{1-x}Cl_x$ for x = 0, 0.3, 0.5, 0.7 and 1.0 was synthesized and analysed. All compounds in the series demonstrate powder diffraction patterns consistent with the same P4/mmm unit cell as reported for YBi_2O_4Cl via X-ray Powder diffraction measurements (XRD), performed on a PANalytical Empyrean powder diffractometer with Cu $K\alpha_1$ radiation. The XRD patterns show a clear peak shift towards lower angles for compositions going from x = 1 to x = 0. This shift is caused due to the larger size of the Se^{2-} ion compared to Cl^- leading to the expansion of unit cell upon replacing Cl atoms with Se in the composition. Both unit cell lattice parameters *a* and *c* expand with Se substitution. The increase is consistent in both dimensions and is approximately linear when fitted.