

Poster Presentation

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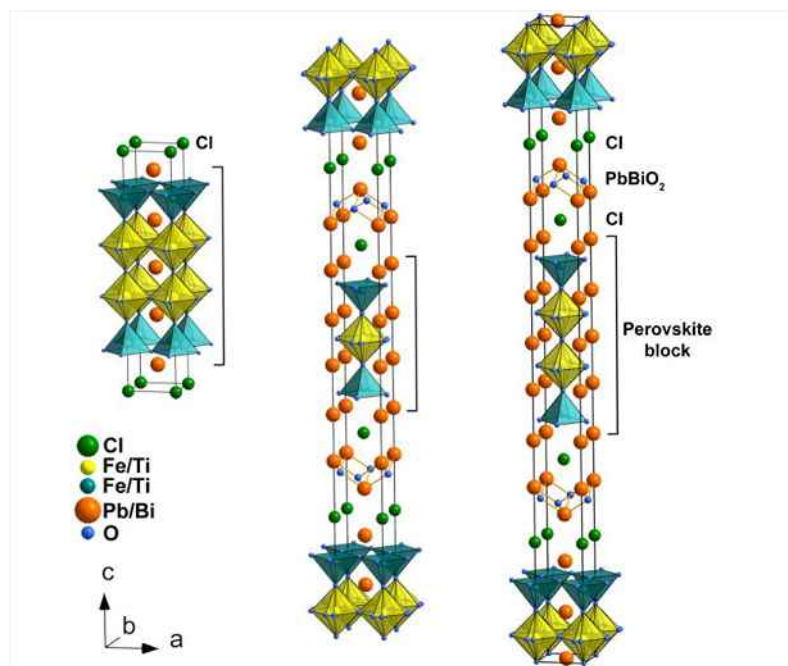
Crystal and magnetic structure of new perovskite-based lead iron oxychlorides

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The hematophanite $\text{Pb}_4\text{Fe}_3\text{O}_8\text{Cl}$ crystal structure is built of incomplete perovskite $\text{Pb}_4\text{Fe}_3\text{O}_8$ blocks separated by layers of chlorine atoms [1,2]. Each perovskite block consists of a corner-sharing FeO_6 octahedral layer sandwiched between the sheets of the FeO_5 square pyramids. We have proven that the thickness of the perovskite block in the hematophanite structure can be extended to two and even three octahedral layers forming homologous series with the general formula $\text{A}_{n+1}\text{B}_n\text{O}_{3n-1}\text{Cl}$ (where hematophanite is the $n=3$ member). The $n=4$ members with composition $\text{Pb}_4\text{BiFe}_4\text{O}_{11}\text{Cl}$ and $\text{Pb}_5\text{Fe}_3\text{TiO}_{11}\text{Cl}$ have been synthesized. We were also able to introduce Aurivillius-type PbBiO_2 blocks between the hematophanite blocks forming another new homologous series $[\text{PbBiO}_2]\text{A}_{n+1}\text{B}_n\text{O}_{3n-1}\text{Cl}_2$. Two successive members with $n=3$ ($\text{Pb}_5\text{BiFe}_3\text{O}_{10}\text{Cl}_2$) and $n=4$ ($\text{Pb}_5\text{Bi}_2\text{Fe}_4\text{O}_{13}\text{Cl}_2$ and isostructural $\text{Pb}_5\text{BiFe}_3\text{TiO}_{13}\text{Cl}_2$) have been obtained. The crystal and magnetic structure has been determined and refined in a wide temperature range (1.5 – 700 K) using a combination of neutron powder diffraction (NPD) and electron microscopy techniques (electron diffraction, high angle annular dark field scanning transmission electron microscopy (STEM), atomic resolution STEM-EDX). Using NPD and STEM-EDX data we demonstrated that Ti^{4+} cations occupy both octahedral and square-pyramidal sites. This makes these structural types rare examples of Ti^{4+} in five-fold oxygen coordination environment. $\text{Pb}_4\text{BiFe}_4\text{O}_{11}\text{Cl}$ and $\text{Pb}_5\text{Fe}_3\text{TiO}_{11}\text{Cl}$ are antiferromagnetically (AFM) ordered below 600(10) and 450(10) K, respectively. $\text{Pb}_5\text{BiFe}_3\text{O}_{10}\text{Cl}_2$, $\text{Pb}_5\text{Bi}_2\text{Fe}_4\text{O}_{13}\text{Cl}_2$ and $\text{Pb}_5\text{BiFe}_3\text{TiO}_{13}\text{Cl}_2$ demonstrate signs of local magnetic ordering below ~ 600 , ~ 600 and ~ 400 K, respectively. However, the long range magnetic ordering does not set in and the magnetic reflections appear enormously broadened merging into a halo. Presumably, AFM ordering establishes within the perovskite blocks but is disrupted along the c -axis, because of a high thickness of the non-magnetic modules.

[1] J. Pannetier, P. Batail, *Journal of Solid State Chemistry*, 1981, 39, 15–21, [2] C.S. Knee, M.T. Weller, *Journal of Materials Chemistry*, 2001, 11, 2350–2357



Keywords: perovskite, neutron powder diffraction, transmission electron microscopy