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

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The hematophanite Pb4Fe3O8Cl crystal structure is built of incomplete perovskite Pb4Fe3O8 blocks separated by layers of chlorine atoms [1,2]. Each perovskite block consists of a corner-sharing FeO6 octahedral layer sandwiched between the sheets of the FeO5 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 An+1BnO3n−1Cl (where hematophanite is the n=3 member). The n=4 members with composition Pb4BiFe4O11Cl and Pb5Fe3TiO11Cl have been synthesized. We were also able to introduce Aurivillius-type PbBiO2 blocks between the hematophanite blocks forming another new homologous series [PbBiO2]An+1BnO3n-1Cl2. Two successive members with n=3 (Pb5BiFe3O10Cl2) and n=4 (Pb5Bi2Fe4O13Cl2 and isostructural Pb5BiFe3TiO13Cl2) 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 Ti4+ cations occupy both octahedral and square-pyramidal sites. This makes these structural types rare examples of Ti4+ in five-fold oxygen coordination environment. Pb4BiFe4O11Cl and Pb5Fe3TiO11Cl are antiferromagnetically (AFM) ordered below 600(10) and 450(10) K, respectively. Pb5BiFe3O10Cl2, Pb5Bi2Fe4O13Cl2 and Pb5BiFe3TiO13Cl2 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.


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