**†Electronic Supplementary Information (ESI) available:** XRD data, HRTEM micrographs in different orientations, magnification of the M(H) data for ilmenite compound, reciprocal susceptibility and χT *vs* T plots as well as different views of magnetic structures. See DOI: 10.1039/b000000x/

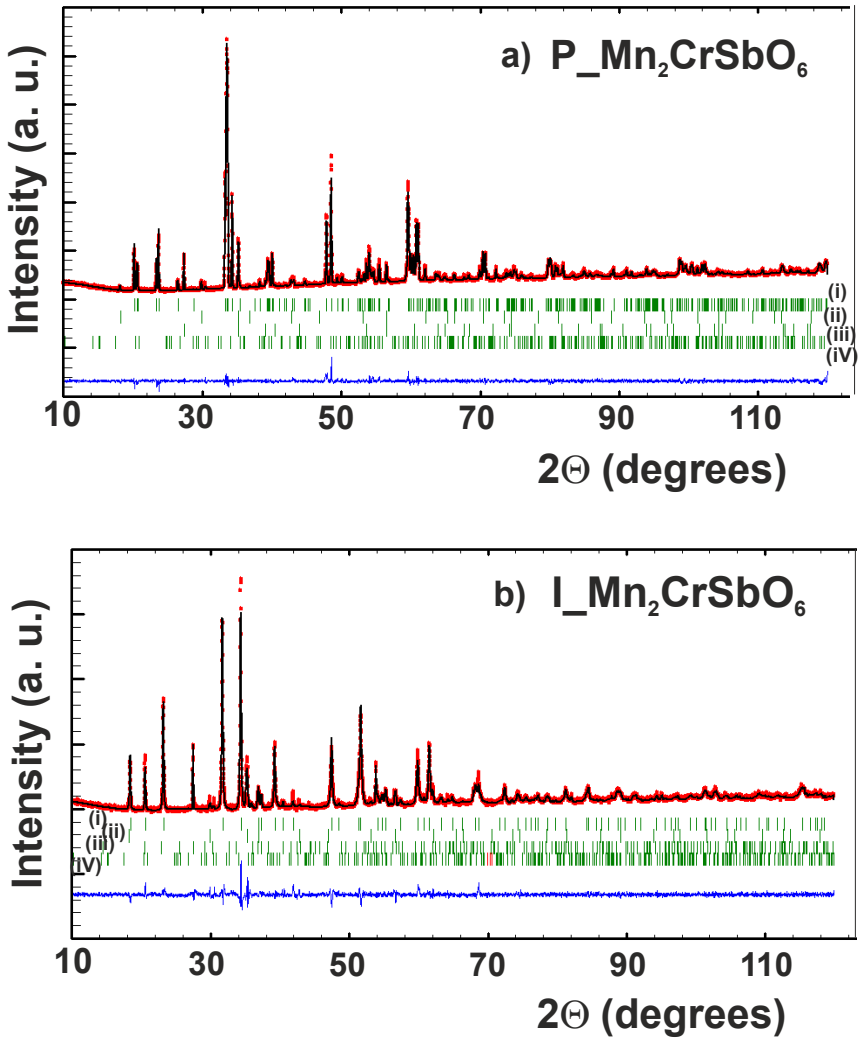


**Figure SF1.** a) Rietveld refinement of the X-ray diffraction pattern of P_$Mn_2CrSbO_6$ compound at room temperature (i). Minor secondary phases are $MnCr_2O_4$ (ii), $Sb_2O_4$ (iii) and $Mn_2Sb_2O_7$ (iv). b) Rietveld refinement of the PND pattern of I_$Mn_2CrSbO_6$ (i). Impurities are $MnCr_2O_4$ (ii) and $MnSb_2O_4$ (iii) and $Mn_2Sb_2O_7$ (iv).

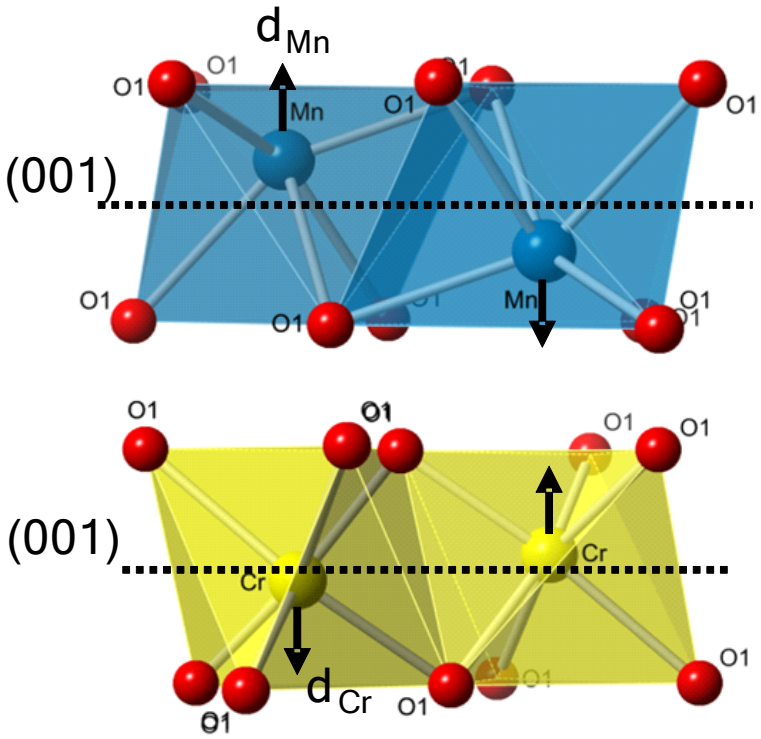


**Figure SF2.** Cation displacements off-centre of the octahedra due to cation-cation repulsions across shared faces and edges of octahedra.

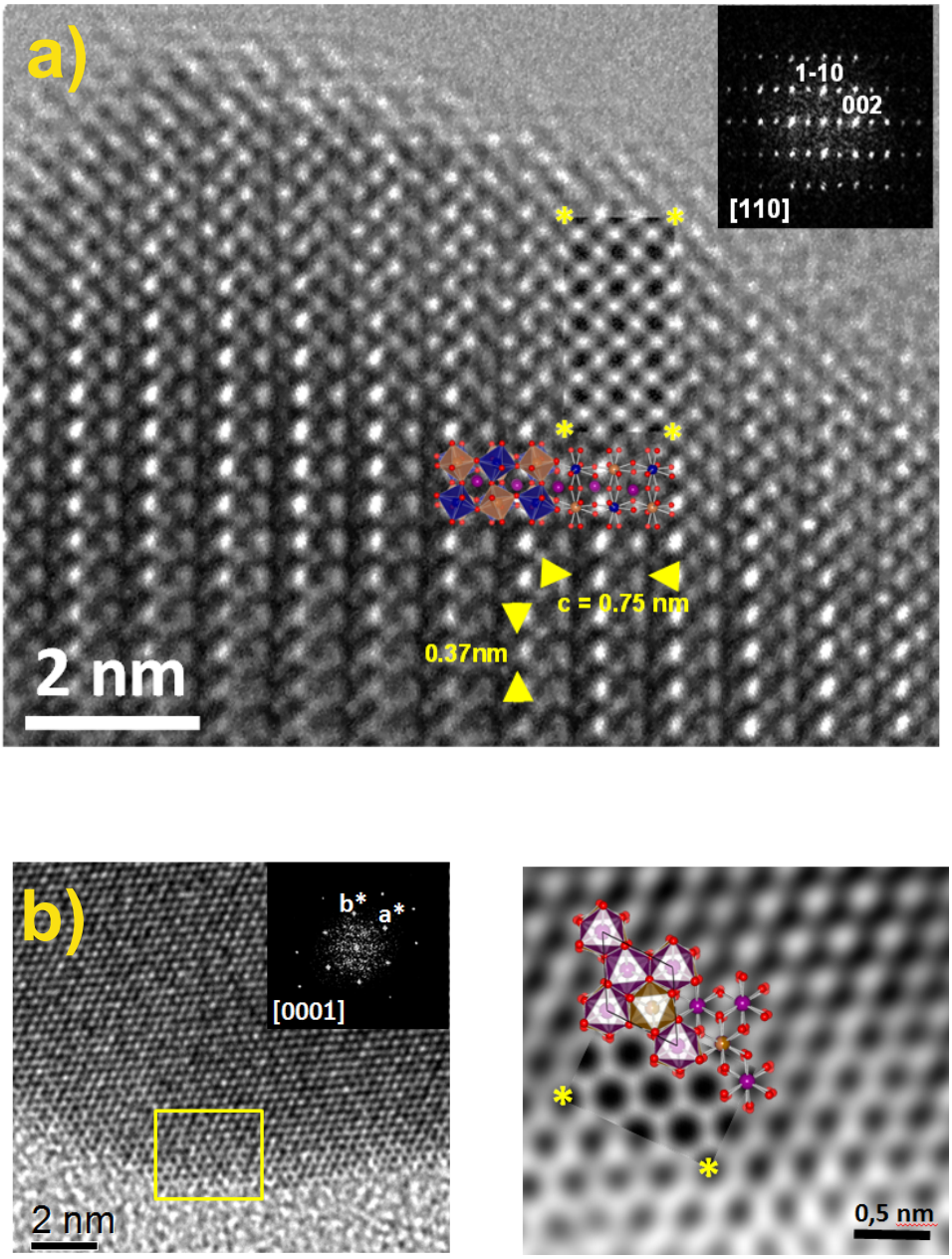


**Figure SF3.** HRTEM micrographs of the a) [110]p-perovskite and b) [0001]-ilmenite orientations.

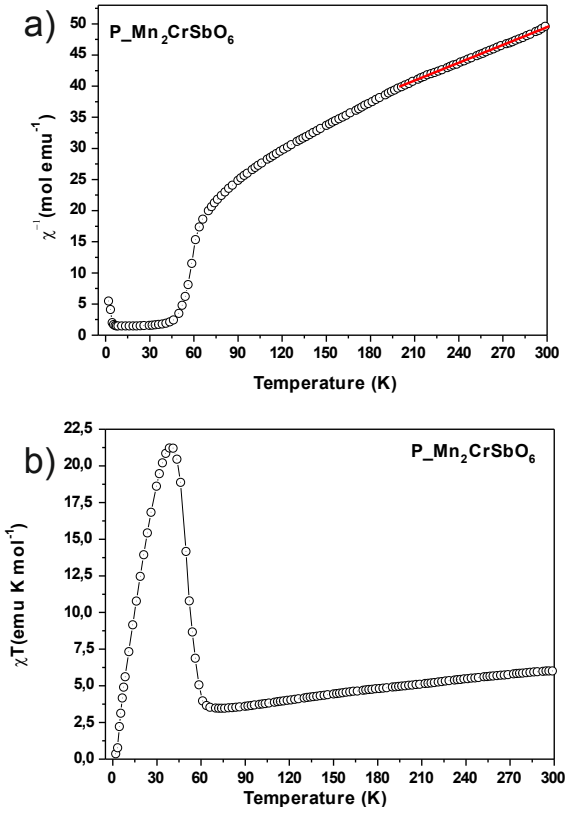


**Figure SF4.** a) Temperature dependence of the reciprocal susceptibility and b) χT vs. T plot for $Mn_2CrSbO_6$ perovskite.

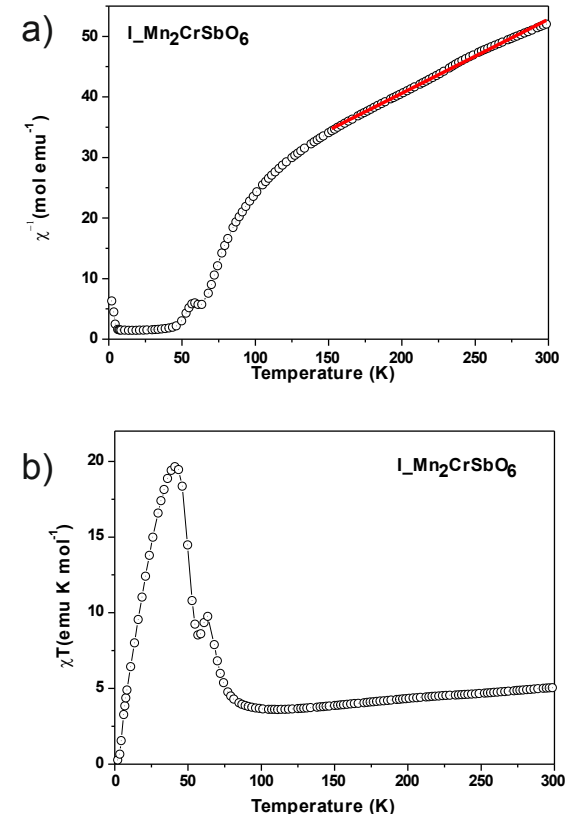


**Figure SF5.** a) Temperature dependence of the reciprocal susceptibility and b) χT vs. T plot for $Mn_2CrSbO_6$ ilmenite.

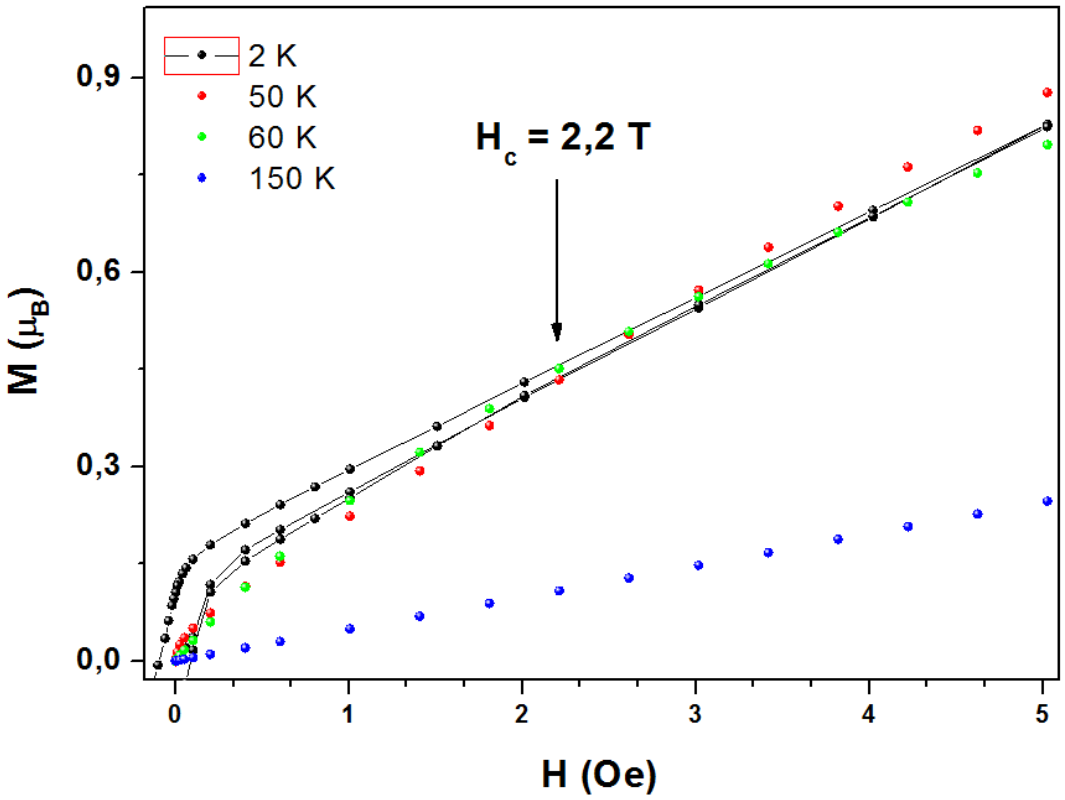


**Figure SF6.** Magnetization isotherms at 2, 50, 60 and 150 K temperatures. A metamagnetic transition occurs at H< 2.2 T.

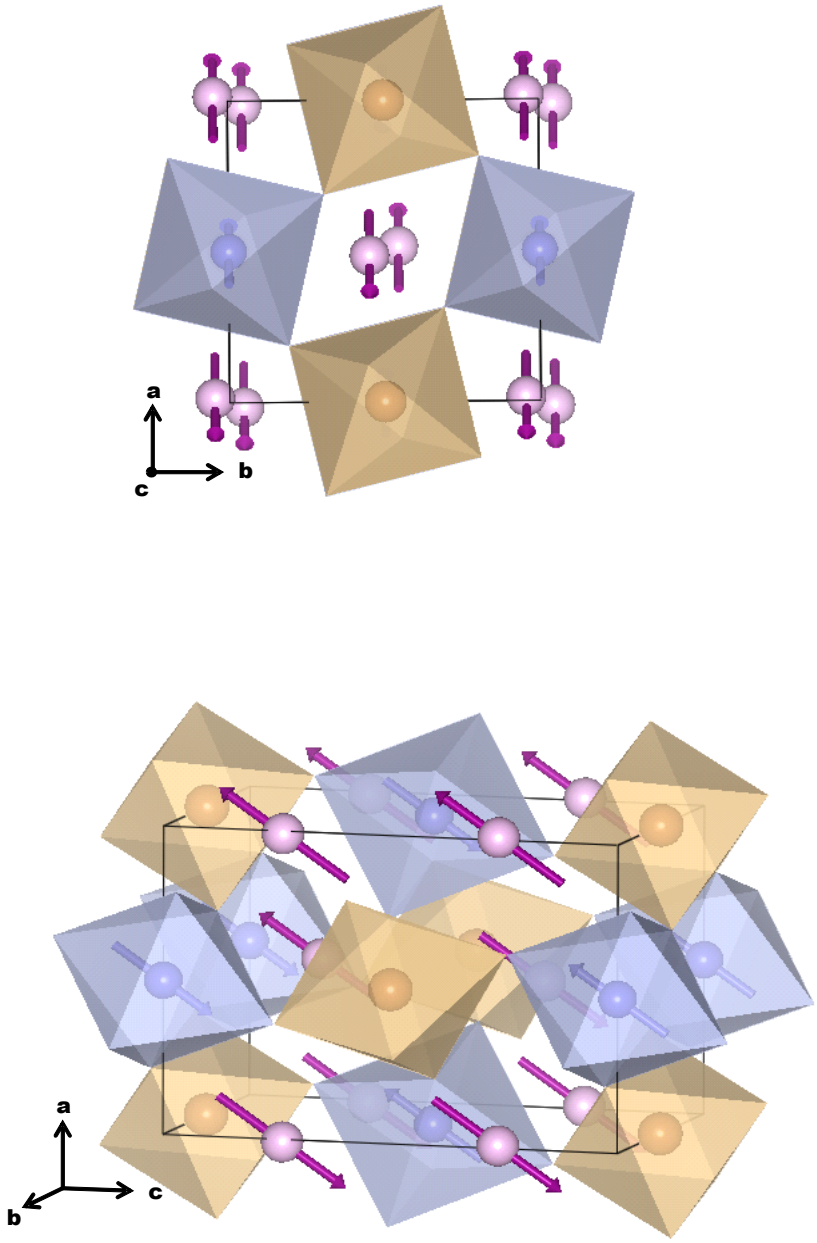


**Figure SF7.** Two different views of the magnetic structure for $Mn_2CrSbO_6$ perovskite polymorph. Magnetic moments for Mn and Cr are represented by pink and blue arrows respectively.

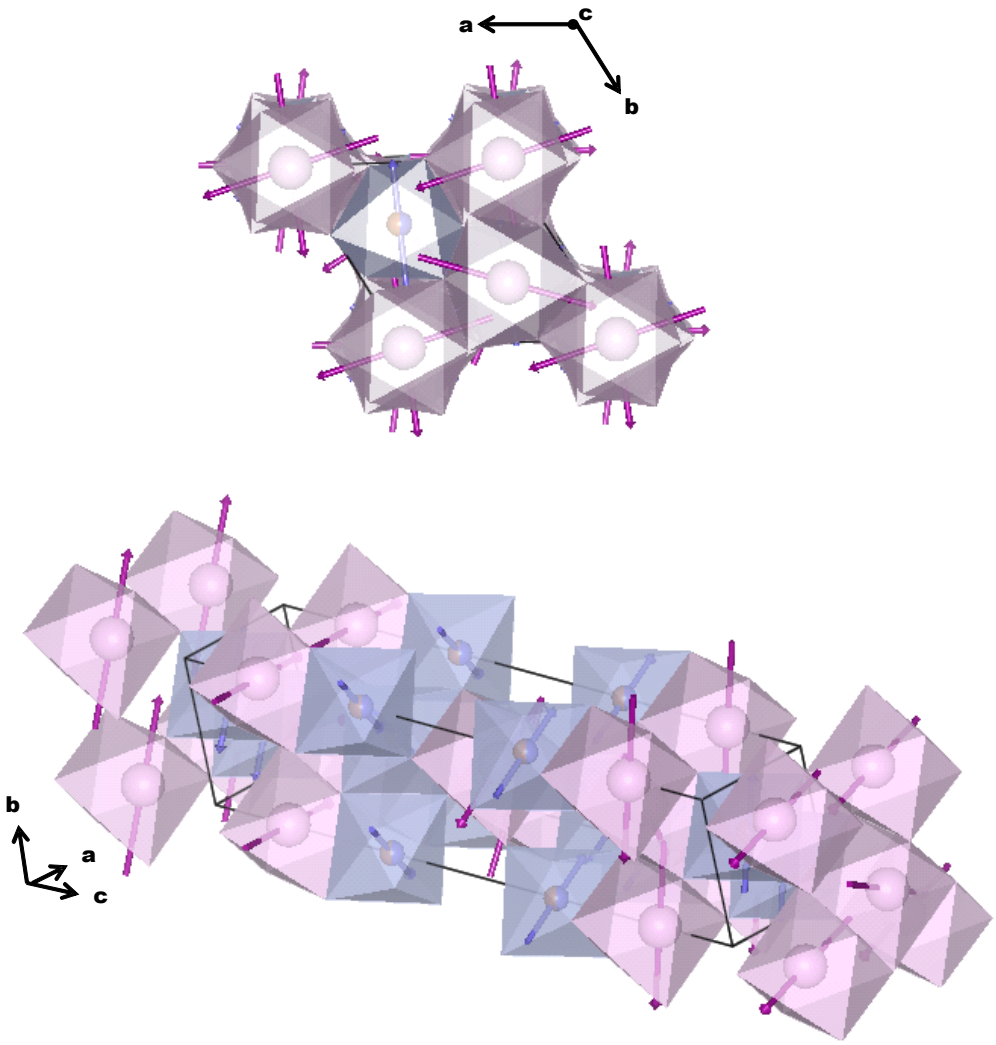


**Figure SF8.** Two different views of the magnetic structure for $Mn_2CrSbO_6$ ilmenite polymorph. Magnetic moments for Mn and Cr are represented by pink and blue arrows respectively.