Structural Studies and High Temperature Properties of Bismuth Vanadate Sillenites; Man-made Minerals!

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Phase formation in the bismuth-rich end of the Bi_2O_3 - V_2O_5 system was investigated and an extensive solid solution of sillenite related phases found ($Bi_{12}(Bi_{1-x^3}+V_x^{5+})O_{20+(x-0.5)}$; 0.065<x<0.705). These materials are metastable and have unusual high temperature behaviour not observed in other sillenite phases. High temperature x-ray diffraction, differential thermal analysis and Impedance Spectroscopy have been used to characterise their high temperature properties. Structural studies of this family of bismuth vanadate sillenite materials have been carried out using neutron diffraction data to try and correlate the metastable nature of these materials to their structure. The structure of these materials is related to the sillenite structure, but a new model was required to take into account Bi^{3+} partially occupying the tetrahedral site along with V^{5+} and the non-stoichiometric nature of the oxygen lattice. It is proposed that the disordered nature of the oxygen lattice is the key to their metastable nature.