Preliminary Structural Refinements And A New Synthetic Route To δ-Bi_2O_3-Related Phases In The Bi-W-O, Bi-Mo-O, Bi-Ta-O And Bi-Nb-O Systems

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The floating zone image furnace is an ideal tool to grow micrometre to millimetre sized metal-oxide crystals. During crystal growth there is no contact with crucibles or quartz/platinum tubes, minimising the formation of impurities. The rapid cooling of the melt produces quenching conditions, allowing synthesis of crystals that do not form with slow cooling; e.g. crystals within the solid-solution range. Here we report the use of the floating zone image furnace technique to grow single crystals of the δ-Bi_2O_3-related solid-solution phases of nominal composition $Bi_8Nb_2O_{17}$, $Bi_{5.6}WO_{11.4}$, $Bi_{16}Ta_2O_{19}$ and $Bi_{38}Mo_7O_{78}$. The $Bi_{5.6}WO_{11.4}$ and line phase $Bi_{38}Mo_7O_{78}$ single crystals were analysed with synchrotron and laboratory based X-ray diffraction to determine metal cation positions and neutron diffraction to determine the oxygen anion positions. The diffraction methods are also applied to the 3-D incommensurately modulated structures of $Bi_8Nb_2O_{17}$ and $Bi_{16}Ta_2O_{19}$. There are challenges encountered in these latter complicated structures; e.g. integration of the collected '6-D' data and subsequent refinements. Each sample studied presents different methods of approaching the structural solutions. The ability to grow single crystals of the Bi-rich transition-metal oxides and solve these structures, highlight the potential for the exploration of phase diagrams by the use of the floating zone technique.