Flux growth and characterization of bulk $InVO_4$ crystals

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Among orthovanadates of the transition metals with common formulae $M^{3+}VO_4$ (M^{3+} = In, Fe, Cr, Ti) compound $InVO_4$ possesses attracting electrochemical and photocatalytic properties, that cause the wide range of its commercial applications. In the literature five different crystal structures of the $InVO_4$ are described: monoclinic phase ($InVO_4$-I) with α-$MnMoO_4$-type structure, an undetermined phase ($InVO_4$-II), the orthorhombic phase with $CrVO_4$-type structure ($InVO_4$-III), all three detected at ambient pressure [1-4]; and $InVO_4$-IV with undetermined structure and $InVO_4$-V with characteristic wolframite structure, detected at high pressure [5-8]. The phase transformation $InVO_4$-III → $InVO_4$-V happened at pressure around 8 GPa and is accompanied by a large volume collapse of 16.6 % and the change of the coordination number for vanadium atom from 4 for $InVO_4$-III to 6 for $InVO_4$-V, that lead to the transformation of physical properties, as was discussed in [6,7]. To the best of our knowledge, no attempts to obtain bulk single crystal samples of $InVO_4$ have been made before and all researches regarding the high-pressure transformation and properties exploration for the $InVO_4$ have been done only for polycrystalline samples. Thus, present study was devoted to obtaining of $InVO_4$ single crystal with orthorhombic structure and characterize obtained samples for a further X-ray high-pressure study for understanding its fundamental properties.
Flux growth of $InVO_4$ bulk single crystals has been explored for the first time. In the proposed method the copper pyrovanadate ($Cu_2V_2O_7$) was applied as the flux material. Low melting point of the flux (785 °C) prevents sublimation of indium oxide from the melt and results in growth of bulk $InVO_4$ single crystals. Surface of obtained crystals is decorated by the flux compound, that have been proved by XRD and EDX analysis. According to XANES analysis oxidation states of the indium and vanadium ions are +3 and +5, respectively, thus, obtained crystals don`t possess any admixture phases with different oxidation states of vanadium ion. EXAFS fitting showed good similarity of obtained data with the crystallographic model, proving high quality of obtained crystals.
The quality of grown by flux technique $InVO_4$ crystals is sufficient for further X-ray diffraction study under high-pressure, that are already in progress at the group of Prof. Dr. J. Geck in TU Dresden, Germany.

References

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