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The Synthesis of HfOS

Rare earth oxysulfides have been reported by Flahaut *et al.* in great detail (*1*), as well as by others, but information about first, second, and third row transition metal oxysulfides is very sparse. The preparation and structural information on ZrOS makes it the only well-documented compound (*2–5*). Recently the synthesis and crystal structure of HfOS was reported by Stocks *et al.* (*6*). A few single crystals of HfOS were found in a reaction product from an experiment which was designed to yield HfS_2. The authors described a number of attempts to prepare HfOS but all were unsuccessful. We repeated their preparative procedures and introduced some additional modifications but all resulted in failure. The inability to synthesize HfOS is puzzling because of the close relationship of properties between Hf and Zr and the ease with which the latter compound forms. We postulated that a mineralizer is required to initiate the reaction and selected NH_4Cl on the basis of its widespread use as a transporting agent for single crystal growth. A mixture of stoichiometric amounts of HfO_2 and HfS_2 was placed into a Vycor tube with id = 7 mm and approximately 15 cm long. About 5 mg NH_4Cl per cubic centimeter of volume was added to the system, which was evacuated, sealed, and placed into a furnace. The temperature was raised to 600°C for about 12 hr, after which the temperature was increased to 900°C and the specimen held there for 3 days. A temperature differential of about 50°C existed between the two ends of the reaction tube. When the ampoule was removed, many yellow, translucent, octahedral crystals about 1 mm in size could be seen at the cooler end of the tube. Energy dispersive qualitative X-ray analysis showed the presence of Hf and S and X-ray wavelength dispersive analysis confirmed the presence of oxygen. Furthermore, the X-ray powder diffraction pattern was identical to that expected for ZrOS and single-crystal precession diagrams yielded the space group $P2_13$ and the lattice parameter $a = 5.68$ Å, in agreement with the reported crystal structure for HfOS (*6*). The same technique works very well for the growth of ZrOS crystals. We were interested to see whether a complete solid-solution range of $Zr_{1-x}Hf_xOS$, $0 \leq x \leq 1$, exists for this system as might be expected on the basis of the strong similarity between Hf and Zr. We prepared mixtures of ZrO_2, ZrS_2, HfO_2, and HfS_2 with NH_4Cl as a transporting agent in the appropriate ratios to yield the compounds $Zr_{0.25}Hf_{0.75}OS$ and $Zr_{0.75}Hf_{0.25}OS$. In all cases single crystals of the mixed metal oxysulfides were grown and the presence of both metals in about the proportions expected from the initial mixture was confirmed by energy dispersive X-ray analysis. No attempts to optimize single crystal growth conditions were made. Studies of the physical properties of the solid solutions and of the pure compounds are currently in progress and will be reported elsewhere.

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