**Toward Inexpensive Superhard Materials: Tungsten Tetraboride-Based Solid Solutions**

Reza Mohammadi,1,2 Miao Xie,1Andrew T. Lech,1 Christopher L. Turner,1 Abby Kavner ,3 Sarah H. Tolbert,1,2,4 and Richard B. Kaner1,2, 4

1 Department of Chemistry, 2 Department of Materials Science, 3 Department of Earth and Space Sciences and 4 California NanoSystems Institute, University of California, Los Angeles, Los Angeles, CA, USA

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, **134**, 20660-20668 (2012)

Late transition metal borides represent an exciting new class of superhard materials. Tungsten tetraboride (WB4) is a notable inexpensive member of this family with a high hardness slightly above 40 GPa. The goal of this study was to enhance the hardness of WB4, by making solid solutions of this material with Ta, Mn and Cr. various concentrations of these three elements, ranging from 0.0-50.0 at.%, were synthesized using arc melting. Microindentation was used to measure the Vickers hardness under loads of 0.49-4.9 N.

 

The bulk modulus for the hardest WB4 solid solution, W0.93Ta0.02Cr0.05B4, was 335 GPa as determined using *in situ* high-pressure X-ray diffraction measurements with data collected up to ~65 GPa (*right Figure*). This bulk modulus value is slightly higher than that of pure WB4 (326 GPa). These experiments were performed at the 12.2.2. ALS, HP-CAT, and also using the COMPRES gas-loading system at GSECARS.



Optimized Vickers hardness values of 52.8, 53.7 and 53.5 GPa were obtained when ~2.0, 4.0 and 10.0 at.% of Ta, Mn and Cr (*left Figure*) were added to WB4, respectively. These results motivated us to create ternary solid solutions of WB4, keeping the concentration of Ta in WB4 constant at 2.0 at.% and varying those of Mn or Cr from 0.0-10.0 at.%. This yielded hardness values of 55.8 and 57.3 GPa for W0.94Ta0.02Mn0.04B4 and W0.93Ta0.02Cr0.05B4, respectively.



The hardest solid solution (W0.93Ta0.02Cr0.05B4) showed suppression of a pressure-induced phase transition previously observed in pure WB4, as is evidenced from the *c/a* ratios plotted as a function of pressure for these two materials (*left Figure*). Solid circle: compression of the solid solution; solid square: decompression of the solid solution; open circle: compression of WB4; open square: decompression of WB4.