Cs₂K(UO)₂Si₄O₁₂: A Mixed-valence Uranium(IV, V) Silicate

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To further establish the valence state of the uranium in $Cs_2K(UO)_2Si_4O_{12}$ (1), X-ray absorption near-edge structure (XANES) spectra were recorded at a wiggler BL01C1 beamline of the National Synchrotron Radiation Research Center, Taiwan, in transmission mode at 293 K. The U L₃-edge XANES spectra of compound 1 and three reference materials, $U^{IV}O_2$, $K_3(U^V_{\ 3}O_6)(Si_2O_7)$ and $U^{VI}O_3$, are shown in Fig. 1. The U^{VI} edge, measured at the position of the half-edge step marked by a horizontal dashed line in the figure, is at 17169.4 eV, which is 0.7 eV above the U^V edge at 17168.7 eV, and 3.2 eV above the U^{IV} edge at 17166.2 eV. The edge of 1 is at 17167.1 eV, a value which is consistent with the presence of U^{IV}/U^V in this material.

Therefore, the electroneutrality principle, polyhedral geometry, bond-valence sum, XPS, and XANES spectroscopy indicate that ${\bf 1}$ is a mixed-valence U^{IV}/U^V oxide material.

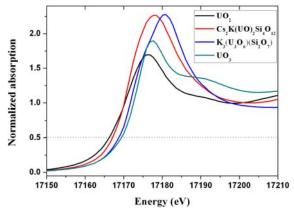


Fig. 1: The U L₃-edge XANES spectra of **1**, along with three standards, $U^{IV}O_2$, $K_3(U^V{}_3O_6)(Si_2O_7)$, and $U^{VI}O_3$. The dashed line at the absorption coefficient value of 0.5 is included to elucidate the chemical shift.

Reference

[1] C.-S. Lee, S.-L. Wang, and K.-H. Lii, J. Am. Chem. Soc. **131**, 15116 (2009).