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Copper site occupancy and valence in lead apatites via XAS at ASTRA/SOLARIS

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We report Cu K-edge XANES/EXAFS results on a series of Cu-substituted lead apatites Pb10-xCux(YO4)6Z (x ≈ 1), Y = P, V; Z = (OH)2, F2, Cl2, Br2, I2. The aim was to test the site preference and valence state of Cu in the apatite lattice, following the experiment proposed at SOLARIS/ASTRA. XANES edge positions and comparison to CuO/Cu_2O standards demonstrate that Cu is unambiguously in the Cu2+ (3d9) state in all measured samples, which is the valence required by band-structure scenarios invoking flat Cu-derived bands near E_n. EXAFS fitting with FEFF-based models shows that for phosphates and vanadates with F_2, Cl_2, and Br_2 channel anions, Cu occupies predominantly the Pb(I) (4f) site, in line with our DFT site-energy hierarchy. A notable exception is found for the iodide and phosphate–hydroxyl members, where the best fits require a mixed Pb(I)/Pb(II) (4f/6h) occupation, indicating that channel size/polarizability and local OH coordination reduce the energetic penalty for Cu on Pb(II). These experimental site fractions constrain the realistic Cu distributions that should be used in electronic-structure models of Cu-Pb apatites and clarify why some compositions may fail to exhibit the predicted correlated or flat-band features. The results are in broad agreement with DFT estimates, and confirm that XAS is an effective discriminator of Cu site and valence in this materials family while.

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