Electronic Supplementary Information (ESI):

FEFF Calculation

FEFF is a computer code based on Real Space Multiple Scattering Theory- it allows for the mathematical modeling of the XANES. It originated from Prof. John Rehr's group of the University of Washington and has been upgraded to the present version- FEFF9 over a period of more than three decades. FEEF is commonly accepted by literature.

The crystal structure of $Ca_3Si_2O_7$ is modelled to have the structure of rankinite,[1] and has space group symmetry of P_{21}/a with lattice constant of a=10.557Å, b=8.885Å, and c= 7.858Å, α=900, ß=119.5860, γ=900. The locations of the atoms in $Ca_3Si_2O_7$ are Ca_1 at (0.0071,0.0552,0.2893), Ca_2 at (0.1677,0.5745,0.2083) Ca_3 at (0.3403,0.9034,0.2839), Si_1 at (0.2948,0.2357,0.4314), Si_2 at (0.0903,0.2145,0.9843), O_1 at (0.3579,0.4038,0.4229), O_2 at (0.1782,0.2344,0.5033) , O_3 at (0.4105,0.1016,0.5523), O_4 at (0.2007,0.1629,0.2120), O_5 at (0.0970,0.3857,0.9810), O_6 at (0.1451,0.1487,0.8437), O_7 at (0.9299,0.1536,0.9394). The XANES (X-ray Absorption Near Edge Structure) spectra of the cluster of the $Ca_3Si_2O_7$ compounds with this crystal models have been calculated by the multiple scattering theory using the FEFF9 code. [2] This theory is based on the real-space Green`s function approach.[3] The XAFS (X-ray Absorption Fine Structure) amplitute of the N-leg (NLEG) path Γ is given by:

$$\chi_{\Gamma}(k) = S_o^2 \, Im \frac{f_{eff}}{kR^2} \, e^{2ikR+2i\delta_l} e^{-2\sigma^2 k^2} \qquad (1)$$

where S_o^2 is the many-body reduction factor, k is the wave-vector of the photo-electron and f_{eff} is the effective scattering amplitude. The structural parameters include the inter-atomic distances *R*. δ_l is the central-atom partial-wave phase shift of the final state of angular momentum *l*. The Debye-Waller factor is given by $e^{-2\sigma^2 k^2}$ which is due to thermal effects and is negligible in XANES when $\sigma^2 k^2 \ll 1$.

The program FEFF9 calculates the potential for each free atom using a relativistic Dirac-Fock-Slater atom code. Then it uses the Mattheiss scheme to overlap the atom charge densities and construct muffin-tin ground-state potentials, where the muffin-tin radii are determined by the Norman prescription. The charge around each atom of atomic number Z is integrated up to the Norman radius r_N of a neutral sphere containing Z electrons. The muffin-tin radii are calculated by scaling of the radii r_N proportionally until the muffin-tins touch. In the case of the absorbing atom in the centre of the cluster considered, the atomic configuration is chosen with a hole in a given core-hole state and an extra electron in the first unoccupied atomic level. This corresponds to the electronic configuration of a neutral atom of atomic number Z with a core hole and local atomic screening. The energy dependent exchange-correlation part is added[4] to get the full potential. The energy is

iterated self-consistently to obtain the ground-state potential. One can then calculate the angular momentum projected density of states. The scattering phase shifts, dipole matrix elements, and x-ray cross-section are also calculated. Full multiple scattering XANES calculations are finally performed to obtain the full Green's function for the specified cluster size.[5]

References:

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