Supplementary Information

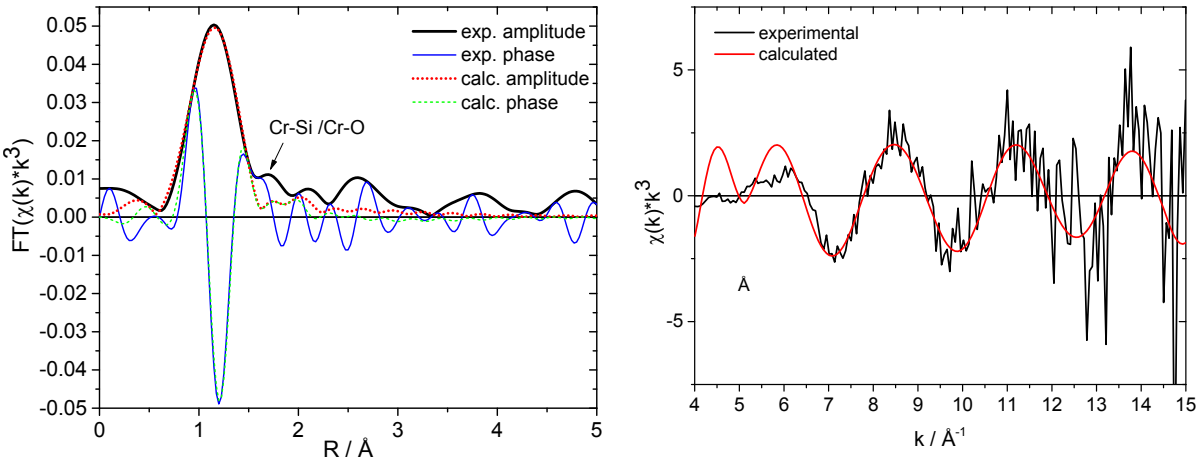
Extended X-ray Absorption Fine Structure (EXAFS):

The EXAFS data of Cr-doped silica was fitted using the theoretical phase and amplitude functions calculated with Feff 8 [38]. The input for Feff 8 was taken from the crystal structure of K_2CrO_4 :

space group:	Pnma;
lattice constants:	a=7.662, b=5.919, c=10.391
coordinates:	Cr(0.22911, 0.2500,0.42061)
	K1 (0.66568, 0.25, 0.41434)
	K2 (0.8901, 0.250, 0.69989
	O1(0.01549, 0.250, 0.42001)
	O2(0.30187, 0.250, 0.57044)
	O3(0.30294, 0.4775, 0.34716)

The fit using just one shell of oxygen atoms did not yield reasonable results, so the fits are done with two shells of oxygen atoms sitting at two distances. Since the chromate species are sitting on an amorphous surface, there are multiple surrounding atoms at fairly close distances, e. g. Cr-Si, Cr-O distances around 2-2.5Å (see figure below). Their presence will impact the fit of the first shell. The distances and coordination numbers for the oxygen atoms, however, stayed fairly stable.

Below is one example of the fits with 2 shells:

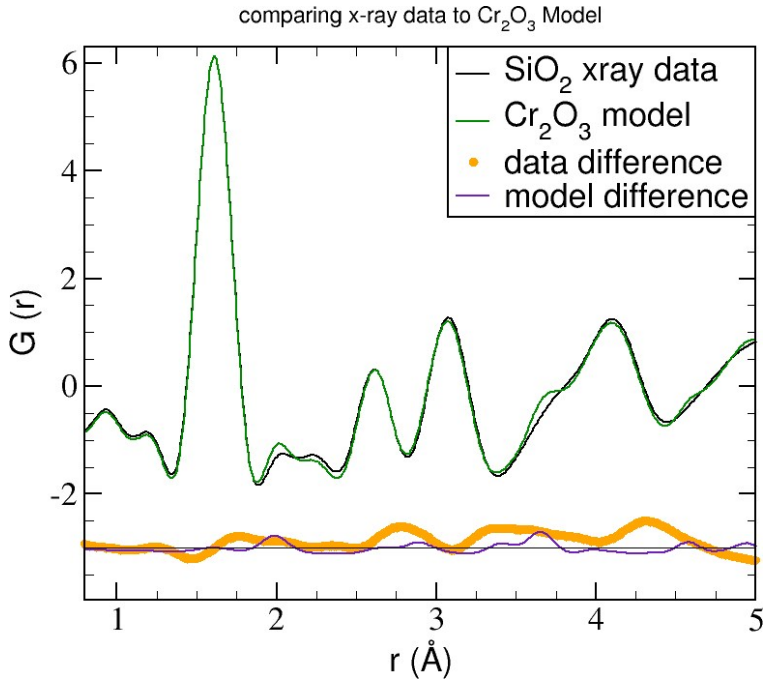


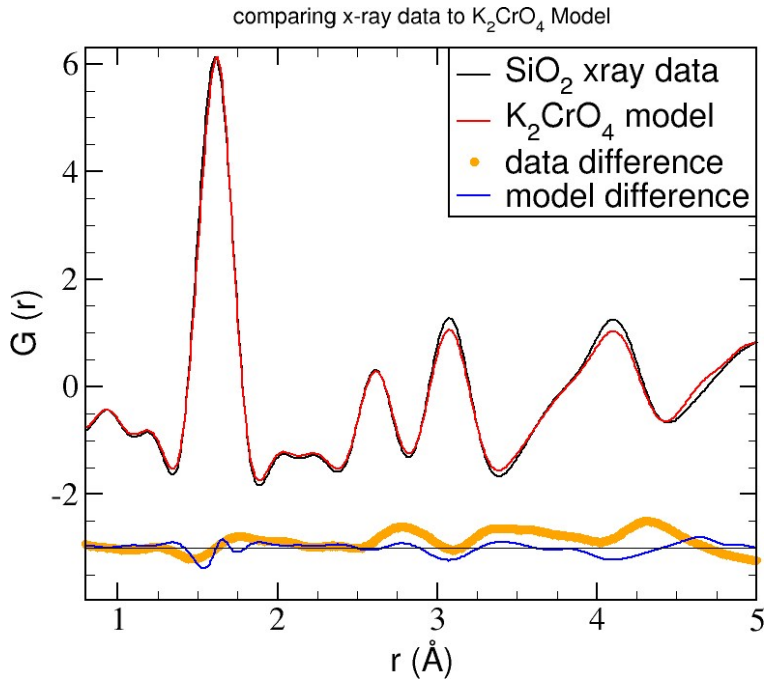
Shell	S_0^2	CN	R / Å	Debye-Waller factor / Å²
Cr-O	0.5	2.06	1.51	0.001
Cr-O		2.00	1.75	0.001

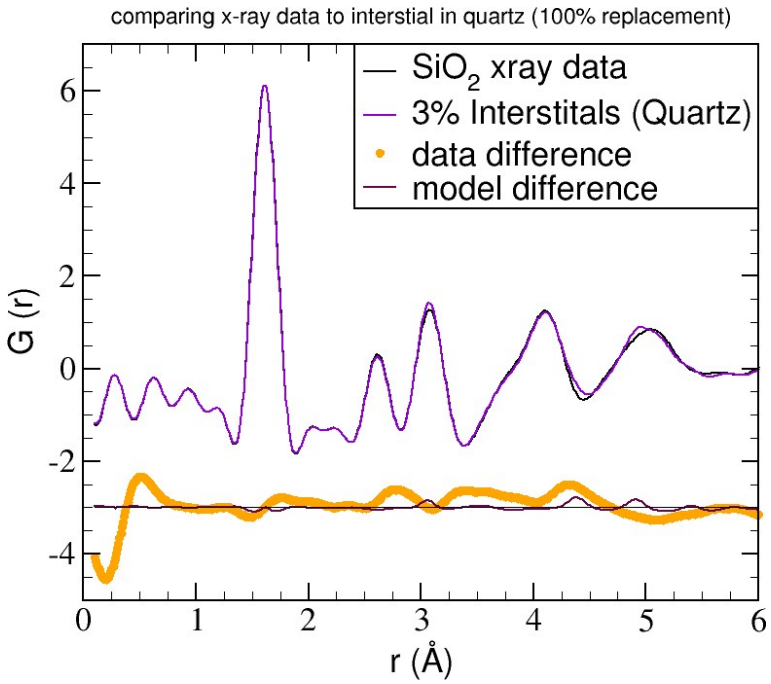
Without having suitable reference substances measured in the same conditions, it makes no sense to include the next shell into the fit and further refine.

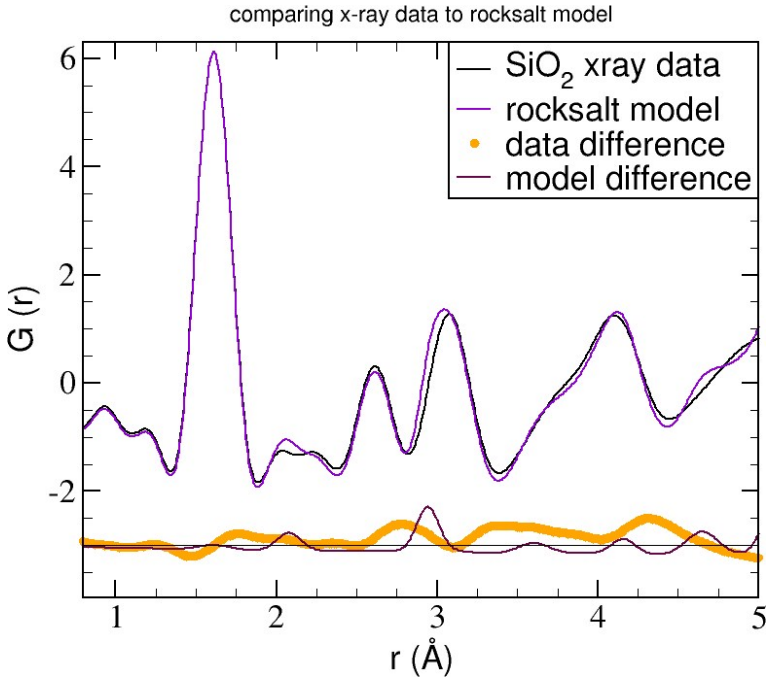
Pair-distribution Function (PDF):

In the Cr-doped silica case, the neutron and x-ray PDFs were compared with corresponding data from neat silica (SiO_2) glass. The datasets were scaled to match the intensities of the first (Si-O) correlations. A difference curve was computed and compared to a series of candidate model structures. The model curves in each case were generated by adding 3% of the model signal to the neat SiO_2 data, scaling the new dataset to match the intensity of the first Si-O correlation in the neat SiO_2 data, and then taking a difference between the scaled model data and collected SiO_2 data. Four cases are shown below: (1) the Cr_2O_3 and (2) K_2CrO_4 models discussed in the paper; (3) a CrO rocksalt model; and (4) a quartz crystalline model with Si replaced by Cr. In each case the scaled SiO_2 data and candidate model datasets are shown together. The data difference (Cr substituted SiO_2 data with SiO_2 reference data subtracted) is shown as orange circles, while the model difference datasets are shown as solid lines.




comparing x-ray data to K_2CrO_4 Model
SiO_2 xray data
K_2CrO_4 model
data difference
model difference
G (r)
r (Å)


comparing x-ray data to interstial in quartz (100% replacement)
SiO_2 xray data
3% Interstitals (Quartz)
data difference
model difference
G (r)
r (Å)


comparing x-ray data to rocksalt model
SiO2 xray data
rocksalt model
data difference
model difference
G (r)
r (Å)
6
4
2
0
-2
1
2
3
4
5