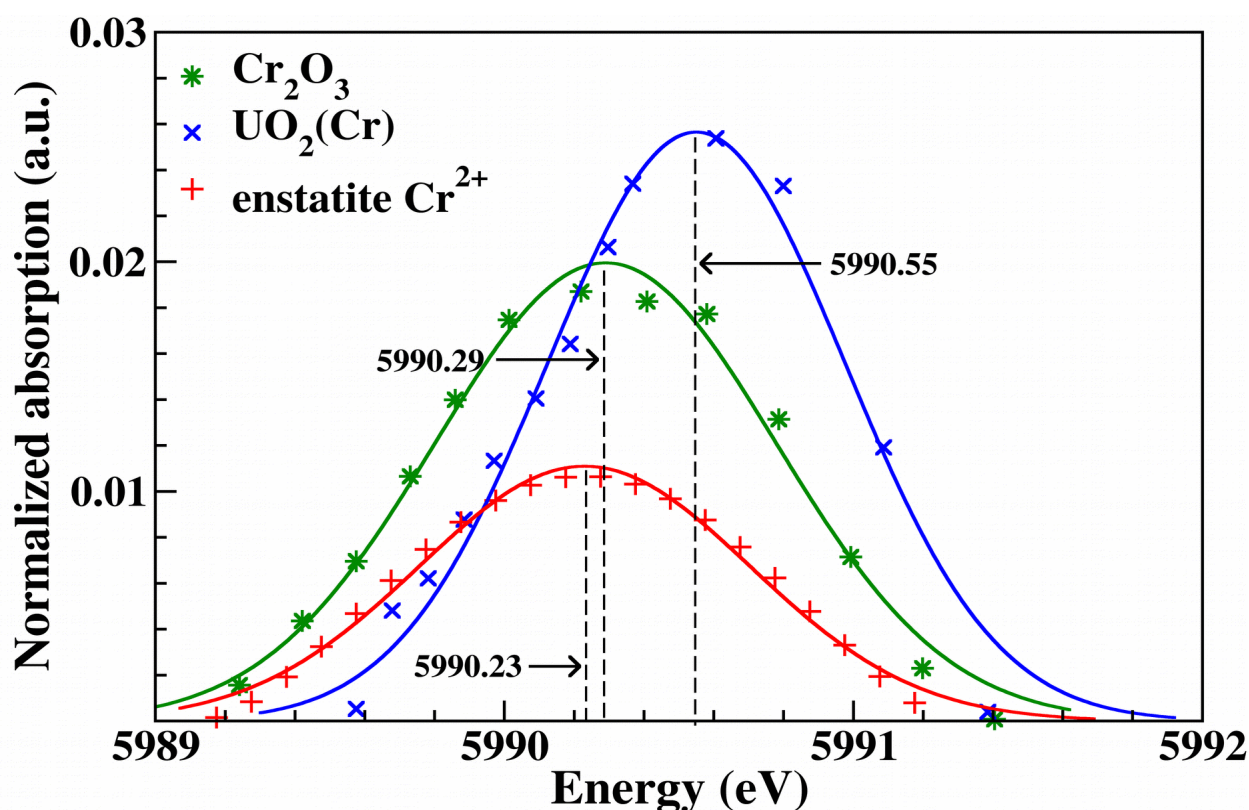


The +2 oxidation state of Cr incorporated into the crystal lattice of UO_2

Supplementary Table 1. The positions of the pre-edge peak features obtained by fits with Gaussian function ($A \cdot \exp(B \cdot (x-C)^2)$).

Materials	First pre-edge peak			Second pre-edge peak		
	A	B	C(position)	A	B	C(position)
Cr-doped UO_2	0.026	-2.74	5990.55 ± 0.02	0.011	-1.25	5992.97 ± 0.10
Cr^{2+} enstatite	0.011	-2.22	5990.23 ± 0.02	0.019	-1.39	5993.13 ± 0.03
Cr^{3+} Cr_2O_3	0.020	-2.09	5990.29 ± 0.03	0.028	-0.60	5993.74 ± 0.05



Supplementary Figure 1. The extracted XANES pre-edge peaks for Cr-doped UO_2 and reference Cr^{2+} and Cr^{3+} structures. The energy resolution of the measured spectra of Cr-doped UO_2 is estimated at 0.3 eV [1]. The Figure is the equivalent of the Fig. 4. in the manuscript but shows the fits (positions) of the lower energy first pre-edge peak features.

Supplementary Note 1. Multi functions fits of the pre-edge features aimed at the derivation of centroid were performed with PeakFit4 software (<https://systatsoftware.com/products/peakfit/>). The procedure is exactly the same as used in studies of Farges (2009) [2].

To analyze the XANES pre-edges, we fitted the measured features using the Pseudo-Voigt functions and the ratios of Gaussian and Lorentz profiles were taken from the previously published studies [2-3]. For pre-edges we applied the full width at half maximum of Gaussian, **FWHM(Gauss)=1.3** and ratio of FWHM(Gauss)/FWHM(Lorentz)=45%/55%=0.82 [2]. For baselines we applied FWHM(Gauss)/FWHM(Lorentz)=50%/50%=1.00 [3].

Supplementary Table 2. Detailed pre-edge fitting parameters. The best solutions (with the coefficient of determination, $R^2 > 0.99$) are given with Bold face font.

	Peak	Area	Position(eV)	Total area	Centroid	R ²
Cr₂O₃	1'	0.0929450	5990.4500	0.4568631	5993.50±0.02	0.996843
	2'	0.1162138	5992.8464			
	3'	0.1518325	5994.2864			
	4'	0.0958718	5996.0231			
	1'	0.1036694	5990.5960	0.4349657	5993.42±0.03	0.978701
	2'	0.1875166	5993.4584			
	3'	0.1437797	5995.4187			
	1'	0.1182806	5990.8437	0.3668657	5993.02±0.07	0.889026
	2'	0.2485851	5994.0619			
UO₂	1'	0.2214381	5990.6969	0.8732953	5992.66±0.02	0.997965
	2'	0.3100726	5992.5914			
	3'	0.3417846	5993.9887			
	1'	0.3305079	5991.2355	0.8334600	5992.62±0.04	0.974973
	2'	0.5029521	5993.5219			
Enstatite	1'	0.0429803	5990.3589	0.1401661	5992.16±0.12	0.997706
	2'	0.0100901	5991.8216			
	3'	0.0870957	5993.0957			
	1'	0.0469276	5990.4421	0.1387141	5992.16±0.04	0.997539
	2'	0.0917865	5993.0453			

Supplementary Table 3. The parameters of baseline of pre-edges.

	Parameter and its meaning	Cr ₂ O ₃	UO ₂	Enstatite
a0	Area	2.4	5.95	3.8
a1	Position of the peak	6000.33	5997.5	5999.3
a2	Width(Guass)	1.3	1.3	1.3
a2	FWHM(Guass)	2.6	2.6	2.6
a3	FWHM(Gauss)/FWHM(Lorentz)	1.00	1.00	1.00

Supplementary References:

1. Riglet-Martial et al., Thermodynamics of chromium in UO₂ fuel: A solubility model. *Journal of Nuclear Materials* **447**, 63–72 (2014).
2. Farges, Chromium speciation in oxide-type compounds: application to minerals, gems, aqueous solutions and silicate glasses. *Phys Chem Minerals* **36**, 463-481 (2009).
3. Wilke *et al.*, Oxidation state and coordination of Fe in minerals: An Fe K-XANES spectroscopic study. *American Mineralogist* **86**, 714-730 (2001).