



Experiment title: Site partitioning and oxidation state of Cr in spinel phases from high temperature refractory ceramics: a resonant scattering powder diffraction and DAFS study	Experiment number: HC-573	
Beamline: D16-BL15	Date of experiment: from: 28/8/1996 to: 01/9/1996	Date of report: 18/8/1 997
Shifts: 9	Local contact(s): Andrew Fitch	<i>Received at ESRF</i> 22 AOUT 1997

Names and affiliations of applicants (* indicates experimentalists):

Gilberto ARTIOLI *, Dip. Scienze della Terra, Univ. Milano
Alessandro PAVESE *, Dip. Scienze della Terra, Univ. Milano
Davide LEVY *, Dip. Scienze della Terra, Univ. Milano
Massimo VALLE, ICRA, S. Paolo d'Argon

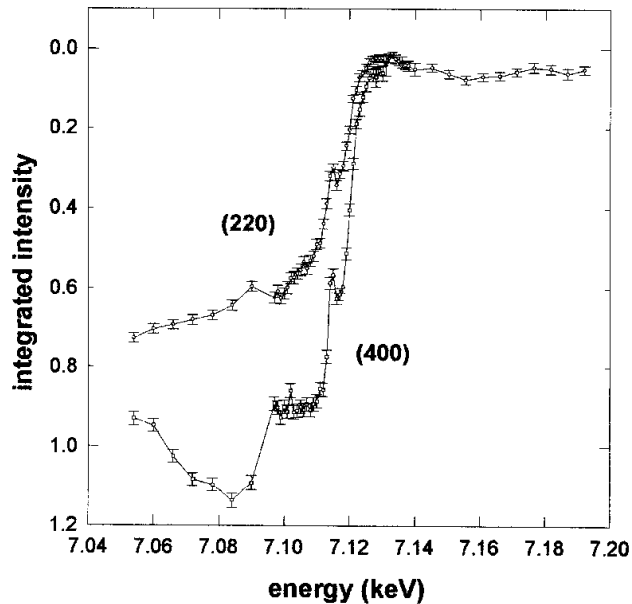
Report:

The spinel structure is a near to ideal case for DAFS studies, since some of the diffraction peaks (i.e. 220, 422, 620) are almost completely due to the scattering of atoms located in the tetrahedral sites, while other peaks (i.e. 400, 444) are due to scattering from octahedral sites only. We are in the process of characterizing the spinel phases formed during the manufacturing of high temperature refractory ceramics. Phase characterization include conventional X-ray powder diffraction, also performed at high temperature, and XAS and Mössbauer spectroscopies. It is of great interest to determine the cation crystal chemistry in the spinel structure of the as synthesized material, and the cation distribution between the spinel and the coexisting phases. As the Diffraction Anomalous Fine Structure (DAFS) technique seems to be of great promise for the site selective characterization of the valence state and coordination of the cation in the spinel structure, we attempted data collection in DAFS mode on synthetic and natural Cr-rich and Fe-rich spinel samples.

Unfortunately, no signal could be obtained on the Bragg diffraction peaks at the Cr K edge

(5.99 keV) on the synthetic and natural Cr-rich samples of interest.

DAFS and resonant scattering data were then successfully collected on pure magnetite and a Fe-rich natural chromite. The resonant scattering data have been treated for the extraction of site resolved information, in order to determine the mean valence of Fe in each site from the chemical shift of the Fe K edge (7.11 keV). Below are shown the raw DAFS spectra measured on the (2 2 0) and (4 0 0) diffraction peaks of magnetite, corresponding to scattering from tetrahedral and octahedral sites respectively.



The spectra have been obtained by integrating the diffraction Bragg peak at each incident radiation energy. In spite of the long counting times, the spectra are rather noisy, due to the low flux of the incident beam in the energy region close to the Fe K edge. It is however possible to discriminate a slight edge shift corresponding to the change in the mean oxidation state of Fe located in the tetrahedral (Fe^{3+}) and the octahedral sites ($\text{Fe}^{2.5+}$). Extraction of quantitative information from the DAFS spectra seems unlikely, given the poor statistical signal of the spectra, however attempts are in progress in order to link the qualitative information obtained from the DAFS measurements with the results of the multispectra Rietveld refinements performed on the powder data collected in resonance scattering mode.