

1.4.P08

Atomic scale determination of the insertion of Cr³⁺ in spinel and garnets: An EXAFS study of site relaxation and element clustering

M.-H. THIBAUT¹, L. GALOISY¹, G. CALAS¹,
J.-L. HAZEMANN² AND O. PROUX²

¹Lab. Minéralogie-Cristallographie, Universités Paris 6/7 and IPGP, Paris, France (thibault@lmpc.jussieu.fr; galoisy@lmpc.jussieu.fr; calas@lmpc.jussieu.fr)

²ESRF, BP 220, 38043 Grenoble, France (hazemann@grenoble.cnrs.fr, proux@esrf.fr)

Trivalent Cr almost exclusively substitutes to Al and Fe in the octahedral sites of many minerals, and participates to extensive solid solutions. We present new spectroscopic data concerning the substitution processes of Cr in natural spinel and garnets, using a combination of Cr K edge x-ray absorption spectroscopy and optical absorption spectroscopy. The local structure obtained from spectroscopic data will be compared to the average mineral structure derived from x-ray diffraction. EXAFS-derived Cr-O distances determined in spinels demonstrate the presence of a structural relaxation around octahedral Cr³⁺ ions, as already evidenced by EXAFS and x-ray linear dichroism in ruby. As in the Al₂O₃-Cr₂O₃ solid solution, crystal field stabilization energy of Cr³⁺ decreases in spinel with increasing Cr concentration. According to Vegard's law, this modification may be related to increasing average Cr-O distances. Our data confirm that metal-ligand distances are not the only control of crystal field intensity and shed light on the modification of the Cr-O bond as a function of Cr concentration. The nature of the next-nearest neighbors indicates the absence of random cation substitution in natural spinels. Cr-Al substitution processes are different in garnets, concerning as well site relaxation as inter-site relationships. The influence of mineral crystal chemistry will be discussed by comparison to the behavior of Cr in other mineral solid solutions.

1.4.P09

A macroscopic and microscopic investigation of the MgCO₃-CdCO₃ solid solution

F.A. BROMILEY¹, T. BOFFA-BALLARAN¹, M. ZHANG²
AND F. LANGENHORST¹

¹Bayerisches Geoinstitut, Universität Bayreuth, Bayreuth, Germany (fiona.bromiley@uni-bayreuth.de)

²University of Cambridge Department of Earth Sciences, Downing Street, Cambridge CB2 3EQ

The binary join within the magnesite (MgCO₃) – Otavite (CdCO₃) system has been investigated in order to gain insight into the mixing behaviour and cation ordering within the magnesite – calcite system, for which this system is an analogue. At intermediate compositions, and temperatures below 700°C, an ordered phase is observed, having the R-3 structure. This phase field is superimposed upon a miscibility gap containing both the ordered R-3 phase and the disordered R-3c phase. Above 700°C a disordering transformation occurs to the R-3c structure across the entire solid solution.

Experiments were performed in piston cylinder apparatus at a pressure of 1GPa and a temperature range of 500-900°C. Samples were characterised using powder X-ray diffraction and Rietveld refinement to give accurate lattice parameters, atomic positions and bond lengths. The variation of unit cell volume across the solid solution is linear for both ordered and disordered samples, hence it is dependent only upon cation substitution and not degree of order.

Infrared powder absorption spectra were collected at room temperature in the range 50-4000cm⁻¹. Variation of peak position due to the substitution of cadmium appears to be linear across the solid solution. Local elastic strains, also due to substitution of cadmium, have been quantified via an autocorrelation function. The autocorrelation function acts to quantify the change in line width of the IR bands with respect to the order – disorder transformation and cation substitution. Ordered samples show bands much sharper than those for disordered samples. Results from the measured ranges all show a positive deviation from linearity for the disordered samples.