Structure of spinel at high temperature using *in-situ* XANES study at the Al and Mg K-edge

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Abstract. We present structural information obtained on spinel at high temperature (298-2400 K) using in situ XANES at the Mg and Al K-edge. Spinel, \([\text{Al}_x\text{Mg}_{1-x}]\)[6](\text{Al}_{2-x}\text{Mg}_x)O_4, with increasing temperature, show a substitution of Mg by Al and Al by Mg in their respective sites. This substitution corresponds to an inversion of the Mg and Al sites. Furthermore, both experiments at the Al and Mg K-edges are in good agreement with XANES calculation made using FDMNES code.

1. Introduction

Only a few studies on the properties and structure of spinel (MgAl_2O_4) and alumina (Al_2O_3) have been carried out at high temperature [1,2] because of technical difficulties associated with their very high liquidus temperatures (i.e., > 2000 K for MgAl_2O_4). Structural determinations are further complicated due to cationic disorder arising from the spinel inversion [3]. It is well known that a spinel inversion can be observed at high temperature [3,4,5,6,7,8]. The general spinel \([\text{Al}_{1-x}\text{Mg}_x]_4(\text{Al}_{2-x}\text{Mg}_x)_6\text{O}_{12}\), has two sites (4-fold and a 6-fold) for each cation. At low temperature \(x=0\) and the 4-fold coordinated site is fully occupied by Mg. As the temperature rises, \(x\) increases, Al moves into the 4-fold coordinated site and Mg into the 6-fold coordinated site. The parameter \(x\) is referred to as the degree of inversion. It has been predicted that the Al and Mg distribution on both sites is not fully random [9]. The weak contrast in X-ray diffraction experiments between Mg and Al prevents precise determination of the site occupancy. Moreover a non-random fluctuation in \(x\) at the nanometer scale as predicted in [10, 8] is even more difficult to identify.

Interpretation of XANES spectra is a difficult task. The features seen around the absorption edge must be compared to reference compounds (fingerprint analysis) or to theoretical calculations, in order to understand the relationship between the spectral features and coordination number or atomic substitution in the neighbor shells of the absorbing element. To allow us to make more quantitative observations from the experimental results we have made XANES simulation of spinels, using the FDMNES (Finite Difference Method Near-Edge Simulation) code of Joly [14], to predict the expected spectral evolution during the conversion of normal to inverse spinel.
2. Experimental methods

2.1. Samples

The three different spinels investigated are:

i) a natural stoichiometric spinel (MgAl$_2$O$_4$) from Myanmar,

ii) a synthetic spinel made from a mixture of Al$_2$O$_3$ and MgO rectapur products from VWR$^\text{®}$.

iii) and finally an Al-rich spinel (Mg$_{0.38}$Al$_{2.67}$O$_4$) described in [16].

From X-ray diffraction the inversion coefficient ($x$) was determined to be 0.07 for the natural sample and 0.32 for the synthetic sample which correspond to equilibrium temperatures of 550K and 1650K respectively using the model [9].

2.2. XANES spectroscopy experiments

By using a home-made heating device consisting of an iridium wire, samples can be heated from ambient temperature up to more than 2800K [11, 12, 13]. This device has been adapted to the experimental vacuum chamber of the LUCIA beamline installed on the Swiss Light Source (Switzerland) [17]. Spectra were recorded in fluorescence mode using a silicon drift diode detector protected by a beryllium cap [17]. We used KTP(110) crystals as the monochromator. The beam size was $20\times20$ $\mu$m and the total sample diameter was $200$ $\mu$m. Some XANES spectra were recorded at room temperature before and after the high temperature experiments and no changes between the before and after spectra were observed [11,12]. In order to prevent data treatment artifacts, the normalization procedures were performed on all spectra with the same parameters using the Athena software [18].

2.3 XANES calculations:

The X-ray absorption spectroscopy is related to the transition of an electron from a deep shell to an empty upper level. The low energy photoelectron produced in the XANES regime has quite a large (a few tens of Å) elastic mean free path and therefore can be used to probe large distances. Results of XANES calculations are used to evaluate the final state of the electron. Calculation were done using the FDMNES software of Joly [14]. The only user input data were the atomic positions and cell parameters taken in [19]. The inverse spinel transformation was modeled by randomly changing Al and Mg within a cluster and without changing the cell parameters or atomic positions. No further normalization of the data was carried out on the output spectra.

3. Results

The room temperature spectra at 300K at the Al K-edge on Fig. 1, present 5 distinct features (labeled a-e) according previous works [20, 21]. A consistent trend between the samples can be noticed on going from natural ($x=0.07$) to synthetic ($x=0.32$) to the Al rich sample, as well as during temperature increases. The trends are:

- i) peak $a$ at 1565.1 eV, which corresponds to a weak pre-edge feature before the main resonance in the natural sample, becomes larger in the synthetic sample and at high temperature. A distinct peak is observed in the Al rich spinel.

- ii) peaks $b$, $c$ and $d$, at 1567.0, 1571.3 and 1575.6 eV respectively, exhibit a decrease in intensity and merge into a broad peak centered at 1570.5 eV on going from the natural to the Al rich sample or to high temperature.

- iii) peak $e$ at 1589.3 eV, due to the first distinct EXAFS oscillation or to a contribution of the multiple scattering within the first neighbors [22] follows a similar trend to that of peaks $b$, $c$ and $d$, in that the intensity decreases from the natural to the Al rich sample or to high temperature.

These peak changes are systematic from the natural spinel at 298K, to the synthetic spinel at 298K, 2070K and 2290K. This behaviour is consistent with the spinel inversion process already observed using neutron diffraction by Redfern et al. [15].
The room temperature Mg K-edge XANES spectra for the three spinels are shown in Fig. 2. All spectra exhibit four peaks at 1308.7, 1313.2, 1318.1 and 1331.4 eV, and labelled a-d, respectively and are in good agreement with previous works [20]. With increasing temperature, important changes are observed (Fig 2). There is a broadening of all peaks accompanied by a decrease in intensity with increasing T. Peaks a and d decrease in intensity relative to peak c, and peak b essentially becomes unresolved. The Mg K-edge spectrum at 2290K is also noisier than the Al K-edge spectrum at this temperature, which may be a result of the very high mobility of Mg in the liquid state [23].

Figures.  1) Al K-edge and 2) Mg K-edge XANES spectra of natural, synthetic and Al-rich spinel, and of the synthetic spinel at high temperatures. 3) and 4) FDMNES calculations of XANES spectra at the Al K-edge and Mg K-edge with different degrees of inversion x with a mixing of tetrahedral and octahedral sites. Vertical lines on the spectra are the positions of the experimental peaks (labelled a-d) identified in Fig. 1 and 2.

4. Discussions

At room temperature, from a comparison between experimental and simulated spectra at the Al K-edge of Figs. 1 and 3, we can infer by looking at the relative amplitude of the main (b+c+d) peak versus the edge step, the following correlation: natural spinel agrees with x=0, synthetic spinel with x=0.33 and Al rich with "vacancies". Here good agreement is found with the inversion coefficient initially determined by X-ray scattering (see the experiments section). In the same way, for the 2070 K XANES spectra we can infer that x for the synthetic spinel in our study is higher than 0.33. For the synthetic sample at 2290 K the strong decrease of peak c is associated with a strong peak a and b suggesting that the sample is moving toward one with full Al occupancy at the four-fold site (x=1 in Fig. 3). These results indicate that the inversion process continues between 2070 K and 2290 K towards x=0.5, with destruction of the medium range order. In situ high temperature inversion determinations using neutron scattering experiments have only been performed up to 1873 K [15] and never measured for x higher than 0.35 [10]. Our results essentially extend these previous studies to higher temperature and are in good agreement with ab initio calculations [24] which predicted x=0.5±0.1 at 2375 K. The loss of intensity of all the peaks at high T can be easily understood by the loss of all medium range order close to the melting point.

Since 100% of the Mg atoms can exchange sites but only 50% of the Al atoms can do so during the inversion process, the Mg K-edge spectra should be more sensitive than the Al K-edge to changes resulting from the inversion. By comparing the experimental (Fig. 2) and calculated (Fig 4) XANES spectra at the Mg K-edge we can conclude that the natural, synthetic and Al rich spinel samples are consistent with x=0 at room temperature, while the synthetic sample at 2070K is more consistent with x=0.5. For the synthetic spinel at 2290 K a temperature-induced flattening of all the
contributions is observed, partially related to the poor experimental signal to noise ratio. However peak \( a \) still exists, and this suggests that Mg is still present in the 4 fold coordinated site and \( x \) is therefore around 0.5 [20]. At high temperature, this is in agreement with the conclusions made above for the Al K-edge.

However, a drastic difference is observed at room temperature in the XANES spectra at both K-edges probably because of the speciation difference between Mg and Al in \( [4]Mg/[6]Al_2O_4 \) spinel. All the samples show a strong peak \( b \) in the Mg K-edge spectra characteristic of medium range order (MRO). This seems in contradiction with the observation on the Al K-edge spectra. This discrepancy implies some Mg-clustering in the spinel. This clustering effect was predicted from calorimetric measurements [10] and from Monte Carlo simulation [8]. Complete cation disorder can be approached only at high temperature as observed in this study at 2070 K and 2290 K. However this has never been observed from a structural point of view. Because XANES probes the local environment on a single species atom such clustering can be observed.

More specifically for the Al rich sample, comparison between the experimental spectra (Fig. 2) and the calculated "vacancies" spectrum (Fig. 4) on the Mg K-edge shows only the first sharp peak \( a \) in common The presence of this peak \( a \) confirms that Mg remains in four-fold coordination because peak \( a \) was assigned specifically to this environment (see results section). However the presence in the experimental spectra of peak \( b \), sensitive to MRO, leads to the suggestion of a strong non-random distribution of the vacancies leading to two sub networks, one with a regular spinel organization with \( [4]Mg \) and \( [6]Al \) elements, and another one enriched with Al where \( [6]Al \) is surrounded mainly by vacancies located in the six fold coordinated site. This structural model is in agreement with the ion vacancy increase with the alumina excess content [25].

References

[1] Maekawa, H., Kato, S., Kawamura, K., and Yokokawa, T. (1997) Amer. Min., 82, 1125-1132.
[2] Fiquet, G., Richet, P., and Montagnac, G. (1999) Phys. Chem. Min., 27, 103-111.
[3] Barth, T.F.W., and Posnjak, E. (1932) Zeil. Kristal, 82, 325-341.
[4] Andréozzi, G.B., Priniville, F., Skogby and Della Giusta, A. (2000) Amer. Mineral., 85, 1164-1171.
[5] Warren, M.C., Dove, M.T., and Redfern, S.A.T. (2000) Mineral. Mag., 64, 311-317.
[6] Lavrentiev M.Yu., Purton J-A. and Allan N.L. (2000) Amer. Mineral., 88, 1522-1531.
[7] Méducin F., Redfern S.A.T., Le Godec Y., Stone H.J., Tucker M.G., Dove M.T. and Marshall W.G. Amer. Mineral., 89, 981-986.
[8] Palin E.J. and Harrison R. (2007) Amer. Mineral., 92, 1334-1345.
[9] O'Neill, H.St.C., and Navrotsky, A. (1983) Amer. Mineral., 68, 181-194.
[10] Wood, B.J., Kirkpatrick, R.I., and Montez, B. (1986) Amer. Mineral., 71, 999-1006.
[11] Neuville D.R. Cormier L., de Ligny D., Flank AM, and Lagarde P. (2008) Amer. Mineral., 93, 228-234.
[12] Neuville D.R., de Ligny D., Cormier L., Henderson G.S., Roux J., Flank AM, and Lagarde P. (2009) Geochimica Cosmoehimica Acta, 73, 3410-3422.
[13] de Ligny D., Neuville D.R., Cormier L., Roux J., and Henderson G.S. G. Panczer, S. Shoval, A.-M. Flank, P. Lagarde (2009) J. of Non Crystal. Sol., 355, 1099-1102.
[14] Joly, Y. (2001) Phys. Rev. B, 63, 125120.
[15] Redfern, S.A.T., Harrison, R.J., O'Neill, H.St.C., and Wood, D. (1999) Amer. Mineral., 84, 299–310.
[16] Basso, R., Carbonin, S., and Della Giusta, A. (1991) Zeil. Kristal, 194, 111-119.
[17] Flank, A.-M., Caucon, G., Lagarde, P., Bac, S., Janousch, M., Wetter, R., Dubuisson, J.-M., Idir, M., Langlois, F., Moreno, T., and Vantelon, D. (2006) Nucl. Inst. Meth. Phys. Res. B, 246, 269-274.
[18] Ravel, B. and Newville, M. (2005) J. Synch. Rad., 12, 537-541.
[19] Yamanaka, T., Takéuchi, Y., and Tokonami, M. (1984) Acta Crystal., B40, 96-102.
[20] Andrault, D., Neuville, D.R., Flank, A.-M., and Wang, Y. (1998) Amer. Mineral., 83, 1045-1053.
[21] Marcelli, A., Mottana, A., and Cibin, G. (2000) J. Appl. Cryst., 33, 234-242.
[22] Cabaret, D., Saintctavit, P., Idelhonse, P., Flank, A.M. (1996) J. Phys. Condens. Mat., 8, 3691-3704.
[23] Magnien V, Neuville D.R., Cormier L., Roux J., Hazemann J-L., de Ligny D., Pascarelli S., Vickridge I., Pinet O. and Richet P. (2008) Geochim. Cosmoehimica Acta., 72, 2157-2168.