

The Order-disorder and Structural Behaviour of Magnesioferrite to about 1000°C

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Beamline(s): X7B

Introduction: Numerous studies have been done on spinels because of their chemical and structural simplicity, their geological importance, and their use as geothermometers, geobarometers, and geospeedometers. *In-situ* measurements are more realistic than measurements on quenched samples to study the detailed structural behaviour of minerals. This study aims to resolve the quench problem of previous studies and to accurately determine the crystal structures and cation ordering at various temperatures to about 1000°C for the spinel magnesioferrite, ideally, MgFe_2O_4 . Accurate order-disorder parameters are necessary to test various thermodynamic models that are commonly used to describe ordering in minerals. Our present results for magnesioferrite are different from previous studies on this mineral, but we have confidence that our new results best describe the order-disorder phenomenon in magnesioferrite, and they will be used to test the applicability of various thermodynamic models.

Methods and Materials: Magnesioferrite spinel was synthesized at 900°C from equimolar amounts of reagent-grade oxides: MgO and Fe_2O_3 . The structural behaviour of magnesioferrite was determined by *in-situ* X-ray diffraction ($\lambda = 0.91997 \text{ \AA}$) at room pressure and temperatures ranging from 25 to 982°C on heating, and again on cooling from 982 to 25°C. Data were collected at a rate of about 9.5°C/min, both on heating as well as on cooling. The crystal structures were refined using the GSAS Rietveld refinement software. Simultaneous differential scanning calorimetry (DSC) and thermogravimetry (TG) data were also obtained using a Netzsch STA 449C simultaneous TG-DSC instrument. Data were collected at a heating rate of 10°C/min from 25 to 1400°C, and at the same rate on cooling down to 25°C.

Results: The *a* unit-cell parameter of magnesioferrite increases quite linearly on heating, but it deviates at 448°C to give a discontinuity in the *a* unit-cell parameter at $T_c = 570^\circ\text{C}$. The variation of the *a* cell parameter above 570°C is linear, and on cooling from the highest temperature (982°C), the *a* unit-cell parameter decreases reversibly back to T_c and then continues linearly to room temperature. Therefore, the above transition is irreversible. The *a* unit-cell parameters at 25°C obtained before heating [8.3869(5) Å] and after cooling [8.3757(2) Å] are, therefore, different. The DSC curve for magnesioferrite contains an endothermic peak at about 550°C, which corresponds to the curie temperature of this sample. This peak was absent on cooling the sample, indicating, again that this transition is irreversible, as mentioned above. The DSC data are in excellent agreement with the structural data. On heating, the derivative of the DSC curve contains an inflection point at 477°C (where ordering begins) and an end temperature of 574°C (= T_c) where equilibrium is achieved, which corresponds well with the structural data. The structure was analyzed in terms of order parameters: (1) the inversion order parameter, *x*, indicated by the formula, ${}^4[\text{Mg}_{1-x}\text{Fe}_x]{}^6[\text{Mg}_{x/2}\text{Fe}_{1-x/2}]_2\text{O}_4$; (2) the order parameter, $Q = 1 - 1.5x$, and (3) the distribution coefficient, $K_D = (1-x)/(2-x)$. When $x = 2/3$, maximum disorder occurs, and when $x = 1$, a perfect inverse ordering occurs. Initially, $x = 0.82$ at room temperature for magnesioferrite. All three order parameters show similar behaviour for cation ordering in magnesioferrite. On heating, there is no change in cation ordering until the temperature is high enough (448°C) to cause exchange of Mg and Fe between the octahedral and tetrahedral sites to occur. This thermal activation barrier begins at 448°C and is overcome at $T_c = 570^\circ\text{C}$, where the sample achieves a more ordered equilibrium state, which also corresponds to the maximum ordered state of the sample on heating, where x (max.) = 0.85 on heating. DSC indicates that the energy required to overcome this thermal barrier is 157 J/g. On further heating beyond T_c , the sample continuously disorders further along the equilibrium pathway to the maximum temperature studied ($T = 982^\circ\text{C}$, $x = 0.767$). On cooling down to T_c , the ordering reverses along the identical equilibrium pathway as that of heating. On cooling further, the ordering overshoots T_c and becomes T_c' , and that maximum equilibrium order is frozen in, and maintained to room temperature, where x (max.) = 0.87 from T_c' to room *T*. After the heating and cooling cycle, if data were re-collected immediately at X7B or by DSC, we expect to observe no activation barrier from 448°C to T_c , and we also expect the ordering to follow the pathway observed on cooling. This indicates that quenching after synthesis, gives rise to a non-equilibrium cation distribution. Although we collected structural data to nearly 1000°C, and because the cell parameter varies linearly in this *T* range, we expect that our results may be applicable to temperatures beyond 1000°C. The order-disorder behaviour of magnesioferrite is similar to that for spinel (proper) MgAl_2O_4 , and FeAl_2O_4 (hercynite), but our results indicate that these spinels should be re-investigated using the method we have employed in the present study. We plan to do these re-investigations when we have additional beam time at X7B, and we also hope to increase the high temperature range to make it comparable to natural conditions (lower-and upper-mantle conditions).

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