Fe-Mg diffusion in spinel: New experimental data and a point defect model†

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ABSTRACT

We have measured Fe-Mg interdiffusion rates ($D_{Fe-Mg}$) in synthetic Mg-Al spinel and a natural (Mg,Fe) alumino spinel from Sri Lanka ($X_{Fe} \approx 0.07$) at atmospheric pressure over a range of different oxygen fugacities ($\log_{10}(f_{O_2}/Pa) = -14$ to $-10$) and temperatures ($750–900 \degree C$). Diffusion couples made of single-crystal spinel and thin films of hercynitic composition ($X_{Fe} \approx 0.5$) were used for the diffusion anneals. The experimentally induced diffusion profiles were analyzed by Rutherford backscattering Spectroscopy to retrieve true depth concentration profiles for Fe. These were fitted numerically by an explicit finite difference scheme that allows compositionally dependent interdiffusion processes to be modeled by relating self- and interdiffusion coefficients. Synthesis of data from the two diffusion couples indicate that: (1) $D_{Fe-Mg}$ depends on $X_{Mg}$ of spinel, with increasing diffusion rates with increasing $X_{Mg}$. This behavior is opposite of that found in silicates. (2) Self-diffusion coefficients could not be determined from these experiments, but the results indicate that $D_{Fe}/D_{Mg} > 100$. (3) $D_{Fe-Mg}$ in Mg-spinel is independent of oxygen fugacity, whereas it depends strongly and nonlinearly on oxygen fugacity for the natural spinel. This observation indicates that the mechanisms of diffusion are different in the two kinds of spinel (Fe-bearing vs. Fe-free), which is also seen in the difference in activation energy obtained for these. Moreover, the nonlinear dependence on oxygen fugacity indicates that diffusion occurs by an interstitial mechanism at low-oxygen fugacities and by a vacancy mechanism at high-oxygen fugacities in natural, Fe-bearing spinel. (4) Simple Arrhenius relations that describe the data within the range of experimental conditions are: Synthetic magnesium spinel: $Q_{Fe-Mg} = 219 \pm 19 \text{ kJ/mol, }$ $\log_{10}D_{Fe-Mg} = -7.76 \pm 0.90 \text{ [m/s].}$ Natural Fe-bearing spinel for $\log_{10}(f_{O_2}/Pa) = -12$: $Q_{Fe-Mg} = 139 \pm 18 \text{ kJ/mol, }$ $\log_{10}D_{Fe-Mg} = -12.33 \pm 0.85 \text{ [m/s].}$ A model based on point defect considerations that describes the temperature as well as oxygen fugacity dependence of $D_{Fe-Mg}$ in Fe-bearing spinel is: $D \text{ [m}^2\text{/s]} = D_i \text{ [m}^2\text{/s]} f_{O_2} \text{ [Pa]} \exp(–Q_i \text{ [J/mol]} / RT \text{ [K]} + D_s \text{ [m}^2\text{/s]} f_{O_2} \text{ [Pa]} \exp(–Q_s \text{ [J/mol]} / RT \text{ [K]}),$ with $D_i = 1.07 \times 10^{-9} \pm 1.55 \times 10^{-9} \text{ m}^2\text{/s, } Q_i = 131 \pm 66 \text{ kJ/mol, } D_s = 1.03 \times 10^{-17} \pm 7.32 \times 10^{-17} \text{ m}^2\text{/s, } Q_s = 130 \pm 80 \text{ kJ/mol and } m = 0.34 \pm 0.18$. Poor coverage of $T-f_{O_2}$ space by available experimental data results in large uncertainties in the fit parameters. As a result, these expressions are useful for understanding the diffusion behavior in spinels, but not for extrapolation and calculation of diffusion coefficients for cooling rate or other related calculations. Until the parameters can be better constrained through the availability of more data, we recommend that for such calculations, the parameters noted above for Fe-bearing spinels be used for compositions and $f_{O_2}$ conditions that are close to those of the experiments. (5) $D_{Fe-Mg}$ in spinel is faster than $D_{Fe-Mg}$ in olivines, pyroxenes, and garnets at most conditions.  

Keywords: Spinel, diffusion coefficient, diffusion mechanism, point defect, thin films, pulsed laser deposition, Rutherford backscattering spectroscopy

INTRODUCTION

Spinel ($\text{Fe}_{x}\text{Mg}_{1-x}\text{Al}_2\text{O}_4$) is one of the major minerals in Earth’s uppermost mantle, a common mineral in a wide range of metamorphic and ultramafic rocks, an important mineral inclusion found in chondritic meteorites of the early Solar System, and it has also been found in lunar rocks (see references in the review by Van Orman and Crispin 2010). Because of its wide range of thermodynamic solid solutions, spinel may form in various different tectonic environments and its chemical composition has been used to infer the physicochemical conditions under which its host rocks have formed (e.g., Irvine 1965; O’Neill and Wall 1987; Ballhaus et al. 1991). Hence, knowledge of diffusion rates in spinel is of interest in several geological and planetary science problems. For example, Sheng et al. (1992) studied the Mg isotopic variations in spinel and coexisting silicates of the plagioclase-olivine inclusions in the Allende meteorite to evaluate cooling rates based on Mg-self diffusion in spinel and equilibrium melt. Ozawa (1983) used zoning patterns in spinel and coexisting olivine to constrain cooling rates of ultramafic rocks of the Miyamori ultramafic complex. Similarly, Coogan et al. (2007) used the partitioning of Mg and Fe$^{2+}$ between olivine and different tectonic environments and its chemical composition has been used to infer the physicochemical conditions under which its host rocks have formed (e.g., Irvine 1965; O’Neill and Wall 1987; Ballhaus et al. 1991). Hence, knowledge of diffusion rates in spinel is of interest in several geological and planetary science problems. For example, Sheng et al. (1992) studied the Mg isotopic variations in spinel and coexisting silicates of the plagioclase-olivine inclusions in the Allende meteorite to evaluate cooling rates based on Mg-self diffusion in spinel and equilibrium melt. Ozawa (1983) used zoning patterns in spinel and coexisting olivine to constrain cooling rates of ultramafic rocks of the Miyamori ultramafic complex. Similarly, Coogan et al. (2007) used the partitioning of Mg and Fe$^{2+}$ between olivine and