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SPINELS RENAISSANCE: THE PAST, PRESENT, AND FUTURE OF THOSE UBIQUITOUS MINERALS AND MATERIALS

Spectroscopic study of ordering in non-stoichiometric magnesium aluminate spinel†

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ABSTRACT

FTIR and RAMAN spectroscopic methods were used to study the ordering of non-stoichiometric nano-magnesium aluminate spinels ($MgO{\it n}Al_2O_3$, $0.4 < n < 12$) synthesized using a combustion synthesis method. It was established that the degree of structural disorder (i.e., the inversion parameter, *i*) can be quantified using the intensities of the γ_1 and γ_5 IR modes or 670 and 723 cm^{-1} Raman shifts. The results indicated that the as-synthesized materials were heavily disordered and obey earlier conclusions that the defect chemistry of non-stoichiometric spinels is dominated by clusters formed from anti-site defects. Analysis of the temperature dependency of cation distribution in the Mg- and Al-rich samples showed that the spinel phase moved toward equilibrium upon increases in temperature. Where decomposition occurred, the disordered level decreased at temperatures up to 1000 °C. Above this temperature, the order level dropped far below the expected equilibrium value and the γ_3 mode (a mode that is characterized for ordered structures, such as a natural spinel) that appears. These findings, together with Raman results of partly decomposed Al-rich samples, support the hypothesis that a $MgAl_2O_4$-γ-$Al_{8/3}\square_{1/3}O_4$ solid solution comprises of series of complex micro-phases with considerable short-range order.

Keywords: FTIR, inversion parameter, magnesium aluminate spinel, Raman