

Cation ordering and structural variations with temperature in MgAl₂O₄ spinel: An X-ray single-crystal study

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ABSTRACT

The equilibrium distribution of Mg and Al between the tetrahedral and octahedral sites of a flux grown, stoichiometric MgAl₂O₄ spinel was investigated between 600 and 1100 °C by single-crystal X-ray diffraction of quenched samples. The cation distribution for both ordering and disordering runs was obtained by minimizing accurate crystallographic parameters and effective ionic radii. Along with the variation of the degree of inversion from 0.18 to 0.29 between 600 and 1100 °C, both unit cell and oxygen positional parameter decreased linearly. Multiple non-linear least-squares fit of our data with the thermodynamic model of O'Neill and Navrotsky (1983) gave $\alpha = 23 \pm 2$ KJ/mol and $\beta = 13 \pm 4$ KJ/mol. The influence of both cation inversion and thermal expansion on T-O and M-O bond length variation was determined by comparison of our data with previous in situ studies. In the thermal interval investigated, the inversion accounts for change of -0.014 \AA for T-O and $+0.007 \text{ \AA}$ for M-O. Mean linear polyhedral thermal expansion coefficients of $6.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ and $8.9 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ were calculated for T and M sites, respectively.